Supporting Information for

Electrocatalytic Reduction of CO_2 using Mn Complexes with Unconventional Coordination Environments

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Experimental: All cyclic voltammetry experiments have been carried out in a three neck round bottom flask wrapped with aluminum foil. Samples were prepared in glove box and sealed before removing for measurement. Cyclic voltammetry was performed using a VersaSTAT 3 (Princeton Applied Research) potentiostat. A conventional three electrode system was employed. A glassy carbon electrode (diameter = 0.2 cm) was used as the working electrode, a Pt wire as the auxiliary electrode, and an Ag wire was used as pseudo-reference electrode. For bulk electrocatalytic reduction experiments, a glassy carbon rod (diameter = 0.4 cm; length 2 cm) was used as the working electrode, a Pt gauze as the auxiliary electrode, and an Ag wire was used as pseudo-reference electrode. Ferrocene was added after purging CO_2 and measured before and after water addition. Dried acetonitrile was purchased from Sigma-Aldrich and stored on molecular sieves in a glove-box. Tetrabutylammoniumhexafluorophosphate, the supporting electrolyte, was crystallized two times with dried methanol and dried in vacuum at 90 °C for 24 h before use and stored in glove box. The electrolyte solution, 0.1 M $(n\text{-}Bu)_4N.PF_6$ in CH_3CN, was saturated with N_2 or CO_2 by purging with N_2 or CO2 (purity $\geqslant$ 99.8%, BOC gases) for 15 min prior to each experiment. The concentration of catalyst was 1 mM (15 mL acetonitrile) in each experiment. Carbon monoxide and hydrogen production was measured using an Agilent 7820A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) analyzer using an Agilent select permanent gases column.

For complex **1⁺Br⁻** and ligands, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 400, 100 and 162 MHz; for complex **2**, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.0, 75.0 and 121.5 MHz respectively with chemical shifts reported in ppm using the residual protons of the NMR solvent as internal standards. Carbon-13 DEPT NMR experiments were used routinely to determine the number of hydrogen atoms linked to carbon atoms. IR spectra were collected using an Agilent Cary FTIR spectrometer

X-ray Crystallography

Data collection results for compounds represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200.15 °K. Data were collected on a Bruker

AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.[1] Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[2] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with triclinic P$\overline{1}$ for compound **1Br**, and monoclinic P2_1 for compound **2**. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. All hydrogen atoms positions were calculated based on the geometry of the related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.[3]

Synthesis of κ^3-[2,6-{Ph$_2$PNMe}$_2$(NC$_5$H$_3$)]Mn(CO)$_3$+Br⁻ (1+Br⁻, PN$_3$PMn(CO)$_3$+Br⁻) In a glove box, a solution of ligand N,N'-bis(diphenylphosphino)-2,6-di(methylamino)pyridine (0.253 g, 0.5 mmol) was prepared in 15 mL of tetrahydrofuran. Mn(CO)$_5$Br (0.137 g, 0.5 mmol) was added via stirring to the THF solution of ligand. The flask was wrapped with aluminum foil, removed from the glovebox and connected to a Schlenk line via a reflux condenser. The reaction mixture was heated to 100 °C under N$_2$ and stirred for an additional 3 hThe solution was cooled and the volume was reduced to ~10 mL *invacuo*. White precipitate was filtered off to give complex **1+Br⁻**. Single crystals of this complex were grown by slow diffusion of hexane into the solution of complex made in chloroform. Yield 0.269 g (74%); ¹H NMR (400 MHz, CDCl$_3$, 25°C): δ = 3.25 (s, 6H, CH$_3$,), 6.95 (s, 2H**)**, 7.47–7.63 (m, 20 H), 8.10 (s, 1 H).¹³C{¹H} NMR (100 MHz, CDCl$_3$, 25 ºC): δ = 37.7 (s, CH$_3$), 102.6, 129.7 (t, J = 5.0 Hz), 130.5 (t, J = 5.7 Hz), 131.6 (t, J = 24.1 Hz), 132.0, 143.5, 161.3 (t, J = 11.1 Hz). ³¹P{¹H} NMR (162 MHz, CDCl$_3$, 25°C): δ = 134.3. HR-MS (CH$_3$CN): [M−Br] m/z 644.1048; calcd value for C$_{34}$H$_{29}$N$_3$O$_3$P$_2$Mn 644.1065 (δ −2.6). Infrared data (cm⁻¹): ν(CO) 1852, 1930, 1973.

