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Supporting Information

Unsymmetric Dirhodium Single Molecule Photocatalysts for H₂ Production with Low-Energy Light

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Materials

The starting material [RhCl(COD)]₂ was purchased from Pressure Chemicals and used as received. The partially solvated compound *cis*-[Rh₂(DTolF)₂(MeCN)₆][BF₄]₂ was synthesized by addition of two equivalents of the formamidinate ligand to [RhCl(COD)]₂ followed by oxidation with AgBF₄ according to reported procedures.^{S1} Tetrabutylammonium hexafluorophosphate (TBAPF₆) was purchased from Alfa Aesar. The ligands 2-(1,8-naphthyridin-2-yl)quinoxaline (qxnp) and 2-(quinolin-2-yl)-1,8-naphthyridine (qnnp) were prepared according to reported procedures.^{S2,S3} The solvent acetonitrile was dried over 3 Å molecular sieves and distilled under a N₂ atmosphere. The complexes were synthesized under a N₂ atmosphere using standard Schlenk techniques. Additional manipulations of the products were performed in air.

 $cis - [Rh_2(\mu - DTolF)_2(\mu - np)(\mu - qxnp)] / [BF_4]_2$ (1). Equimolar quantities of $cis - [Rh_2(\mu - DTolF)_2(\mu - np)(\mu - qxnp)] / [BF_4]_2$ (1). $np)(\mu-qxnp)$][BF₄]₂ (101.6 mg, 0.095 mmol), np (12.2 mg, 0.094 mmol), and qxnp (24.4 mg, 0.094 mmol) were suspended in 20 mL of acetonitrile and refluxed for 24 hours in an oil bath at 90 °C. The resulting dark purple solution was concentrated to ~5 mL and copious amounts of diethyl ether were added to precipitate the product. The product was filtered through a fine frit and washed three times with 5 mL of diethyl ether. The product was obtained as a 110.3 mg mixture of 1, cis-[Rh₂(µ- $DTolF_2(\mu-np)_2$ [BF₄]₂ and *cis*-[Rh₂(μ -DTolF)₂(μ -qxnp)₂][BF₄]₂ which were separated by column chromatography using neutral alumina as the stationary phase and a gradient of 2-5% methanol in dichloromethane. The desired compound was collected in the second band and evaporated to dryness to yield 39.7 mg (34.4% yield) of a purple powder. ¹H NMR (499 MHz, CD₃CN) δ 10.72 (d, J = 40.2 Hz, 2H), 9.67 (s, 1H), 8.72 (dd, J = 5.3, 1.3 Hz, 1H), 8.70 - 8.65 (m, 2H), 8.54 (ddd, J = 5.3, 1.3 Hz, 1H), 8.70 - 8.55 (m, 2H), 8.54 (ddd, J = 5.3, 1.3 Hz, 1H), 8.70 - 8.55 (m, 2H), 8.54 (ddd, J = 5.3, 1.3 Hz, 1H), 8.70 - 8.55 (m, 2H), 8.55 (m= 8.3, 5.3 Hz, 1H), 7.83 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.33 – 7.29 (m, 2H), 7.17 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.10 (d, J = 8.1 Hz, 2H), 7.03 (dd, J = 8.8, 1.0 Hz, 1H), 6.95 -6.89 (m, 4H), 6.71 (d, J = 8.2 Hz, 2H), 6.27 (d, J = 8.2 Hz, 2H), 6.20 (d, J = 8.2 Hz, 2H), 6.12 (dd, J = 19.1, 7.1 Hz, 4H), 2.40 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H), 1.85 (s, 3H). HRMS (ESI-MS) m/z: $[M]^{2+}$ (C₅₄H₄₆N₁₀Rh₂) 520.0999 calc. $[M]^{2+}$ (C₅₄H₄₆N₁₀Rh₂) 520.1003.

