Supporting Information

for

Cyclopentadiene-Mediated Hydride Transfer from Rhodium Complexes

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I. General Considerations.

Procedures were carried out under nitrogen except where noted. All reagents were commercially available and used without further purification. Commercial HPLC-grade water was used as a solvent, and organic solvents were dried and degassed with argon using a Pure Process Technology solvent system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Electrochemical experiments were performed on a Pine WaveNow potentiostat or Pine WaveDriver bipotentiostat controlled by Aftermath software. Details on specific electrochemical experiments are described below. Solution pH was recorded using an OrionStar A111 pH meter with a Beckman-Coulter or Hanna pH probe. UV-Vis spectra were obtained using an Ocean Optics USB2000+ spectrometer with a DT-MINI-2GS deuterium/tungsten halogen light source controlled by OceanView software.

NMR spectra were obtained on 400, 500, or 600 MHz spectrometers. ¹H NMR spectra were referenced to the residual solvent signals (or dioxane or NaOTs as an internal standard in D_2O).¹ Spectra were processed using the MestReNova software suite from Mestrelab Research S. L. The solution acidity in NMR experiments is reported as pD, obtained by addition of +0.4 to the reading of a pH electrode that was calibrated using H₂O standards.²

Electrochemistry. Electrochemical experiments were carried out with carbon working electrodes (glassy carbon for cyclic voltammetry and reticulated vitreous carbon for bulk electrolysis), platinum wire counter electrodes, and Ag/AgCl (3M NaCl) reference electrode in a small glass tube fitted with a Vycor glass frit. Solutions were thoroughly degassed by sparging with nitrogen for at least 15 minutes before beginning an experiment or the experiments were carried out in a N₂ filled glovebox. All potentials are reported relative to NHE, with values obtained by adding 0.21 V to the experimentally observed potential *vs*. Ag/AgCl.³ The glassy

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carbon working electrode was polished with 0.05 micron alumina powder between scans and cyclic voltammetry was performed in an undivided cell. Controlled potential electrolysis experiments were carried out in a divided H-cell with the working electrode chamber and counter electrode chamber separated by a fine frit.

II. Synthetic Methods

The complexes [Cp*RhCl₂]₂,⁴ [Cp*Rh(bpy)(Cl)][Cl] (**4**),⁵ [Cp*Rh(bpy-COOH)(Cl)][Cl],⁵ [Cp*Ir(bpy-COOH)(Cl)][Cl],⁶ [(C₆Me₆)Ru(bpy)(H)][Cl]⁷ were prepared according to literature procedures.

Cp*Rh(bpy) (5). In a nitrogen filled glovebox, [Cp*Rh(bpy)(Cl)][Cl] (15.6 mg, 0.034 mmol) and excess NaBH₄ (10.3 mg, 0.272 mmol) were allowed to stir in 3 mL of 1 M NaOH. Dark purple solids quickly formed. After letting stir for two hours, the solid was filtered off, washed 3× with water, collected in benzene, and evaporated to dryness, yielding Cp*Rh(bpy) (11.6 mg, 88 % yield). The ¹H NMR spectrum of **1** prepared in this way matched previously reported data.⁸



Figure S1. ¹H NMR spectrum of Cp*Rh(bpy) in C₆D₆.

(Cp*H)Rh(bpy)(Cl) (1). To a stirring solution of Cp*Rh(bpy) (10.3 mg, 0.026 mmol) in ether, a dilute solution of HCl·Et₂O (50 mM) was added dropwise until a change from a dark purple solution to fine red solids was observed. Typically 1-1.5 eq of HCl were added with the excess acid immediately pumped off after completion of the addition. Alternatively, a subsess of 50 mM HCl in pentane was added to a solution of Cp*Rh(bpy) (10.6 mg, 0.027 mmol) stirring at -30 °C. The red solid that precipitated was filtered off and washed 3× with pentane. Samples of hydride prepared in this way typically contained small amounts [Cp*Rh(bpy)(Cl)][Cl] (presumably formed by protonation of the diene complex to release H₂). ¹H NMR (600 MHz, CD₂Cl₂) δ 8.92 (d, J = 5.2 Hz, 2H), 8.09 (dt, J = 7.9, 1.2 Hz, 2H), 7.87 (td, J = 7.8, 1.6 Hz, 2H), 7.47 (ddd, J = 7.6, 5.3, 1.3 Hz, 2H), 2.50 (q, J = 6.3 Hz, 1H), 1.85 (s, 6H), 0.91 (s, 6H), 0.53 (d, J = 6.2 Hz, 3H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 154.11, 151.38, 136.47, 125.90, 121.87, 92.17 (d, *J* = 10.1 Hz), 56.10 (d, *J* = 3.7 Hz), 53.26 (br s), 19.38, 12.03, 10.56.



