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Reductive Deprotonation and Hinders CO₂ Reduction Catalysis
in [Ru(tpy)(6DHBP)(NCCH₃)]²⁺ (6DHBP = 6,6'- (OH)₂bpy)***

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A Non-Innocent Proton-Responsive Ligand Facilitates Reductive Deprotonation and Hinders CO₂ Reduction Catalysis in [Ru(tpy)(6DHBP)(NCCH₃)]²⁺ (6DHBP = 6,6'-(OH)₂bpy)

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Abstract

Ruthenium complexes with proton-responsive ligands [Ru(tpy)(nDHBP)(NCCH₃)](CF₃SO₃)₂ (tpy = 2,2':6',2''-terpyridine; nDHBP = n,n'-dihydroxy-2,2'-bipyridine, n = 4 or 6) were examined for reductive chemistry and as catalysts for CO₂ reduction. Electrochemical reduction of [Ru(tpy)(nDHBP)(NCCH₃)]²⁺ generates deprotonated species through inter-ligand electron transfer in which the initially formed tpy radical anion reacts with a proton source to produce singly- and doubly-deprotonated complexes that are identical to those obtained by base titration. A third reduction (i.e., reduction of [Ru(tpy)(nDHBP-2H⁺)]⁰) triggers catalysis of CO₂ reduction; however, the catalytic efficiency is strikingly lower than that of unsubstituted [Ru(tpy)(bpy)(NCCH₃)]²⁺ (bpy = 2,2'-bipyridine). Cyclic voltammetry, bulk electrolysis and spectroelectrochemical infrared (SEC-IR) experiments suggest the reactivity of CO₂ at both the Ru center and the deprotonated quinone-type ligand. The Ru carbonyl formed by the intermediacy of a metallocarboxylic acid is stable against reduction, and mass spectrometry analysis of this product indicates the presence of two carbonates formed by the reaction of DHBP-2H⁺ with CO₂.

Introduction

Artificial photosynthesis for the conversion of carbon dioxide and water to hydrocarbon fuels and H_2 is an appealing approach to alleviate the historically high atmospheric CO_2 concentration while providing energy security against the uneven distribution and the exhaustibility of fossil fuels.¹⁻¹² This process consists of two half-reactions: CO_2 reduction¹² and water oxidation.¹³ Although the one-electron reduction of CO_2 is energy intensive (for CO_2 to $CO_2^{\bullet-}$ $E^0 = -1.90$ V)¹⁴, multielectron, multiproton pathways offer significant diminution of the energy requirement for reduction to C1 products (e.g., $E^0 = -0.53$ V for CO and -0.48 V for HCHO at pH 7). Unfortunately, the low energy pathways are difficult to catalyze efficiently owing to their multielectron nature, and practical reaction rates often require significant overpotentials. Furthermore, product selectivity remains a challenge due to competitive reaction mechanisms including reduction of protons to H_2 .

The availability of multiple oxidation states and tunable properties through structural tailoring distinguish transition metal complexes as versatile catalysts for CO_2 reduction via multi-electron pathways. Accordingly, many molecular complexes, metal electrodes, and semiconductor materials have been discovered to catalyze the reduction of CO_2 ,^{5,6,9-12,15-28} yet improvements in rates and stability are needed. Additionally, most catalysts yield HCOOH and/or CO as $2e^-/2H^+$ reduction products and further reduction is rare. Nagao et al. reported that $[Ru(tpy)(bpy)(CO)]^{2+}$ (tpy = 2,2':6',2''-terpyridine, bpy = 2,2'-bipyridine, Chart 1) catalyzes the electrochemical reduction of CO_2 to HCOOH, CO, and H_2 at room temperature in DMF/ H_2O (1/5 v/v, pH 9) by applying -1.60 V.²⁹ The same catalyst produced HCOOH, CO, $H(O)CCOOH$, $HOCH_2COOH$, and CH_3OH by the two-, four- and six-electron reduction of CO_2 in C_2H_5OH/H_2O (4/1 v/v) at -20 °C by applying -1.75 V vs Ag/Ag^+ . They confirmed such CO_2 reduction by detecting $H(O)^{13}C^{13}COOH$ and $HO^{13}CH_2^{13}COOH$ using $^{13}CO_2$.²⁹ More recently, electrolysis conditions were optimized to produce syngas ($H_2 + CO$), and a carbene analogue, $[Ru(tpy)(Mebim-py)(NCCH_3)]^{2+}$ (Mebim-py = 3-methyl-1-pyridyl-benzimidazol-2-ylidene, Chart 1) with greater activity was discovered ($k_{cat} = 19$ s⁻¹ vs 5 s⁻¹ for $[Ru(tpy)(bpy)(NCCH_3)]^{2+}$).^{30,31} In CH_3CN , solvent dissociation from the doubly reduced species, $[Ru(tpy)(bpy)(NCCH_3)]^0$, is slow and rate limiting,³¹ and the faster catalysis using $[Ru(tpy)(Mebim-py)(NCCH_3)]^{2+}$ was attributed to accelerated ligand exchange. The relationship between polypyridyl ligand properties, ligand exchange rates, and catalytic current for CO_2 reduction has been quantified.³² A key intermediate during CO formation is considered to be the metallocarboxylic acid, produced by the reaction of the doubly reduced species with CO_2 and a proton.²⁹⁻³¹

The reduction of CO₂ via the metallocarboxylate intermediate [Ru(tpy)(bpy)(CO₂)]⁰ is closely related to the same catalysis by iron(II) porphyrins in which subsequent protonation is facilitated by weak acids³³ and is dramatically enhanced using phenolic ligands as a pre-positioned internal proton source.³⁴ The effects of proximal bases on proton reduction/hydrogen oxidation,^{9,35} alcohol dehydrogenation,³⁶ and CO₂ reduction^{37,38} have been documented as well. Our primary interest in this field pertains to the second coordination sphere and electronic effects of hydroxy substituted bipyridine ligands on CO₂ hydrogenation (the thermal reduction of CO₂ with H₂) and formic acid dehydrogenation.^{6,39-41} The proton responsive ligands impart pH-dependent solubility and reactivity while the proximity of bases to the metal, e.g., [Ir(Cp*)(6DHBP)(OH₂)]²⁺ (6DHBP = 6,6'-dihydroxy-2,2'-bipyridine), enhances reactivity. We have obtained clear evidence of the involvement of a water molecule in the rate-determining heterolysis of H₂ and accelerated proton transfer by formation of a water bridge in CO₂ hydrogenation catalyzed by the complexes bearing a pendent base.⁴²

Outer sphere ligand acid/base properties in reductive catalysis using the [Ru(tpy)(bpy)L]²⁺ motif have received little attention. Our group investigated p- and d-[Ru(tpy)(pynap)(OH₂)]²⁺ (pynap = 2-(pyrid-2'-yl)-1,8-naphthyridine, Chart 1), for which there are two separable isomers differing by the orientation of the asymmetric pynap ligand. Catalytic proton reduction was observed only for the isomer with the pendent naphthyridine nitrogen atom near the coordinating water molecule (and the active site).⁴³ Tanaka investigated the reductive electrochemistry of *cis* and *trans* isomers of [Ru(tpy)(bpyO)(CO)]⁺ (bpyO = 2,6'-bipyridin-6-onato, Chart 1) and found CO dissociation in the doubly reduced *trans* isomer but cyclometallation in the *cis* isomer via attack on the CO ligand by the pyridinolate oxygen.⁴⁴

To further examine the role of proton responsive bipyridine ligands on reductive electrochemistry and reactivity toward CO₂, we prepared the Ru complexes [Ru(tpy)(6DHBP)(NCCH₃)]²⁺ and [Ru(tpy)(4DHBP)(NCCH₃)]²⁺ (4DHBP = 4,4'-dihydroxy-2,2'-bipyridine). We hypothesized that the proximity of 6,6'-OH groups to the Ru center might facilitate protonation of a putative metallocarboxylate intermediate or accelerate protonolysis of the metallocarboxylic acid into CO and H₂O while the strongly donating 4,4'-OH groups could: 1) influence transfer of charge from ligand-based orbitals to Ru for CO₂ binding and 2) accelerate the ligand exchange reactions at the metal center. Instead, our results demonstrate the formation of doubly deprotonated ligands (i.e., removal of protons from the two hydroxy groups) during cathodic electrolysis to form [Ru(tpy)(6DHBP-2H⁺)(NCCH₃)] and [Ru(tpy)(4DHBP-

$2\text{H}^+(\text{NCCH}_3)]$. Such a consecutive electrochemical reduction coupled with deprotonation has been observed for $\text{Re}(\text{nDHBP})(\text{CO})_3\text{Cl}$ to form complexes identical to those obtained by chemical deprotonation.⁴⁵ Here we will report the electrochemical reduction of CO_2 with these deprotonated complexes and a possible reductive deprotonation mechanism investigated by density functional theory (DFT) calculations.

Chart 1. Chemical structures of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{L})]^{2+}$ type complexes studied as CO_2 reduction catalysts or for second coordination sphere effects. The letters p and d for the pynap complexes indicate the proximal and distal naphthyridine (to the bound water) isomers, respectively.

Experimental Details

Materials. All solvents for synthesis and electrochemistry are used as received. The 2,2':6',2''-terpyridine was purchased from Sigma-Aldrich, and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was from Colonial Metals. $[\text{Ru}(\text{tpy})\text{Cl}_3]$, $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2$, 6DHBP and 4DHBP were synthesized according to literature methods.^{46-48,49} Certified gas mixtures (3, 10, and 30% CO_2 balanced with N_2) from MG Industries were used for electrochemistry measurements. The ^1H NMR spectra were recorded with a Bruker Avance 400 spectrometer, and coupling constants are reported in Hz. Mass spectrometry was performed on a LCQ ADVANTAGE MAX (Finnigan) mass spectrometer

using methanol as the eluent. Elemental analyses were conducted by Robertson Microlit Laboratories (Ledgewood, NJ). Electronic absorption spectra were recorded using an Agilent 8454 UV-vis spectrophotometer. Sodium reduction was performed in a home-made air tight vessel equipped with a quartz spectrophotometric cell separated by a fine glass frit from a second compartment containing 1% Na in Hg. Samples were prepared under high vacuum with dry CH₃CN and were reduced gradually by introducing small portions to the amalgam chamber. Synthesis and characterization of a series of Ru complexes can be found in the SI.

Electrochemistry. Electrochemical measurements were carried out with a BAS100B potentiostat or BASi Epsilon potentiostat. Cyclic voltammetry (CV) was performed with a standard three-electrode configuration using a glassy carbon disk (3 mm) working electrode, a Pt wire counter-electrode, and an Ag/AgCl or Ag/AgNO₃ reference electrode in aqueous or organic solutions, respectively. All experimental data are calibrated with reference to the Fc⁺⁰ couple measured using an internal ferrocene standard. For bulk electrolysis, a gas-tight three-compartment cell containing a mercury pool working electrode, a Pt mesh counter electrode and an Ag/AgNO₃ reference electrode was used. Each compartment was separated by a fine porosity glass frit. Typically, an acetonitrile solution of a catalyst (0.5 mM, 8 mL) with 0.1M Bu₄NPF₆ electrolyte was purged with CH₃CN saturated CO₂ for 15 min prior to electrolysis. The gas products were analyzed by gas chromatography (GC) on an Agilent 6890N network GC system (columns: GS-CARBON-PLOT 15 m × 0.32 mm × 1.5 μm; HP-MOLSIV 30 m × 0.32 mm × 12 μm). The CO was quantified using a FID detector via a methanizer, and the H₂ was quantified using a TCD detector. Quantitative detection of formate was performed using a Dionex ICS-1600 ion chromatography system (cell temperature = 35 °C, column temperature = 40 °C, eluent = 0.45 mM carbonate /0.8 mM bicarbonate, flow rate = 1 mL min⁻¹, data collection rate = 5 Hz). Spectroelectrochemical IR (SEC-IR) experiments were performed using a 200 μM OTTE (optically-transparent thin-layer electrode) cell from Specac equipped with an Rh minigrid working electrode, a Rh counter electrode, a Ag wire electrode and CaF₂ windows. Solutions were approximately 2 mM Ru complex and 0.1 M Bu₄NPF₆ and were purged with Ar or CO₂ prior to introduction into the cell via syringe. Data were collected with 2 cm⁻¹ resolution using an MCT detector. Since the Ag wire is a pseudo-reference and changed frequently, the potential was stepped increasingly negative until IR changes were observed. At the commencement of a sequence of IR changes, the potential was stepped again and data collection was repeated.

Collection and Refinement of X-Ray Data. Single crystals of [Ru(tpy)(6DHBP)(OH₂)](CF₃SO₃)(ClO₄) suitable for X-ray analysis were grown from a pH 1.0

triflic acid solution of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2$ containing a few drops of 70% perchloric acid. *Warning: perchlorate salts are potentially explosive and should be handled with caution.* Single crystals of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$ suitable for X-ray analysis were grown from a pH 1.0 HCl $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ solution by slow evaporation of CH_3OH . Single crystals of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$ were obtained upon cooling the resulting solution in a Parr reactor to room temperature. Crystals were mounted on the end of glass fibers, and X-ray data were collected with a Bruker Kappa Apex II diffractometer.

X-ray diffraction data collected at 173 K indicated monoclinic symmetry and systematic absences consistent with space group $P2_1/c$ for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)$ and $C2/c$ for $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$, triclinic symmetry and space group $P\bar{1}$ for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$. These space groups were used for the solution and refinement of the structure. Crystal data are provided in the Table S1. The structures of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)$ and $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$ were solved by the Patterson heavy atom method while $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$ was solved by direct methods.⁵⁰ In the least-squares refinement, anisotropic temperature parameters were used for all the non-hydrogen atoms, except for one nitrogen atom (N11, see Figure 1) of the 6DHBP and the two partial water molecules in $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$. The problem with the anisotropic refinement of N11, which is trans to Cl(1), may be due to disorder. There is likely a partial (<5%) disordering in the crystal in which the tpy ligand remains in place while the Cl and the 6DHBP flip by 180 degrees. Hydrogen atoms were placed at ideal positions and refined as rider atoms except for the H atoms on O16 and O26 of the 6DHBP ligand in $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ and the waters of crystallization in all the structures. The ligand H_2O protons were located on a difference Fourier map and included in fixed positions. The hydrogen atoms on the waters with partial occupancy factors were not included. The data were corrected for absorption using the multi-scan method (SADABS).⁵¹ The isotropic thermal parameters for the hydrogen atoms were determined from the atom to which they are attached.

DFT calculations. All calculations were carried out using DFT (RKS states for closed shells, UKS states for open shells) and the B3LYP functional.⁵²⁻⁵⁵ The ECP28MWB(1f,0g) effective core potential and basis^{56,57} was used for the ruthenium center, and the 6-31+G(d,p) 5d basis set⁵⁸⁻⁶³ was used for all other atoms. All species considered in the suggested reductive deprotonation and CO_2 reduction processes were fully optimized in a continuum model of the solvent, and frequency analyses were carried out to exclude any transition state geometries, and to confirm a minimum in the energy. The CPCM solvation model⁶⁴⁻⁶⁶ as implemented in the Gaussian 09

program package⁶⁷ was used along with UAHF radii⁶⁸ and water or acetonitrile as solvent. TD-DFT calculations with the CPCM solvation model and the same basis set were performed for selected species to help characterize their spectral signature in the UV-vis spectra. The standard Gibbs free energy in aqueous solution was obtained to calculate pK_a values in the manner we previously published.⁶⁹

Results and Discussion

Synthesis, Characterization, and X-ray Structures. The syntheses of $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{OH}_2)]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{Cl})]^+$ ($n = 4, 6$) have been reported⁷⁰ although we used slightly different procedures. Complexation of $[\text{Ru}(\text{tpy})\text{Cl}_3]$ and nDHBP ($n = 4, 6$) in the presence of Et_3N in $\text{EtOH}/\text{H}_2\text{O}$ ($v/v = 4/1$) afforded $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{Cl})]\text{Cl}$ which was treated with $\text{CF}_3\text{SO}_3\text{H}$ in water to form $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2$. These complexes were isolated in the diprotic form of the ligand and spectroscopic characterization agreed with the previous data.⁷⁰ Complexes $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{NCCH}_3)](\text{CF}_3\text{SO}_3)_2$ ($n = 4, 6$) were prepared from the aqua complexes by ligand exchange in CH_3CN . The CO complex was prepared by the reaction of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ with CO in a Parr reactor. When CO is bound to the Ru center, a deprotonated complex $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$ similar to $[\text{Ru}(\text{tpy})(\text{bpyO})(\text{CO})]^+$, which contains a deprotonated pyridinone ligand,⁴⁴ was obtained.

