Electronic Supplementary Material (ESI) for Dalton Transactions.

Interrogating Heterobimetallic Co-Catalytic Responses for the Electrocatalytic Reduction of CO_2 Using Supramolecular Assembly

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Supporting Information

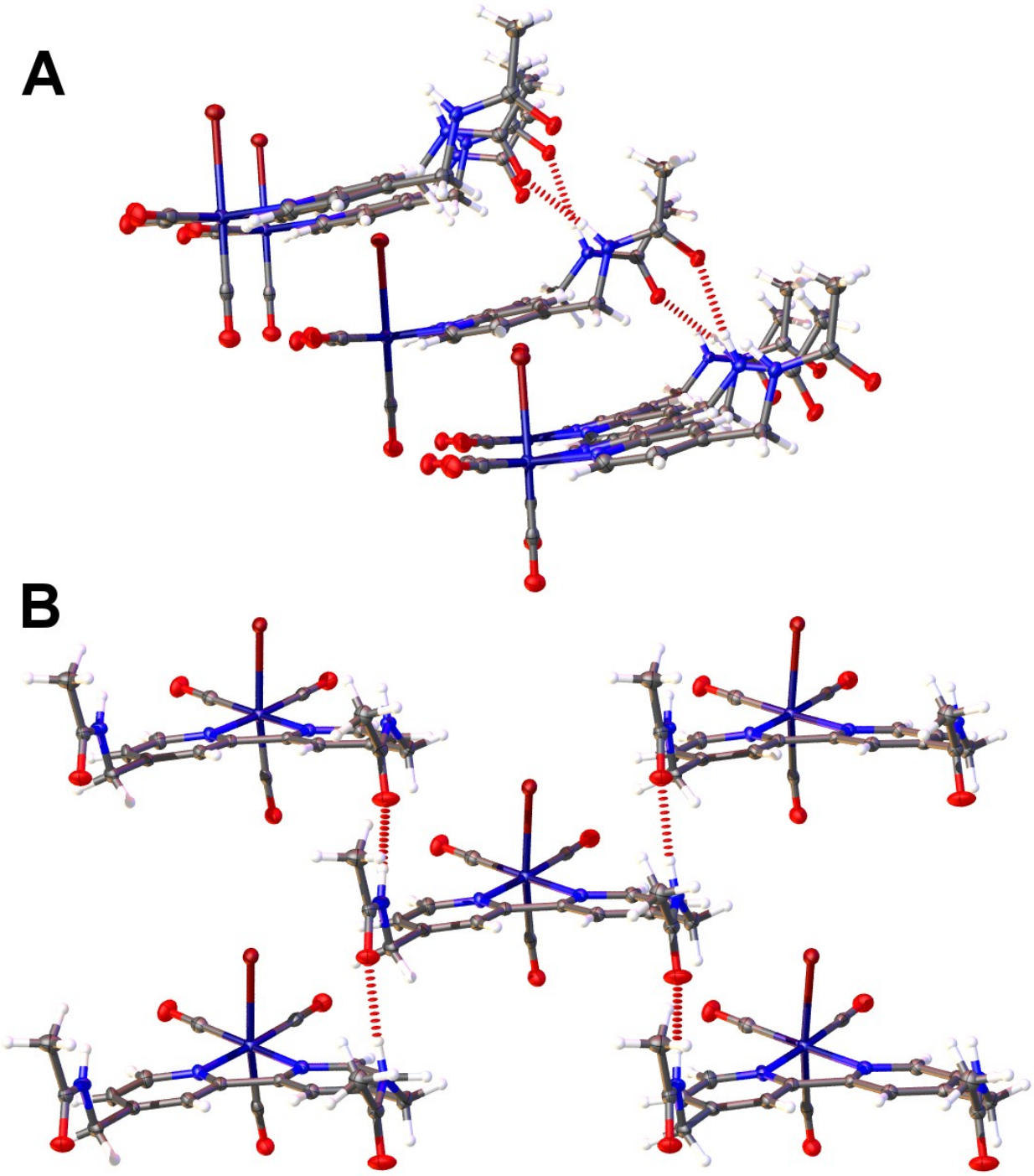

Figure S1. Side (**A**) and back (**B**) projections of Mn(**dacbpy**)$(CO)_3$Br **2** obtained from the single crystal X-ray data. Thermal ellipsoids at 50%; C = gray, H = white, N = blue, O = red, Br = maroon, Mn = navy. Occluded MeCN molecule omitted for clarity, hydrogen bonds denoted by red disks.

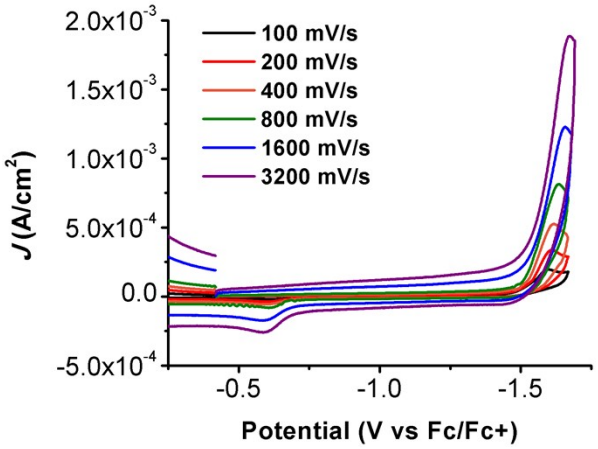

Figure S2. Variable-scan rate study of the cocat mixture under Ar saturation. Conditions: 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3$Cl **1** and Mn(**dacbpy**)$(CO)_3$Br **2** in **cocat** mixture.