Figure S2. ¹H NMR spectrum of (Cp*H)Rh(bpy)(Cl) in CD_2Cl_2 . Trace pentane is marked with

х.



Figure S3. ¹³C NMR spectrum of (Cp*H)Rh(bpy)(Cl) in CD₂Cl₂.

Alternatively, [Cp*Rh(bpy)(Cl)][Cl] (5.8 mg, 0.012 mmol) was dissolved in pH 5 3 M NaO₂CH. After stirring for 30 min, the solution had turned from yellow to dark red, and addition of excess $[NH_4][PF_6]$ resulted in the precipitation of a light green solid. Dissolving this solid in CD₃CN produced a red solution of $[(Cp*H)Rh(bpy)(NCCD_3)][PF_6]$. ¹H NMR (400 MHz, CD₃CN) δ 8.98 (dd, *J* = 5.2, 1.3 Hz, 1H), 8.34 (dt, *J* = 8.3, 1.1 Hz, 1H), 8.10 (td, *J* = 7.9, 1.6 Hz, 1H), 7.67 (ddd, *J* = 7.6, 5.3, 1.2 Hz, 1H), 2.31 (q, *J* = 6.2 Hz, 1H), 1.92 (s, 3H), 0.79 (s, 3H), 0.53 (d, *J* = 6.2 Hz, 1H).



Figure S4. ¹H NMR spectrum of [(Cp*H)Rh(bpy)(NCCD₃)][PF₆] in CD₃CN.



Figure S5. ¹H NMR spectra showing the low temperature protonation of Cp*Rh(bpy) (4.8 mg, 0.012 mmol) in C₆D₅Cl (red). After injection of 5.5 μ L 2.0 M HCl·Et₂O in an acetonitrile/dry ice bath. Spectrum recorded at 238 K (blue). After warming to 293 K (purple). A hydride resonance at –9.60 ppm at low temperatures is evidence for the intermediacy of [Cp*Rh(bpy)(H)]⁺ in the formation of (Cp*H)Rh(bpy)(Cl).

 $[Cp*Rh(bpy-COO)]^{2-}$ (**5**_{COO}). Electrolysis at -0.89 V of [Cp*Rh(bpy-COOH)Cl][Cl] (4.9 mg, 0.009 mmol) in 1.8 mL 0.1 M Na₂SO₄ electrolyte in D₂O passed -1.67 C (2.0 e⁻/Rh) resulting in a royal blue solution of [Cp*Rh(bpy-COO)]²⁻. ¹H NMR (600 MHz, D₂O) δ 8.85 (br s, 1H), 8.35 (s, 1H), 7.06 (dd, *J* = 6.5, 1.9 Hz, 1H), 1.80 (br s, 7H).



Figure S6. ¹H NMR spectra of $[Cp*Rh(bpy-COO)]^{2-}$ formed electrochemically under basic conditions (bottom) and with dropwise addition of pD 7 0.1 M sodium phosphate buffer to protonate (top) both referenced to trace MeOH. The three resonances in the aliphatic region display upfield shoulders from scrambling of deuterium into the Cp* methyl groups and the Cp*H proton—and coupling to it—are not observed because of deuteration.



III. Hydricity Determination for [(Cp*H)Rh(bpy-COO)]⁻

Figure S7. The shift of the 2e⁻ reduction of $[Cp*Rh(bpy-COO)(OH)]^-$ at 100 mV/s as the pH increases from 9.5 to 13.0 (left). $E_{1/2}$ of the reduction plotted against pH to extrapolate to pH 0 (right).



Figure S8. UV-vis spectra of $[Cp*Rh(bpy-COO)]^{2-}$ formed electrochemically at pH 11.2 (blue) and added to a pH 7 0.1 M sodium phosphate buffer to protonate (yellow).



Figure S9. Spectrophotometric titration of $[Cp*Rh(bpy-COO)]^{2-}$ with addition of acid to form $[(Cp*H)Rh(bpy-COO)]^{-}$ (left) and analysis of the absorbance at 610 nm to the Henderson-Hasselbalch equation giving $pK_a = 9.9$ (right). Both species were observed to react on the timescale of the experiment, which leads to lower than expected absorbance at 610 nm and produces an artificially low [Cp*Rh]/[(Cp*H)Rh] ratio — and thus an overestimation of the pK_a .



