Same ligand, three first-row metals: Comparing M-amido bifunctional reactivity (Mn, Fe, Co)

Matthew R. Elsby,[†] Scott Y. H. Kim,[†] Stephan N. Steinmann,*[,‡] and R. Tom Baker*[,†]

[†] Department of Chemistry and Biomolecular Sciences and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

[‡] Univ Lyon, ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie, Lyon, France

rbaker@uottawa.ca; stephan.steinmann@ens-lyon.fr

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I. General Considerations.

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen by standard Schlenk or glovebox techniques. Benzene-d_6 (C_6D_6) was degassed by three freeze-pump-thaws and further dried by running through a short column of activated alumina. Diethyl ether, THF, and hexanes were dried on columns of activated alumina using a J. C. Meyer solvent purification system and stored over 4 Å molecular sieves. ^{1}H NMR spectra were recorded on a Bruker Avance Spectrometer operating at 300 MHz with respect to proton nuclei. ^{1}H NMR spectra were referenced to residual protons (C_6D_6 δ 7.15) with respect to tetramethylsilane. EPR spectra were recorded on a Bruker Elexsys E580 X-band spectrometer. Electron impact mass spectra were recorded on a Kratos Concept Magnetic Sector Mass Spectrometer. Solution state magnetic susceptibility was determined by the Evans method.[1] The compounds **Mn1**[2] and **Fe1**[3] have been previously reported and characterized. $Co[N(SiMe_3)_2]_2$ was prepared according to literature procedures.[4]

II. Synthesis, Reactivity, and Spectroscopy

Synthesis of Co(κ^3-S^{Me}NS^{Me})$_2$ (Co1). Solid $Co[N(SiMe_3)_2]_2$ (0.120 g, 0.267 mmol) and H**L** (0.150g, 0.533 mmol, 2 equiv.) were charged to a 20 mL scintillation vial equipped with a stir bar. The vial was charged with 5 mL of diethyl ether and the purple solution was stirred for 6 h, resulting in the formation of a precipitate. The solution was filtered through a glass frit and the resulting purple solid was washed with diethyl ether (3 x 2 mL), and dried under reduced pressure to yield 0.160 g of **Co1** (92% yield). Crystals suitable for single crystal X-ray diffraction were grown from a concentrated THF solution layered with hexanes at –35 °C. ^{1}H NMR (C_6D_6, 23 °C, 300 MHz): δ -47.81 (br s, 1H); -16.20 (br s, 1H); -1.58 (br s, 1H); 14.23 (br s, 1H); 41.16 (br s, 1H); 46.68 (br s, 3H, S–CH_3); 63.71 (br s, 1H); 111.77 (br s, 3H, S–CH_3). Magnetic susceptibility (Evans method in benzene-d_6, 23 °C): μ_{eff} = 3.9 μ_B. HRMS (EI-QTOF): calcd for $C_{30}H_{32}CoN_2S_4$ m/z 607.07803. Found m/z 607.07634.

Reactions with Hydrogen. The metal complex (**Mn1**, **Fe1**, or **Co1**) (0.008 mg, 0.013 mmol) was dissolved in 0.6 g of THF and added to a J. Young tube. The nitrogen atmosphere was evacuated and 1 atm of H_2 was added through a gas inlet in the glovebox. The solution was monitored for color change and by ^{1}H NMR.

Mn1 - changed color from yellow to light brown. EPR shows new signal (Figure S2)

Fe1 - no color change. ^{1}H NMR showed no change (Figure S4).

Co1 - no color change. ^{1}H NMR showed no change (Figure S5).

Complexes Fe1 and Co1 were then heated under H_2 at 60°C, resulting in formation of black precipitates.

Hydrogenation of benzaldehyde. A solution of **Mn1** (0.011 mg, 0.018 mmol) and benzaldehyde (0.01 g, 0.096 mmol) in 0.6 g of C_6D_6 was added to a J. Young tube. The nitrogen atmosphere was evacuated and 1 atm of H_2 was added through a gas inlet in the glovebox. The solution was monitored for color change and by ^{1}H NMR (Figure S5).

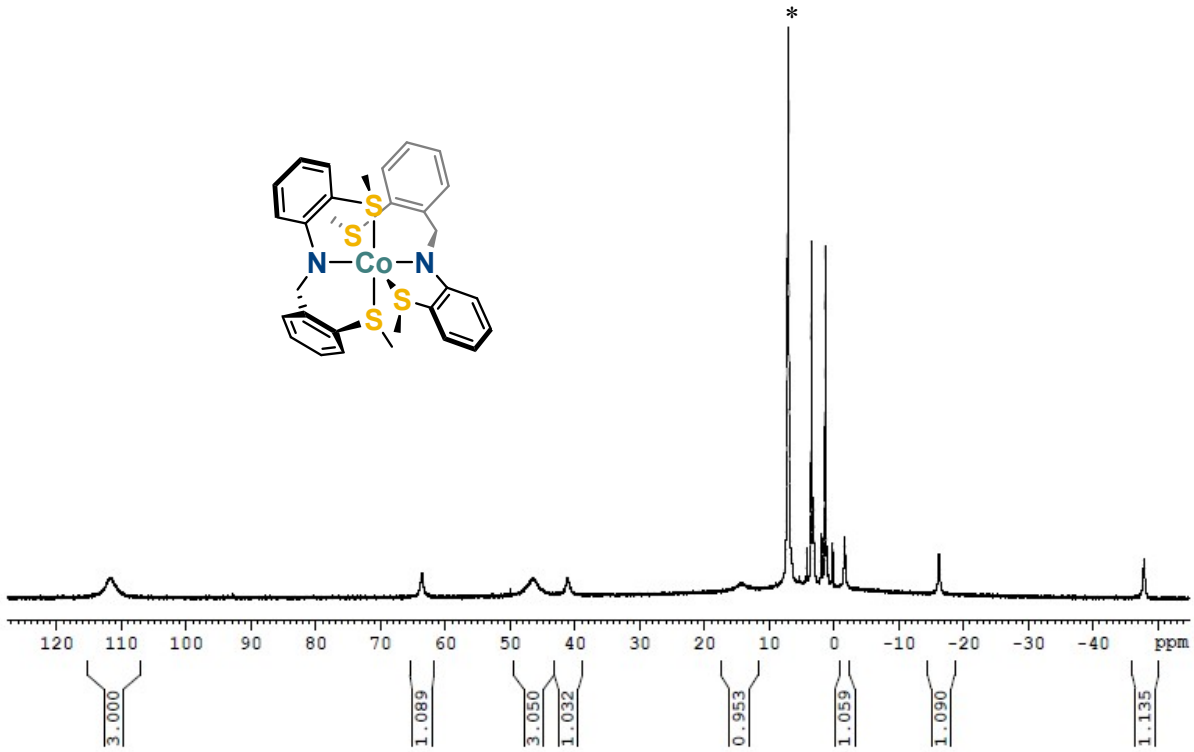


Figure S1. ^{1}H NMR spectrum of Co(κ^3-S^{Me}NS^{Me})$_2$ **(Co1)**. * is C_6D_6.

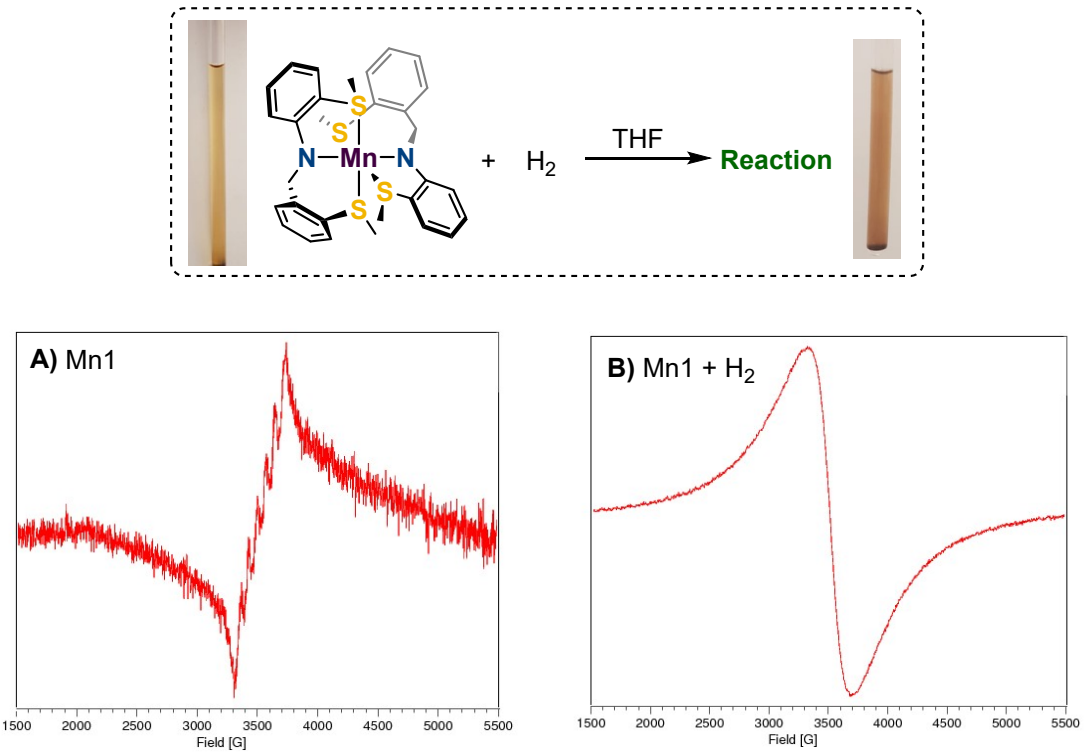


Figure S2. EPR spectra of: A) **Mn1**, and B) **Mn1** + H_2.

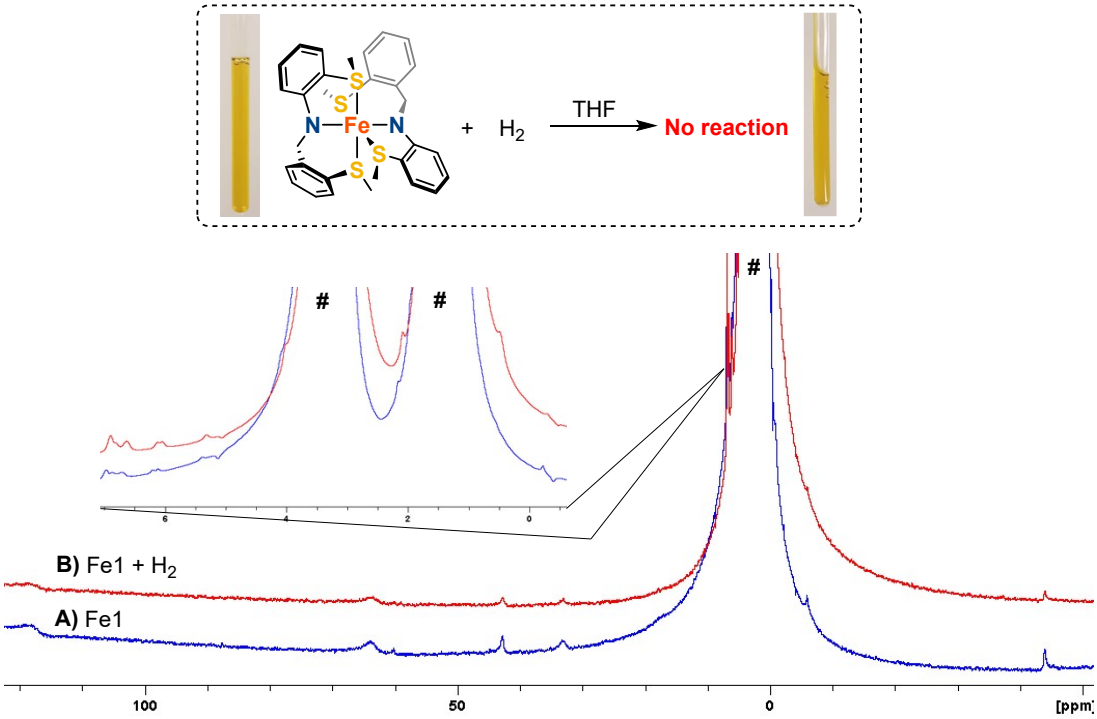


Figure S3. Stacked plot of ^{1}H NMR spectra: A) **Fe1**, and B) **Fe1** + H_2. # is THF.

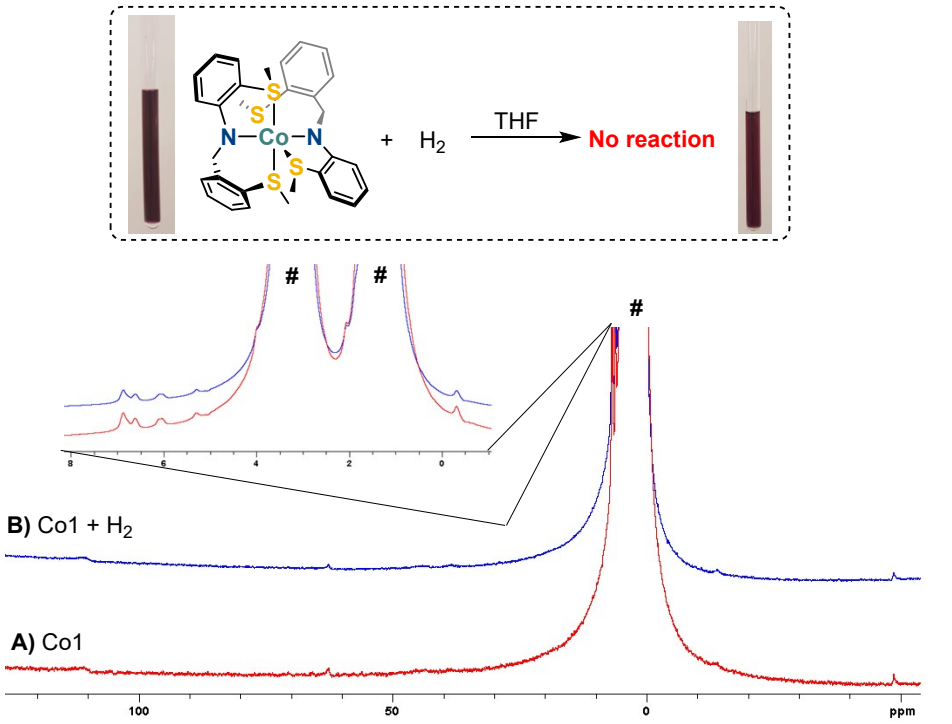


Figure S4. Stacked plot of ^{1}H NMR spectra: A) **Co1**, and B) **Co1** + H_2. # is THF.