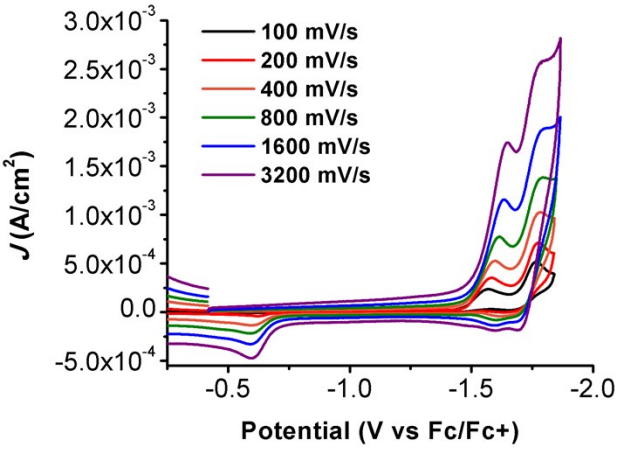

Figure S3. Variable-scan rate study of the cocat mixture under Ar saturation. Conditions: 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3$Cl **1** and Mn(**dacbpy**)$(CO)_3$Br **2** in **cocat** mixture.

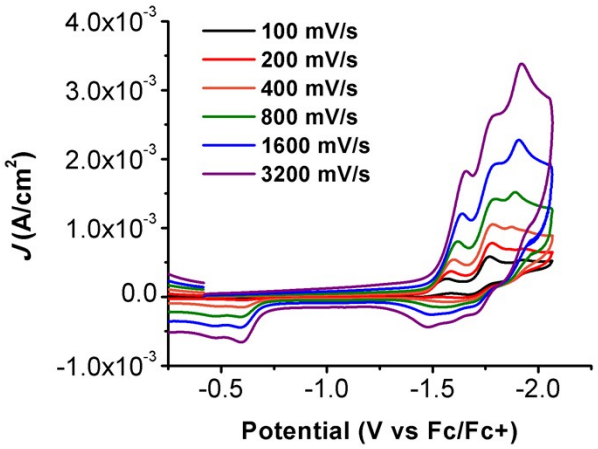

Figure S4. Variable-scan rate study of the cocat mixture under Ar saturation. Conditions: 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3$Cl **1** and Mn(**dacbpy**)$(CO)_3$Br **2** in **cocat** mixture.

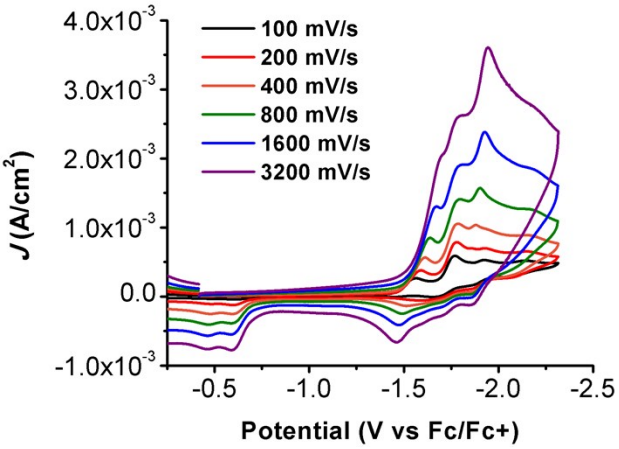

Figure S5. Variable-scan rate study of the cocat mixture under Ar saturation. Conditions: 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3$Cl **1** and Mn(**dacbpy**)$(CO)_3$Br **2** in **cocat** mixture.

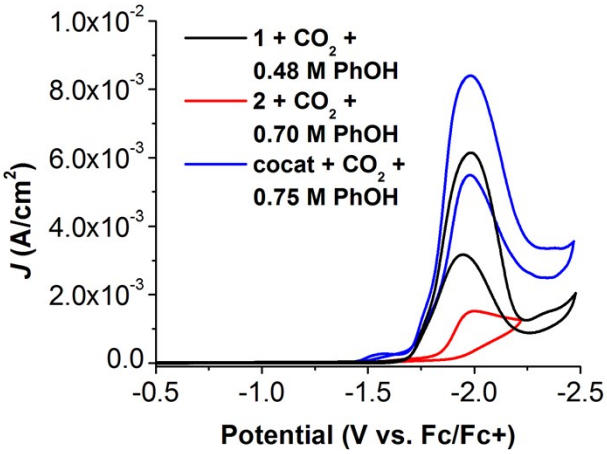

Figure S6. CVs showing the maximum current achieved through titration with PhOH for **1** (black), **2** (red), and **cocat** (blue) in MeCN under CO_2 saturation. CVs taken in 0.1 M $TBAPF_6$/MeCN at 100 mV/s; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2** in **cocat** mixture and 1 mM otherwise.

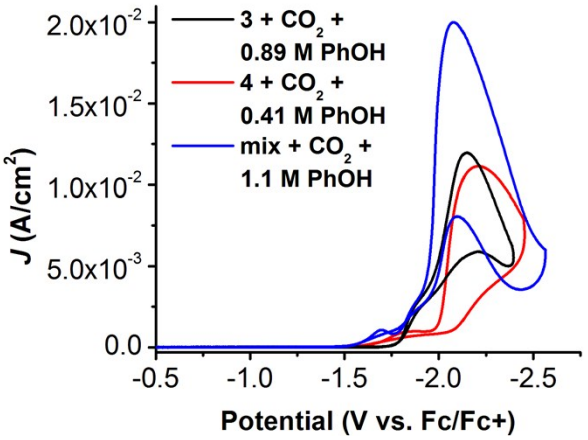

Figure S7. CVs showing the maximum current achieved through titration with PhOH for **3** (black), **4** (red), and an equimolar mixture of the two (blue) in MeCN under CO_2 saturation. CVs taken in 0.1 M $TBAPF_6$/MeCN at 100 mV/s; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dmb**)$(CO)_3Cl$ **3** and Mn(**dmb**)$(CO)_3Br$ **4** in the mixture and 1 mM otherwise.