An ORTEP drawing of the cation of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)\cdot\text{H}_2\text{O}$ is presented in Figure 1. The intramolecular hydrogen bond between O(26) and the coordinated water molecule O(11) agrees with the reported structure of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2$ with the primary difference in these structures being the triflate and perchlorate anions.⁷⁰ An intramolecular hydrogen bonding arrangement is present in both structures even though the crystal lattice changes with replacement of a triflate anion with perchlorate in $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)\cdot\text{H}_2\text{O}$ (Figure S1). Complex $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$ was crystallized from water and contains 3.75 waters of crystallization rather than CH_3OH as in the published structure.⁷⁰ In the present $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$, the hydroxy group of the 6DHBP ligand participates in a 2.169 Å intramolecular hydrogen bond with the coordinated chloro ligand in contrast to the reported structure in which the OH hydrogen is H-bonded to a methanol of crystallization. The bond angles of N(41)–Ru(1)–O(11) in $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ and N(41)–Ru(1)–Cl(1) in $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]^+$ are slightly smaller than the 90° of an ideal octahedral configuration reflecting steric repulsion between the aqua/chloro ligand and the hydroxy group. In the structure of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$ the

coordinated 6DHBP is doubly deprotonated which results in a neutral complex. As can be seen in Figure 1, the two deprotonated oxygen atoms of the 6DHBP ligand are involved in hydrogen bonds with water molecules of crystallization. In addition, one of the deprotonated oxygen atoms of the 6DHBP, O(116), forms close intramolecular contacts with the coordinated carbonyl group. The distances O(116)⋯C(161) and O(116)⋯O(161) are 2.588(3) and 2.814(3) Å, respectively. These are similar to the H⋯C and H⋯O contacts of 2.600 and 2.816 Å, which are found in the structure of [Ru(tpy)(bpyO)(CO)]⁺ reported by Tanaka et al.⁴⁴ In [Ru(tpy)(6DHBP-2H⁺)(CO)] the carbonyl is bent away from the 6DHBP ligand while in [Ru(tpy)(bpyO)(CO)] it is bent towards the bpy. This is illustrated by the distance between the nitrogen atom of the ligand involved in these contacts and the oxygen atom of the carbonyl which is 3.902(3) in [Ru(tpy)(6DHBP-2H⁺)(CO)] and 3.716(8) Å in [Ru(tpy)(bpyO)(CO)]. In [Ru(tpy)(bpyO)(CO)] the Ru–C(carbonyl) bond length is 1.862(2) Å and the Ru–C–O bond angle is 173.3(2) degrees while in the bpyO complex the Ru–CO band length is 1.843(5) Å and the Ru–C–O angle is 175.3(4) degrees. The C–O bond length of 1.260(3) Å in [Ru(tpy)(6DHBP-2H⁺)(CO)] is longer than that in the bpyO compound (1.161(7) Å).

Figure 1. X-ray structures of cations of [Ru(tpy)(6DHBP)(OH₂)]²⁺ (top left), [Ru(tpy)(6DHBP)(Cl)]⁺ (top right), and [Ru(tpy)(6DHBP-2H⁺)(CO)] with water molecules that are hydrogen-bonded to the pyridine ligand (bottom).

Ligand Exchange Reactions. The ligand exchange process, for instance coordination of a substrate along with release of a product, is a critical component of catalytic reactions. The ligand

exchange reaction $[\text{Ru}-\text{OH}_2]^{2+} + \text{CH}_3\text{CN} \rightarrow [\text{Ru}-\text{NCCH}_3]^{2+} + \text{H}_2\text{O}$ was examined by electronic absorption spectroscopy. Upon mixing aqueous solutions containing $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ and CH_3CN , the $^1\text{MLCT}$ absorption maximum of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ shifted from 478 to 460 nm (Figure S2), indicating the formation of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$. Kinetic measurements revealed that this reaction is first order in both the ruthenium complex and CH_3CN with a second-order rate constant of $(9 \pm 1) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for the 6DHBP complex. In the case of the 4DHBP complex the reaction is ~ 5 times slower. These results demonstrate that the proximal $-\text{OH}$ group of 6DHBP, which is hydrogen bonded to the aqua ligand, should not hinder ligand exchange. It should be noted that the exchange reaction of $[\text{Ru}(\text{tpy})(\text{N}-\text{N})(\text{OH}_2)]^{2+}$ complexes with large cone angle N-N ligands such as 2,2'-biquinoline or 6,6'-dichloro-2,2'-bipyridine is faster than that with N-N = 2,2'-bipyridine or 1,10-phenanthroline.⁷¹ Our results for the nDHBP complexes are consistent with this published conclusion. The calculated spectra of the exchange reactions model the experimental blue shifts with λ_{max} of the $^1\text{MLCT}$ bands shifting from 452 to 434 nm in the 6DHBP complex and from 450 to 432 nm in the 4DHBP complex (Figure S3).

Acid-Base Titration. The aqueous $\text{p}K_{\text{a}}$ values of complexes $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{OH}_2)]^{2+}$ ($n = 4$ and 6) were measured by a spectrophotometric titration (Figures S4 and S5). The first two $\text{p}K_{\text{a}}$ values of 6DHBP in $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ are 3.2 and 6.0, and are similar to those of the chloro complex (3.4 and 5.8).⁷⁰ Two separate $\text{p}K_{\text{a}}$ values were observable due to the asymmetry of the complex. The third $\text{p}K_{\text{a}}$ was greater than 12 and is assigned as deprotonation of the aqua ligand. This value is reasonable in comparison to $\text{p}[\text{Ru}(\text{tpy})(\text{pynap})(\text{OH}_2)]^{2+}$ ($\text{p}K_{\text{a}} = 11.3$) where one of protons of the water ligand is hydrogen-bonded to the naphthyridine N atom of the pynap ligand.⁴³ For $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$ a single acid/base reaction of 4DHBP was observed with the average $\text{p}K_{\text{a}} = 6.2$ in good agreement with 6.35 reported in $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{Cl})]^+$.⁷⁰ The $\text{p}K_{\text{a}}$ of the aqua ligand in $[\text{Ru}(\text{tpy})(4\text{DHBP}-2\text{H}^+)(\text{OH}_2)]$ is 11.0. Our titration data for $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$ suggest that ligand $\text{p}K_{\text{a}}$ values for $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{Cl})]^+$ of 6.35 and 11.0 were improperly assigned in the literature. The first $\text{p}K_{\text{a}}$ should be assigned to two deprotonations of the ligand while the second is in the range typical of a coordinated aqua ligand produced *in situ* by exchange with chloride. Values of the $\text{p}K_{\text{a}}$ of the bound water ligand in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ and $\text{d}[\text{Ru}(\text{tpy})(\text{pynap})(\text{OH}_2)]^{2+}$ have been reported as 9.7 and 9.1, respectively.^{43,72} The deprotonated nDHBP ligands are stronger electron donating ligands than bpy or bynap,⁷³ rendering the coordinated water molecule more basic. The calculated $\text{p}K_{\text{a}}$ values (2.5, 7.0, and 12.1) of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ reasonably reproduce the experimental data and show that the first proton is removed from the OH group closest to the aqua ligand, the second

proton dissociates from the other OH of 6DHBP- H^+ , and the last proton dissociation is from the aqua ligand (Scheme 1)

Scheme 1. Acid-base properties of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$.

Cyclic Voltammetry. The electrochemical CO_2 reduction by $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{OH}_2)]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ was studied in aqueous solutions (pH 4.3 phosphate buffer; Figures S6-S8), however, proton reduction is the dominant reaction as shown in the CV data and in the GC analysis after bulk electrolysis using a mercury pool working electrode at an applied potential of -1.3 V vs NHE. Therefore, the following experiments were performed in organic solvent.

The free ligands are poorly soluble in CH_3CN and the cyclic voltammetry was recorded in DMF (Figure S9). For these ligands, irreversible waves were observed at -2.11 V (E_p°) and -2.40 V (E_p°) for 6DHBP and ca. -2.3 V (E_p°) and -2.47 V (E_p°) (overlapping) for 4DHBP. Reversible couples were measured at -2.57 V ($E_{1/2}$) for tpy and -2.63 V ($E_{1/2}$) for bpy^{74,75} vs $\text{Fc}^{+/0}$ ($\text{Fc}^{+/0} = 0.45$ V vs SCE in DMF).⁷⁶ While the reduction potential of tpy is more negative than those of 6DHBP and 4DHBP, the measurements correspond to the lowest energy *trans* configurations of the C–C bond(s) of the pyridyl rings indicating that these reduction potentials may not correlate with those of the corresponding Ru complexes. Accordingly, the calculated reduction potentials of *trans-trans*-tpy and *trans*-6DHBP are -1.63 V and -1.53 V in DMF. Conversely, the calculated potential of -0.95 V for the *cis-cis* configuration of tpy is less negative than that of the *cis* configuration of 6DHBP (-1.49 V). A more detailed description of the calculations is presented in Tables S4-S7 and Figure S10 in the SI.

The CV of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ in CH_3CN exhibits two irreversible one-electron reduction waves R1 and R2 at $E_p = -1.70$ V and -1.85 V, respectively, a reversible couple (R3/O₂) at $E_{1/2} = -2.10$ V, and a quasi-reversible couple R4 at $E_{1/2} = -2.35$ V (Table 1 and Figure 2). The doubly deprotonated species $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$ was prepared *in situ* by treatment with two equivalents of Bu_4NOH , and the CV exhibits two reversible redox couples

with $E_{1/2} = -2.10$ and -2.35 V. Data collected in DMF reveal similar behavior (Figure S11). Two irreversible waves are observed at $E_p^c -1.43$ and -1.65 followed by a reversible couple with $E_{1/2} = -1.97$ V. In the presence of 10 equiv Et_3N , the 6DHBP ligands are deprotonated, the irreversible couples are absent, the Et_3NH^+ reduction appears at -1.75V ,⁴⁴ and the reversible couple at -1.97 remains unchanged.

The CV of $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ in CH_3CN (Figure S12) is complicated by insolubility of reduced species as indicated by surface desorption waves. Likewise, precipitation occurred in DMF. By comparison of data in Figure S12 for 4DHBP complexes and data in Figure 2 for 6DHBP complexes, the first composite wave from -1.7 to -2 V vs $\text{Fc}^{+/0}$ for 4DHBP complexes is identified as a three-electron wave. In the presence of base, the first two reductions are absent and a reversible couple remains at $E_{1/2} = -1.88\text{V}$.

Figure 2. CVs of complex $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (1 mM, solid line), after deprotonation with 2 equiv. of Bu_4NOH (dashed line), or after exhaustive $2e^-$ reduction (dotted line) in CH_3CN .

Table 1. Summary of Reduction Potentials.^a

Complex	$E / \text{V vs Fc}^{+/0}$	Reference
$[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$	$-1.70,^b -1.85,^b -2.10, -2.40$	<i>this work</i>
$[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$	$-2.10, -2.35$	<i>this work</i>
$[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$	$-1.7 \text{ to } -1.8,^c -1.9, -2.3$	<i>this work</i>
$[\text{Ru}(\text{tpy})(4\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$	$-1.88, -2.3^b$	<i>this work</i>
<i>trans</i> - $[\text{Ru}(\text{tpy})(\text{bpyO})(\text{CO})]^+{}^d$	$-1.75, -2.17^b$	44
<i>trans</i> - $[\text{Ru}(\text{tpy})(\text{bpyOH})(\text{CO})]^{2+}{}^d$	$-1.50,^b -1.79, -1.95,^b -2.15^b$	44

$cis\text{-Ru(tpy)(bpyO)(CO)]}^{+e}$	$-1.61, -2.23^b$	44
$cis\text{-[Ru(tpy)(bpyOH)(CO)]}^{2+ef}$	$-1.68, -2.24^b$	44
$\text{[Ru(tpy)(bpy)(NCCH}_3\text{)]}^{2+g}$	$-1.64, -1.94$	30

^a In CH₃CN. Potentials reported vs Ag/AgNO₃ in Ref. ⁴⁴ were adjusted to Fc⁺⁰ by subtraction of 0.10 V. Potentials reported vs NHE in Ref. 30 were adjusted to Fc⁺⁰ by subtraction of 0.64 V.

^b E_p^c for an irreversible couple.

^c Overlapping 2e⁻ wave.

^d Isomer with the C=O or C-OH group of bpy *trans* to the CO ligand.

^e Isomer with the C=O or C-OH group of bpy *cis* to the CO ligand.

^f The first and second reduction potentials were assigned as tpy- and bpyOH-localized redox reactions, respectively.⁴⁴

^g The first reduction potential has been assigned as tpy-localized redox reactions.^{30,77}

The cyclic voltammetry of $\text{[Ru(tpy)(nDHBP)(NCCH}_3\text{)]}^{2+}$ is interpreted with reference to the isomeric forms of $\text{[Ru(tpy)(bpyO)(CO)]}^{+}$ and $\text{[Ru(tpy)(bpy)(NCCH}_3\text{)]}^{2+}$ (Table 1).^{30,44} The pyridinone complex *trans*- $\text{[Ru(tpy)(bpyO)(CO)]}^{+}$ undergoes a reversible tpy^{0/-} reduction at -1.75 V while the protonated pyridinol is reduced irreversibly at -1.50 V, and reversibly at -1.79 V. On a second sweep or in the presence of base, the wave at -1.50 V is absent indicating formation of the deprotonated *trans*- $\text{[Ru(tpy)(bpyO)(CO)]}^{+}$ upon electrochemical reduction. The pyridinone complex *cis*- $\text{[Ru(tpy)(bpyO)(CO)]}^{+}$ undergoes a reversible reduction at -1.68 V and an irreversible reduction at -2.24 V while the pyridinol complex *cis*- $\text{[Ru(tpy)(bpyOH)(CO)]}^{2+}$ shows a poorly resolved peak at about -1.7 V and an irreversible reduction at -2.24 V. Tanaka and co-workers noted that H₂ evolution was observed at -1.5 V. They assigned the first and second reductions of *cis*- $\text{[Ru(tpy)(bpyO)(CO)]}^{+}$ as tpy- and bpyO-localized redox reactions, respectively. The tpy-based reduction of -1.75 V for *trans*- $\text{[Ru(tpy)(bpyO)(CO)]}^{+}$ is slightly cathodic of that observed for $\text{[Ru(tpy)(bpy)(NCCH}_3\text{)]}^{2+}$ (-1.64 V) and is logical considering the electron-rich nature of the bpyO ligand. Likewise, the two irreversible reductions in $\text{[Ru(tpy)(nDHBP)(NCCH}_3\text{)]}^{2+}$ seem to be associated with sequential reductive deprotonation events of the DHBP ligands. This phenomenon is proven by the coincidence of the first *reversible* redox wave in the absence or presence of base or after exhaustive two-electron reduction of a solution of $\text{[Ru(tpy)(6DHBP)(NCCH}_3\text{)]}^{2+}$ (Figure 2). We recently reported a similar reaction in $\text{[Re(nDHBP)(CO)}_3\text{Cl]}$ (n = 4 and 6) for which reductive electrolysis consecutively generates singly and doubly deprotonated complexes in CH₃CN, which are equivalent to those obtained by chemical deprotonation.⁴⁵

It is widely accepted that the first reduction of $[\text{Ru}(\text{tpy})(\text{bpy})\text{L}]^{\text{m}+}$ ($\text{L} = \text{halide}$, $\text{m} = 1$; $\text{L} = \text{CH}_3\text{CN}$, $\text{m} = 2$) yields a tpy radical anion.^{30,77} The $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{NCCH}_3)]^{2+}$ should retain this property considering the electron rich nature of the DHBP ligands. In fact, the DFT calculations for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ predict the first reduction is the tpy-based reduction as shown in detail below. Thus, the irreversibility of the first redox waves in this work and in that reported for $[\text{Ru}(\text{tpy})(\text{bpyO})(\text{CO})]^+$ is an interesting phenomenon. Furthermore, electrochemical reductive deprotonation of complexes with protic ligands has been reported for $[\text{Re}(\text{bpy})(\text{imidazole})(\text{CO})_3]$ and $[\text{Re}(\text{phen})(\text{imidazole})(\text{CO})_3]$ ^{78,79} in which the initial $\text{bpy}^{\bullet-}$ or $\text{phen}^{\bullet-}$ radical is quasi-stable but the deprotonated imidazolate slowly forms. The reaction is formally inter-ligand electron transfer with net loss of an H atom but the dubious fate of the net H atom loss was not discussed.^{78,79}

In the present case, no tpy radical intermediates were detected; therefore, the reaction must be a fast and possibly inter-ligand electron-transfer reaction. In the case of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, bulk electrolysis in an air-tight vessel at the potential of the second reduction liberated H_2 suggesting a possible reductive deprotonation mechanism.

Chemical Reduction. To further investigate the reduction/deprotonation of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, chemical reduction with sodium amalgam was performed and monitored by UV-vis spectroscopy. In this experiment, the reaction of Na with the phenolic OH groups generates the doubly deprotonated $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$, which can be reduced again at tpy as shown in Figure 3. For comparison, Figure 3 includes the acid/base titration data for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ for which similar features were observed. Decreased absorbance for chemical deprotonation with Na vs OH^- is attributed to precipitation or slow decomposition. The stepwise red shifts of the $^1\text{MLCT}$ band are consistent with destabilization of the Ru highest occupied d orbital as 6DHBP is deprotonated. After deprotonation, a third change in the spectrum was observed for Na-reduction of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$ to $[\text{Ru}(\text{tpy}^{\bullet-})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^-$. This final step includes loss of absorptivity at 370 nm and formation of new bands with $\lambda_{\text{max}} = 450$ and 550 nm. The features of the final spectrum are similar to those of singly reduced $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ and $[\text{Ru}(\text{tpy})_2]^{2+}$ verifying reduction of the terpyridine ligand after deprotonation of the 6DHBP ligand.^{77,80}

Figure 3. Top: sodium reduction of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCCH}_3)]^{2+}$ in CH_3CN . Bottom: Acid-base titration of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ in water. Initial spectra are shown in green, singly deprotonated species in red, doubly deprotonated species in blue, and doubly deprotonated / $1e^-$ reduced species in black.