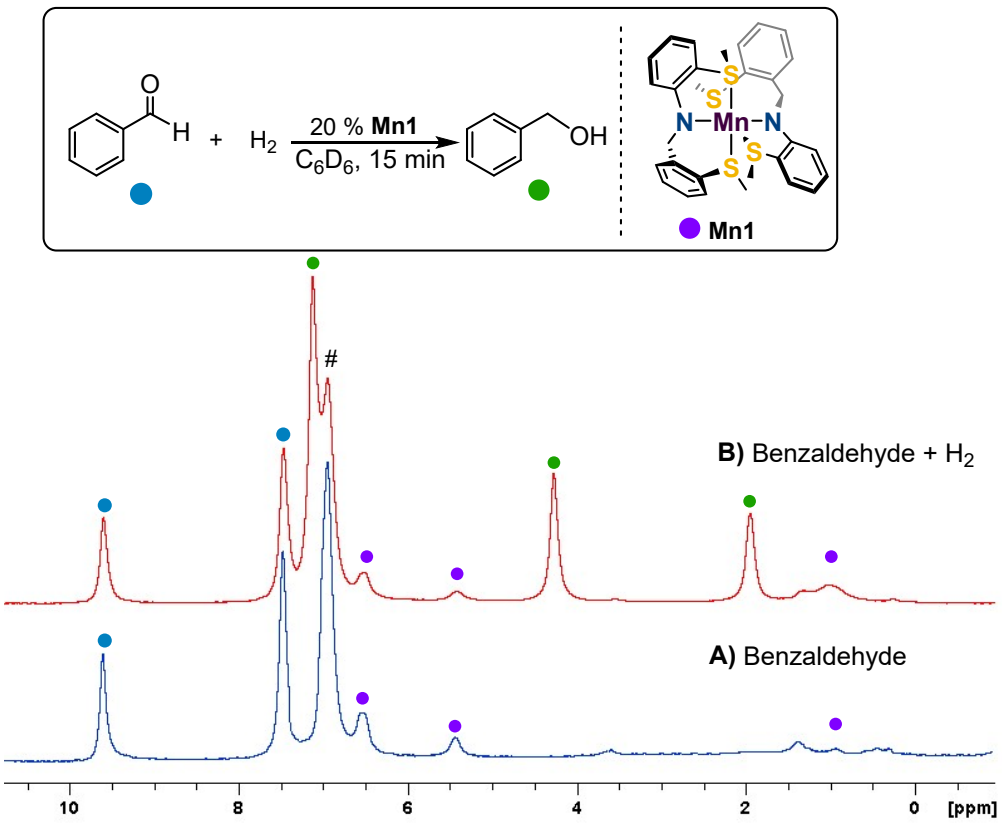


Figure S5. Stacked plot of ^{1}H NMR spectra showing reaction of benzaldehyde and H_2 with 20% loading of **Mn1**.

III. Electrochemistry

Cyclic voltammetry (CV) data were obtained using a VeraSTAT 3 potentiostat, and performed under a nitrogen atmosphere in a sealed one-compartment, three electrode electrochemical cell (Pt working, Pt counter, Ag wire pseudoreference). Tetrabutylammonium hexafluorophosphate in anhydrous DCM was used as supporting electrolyte (0.1 M). All potentials are referenced to internal standard redox potential of Fc/Fc^+ (Fc = ferrocene). An automatic ohmic drop compensation procedure was systematically implemented prior to recording CV data. All the electrodes were purchased from EDAQ. Platinum (Ø = 1 mm) working electrode was polished with 50 micron alumina paste before each recording.

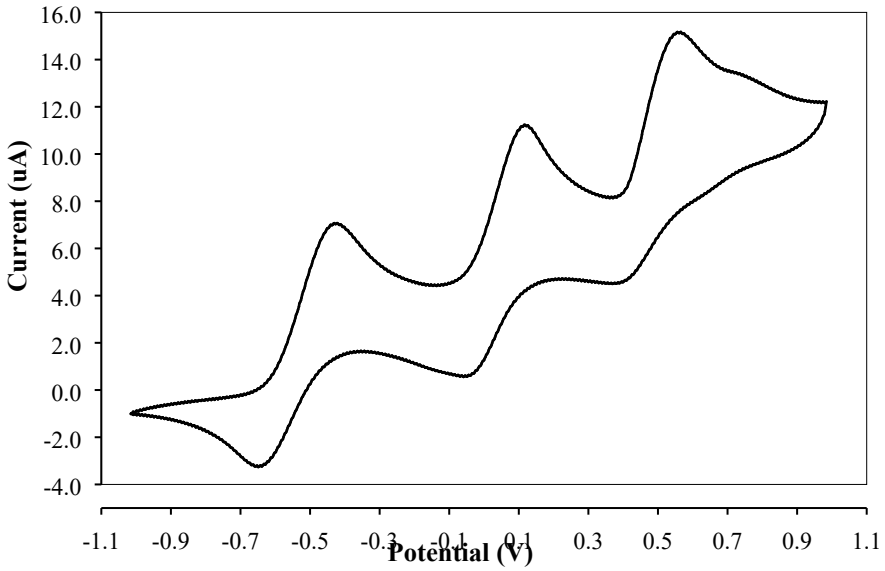


Figure S6. Cyclic voltammogram of **Fe1** referenced to internal standard Fc/Fc^+. Conditions: scan rate, 100 mV/s, electrolyte, 0.1 M $[^nBu_4N][PF_6]$ in DCM, under N_2.

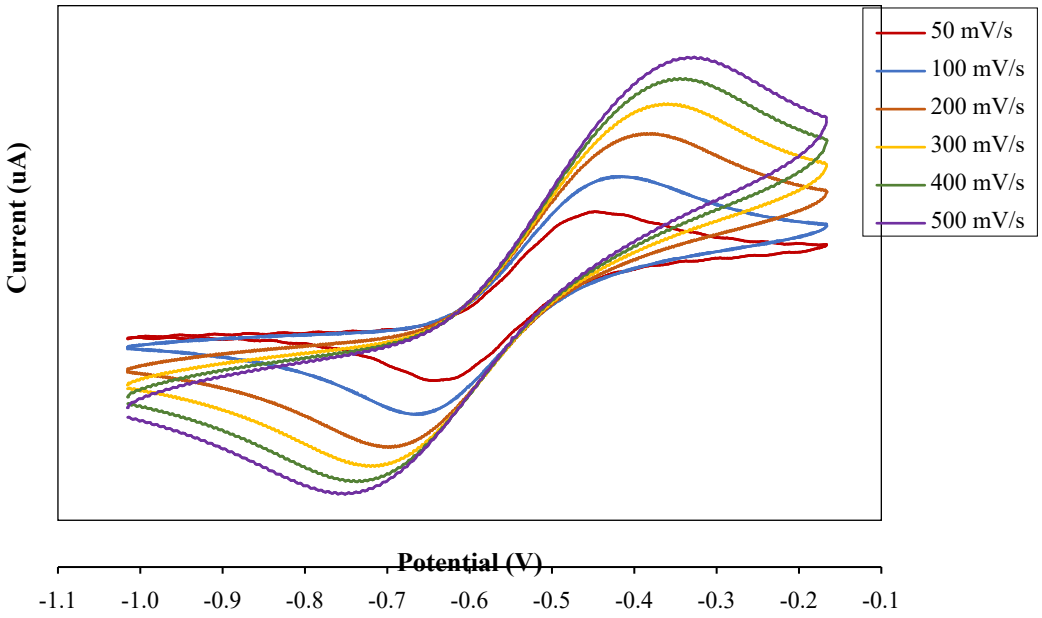


Figure S7. Cyclic voltammograms of **Fe1** recorded at various scan rates (50-500 mV/s) referenced to internal standard Fc/Fc^+. Conditions: scan rate, 100 mV/s, electrolyte, 0.1 M $[^nBu_4N][PF_6]$ in DCM, under N_2.

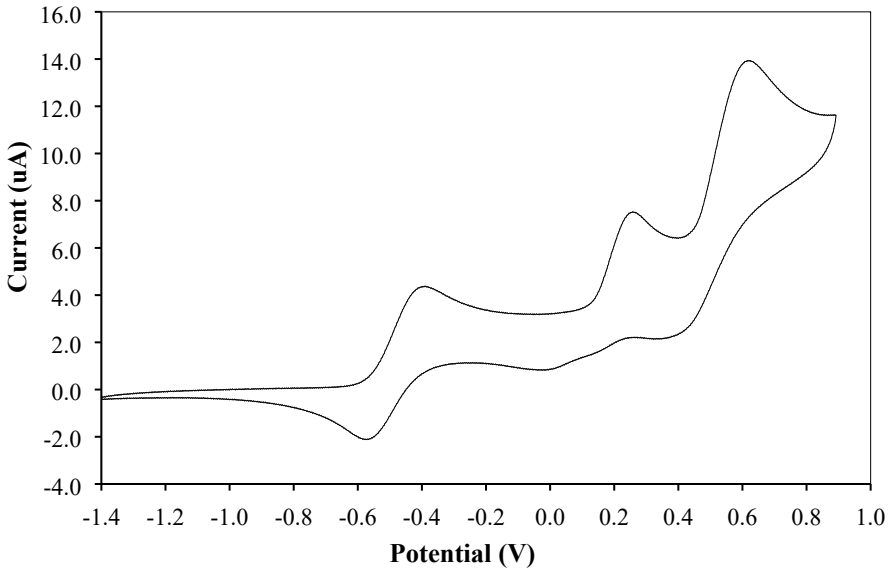


Figure S8. Cyclic voltammogram of **Co1** referenced to internal standard Fc/Fc^+. Conditions: scan rate, 100 mV/s, electrolyte, 0.1 M $[^nBu_4N][PF_6]$ in DCM, under N_2.

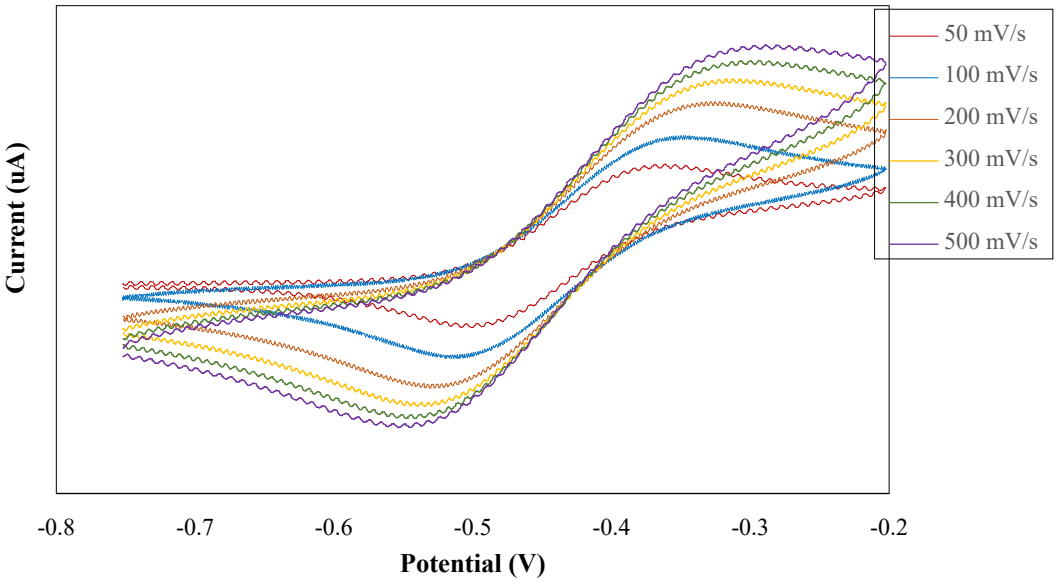


Figure S9. Cyclic voltammograms of **Co1** recorded at various scan rates (50-500 mV/s) referenced to internal standard Fc/Fc^+. Conditions: scan rate, 100 mV/s, electrolyte, 0.1 M $[^nBu_4N][PF_6]$ in DCM, under N_2.

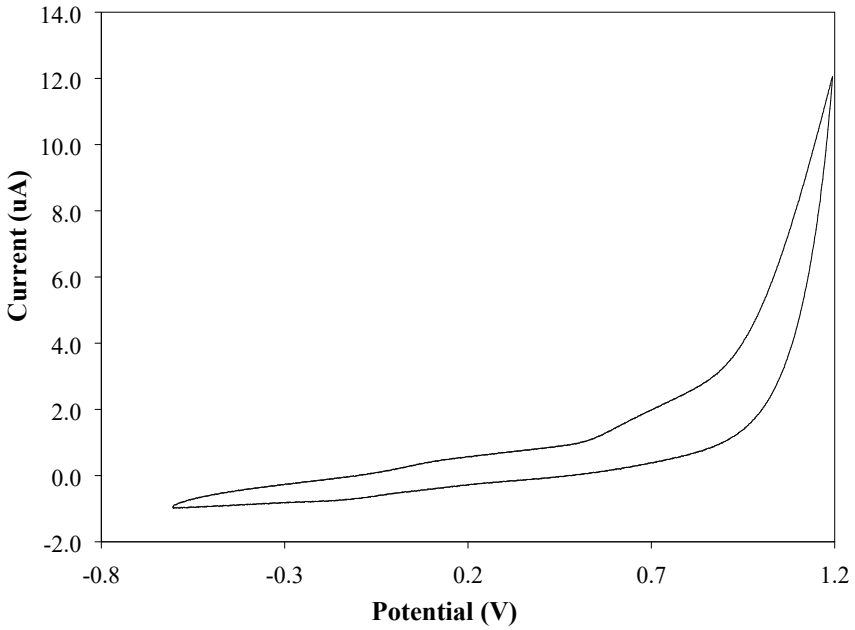


Figure S10. Cyclic voltammogram of **Mn11** referenced to internal standard Fc/Fc^+. Conditions: scan rate, 100 mV/s, electrolyte, 0.1 M $[^nBu_4N][PF_6]$ in DCM, under N_2.

IV. Crystallographic Details

The crystals were mounted on thin glass fibers using paraffin oil. The crystals of **Co1** were cooled to 200 ± 2 K during data collection. The data were collected on a Bruker single-crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. The raw data collection and processing were performed with Bruker APEX II software package.[5] Semi-empirical absorption correction based on equivalent reflections was applied.[6] Systematic absences and unit cell parameters were consistent with monoclinic $P2_1/n$ (#14) for **Co1**. The structure was solved by intrinsic phasing and refined with a full-matrix least-squares procedure based on F^2, using SHELXL.[7] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon atoms were placed in idealized positions.

Refinement details for Co(κ³-S^{Me}NS^{Me})$_2$ (Co1).

The structure was refined without additional restraints / constraints. No disorder was present.

Table S1. Crystal data and structure refinement for Co(κ³-S^{Me}NS^{Me})$_2$ **(Co1)**.

Empirical formula	$C_{30}H_{32}CoN_2S_4$
Formula weight	607.74
Temperature/K	200(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	14.3526(5)
b/Å	10.3708(4)
c/Å	19.8110(6)
α/°	90
β/°	107.760(2)
γ/°	90
Volume/Å^3	2808.29(17)
Z	4
ρ_{calc}g/cm^3	1.437
μ/mm^{-1}	0.932
F(000)	1268.0
Crystal size/mm^3	0.542 × 0.211 × 0.064
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.482 to 56.758
Index ranges	-19 ≤ h ≤ 19, -13 ≤ k ≤ 13, -26 ≤ l ≤ 21
Reflections collected	27717
Independent reflections	7003 [R_{int} = 0.0516, R_{sigma} =

	0.0523]
Data/restraints/parameters	7003/0/338
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.0920
Final R indexes [all data]	R_1 = 0.0783, wR_2 = 0.1076
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.32

Table S2. Bond lengths for Co(κ^3-$S^{Me}NS^{Me}$)$_2$ **(Co1)**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	N9	1.967(2)	C15	C16	1.390(4)
Co1	N29	1.974(2)	C16	S17	1.767(3)
Co1	S2	2.4723(7)	S17	C18	1.795(3)
Co1	S22	2.4780(7)	C21	S22	1.801(3)
Co1	S17	2.6481(7)	S22	C23	1.782(3)
Co1	S37	2.7027(7)	C23	C24	1.376(4)
C1	S2	1.795(3)	C23	C28	1.424(4)
S2	C3	1.772(3)	C24	C25	1.358(4)
C3	C4	1.376(3)	C25	C26	1.386(5)
C3	C8	1.424(3)	C26	C27	1.364(4)
C4	C5	1.373(4)	C27	C28	1.415(4)
C5	C6	1.390(4)	C28	N29	1.363(3)
C6	C7	1.374(4)	N29	C30	1.463(3)
C7	C8	1.409(3)	C30	C31	1.517(3)
C8	N9	1.363(3)	C31	C36	1.391(3)
N9	C10	1.472(3)	C31	C32	1.394(3)
C10	C11	1.511(4)	C32	C33	1.380(4)
C11	C12	1.386(4)	C33	C34	1.374(4)
C11	C16	1.400(4)	C34	C35	1.387(4)
C12	C13	1.386(4)	C35	C36	1.389(3)
C13	C14	1.375(5)	C36	S37	1.772(3)
C14	C15	1.378(5)	S37	C38	1.789(3)

V. DFT Calculations

Computational Details. All calculations were carried out using DFT at the M06L level of theory using the Gaussian 09 package[8] on the WebMO platform.[9] Geometry optimizations and vibrational frequency calculations were carried out using the def2-SVP basis set. The energies of optimized structures were reevaluated by additional single-point energy calculations on each optimized geometry using the def2-TZVP basis set. Additional functionals (PBE-D3, PBE0-D3, B3LYP-D3, TPSS-D3, wB97XD) were evaluated using the def2-TZVP basis set to benchmark the M06L method. Solvation energies were evaluated by a self-consistent reaction field (SCRF) approach.[10-12] Fukui indices were calculated using the Hirshfeld charges from single point energy calculations.[13]

The energy components have been computed with the following protocol. The free energy in solution-phase, G(sol), has been calculated as follows, with T = 298 K to match the experimental room temperature conditions:

$$G_{(sol)} = G_{(gas)} + G_{solv}$$

$$G_{(gas)} = H_{(gas)} - TS_{(gas)}$$

$$H_{(gas)} = E_{(SCF)} + \text{ZPE}$$

$$\Delta E_{(SCF)} = \Sigma\, E_{(SCF)} \text{ for products} - \Sigma\, E_{(SCF)} \text{ for reactants}$$

$$\Delta G_{(sol)} = \Sigma\, G_{(sol)} \text{ for products} - \Sigma\, G_{(sol)} \text{ for reactants}$$

Fukui indices were calculated from the Hirshfeld charges using the following formulae:

Electrophilicity of atom A in molecule M (of N electrons)

$$f_A^+ = P_A(N+1) - P_A(N)$$

Nucleophilicity of atom A in molecule M (of N electrons)

$$f_A^- = P_A(N) - P_A(N-1)$$

Table S3. Comparison of energies for ground state determination for **Mn1**, **Fe1**, and **Co1**.

energy (kcal/mol) of spin state, *I*	Mn1	Fe1	Co1
1/2	5.8		
5/2	0		
1		13.2	
3		0	
1/2			3.6
3/2			0

Table S4. Comparison of key bond lengths (Å) of **Mn1** to DFT optimized structures for ground state determination.

