Supporting information for:

Structural investigations into the deactivation pathway of the CO_2 reduction electrocatalyst $Re(bipy)(CO)_3Cl$

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General Considerations:

$Re(bpy)(CO)_3Cl$ and KC_8 were synthesized by previously reported methods.[1] THF and Pentane were sparged with argon and dried over basic alumina with a custom dry solvent system and then stored over activated molecular sieves. 18-crown-6 was recrystallized from acetonitrile, tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized twice from methanol, and both were dried *in vacuo*. All other chemicals were purchased from commercial sources and used as received. Elemental analysis was performed by Midwest MicroLab, LLC, Indianapolis, IN.

Synthesis of $[Re(bpy)(CO)_3]_2$ (2). $Re(bpy)(CO)_3Cl$ (0.100 g, 0.217 mmol) was added to ~20 mL THF under an inert atmosphere. The solution was then cooled to –35 °C and 1.1 eq (0.032 g, 0.238 mmol) of KC_8 was added to the solution and allowed to warm to room temperature. After an hour, the solution was filtered through a plug of silica gel, and the column was washed with an additional 20 mL of THF. The solvent was removed *in vacuo* to afford the sparingly soluble (**2**) with a total yield of 54% (0.050 g, 0.117 mmol). ^1H NMR (500 MHz, THF-d_8, 20 °C): δ 7.08

(dt, 4H, *J* = 6 Hz, 1 Hz), δ 7.66 (dt, 4H, *J* = 8 Hz, 2 Hz), δ 8.25 (d, 4H, *J* = 6 Hz), δ 8.36 (d, 4H, *J* = 8 Hz). IR(THF) ν(CO): 1990, 1952, 1986, 1862 cm^{-1}. Anal. Calcd for **1**, $C_{26}H_{16}N_4O_6Re_2$: C, 36.63; H, 1.89; N, 6.57. Found: C, 36.68; H, 2.06; N, 6.43.

Synthesis of [Re(bpy)(CO)$_3$]$_2$ [K(18-crown-6)] (4). To 16 mL of THF, Re(bpy)(CO)$_3$Cl (0.100 g, 0.217 mmol) and 18-crown-6 ether (0.0858 g, 0.325 mmol) were added under an inert atmosphere. The solution was then cooled to –35 °C, and 1.5 eq (0.044 g, 0.325 mmol) of KC_8 was added to the solution and allowed to warm to room temperature. After warming to room temperature for an hour, the solution was filtered, affording a deep purple solution. Additionally, **4** can be prepared by the oxidation of complex **3** with 0.5 equivalents of [FeCp$_2$][PF$_6$]. IR(THF) ν(CO): 1990, 1974, 1951, 1886, 1862, 1837 cm^{-1}. UV-Vis (THF), λ_{max}, nm (ε, M^{-1}cm^{-1}); 533(br) (7200), 812 (11,000).

Synthesis of [Re(bpy)(CO)$_3$] [K(18-crown-6)] (3). To 20 mL of THF, Re(bpy)(CO)$_3$Cl (0.100 g, 0.217 mmol) and 18-crown-6 ether (0.120 mg, 0.455 mmol) were added under an inert atmosphere. The solution was then cooled to –35 °C, and 2.1 eq (0.061 g, 0.455 mmol) of KC_8 was added to the solution and allowed to warm to room temperature. After warming to room temperature for an hour, the solution was filtered, affording a spectroscopically pure deep purple solution. The solution was concentrated under vacuum, and then ~15 mL of pentane was added to the solution before placing the vial in a freezer. After 2 hours the product was obtained by decanting the supernatant and dried *in vacuo* to yield 0.116 mg of **(3)** (0.159 mmol, 73% yield). An analogous procedure using **2** as the starting material yields **3** quantitatively as shown by FTIR. ^{1}H NMR (500 MHz, THF-d$_8$, 20 °C): δ 3.55 (s, 24H), δ 5.26 (dt, 2H, *J* = 7 Hz, 1 Hz), δ 5.92 (ddd, 2H, *J* = 9 Hz, 6 Hz, 1 Hz), δ 7.23 (d, 2H, *J* = 9 Hz), δ 8.88 (d, 2H, *J* = 6 Hz). IR(THF) ν(CO): 1945, 1839 cm^{-1}. Anal. Calcd for **1**, $C_{25}H_{32}KN_2O_9Re$: C, 41.14; H, 4.42; N, 3.84. Found: C, 42.20; H, 4.23; N, 3.62

X-ray structure determination.