Synthesis of κ²-(Ph₂P)NMe(NC₅H₄)Mn(CO)₃Br (2) In a glove box, a solution of N-(diphenylphosphino)-2-methylaminopyridine (0.146 g, 0.5 mmol) was prepared in 15 mL of tetrahydrofuran. Mn(CO)₅Br (0.137 g, 0.5 mmol) was added via stirring to the THF solution of ligand. The flask was wrapped with aluminum foil, removed from the glovebox and connected to a Schlenk line via a reflux condenser. The reaction mixture was heated to 100 °C under N_2 and stirred for an additional 3 h. The solution was cooled and the volume was reduced to ~3 mL and 50 mL of hexane was added to get complex **2** as a yellow solid. Single crystals of **2** were grown by slow diffusion of hexane to the solution of **2** in THF. Yield 0.177 g (78%); ^{1}H NMR (300 MHz, CDCl₃, 25°C): δ = 3.14 (s, 6H, CH₃,), 6.93–7.85 (m, 13 H), 8.72 (s, 1 H). ^{13}C{^{1}H} NMR (75 MHz, CDCl₃, 25 ºC): δ = 34.6 (s, CH₃), 109.9 (d, J = 6.8 Hz), 116.2, 17.4 (d, J = 10.0 Hz), 128.3 (d, J = 9.5 Hz), 128.5 (d, J = 43.5 Hz), 129.7, 130.3 (t, J = 30.3 Hz), 133.1 (d, J = 10.9 Hz), 133.3 (d, J = 44.4 Hz), 139.53, 154.0 (d, J = 4.8 Hz), 161.3 (d, J = 19.2 Hz). ^{31}P{^{1}H} NMR (122 MHz, CDCl₃, 25°C): δ = 122.7. HR-MS (CH₃CN): [M−Br+2CH₃CN] m/z 486.0914; calcd value for C₂₄H₂₃N₄O₂PMn 486.0970 (δ 11.0). Infrared data (cm⁻¹): ν(CO) 1880, 1903, 1936.

Synthesis of N-(diphenylphosphino)-2-methylaminopyridine: This ligand was synthesized following a modified literature procedure.[1] A solution of 1.08 g (10.0 mmol) of 2-(methylamino)pyridine made in 25 mL of diethyl ether was cooled to −78 °C. *n*-BuLi (10 mmol, 1.6 M in hexane, 6.25 mL) was added drop wise and the solution was stirred for 2 h. A solution of PPh₂Cl (10 mmol, 2.2 g) taken in 10 mL diethylether was added dropwise and the solution was allowed to warm at room temperature. This reaction mixture was stirred overnight. The reaction mixture was filtered twice and the solvent was removed to give a colorless liquid which was further kept under vacuum for 24 h at room temperature to give colorless solid. Yield; 2.28 g (78%). NMR (400 MHz, CDCl₃, 25°C): δ = 2.96 (3H, d, J = 1.56 Hz), 6.75–6.79 (m, 1H), 7.39–7.55 (m, 12 H), 8.28–8.30 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl₃, 25 ºC): δ = 34.1 (d, J = 8.6 Hz), 110.5 (d, J = 41.4 Hz), 114.6 (d, J = 1.0 Hz), 128.4 (d, J = 5.8 Hz),

[1] P. A. Aguirre, C. A. Lagos, S. A. Moya, C. Zúῆiga, C. Vera-Oyarce, E. Sola, G. Peris and J. C. Baýon, *Dalton Trans.*, 2007, 5419–5426.

129.0, 131.9 (d, J = 20.4 Hz), 136.6 (d, J = 14.8 Hz), 137.0 (d, J = 3.0 Hz), 147.6 (d, J = 1.7 Hz), 161.3 (d, J = 26.9 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 25°C): δ = 51.0.

