Electronic Supplementary Material (ESI) for Dalton Transactions.

Electrocatalytic Reduction of Carbon Dioxide with Mn(terpyridine) Carbonyl Complexes

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Supporting Information

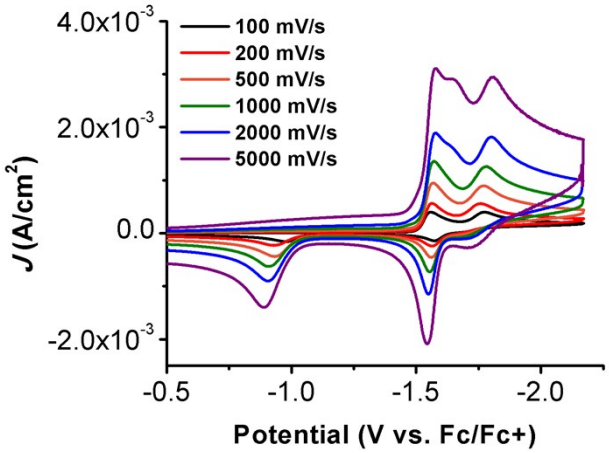

Figure S1. CVs showing the variable-scan rate current response of Mn(κ^2-tpy)$(CO)_3$Br (**1**) at negative potentials. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

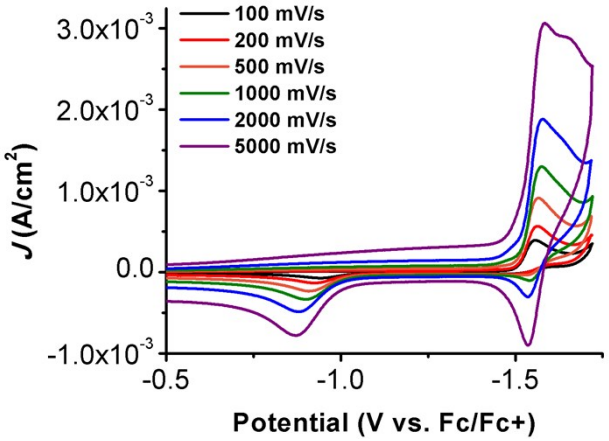

Figure S2. CVs showing the variable-scan rate current response of Mn(κ^2-tpy)$(CO)_3$Br (**1**) at negative potentials. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

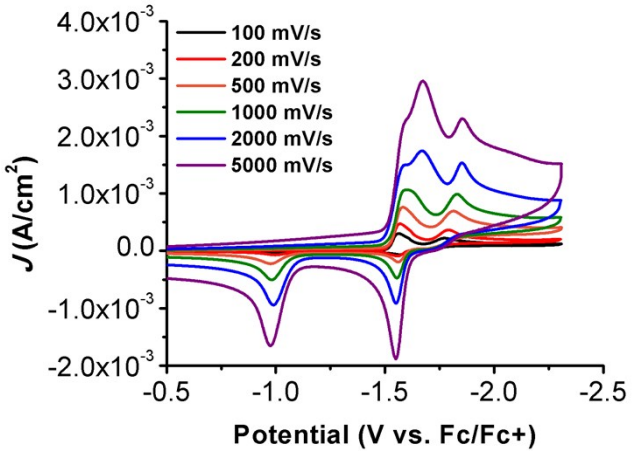

Figure S3. CVs showing the variable-scan rate current response of Mn(κ^3-tpy)$(CO)_2$Br (**2**) at negative potentials. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

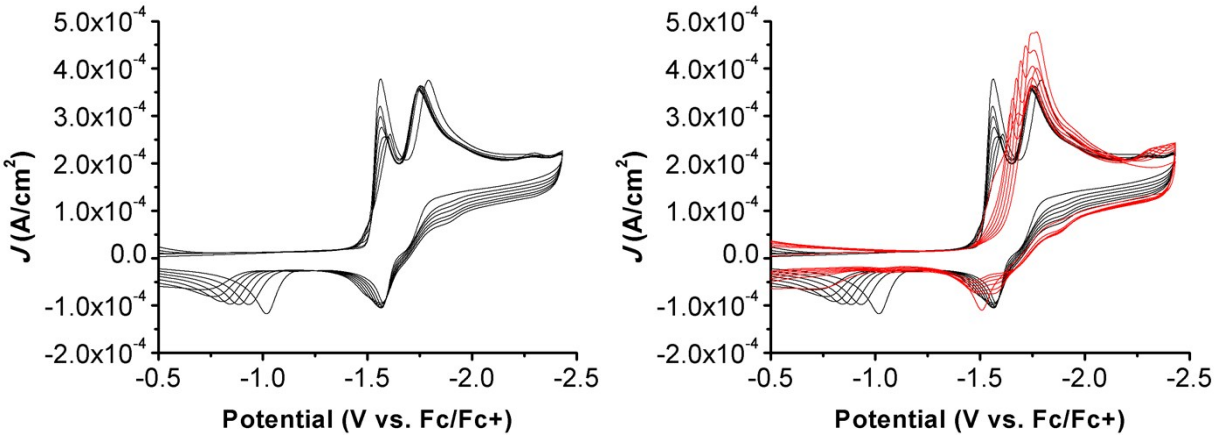

Figure S4. CVs showing the current response for 14 consecutive scans to negative potentials with Mn(κ^3-tpy)$(CO)_2$Br (**2**); (L) scans 1-7, (R) all scans, scans 7-14 in red. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

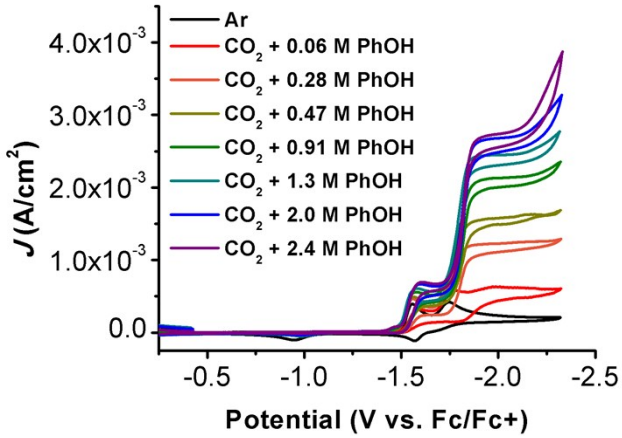

Figure S5. CVs showing the current response of Mn(κ^2-tpy)(CO)$_3$Br (**1**) at negative potentials under Ar and CO_2 atmospheres with added PhOH. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

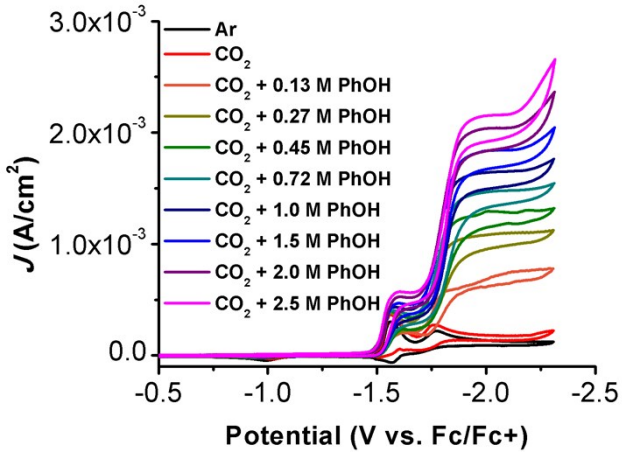

Figure S6. CVs showing the current response of Mn(κ^3-tpy)(CO)$_2$Br (**2**) at negative potentials under Ar and CO_2 atmospheres with added PhOH. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

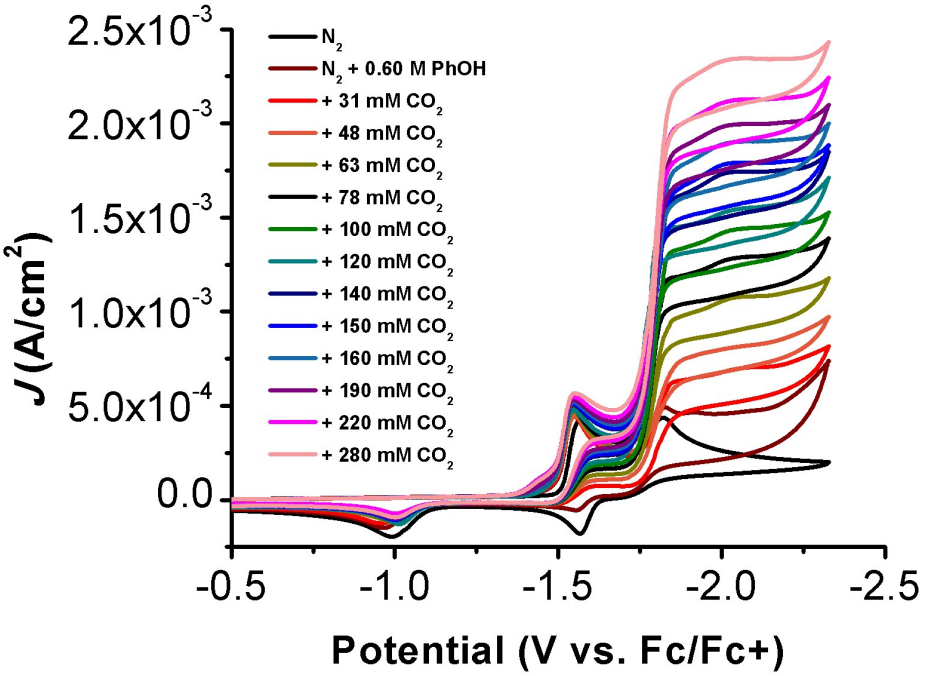

Figure S7. CVs showing the current response of Mn(κ^2-tpy)$(CO)_3$Br (**1**) at negative potentials with added PhOH (0.60 M) and variable CO_2 concentration. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

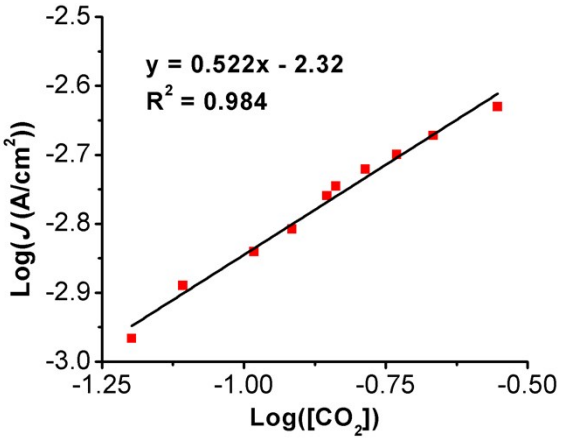

Figure S8. Log-Log plot of peak current response versus CO_2 concentration for Mn(κ^2-tpy)$(CO)_3$Br (**1**); a slope of ~0.5 is consistent with first order kinetics in CO_2.