The single crystal X-ray diffraction studies were carried out on either a Bruker Kappa APEX-II CCD diffractometer or Bruker Platform APEX CCD diffractometer, and both instruments were equipped with Mo Kα radiation (λ = 0.71073 Å). The crystals were mounted on a Cryoloop with Paratone oil, and data was collected under a nitrogen gas stream at 100(2) K using ω and ϕ scans. Data was integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXS) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods (SHELXL-97).[2] All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Crystallographic data are summarized in Table S1.

Table S1. Crystallographic Data and Refinement Information

Compound	**[Re(bpy)(CO)$_3$]$_2$**	**[Re(bpy)(CO)$_3$]$_2$ [K(18-crown-6)•Et$_2$O]**	**[Re(bpy)(CO)$_3$]$_2$ [K(THF)$_2$]**	**Re(bpy)(CO)$_3$ [K(18-crown-6)THF]**
empirical formula	$C_{26}H_{16}N_4O_6Re_2$	$C_{42}H_{50}KN_4O_{13}Re_2$	$C_{34}H_{32}KN_4O_8Re_2$	$C_{29}H_{40}KN_2O_{10}Re$
formula weight	852.83	1305.50	1036.14	801.93
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
lattice parameters				
a (Å)	9.620(3)	8.9201(8)	8.8574(5)	23.3023(13)
b (Å)	19.620(6)	12.4212(12)	11.5882(7)	18.0705(9)
c (Å)	12.933(4)	38.087(4)	32.4500(18)	16.0034(8)
α (deg)	90	90	90	90.00
β (deg)	103.710(4)	95.7410(10)	95.504(3)	73.240(3)
γ (deg)	90	90	90	90.00
V (Å3)	2371.5(13)	4198.8(7)	3315.4(3)	6452.5(6)
space group	C 2/c	P 2_1/n	P 2_1/n	P 2_1/c
Z value	4	4	4	8
ρcalc (g/cm3)	2.389	1.829	2.076	1.651
μ (Mo Kα) (mm-1)	0.71073	0.71073	0.71073	0.71073
temperature (K)	100(2)	100(2)	100(2)	100(2)
2Θ max (deg)	56.52	50.88	50.7	51.12
no. obs. ($I > 2\alpha(I)$)	2666	7756	6067	11977
no. parameters	173	508	441	798
goodness of fit	1.006	1.165	1.137	1.079
max. shift in cycle	0.001	0.001	0.001	0.027
residuals: R1; wR2	0.0489; 0.1094	0.0512; 0.1050	0.0207; 0.0412	0.0331; 0.0578
largest peak	2.355	1.960	0.625	1.705
deepest hole	-2.666	-2.675	-0.789	-0.756

Table S2. Selected bond lengths and angles for complexes presented.