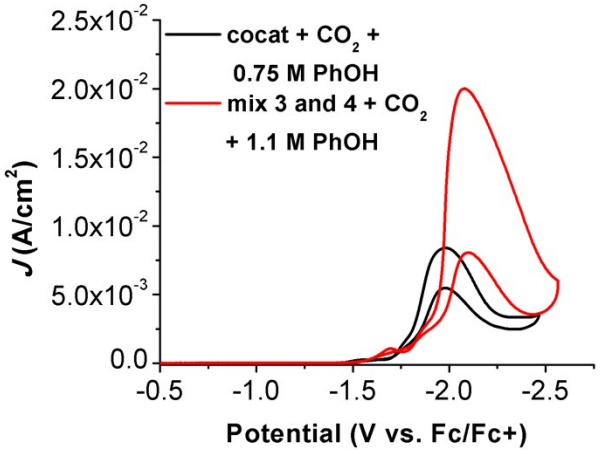

Figure S8. CVs showing the maximum current achieved through titration with PhOH for **cocat** (black) and a comparable equimolar mixture of **3** and **4** (red) in MeCN under CO_2 saturation. CVs taken in 0.1 M $TBAPF_6$/MeCN at 100 mV/s; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Catalyst concentration 1 mM each Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2** for **cocat** or Re(**dmb**)$(CO)_3Cl$ **3** and Mn(**dmb**)$(CO)_3Br$ **4** for the mix.

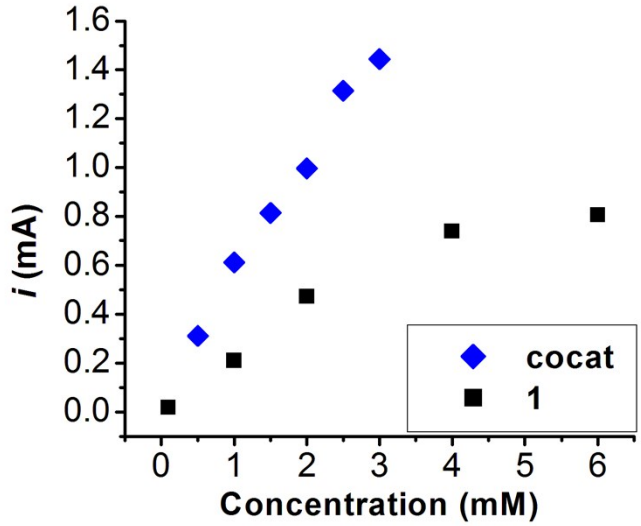

Figure S9. Plot of peak current response versus concentration for **cocat** (blue) and **1** (black); a linear trend is consistent with a first-order response according to the following equation:

$$i_{cat} = n_{cat}FA[cat](Dk_{cat}[Q])^{y})^{1/2}$$

(1) Saveant, J.-M.; Vianello, E. Electrochim. Acta **1962**, *8*, 905−923.
(2) Sampson, M.D.; Nguyen, A.D.; Grice, K.A.; Moore, C.E.; Rheingold, A.L.; Kubiak, C.P. *J. Am. Chem. Soc.* **2014**, *136*, 5460–5471.

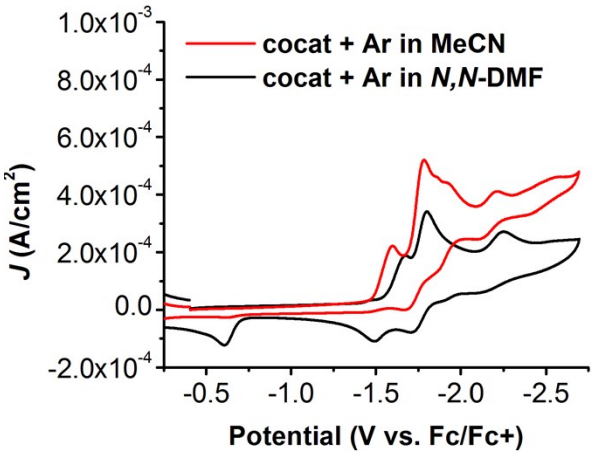

Figure S10. CVs of the **cocat** mixture taken at in MeCN (red) and *N,N*-DMF (black) under Ar saturation. CVs taken in 0.1 M $TBAPF_6$/MeCN or *N,N*-DMF at 100 mV/s; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2** in **cocat** mixture.

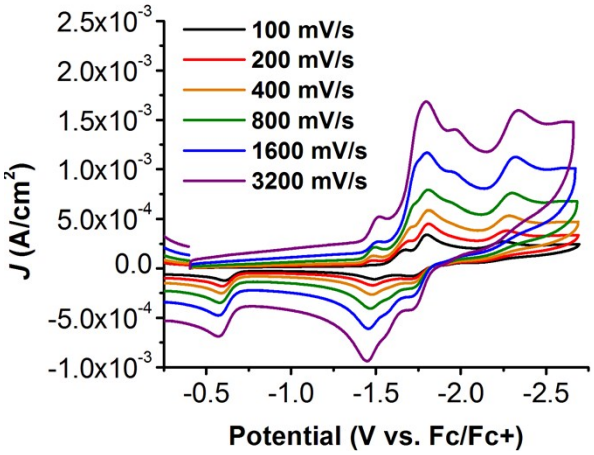

Figure S11. CVs of the **cocat** mixture taken *N,N*-DMF under Ar saturation at variable scan rates. CVs taken in 0.1 M $TBAPF_6$/*N,N*-DMF; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2** in **cocat** mixture.