Figure S10. (A) CV of [Cp*Rh(bpy-COOH)(Cl)][Cl] in pH 5.8 to pH 10 phosphate electrolyte at a scan rate of 100 mV/s, expanded to highlight the return wave attributed to oxidation of [Cp*Rh(bpy-COO)]^{2–}. In acidic water, [Cp*Rh(bpy-COO)]^{2–} is protonated to form [(Cp*H)Rh(bpy-COO)][–]. The increasing oxidative peak current with increasing pH indicates higher concentrations of [Cp*Rh(bpy-COO)]^{2–} as pH increases. (B) Plot of oxidative peak current vs. pH. At each scan rate this sigmoid was fit to the Henderson-Hasselbalch equation to determine a pK_a. (C) Plot of apparent pK_a vs. scan rate. The scan rate dependence indicates that protonation is slow on the electrochemical time scale. As the scan rate decreases, the reaction has longer to approach equilibrium, leading to an increase in apparent pK_a — and therefore an underestimation of the true pK_a.



Figure S11. ¹H NMR spectra showing 17.2 mM $[(C_6Me_6)Ru(bpy)(H)]^+$ in 0.5 mL (8.6 µmol) pD 7 0.1 M NaP_{*i*} (bottom) and the same sample after addition of 2.6 mg [Cp*Rh(bpy)(Cl)][Cl] (5.6 µmol) (top). The $[(C_6Me_6)Ru(bpy)(H)]^+$ resonances disappear and the characteristic 6:6:3 pattern in the aliphatic region of (Cp*D)Rh appears. The Cp*H proton quartet is detectable at 2.66 ppm, but due to scrambling, accounts for only 4% of the diene species in solution.



Figure S12. ¹H NMR spectrum of a solution of (Cp*H)Rh(bpy)(Cl) after addition of 2.8 mg [Cp*Ir(bpy-COOH)(Cl)][Cl] (4.3 µmol) in pD 7 0.1 M NaP_{*i*} (top). Mixture of $[Cp*Ir(bpy-COO)(Cl)]^-$ and $[Cp*Ir(bpy-COO)(H)]^-$ under the same conditions, included for comparison (bottom). Though (Cp*D)Rh(bpy)(Cl) remains, all of the Ir species has been converted to Ir–H.



Figure S13. ¹H NMR spectra of a mixture of $[Cp*Ir(bpy-COO)(H)]^-$, $[Cp*Ir(bpy-COO)(Cl)]^-$, and $[Cp*Rh(bpy)(Cl)]^+$ in pD 7 0.1 M NaP_{*i*} showing no hydride transfer from Ir to Rh over the course of 9 days. The only change is the diminishing Cp* peaks as a result of deuteration.

IV. Hydricity of NADH

There have been discrepancies in the literature regarding ΔG°_{H-} of NADH. Mayer notes that there is disagreement on the reduction potential of 1,4-C₆H₄(NMe₂)₂ (TMPA) on which the derivation of some of the hydricity values have been based.⁹ Regardless, enough of the thermochemistry of NADH and its oxidation and deprotonation products exist to calculate a hydricity value while avoiding the conflict over TMPA.

		kcal ·mol ^{−1}	Ref
$\rm NADH \rightarrow \rm NADH^{*+} + e^-$	$-E^\circ = -(0.94 \text{ V})$	-21.7	10, 11
$NADH^{\bullet+} \rightarrow NAD^{\bullet} + H^+$	$pK_a = -3.5$	-4.8	11
$NAD^{\bullet} \rightarrow NAD^{+} + e^{-}$	$-E^\circ = -(-0.92 \text{ V})$	21.2	11
$\mathrm{H^{+}} + 2\mathrm{e^{-}} \rightarrow \mathrm{H^{-}}$		34.2	12
$NADH \rightarrow NAD^+ + H^-$		28.9	

This value is consistent with the reduction potential for NAD⁺ to NADH. Rodkey reported this potential over a four unit pH range from 6.5 to 10.5 using potentiometric titration. The potential varied according to $E'^{\circ} = -0.1054 - 0.0303^{\circ}$ pH.¹³ Extrapolation to pH 0 gives $E^{\circ} = -0.1054$ V or $\Delta G^{\circ}_{H^{-}} = 29.3$ kcal·mol⁻¹.

V. (Cp*H)Rh as an Intermediate in NAD⁺ Reduction



Figure S14. ¹H NMR spectrum of a solution of (Cp*H)Rh(bpy)(Cl) after addition of 2.7 mg NAD⁺ (4.1 µmol) in pD 7 0.1 M NaP_i. The Rh species has reacted completely (best seen by the absence of any resonance at 0.7 ppm), and NADH has appeared. The nicotinamide singlet shifts from 9.3 ppm to 6.9 ppm upon reduction and a pair of diastereotopic protons appear at 2.6 and 2.7 ppm. Assignments where made by comparison to authentic samples in the same solutions and by comparison to ref. 14.