Synthesis of N,N'-bis(diphenylphosphino)-2,6-di(methylamino)pyridine:[2] *n*-Butyllithium (1.6 M in hexane, 8.0 mmol, 5.0 mL) was drop wise added to a toluene (100 mL) solution of N,N'-dimethyl-2,6-diaminopyridine (1.0 g, 7.3 mmol) cooled on ice-salt bath. The mixture was stirred at room temperature for 2 h and was then cooled to −78 °C using dry ice-acetone bath. To this mixture 1.3 mL (7.3 mmol) of chlorodiphenylphosphine was added. The resulting reaction mixture was stirred for 2 h at room temperature and refluxed for 18 h. The solution was cool to room temperature and filtered twice with a frit. The above procedure was then repeated with the resulting yellow solution. After filtering, the solvent of resulting reaction mixture was removed under vacuum yielding a yellow oil. This oil dissolved in acetonitrile and the mixture was heated to reflux for 10 minutes. Upon cooling at room temperature a white precipitate formed. The acetonitrile was decanted off and the compound was dried under vacuum. Yield: 1.70 g (46%). NMR (400 MHz, CDCl$_3$, 25°C): δ = 2.92 (6H, d, J = 1.72 Hz), 6.90 (dd, 2H, J = 2.44, 8.04), 7.38–7.49 (m, 21 H). $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$, 25 ºC): δ = 33.9 (d, J = 8.6 Hz), 99.7 (d, J = 21.1 Hz), 128.3 (d, J = 5.8 Hz), 128.7, 132.0 (d, J = 20.7 Hz), 137.4 (d, J = 15.8 Hz), 138.2 (t, J = 3.2 Hz), 159.5 (dd, J = 2.08, 27.2 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 25°C): δ = 49.5.