 $cis - [Rh_2(\mu - DTolF)_2(\mu - np)(\mu - qnnp)] [BF_4]_2$ (2). Quantities of $cis - [Rh_2(\mu - DTolF)_2(\mu - np)(\mu - qnnp)]$ qxnp)][BF₄]₂ (100.3 mg, 0.094 mmol), np (12.1 mg, 0.093 mmol), and qnnp (23.9 mg, 0.093 mmol) were suspended in 20 mL of acetonitrile and refluxed in an oil bath at 90 °C for 24 hours. The dark purple solution was cooled and the solvent was evaporated to near dryness. Diethyl ether was used to precipitate the product which was collected by vacuum filtration on a fine frit to yield 98.6 mg of a dark blue powder. As in the case of 1, the product was obtained as a mixture of 2 and the bis-substitution products $cis-[Rh_2(\mu-DTolF)_2(\mu-np)_2][BF_4]_2$ and $cis-[Rh_2(\mu-DTolF)_2(\mu-np)_2][BF_4]_2$ qnnp)₂][BF₄]₂. The desired product was obtained by evaporation of the second fraction from column chromatography using neutral alumina and 2-5% methanol in dichloromethane; 42.1 mg of 2 (36.9 % yield). ¹H NMR (499 MHz, cd₃cn) δ 10.67 (d, J = 16.4 Hz, 2H), 8.81 (dd, J = 5.3, 1.4 Hz, 1H), 8.58 (d, J = 8.8 Hz, 1H), 8.51 (d, J = 7.7 Hz, 2H), 8.46 (dd, J = 8.3, 1.7 Hz, 1H), 8.41 (dd, J = 8.6, 3.1 Hz, 2H), 8.20 (d, J = 8.7 Hz, 1H), 7.90 (dd, J = 8.2, 1.2 Hz, 1H), 7.80 (dd, J = 8.2, 1H), 7.80 (dd, J = 85.3 Hz, 1H), 7.70 (dd, J = 8.1, 5.4 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.36 (dd, J = 8.1, 4.8 Hz, 2H), 7.26 (dd, J = 8.2, 5.3 Hz, 1H), 7.11 (ddd, J = 8.5, 5.1, 1.7 Hz, 3H), 6.85 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.3 Hz, 2H), 6.36 (d, J = 8.3 Hz, 2H), 6.29 - 6.23 (m, 4H), 6.12(d, J = 8.0 Hz, 2H), 2.41 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.87 (s, 3H). HRMS (ESI-MS) m/z: $[M]^{2+}$ (C₅₄H₄₆N₁₀Rh₂) 519.6026 calc. $[M]^{2+}$ (C₅₅H₄₇N₉Rh₂) 519.6027.

Instrumentation and methods

¹H NMR spectra were obtained on an Inova 500 MHz spectrometer; the chemical shifts were referenced to the residual peak of the residual CD₃CN- d_3 deuterated solvent signal at 1.96 ppm. Electronic spectroscopy was performed on a Shimadzu UV-1601PC spectrophotometer in 1×1 cm quartz cuvettes. Extinction coefficients in acetonitrile were determined in triplicate. An acid titration of a solution of the compounds in acetonitrile was followed by UV-Vis spectroscopy with a solution of TsOH in acetonitrile. The acid was added in amounts of 0.3 equivalents and the absorption profile was recorded. The number of equivalents of acid required to fully protonate the complex was determined from a plot of the absorbance at 581 nm as a function of the amount of acid added.

Electrochemical measurements for **1** and **2** $(1 \times 10^{-3} \text{ M})$ were recorded under an inert atmosphere using dry acetonitrile and 0.1 M [n-Bu₄N][PF₆] as the supporting electrolyte with a CH Instruments electrochemical analyzer model CH1620A. A three-electrode cell was used with a Ag/AgCl reference electrode standardized to ferrocene (E_{1/2} = +0.55 V vs Ag/ AgCl), a Pt wire as the counter electrode, and a glassy carbon disk as the working electrode. High-resolution Electrospray Ionization mass spectrometry (ESI-MS) data were obtained in the Laboratory for Biological Mass Spectrometry at Texas A&M University using a using a Thermo Scientific Q Exactive Focus. The sample was directly infused at a flow rate of 10 µL/min. The Q Exactive Focus HESI source was operated in full MS in positive mode. The mass resolution was tuned to 17500 FWHM at m/z 200, the spray voltage was set to 3.75 kV, and the sheath gas and auxiliary gas flow rates were set to 7 and 0 arbitrary units, respectively. The transfer capillary temperature was held at 250 °C and the S-Lens RF level was set at 50 v. Exactive Series 2.8 SP1/Xcalibur 4.0 software was used for data acquisition and processing.

