Electronic Supplementary Information for

Metalloradical intermediates in electrocatalytic reduction of CO_2 to CO: Mn versus Re bis-N-heterocyclic carbene pincers

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1. General Methods

Reagents were used as purchased from commercial sources unless otherwise noted. Solvents for use in synthesis were distilled and degassed using the freeze-pump-thaw method before storing over molecular sieves. Likewise, solvents for electrochemical experiments were distilled and degassed before use. For electrochemical experiments, tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized from ethanol and dried thoroughly under high vacuum before use as supporting electrolyte. The ligand 1,1'-(2,6-pyridinediyl)bis(3-benzylimidazolium) dibromide ($CNC^{Bn}Br_2$) was synthesized as previously reported.[1] Metal complex **1** was stored in air-free conditions inside of a nitrogen glovebox. All ^1H and ^{13}C NMR spectra were collected using a Bruker Avance-III 300 MHz NMR Spectrometer. Diffusion ordered spectroscopy (DOSY) data was collected on a Varian INOVA 500 MHz NMR Spectrometer at 22°C. Residual internal proton or carbon solvent was used for chemical shift reference. Robertson Microlit Inc. performed elemental analyses.

All spectra were acquired on an Agilent INOVA 500 spectrometer with VNMRJ 3.2 software operating at 499.599 MHz equipped with a 5 mm triple resonance HCN Agilent probe at 295 K on ~500 μL samples at 22°C. A 5/3 mm Precision NMR sample glass tube from Wilmad was used to avoid convection. The following are the parameters for the 1HNMR data acquisition: acquisition time 3.0 s, spectral width 8 KHz, pulse width 6.12 S3 μs, relaxation delay 2.0 s, and no. of scans 16.

For the 2D DOSY NMR experiment, a gradient compensated stimulated DOSY (DgcsteSL_cc) pulse sequence was used. The duration of the magnetic field pulse gradients (δ) was optimized for each diffusion time (t) in order to obtain 5-10% residual signal with maximum gradient strength. A pulse field gradient length (gt1) of 1.7 ms and a diffusion delay (δ) of 35 ms were used (along with a 35s relaxation delay and 16 scans), and a series of 30 spectra on 32 K data points were collected with pulse gradients (g) increasing from 8.8 to 56 G cm^{-1} in a linear ramp.

All data were processed using Mnova software using the "peak heights" fit. After a two-dimensional Fourier transformation in magnitude mode, the DOSY dimension was reconstructed on a logarithmic scale using a mono-exponential fit to all resonances, and the peaks were reconstructed in the diffusion constant dimension on a grid of 128 data points. DOSY spectra are presented with chemical shifts (expressed in ppm) on the horizontal axis and diffusion coefficients on the vertical axis (expressed in cm^2 /s).

2. Synthesis of compound ReCNC^{Bn} (I^{Re})

The synthetic procedure including work-up was performed in a nitrogen atmosphere glovebox. A borosilicate glass vial with a stir bar was used for the reaction of 0.1211 g (0.218 mmol) CNC^{Bn}Br$_2$, 0.1438 g (0.391 mmol) $Re(CO)_5Cl$, and 0.2056 g (0.631 mmol) cesium carbonate in 5 mL acetonitrile. After sealing, the reaction was stirred and heated in an aluminum heating block at 60°C for 16 hr. The initially yellow solution became red and was cooled to room temperature before filtration to remove the remaining cesium salts. After stripping to remove solvent, the solid was taken up in a minimal amount of dichloromethane/methanol 94:6 v:v and pushed through a neutral alumina plug. 0.0923 g

(64% yield) of red product was recovered. ^{1}H NMR (300 MHz, Acetonitrile-d_3) δ 8.21 (t, J = 8.2 Hz, 1H), 8.07 (d, J = 2.3 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 2.2 Hz, 2H), 7.41 – 7.33 (m, 10H), 5.43 (s, 4H). ^{13}C NMR (75 MHz, CD_3CN) δ 183.40, 183.13, 153.24, 144.35, 136.03, 128.92, 128.24, 127.31, 124.43, 119.32, 107.13, 55.41, 1.15. HR-MS (CH_3CN): 662.1200 m/z and 634.1254 m/z; calculated value for $(C_{28}H_{21}N_5O_3Re)^{+1}$ $[ReCNC^{Bn}]^{+1}$ 662.1203 and for $(C_{27}H_{21}N_5O_2Re)^{+1}$ 634.1248. Infrared data (cm^{-1}): ν(CO) 2050, 1956, 1895 cm^{-1}. C, H, N analysis found: C: 41.56, H: 2.91, N: 8.08. C, H, N calculated for 1^{Re}+$2CH_2Cl_2$ C 41.43, H: 2.6, N: 8.46.