[2]: S. R. M. M. de Aguiar, B. Stöger, E. Pittenauer, M. Puchberger, G. Allmaier, L. F. Veiros, K. Kirchner, *J. Organomet*. *Chem*., 2014, 760, 74–83.
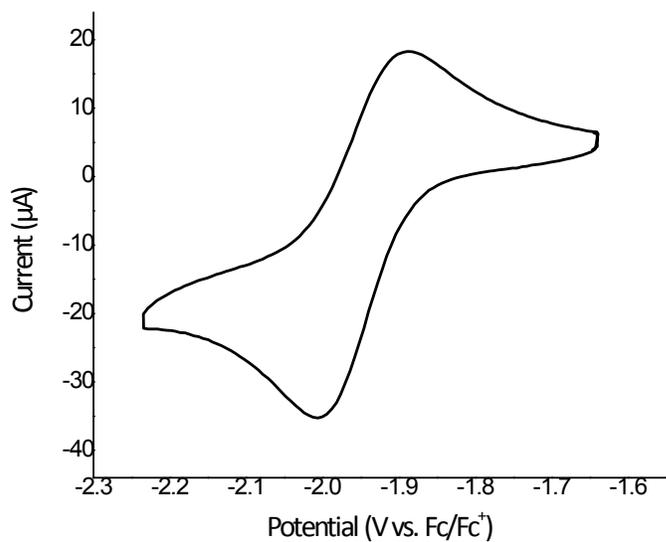
Figure S1. A portion of the cyclic voltammagram of **1⁺Br⁻**(1.0 mM) showing the reversible reduction. Potential is vs Fc/Fc⁺. Measurement was carried out under N_2 in CH_3CN with 0.1M tetrabutylammoniumhexafluorophosphate (TBAHFP) supporting electrolyte at a scan rate of 100 mV/s.
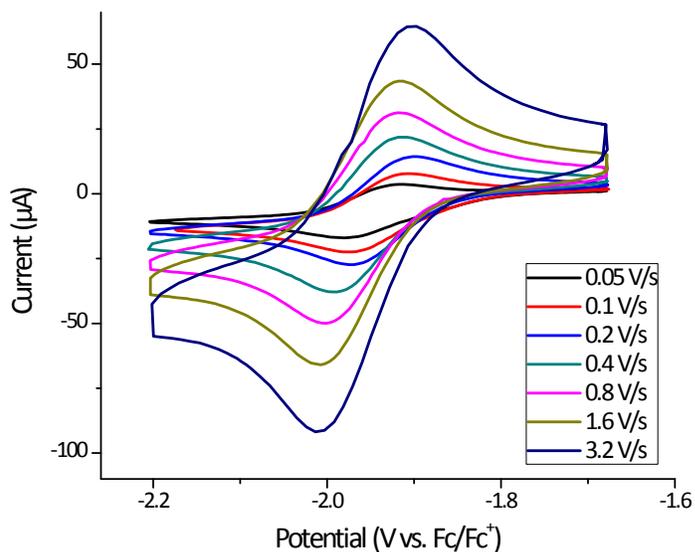
Figure S2. Cyclic voltammagrams of the first reduction for 1^+Br^- (1.0 mM) under N_2 in CH_3CN with 0.1M tetrabutylammoniumhexafluorophosphate (TBAHFP) supporting electrolyte with different scan rates.