Nanosecond transient absorption spectra were obtained on a setup that was previously reported.^{S4} The pump beam (~5 mJ) was generated using a BasiScan OPO (Spectra Physics) pumped with the third harmonic of an Nd:YAG laser (Spectra Physics, INDI-40) at a rate of 10 Hz and power of 130 mJ. The output of a continuous 150 W xenon arc lamp gated using a Uniblitz shutter was used as the probe. The pump and probe pulse were overlapped at a 90° geometry at the sample. Time-resolved absorption spectra were obtained on an Edinburgh LP980 spectrometer with an ICCD-based broadband camera. The kinetic traces were collected with a PMT and an oscilloscope. All transient absorption samples were deoxygenated prior to study and UV-vis spectra were collected before and after to ensure no sample degradation occurred upon irradiation. All samples were prepared to an optical density of ~ 0.5 OD in acetonitrile at the 650 nm excitation in a 1 by 1 cm cell and all fits were performed as the sum of exponentials using Igor Pro (6.3) software with instrument response deconvolution.

Ultrafast transient absorption (fsTA) experiments were performed on a system previously described in detail.^{S5} Briefly, the output of a Ti:sapphire regenerative amplifier (Astrella 1K-USP, Coherent) was split to generate the white light probe through rotating CaF₂ crystal and to pump an OPA (OPerA Solo, Coherent/Positive Light) to generate the pump pulse at 720 nm. A thermally cooled CCD camera and home-built software written in LabVIEW 2015 were used to collect and manipulate data. The sample solution was prepared with ~ 0.5 OD in acetonitrile at the excitation wavelength and ~ 5 mL of the solution containing the sample was flowed through a 1 mm pathlength Harrick Scientific flow cell (1 mm thick CaF₂ windows) and excited with ~ 2.5 μ J at the pump wavelength. The protonated samples were prepared in acetonitrile with the addition of p-

toluenesulfonic acid (TsOH) until no blue shift was observed in the spectra. An instrument response of fwhm ~ 85 fs was measured using the Kerr effect in cyclohexane. The polarization angle between the pump and probe was set to 54.7° to avoid the rotational diffusion effects. All fits were performed as the sum of exponentials using Igor Pro (6.3) software with instrument response deconvolution.

All irradiation studies were performed using light emitting diodes (Luxeon Star), where 655 nm irradiation was performed with 2 LEDs on a homebuilt irradiation apparatus, where the sum of all the LED output was found to be 500 mW. Acrylic plates were designed to hold a 1 cm cuvette in the center of the LEDs, each at a 1.6 cm distance from the photolysis vials. All samples were prepared with ~ 0.5 OD at a 655 nm irradiation wavelength in DMF with the addition of 120 mM BNAH as the electron donor and 100 mM TsOH as the acid source. All samples were purged under N₂ for 15 min before irradiation. Dark controls were performed by irradiating the samples in an aluminum foil sleeve to ensure that the effect was not merely temperature dependent. Quantification of hydrogen was performed by irradiation in septum capped vials. Volume measurements of vials were performed by weight when filled with deionized water with all measurements being made in triplicate.

Gaseous products were qualified and quantified with a Shimadzu GC-2014 gas chromatograph (GC). Aliquots of headspace were removed using a Hamilton gastight syringe and injected into a GC (He carrier gas for H₂ generation) with a ShinCarbon column (2 m long × 1/8 in. OD × 2.0 mm ID) and a Shimadzu TCD-2014 thermal conductivity detector. The GC conditions were as follows: injector temperature, 41.0 °C; column temperature, 30 °C; detector temperature, 150 °C; and gas flow, 25 mL/min. The calibration curve was constructed by injecting a series of known amounts of 5% H₂/N₂ mixture in triplicate.