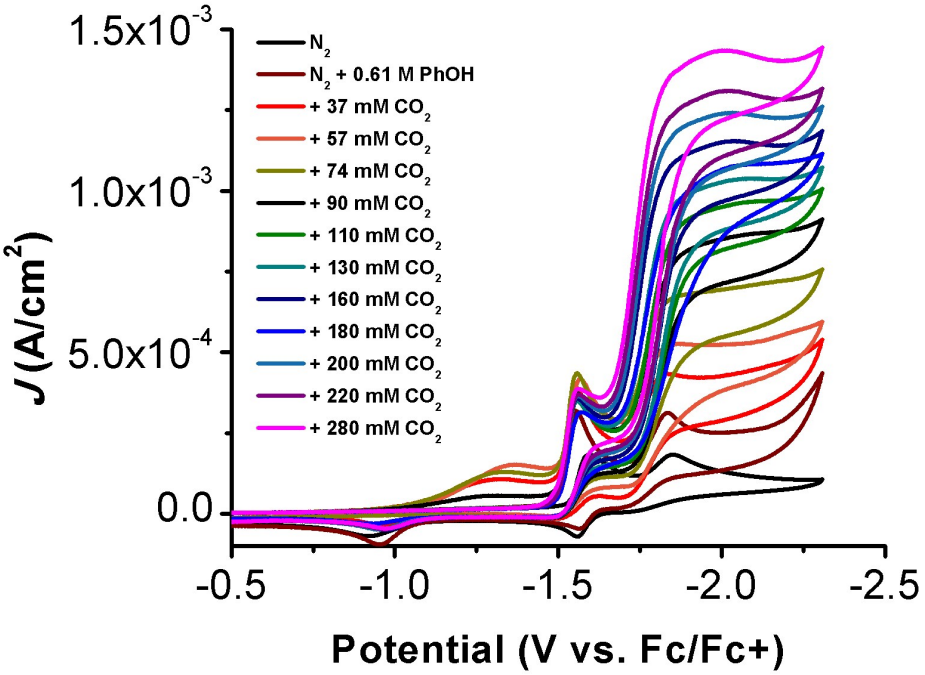

Figure S9. CVs showing the current response of Mn(κ^3-tpy)(CO)$_3$Br (**2**) at negative potentials with added PhOH (0.61 M) and variable CO_2 concentration. Conditions: 1 mM analyte in 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudo-reference electrode behind CoralPor; referenced to internal Fc standard.

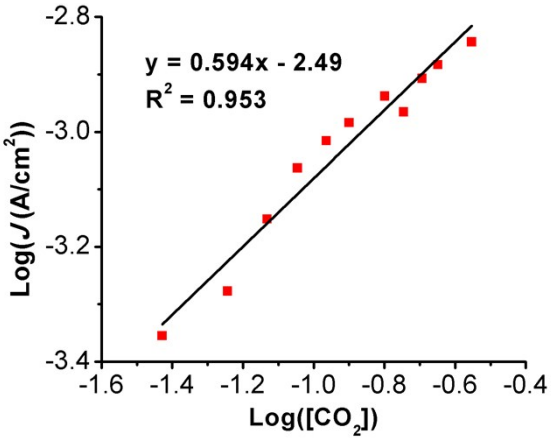

Figure S10. Log-Log plot of peak current response versus CO_2 concentration for Mn(κ^3-tpy)(CO)$_2$Br (**1**); a slope of ~0.5 is consistent with first order kinetics in CO_2.

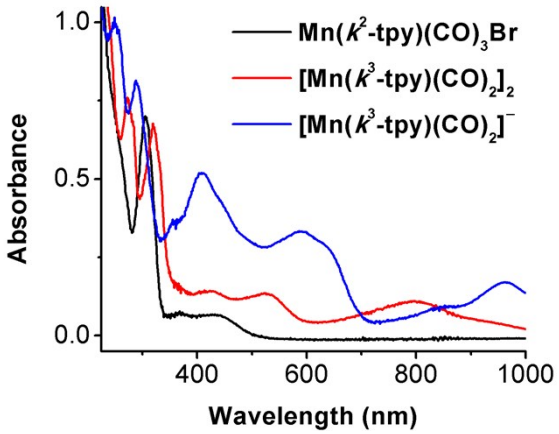

Figure S11. UV-vis absorbance data obtained from the chemical reduction of Mn(κ^2-tpy)(CO)$_3$Br (**1**) with KC_8 in THF solution; total equiv of added KC_8: 0 (black), 1.1 (red), 2.5 (blue, K^+ counterion). Conditions: 0.3 mM **1** starting; Specac CaF_2 liquid transmission cell with 0.1 mm spacer.

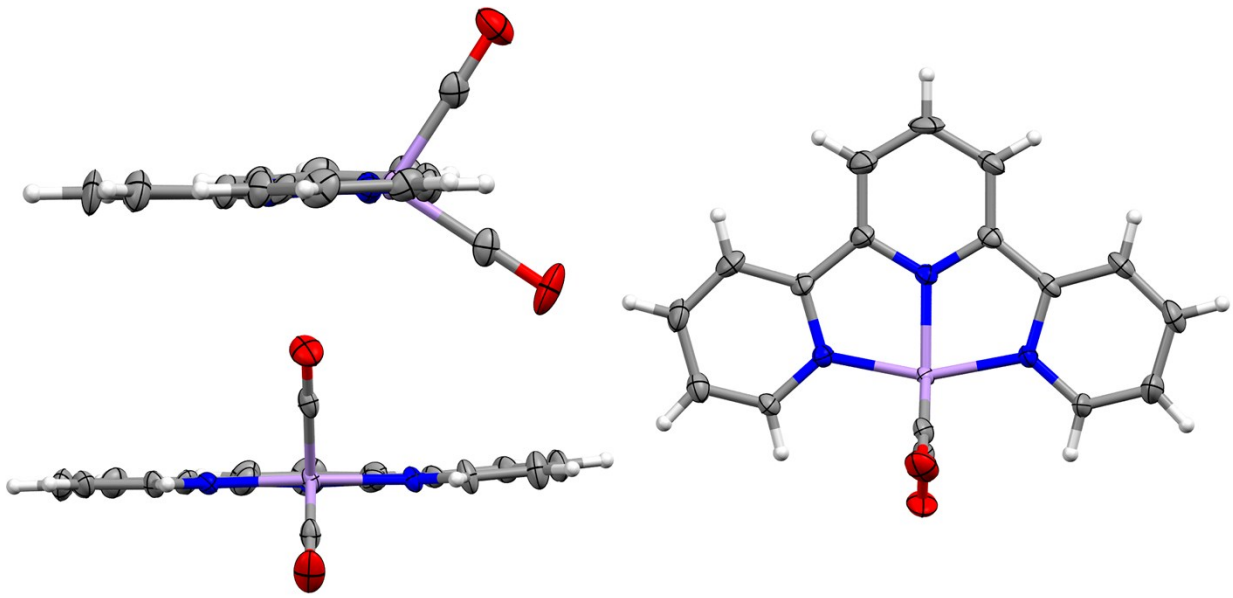

Figure S12. Alternate views of the single crystal X-ray crystallographically derived molecular structure of [Mn(κ^3-tpy)(CO)$_2$]$^-$. Thermal ellipsoids at 50%; occluded THF molecule and 0.5 occupancy (18-crown-6)K(THF)$_2$ complex (Z = 2) omitted for clarity. C = gray, H = white, N = blue, O = red, Mn = lilac.

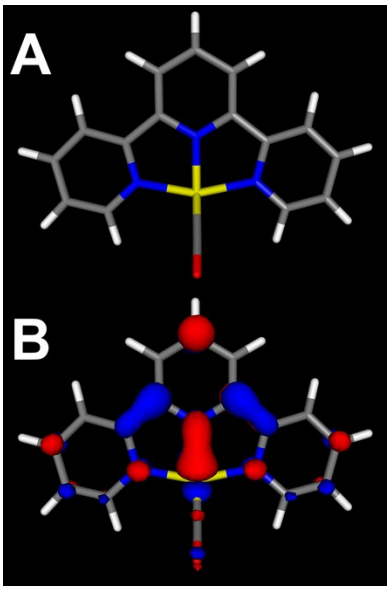

Figure 13. Molecular structure of $[Mn(\kappa^3\text{-tpy})(CO)_2]^-$ (**A**) and Kohn-Sham representation of the corresponding HOMO (**B**) obtained from DFT calculations using with B3LYP/G functionals, def2-TZVP basis sets, dispersion corrections, and COSMO, geometry was verified as a minimum through frequency calculations as implemented in ORCA 3.0.3. C = gray, H = white, N = blue, O = red, Mn = yellow.

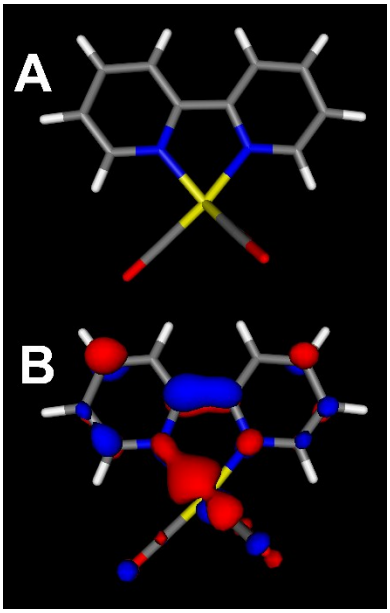

Figure 14. Molecular structure of $[Mn(bpy)(CO)_3]^-$ (**A**) and Kohn-Sham representation of the corresponding HOMO (**B**) obtained from DFT calculations using with B3LYP/G functionals, def2-TZVP basis sets, dispersion corrections, and COSMO, geometry was verified as a minimum through frequency calculations as implemented in ORCA 3.0.3. C = gray, H = white, N = blue, O = red, Mn = yellow.

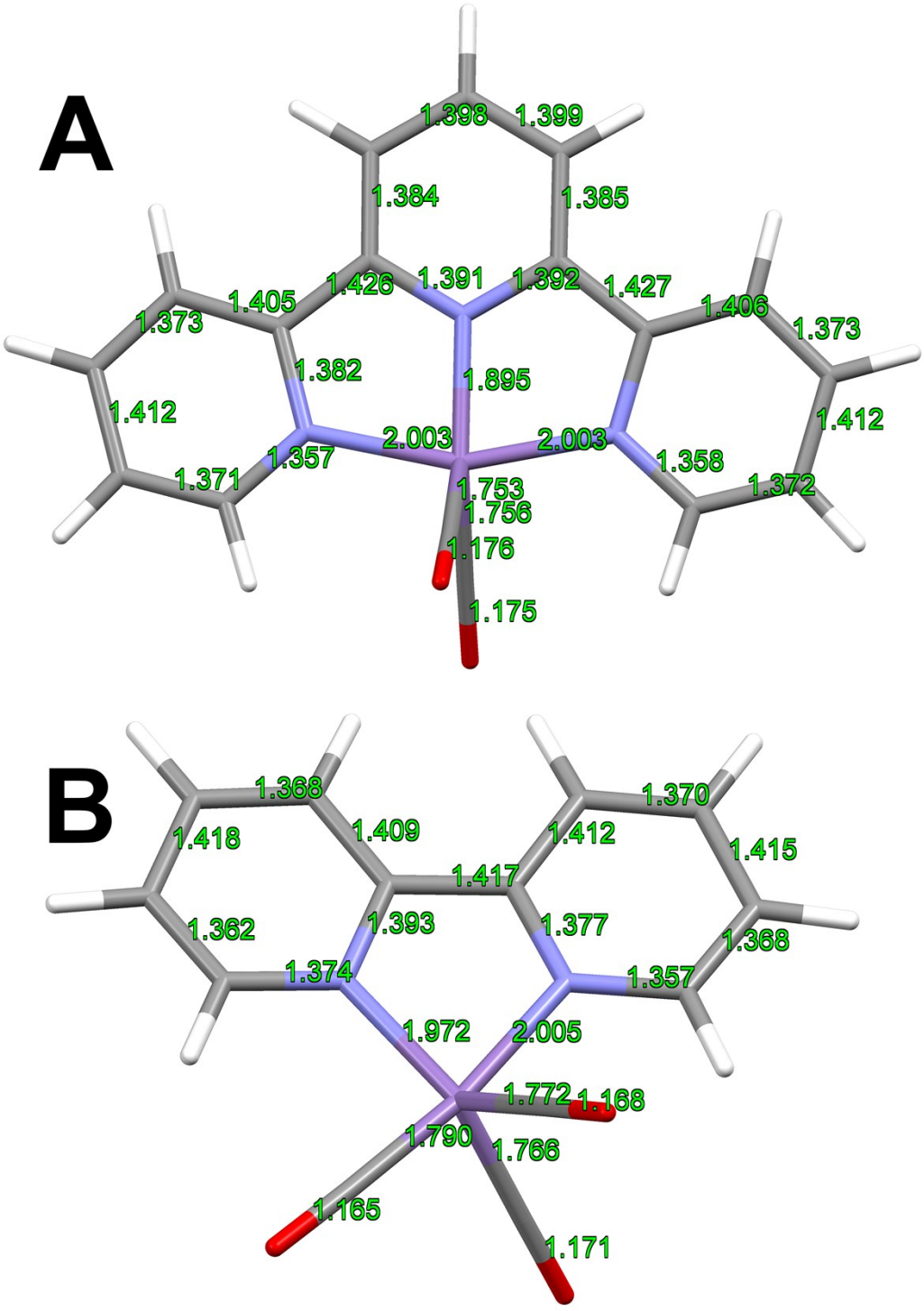

Figure 15. Molecular structures with bond distances of $[Mn(\kappa^3\text{-tpy})(CO)_2]^-$ (**A**) and $[Mn(bpy)(CO)_3]^-$ (**B**) obtained from DFT calculations using with B3LYP/G functionals, def2-TZVP basis sets, dispersion corrections, and COSMO, geometry was verified as a minimum through frequency calculations as implemented in ORCA 3.0.3. C = gray, H = white, N = blue, O = red, Mn = lilac.