Figure S15. ¹H NMR spectra showing the formation of diene products (indicated by a 6:6:3 pattern in the aliphatic region) under catalytic conditions. (top) $[Cp*Rh(bpy)(OH_2)]^{2+}$ under an atmosphere of H₂ in pD 7 0.1 M NaP_{*i*}, referenced to sodium tosylate. (middle) Product of electrolysis of $[Cp*Rh(bpy)(Cl)]^+$ at -0.64 V in 80:20 pD 7:pH 7 0.1 M NaP_{*i*}, referenced to dioxane. (bottom) $[Cp*Rh(bpy)(Cl)]^+$ in D₂O with 10 eq of sodium formate, referenced to formate.



Figure S16. ¹H NMR spectra showing an equilibrium mixture of $[Cp*Ir(bpy)(H)]^+$, $[Cp*Ir(bpy)(Cl)]^+$, $[Cp*Ir(bpy-COO)(H)]^-$, and $[Cp*Ir(bpy-COO)(H)]^-$ (formed by mixing electrochemically produced $[Cp*Ir(bpy-COO)(H)]^-$ with $[Cp*Ir(bpy)(Cl)][Cl])^7$ shortly after equilibrium had been achieved (bottom) and 7 weeks later (top). The Cp* peaks have disappeared with no changes to the aromatics indicating per-deuteration of the Cp* protons. Deuteration was also observed by ²H NMR. $[(Cp*-d_{15})Ir(bpy)(Cl)]^+$ (m/z = 534.21 (calc), 534.33 (obs)) and $[(Cp*-d_{15})Ir(bpy-COONa)(Cl)]^+$ (m/z = 666.16 (calc), 666.20 (obs)) were also observed by mass spec.

VI. Crystallographic Details

Table 51. Ciystal uata allu structi	$(Cp^{-11})(Cl)(Cl)(1, x131)$
Identification code	x1511015
Empirical formula	$C_{21}H_{26}Cl_3N_2Rh$
Formula weight	515.70
Temperature/K	100
Crystal system	orthorhombic
Space group	Pnma
a/Å	22.5211(11)
b/Å	12.1599(6)
c/Å	7.8427(4)
α/°	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	2147.76(19)
Z	4
$\rho_{calc}g/cm^3$	1.595
μ/mm^{-1}	9.921
F(000)	1048.0
Crystal size/mm ³	$0.282 \times 0.143 \times 0.035$
Radiation	$CuK\alpha \ (\lambda = 1.54178)$
2Θ range for data collection/°	7.852 to 144.676
Index ranges	$-27 \le h \le 27, -14 \le k \le 14, -9 \le l \le 9$
Reflections collected	18815
Independent reflections	2224 [$R_{int} = 0.0258$, $R_{sigma} = 0.0153$]
Data/restraints/parameters	2224/0/136
Goodness-of-fit on F ²	1.112
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0220, wR_2 = 0.0549$
Final R indexes [all data]	$R_1=0.0224,wR_2=0.0552$
Largest diff. peak/hole / e Å ⁻³	0.37/-0.69

Table S1. Crystal data and structure refinement for (Cp*H)Rh(bpy)(Cl) (1, x1511015).

Table S2. Bond Lengths for x1511015.

Atom	n Atom	Length/Å	Ator	n Atom	Length/Å
Rh1	Cl1	2.5440(6)	C2	C3	1.440(3)
Rh1	N1	2.1157(15)	C2	C5	1.503(3)
Rh1	$N1^1$	2.1156(15)	C3	C3 ¹	1.430(4)
Rh1	$C2^1$	2.1334(18)	C3	C6	1.499(3)
Rh1	C2	2.1334(18)	C7	C8	1.378(3)
Rh1	C3	2.1032(17)	C8	C9	1.390(3)

Rh1	C3 ¹	2.1031(17) C9	C10	1.382(3)
N1	C7	1.345(2) C10) C11	1.390(3)
N1	C11	1.359(2) C11	C11 ¹	1.480(4)
C1	C2	1.517(2) Cl2	C12	1.763(4)
C1	$C2^1$	1.517(2) Cl3	C12	1.734(3)
C1	C4	1.545(4)		

 $^{1}+X,1/2-Y,+Z$

Table S3. Bond Angles for x1511015.