The experimental UV-vis spectra of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ and $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCCH}_3)]^{2+}$ and their deprotonated species in water and acetonitrile were successfully reproduced and assigned by a TD-DFT study (Figures S13 and 14). Characteristic ¹MLCT and ligand-to-ligand charge transfer (¹LLCT) bands were observed. The dominant transitions of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCCH}_3)]^{2+}$ and $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ in the protonated and deprotonated complexes in order of increasing energy are $\text{Ru}(\text{d}\pi) \rightarrow \text{tpy}(\pi^*)$, $\text{Ru}(\text{d}\pi) \rightarrow 6\text{DHBP}(\pi^*)$, and $6\text{DHBP}(\pi) \rightarrow \text{tpy}(\pi^*)$ charge transfer bands. The assignment of electronic transitions (nm) and the oscillator strengths (f) in water and in acetonitrile are summarized in Tables S6 and S7. Although the calculated absorption maxima are shifted, the features of the experimental electronic transitions are reasonably reproduced.

Proposed Mechanism of Hydrogen Production via Reductive Deprotonation. Calculations were carried out on $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCCH}_3)]^{2+/1+/0}$ in acetonitrile, with and without the

coordinated solvent molecule. A proposed “proton catalyzed hydrogen production” mechanism has been described recently for similar rhenium complexes⁴⁵ for which *electrochemical reduction and chemical deprotonation lead to the same Re complex*. The proposed mechanism for $\text{Re}(\text{CO})_3(\text{nDHBP})\text{Cl}$ shows that a reduced nDHBP ligand is protonated and that leads to the production of $\frac{1}{2} \text{H}_2$ in each one-electron reduction step. In the present study the ruthenium complex has a tpy ligand that is likely to be the site of initial reduction and that may accept and lose a proton, thus increasing the number of possible intermediates and pathways. The proposed mechanism for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ shows that the production of hydrogen during the reductive deprotonation via the 6DHBP ligand is thermodynamically feasible (see Figure 4). Detailed descriptions of other possible intermediates (with a proton on the tpy ligand, the formation of a ruthenium hydride intermediate, etc.) that might be formed are shown in Figures S15 and S16 and Table S8. The structures of possible intermediates are shown in Scheme 2.

Hydrogen production requires two protons and two electrons. Consideration of the initial Ru complex with a proton-responsive 6DHBP ligand (the source of the two protons), an initial “reservoir” of additional species required for the reaction consists of two electrons and one proton (the latter to initiate each step of the reaction but is returned to the solution after each step). Since acetonitrile is a polar aprotic solvent with $\text{p}K_a$ 25, it is not easy to measure the experimental pH. The calculated $\text{p}K_a$ of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, the strongest acid in the solution, is 15.69. Thus the ruthenium complex present in 1 mM concentration is the source of a proton in the solution. We have estimated the experimental pH to be 9.34 by using the calculated $\text{p}K_a$ of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and the concentration of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ used in the experiment (see Table S8 for details).

The first irreversible peak R1 observed in the CV experiment (Figure 2, $E_p = -1.06$ eV vs NHE) can be assigned to a reduction of the tpy ligand ($E_{\text{calc}} = -1.30$ eV vs NHE) associated with CH_3CN ligand dissociation and by inter-ligand electron transfer from the $\text{tpy}^{\bullet-}$ to the 6DHBP accompanied by proton transfer from the solution to the C5 position (see Scheme 2) of the transient $[\text{Ru}(\text{tpy})(6\text{DHBP}^{\bullet-})]^+$. This net H-atom addition forms $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}})]^{2+}$ (Scheme 2), a 6DHBP radical species. A number of possibilities were taken into consideration as the site for an external (i.e., from the solution) or an internal (i.e., from an $-\text{OH}$ of the 6DHBP ligand) proton (e.g., formation of ruthenium hydride, placing the proton on the tpy ligand or different locations of the 6DHBP ligand as shown in Scheme 2), and the one with the lowest free energy was selected (see Figure S15 and Table S8 for details). Owing to an overpotential being

applied in the CV experiments, the slightly uphill proton transfer from the solution to $[\text{Ru}(\text{tpy}^{\bullet-})(6\text{DHBP})]^+$ to form $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{c}})]^{2+}$ is thermodynamically feasible.

Scheme 2. Calculated structures of the investigated species and the pK_a values associated with their losing the proton indicated in red. The tpy ligand is omitted for clarity in some structures.

After the first combined one-electron reduction and proton transfer step, the reservoir contains one electron and a solvent molecule. The $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}})]^{2+}$ species is capable of releasing $\frac{1}{2} \text{H}_2$ and H^+ to the solution in an exoergic process through a net disproportionation reaction.

This process could involve an intermolecular association of the $\text{H}^\bullet$ radicals at the C5 carbon atoms and the loss of a proton from an $-\text{OH}$ group on the two 6DHBP ligands to form H_2 and a two protons in solution. After this step, the complex has become $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)(\text{S})]^+$ and the reservoir species are an electron, $\frac{1}{2}\text{H}_2$ and H^+ .

The second irreversible peak R2 (see Figure 2, $E_p = -1.21$ eV vs NHE) can be assigned as a reduction ($E_{\text{calc}} = -1.53$ eV vs NHE) of the singly-reduced and singly-deprotonated species, $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)(\text{S})]^+$. This reduction is coupled to proton transfer from solution and loss of a solvent molecule to form $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$, the possible intermediate of lowest free energy. Here $+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}}$ indicates the protonation of the C5 site of the deprotonated hydroxypyridine ring proximal to the $-\text{O}$ group. Again, a number of possibilities were considered as the site for an external or internal proton, and the one with the lowest free energy was selected (see Figure S16 and Table S8). Thus the next proposed step is the exoergic production of $\frac{1}{2}\text{H}_2$ and H^+ via a net disproportionation of $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$ to produce the experimentally observed $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H})(\text{S})]^0$ ($E_{\text{calc}} = -1.98$ vs NHE).

The reservoir after this second reduction step contains H_2 and H^+ so that the net overall reaction is

in agreement with the experimental observation that the same product complex is obtained by double deprotonation and double reduction of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{S})]^{2+}$.

Figure 4. The energetics of hydrogen production at pH 9.34, the calculated pH of a 1 mM solution of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{S})]^{2+}$. The presented structures are associated with a reservoir of two electrons and a proton that are needed to produce H_2 . Owing to the number of possibilities for selecting an active site for proton reduction within the complex, only species with the lowest free energy at each stage of reduction are presented along with the corresponding reservoir species (in orange font). Since the $\text{p}K_a$ of CH_3CN is 25, the proton in the reservoir comes from $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{S})]^{2+}$ with a calculated $\text{p}K_a$ of 15.69. $\text{S} = \text{NCCH}_3$. ET denotes electron-transfer steps, and PCET denotes proton-coupled, electron-transfer steps.

Spectroelectrochemical Infrared Spectroscopy (SEC-IR). In a previous report, the reductive deprotonation of $[\text{Re}(\text{CO})_3(\text{nDHBP})\text{Cl}]$ was studied by SEC-IR.⁴⁵ For these complexes, the strong ν_{CO} vibrations were diagnostic, but changes in the bipyridine vibrations were also apparent. Notably, a band at *ca.* 1510 cm^{-1} appeared in the doubly deprotonated species and was assigned as a pure phenolate $\text{C}=\text{O}$ stretching mode according to DFT modeling. The SEC-IR data from 1500 to 1650 cm^{-1} collected during reductive deprotonation of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ are shown in Figure 5. The initial spectrum exhibits two bands at 1608 and 1587 cm^{-1} , which by comparison to $[\text{Ru}(\text{bpy})_3]^{2+}$, are assigned as bipyridine stretching modes.⁸¹ Upon initial

electrolysis, the absorbance at 1608 cm^{-1} decreased and a weak, broad band appeared at 1612 cm^{-1} . This species is tentatively assigned as the $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}})]^{2+}$ formed via the first two steps of Figure 4. Next, the 1612 cm^{-1} band increased and broad absorptions appeared at 1542 and 1521 cm^{-1} (Figure 5a, black spectrum). This species is assigned as $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)]^+$ in accord with the appearance of ligand C=O stretches at 1542 and 1521 cm^{-1} . The next reduction caused a shift of the 1612 cm^{-1} band to 1610 cm^{-1} and appearance of a sharp feature at 1512 cm^{-1} . For comparative purposes, the experiment was repeated using $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ (Figure 5b). In this case, no changes were observed from 1510 – 1540 cm^{-1} during the first two reductions. A band at 1603 cm^{-1} decreased in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^+$ while the spectrum of $[\text{Ru}(\text{tpy})(\text{bpy})]$ showed bands at 1570 , 1587 , and 1606 cm^{-1} . The vibrational modes unique to the hydroxy-bipyridine ligand of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ from 1510 – 1540 cm^{-1} are clear when noting the absence of these features in the $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ congener. Further support for reductive deprotonation is available by comparison to $[\text{Re}(\text{CO})_3(6\text{DHBP})\text{Cl}]$ (Figure 5c) which exhibits IR changes for sequential reductive deprotonations which are very similar to those of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$. Additionally, theoretical spectra obtained by DFT calculation of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and six-coordinate $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$ accurately predict the spectral changes observed upon deprotonation. Two bpy stretching modes are calculated at 1636 and 1616 cm^{-1} for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$. For the singly-deprotonated species, a 1516 cm^{-1} band and two medium-intensity bands are predicted at 1620 and 1634 cm^{-1} . For the doubly-deprotonated species, new strong absorptions due to the C=O stretch are predicted at 1516 cm^{-1} together with a bpy stretching mode at 1627 cm^{-1} (see Figure S17).

Figure 5. Spectroelectrochemical infrared spectroscopy of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (a), $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ (b), and $[\text{Re}(\text{CO})_3\text{Cl}(6\text{DHBP})]$ (c) in CH_3CN . For complexes with 6DHBP ligands, red spectra are initial species, blue spectra are singly deprotonated species, and black spectra are products of double deprotonation.

Reactivity Toward Carbon Dioxide. Catalytic reduction of CO_2 was initially evaluated by CV. In CO_2 -saturated CH_3CN , current enhancement was observed for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ indicating the interaction of reduced complexes with CO_2 , but solubility remained problematic for $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ and this complex was not studied further. For $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ the current at $E_p = -2.13$ V increased in proportion to $[\text{CO}_2]^{1/2}$ indicating a process which is first order in CO_2 , and the current enhancement reached ~ 1.8 (Figure S11). The catalytic wave for the deprotonated $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$ notably appeared at its first reduction (Figure 6). The strong electron donating ability of the anionic $[6\text{DHBP}-2\text{H}]^{2-}$ ligand likely increases the nucleophilicity of Ru in $[\text{Ru}(\text{tpy}^{\bullet-})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^{-1}$ while the *trans* labilization effect of $[6\text{DHBP}-2\text{H}]^{2-}$ can accelerate exchange of CH_3CN for CO_2 . The $[\text{CO}_2]^{1/2}$ dependence is non-linear suggesting saturation kinetics while the peak-shape indicates deactivation processes are occurring (consumption of CO_2 , product inhibition, product precipitation, etc.) since sustained catalysis in the presence of excess substrate should show a current plateau.⁸² Further support for deactivation is evident in the second reduction wave which is $[\text{CO}_2]$ -independent and does not accelerate catalysis and is therefore assigned as reduction of an intermediate or product of catalysis. As will be discussed below, bulk electrolysis generates a catalytically inactive species.

Figure 6. CVs of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$ in Ar-saturated CH_3CN and in N_2/CO_2 mixtures with $[\text{CO}_2]$ concentrations of 8, 28, 84, and 280 mM (bottom to top). Inset: plot of peak current at -2.11 V divided by the current of the 1-electron wave at -2.2 V vs $[\text{CO}_2]^{1/2}$.

Controlled potential electrolysis experiments were carried out in order to examine the products of CO_2 reduction using $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$

in acetonitrile. When a glassy carbon electrode was used in the electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, current dropped within 4 minutes due to the insulating effect of precipitation on the electrode (Figure S18). Therefore, a mercury pool electrode was used (Figure S19), and the results are summarized in Table S9. Electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ at -2.3 V generated small amounts of CO ($0.54 \mu\text{mol}$) and formate ($0.76 \mu\text{mol}$) with Faradaic efficiencies of 4.1% and 5.9%, respectively. A trace amount of H_2 was also detected. Complex $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ produced $2.1 \mu\text{mol}$ of CO and $2.6 \mu\text{mol}$ of formate (FE = 11% and 14%, respectively). Formate and bicarbonate were detected by ^1H and ^{13}C NMR spectroscopy after electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (Figure S20) suggesting CO_2 as the oxide acceptor in the production of CO and formate. Electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$ for 2 h at -2.50 V yielded small amounts of H_2 ($1.6 \mu\text{mol}$, FE = 6%) and CO ($1.8 \mu\text{mol}$, FE = 7%). Electrolysis results obtained in this work differ greatly from the reported electrocatalysis using $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ in which CO and formate were produced in 76% and 20% charge yields at a glassy carbon electrode.³⁰ We repeated the $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ at the Hg pool electrode and obtained CO and formate with 29.8 % and 8.3 % charge yields, respectively. While the efficiency of this catalyst is clearly lower at Hg, the adverse effects of the hydroxy groups on the bpy ligand catalysis of CO_2 reduction are evident in preparative scale experiments. We should point out that under the same conditions, $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(4,4'\text{-tBu}_2\text{-bpy})(\text{CO})_3\text{Cl}]$ gave 91% and 100% Faradic efficiencies for CO production.

In order to scrutinize the poor catalytic performance, we investigated the products of electrolysis by mass spectrometry and IR spectroscopy (Figures S20-S21 and Table S10). After bulk electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ under CO_2 , KPF_6 was added to induce precipitation. The IR spectrum of this precipitate exhibits peaks at 1940, 1685, 1644, and 1604 cm^{-1} (Figure 7a).

SEC-IR experiments were executed on $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ under catalytic conditions. Initially, the ligand OH protons are lost sequentially as discussed above without significant interaction with CO_2 (solid red to blue to green spectra). Further reduction of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$ triggered CO_2 reactivity as indicated by the appearance of a broad band at 1930 cm^{-1} (Figure 7b). New IR bands were also observed at 1349, 1300, and 1214 cm^{-1} (not shown). Intense peaks at 1684, 1645, and 1605 cm^{-1} appeared; however, these peaks were also observed in control experiments in the absence of catalyst. Apparently the Rh mesh electrode exhibited significant activity for CO_2 reduction and the peaks at 1684, 1645, and 1605 cm^{-1} were observed indicating that these features are due to a

combination of dissolved or adsorbed carbonate and formate, and are indistinguishable from ruthenium metallocarboxylate intermediates.

Figure 7. IR spectra of the precipitate obtained after electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ under CO_2 and re-dissolved in CH_3CN (a), SEC-IR data for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (b) and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ (c).

For comparison, the SEC-IR results for $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ under CO_2 are shown in Figure 7c. Initial reduction leads to an immediate growth of peaks at 1950 and 1900 cm^{-1} that were not present during electrolysis without CO_2 . A feature at 1841 cm^{-1} grew in intensity when the potential was further decreased. Peaks at 1350, 1300, and 1214 cm^{-1} appeared similarly to experiments with $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$.

Several of the IR peaks can be assigned with reasonable accuracy with reference to literature data (Table 2). Although the electrode reaction yielded peaks from 1586 to 1684 cm^{-1} , the contribution of CO_2 bound to the catalyst to the IR data in this region is confirmed by the precipitation experiment shown in Figure 7a. The 1618 cm^{-1} and 1608 cm^{-1} C=O stretch of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OCHO})]^+$ or dissolved formate, respectively, are also found in this region.^{83,84}

Table 2 Summary of Infrared Data.

Complex	ν	Reference
$\{K[Ru(tpy)(CO)(6DHBP-2H^+ + 2CO_2)]\}^+{}^a$	1940, 1685, 1644, 1604	<i>this work</i>
$[Ru(tpy)(6DHBP-2H^+)(CO)]^b$	1984	<i>this work</i>
$[Ru(tpy)(6DHBP-2H^+ + 2CO_2)(CO)]$	1930 ^c	<i>this work</i>
$[Ru(tpy)(bpy)(CO)]^+$	1950	<i>this work</i>
$[Ru(tpy)(bpy)(CO)]^0$	1900	<i>this work</i>
$[Ru(tpy)(bpy)(CO)]^-$	1841	<i>this work</i>
$[Ru(tpy)(bpy)(CO)]^{2+}$	2004	29
$[Ru(tpy)(bpy)(C(O)OH)]^+$	1653 ^d	29
<i>trans</i> - $[Ru(tpy)(bpyO)(CO)]^+$	1979, 1620, 1605	44
<i>trans</i> - $[Ru(tpy)(bpyO)(CO)]^0$	1932, 1618, 1602	44
<i>trans</i> - $[Ru(tpy)(bpyO)(CO)]^-$	1853, 1595, 1581	44
<i>cis</i> - $[Ru(tpy)(bpyO)(CO)]^+$	1996, 1612	44
<i>cis</i> - $[Ru(tpy)(bpyO)(CO)]^0$	1950,	44
<i>cis</i> - $[Ru(tpy)(bpyO-CO)]^-$	1587 ^e	44
$[Ru(bpy)_2(CO)_2]^{2+}$	2091, 2039	29
$[Ru(bpy)_2(CO)(CHO)]^+$	1950, 1608	85
$[Ru(tpy)(bpy)(OCHO)]^+$	1618, 1318	83
<i>cis</i> - $[Ru(dmpe)_2(OCHO)_2]$	1613, 1317	86

^a Precipitate obtained from bulk electrolysis and isolated by addition of KPF₆.