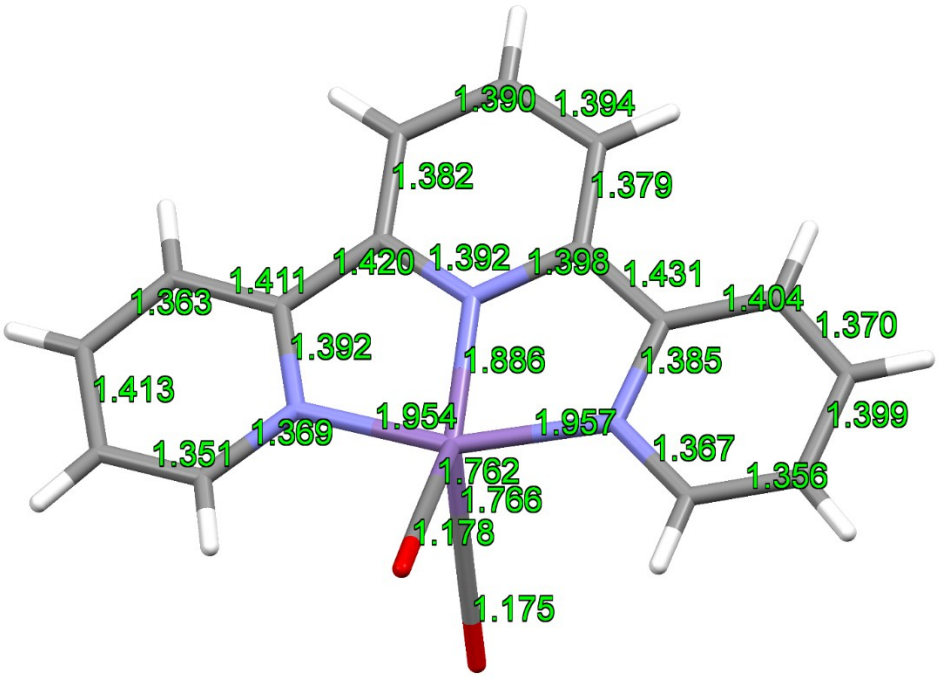

Figure 16. Molecular structure of $[Mn(\kappa^3\text{-tpy})(CO)_2]^-$ obtained from X-ray crystallographic data showing bond distances in Angstroms. C = gray, H = white, N = blue, O = red, Mn = lilac.

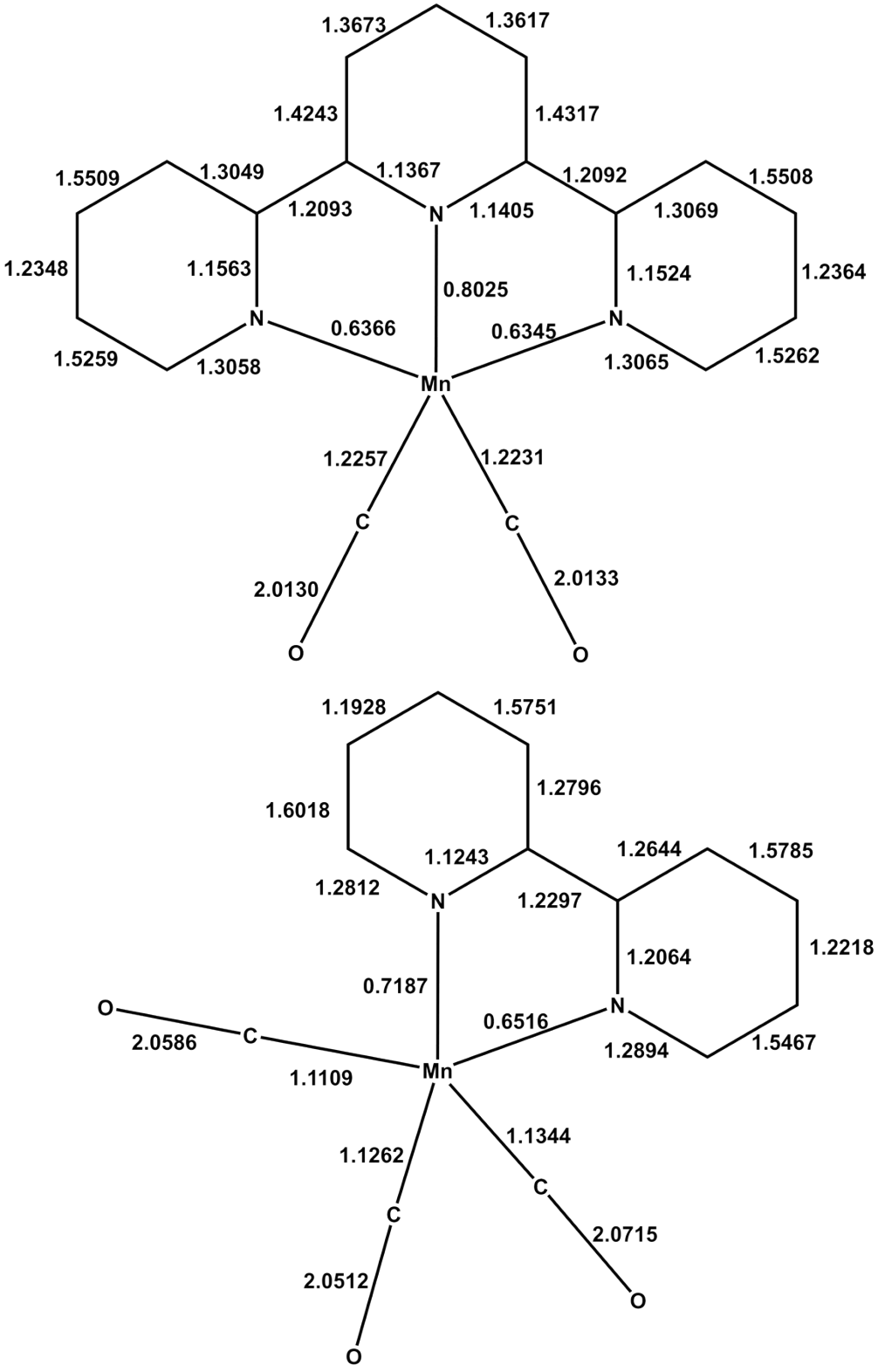

Figure 17. Molecular structures with Mayer bond orders showing connectivity only for [Mn(κ^3-tpy)$(CO)_2]^-$ (**top**) and $[Mn(bpy)(CO)_3]^-$ (**bottom**) obtained from DFT calculations using with B3LYP/G functionals, def2-TZVP basis sets, dispersion corrections, and COSMO, geometry was verified as a minimum through frequency calculations as implemented in ORCA 3.0.3.

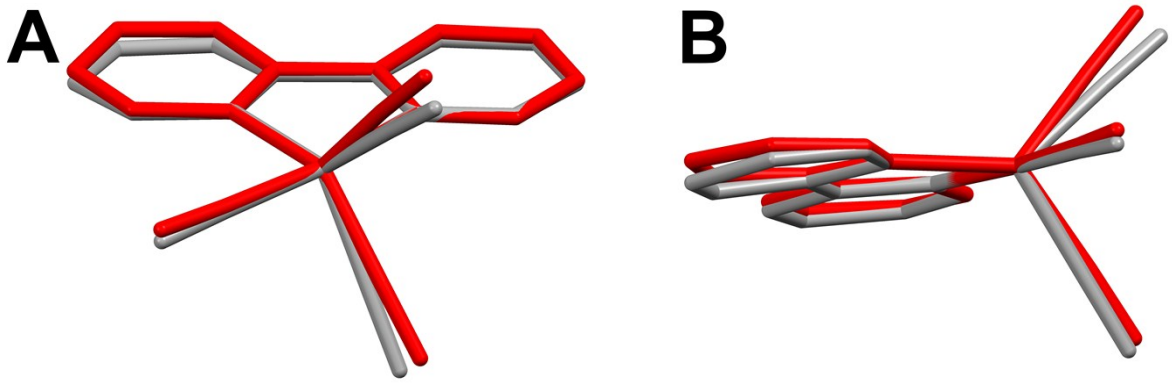

Figure 18. Overlay of the molecular structure obtained with theory for $[Mn(\kappa^3\text{-tpy})(CO)_2]^-$ (**red**) and experimental structural data from $[Mn(4,4\text{-ditertbutyl-}2,2\text{-bpy})(CO)_3]^-$ (gray, *Inorg. Chem.*, **2013**, *52*, 2484–2491) edited to remove tert-butyl groups. DFT calculations used B3LYP/G functionals, def2-TZVP basis sets, dispersion corrections, and COSMO, geometry was verified as a minimum through frequency calculations as implemented in ORCA 3.0.3.

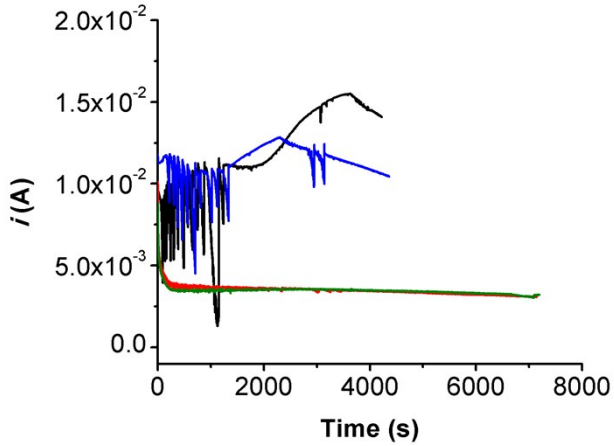

Figure S19. Data from the CPE experiments of $Mn(\kappa^2\text{-tpy})(CO)_3Br$ (**1**) and $Mn(\kappa^3\text{-tpy})(CO)_2Br$ (**2**) showing current over time. Plots overlaid showing data taken at –2.2 V vs Fc/Fc+ for **1** – black and **2** – blue as well as at –1.65 V vs Fc/Fc+ for **1** – red and **2** – green. For complete experimental details see **Table S1**.

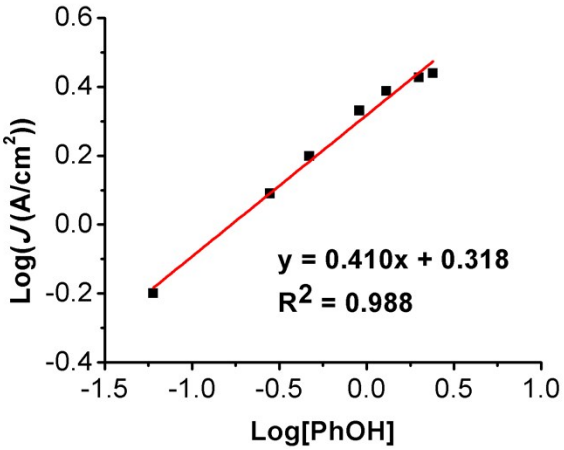

Figure S20. Log-Log plot of peak current response versus PhOH concentration for Mn(κ^2-tpy)(CO)$_3$Br (**1**); a slope of ~0.4 is consistent with first order kinetics in PhOH, suggesting a rate-limiting protonation step, likely C–O bond cleavage from hydroxycarbonyl protonation:

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

(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.