3. Electrochemical Experiments

A standard three electrode setup with a glassy carbon working electrode (3mm, Bioanalytical Systems), a platinum wire counter electrode, and a silver wire single junction pseudo-reference were used for Cyclic Voltammograms (CVs) and Normal Pulse Voltammograms (NPV). Pseudo-references were compared against ferrocene as an external standard. All experiments were performed under rigorously air-free conditions following an argon purge. In the case of NPVs, concentrations were adjusted for evaporated solvent in order to calculate the number of electrons accurately. All data workup was done via OriginPro vb9.4.0.220 software.

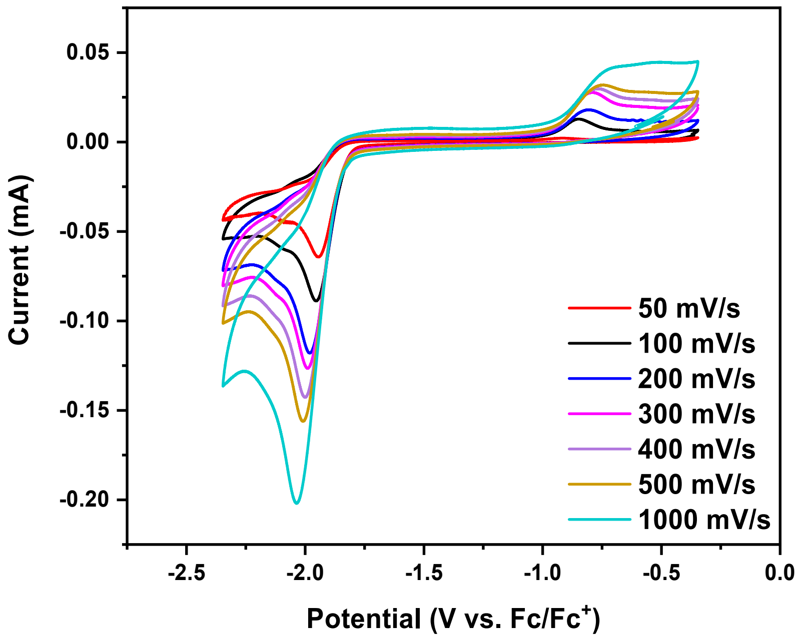

Figure S3.1. 4 mM **I^{Re} (ReCNC^{Bn})** solution using 0.1 M TBAH in acetonitrile. Scan rate dependence overlay of reductive CVs at 50 mV/s (red), 100 mV/s (black), 200 mV/s (blue), 300 mV/s (pink), 400 mV/s (violet), 500 mV/s (tan), and 1000 mV/s (light blue).