^b Synthesized independently.

^c Observed *in-situ* during SEC-IR experiments.

^d Stretching mode of the O=C=O

^e Metallacycle formed by the reaction of bpyO with bound CO.

The most notable differences in SEC-IR data for $[Ru(tpy)(6DHBP)(NCCH_3)]^{2+}$ and $[Ru(tpy)(bpy)(NCCH_3)]^{2+}$ are found in the 1850–1950 cm⁻¹ region. Peaks at 1950 and 1900 cm⁻¹ appeared during the first reduction for $[Ru(tpy)(bpy)(NCCH_3)]^{2+}$ while the 1841 cm⁻¹ signal required more negative potentials. The electrochemical reduction of CO₂ to CO catalyzed by $[Ru(tpy)(bpy)(NCCH_3)]^{2+}$ has been studied in detail.³⁰ The proposed initiation step is the reaction of CO₂ with the 2e⁻ reduced complex as indicated in either eq. 4 or eq. 5.⁷⁷

Previous work³¹ suggested that further $2e^-$ reduction of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO}_2^{2-})]^0$ to $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO}_2^{2-})]^{2-}$ followed by the reaction with CO_2 as an oxide acceptor could yield $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^0$ and CO_3^{2-} ; (eq 6 and 7) however direct observation of the carbonyl intermediate was absent.

The metal carbonyl as a precursor to CO is formed by the reaction of the metallocarboxylate with protons or CO_2 yielding water and carbonate byproducts, respectively. The data in Figure 7c suggest that ruthenium carbonyl species are formed at positive potentials in contrast to those assigned to reduction to $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO}_2^{2-})]^{2-}$ in the literature. We interpret this observation as the reaction of the metallocarboxylic acid $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO}_2^{2-})]^0$ with CO_2 or H^+ without further reduction, thereby yielding the $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{2+}$ species at mild potentials. At the applied potential, the $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{2+}$ ($\nu_{\text{CO}} = 2004 \text{ cm}^{-1}$) will be reduced to $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^+$. The CV of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^+$ exhibits a reversible $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{+/0}$ couple, suggesting the possible observation of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^-$ with further reduction due to the slow loss of CO. Thus the set of IR peaks at 1950, 1900, and 1841 cm^{-1} are assigned to a series of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{+/0/-}$ complexes similarly to *trans*- $[\text{Ru}(\text{tpy})(\text{bpyO})(\text{CO})]^+$ (Table 2) and are observed due to slow CO dissociation. The two electron reduction of *cis*- $[\text{Ru}(\text{tpy})(\text{bpyO})(\text{CO})]^+$ is reported to form the five-membered metallacycle by the attack of the pyridinato oxygen at the carbon atom of the CO ligand ($\nu_{\text{O-C-O}}$ at 1587 cm^{-1}). In contrast to the observation of several oxidation states in $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{+/0/-}$, a single oxidation state of a metal carbonyl with stretching band at 1930 cm^{-1} was observed upon reduction of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ at potentials corresponding to the catalytic wave by CV. A precipitate, which was manipulated in air, formed during a controlled potential electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ under CO_2 and exhibits 1940 cm^{-1} band upon re-dissolution suggesting equivalence of the species measured during SEC-IR and obtained on a preparatory scale.

The identity of the isolated precipitate was probed by mass spectrometry after re-dissolving the solid in methanol (Figure S21). The major peak at $m/z^+ = 676.1$ agrees well with

$\{[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)]^0 + 2\text{CO}_2 + \text{CO} + \text{K}^+\}^+$ (calcd. 675.98). Additional peak assignments for minor components are provided in Table S10. The presence of two CO_2 and one CO in the major species provides insight regarding the reaction of CO_2 with Ru-nDHBP complexes. The reaction of CO_2 with reduced quinone,^{87,88} 9,10-phenanthrenequinone,⁸⁹ and quinacridone⁹⁰ to form organic carbonates is known from the literature. These compounds do not catalyze CO_2 reduction but can function as reversible CO_2 carriers. On the basis of these findings, the species $[\text{M} - 2\text{H}^+ + 2\text{CO}_2 + \text{CO} + \text{K}^+]^+$ is proposed as a *bis*-carbonate complex with a structure shown in Figure 8, and DFT calculations support this conclusion (Figure S22). The calculated CO_2 vibrations are $\sim 1720\text{--}1747\text{ cm}^{-1}$, while the stretching mode of the CO ligand is 2010 cm^{-1} in reasonable agreement with the calculated 1984 cm^{-1} of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]^0$ and 2004 cm^{-1} of the $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{2+}$ (Table 2).

Figure 8. Representation of $\{\text{K}[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+ + 2\text{CO}_2)(\text{CO})]\}^+$ and its calculated and observed mass spectra.

These observations explain the poor electrocatalytic efficiency of the Ru-nDHBP complexes. Formation of the metal carbonyl is difficult owing to a combination of negative standard potentials and precipitation of intermediates as observed during the bulk electrolysis. While the nature of the precipitate is not clear at this stage, it must be a neutral-charged species such as $[\text{Ru}(\text{tpy})(6,6'-(\text{O}_2\text{CO})_2\text{bpy})(\text{NCCH}_3)]^0$ shown in Scheme 2. Additionally, the once-formed carbonyl is stable against product release. In consideration of these findings, the total charge consumption during bulk electrolysis can be assigned (Scheme 2). During electrolysis of $5\text{ }\mu\text{mol}$

of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, 26.5 μmol of electrons were consumed. In all, 2.6 μmol generated CO and formate, 10 μmol were used to deprotonate the ligands (which reacted with 2 equiv. CO_2) and 10 μmol were used to convert 1 free CO_2 to a bound CO. The difference of 1 μmol is within uncertainty.

Scheme 2. Deactivation of the catalyst during electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ in the presence of CO_2 .

Conclusions

$[\text{Ru}(\text{tpy})(\text{bpy})(\text{L})]^{2+}$ analogues $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ were examined for electrochemical CO_2 reduction to probe the effects of proton responsive ligands and pendent bases in the second coordination sphere. The introduction of a pendent base proximal to the catalytic center introduces the possibility of rapid protonation or protonolysis of intermediates. Unexpectedly, the first two reductions of the complexes are irreversible due to reductive deprotonation of the ligands. This chemistry was investigated by acid/base titration, chemical reduction with Na/Hg ($E = -2.0$ V vs NHE^{91}), cyclic voltammetry, spectroelectrochemical IR spectroscopy, and DFT calculations. All data indicate reductive deprotonation followed by a third reduction of the tpy which is electrochemically reversible. Under CO_2 , the tpy-based reduction triggers reactivity with CO_2 ; however, catalysis is inefficient in preparative scale experiments. The phenomena responsible for poor catalysis were

investigated by comparison of spectroelectrochemical IR data for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ to the active catalyst $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$. While both complexes undergo reaction of CO_2 to form metallocarboxylic acids, three ruthenium carbonyl species $[\text{Ru}(\text{tpy})(\text{bpy})(\text{CO})]^{+/0/-}$ were formed during reduction of the known catalyst but a single Ru–CO was formed during reduction of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$. The latter is a deactivation pathway since CO is not released. The formulation of this species was investigated by mass spectrometry and is consistent with $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^++2\text{CO}_2)(\text{CO})]$ in which CO_2 has reacted with deprotonated ligands to form carbonates much like the well-known chemistry of reduced quinones. This investigation highlights possible deactivation pathways during electrocatalytic reduction of CO_2 .

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TOC synopsis and graphic

What exactly is “reductive deprotonation” (net loss of an H atom) in metal complexes containing weak acid ligands? The $[\text{Ru}(\text{tpy})(4,4'\text{- and }6,6'\text{-(OH)}_2\text{bpy})(\text{NCCH}_3)]^{2+}$ are new examples that form $[\text{Ru}(\text{tpy})(4,4'\text{- and }6,6'\text{-(O}^-\text{)}_2\text{bpy})(\text{NCCH}_3)]$ upon electrolysis. Spectroelectrochemical-IR measurements and DFT calculations suggest a mechanism of ligand non-innocence whereby sequential reductions, ligand protonations, and net disproportionations yield singly- and doubly-deprotonated molecules and H_2 . Negative consequences for electrocatalytic CO_2 reduction are explained by ligand reactivity and precipitation of a deactivated catalyst.

A Non-Innocent Proton-Responsive Ligand Facilitates Reductive Deprotonation and
Hinders CO₂ Reduction Catalysis in [Ru(tpy)(6DHBP)(NCCH₃)]²⁺ (6DHBP = 6,6'-
(OH)₂bpy)

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Synthesis and characterization of Ru complexes

Synthesis of [Ru(tpy)(6DHBP)(Cl)]Cl. To a mixture of [Ru(tpy)Cl₃] (60 mg, 136 μmol), 6DHBP (26 mg, 138 μmol) and Et₃N (0.4 mL) was added 20 mL of EtOH/H₂O (v:v = 4:1). The resulting solution was purged with Ar for 10 min then heated at reflux for 4 h. After cooling, solvents were removed by rotary evaporation. The residue was treated with 5 mL H₂O and a few drops of conc. HCl under sonication. The resulting solution was left to stand for 4 h after which a black solid was collected by filtration and washed with cold water. Addition of LiCl to the filtrate yielded additional product. The solid was re-dissolved in MeOH, filtered to remove solids, and evaporated to yield the desired product (24 mg, 30% yield). ¹H NMR (400 MHz, CD₃OD, 25 °C) δ (ppm: 6.24 (d, *J* = 8.13, 1H), 7.29 (d, *J* = 8.01, 1H), 7.40 (t, *J* = 6.54, 2H), 7.54 (t, *J* = 8.04, 1H), 7.88 - 8.01 (m, 5H), 8.07 (t, *J* = 7.95, 1H), 8.16 (t, *J* = 7.95, 1H), 8.22 (d, *J* = 7.64, 1H), 8.47 (d, *J* = 8.07, 2H), 8.52 (d, *J* = 8.07, 2H). MS (ESI): *m/z*⁺ = 553.9 ([M-2Cl-H+MeOH]⁺, calc'd = 554.08), 522.2 ([M-2Cl-H]⁺, calc'd = 522.05). Anal. Calcd for C₂₅H₁₉Cl₂N₅O₂Ru·2H₂O: C, 47.70; H, 3.68; N, 11.13. Found: C, 47.38; H, 3.34; N, 10.91.

Synthesis of [Ru(tpy)(4DHBP)(Cl)]Cl. To a mixture of [Ru(tpy)Cl₃] (176 mg, 400 μmol), 4DHBP (76 mg, 404 μmol) and Et₃N (0.5 mL) was added 100 mL of EtOH/H₂O (v:v = 4:1). The resulting solution was purged with Ar for 10 min then heated at reflux for 6 h. The mixture was concentrated to ca. 5 mL, and 1 M NaOH aqueous solution was added dropwise to adjust the pH

to 11. Insoluble material was removed by filtration, and conc. HCl was added to pH 8. A black precipitate formed, which was isolated and re-dissolved in boiling MeOH/H₂O (v:v = 4:1; 50 mL) containing 500 mg of NaCl. The volume was reduced to *ca.* 5 mL, and then 0.5 mL of conc. HCl was added dropwise. The resulting precipitate was isolated, washed with dilute HCl (pH 1), and dried under vacuum (yield: 140 mg, 59%). ¹H NMR (400 MHz, CD₃OD, 25 °C) δ (ppm): 6.42 (dd, *J* = 6.50, 2.32, 1H), 6.81 (d, *J* = 6.36, 1H), 7.30–7.44 (m, 3H), 7.68 (d, *J* = 2.14, 1H), 7.81 (d, *J* = 5.07, 2H), 7.90 (t, *J* = 7.79, 2H), 7.97 (d, *J* = 2.10, 1H), 8.06 (t, *J* = 8.10, 1H), 8.49 (d, *J* = 8.19, 2H), 8.59 (d, *J* = 8.07, 2H), 9.76 (d, *J* = 6.30, 1H). MS (ESI): *m/z*⁺ = 558.1 ([M–Cl]⁺, calcd = 558.03).

Synthesis of [Ru(tpy)(6DHBP)(OH₂)](CF₃SO₃)₂. A vial containing 229 mg of complex [Ru(tpy)(6DHBP)(Cl)]Cl was treated with 1 mL trifluoromethanesulfonic acid. The mixture was stirred at 50 °C for 1.5 h with the vial open to air then 2 mL of water was added together with a small amount of ascorbic acid. An additional 2 mL of water was added to form a precipitate which was isolated by filtration, washed with pH 1.0 CF₃SO₃H and dried under vacuum to yield 170 mg of the title compound in 53% yield. ¹H NMR (400 MHz, D₂O, 25 °C) δ (ppm): 6.34 (d, *J*

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= 8.25, 1H), 7.28 (dd, *J* = 7.12, 2.17, 1H), 7.38–7.42 (m, 2H), 7.57 (t, *J* = 8.04, 1H), 7.82 (d, *J* = 7.09, 1H), 7.92 (d, *J* = 5.32, 2H), 7.99 (td, *J* = 7.87, 1.44, 2H), 8.07–8.16 (m, 3H), 8.37 (d, *J* = 8.01, 2H), 8.41 (d, *J* = 8.13, 2H). MS (ESI): *m/z*⁺ = 539.8 ([M–2CF₃SO₃–H]⁺, calcd = 540.06). Anal. Calcd for C₂₇H₂₁F₆N₅O₉RuS₂: C, 38.67; H, 2.52; N, 8.35. Found: C, 38.48; H, 2.66; N, 8.18.

Synthesis of [Ru(tpy)(4DHBP)(OH₂)](CF₃SO₃)₂. The procedure similar to the synthesis of [Ru(tpy)(6DHBP)(OH₂)](CF₃SO₃)₂ was used yielding 35 mg [Ru(tpy)(4DHBP)(OH₂)](CF₃SO₃)₂. ¹H NMR (400 MHz, D₂O with a small amount of ascorbic acid) δ (ppm): 6.31 (dd, *J* = 6.57, 1.99, 1H), 6.82 (d, *J* = 6.36, 1H), 7.27 (t, *J* = 6.63, 2H), 7.42 (dd, *J* = 6.48, 2.14, 1H), 7.60 (d, *J* = 2.02, 1H), 7.81 (d, *J* = 5.44, 2H), 7.87 (t, *J* = 7.98, 2H), 7.93 (d, *J* = 2.10, 1H), 8.06 (t, *J* = 8.00, 1H), 8.34 (d, *J* = 8.07, 2H), 8.46 (d, *J* = 8.13, 2H), 9.11 (d, *J* = 6.36, 1H). MS (ESI): *m/z*⁺ = 571.9 ([M–CF₃SO₃–H₂O]⁺, calcd = 572.01). Anal. Calcd for C₂₇H₂₁F₆N₅O₉RuS₂·2H₂O·0.4CF₃SO₃H: C, 35.21; H, 2.74; N, 7.49. Found: C, 35.18; H, 2.72; N, 7.48.

Synthesis of [Ru(tpy)(6DHBP–2H⁺)(CO)]. [Ru(tpy)(6DHBP)(OH₂)](CF₃SO₃)₂ (13 mg) was dissolved in acetone (15 mL) and this solution was transferred to a Parr reactor which was then pressurized with CO to 200 psi. The Parr reactor was heated at 80 °C for 10 h and then cooled down to room temperature. The CO gas was released and the solvent was evaporated. The residual solid was purified by chromatography on Al₂O₃ (gradient elution: CH₃CN to CH₃CN/water 5:1), yielding the desired product as an orange powder (5.8 mg, 56 % yield). ¹H

NMR (400 MHz, methanol-*d*₄): δ (ppm) = 6.07 (dd, J = 7.34, 1.96 Hz, 1 H) 6.77 (d, J = 8.31 Hz, 1 H) 7.40–7.54 (m, 5 H) 7.70 (dd, J = 7.90 Hz, 1 H) 7.81 (dd, J = 5.50, 0.86 Hz, 2 H) 8.07 (td, J = 7.95, 1.47 Hz, 2 H) 8.27 (t, J = 7.60 Hz, 1 H) 8.41 (d, J = 8.07 Hz, 2 H) 8.45 (d, J = 8.07 Hz, 2 H). IR (KBr): $\nu(\text{C}\equiv\text{O})$ = 1984 cm^{-1} , $\nu(\text{C}=\text{O})$ = 1604 cm^{-1} . MS (ESI): m/z^+ = 549.9 ($[\text{M}+\text{H}]^+$), calcd = 550.05.

Synthesis of $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{NCCH}_3)](\text{CF}_3\text{SO}_3)_2$ ($\mathbf{n} = \mathbf{4}, \mathbf{6}$). These complexes were prepared from $[\text{Ru}(\text{tpy})(\text{nDHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2$ ($\mathbf{n} = \mathbf{4}, \mathbf{6}$) by replacing the aqua ligand with NCCH₃. The Ru aqua complexes were dissolved in CH₃CN and stirred for 30 min, and the solvent was removed under vacuum. The procedure was repeated three times after which complete exchange was verified by ¹H NMR.