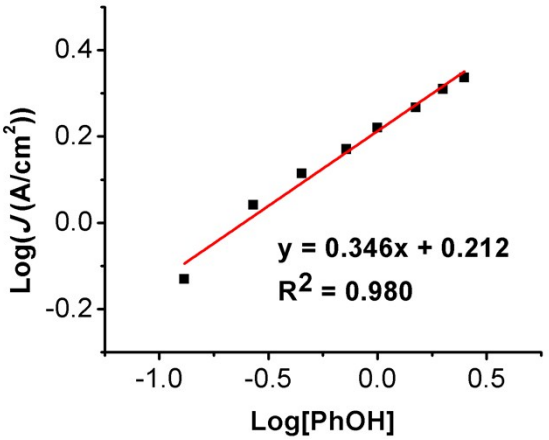

Figure S21. Log-Log plot of peak current response versus PhOH concentration for Mn(κ^3-tpy)(CO)$_2$Br (**2**); a slope of ~0.4 is consistent with first order kinetics in PhOH, suggesting a rate-limiting protonation step, likely C–O bond cleavage from hydroxycarbonyl protonation.

Table S1. Bulk electrolysis data from this study

Catalyst	[conc] (Vol)	Turnovers	mol CO	Efficiency CO	Efficiency H_2
1 –2.2 V*	1.0 mM (42 mL)	4.1 (32.9 C) 6.2 (50.0 C)	2.20E-04 2.74E-04	129% 106%	1% 2%
2 –2.2 V*	0.93 mM (44 mL)	4.1 (32.1 C) 6.2 (49.0 C)	1.54E-04 1.95E-04	93% 77%	6% 14%
1 –1.65 V*	0.90 mM (44 mL)	1.6 (12.5 C) 3.3 (25.0 C)	4.81E-05 9.69E-05	74% 75%	<1% <1%
2 –1.65 V*	0.96 mM (43 mL)	1.6 (13.0 C) 3.1 (25.0 C)	6.25E-05 1.09E-04	93% 84%	<1% <1%

*** - potential is in V vs. Fc/Fc+**

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 (Pt wire), working electrode (graphite rod; 2.2 cm long and 0.6 cm in diameter with only one end exposed), pseudoreference electrode (Ag/AgCl wire in 0.1 M $TBAPF_6$/MeCN behind a vycor tip), and a septum for sampling the headspace. Total cell volume was determined to be 70 mL; solution volumes and catalyst loadings for individual runs are shown in Table S1. 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 (HP 7890A with TCD) 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.

Table S2. Theoretical (Mode) and experimental (Exp.) IR data in MeCN for relevant complexes in cm^{-1}.

Compound	Mode 1	Mode 2	Mode 3	Mode 4	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
$Mn(\kappa^2\text{-tpy})(CO)_3Br$	2031	1893	1878		2025	1935	1921		
$Mn(\kappa^3\text{-tpy})(CO)_2Br$	1888	1823			1925	1853			
$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^+$	1917	1850			1949	1878			
$[Mn(\kappa^2\text{-tpy})(CO)_3Br]^-$	2002	1850	1837						
$[Mn(\kappa^3\text{-tpy})(CO)_2Br]^-$	1862	1775							
$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^0$	1882	1796							
$[Mn(\kappa^3\text{-tpy})(CO)_2]^0$	1937	1790							
$[Mn(\kappa^3\text{-tpy})(CO)_2]_2$*	1920	1908	1867	1862	1921 1911	1883 1882	1860 1860	1798 1836	n/a 1798
$[Mn(\kappa^3\text{-tpy})(CO)_2]^-$	1844	1754			1830	1765			
$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2)]^-$	1868	1809	1648						
$Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)$	1904	1842	1655						
$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)]^-$	1868	1779	1637						
$[Mn(\kappa^3\text{-tpy})(CO)_3]^+$	2061	1925	1912						
$[Mn(\kappa^3\text{-tpy})(CO)_3]^0$	2030	1874	1852						
$[Mn(\kappa^2\text{-tpy})(CO)_3]^0$	2003	1861	1849						
$[Mn(\kappa^2\text{-tpy})(CO)_3(MeCN)]^+$	2053	1927	1912						

* data obtained from IR-SEC of **1** above that obtained for **2**.

Table S3. Scaled theoretical (Mode) and experimental (Exp.) IR data for relevant complexes in cm^{-1}; 0.986, *J. Chem. Theory Comput.* **2010**, *6*, 2872–2887.

Compound	Mode 1	Mode 2	Mode 3	Mode 4	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
$Mn(\kappa^2\text{-tpy})(CO)_3Br$	2003	1866	1852		2025	1935	1921		
$Mn(\kappa^3\text{-tpy})(CO)_2Br$	1862	1797			1925	1853			
$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^+$	1890	1824			1949	1878			
$[Mn(\kappa^2\text{-tpy})(CO)_3Br]^-$	1974	1824	1811						
$[Mn(\kappa^3\text{-tpy})(CO)_2Br]^-$	1836	1750							
$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^0$	1856	1771							
$[Mn(\kappa^3\text{-tpy})(CO)_2]^0$	1910	1765							
$[Mn(\kappa^3\text{-tpy})(CO)_2]_2$*	1920	1908	1867	1862	1921 1911	1883 1882	1860 1860	1798 1836	n/a 1798
$[Mn(\kappa^3\text{-tpy})(CO)_2]^-$	1818	1729			1829	1765			
$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2)]^-$	1842	1784	1626						
$Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)$	1878	1816	1631						
$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)]^-$	1842	1754	1614						
$[Mn(\kappa^3\text{-tpy})(CO)_3]^+$	2032	1898	1873						
$[Mn(\kappa^3\text{-tpy})(CO)_3]^0$	2001	1847	1826						
$[Mn(\kappa^2\text{-tpy})(CO)_3]^0$	1975	1835	1823						
$[Mn(\kappa^2\text{-tpy})(CO)_3(MeCN)]^+$	2024	1900	1885						

* data obtained from IR-SEC of **1** above that obtained for **2**.

Table S4. Calculated Gibbs Free Enthalpies of relevant complexes.

Compound	Hartree
$Mn(\kappa^2\text{-tpy})(CO)_3Br$	-4805.526125
$Mn(\kappa^3\text{-tpy})(CO)_2Br$	-4692.136118
$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^+$	-2250.559583
$[Mn(\kappa^2\text{-tpy})(CO)_3Br]^-$	-4805.647586
$[Mn(\kappa^3\text{-tpy})(CO)_2Br]^-$	-4692.258053
$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^0$	-2250.687911
$[Mn(\kappa^3\text{-tpy})(CO)_2]^0$	-2117.893024
$[Mn(\kappa^3\text{-tpy})(CO)_2]_2$	-4235.736658
$[Mn(\kappa^3\text{-tpy})(CO)_2]^-$	-2118.035443
$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2]^-$	-2306.696607
$Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)$	-2307.16651
$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)]^-$	-2307.275919
$[Mn(\kappa^3\text{-tpy})(CO)_3]^+$	-2231.165125
$[Mn(\kappa^3\text{-tpy})(CO)_3]^0$	-2231.29673
$[Mn(\kappa^2\text{-tpy})(CO)_3]^0$	-2231.273278
$[Mn(\kappa^2\text{-tpy})(CO)_3(MeCN)]^+$	-2363.945347

Table S5. Theoretical (Mode) IR data in MeCN in cm^{-1} and Gibbs Free Enthalpies (Hartree) obtained for $[Mn(\kappa^3\text{-tpy})(CO)_2]^-$ and $[Mn(bpy)(CO)_3]^-$ with Orca 3.0.3 and used in Figures 7 and 8.

Compound	Mode 1	Mode 2	Mode 3	Hartree
$[Mn(\kappa^3\text{-tpy})(CO)_2]^-$	1853	1768		-2120.63677395
$[Mn(bpy)(CO)_3]^-$	1925	1833	1805	-1986.86419889

DFT Coordinates

$Mn(\kappa^2\text{-tpy})(CO)_3Br$ (**1**)

C	2.16165596835828	12.33771854093850	8.23199543058152
C	3.04843816350447	13.55389986820690	10.22116886335573
H	2.82521958407174	14.50532537385618	9.76425695459057
C	1.66508238982479	13.42797738615380	7.53109263664595
H	1.83598365283203	14.42769997370045	7.89922263125421
C	3.61196587132785	9.79045889176306	12.05986670555847
C	2.94444891164646	8.67876165268131	7.38605202758351
C	1.27976620773346	10.86276321986190	6.67080330094459
C	3.86233670281221	8.52860083108415	9.57653789640698
N	2.47976482781663	9.09827945164736	12.22189121698652
C	4.81779401150630	9.42563980847850	12.65101331064876
C	3.49794992334886	11.07289264370698	11.31988073449399
C	2.52749332672648	7.99517783342528	12.96741460240145
H	1.59433735242376	7.45799703609207	13.09076087183114
C	3.59435913248067	13.48114480662649	11.48512850786549
H	3.83159832072230	14.37590714480901	12.04232800706231
C	0.94279330566862	13.21311265713663	6.37288999505508
H	0.54121367773864	14.04517968632653	5.81292948356593
C	3.79718831178299	12.22512651740560	12.03304402184689
H	4.16745101629076	12.11912323505351	13.04158046566236
C	4.85580466955104	8.27016671406469	13.41839561002593
H	5.77969327585710	7.94747013001097	13.87997055479696
C	0.72704260001421	11.90234752827447	5.95726294337714
H	0.14410689977505	11.67877644902111	5.07617874133103
C	2.79117472725357	12.38311574495175	9.53000463732290
C	3.68858762232541	7.53831571378895	13.58185090302549
N	3.04923235977416	11.13704293503565	10.03557166488974
N	2.01854499916687	11.06519835563665	7.78452443630431
O	4.47295312272418	7.65686476629081	10.05773484310701
O	2.96225104151775	7.99268789953909	6.43947851578259
C	1.50586039101049	8.97356433292520	9.31682051932844
Br	5.02865037721747	10.65398944538745	7.87937581245758
Mn	2.92685884999417	9.69102006869805	8.75064459050021
O	0.51504331701376	8.44598593331938	9.65709962274776
H	3.66954595675491	6.63599489301727	14.17699567918112
H	5.70582953415363	10.02173278033772	12.49357842778361
H	1.14470859727889	9.84241175074661	6.35317583369672

$Mn(\kappa^3\text{-tpy})(CO)_2Br$ (**2**)

Mn	6.09247820876734	1.73631589803288	9.89321026982913
C	7.40303307277740	1.58447035727694	10.93088485061529