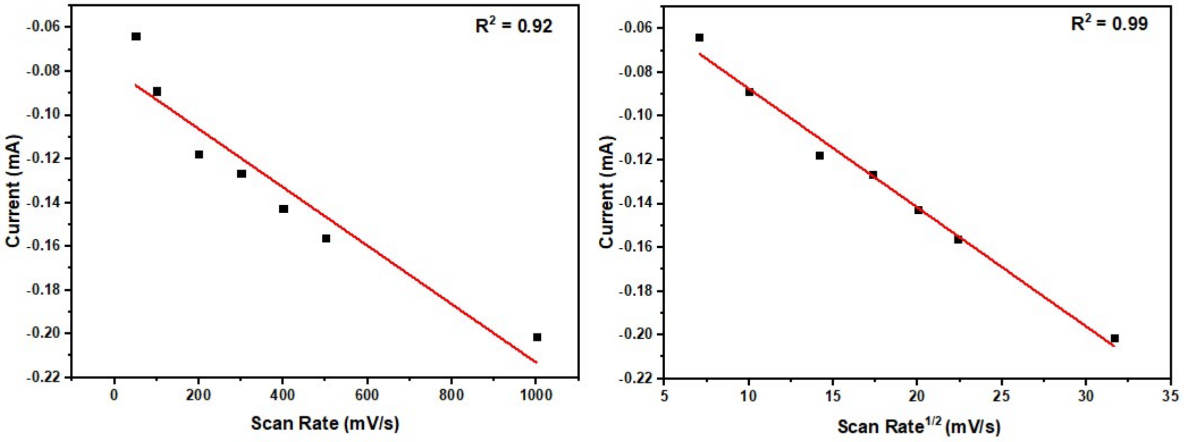

Figure S3.2. 4 mM **I^{Re} (ReCNC^{Bn})** solution using 0.1 M TBAH in acetonitrile. Plots of peak current of the reductive peak vs. scan rate and vs. scan rate$^{1/2}$ for scan rates 50, 100, 200, 300, 400, 500, and 1000 mV/s indicating diffusional behavior.

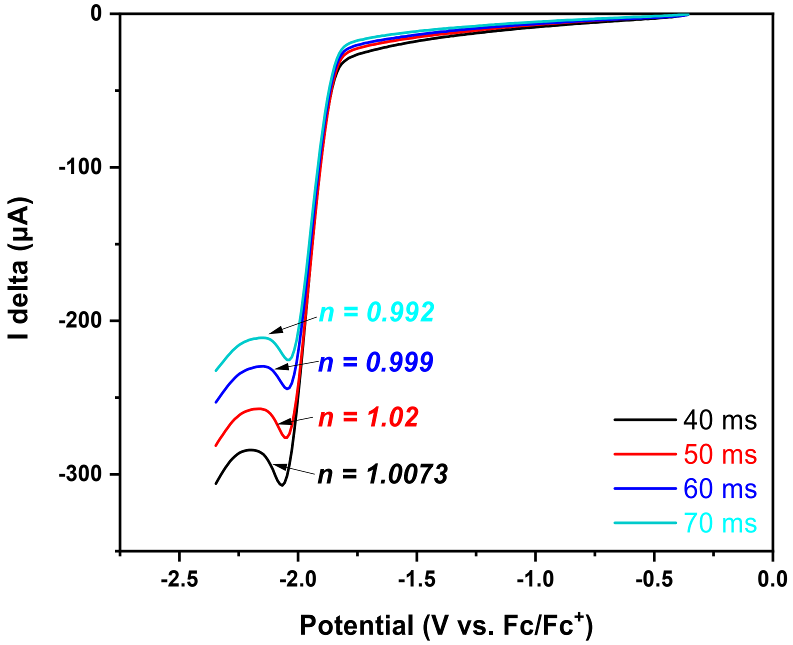

Figure S3.3. Normal pulse voltammograms of a 4mM solution of $\mathbf{I^{Re}}$ **(ReCNC$^{\mathbf{Bn}}$)** with 0.1 M TBAH in acetonitrile at 40 ms (black), 50 ms (red), 60 ms (blue), and 70 ms (light blue). Parameters for the calculation of n shown in Table S1 below.

Plateau currents from Normal Pulse Voltammetry were used to determine the number of electrons exchanged in the CV wave observed using the following equation:

$$i_l = \frac{nFACD^{1/2}}{\sqrt{\pi t_m}}$$

Where i_l is is the plateau current of the Normal Pulse Voltammetry, F is Faraday's constant, C is the concentration of the sample, D is the diffusion coefficient of the analyte, as measured by DOSY NMR, τ_m is the time constant of the experiment. This method was reported by Donadt and coworkers.[2]

