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Exploring Mn-O Bonding in the Context of an Electronically Flexible Secondary Coordination Sphere: Synthesis of a Mn(III)-Oxo.

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Supporting Information Table of Contents:

General Considerations. All manipulations were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. Solvents were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves purchased from Strem following literature procedure prior to use. Acetontrile-d_3 was purchased from Cambridge Isotope Labs and stored over 4 Å molecular sieves prior to use. Manganese(II) chloride was purchased from Strem and used as received. Manganese bis(trifluoromethanesulfonate) was prepared according to literature procedures.[1] $H_3[N(pi^{Cy})_3]$ was prepared according to literature procedures.[2] Lithium oxide was purchased from Sigma-Aldrich and used as received. Lithium hexamethyldisilazane was purchased from Sigma-Aldrich and recrystallized from toluene under an inert atmosphere prior to use. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 ℃ prior to use in a drybox. ^{1}H NMR spectra were recorded on a Varian spectrometer operating at 500 MHz (^{1}H NMR). All chemical shifts were reported relative to the peak of the residual solvent as a standard. Solid-state infrared spectra were recorded using a Perkin-Elmer Frontier FT-IR spectrophotometer equipped with a KRS5 Thallium Bromide/Iodide Universal Attenuated Total Reflectance accessory. ESI-MS data was collected on a Thermo Scientific LTQ Orbitrap. The data was collected using sonic spray ionization (SSI) with a solvent pumping rate of 6 microliters/min and a nitrogen pressure of 200 psi. Elemental analysis was performed the University of Illinois at Urbana-Champaign School of Chemical Sciences Microanalysis Laboratory in Urbana, IL. EPR samples were prepared in an MBraun glovebox. The sample concentration is approximately 5mM in dichloromethane/toluene (1:1) mixture. EPR spectra were recorded on a Varian E-line 12” Century series X-band CW spectrometer and the spectra were simulated using the program SIMPOW6.[3]

Preparation of $K[(N(pi^{Cy})_3Mn(OH_2)]$ (1). $H_3[N(pi^{Cy})_3]$ (0.060 g, 0.103 mmol) was deprotonated by addition of 3.1 equivalent of KH (0.013 g, 0.32 mmol) to an approximately 10 mL of tetrahydrofuran solution. After it was stirred for two hours at room temperature, the mixture was filtered through Celite to remove excess KH. Addition of deprotonated ligand to the $MnCl_2$ (0.013 g, 0.0103 mmol) slurry in tetrahydrofuran resulted in a color change from colorless to yellow. After stirring overnight and all $MnCl_2$ was consumed, the reaction mixture was filtered through Celite to remove KCl. Following removal of the volatiles, the yellow oil was washed with diethyl ether. The product was isolated as a yellow powder in quantitative yields (0.068 g, 0.097 mmol, 95 %). Crystals of **1** suitable for X-ray analysis were grown at room temperature via slow diffusion of hexanes into a concentrated solution of tetrahydrofuran. Analysis for $KMnC_{36}H_{50}N_7O \cdot OC_4H_8$: Calcd. C, 62.97; H, 7.66; N, 12.85. Found C, 63.46; H, 7.60; N, 12.47. IR = 1617 cm^{-1} (C=N). μ_{eff} = 6.15(15) μ_B.

Preparation of $N(pi^{Cy})(afaCy)_2Mn(OH)$ (2). A 20 mL scintillation vial was charged with $Mn(OTf)_2(MeCN)_2$ (0.043 g, 0.100 mmol) and approximately 10 mL of tetrahydrofuran. With vigorous stirring, $H_3N(pi^{Cy})_3$ (0.060 g, 0.103 mmol) was added and resulted in an instantaneous color change from colorless to yellow. After stirring for one hour, lithium oxide (0.003 g, 0.100 mmol) was added as a solid. The mixture was stirred for three hours, giving rise to formation of yellow precipitates. The solvents were removed under reduced pressure and the resulting yellow residue was washed with diethyl ether/ tetrahydrofuran mixture to remove lithium triflate. The product, **2**, was isolated as a yellow powder in quantitative yields (0.075 g, 0.093 mmol, 93%). Crystals of **2** suitable for X-ray analysis were grown at room temperature from a dilute solution of tetrahydrofuran. Analysis for $MnC_{36}H_{51}N_7O$: Calcd C, 66.24; H, 7.87; N, 15.02. Found C, 65.95; H, 7.51; N, 14.91. IR = 1645 cm^{-1} (C=N). 3226 cm^{-1} (NH). μ_{eff} = 5.87(28) μ_B.