Br	4.31647096753859	1.95361846695819	8.22741743094010
C	7.18983496351605	2.05692270261124	8.67278650809979
N	5.69933685952019	3.49422765458774	10.39319783064017
N	4.74138645152593	1.41863266862324	11.15007883269180
N	5.89033961783882	-0.11370586779557	9.68699317484402
C	6.29365653199899	4.60100693521073	9.87440330861783
H	7.04003850753772	4.42767383264244	9.11785931853060
C	5.96469110298020	5.87741720541278	10.27209457885270
H	6.47659342377815	6.70986026624692	9.81122197057749
C	4.98143258519287	6.07926167211832	11.24011054114356
H	4.70418624363133	7.07351867691451	11.55963525963912
C	4.36145174441148	4.96601475776037	11.77756603449524
H	3.59103958733504	5.06378207299015	12.52831450748124
C	4.72637928546366	3.70288891831693	11.34178341694012
C	4.16595395425166	2.45873503456865	11.80124090592512
C	3.18431199132601	2.24903259413215	12.75883542996939
H	2.74050073448836	3.08833074748958	13.27188265836037
C	2.78162792682556	0.95010249162942	13.03429953352275
H	2.02476661779115	0.76537372539572	13.78292993895442
C	3.33908806914422	-0.11110786843321	12.33023153204129
H	3.01410543544756	-1.12486040557914	12.51067943973692
C	4.30660313969893	0.15318140822355	11.37226980986968
C	4.98051049862793	-0.76459836863568	10.48591388147429
C	4.76193325762270	-2.13092000698896	10.41472497352204
H	4.03164868845536	-2.58481071176523	11.06905778169274
C	5.47437488993462	-2.89150357599333	9.50507409842516
H	5.30777817703594	-3.95584973461074	9.42127782408004
C	6.39445845042230	-2.23867370729982	8.68793440236053
H	6.97181551431561	-2.78058457029885	7.95282713727407
C	6.57494940391786	-0.87698341330155	8.79656080491868
H	7.27045732834935	-0.35259119136742	8.16344776080726
O	8.34659115613478	1.47283815063161	11.63652208716837
O	7.98852761239632	2.29557618429541	7.82298016595863

$[Mn(\kappa^2\text{-tpy})(CO)_3Br]^-$ (**3**)

C	2.09268940971466	12.34617880978784	8.27552732933047
C	2.98335749481816	13.55225223350502	10.25889675970961
H	2.74824371409561	14.50642739549462	9.81079660154316
C	1.70004905534283	13.44201128735777	7.49780939904356
H	1.89521263367074	14.44117985413146	7.85845583616143
C	3.59452602052248	9.77499179671496	12.07243738590242
C	2.80408180481335	8.67610126360560	7.48341528400652
C	1.26776532724022	10.87293049183794	6.65230725050025
C	3.82999622607256	8.60857080014605	9.53824898121440
N	2.47516091881973	9.07230131358065	12.27897779255441

C	4.82178002928114	9.40926737747855	12.62213666221780
C	3.46301046429242	11.05708307980179	11.33339734846981
C	2.55768925139081	7.96569207314797	13.01499828686211
H	1.63281551496802	7.41977018363157	13.16471676104531
C	3.56156411852560	13.47481236427818	11.49770266604861
H	3.80898833044752	14.36308657690094	12.06102928739631
C	1.08414087406924	13.23890135688640	6.28940129012895
H	0.77753186148139	14.07372971951395	5.67551314687960
C	3.78448361071843	12.19587720279931	12.03201626997630
H	4.17502266623477	12.08598378800236	13.03292470568850
C	4.89454234264285	8.25719142433004	13.39128887692300
H	5.83654328890019	7.94239862126719	13.82153500554436
C	0.84443799342192	11.91257289028549	5.87620602182968
H	0.33705761986386	11.69787453044443	4.94697678981542
C	2.69268082708890	12.38542051127105	9.55281333940507
C	3.74042663848918	7.51306934025571	13.59033424029284
N	2.96613997932663	11.11070062909014	10.04424000397582
N	1.93109367013535	11.05204302521849	7.83552345915887
O	4.60526603706232	7.80819367119610	9.91488687752394
O	2.90692844405854	7.96764720867211	6.54784280289348
C	1.37229133266148	8.88679204945613	9.46267119827824
Br	5.15513010095253	10.86540797147895	7.66441015742582
Mn	2.71114407630495	9.67918843591259	8.84216767332217
O	0.41050301019627	8.33661758537997	9.87066976342194
H	3.74850503999397	6.60681558267577	14.17992737570026
H	5.70119724972107	10.00734487652550	12.42844936890005
H	1.10073202266026	9.85304467793748	6.34786900090942

$[Mn(\kappa^3\text{-tpy})(CO)_2Br]_2$ (**4**)

C	1.15424044472293	3.14960321199403	-1.08541297222103
C	1.41521269828575	4.48260554847232	-0.82760047440222
C	2.21039395070193	2.27058666938453	-1.29448281481812
C	3.51293097902083	2.74610471747297	-1.25055259068173
C	3.74170132447436	4.08970426691646	-1.00329454916802
N	2.70288594032893	4.96433462908315	-0.78813092407471
C	0.49185613415851	5.54693604560481	-0.56854028704067
C	-0.88845013576078	5.43724134562292	-0.48281672358799
C	-1.65570185746987	6.55522282546491	-0.23434272263312
C	-0.99437909506869	7.77663105691113	-0.07418121915640
C	0.37366754902031	7.84277040377250	-0.15755770486833
N	1.16289365188977	6.74677428410694	-0.38639720887169
C	4.98931662074170	4.78172977203336	-0.87989266273869
C	6.25247839392747	4.21568095760709	-0.94177407868524
C	7.37215885899056	5.00075269104499	-0.75252232541084
C	7.17847439193298	6.36081380591484	-0.50951267818165

C	5.91221285425215	6.88806831978018	-0.45738698427173
N	4.77910690873394	6.13128235569623	-0.60925825735732
H	8.01838258152292	7.02567227085643	-0.36598700042051
H	5.74854349334186	7.93555337708146	-0.26794145560450
H	6.34191637509063	3.15716698238714	-1.13885211455837
H	8.36390076438032	4.57507733970603	-0.79972912168460
H	4.35083976969120	2.08398199627666	-1.40994420890661
H	0.13211394425092	2.80316730287841	-1.12317612628550
H	2.01911030509212	1.22614083348940	-1.49597194105704
H	-1.34482065594459	4.46794662571427	-0.62467238578577
H	-2.73211187863950	6.48868019396274	-0.16747421078206
H	-1.54310640363964	8.68832824280982	0.11481022574758
H	0.90002034863313	8.77238470098450	-0.02583135988273
Mn	3.03624380297694	6.74639634940699	-0.34242451702551
C	3.33722892492858	8.38542565730795	-0.33259073200053
C	3.12838496714047	6.75502275827754	1.32146164513365
O	3.57230082666036	9.55653417370383	-0.26431828933260
O	3.19384702896196	6.76212148221579	2.51058620728491
Mn	2.85203820906794	7.35587126460923	-3.54230759444858
N	1.99915590456908	8.96199553046738	-3.10070127788556
N	4.32847364339755	8.46555417223474	-3.26970763154000
N	4.24080060096827	6.11857524698756	-3.71789005046843
C	4.07649095050707	4.78904482180416	-4.00479481354925
C	5.12216869265199	3.94158493450867	-4.27514914006857
C	6.43571075179066	4.40975718283343	-4.24990794431300
C	6.63808342320962	5.73972775162584	-3.93897690271650
C	5.55841124736775	6.56565066698160	-3.67151033780753
C	5.60724712461124	7.96870110264055	-3.37858840682305
C	4.15858367555553	9.80331562798714	-3.00074082723176
C	5.24361954367706	10.64978886412946	-2.85278479864583
C	6.53016408070055	10.14230206464232	-2.97349579068260
C	6.71168166079722	8.79069913410647	-3.23678105738606
C	2.76151435120929	10.10482028810948	-2.90961844891922
C	0.63980732969039	9.12752922416247	-3.01188722018183
C	0.04796447096644	10.34145625337369	-2.77527000228678
C	0.82949639995450	11.48845099574224	-2.60328835495880
C	2.19935740310832	11.35174850610464	-2.67533483743559
H	0.05431291197603	8.23518722791938	-3.15130847157172
H	-1.03032018025196	10.38575777180760	-2.71504549476467
H	0.37432364268676	12.44930969340547	-2.41110280750661
H	2.85317814927833	12.20114849761679	-2.53897160622157
H	5.07928989246624	11.69314130050042	-2.62794394526549
H	3.05680528749874	4.44303384401207	-4.03059040694319
H	4.90082370280502	2.90773075366225	-4.49923472767054
H	7.26917725849736	3.75471299262008	-4.45717561024989
H	7.63460184145860	6.15468581384193	-3.90123031510374

C	2.50917993239450	7.43207186490763	-5.17195076050825
C	1.55237933689913	6.32615605476270	-3.39310043158183
O	2.25284189565119	7.47235435579505	-6.33475168413485
O	0.59514418245607	5.61018979472347	-3.35306211284706
H	7.38581002673224	10.79102069051931	-2.85152238836917
H	7.70292884832075	8.37177251691228	-3.32464123658280

$[Mn(\kappa^2\text{-tpy})(CO)_3]^0$

C	2.10550484859485	12.32663990318229	8.27130166651679
C	3.16314143431380	13.55167717418637	10.18197433591180
H	2.97305372450914	14.51063832792114	9.72410518914942
C	1.63835926272175	13.40036493690889	7.52490714484522
H	1.86232614265170	14.40627059632498	7.84797486581624
C	3.49250446957302	9.77562419015169	12.06692591402661
C	2.92135205433576	8.75337567296819	7.41299966605764
C	1.13607670832980	10.80963841021467	6.76562581532191
C	4.33118681947489	9.10907008069498	9.25348778609258
N	2.27867642707329	9.33421709245192	12.41279832424743
C	4.66835310104127	9.17492087521050	12.50521762258626
C	3.50764388267557	11.05689551231491	11.30965539446986
C	2.20331262478342	8.25217151880755	13.18662035099357
H	1.20678117580234	7.91304660466846	13.44520967957213
C	3.77947999907814	13.45580412663590	11.40816713787976
H	4.10867034923585	14.33813529673351	11.93789103140566
C	0.88574419417338	13.16800276781034	6.39375740177084
H	0.50193683390919	13.98965861049341	5.80691768105941
C	3.92154494356191	12.18770045891867	11.97593664045453
H	4.31955789100983	12.07659161772654	12.97388205114256
C	4.57771990524314	8.05217219778936	13.31639335071671
H	5.47371004535698	7.56064752986550	13.67198944371695
C	0.61242435323855	11.83861360644329	6.03617904227382
H	-0.00260531635924	11.60718609151593	5.17902537771950
C	2.78654131498431	12.39100717948895	9.52011548221163
C	3.32140496711333	7.57685907908153	13.66411878048674
N	3.01879351284759	11.12857151590610	10.02248841545080
N	1.92434819203441	11.01538174353091	7.87624541162977
O	5.42018294608347	8.74502614987837	9.50133991571383
O	3.03298311940406	8.10969018883891	6.43425738962257
C	1.88531297973245	8.52758754950968	9.58896965735061
Mn	2.80741756155802	9.69825992836750	8.81393730480465
O	1.21562217589028	7.68847125830182	10.07120607354853
H	3.20389466502687	6.70778475810347	14.29642813697016
H	5.62655417464958	9.57345405791169	12.20603570084858
H	0.94808741539474	9.78290741966313	6.50002566018906