	Compound 1	**Compound 1**	**Compound 1**	**Compound 1**
I (microamps)	283.9	257.08	229.87	211.27
F (C/mol)	96485	96485	96485	96485
A (cm^2)	0.070686	0.070686	0.070686	0.070686
D (cm^2/s)	0.0000129	0.0000129	0.0000129	0.0000129
$D^{1/2}$	0.003592	0.003592	0.003592	0.003592
C (mM)	4.078917	4.078917	4.078917	4.078917
pi	3.14159	3.14159	3.14159	3.14159
$pi^{1/2}$	1.77245	1.77245	1.77245	1.77245
t (s)	0.04	0.05	0.06	0.07
$t^{1/2}$	0.20000	0.22361	0.24495	0.26458
N	**1.0073**	**1.02**	**0.999**	**0.992**

Table S1. Data calculations used in the combined normal pulse voltammetry and diffusion-ordered spectroscopy method to determine number of electrons for the reductive wave of **I^{Re} (ReCNC^{Bn})**. Data shown in Figure S4.

4. Chemical Reduction Experiments

A J- Joung NMR tube was charged with 15 mg **1^{Mn}** and 6 mg Bis(pentamethylcyclopentadienyl)cobalt(II), (0.8 equivalents) in a glovebox, sealed and heated at 50°C for 1h in an oil bath. The DOSY NMR spectrum collected from this sample is shown below.

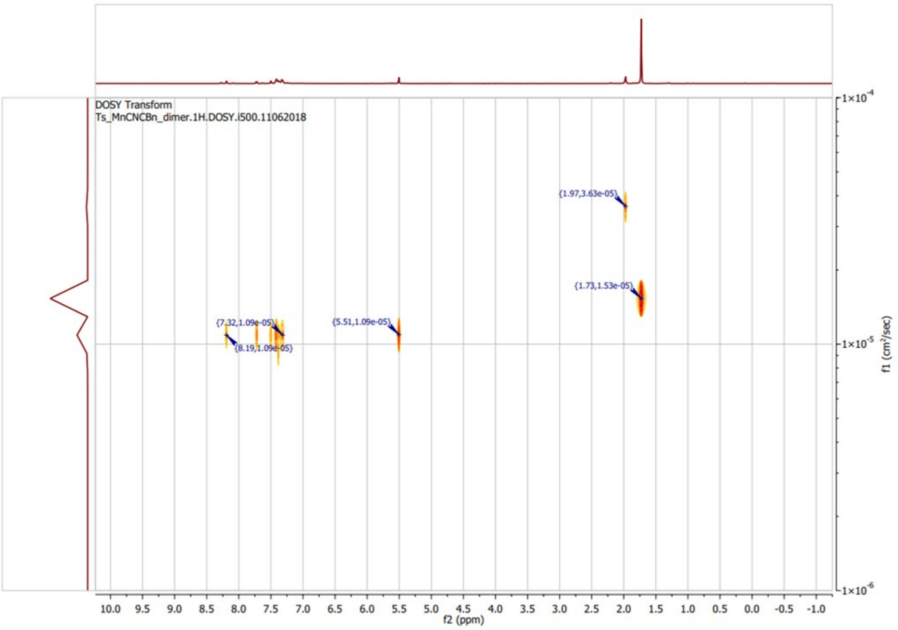

Figure S4.1. DOSY NMR collected from a chemical reduction experiment of $\mathbf{1}^{\mathbf{Bn}}$ with Bis(pentamethylcyclopentadienyl)cobalt(II) in search of a dimeric species.

5. Computational

Computational Methods

Density functional theory calculations were performed based on the MN15 density functional[3] implemented in Gaussian 16.[4, 5] A split basis-set was used to describe Mn and Re atoms with Stuttgart/Dresden SDD basis set/pseudopotentials[6] and all other atoms with the double-zeta 6-31+G(d,p) basis set.[7] Vibrational force constants at this level of theory were calculated to (a) validate that all geometries have only positive vibrational frequencies and (b) compute entropies, zero-point energies, and thermal corrections for the reported free energies at 298 K. Solvation effects of acetonitrile were simulated using an implicit polarized continuum solvation model (CPCM).[8] [9] All charge and spin densities were projected using natural-bond orbitals (NBO).[10]

Reduction Potential Calculations

Reduction potentials E^0 versus the ferrocene electrode (vs. Fc/Fc$^+$) in acetonitrile were calculated using the aforementioned levels of theory according to the following equation:[11]

$$\Delta G_{red} = G_{RH} - G_{RH^+} \qquad (1)$$

$$E^0 = -27.2114\,\Delta G_{red} - 4.988\,V \qquad (2)$$

The computed values were checked against experimental results and found to agree within 0.2 V.