Compound	**[Re(bpy)(CO)$_3$]$_2$**	**[Re(bpy)(CO)$_3$]$_2$ [K(18-crown-6)•Et$_2$O]**	**[Re(bpy)(CO)$_3$]$_2$ [K(THF)$_2$]**	**Re(bpy)(CO)$_3$ [K(18-crown-6)THF][a]**
Re1 – N1	2.165(8)	2.142(7)	2.136(3)	2.074(3)
Re1 – N2	2.141(8)	2.133(8)	2.131(4)	2.085(4)
N1 – Re1 – N2	76.2(3)	75.2(3)	74.96(13)	75.04(14)
Re1 – C1	1.909(11)	1.897(12)	1.906(5)	1.915(5)
Re1 – C2	1.939(11)	1.906(10)	1.911(5)	1.894(5)
Re1 – C3	1.935(11)	1.883(10)	1.895(5)	1.855(5)
C1 – O1	1.150(12)	1.188(13)	1.159(5)	1.167(5)
C2 – O2	1.129(12)	1.177(12)	1.161(5)	1.166(6)
C3 – O3	1.116(13)	1.185(12)	1.161(6)	1.166(6)
N1 – Re1 – C1	97.2(4)	100.9(4)	97.90(15)	98.64(17)
N1 – Re1 – C3	95.8(4)	94.5(4)	94.07(16)	110.33(18)
N2 – Re1 – C3	97.4(4)	98.1(4)	97.25(18)	102.8(2)
N2 – Re1 – C2	95.0(4)	97.3(4)	97.46(16)	95.23(18)
C1 – Re1 – C2	91.0(4)	85.5(5)	88.60(18)	85.78(19)
Re1 – Re1	3.0791(13)			
Re1 – Re2		3.1574(6)	3.1348(3)	
Re2 – N3		2.124(7)	2.131(3)	
Re2 – N4		2.140(8)	2.129(3)	
N3 – Re1 – N4		75.5(3)	75.20(13)	
Re1 – C14		1.906(11)	1.907(5)	
Re1 – C15		1.881(10)	1.901(4)	
Re1 – C16		1.891(10)	1.900(5)	
C14 – O4		1.176(12)	1.155(5)	
C15 – O5		1.187(12)	1.172(5)	
C16 – O6		1.189(12)	1.159(6)	
N3 – Re1 – C14		95.7(4)	98.13(16)	
N3 – Re1 – C16		97.0(3)	95.89(16)	
N4 – Re1 – C15		98.8(3)	98.70(16)	
N4 – Re1 – C16		103.7(4)	97.07(17)	
C14 – Re1 – C15		88.7(4)	86.82(18)	

[a] Distances and angles taken from one of the molecules in the asymmetric unit, Z’=2.