Atom Atom Atom At		Angle/°	le/° Atom Atom A		n Atom	Atom Angle/°	
N1	Rh1	Cl1	85.26(4)	$C2^1$	C1	C2	96.6(2)
$N1^1$	Rh1	Cl1	85.26(4)	C2	C1	C4	115.48(15)
$N1^1$	Rh1	N1	77.04(8)	$C2^1$	C1	C4	115.48(15)
$N1^1$	Rh1	C2	171.82(6)	C1	C2	Rh1	90.56(12)
N1	Rh1	$C2^1$	171.82(6)	C3	C2	Rh1	69.00(10)
$N1^1$	Rh1	$C2^1$	109.18(6)	C3	C2	C1	109.04(16)
N1	Rh1	C2	109.18(6)	C3	C2	C5	125.22(17)
C2	Rh1	Cl1	100.34(5)	C5	C2	Rh1	127.25(13)
$C2^1$	Rh1	Cl1	100.34(5)	C5	C2	C1	120.95(16)
$C2^1$	Rh1	C2	64.14(10)	C2	C3	Rh1	71.26(10)
C3	Rh1	Cl1	140.07(5)	C2	C3	C6	126.39(17)
C3 ¹	Rh1	Cl1	140.07(5)	C3 ¹	C3	Rh1	70.12(5)
C3	Rh1	N1	105.98(6)	C3 ¹	C3	C2	106.86(11)
C3 ¹	Rh1	$N1^1$	105.98(6)	C3 ¹	C3	C6	126.75(11)
C3 ¹	Rh1	N1	134.32(6)	C6	C3	Rh1	123.73(13)
C3	Rh1	$N1^1$	134.32(6)	N1	C7	C8	123.25(18)
C3	Rh1	$C2^1$	65.92(7)	C7	C8	C9	118.46(18)
$C3^1$	Rh1	$C2^1$	39.73(7)	C10	C9	C8	119.21(18)
C3	Rh1	C2	39.74(7)	C9	C10	C11	119.34(18)
C3 ¹	Rh1	C2	65.92(7)	N1	C11	C10	121.62(17)
$C3^1$	Rh1	C3	39.75(10)	N1	C11	$C11^{1}$	115.15(10)
C7	N1	Rh1	125.30(13)	C10	C11	C11 ¹	123.20(11)
C7	N1	C11	118.09(16)	C13	C12	Cl2	113.0(2)
C11	N1	Rh1	116.19(12)				

 $^{1}+X,1/2-Y,+Z$

Table S4. Torsion Angles for x1511015.

A	В	С	D	Angle/°	Α	B	С	D	Angle/°
Rh1	N1	C7	C8	171.66(13)	C4	C1	C2	C3	-90.4(2)
Rh1	N1	C11	C10	-173.91(13)	C4	C1	C2	C5	66.3(3)
Rh1	N1	C11	C11 ¹	3.91(12)	C5	C2	C3	Rh1	121.51(18)
Rh1	C2	C3	C3 ¹	61.45(5)	C5	C2	C3	C3 ¹	-177.04(15)
Rh1	C2	C3	C6	-118.58(18)	C5	C2	C3	C6	2.9(3)
N1	C7	C8	C9	1.0(3)	C7	N1	C11	C10	-0.9(2)
C1	C2	C3	Rh1	-83.02(14)	C7	N1	C11	C11 ¹	176.90(12)
C1	C2	C3	C3 ¹	-21.57(16)	C7	C8	C9	C10	0.2(3)
C1	C2	C3	C6	158.40(18)	C8	C9	C10	C11	-1.6(3)
$C2^1$	C1	C2	Rh1	-36.00(16)	C9	C10	C11	N1	2.0(3)
C2 ¹	C1	C2	C3	31.9(2)	C9	C10	C11	C11 ¹	-175.60(13)
C2 ¹	C1	C2	C5	-171.37(11)	C11	N1	C7	C8	-0.6(3)
C4	C1	C2	Rh1	-158.34(16)					

$^{1}+X,1/2-Y,+Z$

Experimental

Single crystals of $C_{21}H_{26}Cl_3N_2Rh \times 1511015$ (1) were grown by vapor diffusion of dichloromethane and pentane at ambient temperature. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the XL [3] refinement package using Least Squares minimisation.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
- 3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of x1511015