			Length (Å)	
Complex	**Spin**	**Bond**	**DFT**	**Xray**
$Mn(S^{Me}NS^{Me})_2$	6	Mn1-N1	2.118	2.099
		Mn1-N2	2.105	2.112
		Mn1-S1	2.655	2.624
		Mn1-S2	2.755	2.734
		Mn1-S3	2.657	2.647
		Mn1-S4	2.772	2.682
	2	Mn1-N1	2.055	2.099
		Mn1-N2	2.004	2.112
		Mn1-S1	2.305	2.624
		Mn1-S2	2.430	2.734
		Mn1-S3	2.375	2.647
		Mn1-S4	2.334	2.682

Table S5. Comparison of key bond lengths (Å) of **Fe1** to DFT optimized structures for ground state determination.

			Length (Å)	
Complex	**Spin**	**Bond**	**DFT**	**Xray**
$Fe(S^{Me}NS^{Me})_2$	5	Fe1-N1	2.011	2.015
		Fe1-N2	1.965	2.031
		Fe1-S1	2.582	2.5389
		Fe1-S2	2.793	2.7156
		Fe1-S3	2.534	2.5431
		Fe1-S4	2.782	2.7014
	3	Fe1-N1	2.050	2.015
		Fe1-N2	2.035	2.031
		Fe1-S1	2.534	2.5389
		Fe1-S2	2.782	2.7156
		Fe1-S3	2.582	2.5431
		Fe1-S4	2.793	2.7014

Table S6. Comparison of key bond lengths (Å) of **Co1** to DFT optimized structures for ground state determination.

			Length (Å)	
Complex	**Spin**	**Bond**	**DFT**	**Xray**
$Co(S^{Me}NS^{Me})_2$	2	Co1-N1	1.954	1.967
		Co1-N2	1.954	1.974
		Co1-S1	2.421	2.4723
		Co1-S2	2.598	2.6481
		Co1-S3	2.42	2.478
		Co1-S4	2.598	2.7027
	4	Co1-N1	1.989	1.967
		Co1-N2	1.989	1.974
		Co1-S1	2.516	2.4723
		Co1-S2	2.747	2.6481
		Co1-S3	2.516	2.478
		Co1-S4	2.747	2.7027

Table S7. Energies (eV) of alpha and beta frontier orbitals in neutral, cationic, and anionic analogues of **Mn1**.

			Mn1				
			Multiplicity = 6				
Neutral	**Alpha**	**HOMO**	-0.20577	-0.1829	-0.16034	-0.151	-0.14721
		LUMO	-0.04733	-0.04694	-0.04126	-0.03942	-0.03871
	Beta	**HOMO**	-0.21349	-0.2105	-0.20457	-0.16441	-0.15348
		LUMO	-0.05868	-0.05299	-0.04973	-0.04504	-0.04198
			Multiplicity = 5 or 7				
+1 complex	**Alpha**	**HOMO**	-0.23464	-0.2159	-0.1991	-0.18552	
		LUMO	-0.1828	-0.06851	-0.06627	-0.06532	-0.06317
	Beta	**HOMO**	-0.24433	-0.23521	-0.23222	-0.21048	-0.20156
		LUMO	-0.10616	-0.1016	-0.10021	-0.08481	-0.07225
			Multiplicity = 5				
-1 complex	**Alpha**	**HOMO**	-0.16849	-0.13606	-0.1259	-0.12108	-0.09983
		LUMO	-0.01715	-0.0162	-0.01257	-0.01123	-0.00981
	Beta	**HOMO**	-0.02954				
		LUMO	-0.02304	-0.01951	-0.01726	-0.01424	-0.01071

Table S8. Energies (eV) of alpha and beta frontier orbitals in neutral, cationic, and anionic analogues of **Fe1**.

			Fe1				
			Multiplicity = 5				
Neutral	Alpha	HOMO	-0.20411	-0.18387	-0.16242	-0.16111	-0.15603
		LUMO	-0.04478	-0.04332	-0.04167	-0.03922	-0.03609
	Beta	HOMO	-0.12639				
		LUMO	-0.08413	-0.07934	-0.0497	-0.04466	-0.0424
			Multiplicity = 6				
+1 complex	Alpha	HOMO	-0.24194	-0.22649	-0.21467	-0.20253	-0.20035
		LUMO	-0.07327	-0.07	-0.06733	-0.06468	-0.06039
	Beta	HOMO	-0.24727	-0.23642	-0.2322	-0.2137	-0.19057
		LUMO	-0.19375	-0.16315	-0.15288	-0.14785	-0.10282
			Multiplicity = 4				
-1 complex	Alpha	HOMO	-0.13304	-0.12323	-0.11729	-0.10753	-0.08604
		LUMO	-0.01949	-0.01906	-0.01395	-0.01277	-0.00916
	Beta	HOMO	-0.0465	-0.034			
		LUMO	-0.02121	-0.02016	-0.01575	-0.01402	-0.00898

Table S9. Energies (eV) of alpha and beta frontier orbitals in neutral, cationic, and anionic analogues of **Co1**.

			Co1				
			Multiplicity = 4				
Neutral	Alpha	HOMO	-0.20666	-0.18269	-0.16685	-0.15915	-0.15476
		LUMO	-0.04469	-0.04463	-0.04252	-0.03872	-0.03819
	Beta	HOMO	-0.16016	-0.14566			
		LUMO	-0.10652	-0.06207	-0.04811	-0.04291	-0.04238
			Multiplicity = 5				
+1 complex	Alpha	HOMO	-0.2357	-0.21627	-0.21582	-0.20831	-0.20221
		LUMO	-0.07619	-0.07607	-0.06564	-0.06168	-0.06098
	Beta	HOMO	-0.19821				
		LUMO	-0.18471	-0.15567	-0.10996	-0.09717	-0.07202
			Multiplicity = 3				
-1 complex	Alpha	HOMO	-0.12333	-0.11385	-0.11202	-0.09075	-0.07146
		LUMO	-0.02063	-0.01919	-0.01723	-0.01545	-0.01128
	Beta	HOMO	-0.07167	-0.06168	-0.04787		
		LUMO	-0.02075	-0.01986	-0.01775	-0.01623	-0.01056

Table S10. Calculated atomic Hirshfeld charges for **Mn1**, **Mn1**$^{+}$, and **Mn1**$^{-}$.

	Hirshfeld Charges		
Atom	**Mn1**	**Mn1(+)**	**Mn1(-)**
Mn	0.2304	0.282353	0.120311
N	-0.195624	-0.157384	-0.193764
N	-0.199251	-0.132784	-0.19668
S(5)	-0.047066	-0.014378	-0.069367
S(6)	-0.026408	-0.017341	-0.04849
S(5)	-0.053318	-0.012756	-0.096702
S(6)	-0.015684	0.004407	-0.057904
C5(5)-N	0.042347	0.058726	0.040025
C6(5)-S	-0.033822	-0.005598	-0.036593
C12(5)	-0.009868	0.026604	-0.025512
C13(5)	-0.050239	0.029858	-0.071582
C14(5)	-0.023589	0.021344	-0.042151
C15(5)	-0.054436	0.001312	-0.067864
C20-N	0.045082	0.085794	0.028215
C21(6)-C	0.006259	0.006364	-0.002463
C22(6)-S	-0.004044	-0.002646	-0.017405
C28(6)	0.008192	0.020207	-0.019809
C29(6)	0.008767	0.027211	-0.018427
C30(6)	0.002	0.018429	-0.042207
C31(6)	0.006646	0.018905	-0.021004
C38(5)-N	0.050092	0.057669	0.044496
C39(5)-S	-0.033544	-0.019681	-0.040251
C45(5)	0.003664	0.032761	-0.026216
C46(5)	-0.0456	0.011001	-0.074601
C47(5)	-0.009035	0.024292	-0.045908
C48(5)	-0.043501	-0.000424	-0.068489
C1-N	0.041668	0.077249	0.016027
C53(6)-C	0.009821	0.009922	-0.00178
C54(6)-S	-0.002184	-0.002129	-0.026624
C60(6)	0.015743	0.026218	-0.033274
C61(6)	0.016014	0.030501	-0.021144
C62(6)	0.007234	0.022884	-0.056127
C63(6)	0.01438	0.02501	-0.034633

Table S11. Calculated atomic Hirshfeld charges for **Fe1**, **Fe1**$^{+}$, and **Fe1**$^{-}$.

	Hirshfeld Charges		
Atom	**Fe1**	**Fe1(+)**	**Fe1(-)**
Mn	0.245654	0.37401	0.082033
N	-0.184164	-0.147897	-0.18633
N	-0.179387	-0.149218	-0.179683

S(5)	-0.040155	0.012199	-0.082524
S(6)	-0.038665	-0.01593	-0.062657
S(5)	-0.052738	-0.009079	-0.090355
S(6)	-0.030729	-0.011465	-0.044517
C5(5)-N	0.046925	0.052562	0.039333
C6(5)-S	-0.033425	-0.021428	-0.04025
C12(5)	-0.039995	-0.00457	-0.065815
C13(5)	-0.013049	0.020441	-0.042371
C14(5)	-0.042474	0.006768	-0.080468
C15(5)	-0.001104	0.026281	-0.025761
C20-N	0.041001	0.080022	0.008984
C21(6)-C	0.002029	0.003059	-0.001791
C22(6)-S	-0.006521	-0.008816	-0.009228
C28(6)	0.007832	0.025039	-0.019509
C29(6)	-0.002972	0.021933	-0.036068
C30(6)	0.008449	0.028671	-0.017075
C31(6)	0.005684	0.019149	-0.015732
C38(5)-N	0.053053	0.080799	0.025333
C39(5)-S	0.005331	0.006541	0.001377
C45(5)	-0.003796	-0.004046	-0.008113
C46(5)	0.008811	0.023019	-0.007529
C47(5)	0.009949	0.029013	-0.014782
C48(5)	0.000996	0.021963	-0.068489
C1-N	0.006261	0.02022	0.016027
C53(6)-C	0.051341	0.055457	-0.00178
C54(6)-S	-0.035837	-0.027575	-0.026624
C60(6)	0.001715	0.02827	-0.033274
C61(6)	-0.04462	0.002419	-0.021144
C62(6)	-0.008823	0.023479	-0.056127
C63(6)	-0.046452	-0.014751	-0.034633

Table S12. Calculated atomic Hirshfeld charges for **Co1**, **Co 1**$^{+}$, and **Co 1**$^{-}$.

	Hirshfeld Charges		
Atom	**Co1**	**Co1(+)**	**Co1(-)**
Mn	0.15347	0.19826	-0.014792
N	-0.157323	-0.098661	-0.166624
N	-0.15734	-0.098654	-0.166625
S(5)	-0.042628	-0.008568	-0.087835
S(6)	-0.029807	-0.01725	-0.041966
S(5)	-0.042603	-0.008531	-0.087838
S(6)	-0.029817	-0.017262	-0.041965
C5(5)-N	0.053481	0.09302	0.023844
C6(5)-S	0.005229	0.005734	0.005165
C12(5)	-0.004052	-0.002945	-0.004972

C13(5)	0.003091	0.016797	-0.011881
C14(5)	-0.003202	0.016247	-0.025013
C15(5)	0.005593	0.025011	-0.014894
C20-N	0.003421	0.015798	-0.010088
C21(6)-C	0.052399	0.061969	0.040049
C22(6)-S	-0.032568	-0.012749	-0.044242
C28(6)	-0.032568	0.003579	-0.070379
C29(6)	-0.042628	0.032124	-0.043058
C30(6)	-0.038155	0.027541	-0.090012
C31(6)	0.005	0.039814	-0.026087
C38(5)-N	0.053469	0.093016	0.023842
C39(5)-S	0.005226	0.005732	0.004164
C45(5)	-0.004053	-0.002945	-0.004971
C46(5)	0.003414	0.015792	-0.010092
C47(5)	0.005588	0.02501	-0.014892
C48(5)	-0.003209	0.016241	-0.025014
C1-N	0.003086	0.016793	-0.01183
C53(6)-C	0.052395	0.061969	0.040054
C54(6)-S	-0.032576	-0.01275	-0.044239
C60(6)	0.004997	0.039821	-0.026088
C61(6)	-0.038168	0.027548	-0.090006
C62(6)	-0.005396	0.032128	-0.043057
C63(6)	-0.040286	0.003581	-0.070384

Table S13. Calculated Fukui indices for main atoms in **Mn1**.

Atom	Fukui(+)	Fukui(-)
Mn	0.051953	0.110089
N	0.03824	-0.00186
N	0.066467	-0.00257
S(5)	0.032688	0.022301
S(6)	0.009067	0.022082
S(5)	0.040562	0.043384
S(6)	0.020091	0.04222

Table S14. Calculated Fukui indices for main atoms in **Fe1**.

Atom	Fukui(+)	Fukui(-)
Fe	0.128356	0.163621
N	0.036267	0.002166
N	0.030169	0.000296
S(5)	0.052354	0.042369
S(6)	0.022735	0.023992
S(5)	0.043659	0.037617
S(6)	0.019264	0.013788

Table S15. Calculated Fukui indices for main atoms in **Co1**.