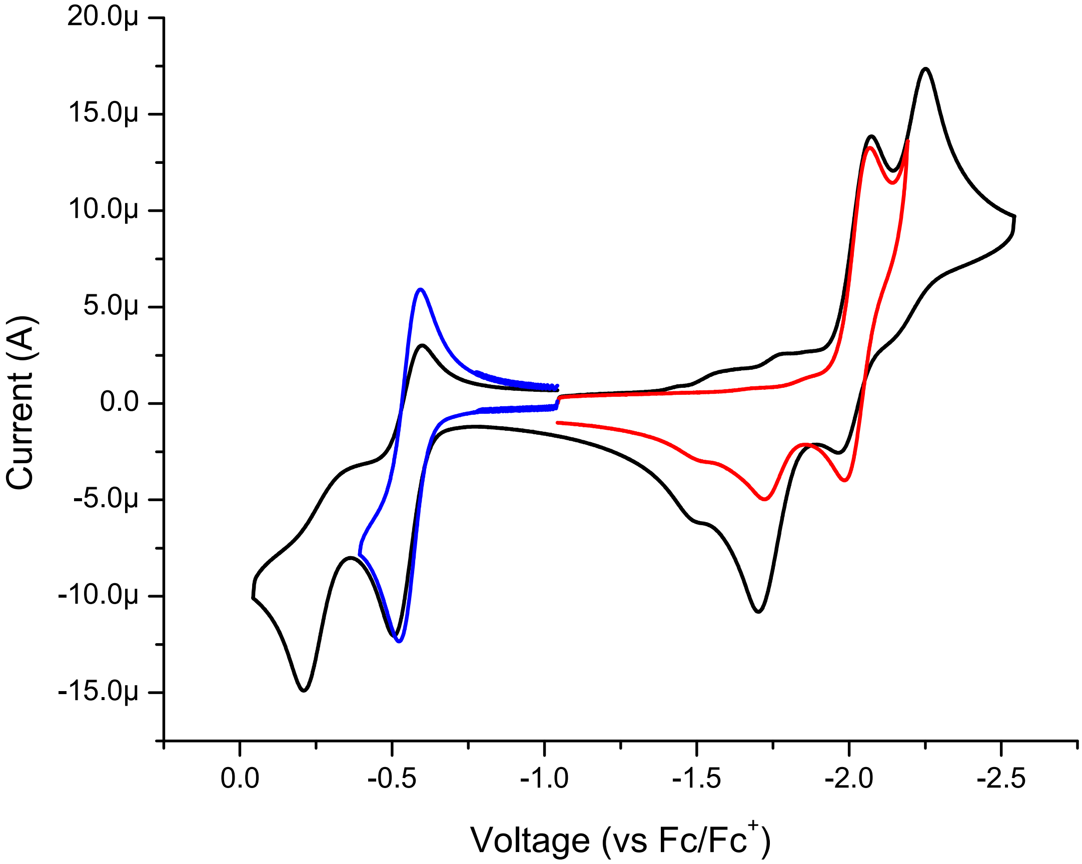

Figure S1. Electrochemistry of $[Re(bpy)(CO)_3]_2$ (**2**) 1mM in THF with a 3 mm glassy counter working electrode, silver wire reference, and Pt counter. A scan with added Fc provided an internal standard (not shown).

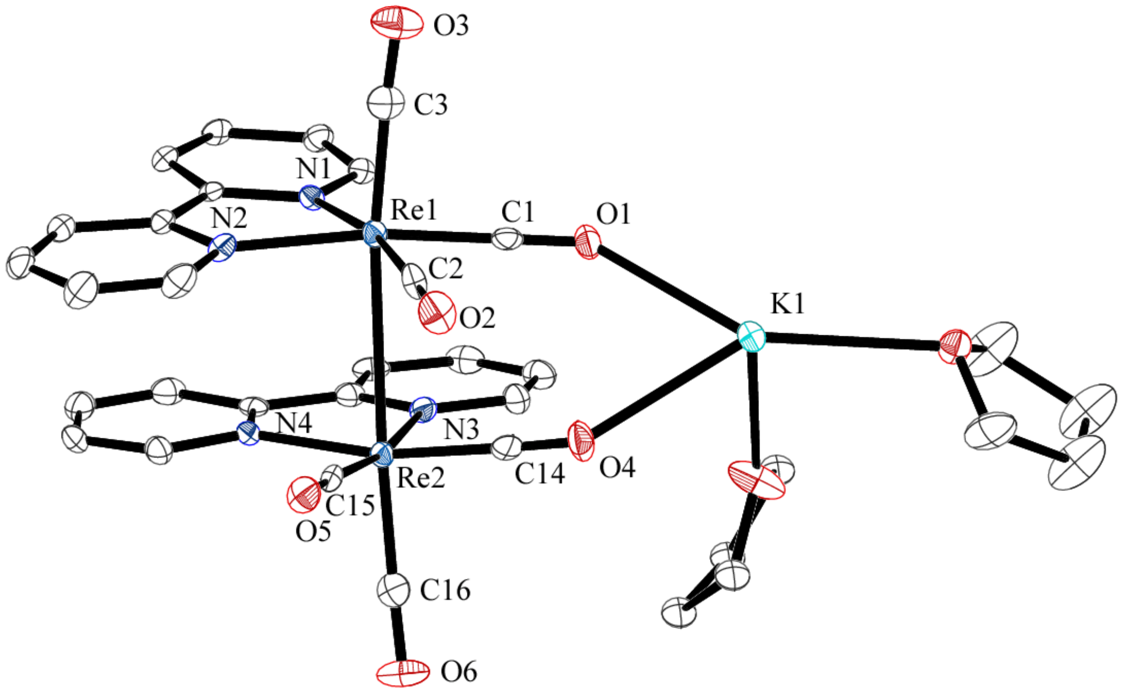

Figure S2. Molecular structure of [[Re(bpy)(CO)$_3$]$_2$][K(THF)$_2$], with hydrogen atoms omitted for clarity. Position 1 of 2 is shown for the disordered THF molecules, and the ellipsoids are set at the 50% probability level.