Table S2. Computed Reduction Potentials.

$Reduction\ Step$	$Reduction\ Potential$
$I^{Mn}\rightarrow II^{Mn}$	$-2.23\ V\ vs\ Fc/Fc^+$
$I^{Re}\rightarrow II^{Re}$	$-2.07\ V\ vs\ Fc/Fc^+$

Geometries of $\mathbf{I^{Mn}}$ and $\mathbf{I^{Re}}$

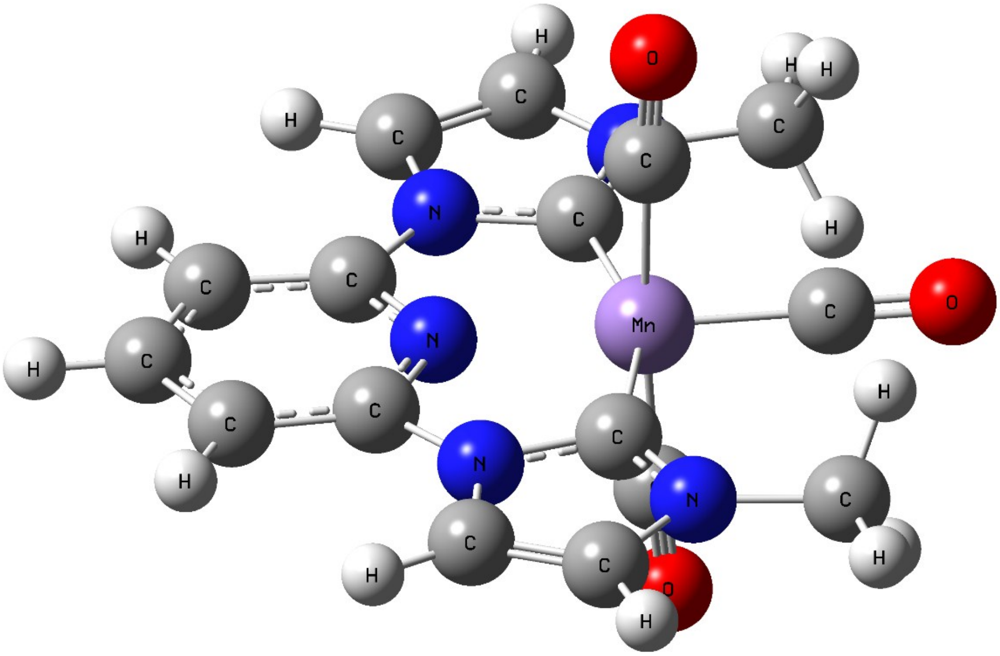

Figure S5.1. Ground state geometry of $\mathbf{I^{Mn}}$. The Mn—N distance is 2.02 Angstroms.