Atom	Fukui(+)	Fukui(-)
Co	0.04479	0.168262
N	0.058662	0.009301
N	0.058686	0.009285
S(5)	0.03406	0.045207
S(6)	0.012557	0.012159
S(5)	0.034072	0.045235
S(6)	0.012555	0.012148

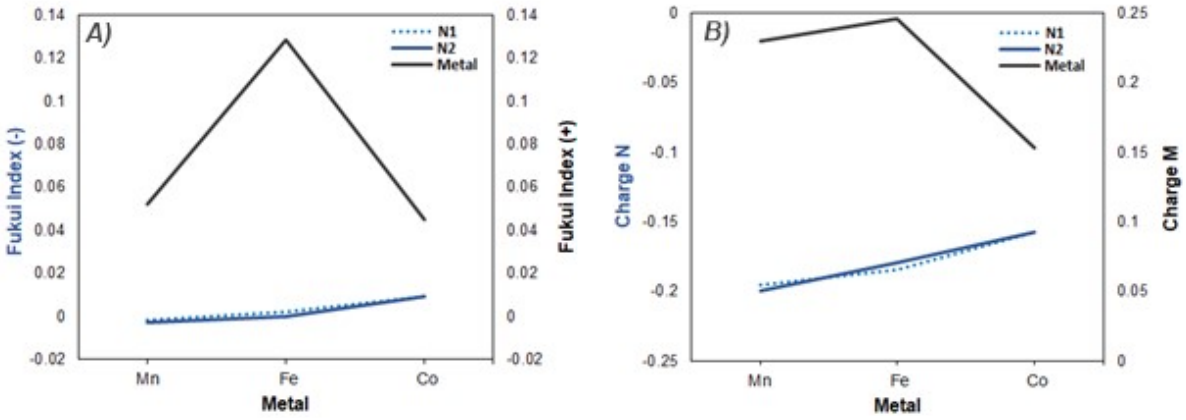


Figure S11. A) Chart of calculated Fukui (-/+) indices for both amido donors and metal of **Mn1**, **Fe1**, and **Co1**; B) Calculated Hirshfeld charges for both amido donors and metals

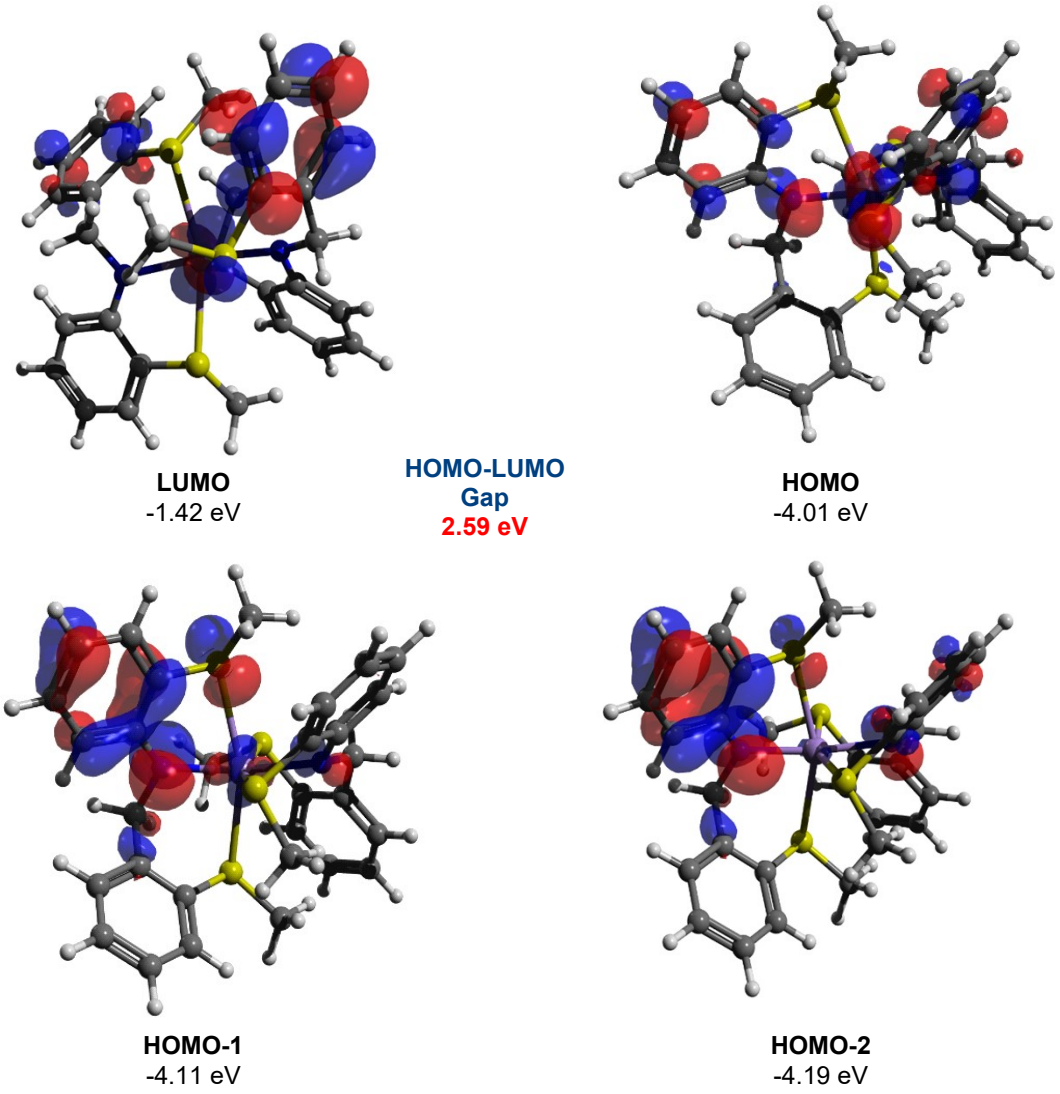


Figure S12. Frontier orbitals and energies of **Mn1**.

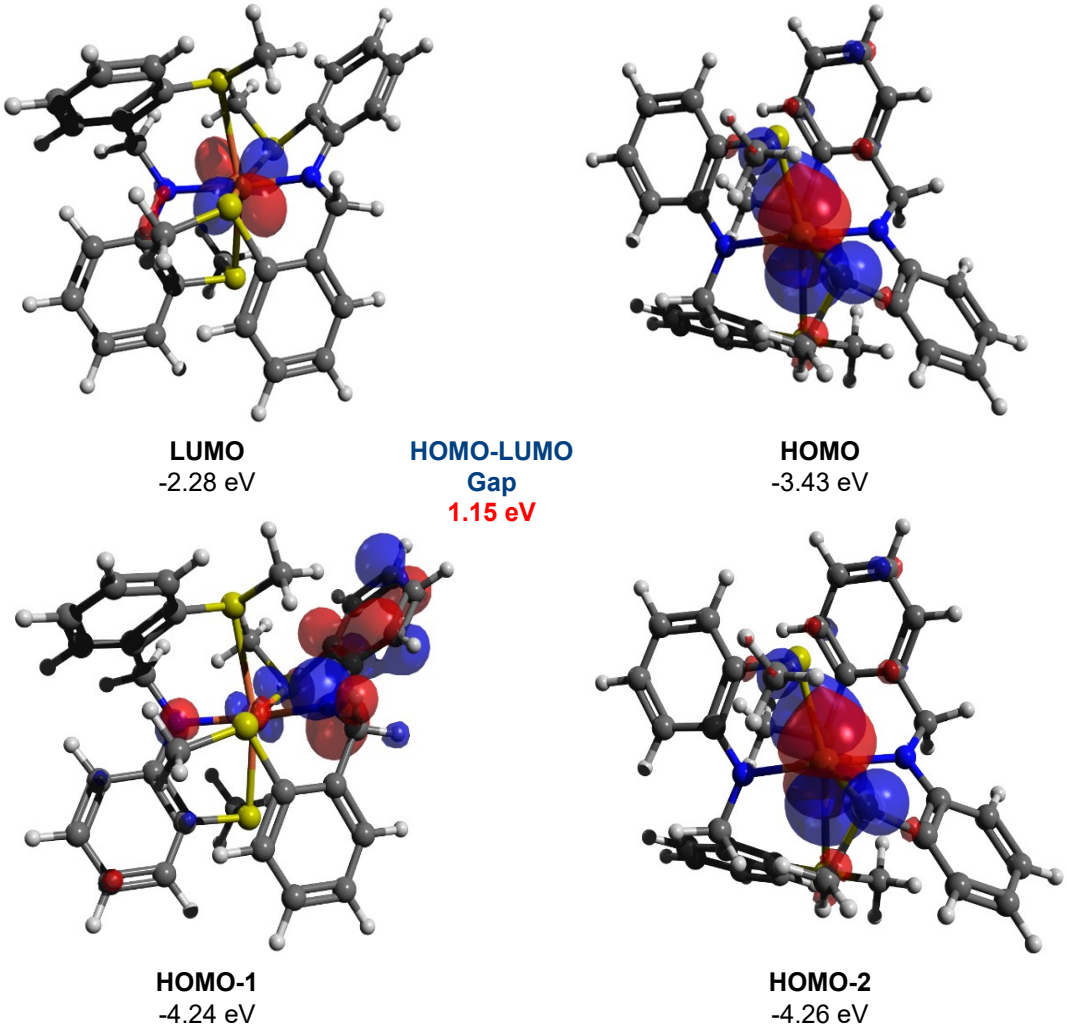


Figure S13. Frontier orbitals and energies of **Fe1**.

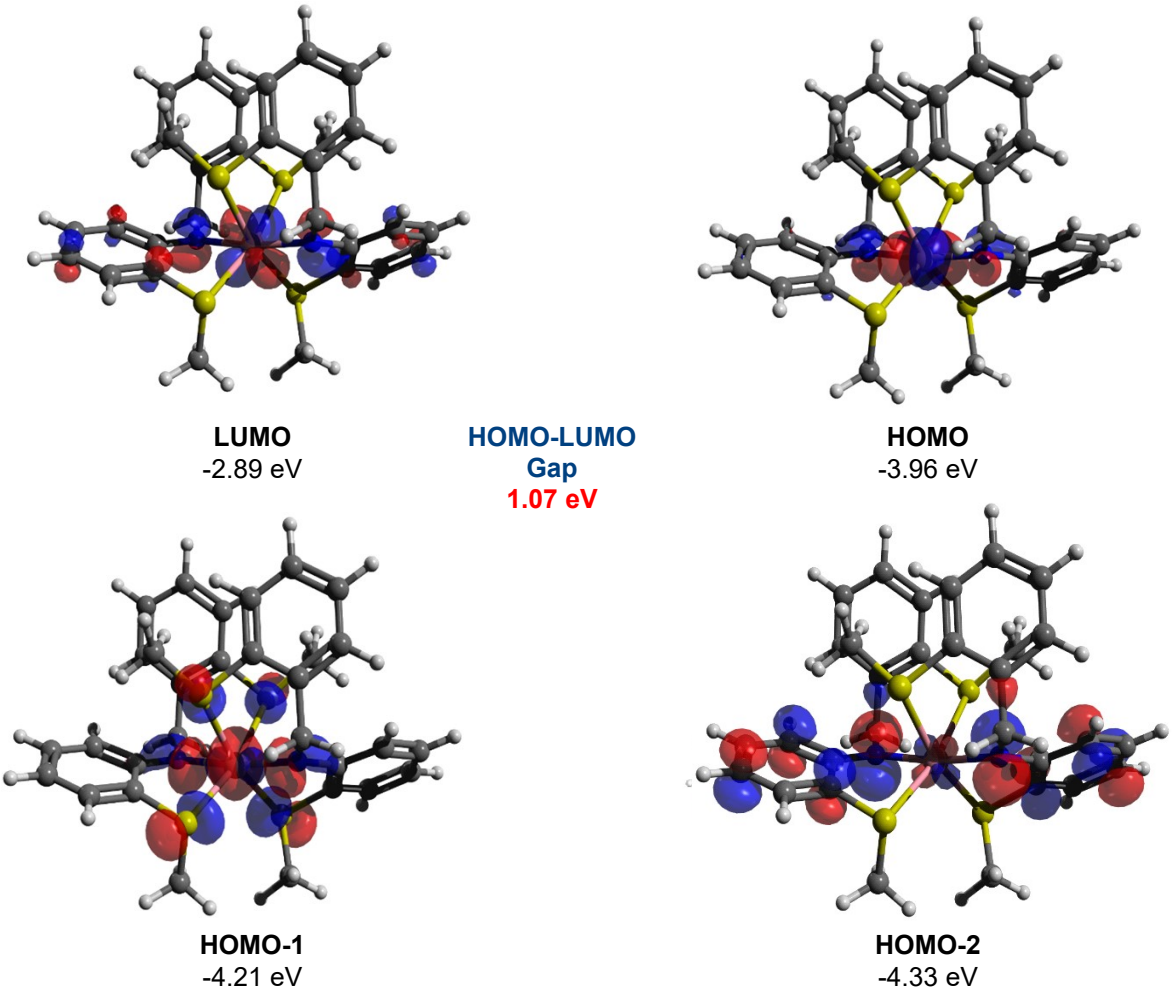
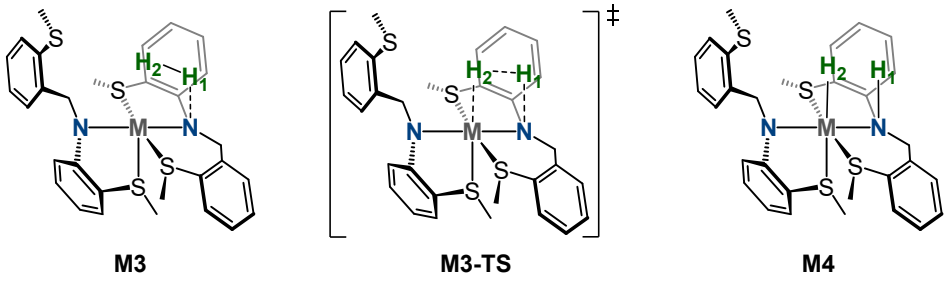


Figure S14. Frontier orbitals and energies of **Co1**.



Bond Lengths (Angstoms)

	H_1-H_2	$N-H_1$	$M-H_2$	H_1-H_2	$N-H_1$	$M-H_2$	H_1-H_2	$N-H_1$	$M-H_2$
[Mn]	0.760	2.621	3.883	1.063	1.293	1.902	1.837	1.026	1.723
[Fe]	0.760	2.589	3.758	1.109	1.232	1.909	1.704	1.032	1.715
[Co]	0.761	2.728	3.653	0.871	1.582	1.861	1.687	1.032	1.645

Figure S15. Key bond lengths in calculated complexes **M3**, **M3-TS**, and **M4** for the Mn, Fe, and Co analogues.

Table S16. Energies (in Hartree) for all DFT compounds, intermediates, and transition states: E_{DZ} and thermal corrections were calculated at the M06-L/def2-SVP level of theory; E_{TZ} energy calculations were performed on the M06-L/def2-SVP at the M06-L/def2-TZVP level of theory with incorporation of solvation energy using the self-consistent reaction field (SCRF) for tetrahydrofuran.