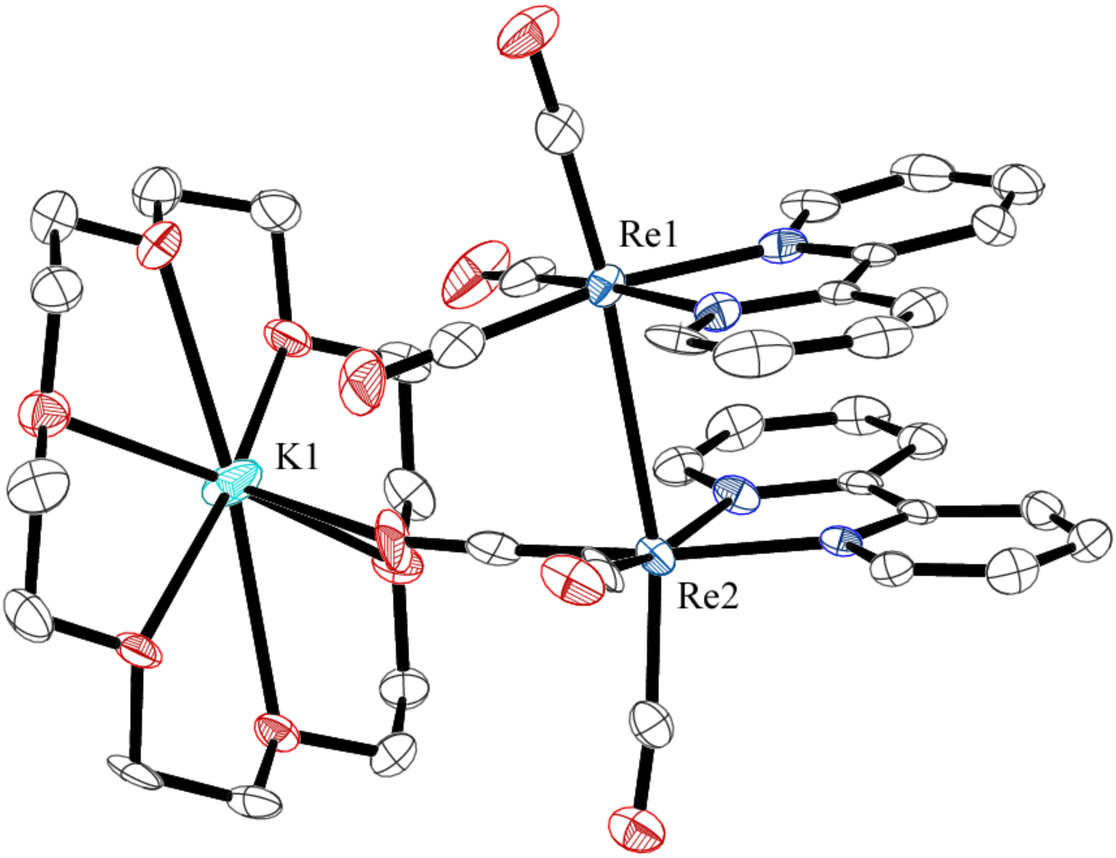

Figure S3. Molecular structure of $[[Re(bpy)(CO)_3]_2][K(18\text{-crown-}6)]$, with hydrogen atoms and disordered Et_2O molecule removed for clarity. The ellipsoids are set at the 50% level.

1. (a) M. A. Schwindt, T. Lejon and L. S. Hegedus, *Organometallics*, 1990, **9**, 2814-2819; (b) J. M. Smieja and C. P. Kubiak, *Inorg. Chem.*, 2010, **49**, 9283-9289.
2. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.