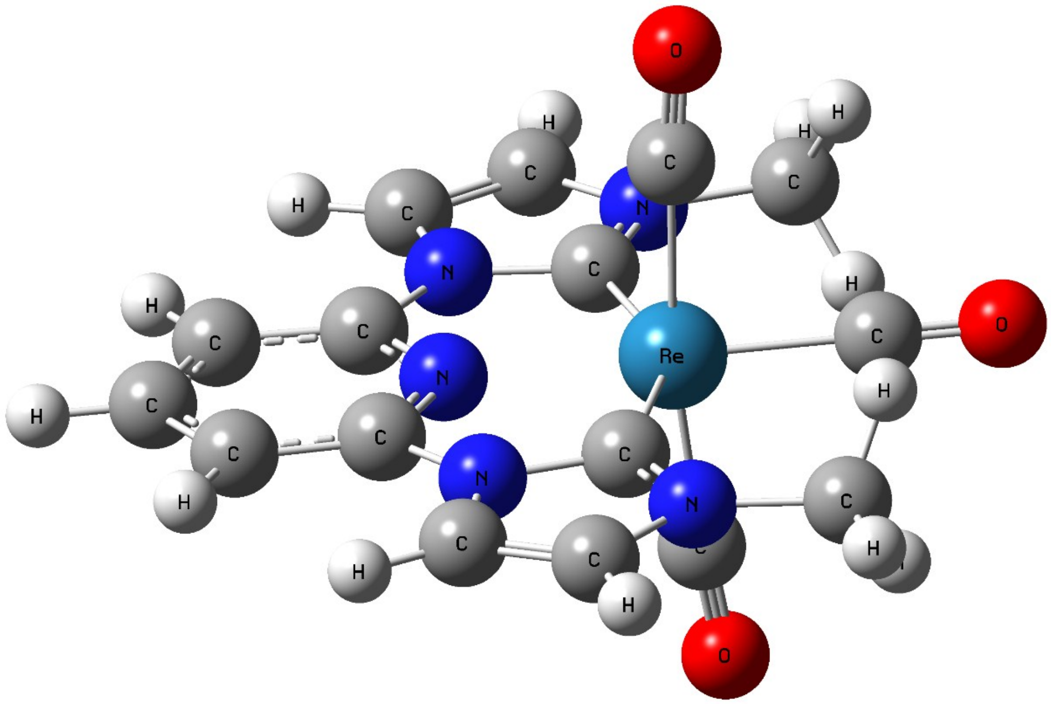

Figure S5.2. Ground state geometry of $\mathbf{I}^{\mathbf{Re}}$. The Re—N distance is 2.16 Angstroms

Spin Density Images

The spin population densities of $\mathbf{II}^{\mathbf{Mn}}$, $\mathbf{II}^{\mathbf{Re}}$, $\mathbf{III}^{\mathbf{Mn}}$, and $\mathbf{III}^{\mathbf{Re}}$ are shown below.

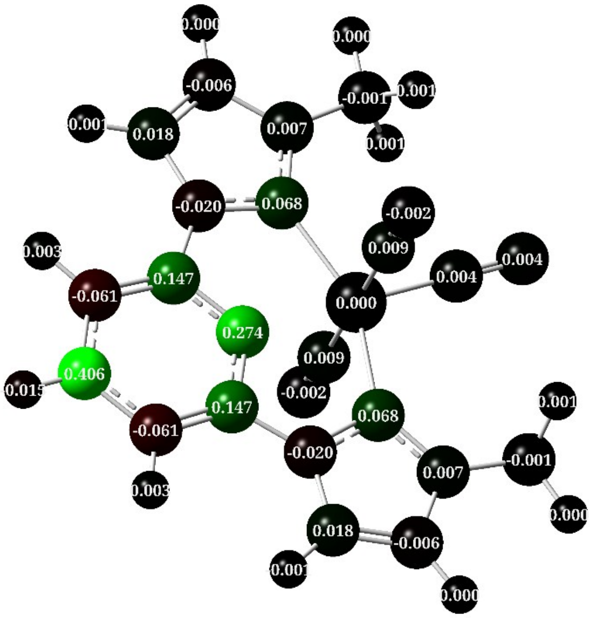

Figure S5.3. Spin population density of $\mathbf{II}^{\mathbf{Mn}}$.

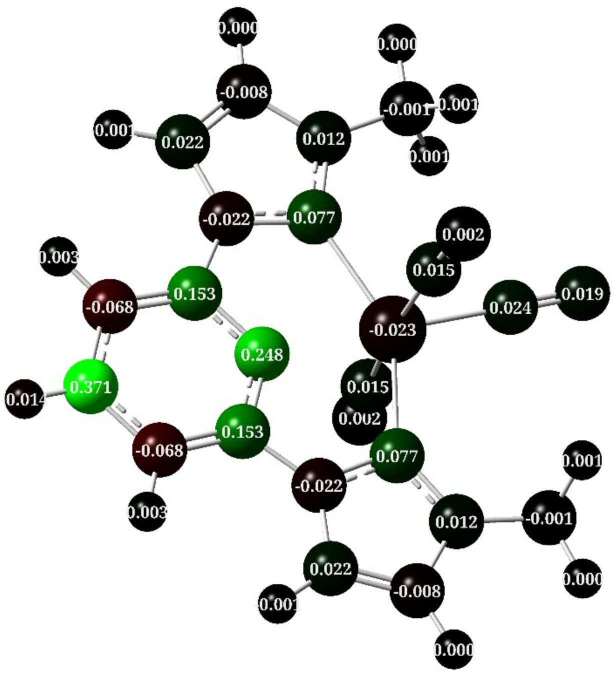

Figure S5.4. Spin population density of **II^{Re}**.