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Table S1. Crystallographic Collection and Refinement Data for three 6DHBP complexes: $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)$, $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$, and $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$

Formula	$[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)$	$[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{Cl})]\text{Cl}$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO})]$
	$\text{C}_{26}\text{H}_{23}\text{O}_{11}\text{N}_5\text{F}_3\text{ClSRu}$	$\text{C}_{25}\text{H}_{26.5}\text{Cl}_2\text{O}_{5.75}\text{N}_5\text{Ru}$	$\text{C}_{26}\text{H}_{23}\text{O}_6\text{N}_5\text{Ru}$
fw	807.07	650.43	602.56
temp	173(2) K	173(2) K	173(2) K
cryst. syst	Monoclinic	Triclinic	Monoclinic
space group	$P2(1)/c$	$P-1$	$C2/c$
a (Å)	16.1735(8)	8.8906(18)	25.4619(7)
b (Å)	15.9616(6)	12.684(3)	13.4074(4)
c (Å)	11.9448(5)	14.297(3)	17.7238(6)
α (deg)	90.0	70.162(10)	90.0
β (deg)	101.142(2)	88.379(10)	124.6270(10)
γ (deg)	90.0	75.563(9)	90.0
V (Å ³)	3025.5(2)	1465.8(5)	4978.8(3)
Z	4	2	8
μ (mm ⁻¹)	0.763	0.762	0.682
λ (Å)	0.71073	0.71073	0.71073
ρ calc (g cm ⁻³)	1.772	1.498	1.608
cryst. size (mm)	0.33 × 0.17 × 0.10	0.20 × 0.20 × 0.07	0.42 × 0.40 × 0.13
θ range (deg)	2.68 to 30.09	2.69 to 24.00	2.33 to 30.09
total no. of reflns	37659	13315	53017
no. of independent reflns,	8796 [R(int) = 0.0576]	4330 [R(int) = 0.0757]	7217 [R(int) = 0.0325]
	5850	3144	5871
$I \geq 3.0 \sigma(I)$			
no. of parameters	433	358	343
Final R indices [$I > 3 \sigma(I)$]	R1 = 0.0404, wR2 = 0.0744	R1 = 0.0747, wR2 = 0.1765	R1 = 0.0262, wR2 = 0.0588
R indices (all data)	R1 = 0.0816, wR2 = 0.0855	R1 = 0.1125, wR2 = 0.1937	R1 = 0.0396 wR2 = 0.0639
Goodness-of-fit on F2	1.003	1.059	1.015
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w F_o^2} \right\}^{1/2}$$

S7

Figure S2. UV-vis spectral changes of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ in water upon addition of acetonitrile. The MLCT band shifts from 478 nm to 460 nm.

Figure S3. Calculated UV-vis spectral changes of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ (top) and of $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$ (bottom) in water upon addition of acetonitrile.

Figure S4. Acid-base titration of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$. UV-vis spectral changes at different pH (top) and absorbance changes at different wavelength (bottom).

Figure S5. Acid-base titration of $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$. UV-vis spectral changes at different pH (top) and absorbance changes at different wavelength (bottom).

S11

250x10⁻⁶

$[2\text{-OH}_2]^{2+}$
 B 500x10 C

$i/\mu\text{A}$
 200
 150
 100
 $[\text{Ru}(\text{tpy})(6\text{DHP})(\text{OH}_2)]$
 Ar CO_2

$i/\mu\text{A}$
 $[\text{Ru}(\text{tpy})(4\text{DHP})(\text{OH}_2)]$
 Ar CO_2

$i/\mu\text{A}$
 $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]$
 Ar CO_2
 0
 -0.4
 -0.8
 -1.2
 0
 -0.4
 -0.8
 -1.2

Figure S6. CVs of complexes $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ (A), $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$ (B), and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ (C) in aqueous phosphate buffer (0.25 M NaH_2PO_4) saturated with Ar (pH 4.3) or CO_2 (pH 4.25). CVs were collected using a mercury drop working electrode with scan rate = 100 mV s^{-1} .

Figure S7. Current versus time plots of controlled potential electrolysis for complexes $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$, $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$ and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ in CO_2 saturated phosphate buffer (0.25 M NaH_2PO_4 , final pH 4.25) at an applied potential of -1.3 V vs NHE. Electrolysis was performed using a mercury pool working electrode, Pt wire counter-

electrode and Ag/AgCl reference electrode. Figure S8 shows representative GC data indicating H_2 as the primary product.

S12

Figure S8. GC analysis of the products in controlled potential electrolysis experiments with $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{OH}_2)]^{2+}$ under the conditions shown in Figure S7.

Figure S9. CVs of 1 mM 6DHBP and 4DHBP in DMF with 0.1 M Bu₄NPF₆ recorded using a glassy carbon working electrode and scan rate = 100 mVs⁻¹.

S13

Electrochemistry of the free ligands

Table S2. Calculated reduction potentials of the free tpy and 6DHBP ligands in the *cis* conformation. Potentials are vs NHE. $G^*(H^+)$ in DMF = -278.700 kcal/mol; $G^*(H^+)$ in CH₃CN =

-264.606 kcal/mol, $\Delta G^*(NHE)$ in CH₃CN = -4.5228 eV, $\Delta G^*(NHE)$ in DMF = -3.9116 eV.

	$E(tpy^{0/-})$	$E(6DHBP^{0/-})$
CH ₃ CN	-1.568	-2.104
DMF	-0.953	-1.490

Table S3. Calculated reduction potentials of the free tpy and 6DHBP ligands in their lowest free-energy conformation: *trans* conformation for 6DHBP and (*trans, trans*) for tpy. Potentials are vs NHE. $G^*(H^+)$ in DMF = -278.700 kcal/mol; $G^*(H^+)$ in CH₃CN = -264.606 kcal/mol, $\Delta G^*(NHE)$ in CH₃CN = -4.5228 eV, $\Delta G^*(NHE)$ in DMF = -3.9116 eV.

	$E(\text{tpy}^{0/-})$	$E(6\text{DHBP}^{0/-})$
CH_3CN	-2.243	-2.179
DMF	-1.630	-1.533

S14

Figure S10. Calculated free energies (eV vs NHE) and potentials (V vs NHE) of the tpy and 6DHBP ligands in DMF and CH_3CN . For 6DHBP, the *trans* conformation is favorable over the *cis* conformation by 0.0525 eV in acetonitrile (0.0643 eV in DMF). The (*trans, trans*) conformation of tpy is 0.8186 eV lower in energy than the (*cis, cis*) conformer in CH_3CN (0.8191 eV in DMF). In 6DHBP, the singly-reduced ligand becomes more planar, and the free energies of the conformers differ by 0.04–0.18 eV. In the singly-reduced tpy, the (*trans, cis*) and (*trans, trans*) conformers are within a 0.006–0.008 kcal mol⁻¹ difference. The singly reduced (*cis, cis*) tpy conformer has a much higher energy owing to the out-of-plane dihedral angles (see Table 3). 1 eV = 23.060550 kcal mol⁻¹.

S15

Table S4. The geometry and numerical value of the dihedral angle (atoms selected for dihedral angle are highlighted in red) of 6DHBP and its reduced form. The *cis* conformer has ~ 30 degrees out-of-plane dihedral angle, whereas the *trans* isomer ~3–8 degrees out-of-plane dihedral angle. The reduced ligand becomes planar in all cases presented in this table.

cis (top view, side view)

trans (top view, side view)

6DHBP ⁰ in DMF	-30.06946	176.95762
6DHBP ^{•-} in DMF	-0.02692	179.85586
6DHBP ⁰ in CH ₃ CN	-30.04648	172.22660
6DHBP ^{•-} in CH ₃ CN	-0.02644	-179.98551

S16

Table S5. The geometry and numerical value of dihedral angle (atoms selected for dihedral angles are highlighted in red and blue) of tpy and its reduced form. The (*cis, cis*) and (*trans, cis*) conformer have higher values of out-of-plane dihedral angle ~30–36 degrees. After reduction the geometry becomes more planar for (*trans, cis*) and (*trans, trans*) conformations. One of the dihedral angles in the (*cis cis*) reduced conformer remains out-of-plane, which is reflected in the higher free energy of that conformer (see Figure S11).

cis, cis (top view, side view)

trans, cis (top view, side view)

trans, trans (top view, side view)

tpy⁰ in DMF tpy^{•-} in DMF

-36.88659, 36.94395

-1.50028, 32.00025

-178.25841, 30.91029

-179.99596, -0.00670
179.54283, -179.57156
-179.95889, -179.99510

tpy⁰ in CH₃CN tpy^{•-} in CH₃CN
-36.89095, 36.95009
-1.51776, 32.03549
-178.64259, 30.93177
-179.99582, -0.00628
179.54373, -179.57251
-179.95199, -179.99656

S17

50 [Ru(tpy)(6DHBP)(NCCH₃)]
catalysis
40 [Ru(tpy)(6DHBP-2H)(NCCH₃)]
30
[Ru(tpy)(6DHBP)(NCCH₃)]
, CO₂
Et₃NH⁺
i / μA
20
10 Fc
+ / 0 R1

R2

2+
+ 0

Figure S11. CVs of complexes $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (1 mM in DMF, 0.1 M Bu_4NPF_6) in the absence or presence of 10 equiv Et_3N under Ar and in the absence of Et_3N in CO_2 -saturated DMF. Reduction peaks R1 and R2 are assigned as the sequential reductive deprotonation of ligand OH protons. While the reversible couple at -1.97 V is assigned as the tpy-based reduction of the deprotonated species $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)]^0$, the irreversible peak at -1.74 V is associated with Et_3NH^+ reduction. CVs were recording using a glassy carbon working electrode with scan rate = 100 mV s^{-1} .

Figure S12. CVs of $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ and the deprotonated species $[\text{Ru}(\text{tpy})(4\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$ produced *in situ* with 2 equiv Bu_4NOH . The cyclic voltammetry of these compounds is complicated by insolubility of reduced species. In the absence of base, the cathodic sweep of $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ exhibits a composite $3e^-$ wave (-1.6 to -2 V). The $3e^-$ reduced species precipitates as indicated by the desorption spike at -1.7 V if the switching potential is kept anodic of -2 V. The desorption spike at -2.25 V shows re-dissolution with further reduction and the absence of surface waves upon the return scan (black curve). In this experiment, an anodic return wave, O1, was observed at -1.8 V. Experiments in the presence of base show behavior similar to $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, i.e., absence of the first two irreversible reductions R1 and R2 and the appearance of the reversible R3/O1 couple assigned as the tpy-based reduction of the deprotonated species, $[\text{Ru}(\text{tpy})(4\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]$. Assignment of further redox processes is not possible at this time although a second tpy-based reduction, $\text{tpy}^{-/2-}$ at -2.3 V is likely. Experiments were attempted in DMF but the solubility of reduced species remained problematic.

Figure S13. Experimental and theoretical spectra of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ (upper figure), and its singly- and doubly-deprotonated species, $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)(\text{OH}_2)]^+$ and $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{OH}_2)]^0$, in water. Experimental spectra (solid lines) are compared to the calculated 6-coordinate equivalent (dashed line). A detailed peak assignment is provided in Table S5. The intensities of the calculated data were reduced and adjusted to the experimental data by a factor of 0.35. The Gaussian width for peak broadening was 0.12 eV.

Figure S14. Experimental and theoretical spectra of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (upper panel) and its doubly deprotonated species $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$ (lower panel) in acetonitrile. Experimental spectra (solid lines) are compared to those of the corresponding calculated 6-coordinate species (dashed and dotted lines, respectively). The intensities of the calculated data were reduced and adjusted to the experimental data by a factor of 0.35. The Gaussian width for peak broadening was 0.12 eV.

S21

Table S6. Molecular orbital assignment of the electronic transitions (nm) in the absorption spectra of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$ in water. Oscillator strengths (*f*) are shown in parentheses.

$[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{OH}_2)]^{2+}$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)(\text{OH}_2)]^+$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{OH}_2)]^0$
562.70 (<i>f</i> = 0.0228) H → L 97% ML(tpy)CT		
H-1 → L 3 % LLCT(6DHBP to tpy)		
598.06 (<i>f</i> = 0.0105)		
565.41 (<i>f</i> = 0.0156)		
H → L 100% ML(tpy)CT		
640.88 (<i>f</i> = 0.233)		
H → L 95% ML(tpy)CT		

452.04 (f = 0.1586)
H-2 → L 33% ML(tpy)CT H-1 → L+2 37% ML(6DHBP)CT

468.66 (f = 0.1139)
H-2 → L 25% ML(tpy)CT H-2 → L+1 37% ML(tpy)CT

460.87 (f = 0.1092)
H-2 → L+1 63% ML(tpy)CT

491.56 (f = 0.0553)
H-2 → L 15% M(tpy)CT H-2 → L+1 66% M(tpy)CT

486.32 (f = 0.071)
H-2 → L 47% M(tpy)CT H-2 → L+1 31% M(tpy)CT

436.05 (f = 0.0458)
H-3 → L+1 82%
LLCT(6DHBP to tpy)

422.79 (f = 0.0578)
H-1 → L+2 56%
ML(6DHBP)CT
H → L+2 28% ML(6DHBP)CT

332.94 (f = 0.1030)
H-3 → L+1 59% LLCT(6DHBP) H → L+4 16% ML(tpy)CT

355.51 (f = 0.2240)
H-3 → L+2 98% LLCT(6DHBP)

370.79 (f = 0.2151) H-3 → L+2 67% LLCT(6DHBP)
H → L+4 14% ML(tpy)CT

313.3 (f = 0.5352)
H-4 → L 93% LLCT(tpy)

312.53 (f = 0.4226)
H-4 → L 100% LLCT(tpy)

309.41 (f = 0.4155)
H-6 → L 94% LLCT(tpy)

H = HOMO, L = LUMO; MLCT = Metal-to-Ligand Charge Transfer, LLCT = Ligand-to-Ligand Charge Transfer

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Table S7. Molecular orbital assignment of the electronic transitions (nm) in the absorption spectra of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ in CH_3CN . Oscillator strengths (f) are shown in parentheses.

$[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)(\text{NCCH}_3)]^+$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{NCCH}_3)]^0$
---	---	--

520.97 (f = 0.0110)
H → L 94% ML(tpy)CT H-1 → L 6% LLCT(6DHBP
to tpy)
525.98 (f = 0.0182)

H-1 → L 89% ML(tpy)CT
590.79 (f = 0.0182)
H-1 → L 51% ML(tpy)CT
H → L 31% LLCT (6DHBP to tpy)

460.19 (f = 0.1218)
H → L+2 77 % ML(6DHBP)CT

451.14 (f = 0.07750)
H-2 → L+1 57% ML(tpy)CT H-3 → L 18% ML(tpy)CT

434.28 (f = 0.1371) H-1 → L+1 68% ML(6DHBP)CT

434.35 (f = 0.0502)
H-2 → L 26% MLCT H-3 → L 20% LLCT(6DHBP to tpy)

405.12 (f = 0.1009)
H-1 → L+2 84% ML(6DHBP)CT

336.07 (f = 0.1504)
330.89 (f = 0.1328) H-3 → L+1 97% LLCT(6DHBP)

367.54 (f = 0.2111) H-3 → L+2 93% LLCT(6DHBP)

375.28 (f = 0.1677)
H-2 → L+2 51% LLCT(6DHBP)

310.69 (f = 0.5597)
H-4 → L 81% LLCT(tpy)

307.48 (f = 0.2583)
H-6 → L 95% LLCT(6DHBP to tpy)

310.44 (f = 0.3509)
H-7 → L 94% LLCT(tpy)

H = HOMO, L = LUMO; MLCT = Metal-to-Ligand Charge Transfer, LLCT = Ligand-to-Ligand Charge Transfer

S23

Computational details and possible hydrogen production mechanism

A calculation of the standard free energy of all possible species involved in all possible electron and proton transfer reactions to $[\text{Ru}^{\text{II}}(\text{tpy})(\text{L})(\text{S})]^{2+}$ (L = 4DHBP, 6DHBP) was carried out. This includes sequential one-electron reductions, proton transfer reactions, proton-coupled electron transfer (PCET) and the energetics of losing a solvent ligand from the sixth coordination position. A study of the different orientation of hydrogens from OH groups in the proton-responsive 6DHBP ligand was also included. The geometry was optimized using DFT (RKS states for closed shells, UKS states for open shells) with the B3LYP hybrid functional and the ECP28MWB (1f, 0g) basis set for the Ru center and the 6-31+G(d,p) for all other atoms. The CPCM continuum solvation model was used for both the geometry optimization and frequency analysis with the United Atom Topological Model (UAHF) radii as implemented in Gaussian09. The $\text{p}K_{\text{a}}$ value is given by

$$\text{p}K_{\text{a}} = \Delta G_{\text{a}}^* / RT \ln(10) \quad (2\text{s})$$

where ΔG_{a}^* represents the standard free energy of the reaction

in the solution.

Owing to the large number of possibilities, only a select set of plausible reactions for hydrogen production are presented here. The singly-reduced species dissociate the solvent (S) ligand from the coordination shell and become 5-coordinate species.

A number of possible of H₂ production mechanisms, from singly-reduced with intermolecular or intramolecular proton transfer (PT), were considered. The free energy of the intermediates is calculated at pH 0 and at the estimated solution pH of 9.34 corresponding to a 1 mM solution of [Ru(tpy)(6DHBP)(NCCH₃)]²⁺, the strongest acid in the solution with calculated pK_a of 15.69.