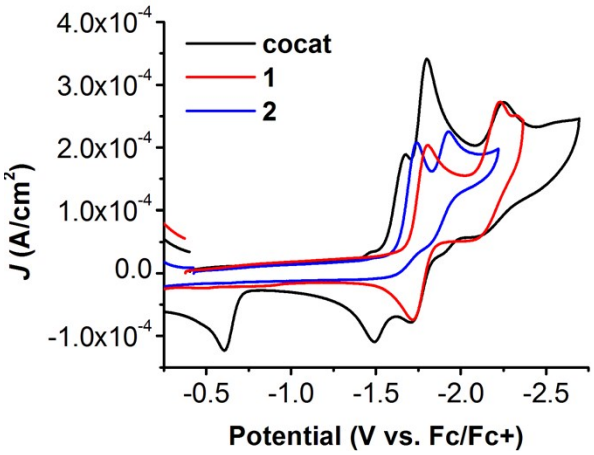

Figure S12. CVs of the **cocat** mixture (black), **1** (red), and **2** (blue) taken in *N,N*-DMF under Ar saturation. CVs taken in 0.1 M $TBAPF_6$/*N,N*-DMF at 100 mV/s; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM each Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2** in **cocat** mixture.

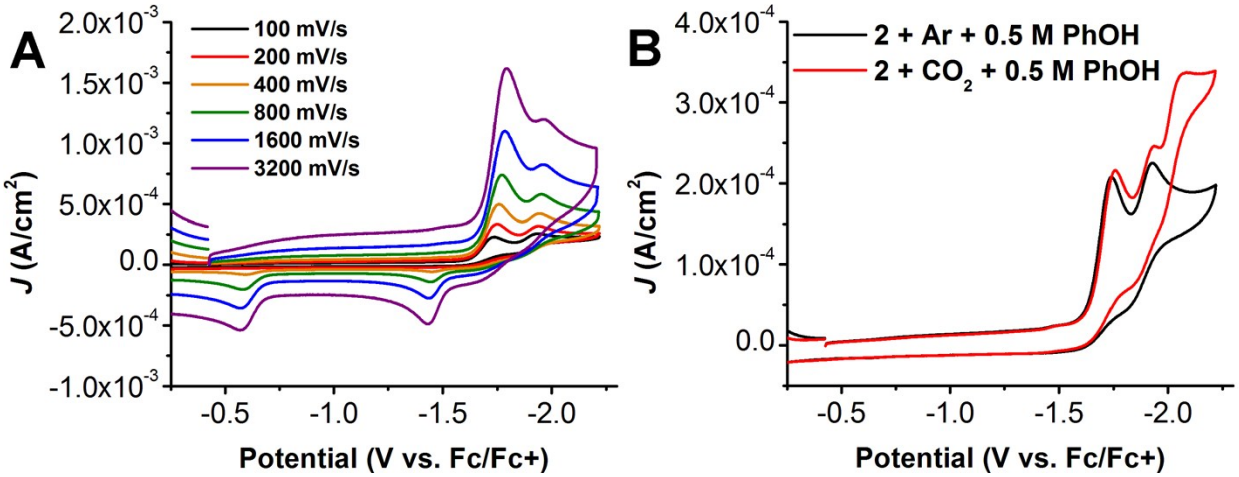

Figure S13. CVs of Mn(**dacbpy**)$(CO)_3Br$ **2** taken *N,N*-DMF under Ar saturation at variable scan rates. CVs taken in 0.1 M $TBAPF_6$/*N,N*-DMF; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM.

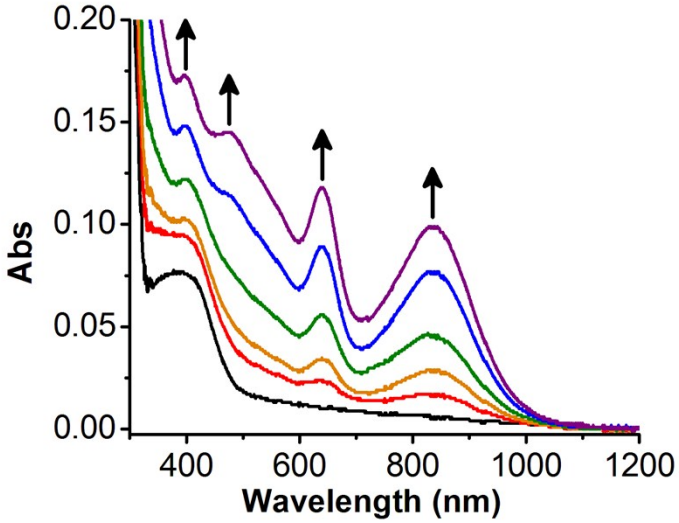

Figure S14. UV-Vis spectra of Mn(**dacbpy**)$(CO)_3$Br **2** taken in MeCN with titration of $CoCp^*_2$. CVs taken in 0.1 M Arrows denote features with increasing intensity. Starting concentration: 3 mM **2** in MeCN; 0.1 mm spacer, CaF_2 windows.