Crystal Data for C₂₁H₂₆Cl₃N₂Rh (M = 515.70 g/mol): orthorhombic, space group Pnma (no. 62), a = 22.5211(11) Å, b = 12.1599(6) Å, c = 7.8427(4) Å, V = 2147.76(19) Å³, Z = 4, T = 100 K, μ (CuK α) = 9.921 mm⁻¹, Dcalc = 1.595 g/cm³, 18815 reflections measured ($7.852^{\circ} \le 2\Theta \le 144.676^{\circ}$), 2224 unique ($R_{int} = 0.0258$, $R_{sigma} = 0.0153$) which were used in all calculations. The final R_1 was 0.0220 (I > 2 σ (I)) and wR_2 was 0.0552 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown. Details: 1. Fixed Uiso At 1.2 times of: All C(H) groups, All C(H,H) groups At 1.5 times of: All C(H,H,H) groups 2. Others Fixed Sof: H4A(0.5) H4B(0.5) H4C(0.5) H12A(0.5) H12B(0.5) 3.a Ternary CH refined with riding coordinates: C1(H1) 3.b Secondary CH2 refined with riding coordinates: C12(H12A,H12B) 3.c Aromatic/amide H refined with riding coordinates: C7(H7), C8(H8), C9(H9), C10(H10) 3.d Idealised Me refined as rotating group: C4(H4A,H4B,H4C), C5(H5A,H5B,H5C), C6(H6A,H6B,H6C)

VII. Computational Details

All calculations were performed using the Gaussian09 software package.¹⁵ The PBE1PBE functional¹⁶ was used for all calculations, with the LANL2DZ basis set¹⁷ and pseudopotential used for Ir and the 6-31G(d,p) basis set^{18,19} used for all other atoms. After optimizing the structure, frequency optimizations were performed for each species to compute Gibbs free energy values, ensuring the absence of imaginary frequencies. A polarizable continuum model (IEFPCM as implemented by Gaussian09) was used to approximate the effects of acetonitrile solvent. The relative free energy of the two isomers for Rh and Ir are collected in Table S5 and illustrated in Figure S17. Geometric coordinates and the corresponding energy, enthalpy, and entropy values for each optimized structure are provided below.

Table S5. Overview of calculated change in electronic energy (ΔE), enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) for the isomerization of rhodium and iridium hydrides.

Reaction	$\Delta \mathbf{E}$ (kcal·mol ⁻¹)	$\Delta \mathbf{H}$ (kcal·mol ⁻¹)	$\Delta \mathbf{S}$ (cal·mol ⁻¹ ·K ⁻¹)	$\Delta \mathbf{G}$ (kcal·mol ⁻¹)
$[Cp*Rh(bpy)(H)]^{+} \rightarrow [(Cp*H)Rh(bpy)]^{+}$	-6.17	-4.02	0.097	-4.05
$[Cp*Ir(bpy)(H)]^{+} \rightarrow [(Cp*H)Ir(bpy)]^{+}$	+5.91	+7.89	-0.62	+8.07



Figure S17. Calculated relative free energies of rhodium (left) and iridium (right) isomers.

Optimized geometry coordinates and energy values

 $[Cp*Rh(bpy)(H)]^+$



Figure S18. Calculated structure of $[Cp*Rh(bpy)(H)]^+$.

SCF Done: E(RPBE1PBE) = -994.478988761	A.U. after	2 cycles
Sum of electronic and zero-point Energies =	-994.0841	79
Sum of electronic and thermal Energies =	-994.06104	40
Sum of electronic and thermal Enthalpies =	-994.0600	96
Sum of electronic and thermal Free Energies =	-994.135	403

Symbol	Х	Y	Z
Rh	0.443446	0.000498	-0.383797
С	-1.07907	2.64232	-0.266256
С	-2.389235	0.736765	-0.049534
С	-3.539251	1.514707	0.076898
С	-3.434779	2.897988	0.037776
С	-2.181579	3.474126	-0.137885
Н	-0.086207	3.044736	-0.424468

Η	-4.508405	1.047905	0.201856
Н	-4.3213	3.515105	0.137347
Н	-2.050265	4.549053	-0.181834
С	-2.38847	-0.732052	-0.038477
С	-3.535144	-1.509445	0.11826
С	-3.430021	-2.893007	0.092943
Н	-4.50173	-1.042046	0.260011
С	-1.079563	-2.639095	-0.250443
С	-2.179594	-3.470185	-0.098479
Н	-4.313931	-3.509634	0.215954
Н	-0.088494	-3.042264	-0.417778
Н	-2.048238	-4.545415	-0.13402
Ν	-1.175823	1.308736	-0.214479
Ν	-1.176583	-1.305099	-0.21058
С	2.279397	1.154471	-0.075658
С	1.919283	0.69564	1.263947
С	1.920144	-0.709437	1.256498
С	2.58798	0.004587	-0.870545
С	2.280199	-1.154212	-0.087835
С	3.193037	0.012078	-2.234759
Н	2.904535	-0.870194	-2.809389
Н	2.902679	0.899428	-2.800609
Н	4.28637	0.012821	-2.147954
С	2.564658	-2.566638	-0.480684
С	1.61123	-1.627749	2.39046
Н	0.931675	-2.429923	2.08599
Н	2.52876	-2.102868	2.756576
Н	1.150258	-1.09797	3.226004
С	1.609697	1.601777	2.407576
Н	1.14879	1.062925	3.237377
Н	2.526836	2.073423	2.779173
Н	0.929713	2.406646	2.111323
С	2.562066	2.571231	-0.453513
Н	2.322852	2.76742	-1.501688
Н	2.005501	3.277686	0.167461
Н	3.626478	2.792058	-0.308605
Н	2.323063	-2.752606	-1.530152
Н	2.010782	-3.280461	0.134262
Η	3.629768	-2.787133	-0.340501
Н	0.109461	0.001876	-1.9073