Based on the calculated data, the singly-reduced species are favorable as 5-coordinate species, e.g., [Ru(tpy)(6DHBP)]⁺ (Table S8) with hydrogens from OH directed toward the ruthenium center in CH₃CN. The singly- and doubly-deprotonated complexes remain as 6-coordinate species only before reduction (see Table S8). Key questions are: Can H₂ be produced the after the first reduction? Although the present system is different from [Re(nDHBP)(CO)₃Cl] (n = 4 or 6), will a similar “proton catalyzed hydrogen production” mechanism be viable? If so, what is the source of the H⁺? Does proton transfer occur by an intermolecular or intramolecular process? The applied potential drives an uphill reaction after which only exoergic processes for hydrogen production are expected.

Table S8. One- and two-electron proton-coupled reduction free-energy pathways with an external (internal) proton transfer to the singly-reduced complex, and the possible attachment of the proton to the Ru center, tpy, or 6DHBP ligand. The investigated structures with relatively higher free energies are listed in gray font. Species listed in black, red, and blue font are presented in Figure 4. The last two columns show the relative free energy of the species at pH 0 and at the calculated pH^a based on the experimental conditions. Here S = CH₃CN. See Scheme S1 for structures.

Net Change to Complex	Species							
				G^*_{species} (Ha)				
Reservoir (Ha)				$G^*_{\text{reservoir}}$ (Ha)				
G^*_{total} (Ha)								
				Rel. $\Delta G^*_{\text{total}}$ (Ha)				
Rel. ΔG^* vs NHE (eV)					Rel. $\Delta G^{*'}_{\text{vs. NHE (eV) at pH = 9.34}^{c,d}}$			
- - -	[Ru(tpy)(6DHBP)(S)] ²⁺	-1615.6119	2e ⁻ , H ⁺	-0.4244	-1616.0364	0.0000	0.0000	0.0000
rotHH								
+e ⁻ -S	[Ru(tpy ^{•-})(6DHBP)] ⁺ ^b							
-1482.9844	S, e ⁻ , H							
+		-133.1704	-1616.1548	-0.1184	1.3008	1.3008		
ex								
+e ⁻ -S +H ⁺								
-1483.4216	S, e ⁻	-132.7487	-1616.1703	-0.1339	0.8790	1.4316		
-1483.4155	S, e ⁻	-132.7487	-1616.1642	-0.1278	1.0454	1.5979		
-1616.1540	e ⁻	-0.0014	-1616.1553	-0.1189	1.2860	1.8386		

$\begin{aligned} & [\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}_c)]^{2+} \\ & +e^- -\text{S} +\text{H}_{\text{ex}} \\ & [\text{Ru} \\ & (\text{H})(\text{tpy})(6\text{DHBP})] \\ & +e^- +\text{H}_{\text{ex}} \\ & [\text{Ru}(\text{tpyH})(6\text{DHBP})(\text{S})] \end{aligned}$								
$+e^- -\text{S}$	$[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_c-\text{H}^+_p)]^+$	-1482.9754	$\text{S}, e^-, \text{H}^+$	-133.1704	-1616.1458	-0.1094	1.5470	1.5470
$+e^- -\text{S}$	$[\text{Ru}(\text{tpyH})(6\text{DHBP}-\text{H}^+)]^+$	-1482.9460	$\text{S}, e^-, \text{H}^+$	-133.1704	-1616.1163	-0.0800	2.3471	2.3471
$+e^-$	$[\text{Ru}(\text{tpyH})(6\text{DHBP}-\text{H}^+)(\text{S})]^+$	-1615.7011	e^-, H^+	-0.4231	-1616.1241	-0.0877	2.1350	2.1350
$+e^- -\text{S}$	$[\text{Ru}^{\text{III}}(\text{H}^-)(\text{tpy})(6\text{DHBP}-\text{H}^+)]^+$	-1482.9690	$\text{S}, e^-, \text{H}^+$	-133.1704	-1616.1394	-0.1030	1.7199	1.7199
$+e^- -\frac{1}{2}\text{H}_2$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)(\text{S})]^+$	-1615.1562	$e^-, \text{H}^+, \frac{1}{2}\text{H}_2$	-1.0130	-1616.1692	-0.1328	0.9100	0.3575
$\begin{aligned} & 0 \\ & + \\ & -1482.5207 \\ & -133.7589 \\ & -1616.2797 \\ & -0.2433 \\ & \mathbf{2.4261} \\ & \mathbf{1.8736} \end{aligned}$								
$+2e^- -\text{S}-\frac{1}{2}\text{H}_2$	$[\text{Ru}(\text{tpy})$ $(6\text{DHBP}-\text{H})]$ $\text{S}, \text{H}, \frac{1}{2}\text{H}$							
$+2e^- -\text{S}-\frac{1}{2}\text{H}_2$	$[\text{RuH}(\text{tpy})(6\text{DHBP}-\text{H})]^+$	-1482.9690	$\text{S}, \frac{1}{2}\text{H}_2$	-133.3373	-1616.3063	-0.2699	1.7019	1.7019
$+2e^- -\frac{1}{2}\text{H}_2$	$[\text{Ru}(\text{tpyH})(6\text{DHBP}-\text{H}^+)(\text{S})]^+$	-1615.7011	$\frac{1}{2}\text{H}_2$	-0.5899	-1616.2910	-0.2546	2.1170	2.1170
$+2e^- -\text{S}-\frac{1}{2}\text{H}_2$	$[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_c-\text{H}^+_d)]^+$	-1482.9657	$\text{S}, \frac{1}{2}\text{H}_2$	-133.3373	-1616.3029	-0.2665	1.7931	1.7931

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$+2e^- -\text{S}-\frac{1}{2}\text{H}_2$	$[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_c-\text{H}^+_p)]^+$	-1482.9754	$\text{S}, \frac{1}{2}\text{H}_2$	-133.3373	-1616.3126	-0.2762	1.5289	1.5289
$+2e^- -\text{H}_2$	$[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{S})]^0$	-1614.6943	H_2, H^+	-1.6015	-1616.2959	-0.2595	1.9848	1.4323

^a $\text{pH} \cong \frac{1}{2}\text{p}K_{\text{a,calc}} + \frac{1}{2}\cdot\text{p}C_0$ for $C_0 \gg K_a$ ($\text{p}K_a = 15.6874$; conc = 0.001M).

^b rotHH hydrogen atoms on OH groups pointing toward the ruthenium center.

^c $\Delta G^*(\text{eV}) = \Delta G^* + RT\ln(10)\cdot\text{pH} = \Delta G^* + 0.059159\cdot\text{pH} = \Delta G^* + 0.55254 \text{ eV}$ (for rxn: $\text{H}^+ + \text{A} \rightarrow \text{HA}^+$).

^d $\Delta G^*(\text{eV}) = \Delta G^* - RT\ln(10)\cdot\text{pH} = \Delta G^* - 0.059159\cdot\text{pH} = \Delta G^* - 0.55254 \text{ eV}$ (for rxn: $\text{HA}^+ \rightarrow \text{H}^+ + \text{A}$).

S26

2.5

Figure S15. The calculated energetics at pH 9.34 of possible intermediates after an initial one-electron transfer followed by proton transfer. Both internal and external proton transfer were considered (blue and red lines, respectively). The most suitable intermediate with the lowest free energy, $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^{+}_{\text{C5}})]^{2+}$, has an external proton attached to the 6DHBP ligand at the C5 position. The reservoir species are indicated in orange. See Scheme S1 for structures. The final one-electron reduced product (i.e., $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^{+})(\text{S})]^{+}$) is formed by the net disproportionation of two $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^{+}_{\text{C5}})]^{2+}$ species.

c d

2

2.0

Figure S16. The calculated energetics at pH 9.34 of possible intermediates after a second electron transfer followed by proton transfer. An internal proton transfer within the $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)]^0$ species is not considered because of the large $\text{p}K_{\text{a}2}$ of the singly-reduced singly-deprotonated species. Since the complex $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)]^0$ is in the doubly-reduced, singly-deprotonated form, a number of possibilities were explored. We have placed an external proton on the ruthenium center, the tpy or the 6DHBP ligand. There were two investigated options for placing the proton on the 6DHBP ligand. (see Scheme S1 for structures). The most suitable intermediate, with the relatively lowest free energy has an external proton attached to the at the C5 position of the pyridine ring that contains the deprotonated $-\text{OH}$ group, $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$, i.e., proximal to the $-\text{O}$ substituent. This result can be understood by the keto resonance structure of the singly-deprotonated 6DHBP. From a thermochemical point of view, there are three exoergic options for placing the proton on $[\text{Ru}(\text{tpy})(6\text{DHBP}-\text{H}^+)]^0$: (1) $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{d}})]^+$, i.e., with the proton on the C5 distal to the $-\text{O}$ substituent; (2) $[\text{Ru}(\text{H}^-)(\text{tpy})(6\text{DHBP}-\text{H}^+)]^+$; and (3) $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$. The first two, (1) and (2), have higher energy than $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$. Moreover, the $\text{p}K_{\text{a}}$ values (12.24 and 10.70, respectively) are lower than the $\text{p}K_{\text{a}}$ 15.17 of $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$. This suggests that the conjugate base of $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$ (i.e., $[\text{Ru}(\text{tpy})(6\text{DHB}-\text{H}^+)]^0$) would compete more effectively for a proton from the solution. Reservoir species are indicated in orange. The final two-electron reduced product (i.e., $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{S})]^0$) is formed by the net disproportionation of two $[\text{Ru}(\text{tpy})(6\text{DHBP}+\text{H}^+_{\text{C}}-\text{H}^+_{\text{p}})]^+$ species.

Figure S17. Calculated IR spectra for $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ and for the singly-, and doubly- deprotonated species. See text for assignments of the lowest energy bands.

Figure S18. (A) Charge vs time plots of the first and second runs of bulk electrolysis of 1 mM $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ in CH_3CN under a CO_2 atmosphere at $E_{\text{app}} = -2.3$ V with constant stirring. (B) CVs of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ before and after bulk electrolysis (scan rate = 100 mV s^{-1}). When glassy carbon was used as the working electrode for the bulk electrolysis, the charge flow stopped after 200 s. CVs were taken before and after the electrolysis: after 200 s electrolysis, the electrode surface was blocked by the precipitated reduced species which insulated the electrode and the redox waves of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ were not visible. Application of an oxidizing potential ($0.1 \text{ V vs Fc}^{+/0}$) restored the initial electrode activity (see the second run).

Figure S19. Current vs time plots of 0.5 mM complexes $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ (green), $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$ (blue) and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ (red). The black plot is a blank experiment. Electrolysis was performed on 8 mL solutions with an applied potential of -2.3 V using a mercury pool working electrode in CH_3CN .

Table S9. Summary of controlled potential electrolysis data of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$, $[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$, and $[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$.^{a,b}

Formate			(μmole)
(μmole)			
Total charge			
passed (C)			
η_{CO} η_{formate}			
<hr/>			
$[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$	0.54	0.78	2.56
			(26.5 μmole electrons)
$[\text{Ru}(\text{tpy})(4\text{DHBP})(\text{NCCH}_3)]^{2+}$	2.13	2.65	3.74
			(38.8 μmole electrons)
4.1%			
(5.8)			
11%			
(13.9)			
5.9%			
(8.5)			
14%			
17.6)			
$[\text{Ru}(\text{tpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$	11.1	3.08	7.2
			(74.6 μmole electrons)
29.8 %	8.3 %		
<hr/>			

^aThe first two electrons were used for reductive deprotonation to form $\text{Ru}(\text{tpy})(\text{nDHBP}-2\text{H}^+)(\text{NCCH}_3)]^{2+}$, not for the reduction of CO_2 . The values in parentheses are the compensated values. ^bUsing the same conditions, η_{CO} of ~100 % was obtained with $\text{Re}(\text{'Bu}_2\text{bpy})(\text{CO})_3\text{Cl}$.

B

Figure S20. ^1H NMR (A; formate: peak at 8.5 ppm) and ^{13}C NMR (B; formate: peak at 170.7 ppm; bicarbonate: peak at 160.4 ppm) in D_2O showing products of controlled potential electrolysis with $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ under CO_2 .

Figure S21. Mass spectra of the red precipitate obtained from bulk electrolysis experiments of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ in the presence of CO_2 . Top: obtained immediately after injecting sample. Bottom: later after injecting sample.

S32

+

+

+

Table S10. Mass spectrometry peak assignments of species produced after electrolysis of $[\text{Ru}(\text{tpy})(6\text{DHBP})(\text{NCCH}_3)]^{2+}$ under CO_2 .

<p>calculated m/z^+: 675.98 observed m/z^+: 676.1</p>	<p>calculated m/z^+: 651.06 observed m/z^+: 651.1</p>	<p>calculated m/z^+: 638.03 observed m/z^+: 638.1</p>
<p>calculated m/z^+: 554.08 observed m/z^+: 553.9</p>	<p>calculated m/z^+: 540.06 observed m/z^+: 539.9</p>	<p>calculated m/z^+: 522.05 observed m/z^+: 522.3</p>

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CO_2 vibrations
@ $\sim 1748 \text{ cm}^{-1}$ ($\nu \text{ CO}$)
@ $\sim 1755 \text{ cm}^{-1}$ ($\nu \text{ CO}$)

CO_2 vibrations
@ $\sim 1727 \text{ cm}^{-1}$ ($\nu \text{ COK}$)
@ $\sim 1748 \text{ cm}^{-1}$ ($\nu \text{ CO}$)

CO_2 vibrations
@ $\sim 1720 \text{ cm}^{-1}$ ($\nu \text{ COK}$)
@ $\sim 1727 \text{ cm}^{-1}$ ($\nu \text{ COK}$)

CO vibration
@ $\sim 2010\text{--}3 \text{ cm}^{-1}$

Figure S22. Calculated infrared spectra of $[\text{Ru}(\text{tpy})(6\text{DHBP}-2\text{H}^+)(\text{CO}_2)_2(\text{CO})]^0$ with 0 to 2 K ions added to the system. The CO vibrations occur at $\sim 2010\text{--}2013 \text{ cm}^{-1}$ in reasonable agreement with the experimental data at $1930\text{--}2004 \text{ cm}^{-1}$ (see Table 2). The calculated CO_2 vibrations occur at $\sim 1720\text{--}1755 \text{ cm}^{-1}$ and are shifted by $70\text{--}100 \text{ cm}^{-1}$ ($0.2\text{--}0.28 \text{ kcal mol}^{-1}$) from the experimental

data.

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H	-0.32402134	-5.30951893	-0.15460246
C	0.32927692	-4.44064828	-0.22070387
C	1.68044726	-4.56496269	-0.54666010
C	2.46775865	-3.41501113	-0.61781406
C	1.89090737	-2.16905936	-0.36161014
N	0.56377966	-2.05733256	-0.03690212
C	-0.18856828	-3.17016211	0.02727478
H	2.11913359	-5.54264881	-0.74507158
H	3.52395413	-3.48419926	-0.87353259
H	-1.23522189	-3.02375757	0.28824878
H	4.62655890	-1.61332132	-0.90744279
C	4.00013171	-0.74476173	-0.71092621
C	4.54296258	0.54271524	-0.73656565
C	3.73802558	1.65331716	-0.47027881
C	2.38421388	1.44950021	-0.18652892
N	1.87985648	0.19610753	-0.18656361
C	2.64041392	-0.89532234	-0.42548647
H	5.60073929	0.68065567	-0.95828876
H	2.68722983	4.20155333	-0.07675161
C	1.67976744	3.85825394	0.15331857
C	0.67572856	4.77429891	0.46907026
C	-0.60434273	4.30099313	0.75957875
C	-0.83720688	2.92686404	0.72241834
N	0.12378088	2.03730570	0.41601421
C	1.38482541	2.49312940	0.13229367
H	-1.81955322	2.51185786	0.94175978
H	0.89398351	5.84188039	0.48776029
H	-1.41907819	4.97766496	1.01336948
H	4.16018445	2.65682796	-0.47789983
H	-0.40671045	0.52478677	-4.94086264
C	-0.98502464	0.41335209	-4.01969845
C	-2.36829660	0.45191336	-4.00573261
C	-3.04015919	0.28884722	-2.79260617
C	-2.30579894	0.10044580	-1.62250231
N	-0.93582928	0.08410410	-1.62218152
C	-0.30262256	0.22541618	-2.80626947
H	-2.92695950	0.60058674	-4.92952313
H	-4.12558138	0.30376639	-2.76946518
H	-4.99455613	0.00941555	-1.05360729
C	-4.35272466	-0.16147610	-0.19461836
C	-4.91776872	-0.42627508	1.05470025
C	-4.08421815	-0.66412446	2.13431183
C	-2.69358614	-0.61420279	1.93771974
N	-2.13074051	-0.32798753	0.74579254
C	-2.96408099	-0.12605209	-0.32039925
H	-6.00042512	-0.45467700	1.17529457
H	-4.47184148	-0.89185081	3.13093184
Ru	-0.02464283	-0.06698357	0.30437386
N	0.71470845	-0.17698728	2.19156812
C	1.23332198	-0.20890998	3.22573459
C	1.84327687	-0.25879475	4.54664218

Table S11. Optimized coordinates of Ru complexes

H	1.07743979	-0.48393504	5.29861068
H	2.61318520	-1.03893640	4.57249292
H	2.30456619	0.70781156	4.78105508
O	1.03514741	0.17525815	-2.76695720
H	1.41159136	0.28612560	-3.69844273
O	-1.84083717	-0.85709690	2.94347001
H	-2.35366246	-1.06027289	3.78934869