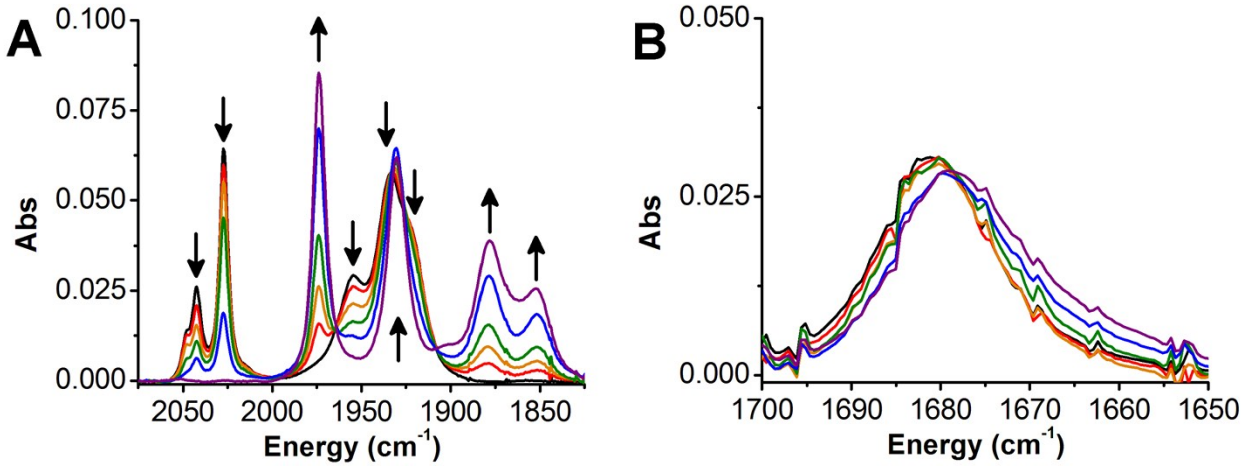

Figure S15. IR spectra of Mn(**dacbpy**)$(CO)_3$Br **2** taken in MeCN with titration of $CoCp^*_2$. Arrows denote features with increasing or decreasing intensity. Starting concentration: 3 mM **2** in MeCN; 0.1 mm spacer, CaF_2 windows.

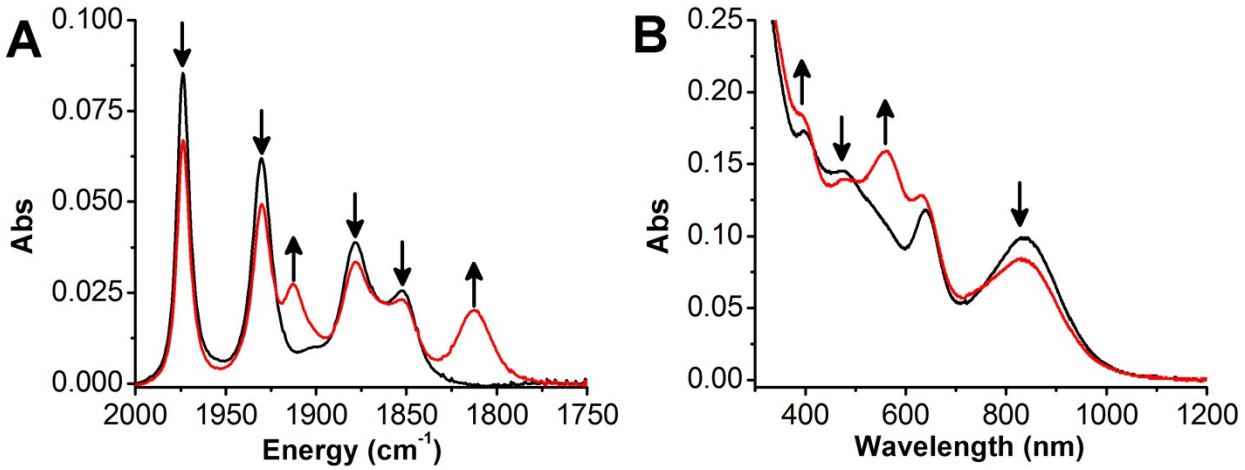

Figure S16. IR spectra (**A**) and UV-Vis spectra (B) of Mn(**dacbpy**)$(CO)_3$Br **2** taken in MeCN showing the generation of the monoanionic $[Mn^0(dabpy^{\bullet})(CO)_3]^-$ from titration of $CoCp^*_2$ to the dimer $[Mn^0$(**dacbpy**)$(CO)_3]_2$. Arrows denote features with increasing or decreasing intensity. Starting concentration: 3 mM in MeCN; 0.1 mm spacer, CaF_2 windows.