			Thermal Corrections (T = 298.15 K, p = 1atm)		
Compound	E_{TZ}	E_{DZ}	E_{zpe}	H	G
H_2	-1.167912861	-1.16791286	0.009919	0.013224	-0.001571
Mn1 (*S*=1/2)	-4016.076284	-4016.067541	0.549369	0.58664	0.482914
Mn1 (*S*=5/2)	-4016.128128	-4014.110838	0.546559	0.58501	0.474914
Mn2	-4016.119331	-4014.099311	0.547363	0.586029	0.474497
Mn3	-4017.289724	-4015.263558	0.557822	0.599921	0.480409
Mn3-TS	-4017.258643	-4015.238565	0.55871	0.598427	0.484071
Mn4	-4017.278808	-4015.253371	0.563279	0.6043463	0.488097
Fe1 (*S*=1)	-4128.804241	-4126.762886	0.547164	0.584844	0.480351
Fe1 (*S*=2)	-4128.828097	-4126.791944	0.546588	0.584821	0.477596
Fe2	-4128.822619	-4126.784552	0.546078	0.584724	0.474418
Fe3	-4129.99799	-4127.953776	0.559685	0.600485	0.487135
Fe3-TS	-4129.961631	-4127.920483	0.560068	0.598964	0.489185
Fe4	-4129.973566	-4127.092979	0.564984	0.604338	0.492823
Co1 (*S*=1/2)	-4247.876133	-4245.817702	0.547716	0.58536	0.480634
Co1 (*S*=3/2)	-4247.883557	-4245.827935	0.547338	0.585275	0.478872
Co2	-4247.875558	-4245.818415	0.546294	0.584742	0.475801
Co3	-4249.04683	-4246.984529	0.559947	0.60047	0.488643
Co3-TS	-4248.999398	-4246.939243	0.561543	0.600484	0.488457
Co4	-4249.028728	-4246.965735	0.565274	0.604576	0.492775

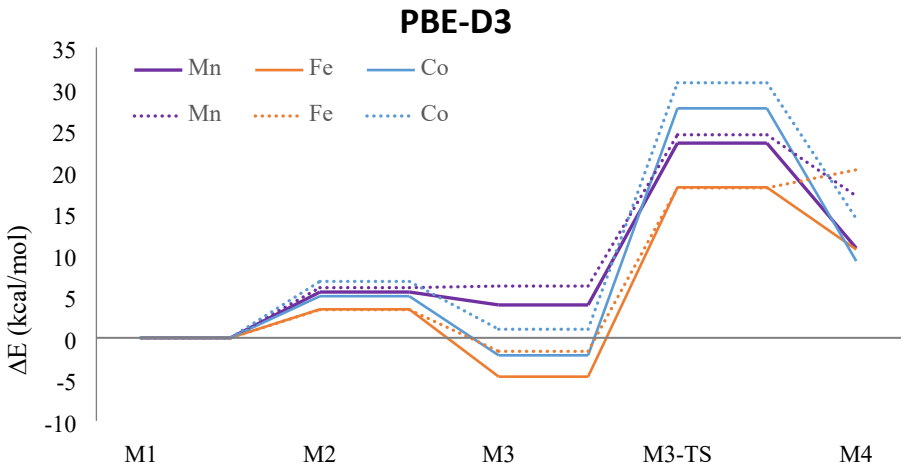


Figure S16. Reaction profiles comparing M06L functional (solid line) vs. PBE-D3 (dotted line).

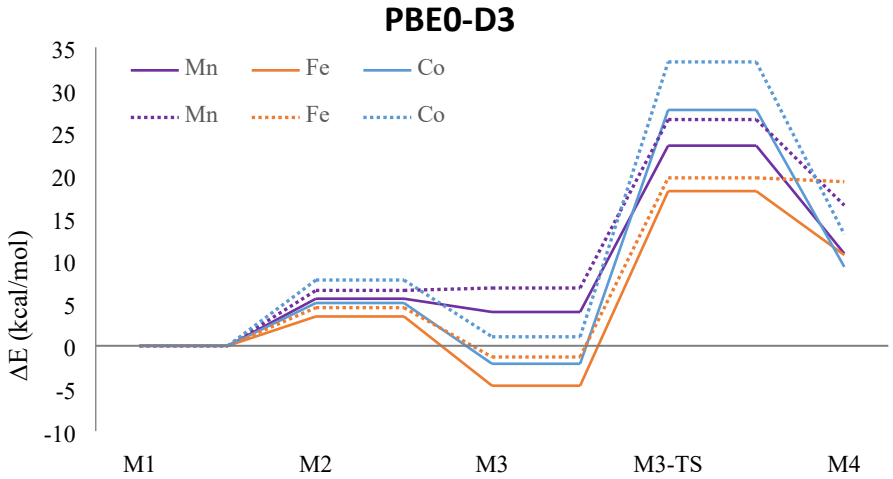


Figure S17. Reaction profiles comparing M06L functional (solid line) vs. PBE0-D3 (dotted line).

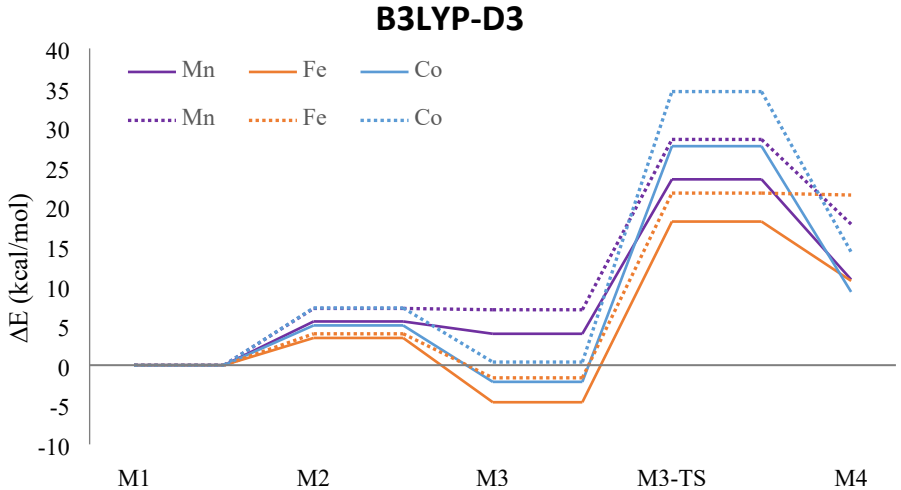


Figure S18. Reaction profiles comparing M06L functional (solid line) vs. B3LYP-D3 (dotted line).

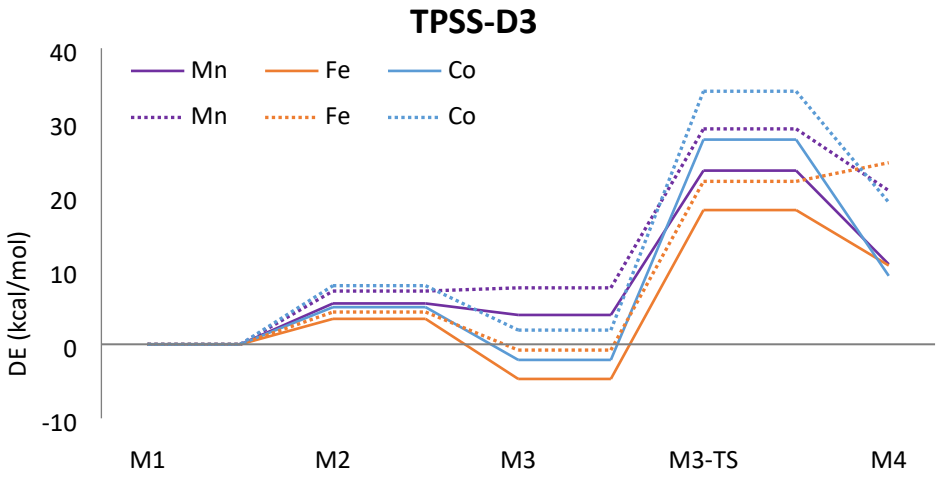


Figure S19. Reaction profiles comparing M06L functional (solid line) vs. TPSS-D3 (dotted line).

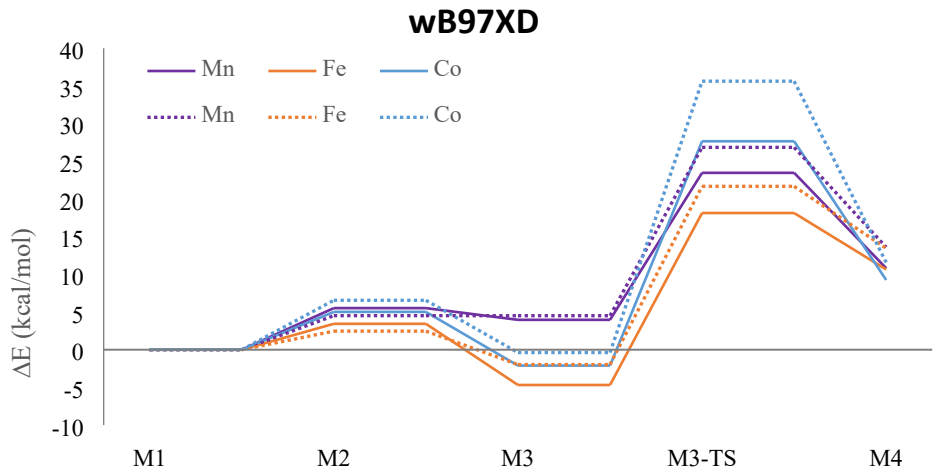


Figure S20. Reaction profiles comparing M06L functional (solid line) vs. xB97XD (dotted line).

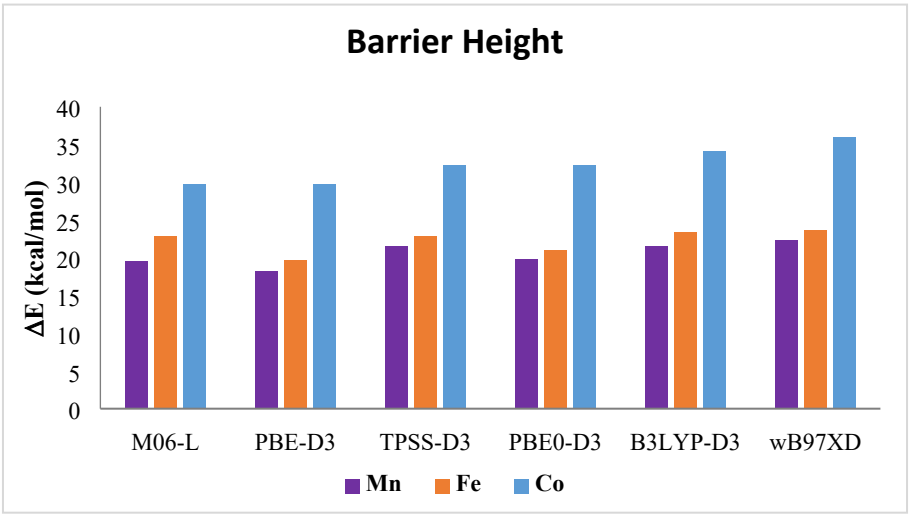


Figure S21. Overall reaction barriers benchmarking different functionals.

Table S17. Cartesian coordinates in Å for optimized structures.

Dihydrogen

H 0.00000000 0.00000000 0.00000000

H 0.00000000 0.00000000 -0.74392600

Mn1 – (*S* = 1/2)

C 0.00000000 0.00000000 0.00000000

N -1.34137600 -0.09425700 0.55620600

Mn -2.81800800 -1.36531200 -0.09824900

N -4.35624100 -2.46198500 -0.76637800

C -5.54971700 -1.84347500 -1.03566700

C -5.51955900 -0.47563500 -1.40367500

S -3.88894200 0.20628200 -1.52098300

C -4.15200600 1.91396800 -0.99443800

H -3.17427300 2.33695200 -0.77478200

H -4.61540200 2.48089900 -1.79868800

H -4.77047800 1.94869500 -0.10059700

C -6.66400500 0.23818300 -1.69872300

C -7.91003200 -0.37266800 -1.62851600

C -7.97372600 -1.71004400 -1.27067400

C -6.82867500 -2.43270400 -0.98051000

H -6.93114800 -3.46407800 -0.67496600

H -8.93570300 -2.20324100 -1.20034700

H -8.80726500 0.18960400 -1.84686400

H -6.58755200 1.27943800 -1.98630900

C -4.38857600 -3.90242100 -0.57408800

C -4.45760600 -4.32024900 0.86951700

C -3.35708300 -4.08421500 1.70740800

S -1.97198700 -3.27437500 0.94472200

C -0.88844300 -2.97102500 2.34814400

H -0.03586500 -2.43170100 1.94818500

H -1.37326500 -2.35371700 3.10161700

H -0.54933800 -3.90940600 2.78162200

C -3.38721900 -4.48270300 3.03828800

C -4.51816500 -5.10026000 3.55272600

C -5.61667900 -5.32787300 2.74117100

C -5.57465600 -4.94276200 1.40867900

H -6.42392200 -5.13764000 0.76358600

H -6.49952300 -5.81035800 3.13952100

H -4.53342900 -5.40299600 4.59191500

H -2.53889600 -4.30915700 3.68557000

H -3.46593000 -4.31811000 -0.99545700

H -5.20563300 -4.37300300 -1.12895300

C -1.75110600 0.99944000 1.24707000

C -3.02068500 0.98142200 1.89141700

S -4.06408700 -0.41489000 1.59255100

C -4.16629400 -1.17717100 3.23758600

H -4.84260600 -2.02558500 3.16061100

H -3.19442200 -1.51246500 3.59085200

H -4.57883900 -0.44996800 3.93329800

C -3.49387000 2.05188600 2.63304100

C -2.73607100 3.20057600 2.79019100

C -1.50351200 3.26362600 2.14858000

C -1.02371600 2.21146900 1.39428700

H -0.07779100 2.33601900 0.88758300

H -0.90628200 4.16493100 2.22309500

H -3.10551300 4.03077700 3.37558800

H -4.47938000 1.98205500 3.08046700

C 0.67154400 -1.31083400 -0.29779500

C 0.15773100 -2.22590300 -1.22730300

S -1.35425800 -1.74921500 -2.00015600

C -1.84138700 -3.20700800 -2.92005300

H -2.86733700 -3.02411900 -3.23086400

H -1.21028300 -3.34558600 -3.79521100

H -1.81185300 -4.09219200 -2.28812100

C 0.81764700 -3.42019400 -1.49149200

C 2.00170700 -3.71933900 -0.83514000

C 2.53334000 -2.82366800 0.07646000

C 1.86816300 -1.63360400 0.33249600

H 2.27694500 -0.92955200 1.04854400

H 3.46047700 -3.04774200 0.58723700

H 2.50673800 -4.65319800 -1.04541400

H 0.41589200 -4.12143900 -2.20936100

H 0.66307200 0.53167500 0.68981800

H -0.00277800 0.60622500 -0.92616900

Mn1 – (*S* = 5/2)