Figure S19. Calculated structure of [(Cp*H)Rh(bpy)]⁺.

SCF Done: E(RPBE1PBE) = -994.488822448	A.U. after	1 cycles
Sum of electronic and zero-point Energies =	-994.09040	08
Sum of electronic and thermal Energies =	-994.06744	9
Sum of electronic and thermal Enthalpies =	-994.06650)4
Sum of electronic and thermal Free Energies =	-994.1418	857

Symbol	Х	Y	Z
Rh	0.338855	0.002499	-0.003766
С	-1.21797	2.6547	-0.073132
С	-2.523507	0.73794	-0.103322
С	-3.685678	1.503666	-0.164942
С	-3.590595	2.889531	-0.176309
С	-2.333433	3.478839	-0.128105
Н	-0.218011	3.067632	-0.039887

Η	-4.658463	1.029808	-0.206867
Н	-4.488291	3.49689	-0.223599
Н	-2.208143	4.555354	-0.135066
С	-2.523202	-0.735986	-0.08147
С	-3.685914	-1.503369	-0.086976
С	-3.589748	-2.88906	-0.066963
Н	-4.660115	-1.030913	-0.103359
С	-1.215528	-2.650811	-0.034075
С	-2.331056	-3.476595	-0.042014
Η	-4.487794	-3.497714	-0.070892
Н	-0.214557	-3.062146	-0.014635
Η	-2.204824	-4.552921	-0.027384
Ν	-1.302667	1.319743	-0.059663
Ν	-1.301216	-1.315997	-0.05009
С	2.169224	1.155169	-0.384109
С	2.112886	0.7199	0.960709
С	2.110483	-0.740785	0.943639
С	2.165537	-1.144105	-0.41132
С	2.238709	-2.548933	-0.910688
С	2.108277	-1.611008	2.155426
Η	1.726439	-2.610658	1.936567
Η	3.131804	-1.724363	2.53317
Η	1.502818	-1.183289	2.958154
С	2.113531	1.561414	2.192466
Η	1.515539	1.111641	2.988667
Η	3.138883	1.671233	2.566373
Η	1.724955	2.56364	1.998768
С	2.250116	2.571801	-0.847747
Η	1.658293	2.727456	-1.75555
Н	1.922903	3.286237	-0.088455
Н	3.289288	2.823671	-1.094363
Η	1.636752	-2.68086	-1.815606
Н	1.918877	-3.282157	-0.166418
Н	3.274744	-2.795755	-1.17485
С	2.636764	0.015051	-1.269297
Η	2.106649	0.026884	-2.232433
С	4.148046	0.016175	-1.544569
Н	4.436032	-0.859889	-2.133218
Н	4.438203	0.905983	-2.111112
Η	4.708459	0.003788	-0.604198

$[Cp*Ir(bpy)(H)]^+$



Figure S20. Calculated structure of $[Cp*Ir(bpy)(H)]^+$.

SCF Done: E(RPBE1PBE) = -989.694211006	A.U. after	1 cycles
Sum of electronic and zero-point Energies =	-989.29870)1
Sum of electronic and thermal Energies =	-989.27569	0
Sum of electronic and thermal Enthalpies=	-989.27474	6
Sum of electronic and thermal Free Energies =	-989.3500)83

Symbol	Х	Y	Ζ
С	0.744335	-2.923426	-0.733539
С	2.252847	-1.199707	-0.333807
С	3.319874	-2.095603	-0.362381
С	3.073569	-3.443802	-0.572727
С	1.760662	-3.863974	-0.762502
Н	-0.288391	-3.200772	-0.899508
Н	4.333864	-1.741587	-0.222352
Н	3.893537	-4.153392	-0.594175
Н	1.517158	-4.905421	-0.937783
С	2.390224	0.241834	-0.133008