[Ru(tpy^{•-})(6DHP)]⁺_{rotHH}

H	-1.87694100	4.81399700	-0.96956300
C	-0.97751100	4.21456500	-0.84206100
C	0.29590200	4.80565200	-0.73546400
C	1.40576600	3.99095600	-0.57366000
C	1.25545900	2.58979400	-0.52260300
N	-0.00435900	2.02122500	-0.62721300
C	-1.07352400	2.83092000	-0.78178700
H	0.41093000	5.88842400	-0.77511900
H	2.39973200	4.42528700	-0.47938700
H	-2.03757500	2.33061400	-0.86054600
H	4.06057300	2.97798800	-0.55518600
C	3.72350100	1.95260300	-0.41019200
C	4.66188000	0.90729400	-0.32868400
C	4.22868100	-0.42953700	-0.25905200
C	2.86604800	-0.70812600	-0.20140400
N	1.96375400	0.34865700	-0.12979200
C	2.36365800	1.66082100	-0.35460600
H	5.72597500	1.12970300	-0.38034300
H	4.01750700	-3.21566800	0.04113700
C	2.93292400	-3.23320500	-0.05353200
C	2.24509300	-4.43673300	-0.03052200
C	0.84122600	-4.42527000	-0.13699200
C	0.19513000	-3.20359100	-0.26825900
N	0.84887500	-2.02226500	-0.30155800
C	2.23092900	-2.01828900	-0.19037000
H	-0.88833100	-3.14463900	-0.35724100
H	2.78665700	-5.37627900	0.07501500
H	0.25981000	-5.34520100	-0.12023000
H	4.95520300	-1.24045600	-0.28409500
H	-0.01749700	0.41164800	4.72841800
C	-0.65568600	0.27368300	3.85346500
C	-2.03625700	0.20524200	3.93806000
C	-2.78559100	0.03630100	2.77001200
C	-2.12891600	-0.06824600	1.54490500
N	-0.76239900	-0.00739400	1.45105400
C	-0.05673000	0.17222500	2.58771800
H	-2.53497800	0.28333400	4.90379100
H	-3.86903800	-0.02508200	2.82136300
H	-4.85283500	-0.07746900	1.07347500
C	-4.24609300	-0.29681300	0.19928100
C	-4.85697100	-0.58344800	-1.02522700
C	-4.06774100	-0.91170900	-2.11716500
C	-2.67391400	-0.90585000	-1.95705900
N	-2.06577900	-0.53707900	-0.81280000

C	-2.85349700	-0.29635500	0.28030500
H	-5.94312200	-0.57533500	-1.11222700
H	-4.48960300	-1.19093300	-3.08466800
Ru	0.03736400	-0.09191000	-0.52478500
O	1.27687100	0.26370200	2.52576400
H	1.56749400	0.28540400	1.57392800
O	-1.92571000	-1.28646600	-3.00449800
H	-0.99053400	-1.48848600	-2.68658500

[Ru(tpy)(6DHBP+H⁺C)]²⁺

H	-0.87400400	5.19387400	-0.55577900
C	-0.11527100	4.41429600	-0.50383200
C	1.24225700	4.72099700	-0.40558600
C	2.16856300	3.67839700	-0.34209700
C	1.72122200	2.35662900	-0.37717700
N	0.38398900	2.06335200	-0.47628100
C	-0.50158700	3.07493100	-0.53560000
H	1.58027200	5.75666600	-0.37754000
H	3.23370300	3.89099500	-0.26335700
H	-1.54887800	2.78763100	-0.61239600
H	4.56313900	2.15896500	-0.29493400
C	4.02347500	1.21332700	-0.29173500
C	4.71762600	0.00017400	-0.26816100
C	4.02357000	-1.21303300	-0.29172900
C	2.62655100	-1.18628800	-0.32139900
N	1.97599700	0.00006800	-0.31482200
C	2.62645800	1.18647300	-0.32140800
H	5.80691000	0.00021700	-0.24393500
H	3.23400600	-3.89076300	-0.26332500
C	2.16884900	-3.67824800	-0.34206200
C	1.24262400	-4.72092100	-0.40553800
C	-0.11492800	-4.41432700	-0.50378300
C	-0.50134800	-3.07499200	-0.53556400
N	0.38414900	-2.06334500	-0.47625700
C	1.72140600	-2.35651500	-0.37715400
H	-1.54866200	-2.78777400	-0.61236000
H	1.58072000	-5.75656300	-0.37748300
H	-0.87360100	-5.19396500	-0.55572100
H	4.56330800	-2.15862800	-0.29492200
H	-0.10817000	0.89617400	4.46085200
C	-0.53865300	-0.00000300	3.91611600
C	-2.02610500	0.00000100	3.95675500
C	-2.75102100	-0.00001700	2.80850900
C	-2.11850800	-0.00003600	1.53032000
N	-0.70707600	-0.00002000	1.42437400
C	0.01299900	-0.00000800	2.52484200
H	-2.51537300	0.00001800	4.93119400
H	-3.84160800	-0.00001600	2.84915300
H	-4.87043200	-0.00010700	1.07625300
C	-4.24940800	-0.00010800	0.18455500
C	-4.83029200	-0.00014400	-1.08104600
C	-4.02735100	-0.00014500	-2.22313100
C	-2.63579800	-0.00010900	-2.04770100

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N	-2.06218600	-0.00007600	-0.83720500
C	-2.84432200	-0.00007300	0.29098300

H	-5.91540400	-0.00017200	-1.18187300
Ru	-0.00234000	-0.00001500	-0.50703700
O	1.33149900	0.00000100	2.39271700
H	1.77326500	0.00001200	3.30778200
O	-1.75720200	-0.00010600	-3.07013800
H	-2.24512900	-0.00013500	-3.95474500
H	-4.44747600	-0.00017300	-3.23163700
H	-0.10817500	-0.89618200	4.46085600

[Ru^{III}(H⁻)(tpy)(6DHP)]²⁺_{rotHH}

H	-2.19691500	4.58477800	-0.91284600
C	-1.24522400	4.06363300	-0.81929500
C	-0.03166000	4.75237800	-0.79952900
C	1.15579000	4.03148900	-0.67805100
C	1.10677900	2.63997100	-0.58199500
N	-0.08934100	1.97256900	-0.60437800
C	-1.23280700	2.67525000	-0.71634100
H	-0.00654500	5.83948700	-0.87566800
H	2.11597400	4.54494900	-0.65594600
H	-2.15826200	2.10218500	-0.73398100
H	3.87127700	3.27440300	-0.47590300
C	3.62808900	2.21610300	-0.39393400
C	4.63746300	1.26405100	-0.24139400
C	4.31409000	-0.08927200	-0.11908100
C	2.97013300	-0.46591700	-0.16594400
N	2.00917500	0.47165800	-0.33429700
C	2.29813800	1.78728000	-0.43631200
H	5.68031100	1.57828900	-0.20893300
H	4.31411100	-2.86916900	0.22168500
C	3.22970000	-2.96265300	0.18165200
C	2.61764100	-4.20733200	0.33470100
C	1.22497700	-4.29345600	0.29151800
C	0.48586400	-3.13103700	0.09053600
N	1.07363000	-1.92997200	-0.07489600
C	2.43819900	-1.83196900	-0.02106600
H	-0.60215000	-3.14311500	0.05042600
H	3.22490500	-5.09895100	0.49152200
H	0.70707600	-5.24380000	0.41307600
H	5.09381600	-0.83750900	0.01621000
H	-0.71282000	0.67643500	4.81746900
C	-1.21027600	0.47528600	3.86641700
C	-2.58807000	0.47261600	3.73066700
C	-3.16238100	0.18148700	2.48718500
C	-2.32626200	-0.08416700	1.40393200
N	-0.96727700	-0.05028400	1.52348200
C	-0.43276500	0.19962600	2.72736700
H	-3.22503800	0.68414800	4.58942900
H	-4.24334700	0.15773100	2.37978800
H	-4.94853300	-0.32173300	0.56772800
C	-4.21365000	-0.56500200	-0.19483100

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C	-4.63325400	-0.99515700	-1.46005100
C	-3.69300200	-1.35979500	-2.40777100
C	-2.33295000	-1.25221500	-2.07408400
N	-1.91660900	-0.74791100	-0.89151600
C	-2.85289300	-0.46328000	0.07284800

H	-5.69717100	-1.06888600	-1.68533400
H	-3.96752300	-1.74551700	-3.39175800
Ru	0.09227100	-0.12884100	-0.52202000
O	0.89894700	0.18573900	2.87969800
H	1.34042000	-0.07431900	2.00603200
O	-1.44511900	-1.67138500	-2.98248700
H	0.56499300	-0.08523800	-2.03531400
H	-0.52221000	-1.75994400	-2.57812300

[Ru(tpyH)(6DHBP)(S)]²⁺_{rotH}

H	3.25702300	2.49605900	3.07720800
C	2.31020400	2.52344200	2.53971300
C	1.52153300	3.67382200	2.50259600
C	0.30985100	3.63768500	1.81340400
C	-0.08475200	2.46288800	1.16791100
N	0.71198800	1.34736100	1.18420900
C	1.87060200	1.38438700	1.86867300
H	1.83804600	4.58513900	3.00950900
H	-0.33235300	4.51625400	1.78085600
H	2.45742300	0.46866600	1.87602000
H	-2.28637400	4.22520800	0.94481100
C	-2.42086200	3.24757300	0.48642600
C	-3.64680500	2.89417500	-0.09622800
C	-3.83277800	1.62321600	-0.62948300
C	-2.76355800	0.70611100	-0.60449300
N	-1.56119000	1.09817800	-0.09445300
C	-1.38811500	2.30844300	0.48717700
H	-4.46272600	3.61616800	-0.11710600
H	-4.92773900	-0.94777200	-0.91382800
C	-3.97526400	-1.43247700	-1.12812100
C	-3.93344500	-2.80107700	-1.39720700
C	-2.66448900	-3.42405000	-1.60231000
C	-1.52299900	-2.68338800	-1.58835100
N	-1.52987700	-1.28803700	-1.32169700
C	-2.81341100	-0.67080400	-1.06220100
H	-0.53656900	-3.09416700	-1.79018500
H	-4.84969300	-3.38676300	-1.42623100
H	-2.59611100	-4.49482900	-1.78950400
H	-4.78723600	1.33713600	-1.06801000
H	1.79912300	2.66620200	-3.98228500
C	2.07105000	1.94203500	-3.21157500
C	3.38503100	1.62523100	-2.91454900
C	3.65164400	0.64234200	-1.95533600

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C	2.59119100	0.04194600	-1.28215900
N	1.28810000	0.40922800	-1.51059500
C	1.04801100	1.28865600	-2.50402300
H	4.20406800	2.11472200	-3.44112300
H	4.67678300	0.35079200	-1.74409300
H	4.93286000	-1.23558400	-0.55346300

C	4.04000200	-1.62815600	-0.07479300
C	4.13259200	-2.72160800	0.79302700
C	2.97853200	-3.24727900	1.35070900
C	1.75143200	-2.63791100	1.04398800
N	1.65384500	-1.53564500	0.27573900
C	2.79073200	-1.06331900	-0.32324500
H	5.10191000	-3.17186400	1.00573100
H	2.98574500	-4.12541000	1.99964000
Ru	-0.05546300	-0.24007400	0.06758000
O	-0.21279500	1.57565800	-2.85969700
O	0.64202300	-3.19179400	1.55262900
H	-0.16939600	-2.83748400	1.06767400
H	-1.01766200	-0.74547900	-2.14692300
N	-1.10940100	-0.85949100	1.68057700
C	-1.75238400	-1.11202700	2.61119000
C	-2.54766600	-1.46136200	3.77881200
H	-2.57181034	-0.61740081	4.47843100
H	-3.57183214	-1.70411838	3.47154096
H	-2.10627428	-2.33181634	4.27908083
H	-0.83856300	0.89648200	-2.44742300

H	-0.87487300	5.18999500	-0.53957200
C	-0.11514300	4.41129800	-0.48932000
C	1.24208600	4.72008500	-0.38665000
C	2.16911100	3.67828000	-0.32406500
C	1.72406500	2.35554200	-0.36527200
N	0.38718100	2.05962600	-0.47071900
C	-0.49919200	3.07170900	-0.52756400
H	1.57844600	5.75606300	-0.35365400
H	3.23364400	3.89166400	-0.24018600
H	-1.54573000	2.78318000	-0.60808200
H	4.56402300	2.15913200	-0.26240400
C	4.02512000	1.21311300	-0.26468700
C	4.72034000	0.00056300	-0.23561100
C	4.02543800	-1.21216200	-0.26484200
C	2.62877700	-1.18560100	-0.30619800
N	1.97536000	0.00021200	-0.30522300
C	2.62846800	1.18619900	-0.30607100
H	5.80923900	0.00070500	-0.20209200
H	3.23458100	-3.89094400	-0.24027700
C	2.17000400	-3.67780500	-0.32423800
C	1.24321500	-4.71981700	-0.38686900

S40

C	-0.11407800	-4.41134100	-0.48965400
C	-0.49842800	-3.07183900	-0.52793600
N	0.38772100	-2.05956500	-0.47101100
C	1.72466100	-2.35516800	-0.36549100
H	-1.54502200	-2.78353900	-0.60854200
H	1.57980800	-5.75571700	-0.35381400
H	-0.87362100	-5.19021800	-0.53996100
H	4.56457400	-2.15805000	-0.26268700
H	-0.10642200	0.88918400	4.47394000

C	-0.52395900	-0.00029800	3.92624100
C	-2.01309000	-0.00053000	3.96463200
C	-2.73156600	-0.00052900	2.81555000
C	-2.08686300	-0.00031200	1.53467800
N	-0.69164300	-0.00012100	1.42076400
C	0.10104000	-0.00011600	2.53744500
H	-2.51116500	-0.00069700	4.93554800
H	-3.82180800	-0.00070300	2.84777300
H	-4.85646300	-0.00036900	1.09857100
C	-4.23962500	-0.00030900	0.20433900
C	-4.82758600	-0.00027300	-1.05441700
C	-4.03232400	-0.00018600	-2.20766600
C	-2.64251400	-0.00012300	-2.03819800
N	-2.05778800	-0.00015500	-0.83282100
C	-2.82919400	-0.00026900	0.30807100
H	-5.91343700	-0.00030500	-1.14741600
H	-4.46000600	-0.00016200	-3.21233600
Ru	0.00381500	-0.00000200	-0.50907400
O	1.34796700	0.00004500	2.46232800
O	-1.76712000	-0.00003900	-3.06933400
H	-2.26266900	-0.00005800	-3.94746700
H	-0.10616100	-0.88975000	4.47380300

[Ru(tpyH)(6DHBP-H⁺)]⁺ rotH

H	-1.99333300	4.59460800	-1.37241200
C	-1.07687500	4.03846100	-1.18074400
C	0.15902400	4.68427600	-1.04607400
C	1.29832400	3.92021800	-0.79168800
C	1.18644300	2.53199300	-0.67311200
N	-0.03481400	1.90428700	-0.80900700
C	-1.13218600	2.65488200	-1.05580600
H	0.23496400	5.76744400	-1.13284100
H	2.26809100	4.39960100	-0.67108100
H	-2.07491900	2.11782700	-1.13680300
H	3.97912600	3.01874700	-0.53530300
C	3.67673700	1.98366000	-0.38951900
C	4.64382300	0.97021000	-0.19225800
C	4.24861800	-0.35965600	-0.03799600
C	2.87587400	-0.66663300	-0.04545500
N	1.95753000	0.33829200	-0.18717500
C	2.32692600	1.62983400	-0.39751500
H	5.70222100	1.22809500	-0.16902500

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H	4.06684200	-3.12545200	-0.49735400
C	3.01022900	-3.19802800	-0.24413000
C	2.34653000	-4.43776700	-0.28479100
C	0.94938500	-4.45031100	-0.02071400
C	0.29314700	-3.27301400	0.30333000
N	0.91833400	-2.05022300	0.35463300
C	2.29027600	-2.01902100	0.04597200
H	-0.77765300	-3.24227700	0.50245900
H	2.87156200	-5.34252900	-0.58547700
H	0.37734700	-5.37762100	-0.05821800

H	4.98927300	-1.14747800	0.08595800
H	-0.18550200	1.03600200	4.65717600
C	-0.78265200	0.75086900	3.78954100
C	-2.14915600	0.52781300	3.88220700
C	-2.88416500	0.15272900	2.72785100
C	-2.20269400	0.00055000	1.51930800
N	-0.85115000	0.22341700	1.42043400
C	-0.08010000	0.59781600	2.54359100
H	-2.66165300	0.63650500	4.83890300
H	-3.95107400	-0.03422600	2.78578400
H	-4.91363700	-0.48210200	0.95042600
C	-4.23711100	-0.62579700	0.11161200
C	-4.73519700	-1.00670800	-1.13971900
C	-3.86431900	-1.18663200	-2.21515200
C	-2.48974200	-0.97936900	-1.99855200
N	-1.99808000	-0.59099600	-0.79812800
C	-2.86542300	-0.41885300	0.26150800
H	-5.80626500	-1.15376400	-1.27748800
H	-4.21034200	-1.46847200	-3.21053300
Ru	0.02201100	-0.13193800	-0.39805800
O	1.17096200	0.78820300	2.44330500
O	-1.63950200	-1.14880900	-3.04240300
H	-0.69156700	-0.92772200	-2.74663600
H	0.77930400	-1.50963400	1.18435200