C 0.00000000 0.00000000 0.00000000

N -1.23171100 -0.46820900 0.60059100

Mn -2.42587200 -2.01099600 -0.22446700

N -3.78292400 -3.34477200 -1.12532500

C -5.09593400 -2.94721800 -1.20231900

C -5.40726600 -1.56738300 -1.42000800

S -4.02659200 -0.47035900 -1.68114800

C -4.63060400 1.09959300 -1.03168900

H -3.75276000 1.73159800 -0.84548900

H -5.28530100 1.60187000 -1.75578000

H -5.16134000 0.94545900 -0.08344400

C -6.71605200 -1.10276500 -1.50168800

C -7.79712400 -1.97535400 -1.37266400

C -7.53154700 -3.32898400 -1.18452500

C -6.22512300 -3.79963400 -1.10013800

H -6.07600600 -4.86459000 -0.93243200

H -8.35638200 -4.04031600 -1.08870100

H -8.82021000 -1.59991500 -1.42964800

H -6.89918600 -0.04103300 -1.68364800

C -3.53306600 -4.77503900 -1.10077800

C -3.44514600 -5.38809100 0.28226000

C -2.28737600 -5.20477600 1.06913900

S -0.95358800 -4.29700100 0.31451300

C 0.30023800 -4.22633000 1.59479500

H 1.13181300 -3.65147600 1.17015500

H -0.06060900 -3.71760800 2.49761600

H 0.65850300 -5.23352900 1.84412700

C -2.19837900 -5.74121200 2.35677100

C -3.26557500 -6.46767300 2.88418300

C -4.40860300 -6.67605400 2.11940400

C -4.48331400 -6.14464500 0.83235800

H -5.37329800 -6.33575900 0.22817200

H -5.24180700 -7.25737000 2.51937900

H -3.19005600 -6.87888900 3.89328000

H -1.29758800 -5.60469600 2.95769500

H -2.57114900 -4.97106400 -1.61224600

H -4.28003500 -5.33302500 -1.69232300

C -1.99147700 0.50483500 1.18069800

C -3.17325700 0.15850300 1.91975700

S -3.63376600 -1.55509500 2.09508400

C -2.30735500 -2.12694500 3.19672500

H -2.38785500 -3.21961900 3.27515100

H -1.33664300 -1.84123500 2.76699400

H -2.42744400 -1.68016400 4.19151900

C -3.98944200 1.12400200 2.50585900

C -3.69109200 2.48198700 2.39945500

C -2.53891800 2.84979200 1.70301100

C -1.71239600 1.90044700 1.11285700

H -0.83890300 2.24751600 0.55928200

H -2.27673500 3.90759200 1.60764700

H -4.33724900 3.23125200 2.85978400

H -4.87382300 0.79280800 3.05685600

C 0.96877200 -1.10159700 -0.34366600

C 0.74622200 -1.98770200 -1.41965900

S -0.72564000 -1.72171900 -2.37295200

C -0.91980800 -3.24731900 -3.30211300

H -1.95990900 -3.24524700 -3.65175600

H -0.24323500 -3.29332100 -4.16522400

H -0.76841600 -4.11980300 -2.65213100

C 1.66703300 -2.99923200 -1.71426000

C 2.83198200 -3.12707400 -0.95937400

C 3.08123500 -2.24842600 0.09233100

C 2.14842300 -1.25486100 0.39109200

H 2.33259300 -0.56762700 1.22200700

H 3.99623200 -2.33686800 0.68183300

H 3.54872900 -3.91362000 -1.20621600

H 1.49040700 -3.68179700 -2.54744800

H 0.52895700 0.69126400 0.68354600

H -0.18616600 0.60643500 -0.91929800

Mn2

Mn 0.00000000 0.00000000 0.00000000

N 1.28900700 -1.27904900 -0.92457600

C 2.09261900 -2.17557300 -0.29090500

C 2.19978800 -2.15405200 1.13761900

S 1.39145800 -0.85856800 2.05597200

C 2.58172500 0.50139400 1.80036700

H 2.75149200 0.66331600 0.72459200

H 2.16615800 1.41292400 2.25102000

H 3.53308200 0.25427200 2.28762900

C 2.94860100 -3.09444200 1.84477900

C 3.65536700 -4.09118600 1.17841800

C 3.60226900 -4.11466200 -0.21744700

C 2.85770500 -3.18779000 -0.93251700

H 2.84079100 -3.26289000 -2.02019800

H 4.15579200 -4.88093100 -0.76763200

H 4.24087800 -4.82507400 1.73437200

H 2.97954600 -3.02696900 2.93539300

C 1.38794600 -1.13480600 -2.36493900

H 0.42775500 -0.73825200 -2.74657600

H 1.52020400 -2.09389300 -2.89546900

C 2.51027600 -0.19041200 -2.72567900

C 2.39213200 1.19691900 -2.48717200

S 0.79950200 1.80573600 -1.96373700

C 1.14960100 3.47236600 -1.39168500

H 0.20613700 3.84768500 -0.97451700

H 1.92145100 3.47754500 -0.60987200

H 1.44551200 4.12685300 -2.22136700

C 3.47693200 2.04920100 -2.70805500

C 4.68857500 1.53573800 -3.17127400

C 4.81635400 0.17533600 -3.42973400

C 3.73047000 -0.67085800 -3.20681200

H 3.82738200 -1.74116800 -3.40759700

H 5.75922700 -0.23041700 -3.80220200

H 5.52930700 2.21326000 -3.33668300

H 3.38770300 3.12250100 -2.53275500

N -1.98593400 0.18932100 -0.41718900

C -2.50269600 1.44423500 -0.51651300

C -1.93356300 2.52082000 0.24119900

S -0.59677900 2.19189300 1.37585900

C -1.46116700 1.29768200 2.70267800

H -2.19807200 1.95785500 3.17611600

H -1.95570800 0.40660100 2.29212700

H -0.71294800 0.99133600 3.44480900

C -2.39666300 3.83359100 0.12888800

C -3.44701300 4.15019600 -0.72711300

C -4.04818900 3.11347000 -1.44728700

C -3.60401600 1.80348600 -1.34375100

H -4.11750000 1.02762200 -1.91499600

H -4.89194600 3.33212800 -2.10772800

H -3.80368400 5.17781200 -0.81350700

H -1.92056600 4.61022900 0.73460000

C -2.60052700 -0.85220800 -1.20274500

H -1.91495000 -1.71995400 -1.23723700

H -2.69908700 -0.56059000 -2.26916200

C -3.93915300 -1.35636700 -0.70843500

C -4.66869200 -2.31669300 -1.43972000

S -4.04660800 -2.96323600 -2.98791600

C -4.60770500 -1.66851100 -4.12289800

H -4.16168100 -0.69060900 -3.89033400

H -4.28449600 -1.96330100 -5.12920500

H -5.70220300 -1.57884000 -4.11701700

C -5.87856800 -2.81452900 -0.94351600

C -6.39006600 -2.35708200 0.26908200

C -5.68569400 -1.39511800 0.98828600

C -4.47501500 -0.90514300 0.50186500

H -3.92171400 -0.15327700 1.06939100

H -6.07871200 -1.02243200 1.93751400

H -7.33675200 -2.75043000 0.64689000

H -6.41571300 -3.56881300 -1.52407100

Mn3

Mn 0.00000000 0.00000000 0.00000000

N -2.03448400 -0.15074900 -0.18597500

C -2.93211600 0.87004100 -0.26744600

C -2.49123100 2.23088400 -0.25437400

S -0.75457500 2.57676500 -0.09565000

C -0.56677700 2.58743600 1.71830000

H -1.08073000 3.45791200 2.14493000

H -0.98423000 1.66925200 2.15623800

H 0.50560100 2.64933500 1.94661500

C -3.37962000 3.29886000 -0.38394000

C -4.74914000 3.08088100 -0.50623400

C -5.21193200 1.76263200 -0.48812000

C -4.34008900 0.68924200 -0.36873500

H -4.75414600 -0.32061400 -0.33125600

H -6.28479400 1.56352700 -0.56165800

H -5.43949400 3.92013500 -0.60434900

H -2.97817800 4.31578800 -0.38452400

C -2.53703100 -1.49107400 -0.34234900

H -1.71759300 -2.13866200 -0.70203100

H -3.28564900 -1.55188100 -1.15935000

C -3.07561200 -2.17033900 0.89454200

C -3.32835000 -3.55921300 0.89372000

S -3.13449600 -4.53348900 -0.59446600

C -4.67385900 -4.11425100 -1.45509400

H -4.74666300 -3.04135100 -1.68385600

H -4.67248700 -4.67025900 -2.40106100

H -5.55179000 -4.41903700 -0.87039700

C -3.68484400 -4.21114300 2.07902700

C -3.82156400 -3.49632200 3.26765700

C -3.60871300 -2.11934100 3.26876400

C -3.23597700 -1.46871200 2.09377900

H -3.03492400 -0.39400500 2.10057600

H -3.72243000 -1.54719700 4.19278600

H -4.10000600 -4.01512400 4.18775900

H -3.85563700 -5.29020100 2.05648600

N 1.16149300 -1.34785500 1.01365500

C 2.52265400 -1.38511700 1.05733800

C 3.28528100 -0.23977400 0.67232500

S 2.41368100 1.21277900 0.12146000

C 2.86328300 1.31086200 -1.63419700

H 2.66582800 0.35785800 -2.14220700

H 2.25020300 2.10604800 -2.07858600

H 3.92219900 1.57515900 -1.74698400

C 4.67707300 -0.21689100 0.75242200

C 5.38734200 -1.34022200 1.16808500

C 4.66904800 -2.48573800 1.51932500

C 3.28208300 -2.51458500 1.46729800

H 2.76497500 -3.43564000 1.74208900

H 5.20331600 -3.38312900 1.84324700

H 6.47719800 -1.32048500 1.21819400

H 5.20778000 0.69838100 0.47517200

C 0.44639300 -2.55607300 1.32212400

H -0.61647800 -2.29216700 1.49007900

H 0.75607800 -2.99695100 2.29140500

C 0.48042300 -3.65642600 0.28036800

C 0.57925100 -3.44949600 -1.10966500

S 0.73481400 -1.81603800 -1.85346200

C -0.38604000 -1.97270300 -3.26901000

H -0.66665400 -0.95360900 -3.56328900

H 0.09105100 -2.46549800 -4.12530000

H -1.29004500 -2.52282400 -2.97417800

C 0.56390800 -4.54285600 -1.98642800

C 0.41109100 -5.84008400 -1.51198900

C 0.29078400 -6.06074200 -0.14218400

C 0.33525000 -4.97762500 0.72708200

H 0.24778500 -5.14385500 1.80579700

H 0.17060400 -7.07332200 0.24845900

H 0.39493500 -6.67507000 -2.21552500

H 0.67239500 -4.37749200 -3.05995900

H -0.33541600 -0.34895600 3.85311100

H 0.08139000 -0.44685000 3.22527000

Mn3 – TS

C 0.00000000 0.00000000 0.00000000

S 0.72402100 -0.04599100 1.67270600

C -0.65846400 0.45711500 2.66945200

C -1.04705600 1.83703000 2.66597500

N -0.32535900 2.74059900 1.95939800

Mn 1.56162300 2.45363100 1.17032400

C -0.69637500 4.12984800 2.02086800

H 0.21564400 4.74840300 1.89894900

H -1.06549000 4.41481900 3.02914800

C -1.68522900 4.59536300 0.97958000

C -1.74210700 5.94572300 0.57048600

S -0.63948400 7.20473600 1.18211600

C -0.86950300 7.16658900 2.97809300

H -1.91470800 6.94399800 3.22913300

H -0.20214900 6.45059000 3.48026400

H -0.63286800 8.17295700 3.34656100

C -2.63009800 6.33694200 -0.44104100

C -3.47004000 5.40910000 -1.04866300

C -3.43637400 4.07867300 -0.63639900

C -2.55156200 3.68425700 0.36404400

H -2.51332800 2.63577600 0.67022200

H -4.09771300 3.34161100 -1.09794900

H -4.15533300 5.72987400 -1.83671900

H -2.65514300 7.38633300 -0.74401900

C -2.20317900 2.14184700 3.44030500

C -2.85193700 1.17838600 4.19917700

C -2.41734300 -0.15019000 4.22440800

C -1.32323000 -0.49952400 3.43703000

H -0.97184500 -1.53431200 3.40376600

H -2.93344900 -0.90129100 4.82448100

H -3.73023000 1.47101300 4.78188000

H -2.60074900 3.15907800 3.43109300

H -0.72496000 -0.81446800 -0.12095100

H -0.49032000 0.96975400 -0.16988200

H 0.81735300 -0.12412800 -0.72277000

H 1.70328200 2.99812800 -0.64651400

N 3.22651600 4.09454600 0.71811700

C 4.57825300 3.85348600 0.82269400

C 5.06109100 2.51772600 0.78977100

S 3.90027800 1.16307600 0.69034600

C 4.26750900 0.26881200 2.22400600

H 3.57205600 -0.57827100 2.27386500

H 5.29536400 -0.11441500 2.21006900

H 4.12422300 0.91968800 3.09699600

C 6.42725300 2.24049000 0.84334900

C 7.35847800 3.26477500 0.98788300

C 6.90138800 4.58029800 1.06734100

C 5.54507500 4.87221200 0.98539500

H 5.21914200 5.91174800 1.05717200

H 7.61490400 5.39883500 1.19194000

H 8.42477000 3.03741900 1.03794100

H 6.76219400 1.20157600 0.78054800

C 2.72007400 5.42400400 0.90138000

H 1.67590500 5.42379500 0.52288100

H 3.22919000 6.17080000 0.25998100

C 2.69337800 5.96509600 2.31461500

C 2.57374900 5.19169500 3.48944400

S 2.60473900 3.39866500 3.47336600

C 1.47947000 2.97206400 4.81801300

H 1.22776800 1.91259500 4.67523800

H 1.93797600 3.09175600 5.80770200

H 0.55115500 3.55529300 4.75332400

C 2.47507700 5.82601000 4.73780500

C 2.47390300 7.21140800 4.84267000

C 2.59129800 7.98840600 3.69198200

C 2.70175400 7.35997000 2.45736900

H 2.78134000 7.96353000 1.54791400

H 2.60075800 9.07869800 3.75560000

H 2.39529000 7.67887700 5.82677000

H 2.40796800 5.22390200 5.64549500

H 2.51493300 3.51205600 -0.19149400

Mn4

Mn 0.00000000 0.00000000 0.00000000

N -1.69917300 0.33685300 1.13473000

C -2.34090500 -0.56416900 1.90781300

C -1.98807300 -1.95218000 1.81307700

S -0.78327600 -2.45035100 0.59932200

C -1.78063900 -2.39981600 -0.92790500

H -2.54063500 -3.19032100 -0.90350200

H -2.25957000 -1.41547700 -1.03127400

H -1.10349100 -2.56083100 -1.77644800

C -2.55740100 -2.92046400 2.64034900

C -3.51835300 -2.57486400 3.58769300

C -3.91889100 -1.23662600 3.66703700

C -3.36369800 -0.26060500 2.85223000

H -3.72821400 0.76640300 2.93034800

H -4.69567400 -0.94702100 4.38068900

H -3.96101000 -3.33487400 4.23326900

H -2.23958000 -3.96051600 2.52746500

C -1.97199900 1.74153400 1.27243100

H -1.03245500 2.30305100 1.07903900

H -2.23307700 2.01860900 2.31717000

C -3.01295300 2.29495300 0.33044400

C -2.96892100 3.63176200 -0.12080700

S -1.67955500 4.77549300 0.33347200

C	-1.76766300	4.82237200	2.14191100
H	-1.18144600	4.02417200	2.62052200
H	-1.35048200	5.78832900	2.45336800
H	-2.81136200	4.77124000	2.47810400
C	-3.91730300	4.09242800	-1.04486900
C	-4.91519900	3.24812800	-1.52156400
C	-4.97824600	1.93251100	-1.06609300
C	-4.03350200	1.46836400	-0.15461400
H	-4.06758800	0.42901900	0.18294900
H	-5.76130700	1.26136200	-1.42647200
H	-5.64585400	3.62230000	-2.24229600
H	-3.86208900	5.12921600	-1.38454900
H	0.13325800	0.53776400	-1.63136900
N	2.25775600	1.69889500	-0.37479300
C	3.55233700	1.33906400	-0.04940900
C	3.91673700	-0.03014800	-0.02643800
S	2.68351400	-1.27117200	-0.39097100
C	2.90221500	-2.39342600	1.01122500
H	2.82710900	-1.84226100	1.95886200
H	2.09175300	-3.13044600	0.95115400
H	3.86092700	-2.92461200	0.96349400
C	5.22083500	-0.39943900	0.30727700
C	6.16301000	0.55621200	0.68177000
C	5.79795900	1.90120900	0.70301100
C	4.51389500	2.28955800	0.33540600
H	4.24339300	3.34740700	0.34271200
H	6.52384700	2.66278900	0.99670300
H	7.17434300	0.24845100	0.95364500
H	5.49853200	-1.45594900	0.29035500
C	1.70207800	2.99924900	-0.12907100
H	0.65621500	2.96110300	-0.49497800
H	2.18190300	3.79789000	-0.72945600

C 1.68617400 3.44089300 1.31473000

C 1.48011900 2.58686000 2.42105800

S 1.36649600 0.81287700 2.22884000

C 0.37415600 0.31637100 3.64863100

H 0.06149800 -0.71719000 3.44744400

H 0.94785700 0.33248000 4.58403600

H -0.52989100 0.93331800 3.74024100

C 1.41212000 3.13046500 3.71321100

C 1.52910600 4.49992800 3.92529200

C 1.72918400 5.35240500 2.84267400

C 1.80800600 4.81374400 1.56320100

H 1.96045900 5.47577800 0.70522800

H 1.82911900 6.42943900 2.99239300

H 1.47379700 4.89346900 4.94264500

H 1.27428100 2.47354000 4.57276100

H 1.77555400 1.18017200 -1.11769300

Fe1 – (*S* = 1)