С	3.603804	0.896616	0.068071
С	3.617527	2.273189	0.233752
Н	4.529231	0.334663	0.09621
С	1.239844	2.259783	-0.027193
С	2.412311	2.96673	0.182326
Н	4.554043	2.795988	0.394786
Н	0.282512	2.759752	-0.095343
Н	2.370891	4.043596	0.297315
Ν	0.978014	-1.620091	-0.514019
Ν	1.221491	0.925309	-0.170257
С	-2.424147	-1.211846	-0.171316
С	-1.936754	-0.961654	1.182533
С	-1.805458	0.436113	1.352382
С	-2.655027	0.062066	-0.79482
С	-2.208521	1.087241	0.108884
С	-3.312574	0.284608	-2.115314
Η	-2.96241	1.204261	-2.587875
Η	-3.127849	-0.544804	-2.800676
Η	-4.396078	0.369632	-1.971456
С	-2.41616	2.555347	-0.072857
С	-1.354113	1.158707	2.57631
Η	-0.674893	1.980762	2.332137
Η	-2.215743	1.592711	3.096569
Η	-0.840462	0.493475	3.272699
С	-1.650783	-2.025467	2.187812
Η	-1.022155	-1.65614	3.000135
Η	-2.586299	-2.393702	2.62455
Η	-1.144992	-2.882476	1.73367
С	-2.890982	-2.531301	-0.693612
Η	-2.752916	-2.612464	-1.77443
Η	-2.370486	-3.365489	-0.216516
Η	-3.959076	-2.660079	-0.482551
Η	-2.248636	2.863739	-1.107536
Η	-1.757607	3.142693	0.571898
Η	-3.44507	2.823883	0.194103
Η	-0.194684	-0.00567	-1.994376
Ir	-0.508773	-0.179331	-0.443815

$[(Cp*H)Ir(bpy)]^+$



Figure S21. Calculated structure of [(Cp*H)Ir(bpy)]⁺.

SCF Done: E(RPBE1PBE) = -989.684788873	A.U. after	1 cycles
Sum of electronic and zero-point Energies =	-989.28586	57
Sum of electronic and thermal Energies =	-989.26311	6
Sum of electronic and thermal Enthalpies =	-989.26217	'2
Sum of electronic and thermal Free Energies =	-989.3372	216

Symbol	Х	Y	Z
С	-1.239171	2.632095	0.042064
С	-2.571833	0.734622	-0.100192
С	-3.722382	1.515114	-0.13696
С	-3.609512	2.898783	-0.080656
С	-2.34527	3.467769	0.013333
Н	-0.23464	3.026894	0.109504
Н	-4.699541	1.05325	-0.203368
Н	-4.498338	3.519927	-0.108162

Η	-2.206586	4.541405	0.061784
С	-2.573674	-0.734756	-0.128761
С	-3.724862	-1.509508	-0.221849
С	-3.616622	-2.894677	-0.213671
Н	-4.698639	-1.042273	-0.300215
С	-1.248481	-2.640765	-0.033691
С	-2.356298	-3.471035	-0.112924
Н	-4.506137	-3.511364	-0.284963
Н	-0.246533	-3.041512	0.035379
Н	-2.221596	-4.546189	-0.100658
Ν	-1.341441	1.296461	-0.012573
Ν	-1.346336	-1.303686	-0.041104
С	2.070157	1.13346	-0.476351
С	2.07597	0.746601	0.894751
С	2.081776	-0.720823	0.917637
С	2.078778	-1.152656	-0.439874
С	2.161195	-2.573663	-0.897222
С	2.152754	-1.560002	2.148588
Н	1.753982	-2.562431	1.977367
Н	3.197532	-1.668077	2.464862
Н	1.597239	-1.109431	2.974749
С	2.141521	1.627231	2.09701
Н	1.593712	1.19846	2.939752
Н	3.185623	1.759325	2.406133
Н	1.729867	2.618772	1.894055
С	2.136284	2.53807	-0.983755
Н	1.515564	2.66833	-1.875932
Н	1.833877	3.277164	-0.237763
Н	3.167959	2.780318	-1.267715
Н	1.551455	-2.740099	-1.79099
Н	1.854969	-3.287057	-0.127791
Н	3.19741	-2.819256	-1.161173
С	2.570933	-0.021478	-1.327936
Н	2.047527	-0.037973	-2.293727
С	4.08416	-0.019911	-1.57893
Н	4.386878	-0.910708	-2.137774
Н	4.381226	0.854547	-2.165935
Н	4.631388	-0.00317	-0.630721
Ir	0.278429	-0.006406	0.041892

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