Density Functional Theory (DFT) calculations were performed to calculate the molecular orbital contributions to the molecular orbitals using the Gaussian (09) package.^{S6} For the Rh atoms, The Stuttgart RSC 1997 Electron Core Potential (ECP)^{S7} basis set was used, and the 6-31G[†] basis set was used for the C, N, and H atoms.^{S8} The B3LYP correlation and exchange functional was used.^{S9,S10} The geometric parameters of a low-resolution crystal structure obtained for **1**, omitting interstitial solvent molecules and counterions, was used as a starting point for the gas optimization of this compound. In addition, this optimized structure was employed as a starting point to model the structure of **2**, as well as the structures of the intermediates of the proposed photocatalytic cycle for H₂ production using 'GaussView'. Time-Dependent Density Functional Theory (TD-DFT) calculations were performed following the gas-phase optimizations using the polarized continuum model (PCM) with acetonitrile as the solvent. The first sixty lowest singlet-to-singlet excited states were calculated from the first ground states calculated for these complexes.

Single crystals of 1 + HCl and 1 in HBF₄ were selected from mineral oil under ambient conditions using a MiTeGen microloop or a nylon loop. Crystals were placed in a cold N₂ stream at 110 K on a Bruker D8-QUEST diffractometer equipped with a IµS Mo microsource ($\lambda = 0.71073$ Å). Initial unit cells were determined using SAINT from a set of three ω -scans consisting of 0.5° frames and a sweep width of 15°. For each structure, the data were corrected for absorption using SADABS and the space group was determined from analysis of the systematic absences using XPREP.¹¹ The structures were solved using the intrinsic phasing routine in SHELXT or by direct methods implemented in SHELXS. The diffraction of both crystals, however, was rather poor which precluded anisotropic refinement of the data.



Figure S1. ¹H NMR spectrum of complex 1 in acetonitrile-d₃.



Figure S2. ¹H NMR spectrum of complex 2 in acetonitrile-d₃.

Cyclic voltammetry and Electrocatalytic H₂ production



Figure S3. Cyclic voltammograms of and 1 (green) and 2 (blue). The insert represents the first oxidation potential for each complex.

In order to assess the electrocatalytic activity of these complexes, cyclic voltammetry experiments were performed in the presence of AcOH as an acid source. Solutions of AcOH in acetonitrile were prepared and added to the complexes in the electrochemical cell in small increments as a function of the quantity of compound. The cathodic potential was scanned for increasing amounts of acid, recorded, and then plotted against the current generated (Figures S4 and S5).

Figure S4. Cyclic voltammograms of 1 in the presence of increasing amounts of AcOH.

Figure S5. Cyclic voltammograms of 2 in the presence of increasing amounts of AcOH.

Electronic structure calculations

In order to better understand the origin of the electronic transitions of **1** and **2**, molecular structure calculations were performed using density functional theory (DFT) in the Gaussian09 (G09) program package.⁶ The B3LYP¹⁰ correlation and exchange functionals were used with the Stuttgart RSC 1997 Electron Core Potential (ECP)¹² basis set for the Rh atoms and the 6-31G[†] basis set for the C, N, and H atoms.⁸ The geometrical parameters of a low-resolution crystal structure obtained for **1** as a starting point for the gas-phase optimizations (Figure S6, Table S1). Crystals for **1** were obtained in the presence of HCl which led to the protonation of the compound with a concomitant blue-shift of its absorption profile. All the ligands were attached to the Rh₂ core in this structure. In contrast, prolonged exposure HBF₄ led to the dissociation of one of the formamidinate ligands as seen in a low-resolution crystal structure for the decomposition product. Due to the low-resolution nature of these structures, they were not able to be refined anisotropically, and are therefore, not presented.

These optimized structures in the gas phase were used for the time-dependent density functional theory (TDDFT)¹³ calculations with a polarized continuum model (PCM) with CH3CN as the solvent.¹⁴ The first 60 lowest singlet-to-singlet excitations were calculated from the optimized singlet ground state as plotted (Figure S8). The molecular orbitals were plotted with the graphic software "Agui" with an isovalue of 0.04 (Table S3).¹⁵ Natural transition orbital (NTO) analyses were performed with the Chemissian program (http://www.chemissian.com).