$[Mn(\kappa^3\text{-tpy})(CO)_2Br]^-$

Mn	6.17237223339612	1.71921008471169	10.01463371057023
C	7.58802951802017	1.59531795751419	10.87938207698554
Br	3.96759222344084	1.96309082622475	8.20119638683495
C	7.06005630284476	2.02982130333573	8.64376422371388
N	5.74628028687082	3.46196126264375	10.45518605780726
N	4.79866778529260	1.41293434355293	11.20882846338641
N	5.93729128666907	-0.09167312971737	9.76116393764741
C	6.34149562807656	4.57831288556128	9.92456110840151
H	7.10553263442410	4.39160722255176	9.18826275343589
C	5.99578635884470	5.85289642625956	10.28175648660131
H	6.51080685115526	6.67941227992864	9.81211786345537
C	4.98239022305948	6.07576349035189	11.23385002503466
H	4.69347790867903	7.07661617174763	11.52250564805003
C	4.36173075623206	4.97482092201221	11.77780996902299
H	3.57132249615058	5.08277660669551	12.50778954818121
C	4.73938201047037	3.69238311021073	11.38451872536784
C	4.17986876241510	2.46767071915318	11.83977501411670
C	3.15604966896799	2.25394952820456	12.74775268959656
H	2.68815750651296	3.09623240449326	13.23634143390066
C	2.72613916853423	0.95438852848574	13.00171330666799
H	1.93134719547226	0.77419591468854	13.71171104420340
C	3.29945573714381	-0.10891660309038	12.30686623448706
H	2.94241755908376	-1.11840370061881	12.45375238025784
C	4.31145075372990	0.13825570791745	11.39338535172658
C	4.98185788435501	-0.76064776162096	10.51742770430139
C	4.74816310302344	-2.12919098559690	10.38846372784061
H	3.98359243133158	-2.58594354025416	11.00206359865358
C	5.47698129380986	-2.87574432574608	9.49162130160964
H	5.29467507341754	-3.93352351711805	9.36444205748671
C	6.45110539244689	-2.20807869863603	8.72630980485660
H	7.05168919273276	-2.74121378339071	8.00237063889035
C	6.64886226050738	-0.86339675661768	8.87696963032438
H	7.37941318317460	-0.33650997253931	8.28589433012428
O	8.60514681997800	1.48733923789526	11.49576160871438
O	7.70376450973644	2.24687884080621	7.65629915774478

$[Mn(\kappa^3\text{-tpy})(CO)_2]^0$

Mn	6.13937919474805	1.69566020283839	10.08566865746495
C	7.81058838397763	1.73326486121971	10.25498791338130
C	6.38810536619470	2.04897976180809	8.46268299663537
N	5.78378850606820	3.42620176625272	10.58602223526695
N	4.74949748951870	1.41225454136755	11.15922483011655
N	5.97468902925284	-0.12204513290748	9.89948420292771

C	6.48496475773989	4.53061454469743	10.13625186688638
H	7.30339952702255	4.31907797389909	9.46803712453648
C	6.16869506493669	5.80229015023117	10.49842663216146
H	6.75530455651244	6.61802930246257	10.10115331611852
C	5.08959708889141	6.04385143346175	11.38053165775352
H	4.82801821231926	7.05132480541281	11.67194883482667
C	4.38230495826077	4.97210900962610	11.85558824159118
H	3.54820671347241	5.10520709100930	12.52981028403972
C	4.72603011737491	3.67434586806748	11.45815618899931
C	4.09939192357925	2.47084202039129	11.81349244834591
C	3.01249083631949	2.25550976221446	12.64005901432613
H	2.54172498375275	3.10425307245258	13.11580600433094
C	2.52743686360403	0.96826365222816	12.84981651685044
H	1.67759036881249	0.79940077464307	13.49415846363740
C	3.14711759718433	-0.09485932048113	12.20036390015410
H	2.78304749796903	-1.10437625314550	12.33328803807042
C	4.22673875396308	0.12398967634625	11.36295458510751
C	4.96231650463606	-0.78673493583857	10.59144640455927
C	4.76143564756644	-2.16782353740876	10.46588946842508
H	3.94965292728768	-2.62683180228041	11.01263260235608
C	5.58014465564586	-2.90882530812774	9.65707402329967
H	5.42752017416363	-3.97234440068129	9.53806642971740
C	6.62668420935737	-2.24849332340459	8.97162291063812
H	7.30199385753240	-2.79719428237268	8.33099360975380
C	6.79312125933149	-0.90606203951052	9.10439401684995
H	7.57759059233347	-0.37879609353897	8.58719770278211
O	8.98557356552503	1.74533275654733	10.37760212302309
O	6.54890681514562	2.31237940252033	7.32333875506650

$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^0$

Mn	6.04764537668470	1.74966893299605	9.78859715294582
C	7.38538926662720	1.59364017978724	10.81941888012714
N	4.65912465717901	1.90323002232007	8.58148081976571
C	7.15926508558649	2.06964539513169	8.58385165594284
N	5.65763732504492	3.51163749125505	10.30744944242748
N	4.69433474156975	1.43202628813783	11.06565116274900
N	5.84737852947365	-0.10975760207510	9.60519033923671
C	6.26288813254765	4.62550620602036	9.79995697815191
H	7.02267094804649	4.44845694691759	9.05647185334222
C	5.93978436599429	5.89774391718967	10.19216381157222
H	6.46251689564914	6.72877897649811	9.74032821365506
C	4.93714208582985	6.10414237346441	11.15986566836206
H	4.66305479436569	7.10031410048216	11.47769158151279
C	4.31043989097107	4.99951842768887	11.68640003905861
H	3.53270102395978	5.10119059239862	12.43036265141520

C	4.66652488705091	3.71941051100934	11.25809620074334
C	4.10242532121381	2.49126373057062	11.70661520479598
C	3.10074476342151	2.27749212698958	12.63833441623487
H	2.64401523797356	3.11725206687939	13.14140106082201
C	2.68145173246549	0.97420098347115	12.90428631373589
H	1.90318769896305	0.79445677664836	13.63225703324692
C	3.24836671502074	-0.09390463398651	12.20831912671427
H	2.90394776710132	-1.10381962155928	12.38017817104892
C	4.23975054948899	0.15150054238354	11.27113901509916
C	4.91527431759789	-0.75824503589030	10.40755272279793
C	4.71033497780481	-2.13847857997708	10.33098560554885
H	3.96930569888726	-2.59076403351965	10.97576446278395
C	5.43748887393004	-2.89935250381369	9.44718398727419
H	5.27619382083777	-3.96524734919285	9.36714561689716
C	6.38326647096266	-2.24483022687598	8.63419438650540
H	6.97934838637250	-2.79246916079059	7.91824161621795
C	6.55322473391142	-0.88901099124409	8.73478948876643
H	7.26456716402097	-0.36729577719162	8.11542321973429
O	8.35915350786957	1.47841470899027	11.47847004645310
O	7.97112988404608	2.31674916907789	7.73873638082397
C	3.76030540147807	1.99600698780177	7.87058078003670
C	2.63736196719423	2.11172472272911	6.96984004575034
H	2.94194460648847	2.64810799984911	6.07039002199518
H	2.27898520653190	1.11974180582966	6.69138095710850
H	1.83004518983726	2.65910653359924	7.45781286859996

$[Mn(\kappa^3\text{-tpy})(CO)_2(MeCN)]^+$

Mn	6.01637920198612	1.74543724357197	9.77438890643590
C	7.34282249173372	1.59133378187871	10.82830861063256
N	4.66308750221059	1.90748132453499	8.55449179185689
C	7.14287661959512	2.06588679418807	8.57008400144245
N	5.63313591055308	3.51389010390431	10.29876901344107
N	4.67697219195728	1.42593141377679	11.06428157985930
N	5.82316199074963	-0.12285428583559	9.59552229362966
C	6.23085013742559	4.61667750926224	9.78431627456173
H	6.98058989701252	4.44625539717037	9.03025240406613
C	5.90785520491722	5.89369982206568	10.19252698853855
H	6.42388099819109	6.72740413823877	9.73882889426178
C	4.92929772170763	6.08971536400909	11.16285558897287
H	4.65721893149902	7.08237716043684	11.49170816584430
C	4.30659006133654	4.97487795910273	11.69703385900655
H	3.54051608111646	5.07144883114568	12.45229909667770
C	4.66772809977516	3.71520725617181	11.25233120096222
C	4.10634855205278	2.46725596737321	11.71202126680229
C	3.12394532985659	2.26211498597894	12.66873725084691

H	2.67922163736814	3.10258715051698	13.17900939383570
C	2.72067695078568	0.96391571964856	12.94629935530457
H	1.96022975439888	0.78190771238770	13.69189739883179
C	3.28221658814947	-0.10021312475293	12.25044960782388
H	2.95828140247300	-1.11322226961417	12.43628559940703
C	4.25102212657840	0.16185355410735	11.29395963664124
C	4.92955934605132	-0.76485098699387	10.41483890247367
C	4.72673671408674	-2.13345755715158	10.37220830229200
H	4.01022316675859	-2.58539772960418	11.04270053059804
C	5.44248966895636	-2.90154007037602	9.46969755828789
H	5.29202007975532	-3.97002105051766	9.41236633641098
C	6.34512171415301	-2.25607499438638	8.63149456445679
H	6.92543525840582	-2.80503556607391	7.90425492935014
C	6.50845235111646	-0.88811159807386	8.71239081483991
H	7.19844644982405	-0.36816209053582	8.06931851162503
O	8.28344682348588	1.48058644064637	11.52159862964916
O	7.94807904499466	2.31034142222732	7.73422376067785
C	3.78375447111434	2.01932704143593	7.82161556283609
C	2.68896558303663	2.16158804476212	6.89441218123593
H	3.02997217876506	2.69990359574057	6.00917973250074
H	2.32225021436311	1.17741693978535	6.59961775955712
H	1.88045955170296	2.72027164984754	7.36742274352560

$[Mn(\kappa^3\text{-tpy})(CO)_2]^-$

Mn	6.13481982518744	1.70338366372861	10.04271179742461
C	7.78622556755323	1.73606127874161	10.22958701708706
C	6.27125916457805	2.05133009922900	8.42260426746722
N	5.79197547661590	3.42036091975270	10.57053481818387
N	4.73908238086284	1.41714716940376	11.13127391652273
N	5.97977929654722	-0.11127718137003	9.88595241260083
C	6.50410387995244	4.53641425680704	10.15494313650912
H	7.32560420905292	4.32790581232755	9.48889528475024
C	6.20271823703339	5.80448851563138	10.54219244114303
H	6.81023274718986	6.61611231184515	10.16539876504603
C	5.11807092166139	6.05534569482857	11.42175948996669
H	4.86840205752269	7.06028106336615	11.73200310068096
C	4.40060349609219	4.97693388177043	11.86294133109780
H	3.56156983877089	5.10014090021068	12.53489285841155
C	4.73284581096058	3.67923322934041	11.44557236899761
C	4.09155458433735	2.48016528966115	11.78945403285670
C	2.99680709266123	2.26418032733307	12.61009177825611
H	2.52400848206322	3.11218652207248	13.08585194442055
C	2.51104652959463	0.97535908050472	12.81266180723292
H	1.65456482887167	0.80742364863550	13.45049044542177
C	3.13507768641764	-0.09333087331966	12.17360105954643

H	2.77045654812905	-1.10253594192690	12.30990258293216
C	4.22114449391344	0.12332454480659	11.34053175222071
C	4.97067479517199	-0.78690877656234	10.58074414060942
C	4.78365638981257	-2.17441215266732	10.47672885102689
H	3.96901363686350	-2.62504323922881	11.02850940908786
C	5.61043452080827	-2.93238235123245	9.69296177556925
H	5.46976963183208	-3.99954319878598	9.59311387688401
C	6.65675356057366	-2.26306659591069	9.00786540296658
H	7.34959005632328	-2.81232410013662	8.38482341532071
C	6.80810251265173	-0.91621173074801	9.11529023659317
H	7.59453150631989	-0.39182979359882	8.59739013405688
O	8.97711857185705	1.74184036723262	10.38188688502636
O	6.34144966221679	2.31804335825847	7.25500946408215