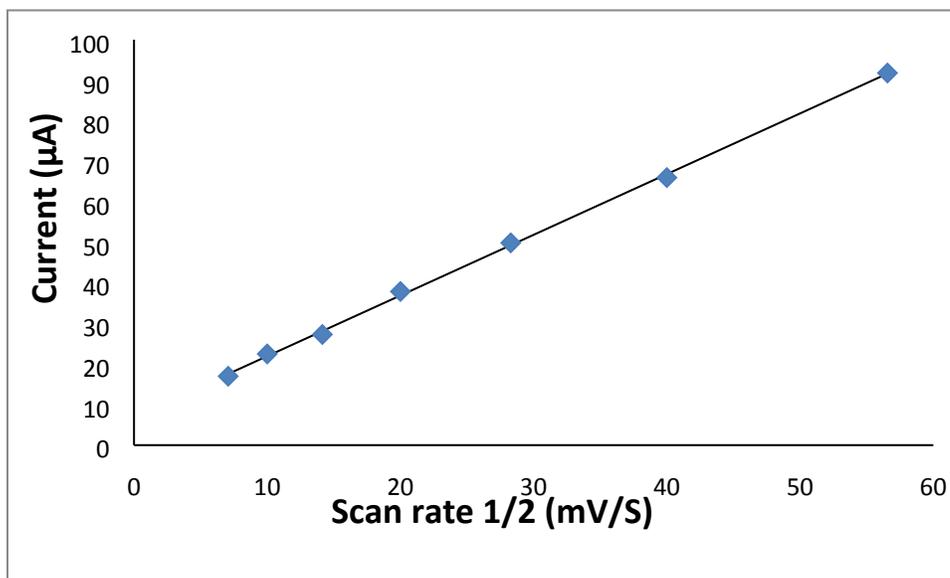
Figure S3. Plot of scan rate$^{1/2}$ versus current for the first reduction peak for compound 1^+Br^-.
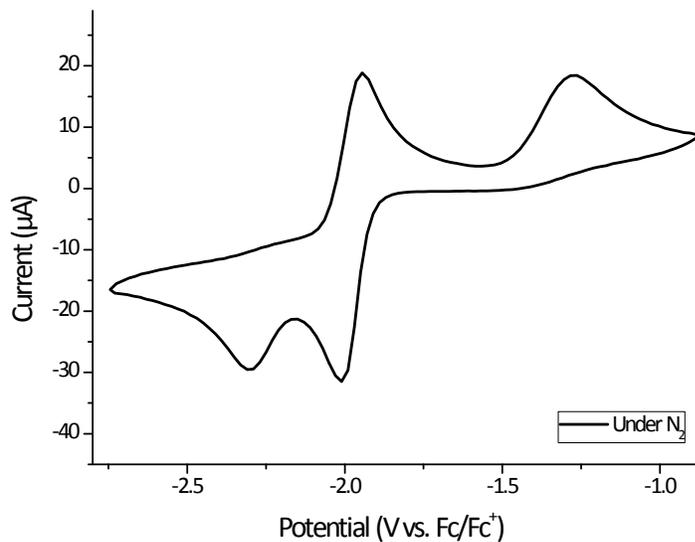
Figure S4. The full cyclic voltammagram of 1^+Br^-(1.0 mM) under N_2 in CH_3CN with 0.1Mtetrabutylammoniumhexafluorophosphate (TBAHFP) supporting electrolyte at a scan rate of 100 mV/s.
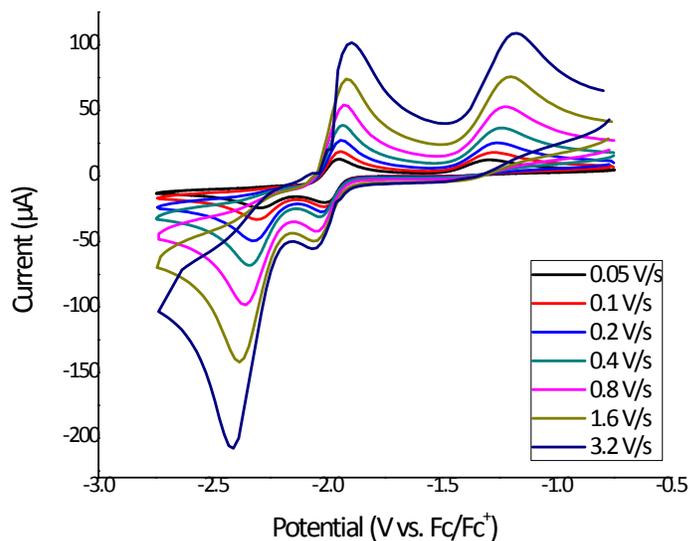
Figure S5. Cyclic voltammagrams for 1^+Br^- (1.0 mM) under N_2 in CH_3CN with 0.1M tetrabutylammoniumhexafluorophosphate (TBAHFP) supporting electrolyte with different scan rates.
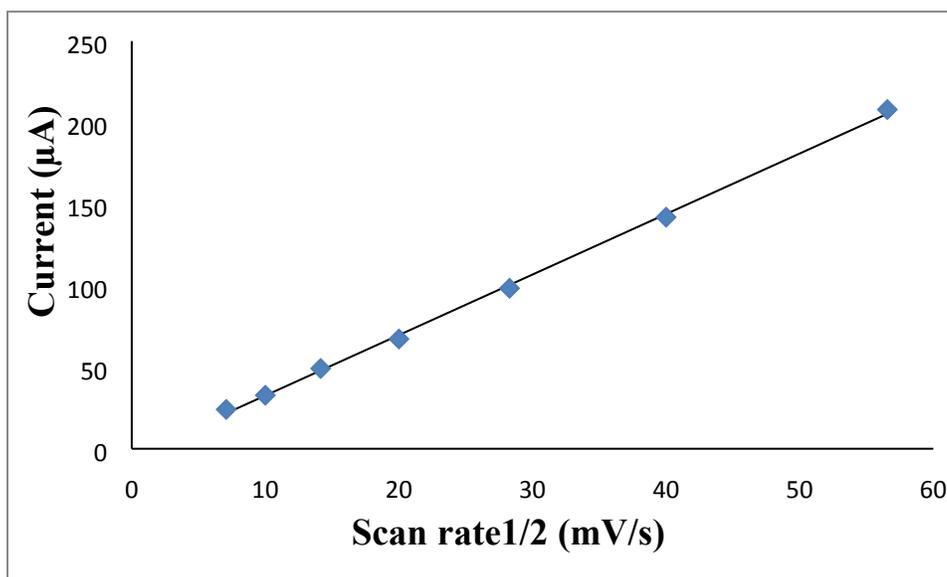
Figure S6. For compound 1^+Br^-, plot of scan rate$^{1/2}$ versus current for the reduction peak at -2.3 V.