The results indicate that the HOMO for complexes 1 and 2 are 31% Rh2(δ^*) in character with a large contribution of 64% from the formamidinate ligands. The LUMOs have 90% qxnp and qnnp character for 1 and 2 respectively (Tables S2, S3, and S4). Since 1 and 2 contain two different π -accepting ligands, the first two LUMOs have markedly different energies due to the orbital contributions of the np to the LUMO+1 and qxnp or qnnp to the LUMO. The lowest energy transitions of 1 - 5 appear in the visible region and extend into the near-IR; TD-DFT calculations

were performed to assign the nature of these transitions (Figure S16 and Table S4). The lowest energy transitions for 1 are assigned as $Rh2(\pi^*)/DTolF \rightarrow qxnp$ and $Rh2(\pi^*)/DTolF \rightarrow np$ ML-LCT which correspond to HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1, respectively. Similarly, 2 displays two MLCT transitions that are $Rh_2(\pi^*)/DTolF \rightarrow qnnp$ and $Rh_2(\pi^*)/DTolF \rightarrow np$ in character.

Figure S6. Gas-phase optimized structures for (a) 1 and (b) 2.

Bond distance (Å) / dihedral angle (°)	1	2
Rh1-Rh2	2.49259	2.49317
Rh1-N1	2.09727	2.10413
Rh1-N3	2.07174	2.07296
Rh1-N5	2.11259	2.10990
Rh1-N7	2.12883	2.12632
Rh1-N9	2.54907	2.54529
Rh2-N2	2.06565	2.06540
Rh2-N4	2.08002	2.08080
Rh2-N6	2.13669	2.13453
Rh2-N8	2.13666	2.13462
Rh2-N10	2.25871	2.26470
N1-Rh1-Rh2-N2	-14.40571	-14.73908
N7-Rh1-Rh2-N8	-15.74080	-15.92198

Table S1. Calculated bond distances and dihedral angles for 1 and 2.

Figure S7. A comparison of the calculated MO diagrams for 1 and 2 with the bis substituted *cis*- $[Rh_2(DTolF)_2(np)_2(MeCN)_2][BF_4]_2$ and *cis*- $[Rh_2(DtolF)_2(qxnp)_2][BF_4]_2$ complexes.

Orbital	1	2
HOMO–5	83% Rh, 11% DtolF	67% Rh, 28% DtolF
HOMO-4	68% Rh, 25% DtolF	59% Rh, 18% DtolF, 20% qnnp
HOMO-3	44% Rh, 51% DtolF	47% Rh, 49% DtolF
HOMO-2	38% Rh, 58% DtolF	53% Rh, 41 DtolF
HOMO-1	9% Rh, 89% DtolF	10% Rh, 88% DtolF
НОМО	31% Rh, 64% DtolF	31% Rh, 64% DtolF
LUMO	7% Rh, 90% qxnp	7% Rh, 90% qnnp
LUMO+1	10% Rh, 86% np	11% Rh, 85% np
LUMO+2	26% Rh, 65% qxnp	56% Rh, 8% DtolF, 27% qnnp
LUMO+3	53% Rh, 7% DtolF, 30% qxnp	24% Rh, 68% qnnp
LUMO+4	10% Rh, 84% qxnp	11% Rh, 68% qnnp
LUMO+5	26% Rh, 15% DtolF, 50% np	17% Rh, 7% DtolF, 56% np, 19% qnnp
LUMO+6	32% Rh, 16% DtolF, 36% np, 16% qxnp	39% Rh, 22% DtolF, 22% np, 16% qnnp

Table S2. Orbital contributions for 1–4 as predicted by TD-DFT calculations in acetonitrile (HOMO-5 through LUMO+6).^a

^aOnly contributions higher than 5% are listed.

Orbital	1	2
LUMO+3		
LUMO+2		
LUMO+1		

Table S3. Electron density maps for **1** and **2** from its HOMO–1 to its LUMO+3 with an isovalue = 0.04.