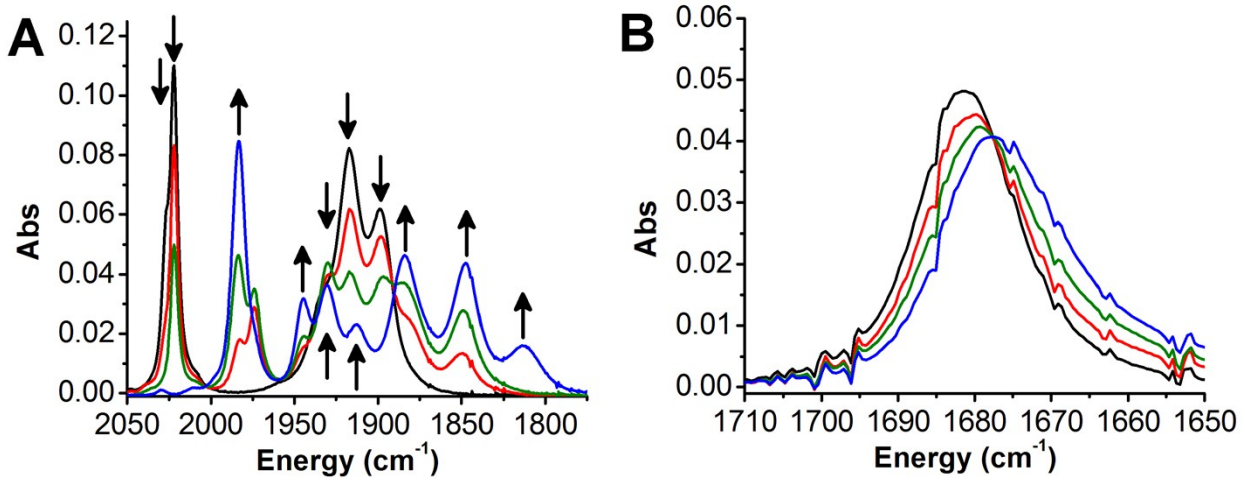

Figure S17. IR spectra of **cocat** taken in MeCN with titration of $CoCp^*_2$. Arrows denote features with increasing or decreasing intensity. Starting concentration 3 mM **cocat** (equimolar mixture of Re(**dacbpy**)$(CO)_3$Cl **1** and Mn(**dacbpy**)$(CO)_3$Br **2**) in MeCN; 0.1 mm spacer, CaF_2 windows.

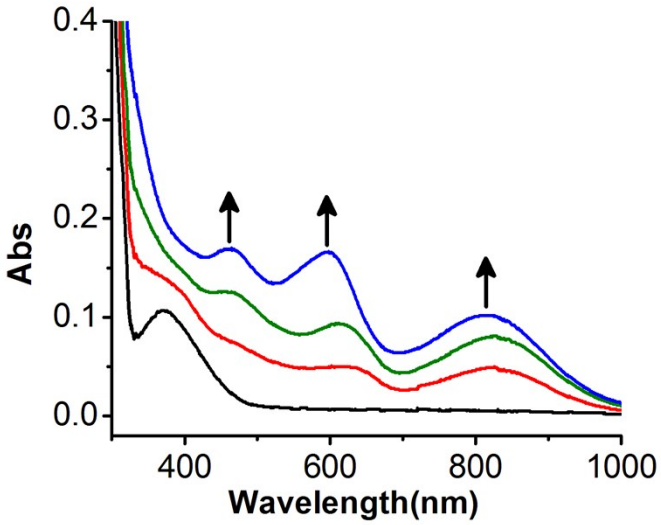

Figure S18. UV-Vis spectra of **cocat** taken in MeCN with titration of $CoCp^*_2$. Arrows denote features with increasing intensity. Starting concentration 3 mM **cocat** (equimolar mixture of Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2**) in MeCN; 0.1 mm spacer, CaF_2 windows.

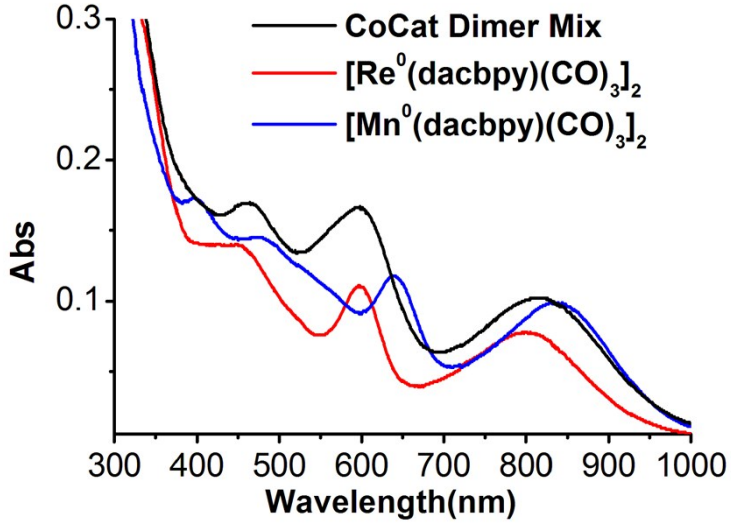

Figure S19. UV-Vis spectra of the metal-metal dimers of Re(**dacbpy**)$(CO)_3Cl$ **1** (red) and Mn(**dacbpy**)$(CO)_3Br$ **2** (blue) obtained through chemical reductions with $CoCp^*_2$ overlaid with that obtained for **cocat** (equimolar mixture of Re(**dacbpy**)$(CO)_3Cl$ **1** and Mn(**dacbpy**)$(CO)_3Br$ **2**; black) after complete consumption of the starting material. The **cocat** mixture contains $[Mn(\textbf{dacbpy})(CO)_3]^-$, resulting in a blue shift for metal-metal dimer absorbances. Starting concentration 3 mM in MeCN; 0.1 mm spacer, CaF_2 windows.