Table S1: Typical bulk electrolysis experiment for **1⁺Br⁻**(1.0 mM) in dry acetonitrile .

Experiment 1		
μmol of CO (Calculated)	μmol of CO (Obtained)	
8.2	4	
16.1	15	
22	21	
24.7	24	
30.1	30	
37.1	35	
44.1	40	
46.4	46	

Table S2: Bulk electrolysis experiments for **1⁺Br⁻**(1.0 mM) in acetonitrile with 5% added H_2O.

μmol of CO + H_2 (Calculated)	μmol of CO (Obtained)	μmol of H_2 (Obtained)
17.28	12	5
29.99	17	10
42.24	20	15
56.13	25	18
70.82	28	23
84.68	28	27
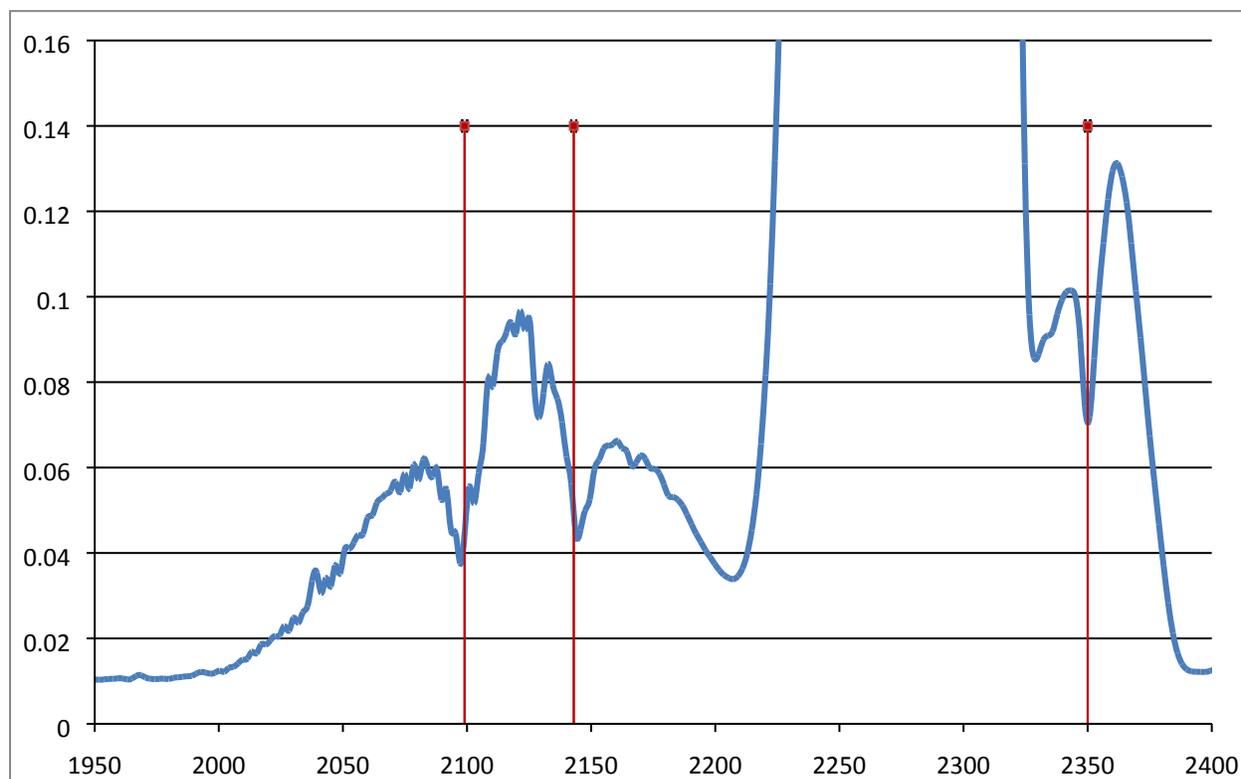
Figure S7. Gas phase FTIR spectrum measured from the bulk electrolysis of $^{13}CO_2$ with compound 1^+Br^-. Vertical indicators are shown for the Q-bands of ^{13}CO 2099 cm^{-1}, ^{12}CO 2143 cm^{-1} and CO_2 2350 cm^{-1} (the P and R-bands are visible on either side of these markers). The band for $^{13}CO_2$ at 2280cm^{-1} is obscured by solvent vapor.