Excited State	1	2
1	11,442 cm ⁻¹ (874 nm), $f = 0.018$, H \rightarrow L (98.0%)	12,579 cm ⁻¹ (795 nm), $f = 0.020$, H \rightarrow L (98.0%)
2	15,152 cm ⁻¹ (660 nm), $f = 0.020$, H–1 \rightarrow L (94.1%)	15,504 cm ⁻¹ (645 nm), $f = 0.032$, H \rightarrow L+1 (94.1%)
3	15,625 cm ⁻¹ (640 nm), $f = 0.029$, H \rightarrow L+1 (88.1%)	16,207 cm ⁻¹ (617 nm), $f = 0.005$, H \rightarrow L+2 (54.8%) H-1 \rightarrow L (32.5%)
4	16,181 cm ⁻¹ (618 nm), $f = 0.004$, H \rightarrow L+2 (47.6%) H \rightarrow L+3 (37.2%)	16,611 cm ⁻¹ (602 nm), $f = 0.017$, H-1 \rightarrow L (64.0%) H \rightarrow L+2 (27.0%)
5	18,553 cm ⁻¹ (539 nm), $f = 0.002$, H-3 \rightarrow L (33.6%) H-4 \rightarrow L (27.0%)	18,727 cm ⁻¹ (534 nm), $f = 0.006$, H–1 \rightarrow L+1 (96.0%)
6	18,832 cm ⁻¹ (531 nm), $f = 0.006$, H-1 \rightarrow L+1 (96.0%)	19,084 cm ⁻¹ (524 nm), $f = 0.003$, H-3 \rightarrow L+2 (15.2%)
7	19,157 cm ⁻¹ (522 nm), $f = 0.003$, H-5 \rightarrow L (34.1%) H-2 \rightarrow L (24.0%)	19,569 cm ⁻¹ (511 nm), $f = 0.001$, H-4 \rightarrow L+2 (22.1%)
8	19,569 cm ⁻¹ (511 nm), $f = 0.005$, H \rightarrow L+3 (44.0%) H \rightarrow L+2 (41.0%)	20,576 cm ⁻¹ (486 nm), $f = 0.009$, H–2 \rightarrow L (46.2%)

Table S4. Vertical energies of the singlet excited states, oscillator strengths, f, and major orbital contributions^a calculated for 1 and 2 in acetonitrile (H = HOMO; L = LUMO)^b

^aOnly contributions of \geq 20% are listed. ^bYellow = ML-LCT (Rh/DtolF \rightarrow qxnp), blue = LLCT (DtolF \rightarrow qxnp), green = ¹MC (Rh₂(π^*) \rightarrow Rh₂(σ^*)).

Ground state protonation

In order to elucidate the number of equivalents required to fully protonate this complex, a titration experiment was carried out by sequential addition of TsOH followed by steady state absorption studies (Figure S5). The maximum at 581 nm for **2** was plotted as a function of the number of equivalents of TsOH added to the solution. Least-squares linear regression analysis of the data indicates that the there is a 1:1 ratio of proton to complex as shown in Figure S7.

Figure S9. Electronic absorption spectra of 1 as a function of TsOH equivalents.

Figure S10. Acid titration of **2** with a solution of TsOH in acetonitrile followed by UV-vis spectroscopy at 581 nm. The change in slope before and after the equivalence point between the blue and green lines occurs around 1 eq of acid suggests a 1:1 proton/complex ratio.

Calculated spectra of protonated complexes

TD-DFT calculations were also performed in order to elucidate the site for protonation of these complexes. To do this, a proton was placed on different N atoms on the ligands and their predicted absorption profiles were compared to the experimentally observed blue-shift in the presence of acid. Compound 2 was protonated at the qnnp ligand and two possible products were proposed, namely one that includes ligand dissociation from the axial position and a second one that involves the formation of a cyclometalated complex with the qnnp ligand (Figure S8). The

calculated spectra for both proposed protonated complexes leads to a red-shift which is not consistent with what is observed experimentally. In contrast, protonation of **1** at the N atom of one of the formamidinate ligands leads to a predicted red-shift, in accord with the experimental results (Figure S9). Protonation at this site would be expected to reduce the electron donating capabilities of the formamidinate ligand which has a large contribution to the HOMO of these complexes.