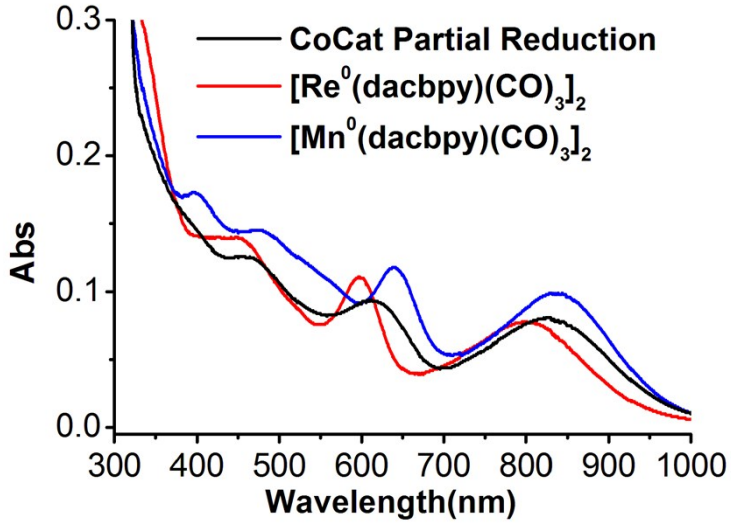

Figure S20. UV-Vis spectra of the metal-metal dimers of Re(**dacbpy**)$(CO)_3$Cl **1** (red) and Mn(**dacbpy**)$(CO)_3$Br **2** (blue) obtained through chemical reductions with $CoCp^*_2$ overlaid with that obtained for **cocat** (equimolar mixture of Re(**dacbpy**)$(CO)_3$Cl **1** and Mn(**dacbpy**)$(CO)_3$Br **2**; black) before the appearance of [Mn(**dacbpy**)$(CO)_3]^-$. Starting concentration: 3 mM in MeCN; 0.1 mm spacer, CaF_2 windows.

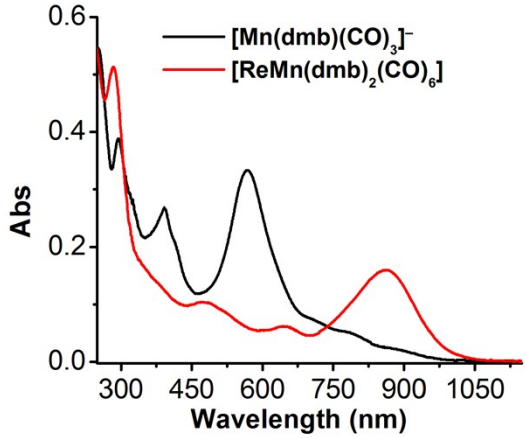

Figure S21. UV-Vis spectra of the [Mn(**dmb**)$(CO)_3$]K (black) and the product of the reaction with an equimolar amount of **3** (red) in chilled THF. Concentration 3 mM [Mn(**dmb**)$(CO)_3$]K and 3.0 mM [ReMn(**dmb**)$_2(CO)_6$]; 0.1 mm spacer, CaF_2 windows.

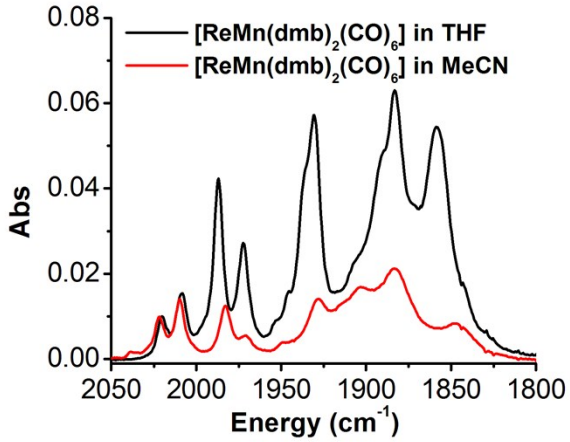

Figure S22. IR spectra of the [ReMn(**dmb**)$_2$(CO)$_6$] in THF (black) and MeCN (red). Concentration 3.0 mM; 0.1 mm spacer, CaF_2 windows.

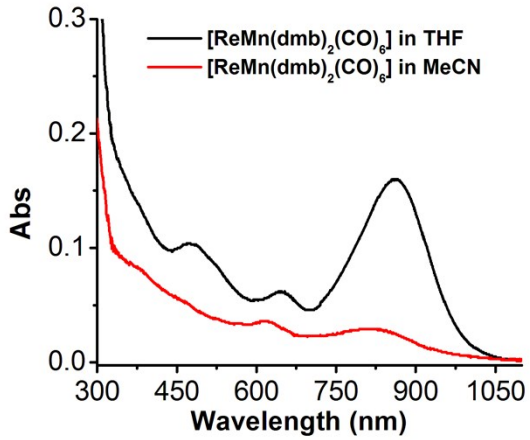

Figure S23. UV-Vis spectra of the [ReMn(**dmb**)$_2$(CO)$_6$] in THF (black) and MeCN (red). Concentration 3.0 mM; 0.1 mm spacer, CaF_2 windows.

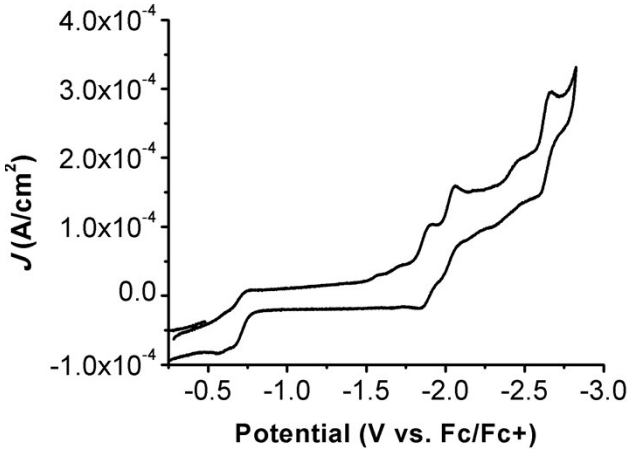

Figure S24. CV of [ReMn(**dmb**)$_2$(CO)$_6$] taken MeCN under Ar saturation. CVs taken in 0.1 M TBAPF$_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard. Analyte concentration 1 mM. Reduction features at –1.90, –2.06, –2.47, and –2.67 V (vs Fc/Fc+); oxidation features at –2.58, –1.97, –1.84, –0.65, and –0.56 V (vs Fc/Fc+).