$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2)]^-$

Mn	6.08618705042858	1.75350729160324	9.90144836615844
C	7.47529104680426	1.58001376673756	10.84575208133053
C	4.63870124586503	1.92089107297158	8.43133109724003
C	7.09997431677160	2.12342311744061	8.62733722105186
N	5.70512365442323	3.49010424319239	10.41322114172709
N	4.74039387918851	1.42768984291193	11.12475036279720
N	5.87253158567674	-0.08129181974206	9.67538839489026
C	6.31753612692065	4.60832206858925	9.92073081963769
H	7.09383326141180	4.43764512823197	9.19375306174889
C	5.96549594587093	5.87944689566757	10.29385745295129
H	6.48993813307413	6.71226869205687	9.84638221529739
C	4.93749742598477	6.08584088692554	11.22492432771546
H	4.64310015008494	7.08161067106761	11.52500965492734
C	4.30648169592891	4.97457105029936	11.73871015032484
H	3.50467476410431	5.06899427595384	12.45739237223689
C	4.68952964918231	3.70440875089000	11.31988823126957
C	4.12534530163403	2.46938073661095	11.75773548698769
C	3.12651889640349	2.24985392700429	12.69886647648014
H	2.66289400228502	3.09123925511029	13.19207760994379
C	2.73717060823133	0.95216732513745	12.98963152965119
H	1.96868015085683	0.76583284585041	13.72624775952690
C	3.32868900254885	-0.10971621656628	12.30867038132489
H	3.01392907173041	-1.12681681396950	12.49226273210221
C	4.30869087826174	0.15230686503726	11.36611786109465
C	4.98550230512943	-0.75519934761924	10.48563021991317
C	4.78147926066402	-2.12641288122567	10.40179310640338
H	4.07331764580739	-2.59438100215958	11.07131084612645
C	5.47321411984310	-2.86688596354758	9.46373706152269
H	5.31997017415999	-3.93296544721818	9.37177364142876
C	6.35517799131236	-2.18642426189628	8.62056420199417

H	6.91012328660818	-2.71130344966537	7.85554284388075
C	6.52233298699591	-0.82663394057852	8.73896939980157
H	7.18232374767274	-0.28251898457593	8.08664410890504
O	8.47182684423758	1.44384712297703	11.47567708628759
O	7.83782685148344	2.41810159660074	7.73623495104963
O	4.72656243769812	1.20315769098270	7.40417675311531
O	3.71724450471538	2.74730500891372	8.65390299115534

$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)]$

Mn	5.99468423240334	1.74483360626170	9.78962531193489
C	7.36802471730782	1.59548799925519	10.77873792356638
C	4.60250341123915	1.87620403480542	8.40685889704220
C	7.06075203391132	2.10247583935276	8.54813055467953
N	5.62419193999101	3.48582629958268	10.34194980534164
N	4.66145490204872	1.41037380538619	11.06368054141548
N	5.82989625385180	-0.11234179973308	9.61694339028485
C	6.24996037032534	4.60061706942313	9.87195363629204
H	7.00028785389690	4.43939295549727	9.11653262664912
C	5.94686859550705	5.86736786716990	10.31071161716071
H	6.48529701808028	6.70270647064051	9.88592082683946
C	4.95506746441241	6.06114939767764	11.27491702069903
H	4.69633445858325	7.05050011610408	11.62409705871745
C	4.31172551276086	4.94456154304831	11.77050233940248
H	3.53956959182105	5.03168071827224	12.52125193510441
C	4.65361457676059	3.68724413216900	11.29553518284043
C	4.08276645881857	2.44360457537085	11.72716133169746
C	3.10020673653957	2.22157916941627	12.68331257118034
H	2.65330931861003	3.05721645010105	13.20015119780320
C	2.70736273324093	0.92110439908837	12.95730395928511
H	1.94677198965662	0.72928655880372	13.70046904967855
C	3.28882087062408	-0.13585087864001	12.26418414869834
H	2.98133532085360	-1.15395052645107	12.45150821247720
C	4.25768431337890	0.13629363667200	11.31132031602937
C	4.96536199646211	-0.77811574373354	10.45052310170352
C	4.83820903630748	-2.15853351058736	10.45397240395216
H	4.16006671681832	-2.62513695896638	11.15415058226129
C	5.57408177733532	-2.91557539159569	9.56095527099752
H	5.48504048348312	-3.99230785462687	9.54105138078912
C	6.42087946018340	-2.24359435225041	8.68184038354431
H	7.00863565537844	-2.78106855619225	7.95146461265224
C	6.51979271675843	-0.86996683711727	8.72691707919953
H	7.16837181766330	-0.33274554200085	8.05623844235125
O	8.35294520644430	1.48947337755023	11.41855646978485
O	7.83017290206201	2.38134907234984	7.68269261785887
O	4.30541468425968	1.03448365177787	7.56970324959051

O	3.89519696553097	3.05249544686810	8.38425490342190
H	3.25241290668986	2.98338475925047	7.65764804707321

$[Mn(\kappa^3\text{-tpy})(CO)_2(\kappa^1\text{-}CO_2H)]^-$

Mn	6.01540963827980	1.74817783337924	9.81678370158163
C	7.38441981082959	1.57703160269627	10.80606418962547
C	4.58581621412169	1.86253745456690	8.47517841554454
C	7.07726442816607	2.12021274867500	8.58919330507286
N	5.61843787768884	3.48538320709888	10.36007233924807
N	4.68231061040463	1.40559813928951	11.10601717061946
N	5.84870556422465	-0.10570911159024	9.63459240859579
C	6.20968351011955	4.61397957027649	9.86215646595749
H	6.95215734048183	4.45155559781467	9.09858320858484
C	5.88726836601062	5.87832807186764	10.27264679200387
H	6.39878469966979	6.71636096750201	9.81979925948864
C	4.89171083652664	6.07304123920369	11.25402407933539
H	4.61446856860558	7.06487592791120	11.58303577372807
C	4.28052851257106	4.95842957173372	11.77500805912296
H	3.51149289375529	5.04552484684784	12.53039362312682
C	4.63869755737935	3.68330306910133	11.32972469277845
C	4.09416571964162	2.44964817609571	11.77593968816643
C	3.12485298983157	2.21209299729449	12.73818373982375
H	2.67241739321036	3.04172587800473	13.26195508892486
C	2.74288866193182	0.89949859560876	13.01538249324506
H	1.99480217661370	0.70124063145518	13.77011004188013
C	3.31764344888091	-0.15571134855354	12.30506275550227
H	3.01103008193527	-1.17472065729730	12.49578178951051
C	4.27470430796638	0.11161165170587	11.33675902002349
C	4.96191575520653	-0.78094431549287	10.46925308767684
C	4.80375230462399	-2.16881901183809	10.41152640654348
H	4.10273987681693	-2.63903333550837	11.08820521464862
C	5.51859370537660	-2.91433833209552	9.50555604376043
H	5.39089907314991	-3.98596528656761	9.43985441744088
C	6.40649966096691	-2.23082084142089	8.64785976623617
H	6.98558507480253	-2.76178221594852	7.90537815626759
C	6.53516571685759	-0.86991718446457	8.73703900652662
H	7.19756718735711	-0.32752959239826	8.08183967982238
O	8.39611020524340	1.45243420876960	11.41634121020056
O	7.85962497659221	2.41479363306254	7.72378304072283
O	3.96881561232670	0.94434542608217	7.94224134978437
O	4.25462599008398	3.13385034473375	8.04809875612771
H	3.56351665174888	3.02121484239859	7.37330376275059

$[Mn(\kappa^3\text{-tpy})(CO)_3]^+$

Mn	5.96359083800139	1.75731524147428	9.74710029054296
C	7.35384954839151	1.58564382253011	10.77234409429907
C	4.84897912148512	1.94851878721740	8.43120888428737
C	7.12865958177191	2.09628643404691	8.56243460219831
N	5.61922048509081	3.53128611802445	10.36293066568731
N	4.65842354861644	1.42677137969253	11.08431747311194
N	5.79971172918074	-0.14566296522996	9.63174909076087
C	6.22953023264473	4.63193336865588	9.86910564407408
H	6.96719445549100	4.47331525653727	9.10056438257777
C	5.92771085231393	5.90331538696618	10.31147918786542
H	6.44813977551463	6.74151661405193	9.87191512774918
C	4.96758410810307	6.08371491468214	11.30101484168839
H	4.71148362599795	7.07110551787556	11.65753272534497
C	4.34520444794836	4.96427958754595	11.82422258625881
H	3.59687487187392	5.05085743054051	12.59777496180685
C	4.68617929395864	3.71282235280718	11.34101621366750
C	4.12069197213766	2.45839501547386	11.77329415688685
C	3.15986635598364	2.24875710802336	12.74863770647709
H	2.73870950388601	3.08719731979897	13.28153298308139
C	2.75473065074034	0.95176475566355	13.02417267955266
H	2.00898248934724	0.76628713183975	13.78338069307265
C	3.31137416320007	-0.10683379773811	12.31863262498566
H	3.00704241041763	-1.12336287565930	12.51752342154485
C	4.25863691187483	0.16014679467380	11.34374423392147
C	4.93705050587933	-0.77715379661601	10.47862737636890
C	4.75668112269526	-2.15018812546680	10.47041875049856
H	4.05895741655316	-2.60033887879370	11.16105038169939
C	5.47409125103536	-2.92269521483620	9.57428105967947
H	5.34471732265097	-3.99508084578998	9.54511288293624
C	6.35486112953610	-2.28267246137812	8.71072223465333
H	6.93902567982639	-2.83738328490267	7.99131922305576
C	6.49514714429637	-0.91029515177360	8.76186525757035
H	7.17097216112231	-0.39261607303940	8.10191628850556
O	8.32629763370451	1.47072375771543	11.38889099626496
O	7.93752707640454	2.35138213728649	7.74667739641689
O	4.16207158232410	2.08471423810028	7.51065588090718

$[Mn(\kappa^3\text{-tpy})(CO)_3]^0$

Mn	5.96239989346010	1.75736124297887	9.75016944990711
C	7.36100045576266	1.58298968267480	10.76382141889320
C	4.86675155564163	1.95284763101572	8.41909645803485
C	7.12349371025339	2.09586641456085	8.57229502577855
N	5.61570072706087	3.52810420118660	10.36853579148263

N	4.66190012554308	1.42782127818639	11.08488625110015
N	5.79520334184658	-0.14329652629493	9.63584245718376
C	6.22535291610176	4.63802132448230	9.87250889482127
H	6.96330238194535	4.47317316519984	9.10466325557359
C	5.92907903335993	5.90551657292487	10.30435229446802
H	6.45002949763512	6.74186345082725	9.86146533486580
C	4.95912538912504	6.09266793232254	11.30453830032531
H	4.70556522117629	7.08299397323384	11.65596338036288
C	4.34020660843834	4.98336376650338	11.82871337249100
H	3.59105658760615	5.07440673040574	12.60203100393553
C	4.67232542946228	3.71147528536621	11.35647081621100
C	4.11310645496127	2.47490815805470	11.78464643783454
C	3.15609739121797	2.25301615240331	12.75656939855991
H	2.73266840339054	3.08980942311339	13.29234951928598
C	2.74881228395752	0.94888057629758	13.03669957043167
H	2.00481194025373	0.76328062673703	13.79754639832048
C	3.30803895389992	-0.11232839658691	12.32611845028160
H	3.00050557335654	-1.12846805770019	12.52832301261672
C	4.25487494201218	0.13948181817411	11.34812384624451
C	4.92243870215471	-0.78148442735510	10.49362828709760
C	4.75561191647926	-2.17011364917796	10.46884465903022
H	4.05900536028548	-2.62499442306881	11.15884149549539
C	5.46869785471989	-2.93270003869684	9.57667156326083
H	5.34274852032843	-4.00576438203146	9.54185063581189
C	6.35748465745667	-2.28092978950259	8.70342321793246
H	6.94176293436409	-2.83302574092527	7.98189127610391
C	6.49072299850079	-0.91684551129242	8.76100260274778
H	7.16420544213448	-0.39360811665731	8.10180056254108
O	8.36129992585855	1.46754387844185	11.34655688663092
O	7.93825457541998	2.35431220502067	7.74989922529058
O	4.22612929482941	2.09762056917792	7.45902644904728