Fe 0.00000000 0.00000000 0.00000000

N 1.43436500 0.95477500 -0.94402500

C 2.72356100 0.59216700 -0.66701000

C 3.83724700 0.78475100 -1.52510200

C 5.10309300 0.31188500 -1.18642600

C 5.33329000 -0.35499600 0.01615500

C 4.26619800 -0.51997000 0.90455500

C 2.99965100 -0.06502300 0.56641800

S 1.60181100 -0.10435400 1.67078600

C 1.80063700 -1.68896300 2.51406400

H 2.63916300 -1.64392900 3.22060700

H 1.95729800 -2.50305100 1.79354300

H 0.87740900 -1.85966400 3.08194600

H 4.43089500 -1.00496600 1.87036900

H 6.32543100 -0.73152900 0.27018600

H 5.92715500 0.46029600 -1.88964500

H 3.69805900 1.27326400 -2.49081900

C 1.25653800 1.80233200 -2.10888500

C -0.05291000 2.53925400 -2.13955200

C -0.08689900 3.93418900 -2.11924600

C -1.29091900 4.63728200 -2.15973200

C -2.49252100 3.93873300 -2.22550900

C -2.49210900 2.54449200 -2.24554700

C -1.28048400 1.85142800 -2.20266000

S -1.16813900 0.08251600 -2.12335000

C -2.87660900 -0.46054400 -2.28285000

H -2.86564000 -1.54882700 -2.14428600

H -3.52841900 -0.01188300 -1.52328000

H -3.24038800 -0.22881300 -3.29247500

H -3.44128400 2.00761200 -2.28333000

H -3.44367300 4.47529800 -2.25617200

H -1.28764400 5.72893200 -2.13660200

H 0.86012100 4.47841700 -2.06442700

H 2.06110700 2.55842200 -2.15596500

H 1.35425900 1.21779800 -3.05424600

N -1.42681100 -1.10116200 0.89188800

C -1.29944700 -2.54593100 0.94361200

C -1.50085900 -3.21752700 -0.40051400

C -0.51229100 -3.12487300 -1.40780400

C -0.76786600 -3.60450700 -2.69756900

C -1.98449900 -4.21785700 -2.99240000

C -2.93911600 -4.38577900 -1.99333900

C -2.68685200 -3.88826200 -0.71459600

H -3.43709000 -4.02636600 0.06776200

H -3.88013200 -4.89720300 -2.20622300

H -2.17065000 -4.58462900 -4.00445600

H -0.01155700 -3.51775100 -3.47903800

S 1.05589900 -2.44153800 -0.94171700

C 1.84721000 -2.10215600 -2.51610800

H 2.78101000 -1.57920500 -2.27243600

H 2.09109500 -3.02449700 -3.05915400

H 1.21828700 -1.44506100 -3.13343500

H -0.28932600 -2.78916000 1.31624500

H -1.99385500 -2.99187600 1.67879200

C -2.67191500 -0.55478400 0.92803200

C -2.81360100 0.87309700 0.89287000

C -4.06002900 1.49191000 0.81654900

C -5.23616600 0.74253100 0.80798600

C -5.12999800 -0.64426800 0.94353200

C -3.89501800 -1.27626300 1.01209800

H -3.87324300 -2.35998300 1.11181200

H -6.03567900 -1.25611700 0.98682700

H -6.20969000 1.23050000 0.73689800

H -4.09469100 2.58447500 0.77466700

S -1.35429800 1.88380300 1.03765100

C -1.03361700 1.66082000 2.80879700

H -0.06944800 2.13086100 3.03907800

H -1.82569300 2.13419200 3.40293500

H -0.97887200 0.58779600 3.04138300

Fe1 – (*S* = 2)

Fe 0.00000000 0.00000000 0.00000000

N -1.45979800 -0.93240500 -1.06833900

C -2.75424000 -0.57508000 -0.83314800

C -3.80019100 -0.65004700 -1.79283600

C -5.08505200 -0.19372800 -1.51759500

C -5.40830600 0.35054900 -0.27449800

C -4.42139800 0.38758000 0.71265200

C -3.13156300 -0.06148600 0.44894200

S -1.90203900 -0.16894800 1.73804700

C -2.10209900 1.38747300 2.62999400

H -3.00900300 1.38054500 3.24823700

H -2.12949700 2.23667300 1.93423900

H -1.23255500 1.48527200 3.29292500

H -4.66801600 0.75848400 1.71113600

H -6.41469000 0.71497000 -0.06209700

H -5.84826200 -0.25741900 -2.29814300

H -3.58215500 -1.03707000 -2.78959400

C -1.20571500 -1.62745000 -2.31434000

C 0.14806000 -2.28368100 -2.34228500

C 0.25825900 -3.67141700 -2.24026900

C 1.49642900 -4.31199200 -2.22674400

C 2.65827900 -3.55178100 -2.31613900

C 2.58302200 -2.16392800 -2.42134500

C 1.33693200 -1.52841900 -2.43515500

S 1.15713700 0.23718900 -2.53051400

C 2.85039300 0.83596500 -2.54466900

H 2.77950500 1.93103400 -2.51755800

H 3.40975800 0.49849600 -1.66190700

H 3.36743000 0.53468400 -3.46543000

H 3.50484500 -1.58341800 -2.48020500

H 3.63869800 -4.03408600 -2.30176500

H 1.55103300 -5.39910400 -2.14133400

H -0.66064700 -4.25913400 -2.16023300

H -1.96525700 -2.41479000 -2.47978600

H -1.30110000 -0.94967600 -3.19573900

N 1.46852600 1.10369400 0.90936500

C 1.34949700 2.54251100 1.07596600

C 1.47536100 3.31349100 -0.22150800

C 0.43835000 3.26641100 -1.18016200

C 0.60076900 3.86895300 -2.43215100

C 1.77549400 4.55866400 -2.73205600

C 2.78113000 4.67013800 -1.77657700

C 2.62064600 4.04900500 -0.53737700

H 3.40948900 4.14392600 0.21323400

H 3.69098800 5.23374200 -1.99304200

H 1.88947700 5.02353700 -3.71403200

H -0.19137400 3.81716100 -3.18014600

S -1.07142200 2.47318700 -0.68962800

C -1.99006200 2.34092800 -2.22378600

H -2.92730700 1.83075400 -1.97138700

H -2.22745000 3.33133100 -2.63252300

H -1.44091200 1.73837100 -2.96092800

H 0.36073200 2.75540500 1.52184200

H 2.08014700 2.93542000 1.80543300

C 2.72283600 0.56462900 0.89619000

C 2.88119600 -0.85762700 0.81011700

C 4.13184300 -1.46213800 0.70334200

C 5.30026500 -0.70137900 0.70743200

C 5.18153100 0.68035300 0.86777300

C 3.93981400 1.29665700 0.96561900

H 3.90964400 2.37876900 1.07903100

H 6.08073700 1.30164400 0.90979300

H 6.27759100 -1.17824100 0.61660000

H 4.17677900 -2.55200200 0.62511900

S 1.43162400 -1.89119900 0.89169000

C 1.06105000 -1.73702500 2.66291200

H 0.10438600 -2.24075800 2.84897500

H 1.84995100 -2.21236300 3.25947800

H 0.97228400 -0.67440900 2.92871500

Fe2

Fe 0.00000000 0.00000000 0.00000000

S	1.41290000	-1.93822200	0.85268800
C	2.88746300	-0.93789800	0.81615900
C	2.75668500	0.48635200	0.81178100
N	1.51153800	1.05484800	0.82344400
C	1.42360700	2.49038100	1.04465900
H	2.21764400	2.84151200	1.72652500
H	0.47818600	2.69449600	1.58185100
C	1.44596100	3.32886500	-0.21600500
C	0.31255900	3.37714900	-1.05669800
S	-1.13628300	2.53540700	-0.47572100
C	-2.23560400	2.52460200	-1.89258300
H	-2.53490400	3.54184900	-2.17608000
H	-3.12769900	1.96863600	-1.57802200
H	-1.78787400	2.00599300	-2.75229800
C	0.34854000	4.07980000	-2.26491500
H	-0.52509500	4.10666700	-2.91850300
C	1.50411500	4.76346000	-2.64123800
H	1.52293600	5.30565300	-3.58931100
C	2.61403200	4.77062400	-1.80161200
H	3.51244200	5.32648300	-2.07750600
C	2.57171800	4.06025200	-0.60191900
H	3.44097100	4.07972100	0.06076200
C	3.98461600	1.19916600	0.81353000
C	5.21583200	0.55532800	0.78507400
C	5.30985300	-0.83678200	0.76199500
C	4.12649100	-1.57253100	0.78680500
H	4.15434900	-2.66609800	0.78916200
H	6.27878700	-1.33817400	0.73631800
H	6.12588300	1.16186500	0.77355600
H	3.97170200	2.28764300	0.81384800
C	1.01698200	-1.82990100	2.62251400
H	1.79671500	-2.32462100	3.21514400