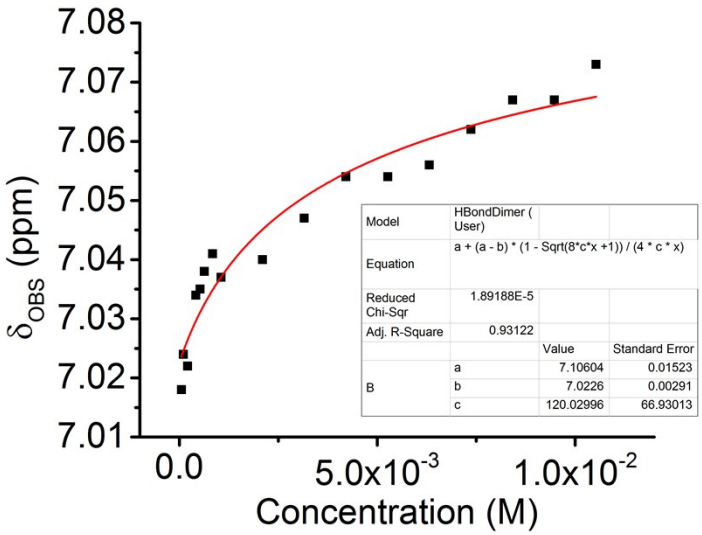

Figure S25. Determination of K_a for ^{1}H NMR data of Mn(**dacbpy**)(CO)$_3$Br **2** by fitting to a 1:1 dimerization model.

Table S1. Crystal data for complex **2**.

Empirical formula	$C_{19}H_{18}BrMnN_4O_5 \cdot C_2H_3N$
Formula weight	558.27
Temperature/K	100(2)
Crystal system	triclinic
Space group	P_{-1}
a/Å	8.4602(13)
b/Å	8.6080(15)
c/Å	17.623(3)
α/°	101.163(6)
β/°	95.668(5)
γ/°	112.647(5)
Volume/Å^3	1140.5(3)
Z	2
ρ_{calc}g/cm^3	1.626
μ/mm^{-1}	2.37
F(000)	564.3709
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.80 to 52.82
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-22 \le l \le 22$
Reflections collected	18832
Independent reflections	4653 [R_{int} = 0.0685, R_{sigma} = 0.0667]
Data/restraints/parameters	3660/0/300
Goodness-of-fit on F^2	1.0295
Final R indexes [I>=2σ (I)]	R_1 = 0.0154, wR_2 = 0.0356
Final R indexes [all data]	R_1 = 0.0169, wR_2 = 0.0362
Largest diff. peak/hole / e Å^{-3}	0.5595/-0.6397

Table S2. Selected bond distances for complex **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1—Mn1	2.5355 (6)	N31—C29	1.133 (4)	Br1—Mn1	2.5355 (6)
Mn1—N4	2.047 (2)	C19—C20	1.388 (4)	Mn1—N4	2.047 (2)
Mn1—C21	1.812 (3)	C19—C25	1.387 (4)	Mn1—C21	1.812 (3)
Mn1—C22	1.809 (3)	C13—C20	1.478 (4)	Mn1—C22	1.809 (3)
Mn1—C10	1.803 (3)	C13—C14	1.392 (4)	Mn1—C10	1.803 (3)
Mn1—N0AA	2.040 (2)	C16—C1	1.518 (4)	Mn1—N0AA	2.040 (2)
O1—C15	1.231 (3)	C20—N0AA	1.362 (3)	O1—C15	1.231 (3)
O9—C21	1.148 (4)	C14—C26	1.386 (4)	O9—C21	1.148 (4)
O3—C10	1.151 (3)	C18—C24	1.383 (4)	O3—C10	1.151 (3)
O7—C22	1.137 (3)	C18—N0AA	1.343 (3)	O7—C22	1.137 (3)
O5—C16	1.235 (3)	C23—C17	1.388 (4)	O5—C16	1.235 (3)
N4—C13	1.351 (4)	C23—C26	1.380 (4)	N4—C13	1.351 (4)
N4—C17	1.341 (4)	C15—C33	1.497 (4)	N4—C17	1.341 (4)

Table S3. Bulk electrolysis data.

Catalyst	[conc] (mM)	V (vs Ag/AgCl)	Efficiency for CO	Turnovers	PhOH (M)
1	1.0	–2.2	76%	4.14	0.5
2	1.0	–2.2	100%	4.14	0.5
cocat	0.5	–2.2	86%	4.15	0.5

Bulk electrolyses were performed in a custom threaded glass jar from Chemglass fitted with a custom PEEK top containing ports for venting, fritted glass insert with counter electrode, working electrode, counter electrode, and a septum for sampling the headspace. The system was sealed with a combination of o-rings, Teflon tape, and electrical tape and tested for airtightness before each run. For an individual run the jar was charged with a known amount of catalyst, known amount of PhOH (0.5 M), stir bar, and an electrolyte solution (0.1 M $TBAPF_6$/MeCN) before being sparged to saturation with CO_2. In order to prevent polymerization of PhOH on the counter electrode, 0.1 M Fc was added to the electrolyte solution as a sacrificial oxidant. After a run was completed, the headspace was sampled via airtight syringe and characterized by GC such that Faradaic efficiency could be determined by using a calibration curve. A turnover for this system is based on two electron equivalents being passed for every catalyst molecule in solution; for every mole of catalyst two electrons are passed to achieve one turnover.