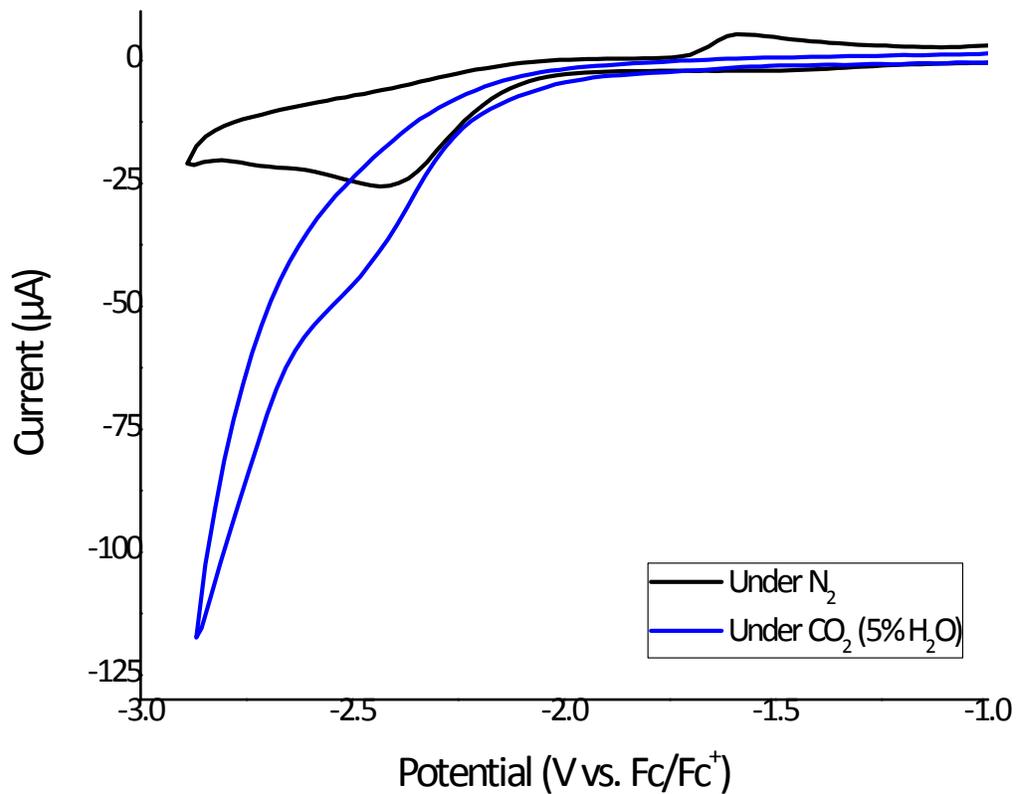
Figure S8. Cyclic voltammograms of 1.0mM MnBr(PN)(CO)$_3$ (**2**) under N$_2$ (black), and CO$_2$/5% H$_2$O (blue) in CH$_3$CN with 0.1M (n-Bu)$_4$NPF$_6$ supporting electrolyte at 100 mV/s.
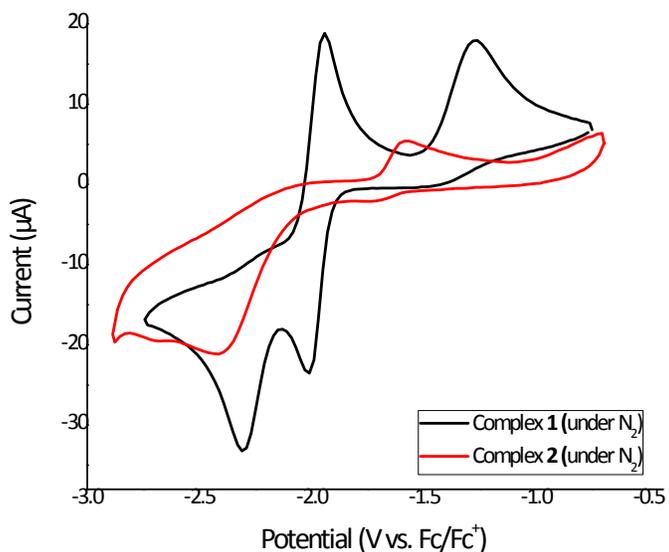
Figure S9. Cyclic voltammagrams of 1^+Br^-(1.0 mM) and 2 (1.0 mM) under N_2 in CH_3CN with 0.1M tetrabutylammoniumhexafluorophosphate (TBAHFP) supporting electrolyte at 100 mV/s.
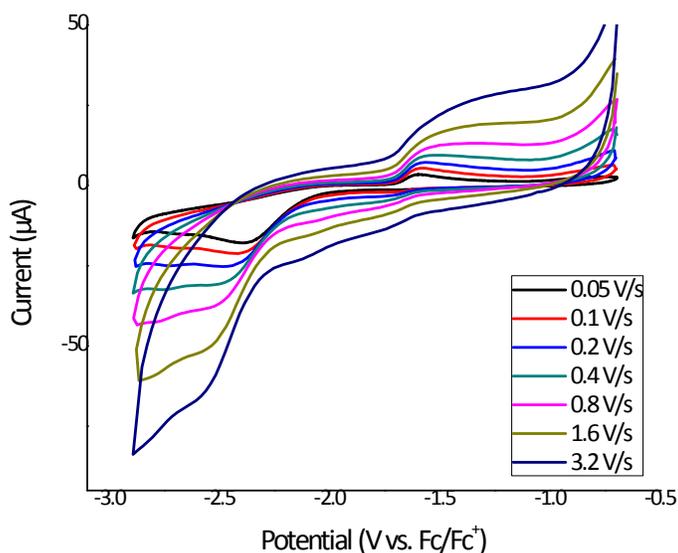
FigureS10. Cyclic voltammagramsof 2 (1.0 mM) under N_2 in CH_3CN with 0.1M tetrabutylammoniumhexafluorophosphate (TBAHFP) supporting electrolyte with different scan rates.
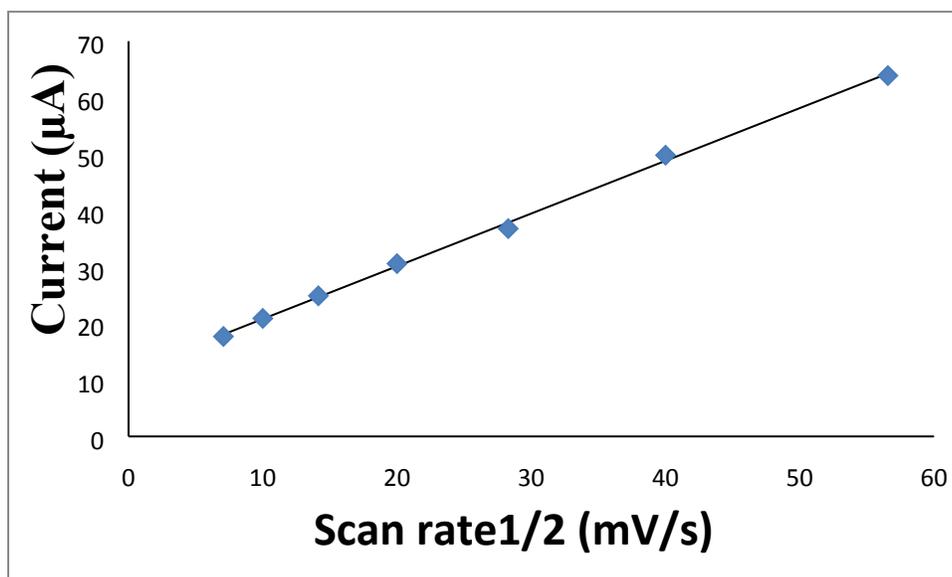
Figure S11. For compound 2, plot of scan rate$^{1/2}$ versus current at first reduction peak at -2.37 V.