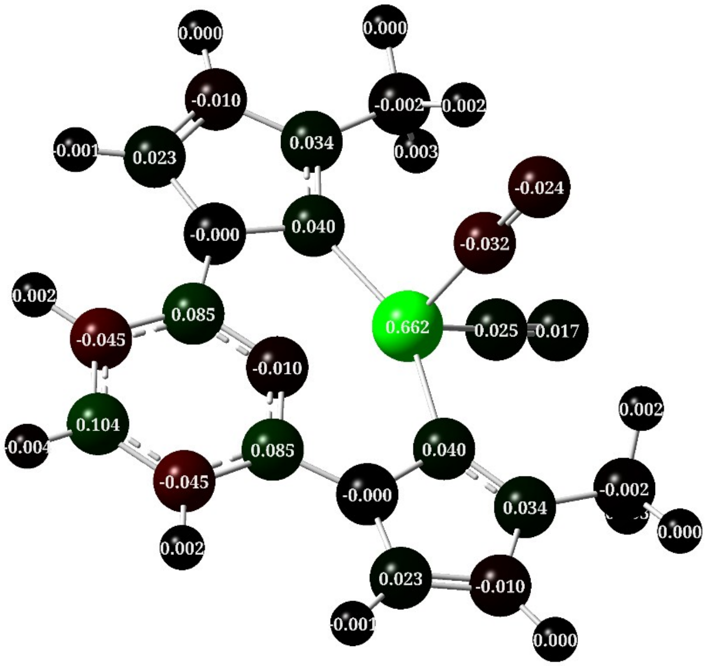

Figure S5.5. Spin population density of **III^{Mn}**.

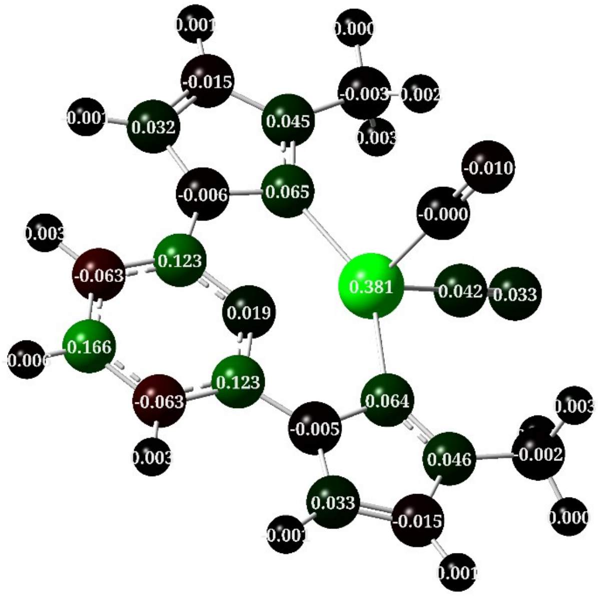

Figure S5.6. Spin population density of **III$^{\mathbf{Re}}$**.

CO Release Calculations:

Table S3. Computed CO release free energy of reactions of Mn and Re complexes.

$Reaction$	ΔG_{rxn}
$MnCNC(CO)_3 \rightarrow MnCNC(CO)_2 + CO$	$-2.4\ kcal/mol$
$MnCNC(CO)_3 \rightarrow MnCNC(CO) + 2CO$	$+5.4\ kcal/mol$
$ReCNC(CO)_3 \rightarrow ReCNC(CO)_2 + CO$	$+2.7\ kcal/mol$
$ReCNC(CO)_3 \rightarrow ReCNC(CO) + 2CO$	$+50.9\ kcal/mol$

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