H 0.05564200 -2.33303400 2.78396100

H 0.93263900 -0.77473200 2.91701100

S -1.96984100 -0.38271600 1.62882000

C -3.18980800 -0.38993600 0.32576300

C -2.72337700 -0.66690600 -0.99838500

N -1.38955200 -0.72336000 -1.24797900

C -0.95733700 -1.00528500 -2.59788800

H -1.41243700 -0.30443500 -3.33269600

H -1.27376100 -2.01329100 -2.93186100

C 0.54061600 -0.85475100 -2.65764200

C 1.42976500 -1.94752200 -2.54614200

S 0.73426900 -3.57057200 -2.45210600

C 2.14344900 -4.56588400 -1.95186500

H 2.57918700 -4.18834600 -1.01538500

H 2.91642400 -4.63014000 -2.72985600

H 1.75151300 -5.57413900 -1.77324100

C 2.80978500 -1.70332800 -2.50169300

H 3.51484900 -2.53084700 -2.41107700

C 3.30642700 -0.40093500 -2.53639200

H 4.38481800 -0.23989800 -2.46419700

C 2.44019900 0.68275700 -2.63812900

C 1.06781300 0.44069000 -2.70653000

H 0.37296600 1.27973300 -2.80929200

H 2.82006100 1.70712800 -2.65616600

C -3.73184300 -0.82850700 -1.98646100

C -5.07934300 -0.66369600 -1.68940500

C -5.50340000 -0.35125300 -0.39622000

C -4.54433900 -0.24565300 0.61187100

H -4.85809800 -0.05513800 1.64192000

H -6.56220500 -0.22225400 -0.16599900

H -5.81672100 -0.78535700 -2.48762500

H -3.43953800 -1.07530300 -3.00867500

C -2.37144800 1.10260800 2.57692900

H -3.31261300 0.97666600 3.12682100

H -2.42920500 1.98599000 1.92812100

H -1.56175300 1.23976600 3.30534500

Fe3

Fe 0.00000000 0.00000000 0.00000000

S 1.36540300 -2.05059400 0.60410100

C 2.89030700 -1.13302800 0.60221500

C 2.83957200 0.29549100 0.64406200

N 1.63096700 0.93360400 0.73454300

C 1.63346900 2.37953700 0.90402400

H 2.55925200 2.73958200 1.37862300

H 0.83773000 2.65276800 1.62083400

C 1.39928700 3.12821000 -0.38454900

C 0.09044700 3.24611200 -0.90044100

S -1.22287400 2.58818000 0.10081900

C -2.63130500 2.60905100 -1.01385500

H -2.97571400 3.63404700 -1.20486400

H -3.43417000 2.04960200 -0.51696400

H -2.39706500 2.09930900 -1.95736700

C -0.13599100 3.87520600 -2.12873900

H -1.14712400 3.97610700 -2.52603200

C 0.93706400 4.38853000 -2.85741400

H 0.74972500 4.87418000 -3.81775600

C 2.23275000 4.29181100 -2.35751300

H 3.07385700 4.70104500 -2.92112200

C 2.45006900 3.66782600 -1.12873200

H 3.46731700 3.59145200 -0.73483100

H 0.21392500 0.98874000 2.90027900

C 4.10752900 0.93692000 0.59940500

C 5.29737400 0.22545800 0.51922400

C 5.31218100 -1.16972900 0.47723900

C 4.09003600 -1.83574300 0.51890600

H 4.05190800 -2.92845600 0.47955900

H 6.24970500 -1.72442600 0.41150500

H 6.23890500 0.78070400 0.48072000

H 4.16430700 2.02512300 0.61152700

C 1.05251300 -2.16781700 2.39056500

H 1.82133200 -2.78953100 2.86633500

H 0.06891200 -2.63515500 2.52636200

H 1.05195500 -1.16889600 2.84586900

S -2.06036700 -0.92966800 1.26791700

C -3.12730900 -0.82458000 -0.16338900

C -2.52512900 -0.60339500 -1.44018700

N -1.18423700 -0.40966400 -1.54302900

C -0.61580100 -0.25570300 -2.86536600

H -0.83288400 0.74540100 -3.30020000

H -1.05663100 -0.98518800 -3.57465400

C 0.87405000 -0.46184100 -2.82906500

C 1.41820200 -1.76716200 -2.74503800

S 0.28029800 -3.11964500 -2.70550000

C 1.36566200 -4.53533400 -2.50694400

H 1.94560800 -4.46587100 -1.57520700

H 2.04351100 -4.67090200 -3.36107500

H 0.70981500 -5.41153300 -2.44305200

C 2.80860200 -1.92977200 -2.70757700

H 3.24912200 -2.92568200 -2.64120300

C 3.65423000 -0.82128100 -2.73614500

H 4.73515100 -0.97340900 -2.68679700

C 3.12840900 0.46423800 -2.80059600

C 1.74362900 0.63006800 -2.85106200

H 1.31540500 1.63477100 -2.92102700

H 3.78701700 1.33565000 -2.80995600

C -3.42348900 -0.57104200 -2.54228100

C -4.79155800 -0.74383900 -2.38169700

C -5.35060500 -0.96955100 -1.12190700

C -4.49807300 -1.02604600 -0.02044500

H -4.90785000 -1.23332900 0.97216700

H -6.42477200 -1.11581400 -0.99805800

H -5.43753400 -0.70013900 -3.26284400

H -3.03075400 -0.38116400 -3.54238700

C -2.83345400 0.24929600 2.40234400

H -3.88299100 -0.01938900 2.57252800

H -2.76558200 1.27945400 2.02764500

H -2.29889600 0.17798000 3.35663600

H -0.09703800 1.25915100 3.53934200

Fe3 – TS

C 0.00000000 0.00000000 0.00000000

N 0.11951900 -1.43150000 0.23013000

C -1.00149100 -2.19837000 0.48673000

C -0.88362100 -3.61095000 0.59260000

S 0.72484900 -4.37729000 0.53990000

C 0.89911900 -4.78725000 -1.21721000

H 0.16600800 -5.55184000 -1.50498000

H 1.91342900 -5.18728100 -1.34427000

H 0.79031900 -3.89175000 -1.84185000

C -1.99894100 -4.41530000 0.82573000

C -3.26898100 -3.86188900 0.96200000

C -3.40189100 -2.47636900 0.87717000

C -2.29895100 -1.66357000 0.64583000

H -2.44488000 -0.58450900 0.59675000

H -4.38512100 -2.01339900 0.99641000

H -4.13558100 -4.50011900 1.14438000

H -1.85301200 -5.49568000 0.91498000

H -0.97156000 0.26795000 -0.44686000

H 0.75228000 0.25186000 -0.77193000

C 0.24927000 0.83156000 1.22901000

C 1.56835000 1.03823000 1.69142000

S 2.88409000 0.38228900 0.69281000

C 4.34320000 0.68644900 1.69328000

H 4.55570000 1.76080900 1.77289000

H 5.17943000 0.19604900 1.17875000

H 4.25087000 0.23253900 2.68860000

C 1.79626000 1.75777900 2.86940000

H 2.81080000 1.92172900 3.23533000

C 0.72343000 2.28025000 3.59020000

H 0.91722100 2.83822000 4.50917000

C -0.58032000 2.10181000 3.13630000

H -1.42174000 2.52021000 3.69253000

C -0.80256000 1.38378000 1.96225000

H -1.82548000 1.24512000 1.60021000

H 0.94395900 -1.83267000 -0.59239000

Fe 2.20199900 -2.32139100 0.83002000

N 3.31310900 -2.37386100 2.49910000

C 4.67214900 -2.45801100 2.48687000

C 5.35872900 -2.91328100 1.31867000

S 4.38149900 -3.44721100 -0.07203000

C 4.83580900 -2.24674100 -1.34848000

H 5.89988900 -2.32669200 -1.60663000

H 4.59400000 -1.22417100 -1.02840000

H 4.22860900 -2.48132100 -2.23159000

C 6.74846900 -2.99678200 1.26586000

C 7.53375900 -2.60302200 2.34783000

C 6.89006900 -2.15650200 3.50381000

C 5.50515900 -2.08943100 3.57983000

H 5.04958900 -1.71103100 4.49664000

H 7.48236900 -1.84870200 4.37024000

H 8.62224900 -2.66015200 2.29417000

H 7.21982900 -3.38182200 0.35682000

C 2.67426900 -2.03334100 3.75121000

H 2.72859000 -0.94350100 3.97469000

H 3.19053900 -2.53469100 4.59591000

C 1.23536900 -2.46509000 3.77960000

C 0.90270900 -3.84293000 3.81582000

S 2.23533900 -5.00663100 3.77645000

C 1.39078800 -6.56718000 4.05467000

H 0.72734800 -6.82868000 3.21759000

H 0.82178800 -6.57260000 4.99485000

H 2.17765800 -7.32805100 4.11939000

C -0.44325100 -4.22063000 3.89769000

H -0.72140100 -5.27556000 3.91745000

C -1.45125100 -3.25807000 3.94297000

H -2.49468100 -3.57860900 3.99535000

C -1.13396100 -1.90519000 3.89672000

C 0.20545900 -1.52396000 3.81974000

H 0.47067000 -0.46271000 3.81135000

H -1.92027000 -1.14675000 3.92035000

H 1.93920900 -2.03461100 -1.03889000

Fe4

C 0.00000000 0.00000000 0.00000000

N 0.32412100 -1.39554500 0.23357000

C -0.58471500 -2.32574200 0.67848500

C -0.21966400 -3.68630200 0.87290900

S 1.46565500 -4.25705200 0.71915800

C 1.57304500 -4.64748900 -1.04808800

H 0.85688900 -5.43914000 -1.30257200

H 2.59543300 -5.00375500 -1.22862100

H 1.40531900 -3.75212400 -1.66033500

C -1.16712100 -4.62565200 1.28597000

C -2.48828900 -4.26759700 1.53138400

C	-2.85099300	-2.93066100	1.37560200
C	-1.92444100	-1.98243500	0.96328000
H	-2.24787800	-0.94841800	0.84694900
H	-3.87828700	-2.61453900	1.57461800
H	-3.21525900	-5.01525000	1.85358400
H	-0.83885200	-5.65828900	1.43332100
H	1.13545600	-1.73564500	-0.30629900
H	-1.02557000	0.10889300	-0.39158400
H	0.66244400	0.34207300	-0.81167800
C	0.17752400	0.89349200	1.20545400
C	1.46737300	1.31014400	1.61414100
S	2.83701000	0.78514900	0.63027200
C	4.26098700	1.45136900	1.49409800
H	4.26488200	2.54966200	1.49600300
H	5.13986700	1.09592200	0.94187700
H	4.33548500	1.06754100	2.52067400
C	1.61269600	2.11220000	2.75335200
H	2.60212600	2.43842800	3.07774000
C	0.49592000	2.50124200	3.49032600
H	0.63044600	3.12199500	4.37924000
C	-0.77933300	2.11091600	3.09129200
H	-1.65835300	2.42250300	3.65897200
C	-0.92245600	1.31953900	1.95207600
H	-1.92450500	1.02458800	1.62670200
Fe	3.06381100	-2.29625300	0.85273400
N	4.05508000	-1.77866800	2.50256100
C	5.41195700	-1.67571700	2.54664600
C	6.21703400	-2.29036800	1.53908100
S	5.41163800	-3.21385800	0.24144300
C	5.64993800	-2.09841700	-1.16962100
H	6.71708600	-2.00675500	-1.41050000
H	5.21449300	-1.11269800	-0.95823900

H 5.11327300 -2.53244400 -2.02215800

C 7.60876700 -2.22446800 1.56694800

C 8.27515300 -1.52414400 2.57048400

C 7.51278600 -0.90710800 3.56447500

C 6.12623600 -0.97949800 3.56075100

H 5.57162700 -0.46527700 4.34816700

H 8.01098800 -0.35192700 4.36439700

H 9.36514500 -1.47191100 2.58131900

H 8.17492700 -2.73889300 0.78502900

C 3.30381100 -1.36676500 3.66455700

H 3.11330800 -0.26993200 3.69447800

H 3.87726300 -1.59090000 4.58834600

C 1.98387100 -2.08011400 3.78055500

C 1.93258800 -3.49157600 3.91192200

S 3.45543200 -4.39216600 3.79591300

C 2.94799700 -6.05666100 4.24980300

H 2.25935000 -6.49101000 3.51095100

H 2.49624500 -6.10113600 5.25058600

H 3.86626600 -6.65613000 4.25522400

C 0.69856400 -4.11158000 4.14652600

H 0.63727300 -5.19555800 4.25383100

C -0.47177800 -3.35960900 4.24607800

H -1.42066700 -3.87007600 4.42805100

C -0.43458700 -1.97955000 4.08584600

C 0.79241500 -1.35711500 3.86016900

H 0.84050800 -0.26919300 3.76674200

H -1.34867100 -1.38358100 4.13836200

H 2.74909400 -1.97077800 -0.80177000

Co1 – (*S* = 1/2)

Co 0.00000000 0.00000000 0.00000000

N -1.70465300 0.03651300 -0.95418700

C -1.77920300 0.65173200 -2.26429500

C -1.72024000 2.16199400 -2.21386000

C -2.84492900 2.95854600 -2.44066500

C -2.79877400 4.34808800 -2.31674700

C -1.60241000 4.96748900 -1.96445400

C -0.45466700 4.20317500 -1.75224400

C -0.50998100 2.81134200 -1.87806400

S 0.89881700 1.76365400 -1.68299200

C 2.22489000 2.88327900 -1.22351200

H 2.45148800 3.56251600 -2.05581900

H 1.99232600 3.45315500 -0.31501400

H 3.09907200 2.24761900 -1.03349700

H 0.48111000 4.69960500 -1.48855700

H -1.55133400 6.05424000 -1.86340500

H -3.69550900 4.94361900 -2.50037800

H -3.78152800 2.47632400 -2.73382200

H -2.68571700 0.33997000 -2.81169400

H -0.93228000 0.27235900 -2.86516900

C -2.83915800 -0.10804700 -0.23002100

C -4.14719300 0.29361300 -0.63070100

C -5.24430000 0.14984400 0.20715600

C -5.12800800 -0.39951000 1.48869200

C -3.87219800 -0.84329700 1.89876400

C -2.76413000 -0.71361600 1.06525200

S -1.19889900 -1.41821900 1.55263300

C -1.43303900 -3.08550400 0.87353200

H -1.57607600 -3.03541400 -0.21401800

H -0.54935900 -3.68886800 1.11254000

H -2.31447600 -3.54287200 1.34026100

H -3.73897600 -1.30721500 2.88033900

H -5.99437800 -0.48916100 2.14564300

H -6.22173500 0.48857400 -0.14839700

H -4.29656400 0.73633400 -1.61512100

N 1.70472600 0.03649500 0.95401600

C 1.77946800 0.65162900 2.26414600

C 1.72048000 2.16186800 2.21366800

C 0.51017500 2.81110200 1.87789600

C 0.45473200 4.20292100 1.75199200

C 1.60244600 4.96731800 1.96407400

C 2.79889900 4.34801000 2.31622200

C 2.84517400 2.95847800 2.44022900

H 3.78186700 2.47632300 2.73319000

H 3.69563600 4.94361100 2.49962700

H 1.55129100 6.05406100 1.86297900

H -0.48107700 4.69925600 1.48823900

S -0.89849600 1.76322100 1.68277500

C -2.22467500 2.88271000 1.22329300

H -1.99275500 3.45193700 0.31422300

H -3.09908200 2.24702600 1.03443000

H -2.45064600 3.56250900 2.05530800

H 2.68605300 0.33987300 2.81142000

H 0.93261700 0.27227600 2.86512700

C 2.83914300 -0.10831800 0.22980000

C 2.76387700 -0.71373900 -1.06552500

C 3.87182600 -0.84362600 -1.89914500

C 5.12778000 -0.40018500 -1.48913000

C 5.24429500 0.14910000 -0.20758600

C 4.14729300 0.29308600 0.63037500

H 4.29685500 0.73570600 1.61481900

H 6.22183900 0.48759200 0.14789600

H 5.99406700 -0.48995700 -2.14617300

H 3.73841700 -1.30742100 -2.88075500

S 1.19835300 -1.41776800 -1.55280100

C 1.43250100 -3.08557200 -0.87497100

H 2.31378100 -3.54264700 -1.34228400

H 1.57586800 -3.03632900 0.21258000

H 0.54869700 -3.68867400 -1.11416900

Co1 – (*S* = 3/2)

Co 0.00000000 0.00000000 0.00000000

N -1.72456800 0.13602200 -0.98132300

C -1.77789400 0.74150500 -2.30067100

C -1.68436100 2.25289200 -2.25194500

C -2.79755000 3.06933700 -2.46536400

C -2.73682700 4.45572500 -2.31570700

C -1.53449500 5.05190500 -1.94725700

C -0.39380200 4.27003200 -1.76466100

C -0.45959100 2.88173700 -1.92744100

S 0.95971400 1.83335600 -1.80589000

C 2.27139900 2.94082500 -1.28187100

H 2.47372300 3.69656600 -2.05217100

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Co3

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S 2.02561800 -1.24238600 0.63225200

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C -1.64125100 2.78436500 -1.01572600

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C -2.29171300 2.96644400 -2.24209600

H -3.32895200 2.65478300 -2.37349400

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C 5.28210100 1.11184400 0.17516800

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H -0.69689000 -0.87907600 -3.67887700

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C 1.76908800 -1.59625400 -2.60088500

S 0.68172800 -2.96487500 -2.31945600

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C -3.13269200 -0.67429200 -2.71195600

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C -4.98706200 -1.55596600 -1.41895600

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H -5.11716500 -0.94689700 -3.48597900

H -2.76019300 -0.25959500 -3.65060000

C -2.60989900 -1.01387800 2.37403000

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Co3 – TS

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N 0.73177300 -1.08764600 0.61916800

C 0.04922700 -2.15732000 1.07575400

C 0.72270400 -3.39644500 1.34797200

S 2.45942300 -3.53560600 1.01345000

Co 3.31943200 -1.29366400 1.43549200

N 4.30522800 -0.20500900 2.68397800

C	5.65805100	-0.03199500	2.62272500
C	6.43483200	-0.71327100	1.63921800
S	5.60340300	-1.76597800	0.46780700
C	5.59228600	-0.67770800	-0.98731900
H	6.61721500	-0.51511700	-1.34473500
H	5.11895200	0.28325200	-0.74353500
H	5.00882800	-1.17418100	-1.77331400
C	7.82014600	-0.58307500	1.57374600
C	8.50100400	0.25444900	2.45413700
C	7.76350400	0.95157100	3.41291500
C	6.38476600	0.81378000	3.50372900
H	5.84813500	1.38461200	4.26287500
H	8.27488500	1.61954000	4.11126300
H	9.58591700	0.35591200	2.39547800
H	8.36723300	-1.15050500	0.81562200
C	3.63326100	0.30599000	3.86334200
H	3.52746100	1.40865400	3.83218600
H	4.24126700	0.09050300	4.76761000
C	2.27557900	-0.30555900	4.05127100
C	2.12273100	-1.70269700	4.20741400
S	3.59847900	-2.70008900	4.16011600
C	2.96661900	-4.34766000	4.49792100
H	2.25323300	-4.67492000	3.72845300
H	2.50292200	-4.41348300	5.49162800
H	3.83721600	-5.01354800	4.47013200
C	0.84897300	-2.24334900	4.41828600
H	0.71115600	-3.31867700	4.53547600
C	-0.27082600	-1.41641700	4.45702100
H	-1.25685000	-1.86604500	4.59467300
C	-0.13366800	-0.03949300	4.30821500
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S 2.16717200 1.83636400 1.00606900

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Co4

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C	-4.29388100	-0.02606300	-1.45430100
C	-5.50531100	0.57783400	-1.79270500
C	-6.45403400	0.81253800	-0.80219400
C	-6.19410000	0.43877200	0.51559700
C	-4.97893500	-0.17022200	0.85401200
S	-4.56551400	-0.64132200	2.51177800
C	-6.02669000	-0.16384400	3.44059100
H	-6.21524800	0.91771100	3.39540200
H	-6.92235800	-0.70785100	3.11073800
H	-5.82220000	-0.43528200	4.48286100
H	-6.95012400	0.63093000	1.27836600
H	-7.40783000	1.28591100	-1.04756100
H	-5.70536100	0.85902900	-2.82903200
H	-3.54635900	-0.21363400	-2.22813900
H	-2.84596800	-2.09461900	0.50369600
H	-2.33657500	-0.57235400	1.17818300
C	-1.51275600	-1.65742200	-1.80935400
C	-2.26300300	-2.84236600	-2.03879800
C	-2.00033500	-3.66486300	-3.12697500
C	-1.00811000	-3.34632400	-4.05995200
C	-0.31056200	-2.14752400	-3.90778500
C	-0.56108600	-1.30855700	-2.82337900
S	0.26306700	0.27251600	-2.71507500
C	-1.11117100	1.38768600	-3.09996200
H	-1.86480300	1.33787600	-2.30000400
H	-0.70311600	2.40541900	-3.16222300
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H 1.40729000 1.82557600 1.05032400

H 0.20222700 -0.31290700 1.60689200

V. References

(1) D. F. Evans, *J. Chem. Soc.* 1959, 2003.

(2) M.R. Elsby, M. Son, C. Oh, J. Martin, M. H. Baik, and R. T. Baker, *A.C.S. Catal.* 2021, **11**, 9043-9051.

(3) U. K. Das, S. L. Daifuku, T. E. Iannuzzi, S. I. Gorelsky, I Korobkov, B. Gabidullin, M. L. Neidig, and R. T. Baker, *Inorg. Chem.* 2017, **56**, 22, 13766-13776.

(4) M. M. Olmstead, P. P. Power, and S. C. Shoner. *Inorg. Chem.* 1991, **30**, 2547-2551.

(5) APEX 2, Bruker AXS Inc., Madison, Wisconsin, USA, 2012

(6) G. M. Sheldrick, SADABS, Program for empirical absorption correction of area detector data, University of Göttingen, Germany, 1996.

(7) G. M. Sheldrick, Acta Cryst. 2015, **71**, 3-8.

(8) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09* (Gaussian, Inc., Wallingford CT, 2009)

(9) J. R. Schmidt, and W. F. Polik, *WebMO Enterprise*, version .0; WebMO LLC: Holland, MI, USA, 2020.

(10) B. Marten, K. Kim, C. Cortis, R. A. Friesner, R. B. Murphy, M. N. Ringnalda, D. Sitkoff, and B. Honig, *J. Phys. Chem.* 1996, **100**, 11775.

(11) M. Friedrichs, R. H. Zhou, S. R. Edinger, and R. A. Friesner, *J. Phys. Chem. B.* 1999, **103**, 3057.

(12) S. R. Edinger, C. Cortis, P. S. Shenkin, and R. A. Friesner, *J. Phys. Chem. B.* 1997, **101**, 1190.

(13) F. De Proft, C. Van Alsenoy, A. Peeters, W. Langenaeker, and P. Geerlings, *J. Comput. Chem*. 2002, **23**, 12, 1198-1209.