Figure S11. Calculated oscillator strengths for 2 (blue), for the complex protonated at the qnnp ligand (purple), and the protonated cyclometalated qnnp ligand on the dirhodium unit (red).

Figure S12. Calculated oscillator strengths for 1 (green) and the protonated analogues with acetonitrile (purple) or a chloride ion (red) in the axial positions respectively.

¹H NMR acid titrations

Acid titrations with dilute DCl in D₂O were followed by ¹H NMR spectroscopy for solutions of both complexes in CD₃CN- d_3 (Figures S10 and S11)

Figure S13. ¹H NMR spectroscopic data for **1** in acetonitrily- d_3 after protonation with DCl in D₂O. The peaks correspond to the protons in the qxnp ligand which are *trans* to the formamidinate ligand. The observed shift is a result of the change in *trans* effect as the formamidinate is protonated with increasing addition of acid.

Figure S14. ¹H NMR spectroscopic data for **2** in acetonitrily- d_3 after protonation with DCl in D₂O. The peaks shown correspond to the protons in the qnnp ligand that are *trans* to the formamidinate ligand. The observed shift is a result of the change in *trans* effect as the formamidinate is protonated with increasing addition of acid.

Transient absorption spectroscopy

Figure S15. fsTA of 2 in CH₃CN (λ_{ex} = 720 nm, 2.5 µJ).

Figure S16. nsTA kinetic trace of **2** measured at 470 nm and fitted with IRF ($\lambda ex = 650$ nm, 5 mJ in CH₃CN).

Figure S17. Kinetic trace of 2 measured at 470 nm ($\lambda ex = 720$ nm, 2.5 µJ in CH₃CN).

Figure S18. Kinetic trace of 1 measured at 460 nm ($\lambda ex = 650$ nm, 2.5 µJ in CH₃CN).

Figure S19. nsTA spectra of 1 (red) and 2 (blue) in CH_3CN in the presence of *p*-phenylenediamine collected at 10 µs after a 650 nm pulse (5 mJ).

Figure S20. (a) fsTA spectra of protonated 1 in CH₃CN and (b) kinetic trace at 430 nm and biexponential fit with $\tau_1 = 6$ ps (64%) and $\tau_2 \sim 2$ ns (36%, $\lambda_{ex} = 720$ nm, 2.5 µJ).

Figure S21. (a) fsTA spectra of protonated **2** in CH₃CN and (b) kinetic trace at 460 nm and insert with shorter time range fitted with $\tau_1 = 11$ ps (50%, $\lambda_{ex} = 720$ nm, 2.5 µJ).

Figure S22. Electronic absorption spectra of the chemically generated (a) one-electron reduced $[1]^{1-}$ by cobaltocene (dark green) and $[1]^{1-}$ add TsOH (purple); (b) one-electron reduced $[2]^{1-}$ by cobaltocene (dark green) and $[2]^{1-}$ add TsOH (purple).

Complex	Donor	Proton	λ_{irr}/nm	TON
1	BNAH	TsOH	655	1.9 (0.5)
2	BNAH	TsOH	655	23.3 (2.8)
-	BNAH	TsOH	655	0
1	-	TsOH	655	0
1	BNAH	-	655	0
1	BNAH	TsOH	-	0
2	BNAH	TsOH	-	0
2	-	TsOH	655	0
2	BNAH	-	655	0

Table S5. Photocatalytic H₂ production of 1 and 2 in DMF.^a

^{*a*}Photocatalytic solution of 3 mL total volume of photocatalyst ~0.2 mM, 120 mM BNAH, 100 mM TsOH, 24 h irradiation.

Table S6. H_2 generation of chemically generated $[2]^{1-}$ with the addition of surplus TsOH.

Trial	Rh ₂ /µmol	H ₂ /µmol	H ₂ /Rh ₂
1	1.5	0.56	0.37
2	1.9	0.87	0.39
3	2.3	1.0	0.36

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