$[Mn(\kappa^3\text{-tpy})(CO)_3]^-$; dissociation of a CO ligand occurs

Mn	6.25052604966056	1.67137562136471	10.09566248912826
C	7.86484427710259	1.68888670792414	10.49684861661580
C	3.50048295958605	1.91182588777290	8.39739677250927
C	6.62606968444532	1.99847342941144	8.51202810301445
N	5.83288338844610	3.39812238968340	10.53137409062491
N	4.80680330614707	1.39134990907561	11.13244356147349
N	6.05377591028221	-0.13171694651075	9.88212954772384
C	6.49720729697138	4.51887822304378	10.05556981594614
H	7.32522807137317	4.31116855576871	9.39761298545205
C	6.14078008086065	5.79268547037161	10.37188580096888
H	6.71010980532726	6.60736409429313	9.94524117056129
C	5.04488571911110	6.04492480629668	11.23545980701802

H	4.75262825555143	7.05377460113888	11.49103320370345
C	4.36459541659785	4.96256071880688	11.72362556341732
H	3.51211348259772	5.08612773528751	12.37817802277484
C	4.74779692114100	3.66043081315623	11.37091151992569
C	4.13145992830832	2.45765558531010	11.74872130429791
C	3.02915681984919	2.24365122748596	12.55943984138893
H	2.54043846748131	3.09384082837771	13.01449922691255
C	2.55285563604320	0.95308000457028	12.77191718343876
H	1.69521193971065	0.78427770261681	13.40798075195091
C	3.17792271210753	-0.11467132590858	12.13290869445648
H	2.80630966156963	-1.12274742617845	12.25764768823610
C	4.27210613036262	0.10368784298506	11.31062793352723
C	5.01467424789687	-0.80183169465640	10.53668769266310
C	4.78671618777510	-2.17729149261505	10.38009012334247
H	3.95160179319855	-2.62183255531819	10.90565559826597
C	5.59504402527926	-2.93046873764063	9.57243958164950
H	5.41811366433455	-3.98673610078372	9.42500345891251
C	6.66524212499211	-2.26739049211905	8.92007345448725
H	7.33966845014164	-2.81137804800353	8.27266341368284
C	6.86066143464492	-0.93181722047473	9.08493660356926
H	7.66227773091939	-0.41261168139201	8.58563107830442
O	9.02685827705988	1.68925822754745	10.79754527690418
O	6.87232569024968	2.24436277025888	7.36468344088272
O	3.14039545287412	2.95649756905320	8.63261358226905

$[Mn(\kappa^2\text{-tpy})(CO)_3(MeCN)]^+$

C	2.19350844241305	12.39438448396919	8.18640042571231
C	3.05368753511104	13.60948928781020	10.18936839804361
H	2.82228644396199	14.56090796391454	9.73679732073613
C	1.67175182467735	13.48194565812517	7.50157403703400
H	1.82378581877378	14.48119138402071	7.87873423570151
C	3.70385463387238	9.83739843454953	11.99029941055659
C	3.02038197178154	8.74273413997977	7.31112829614744
C	1.32485987716283	10.91916966654540	6.61723817646055
C	3.91247629678443	8.55786071614839	9.51339040237304
N	2.60416802716105	9.08949959023303	12.12511887856065
C	4.92727054033311	9.50932362306642	12.56599233578959
C	3.53841483058588	11.12905489823640	11.27867237997767
C	2.70302294760829	7.96662680941961	12.83499675134115
H	1.79684144956274	7.38156972174133	12.93758657408258
C	3.58563814234474	13.53616366674244	11.46110309633115
H	3.80096337045952	14.43218494857618	12.02498839732945
C	0.93683693026465	13.26392325870748	6.35033442297481
H	0.51018057157017	14.09433378208029	5.80664906759133
C	3.80763737081613	12.28297425995657	12.00409169761048

H	4.17559848741742	12.17782207015360	13.01334665272600
C	5.01938093929477	8.33025370887228	13.29234939440813
H	5.95870414997412	8.03182385859367	13.73847527498359
C	0.73860560080256	11.95562552436443	5.92363848262015
H	0.14479838595141	11.72972445771068	5.05053474199921
C	2.81762516848644	12.43952154029170	9.49160407967846
C	3.88586614644761	7.54367048643018	13.43262735323877
N	3.08713216237282	11.19804742343609	9.99898681325331
N	2.07127446013224	11.12688254771394	7.72226396203055
O	4.49857488034375	7.66983779760320	9.98765374819282
O	3.03792058395604	8.06707406496463	6.36131325465822
C	1.56461722882722	9.04492963014544	9.25549572565686
N	4.58629131881905	10.53786606040987	8.11283755836712
Mn	3.01682291140093	9.75445350339717	8.68271678324399
O	0.57880211397087	8.53262369687955	9.59639303138836
H	3.91010055636070	6.62071217594378	13.99476399578776
H	5.78702947546885	10.15060075845889	12.42959435160808
H	1.20697256095717	9.90015730824216	6.28817419038430
C	5.60902679608631	10.93530937760690	7.77593777958016
C	6.92362165964226	11.35910273670850	7.36478331982664
H	7.05852392155192	11.14026526006361	6.30439419836814
H	7.66924996519147	10.81191007241461	7.94337811984270
H	7.04475350129932	12.42843464577254	7.53954188380270

$[Mn(\kappa^2\text{-tpy})(CO)_3(MeCN)]^0$, MeCN ligand dissociates

C	2.08788225342293	12.35062893127869	8.27667122588602
C	3.37847019018145	13.51918127948724	10.07086437431265
H	3.14554072652947	14.48811848969379	9.65474240536107
C	1.48053772266096	13.43154634123093	7.64254502456614
H	1.63887521318718	14.43035704185215	8.02141658160449
C	3.78521289743310	9.72629029741770	11.87387384166355
C	3.53476665791397	9.25296087346364	7.15591828350386
C	1.13024482854610	10.86072097621083	6.75543129874086
C	4.11706143706119	8.67452581566104	9.33928289689973
N	2.61666753635744	9.06994316763122	11.87453707465372
C	4.89378053338597	9.28289292567595	12.59360604237645
C	3.82361345567530	11.00254812374826	11.12908078282065
C	2.53175692330506	7.93851737199858	12.56752728065727
H	1.57304169096332	7.43288555306156	12.54544005386195
C	4.15404053109991	13.39903561133738	11.20649152389491
H	4.55954911578857	14.26887961924333	11.70166603737317
C	0.68093203103705	13.20610454035759	6.54499368447839
H	0.19655790288588	14.02815136720264	6.03794841764967
C	4.32199045260273	12.12071626220601	11.75180289940557
H	4.78803360894475	12.00450448670761	12.71884882168807

C	4.79376509667375	8.10067218198816	13.31157337213258
H	5.64495528545801	7.72262001459427	13.86208670658303
C	0.49961462859500	11.88815159718818	6.10520594377348
H	-0.12969627537226	11.66239594595049	5.25681428955833
C	2.90050688513254	12.38290760021634	9.44369683739787
C	3.59215897675626	7.40669656801362	13.29565352457190
N	3.23336823709226	11.08853922068013	9.86161406730004
N	1.94007680861191	11.06988855526339	7.83088067679417
O	4.93420801717005	7.91424246405274	9.70922110462618
O	3.95888943914004	8.96591252586489	6.09893705309666
C	1.76453038992831	8.54752212707487	8.79379600346743
N	4.84792132956442	12.50061097148285	6.52050239112524
Mn	2.96187485825798	9.72301687074467	8.67369302926863
O	0.92360454374294	7.73512825777700	8.92109169116583
H	3.47192118209161	6.47603711424720	13.83229681196018
H	5.82305439654677	9.83404062839738	12.56310832981211
H	1.01864868751571	9.83625553368536	6.43952251048370
C	5.50733791720928	12.03458557238659	7.33945323489968
C	6.34078613405895	11.45491609340062	8.37479520004583
H	6.23903523930483	10.37036763803937	8.36833324788519
H	6.03994575053543	11.83548294720112	9.34995473215488
H	7.38379676300386	11.71888549628462	8.20034969049894

ORCA 3.0.3 Data used in Figures 7 and 8

$[Mn(\kappa^3\text{-tpy})(CO)_2]^-$

Mn	6.21148870869571	1.72447157105618	9.94610892506642
C	7.96255370010472	1.76618168287106	10.07214366681466
C	6.28945544387628	2.10269227078177	8.23648488271035
N	5.82416318469129	3.58710359789234	10.57377385046365
N	4.73436356317792	1.42207452476689	11.09448444189958
N	6.02996639209019	-0.26721854660332	9.83302307353569
C	6.49946847003631	4.71480241628161	10.23550600545474
H	7.34152857123381	4.56807795719966	9.57354895190718
C	6.16221915304145	5.96658302374726	10.68306707836981
H	6.74660795618082	6.82095148721633	10.37050032586750
C	5.05219538876443	6.11284613570195	11.54401688004763
H	4.75640670789047	7.08716239642269	11.90976685691135
C	4.35384448109242	4.98759537448429	11.90662712217614
H	3.49820478412846	5.05827624228981	12.56450772628232
C	4.74285447410188	3.72642226344968	11.42368224584845
C	4.10688139498053	2.48740137325741	11.73123324403833
C	3.00956288775481	2.28189974990324	12.54938192161895
H	2.52903265025987	3.12387991227453	13.02947855364076
C	2.52210057238826	0.98792324233887	12.75603644549615

H	1.66516085480390	0.82123684960719	13.39355888381334
C	3.15395396660421	-0.08696466448653	12.12209445607716
H	2.78628960470024	-1.09340373854317	12.27458498997809
C	4.24138515792043	0.13576700652656	11.29420510232627
C	4.99334767985041	-0.82678089912663	10.55725818010603
C	4.75093483342961	-2.21194410673814	10.52918385368144
H	3.92151261788058	-2.61297978520822	11.09633905097219
C	5.55667716788685	-3.04082235651364	9.78810679706042
H	5.37046246339911	-4.10611170592927	9.75425682388344
C	6.62915506828643	-2.46882573169893	9.06925223080298
H	7.29734534302720	-3.08058420753655	8.47895425025488
C	6.81661348155354	-1.11099800575334	9.11733517756974
H	7.62213352030128	-0.63984919736454	8.57181237989915
O	9.13595887826008	1.77541544687247	10.14069662292693
O	6.34921887760652	2.38651442056047	7.09716100249826

$[Mn(bpy)(CO)_3]^-$

C	2.12281662147065	12.34081848311738	8.21338997509975
C	2.88546444324111	13.51338330440697	10.30353804521297
H	2.67298222334720	14.48604959891175	9.88349215161164
C	1.76470238269490	13.48982851281749	7.48026994268752
H	1.92220852092516	14.46328463897130	7.92330536418489
C	2.11263612007852	8.32495703442959	7.58988448965194
C	1.42913964537742	10.98986341106119	6.42708645627384
C	4.17945847587534	8.91493121518445	9.06214605473780
C	3.40385351488850	11.01887445196498	11.29726394688200
C	3.38080124171111	13.40217544819879	11.57559323842611
H	3.56869049537356	14.28372942089790	12.17316694877018
C	1.23483579414752	13.37891861332588	6.22403699207745
H	0.95042275688708	14.25268883645782	5.65420421721215
C	3.64493465608050	12.10948122507741	12.08747867394326
H	4.04113458130486	11.97332906696979	13.08402948975523
C	1.05951448115702	12.07571005690895	5.69267646416417
H	0.63552459285097	11.92636509000485	4.70897459126794
C	2.64576926012039	12.35633711340315	9.53063157929695
N	2.90911479628018	11.10324521927308	10.03632322975207
N	1.96848800332723	11.05999470798299	7.68848751298594
O	5.27309971798775	8.52903236235188	9.22376784366308
O	1.79449996879801	7.53861260731529	6.79201188720138
C	1.67323280672025	8.63894720591566	10.05760233082548
Mn	2.55005597551028	9.55151116221847	8.81763809656348
O	1.14337708462393	8.03912276827471	10.90842578608735
H	1.30420114842402	9.99629472597657	6.02477092362989
H	3.59971069079651	10.01881371858184	11.65740376803554