Table S3: Bulk electrolysis experiments for **2**(1.0 mM) in acetonitrile with 5% added H_2O.

μmol of CO + H_2 (Calculated)	μmol of CO (Obtained)	μmol of H_2 (Obtained)
6.57	6	0
11.69	10	0
16.17	11	4
19.96	13	7
28.63	16	12
42.3	26	16
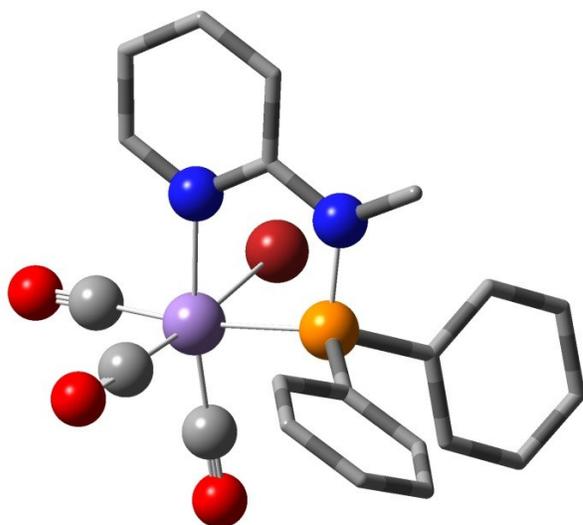
Figure S12. Structural representation for computationally optimized compound 2. DFT calculations used the B3LYP functional and the mixed TZVP/DZVP basis set. Hydrogen atoms are not shown for clarity. Some carbon atoms have been removed for clarity.
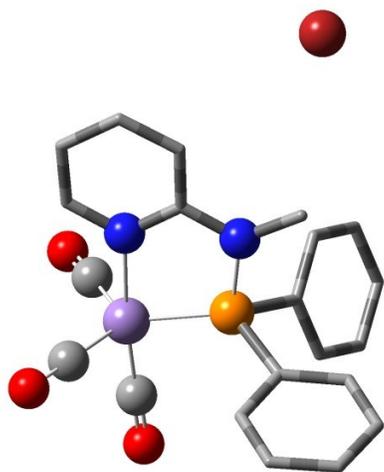
Figure S13. Structural representation for computationally optimized compound 2^{2-} showing the dissociation of the bromide anion. DFT calculations used the B3LYP functional and the mixed TZVP/DZVP basis set. Hydrogen atoms are not shown for clarity. Some carbon atoms have been removed for clarity.

References

1   APEX Softward Suite v 2010; Bruker AXS: Madison WI.

2   B. Y. R. H. Blessing, *Acta Crystallogr. Sect. A*, 1995, 33–38.

3   G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, 112–122.