[Ru(tpyH)(6DHBP-H⁺)(S)]⁺ rotH

H	2.64020200	3.40648800	2.88639200
C	1.71477600	3.18886700	2.35443400
C	0.69805100	4.13818100	2.23727700
C	-0.46504000	3.79684800	1.54836200
C	-0.59081700	2.52164800	0.99010400
N	0.41615700	1.59793000	1.10537900
C	1.53513600	1.93457600	1.77552200
H	0.80498100	5.12950400	2.67711100
H	-1.27572100	4.51620800	1.44404000
H	2.30234300	1.16626600	1.84436500
H	-3.06640800	3.80467100	0.48242500

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C	-2.97996500	2.78688900	0.10760400
C	-4.05839600	2.17083100	-0.54122400
C	-3.95490000	0.85320600	-0.97894400
C	-2.74654700	0.15872300	-0.78099000
N	-1.69666600	0.79897900	-0.20174100
C	-1.79819600	2.05955100	0.27371000
H	-4.98582300	2.72213900	-0.69307200
H	-4.55047000	-1.89065500	-1.03327800
C	-3.51214800	-2.20996500	-1.12589800
C	-3.20509100	-3.57146100	-1.19998700
C	-1.83245400	-3.96607800	-1.21832500
C	-0.84624500	-3.02886200	-1.23708400

N	-1.12405100	-1.63288000	-1.19797600
C	-2.51596300	-1.24234900	-1.09030800
H	0.21182000	-3.27016400	-1.30492800
H	-3.99665900	-4.31747100	-1.20612800
H	-1.55802500	-5.02020500	-1.23205000
H	-4.79200300	0.36235100	-1.47206500
H	1.13894600	2.23167800	-4.41958600
C	1.55750800	1.66301600	-3.58719700
C	2.90521700	1.41061600	-3.48803700
C	3.39205400	0.65548400	-2.40532300
C	2.48943000	0.20020700	-1.45039000
N	1.14595100	0.46205200	-1.51516400
C	0.62887700	1.16764100	-2.60184000
H	3.59619200	1.78017900	-4.24692300
H	4.44977400	0.42363000	-2.33169900
H	5.04944000	-0.56023300	-0.73512100
C	4.27053600	-0.97079400	-0.09963600
C	4.60612600	-1.82890500	0.94985400
C	3.59754700	-2.37266000	1.73118700
C	2.27223100	-2.01399900	1.44796300
N	1.93335900	-1.13921200	0.47885200
C	2.93003500	-0.65158100	-0.32466500
H	5.64847200	-2.08624800	1.13679200
H	3.79457400	-3.07928300	2.53936500
Ru	0.00309700	-0.20351700	0.14888700
O	-0.61699800	1.35841300	-2.71727700
O	1.31019000	-2.57770100	2.19829700
H	0.42599100	-2.49357500	1.72428800
H	-0.67777800	-1.15119900	-2.07168700
N	-1.02573000	-0.83599400	1.80296600
C	-1.67795400	-1.06177400	2.73562100
C	-2.47335900	-1.35802900	3.91873200
H	-2.06892900	-0.81639800	4.78258300
H	-3.51272100	-1.04919200	3.75589900
H	-2.44585900	-2.43452800	4.12476900

S43

H	0.43701300	-5.25080800	-0.17039600
C	-0.26822000	-4.42100200	-0.17939300
C	-1.64438400	-4.62871200	-0.06748700
C	-2.49901100	-3.52696000	-0.08116500
C	-1.96277100	-2.24432600	-0.21195900
N	-0.61339200	-2.05228400	-0.32501800
C	0.20975700	-3.11901000	-0.30163700
H	-2.04978500	-5.63541100	0.03233800
H	-3.57602300	-3.65952600	0.00971600
H	1.27363300	-2.90676400	-0.38862300
H	-4.75780500	-1.82817000	-0.02711400
C	-4.15559900	-0.92639100	-0.12576600
C	-4.75799000	0.33318400	-0.14645500

C	-3.97195400	1.48127700	-0.26038400
C	-2.58509900	1.34165600	-0.36077000
N	-2.02027700	0.11247600	-0.35082200
C	-2.76487400	-1.01064800	-0.22902200
H	-5.84113900	0.42022200	-0.06790000
H	-2.98453100	4.09114600	-0.41971000
C	-1.94063700	3.78893100	-0.48894200
C	-0.93032300	4.74413800	-0.59165000
C	0.39758400	4.32010900	-0.67204500
C	0.67228600	2.95550300	-0.64705900
N	-0.30147800	2.02837100	-0.55667400
C	-1.60511600	2.43333300	-0.47454900
H	1.69171600	2.57809600	-0.70479100
H	-1.17849700	5.80525000	-0.60613500
H	1.21989400	5.02969300	-0.75149800
H	-4.42964300	2.46922700	-0.26711500
H	0.25336100	0.36074200	4.83056400
C	0.84164800	0.27457600	3.91345600
C	2.23007800	0.27580300	3.92155500
C	2.93256400	0.15905700	2.71987400
C	2.21561600	0.04284200	1.52513800
N	0.85645500	0.04647000	1.51643900
C	0.19123100	0.15769000	2.67502900
H	2.77103400	0.36569700	4.86355900
H	4.01851100	0.15609600	2.72474800
H	4.88754400	0.00836100	0.95748100
C	4.25205800	-0.10881200	0.08536900
C	4.83295900	-0.26427900	-1.19390900
C	4.02924500	-0.43568800	-2.28949400
C	2.58911800	-0.46939000	-2.16415500
N	2.03919300	-0.24487600	-0.88997600
C	2.87366400	-0.10471500	0.20328500
H	5.91856700	-0.25475400	-1.29851100
H	4.43979500	-0.57211600	-3.29156400

S44

Ru	-0.01356800	-0.05528900	-0.57181800
O	-1.15122200	0.14858000	2.56820700
H	-1.56888900	0.22984400	3.48314500
O	1.85733400	-0.69662000	-3.16183100
H	-0.39115000	-0.10987500	-2.10402700

[Ru(tpy)(6DHBP-H⁺)(S)]⁺

H	0.09882300	-5.31550800	-0.46249000
C	0.68271500	-4.39625600	-0.47040800
C	2.04206100	-4.39626900	-0.78705200
C	2.73674100	-3.18619000	-0.78293800
C	2.06296900	-2.00500200	-0.46273600
N	0.72860600	-2.01558100	-0.14704600
C	0.06573100	-3.18626000	-0.15623500
H	2.55736800	-5.32342200	-1.03683900

H	3.79636300	-3.15810000	-1.03196900
H	-0.99104800	-3.13717100	0.09995000
H	4.75056000	-1.20357600	-0.94008100
C	4.05264700	-0.39957600	-0.71250600
C	4.48840400	0.92816300	-0.67621400
C	3.59171200	1.95498400	-0.37121100
C	2.25779600	1.62701900	-0.10898000
N	1.85671800	0.33805700	-0.17089900
C	2.70770800	-0.67437600	-0.45198000
H	5.53263500	1.16226100	-0.88016900
H	2.32900200	4.38795200	0.12400800
C	1.35313000	3.95172000	0.33133300
C	0.27429200	4.76567700	0.67755300
C	-0.96314700	4.17376400	0.93563900
C	-1.07869600	2.78804300	0.83727000
N	-0.04477600	1.99536100	0.50222600
C	1.17468600	2.56835500	0.24848600
H	-2.02398400	2.28381800	1.03057800
H	0.40142700	5.84594800	0.74411000
H	-1.83356300	4.76776700	1.21055200
H	3.92807400	2.98961000	-0.33134700
H	-0.38896900	0.77631100	-4.91095600
C	-0.95671600	0.59220900	-3.99713500
C	-2.33086800	0.62909900	-3.97893900
C	-3.01551600	0.36583400	-2.77884600
C	-2.27440400	0.09777800	-1.63244300
N	-0.90456200	0.09151300	-1.62054000
C	-0.19935500	0.29795700	-2.80621400
H	-2.89195600	0.84969300	-4.88782600
H	-4.10034600	0.36545800	-2.75743900
H	-4.97132800	-0.09609500	-1.07001700
C	-4.32532800	-0.33157100	-0.22994300

S45

C	-4.88058100	-0.73177000	0.98578500
C	-4.03999400	-1.06009400	2.03872200
C	-2.65394800	-0.95347600	1.84781700
N	-2.10154900	-0.52700600	0.69329800
C	-2.93639000	-0.24897400	-0.35538300
H	-5.96203100	-0.79889800	1.10234700
H	-4.42094300	-1.40066400	3.00494100
Ru	-0.01605100	-0.10270500	0.29391400
N	0.71518600	-0.24772700	2.19509100
C	1.22306900	-0.28725200	3.23529700
C	1.82504300	-0.35133600	4.55992300
H	1.09723000	-0.02846000	5.31391700
H	2.13530900	-1.38011600	4.77822100
H	2.70256000	0.30423200	4.60475300
O	1.06360800	0.22889000	-2.83076400
O	-1.78816900	-1.28130000	2.82167300
H	-2.29239100	-1.58824200	3.63939200

[Ru(tpy^{•-})(6DHBP-H⁺)]⁰ rotH

H	0.77299900	-5.18162500	-0.29506700
C	0.00958900	-4.40616300	-0.25617100
C	-1.35475500	-4.72488200	-0.15065100
C	-2.28138600	-3.69054100	-0.10534600
C	-1.84925100	-2.35579700	-0.16832400
N	-0.50443700	-2.04916400	-0.27720000
C	0.38495800	-3.07189900	-0.31440800
H	-1.68347500	-5.76229100	-0.10214500
H	-3.34512800	-3.90589300	-0.01700700
H	1.43045100	-2.78150800	-0.39918000
H	-4.67486500	-2.15895800	-0.13952800
C	-4.13540600	-1.21309000	-0.12587500
C	-4.83793700	0.00032800	-0.11721400
C	-4.13522300	1.21364200	-0.12582900
C	-2.74099400	1.20180400	-0.12907500
N	-2.06011500	0.00011800	-0.11972800
C	-2.74117400	-1.20146200	-0.12912000
H	-5.92635900	0.00041500	-0.11734400
H	-3.34452200	3.90631000	-0.01677200
C	-2.28081400	3.69080800	-0.10515500
C	-1.35402500	4.72501100	-0.15041200
C	0.01026500	4.40608500	-0.25597900
C	0.38542800	3.07176500	-0.31430400
N	-0.50412300	2.04916600	-0.27714400
C	-1.84889100	2.35600400	-0.16822700
H	1.43087600	2.78121900	-0.39910300
H	-1.68258500	5.76246700	-0.10183200
H	0.77379700	5.18142900	-0.29484200

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H	-4.67454300	2.15959000	-0.13944400
H	1.32033100	-0.00026800	4.80693000
C	1.71332800	-0.00026800	3.78858600
C	3.07495300	-0.00050500	3.51341500
C	3.51090500	-0.00047400	2.18560700
C	2.56665500	-0.00023800	1.15735200
N	1.22276900	-0.00005300	1.42256400
C	0.81904500	-0.00002400	2.70909500
H	3.79856900	-0.00070900	4.32824800
H	4.57277900	-0.00064300	1.95453800
H	5.07302000	-0.00012600	-0.06083300
C	4.22977300	-0.00010800	-0.74562800
C	4.43011000	-0.00000700	-2.13696300
C	3.34553000	0.00003300	-2.99474900
C	2.00423300	-0.00001200	-2.48329300
N	1.84185200	-0.00011100	-1.10843000
C	2.91735900	-0.00016300	-0.27554000
H	5.44452400	0.00004300	-2.53761500
H	3.47668000	0.00010700	-4.07848000
Ru	-0.10471400	-0.00002000	-0.28265100
O	-0.49764700	0.00024800	2.96992400

H	-0.98329600	0.00037900	2.07352800
O	0.97300700	0.00002100	-3.23475000

[Ru(tpy)(6DHBP+H⁺_c-H⁺_d)]⁺

H	-0.86996800	5.19068000	-0.47019500
C	-0.10918700	4.41192800	-0.44171500
C	1.25006300	4.72051800	-0.36991600
C	2.17849000	3.67863000	-0.33409100
C	1.73272700	2.35600700	-0.37050800
N	0.39375900	2.06019000	-0.44548600
C	-0.49373500	3.07237200	-0.47694000
H	1.58698300	5.75640600	-0.33997100
H	3.24465200	3.89193900	-0.27418700
H	-1.54188100	2.78404200	-0.53402900
H	4.57375400	2.15931100	-0.35712000
C	4.03522300	1.21322000	-0.34072800
C	4.73123200	0.00082300	-0.33332800
C	4.03563900	-1.21181600	-0.34101500
C	2.63846100	-1.18546700	-0.33733900
N	1.98499100	0.00035200	-0.31417300
C	2.63804900	1.18639600	-0.33707100
H	5.82063200	0.00101100	-0.33516000
H	3.24592500	-3.89083700	-0.27472200
C	2.17969800	-3.67785800	-0.33465100
C	1.25159100	-4.72003000	-0.37056100

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C	-0.10775200	-4.41185700	-0.44238400
C	-0.49271600	-3.07241700	-0.47753900
N	0.39447100	-2.05997100	-0.44596700
C	1.73352800	-2.35537300	-0.37098000
H	-1.54094600	-2.78440100	-0.53466300
H	1.58882900	-5.75581400	-0.34065600
H	-0.86828600	-5.19084700	-0.47093200
H	4.57448800	-2.15772200	-0.35763400
C	-0.45225200	-0.00080900	3.87517500
C	-1.82527300	-0.00092400	4.01160300
C	-2.63733900	-0.00071500	2.87060800
C	-2.03406200	-0.00045400	1.60263500
N	-0.65244400	-0.00035200	1.45859800
C	0.17681300	-0.00048700	2.57554300
H	-2.28048600	-0.00113300	5.00273000
H	-3.71935300	-0.00076400	2.95873000
H	-4.81625500	-0.00022300	1.25292500
C	-4.24073600	-0.00024200	0.32604400
C	-4.88546100	-0.00017900	-0.87122200
C	-4.13356700	-0.00020300	-2.16488000
C	-2.65462300	-0.00021100	-1.94923000
N	-2.06324100	-0.00022900	-0.78557100
C	-2.81236100	-0.00030900	0.39262800

H	-5.97494400	-0.00010400	-0.91634300
H	-4.40563800	-0.89513400	-2.80167900
Ru	0.01398100	0.00002400	-0.47770900
O	1.43607700	-0.00035000	2.45562700
O	-1.84467300	-0.00019700	-3.01444600
H	-2.38743300	-0.00006900	-3.86936500
H	-4.40562000	0.89473600	-2.80169900
H	0.21168000	-0.00094200	4.74107500

[Ru(tpy)(6DHBP-2H⁺)(S)]⁰

H	0.74178600	-5.28163800	-0.64498700
C	1.21090400	-4.29934900	-0.61304100
C	2.56503100	-4.12584400	-0.90429200
C	3.10798800	-2.84184800	-0.84814300
C	2.29242100	-1.76129900	-0.50276500
N	0.96388000	-1.94172200	-0.21194900
C	0.44843000	-3.18336600	-0.27144300
H	3.19198300	-4.97541100	-1.17380000
H	4.16009300	-2.67773000	-1.07547900
H	-0.60984500	-3.26979400	-0.03298000
H	4.87069200	-0.63254700	-0.91653500
C	4.08053100	0.07485900	-0.67084300
C	4.35572100	1.44315000	-0.58443700
C	3.34118800	2.34564900	-0.25529700

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C	2.05333800	1.85305100	-0.01917400
N	1.80682900	0.52827400	-0.13164900
C	2.77524200	-0.36544500	-0.43745700
H	5.36639100	1.80602400	-0.76763800
H	1.79687800	4.59000800	0.32736700
C	0.87755900	4.03441200	0.50562900
C	-0.29060700	4.70126000	0.87498900
C	-1.45118700	3.95773100	1.09656700
C	-1.40282300	2.57355000	0.93901700
N	-0.28181100	1.92148900	0.58007600
C	0.86376200	2.64418800	0.36308400
H	-2.28253100	1.95408900	1.10280000
H	-0.29130100	5.78509800	0.98811100
H	-2.38635600	4.43346800	1.38836800
H	3.55289800	3.41053200	-0.17572500
H	-0.44278200	0.93207000	-4.87081200
C	-0.99285400	0.67976200	-3.96261700
C	-2.36905300	0.67481900	-3.92589100
C	-3.03237900	0.31789900	-2.73927200
C	-2.27283600	0.00437400	-1.61476000
N	-0.90353900	0.05047300	-1.62006900
C	-0.21652300	0.33807700	-2.79921600
H	-2.94649700	0.93184600	-4.81499400
H	-4.11601900	0.27584900	-2.70855500
H	-4.95024100	-0.31401400	-1.02868700

C	-4.28136800	-0.59661100	-0.22257400
C	-4.79492300	-1.11915300	0.97678500
C	-3.93020600	-1.52359100	1.97023400
C	-2.50460500	-1.41077400	1.80419400
N	-2.02973100	-0.80039700	0.64640900
C	-2.90024100	-0.46243700	-0.35286600
H	-5.87319200	-1.21868800	1.10881200
H	-4.29198500	-1.95918500	2.90328100
Ru	-0.00827400	-0.14864700	0.28783600
N	0.69253200	-0.28458900	2.19909600
C	1.17602700	-0.29516400	3.25215800
C	1.73887600	-0.33735500	4.59493500
H	1.08012800	-0.91546700	5.25415300
H	2.72752100	-0.81063300	4.57168600
H	1.83968100	0.67990900	4.99120700
O	1.04991500	0.29833100	-2.83670700
O	-1.69927100	-1.85349000	2.68110700