Alternetive Synthesis of 2. $H_3[N(pi^{Cy})_3]$ (0.060 g, 0.103 mmol) was deprotonated by addition of 2.1 equivalents of $LiN(SiMe_3)_2$ (0.036 g, 0.216 mmol) to an approximately 10 mL of tetrahydrofuran solution. After was stirring for one hour at room temperature, the deprotonated ligand was added dropwise to another 20 mL scintillation vial, charged with $MnCl_2$ (0.012 g, 0.100 mmol), 2 drops of pyridine (to aid in solubility), and approximately 2 mL of tetrahydrofuran with vigorous stirring. After this solution was stirred for 3 h at room temperature and the solvents were removed under reduced pressure. The product was isolated as yellow powder with LiCl as a contaminant.

Preparation of [N(afa^{Cy})$_3$Mn(OTf)](OTf) (3). A 20 mL scintillation vial was charged with $Mn(OTf)_2(MeCN)_2$ (0.043 g, 0.100 mmol) and approximately 10 mL of tetrahydrofuran. With vigorous stirring, $H_3N(pi^{Cy})_3$ (0.060 g, 0.103 mmol) was added and resulted in an instantaneous color change from colorless to yellow. The mixture was stirred for one hour, after which time solvents were removed under reduced pressure. The yellow oil was washed with diethyl ether three times. The product, **3**, was isolated as a yellow powder in quantitative yields (0.087 g, 0.094mmol, 94%). Crystals of **3** suitable for X-ray analysis were grown at room temperature from a concentrated solution of tetrahydrofuran layered with pentane. Analysis for $MnC_{38}H_{51}N_7S_2F_6O_6 \cdot OC_4H_8$: Calcd. C, 50.47; H, 5.87; N, 9.91. Found C, 50.31; H, 5.82; N, 9.81. IR = 1641 cm^{-1} (C=N), 3230, 3290 cm^{-1} (N-H). μ_{eff} = 5.89(7) μ_B.

Preparation of [N(afa^{Cy})$_3$MnO](OTf) (4) from O_2. A 20 mL scintillation vial was charged with [N(afa^{Cy})$_3$Mn(OTf)](OTf) (0.100 g, 0.108 mmol) approximately 10 mL of acetonitrile. The vial was sealed with a 14/20 septum and tape and removed from the glovebox. A standard party balloon attached to a syringe was filled with O_2 and injected through the septum with a needle. The atmosphere was purged with O_2, resulting in an instantaneous color change to green. The mixture was stirred overnight to ensure completion. Volatiles were removed under reduced pressure and the product, [N(afa^{Cy})MnO](OTf) (0.065 g, 0.081 mmol, 75 %) was isolated via recrystallization in good yields via slow diffusion of diethyl ether through a concentrated acetonitrile solution at room temperature.

Independent Preparation of [N(afa^{Cy})$_3$MnO](OTf) (4). A 20 mL scintillation vial was charged with **4** (0.050 g, 0.054 mmol) approximately in 10 mL of acetonitrile. The mixture was cooled to -35 °C. An equivalent of iodosylbenzene (0.012 g, 0.054 mmol) was weighed and added as a solid to the pale-yellow solution. A gradual color change to green was noted over the course of two hours. Volatiles were removed under reduced pressure, leaving a brown-green residue. The oil was washed with tetrahydrofuran and filtered over Celite until the filtrate ran clear. The product was subsequently washed through the frit with acetonitrile. After removing solvents *in vaccuo*, the product, [N(afa^{Cy})$_3$MnO](OTf), was isolated as a green, crystalline powder in modest yields (0.018 g, 0.022 mmol, 41 %). Crystals suitable for X-ray analysis were grown from the slow evaporation of a concentrated acetonitrile solution of **4** via slow diffusion of diethyl ether. Analysis for $C_{37}H_{51}N_7MnO_4F_3S$: Calcd. C, 55.42; H, 6.41; 12.23. Found C, 55.28; H, 6.37; N, 12.08. ^{1}H NMR (CD_3CN, 21 °C): δ = 13.06 (539, 3H, C*H*), 6.78 (447, 3H, C*H*), 4.17 (348, 3H, C*H*), 1.47 – 0.75 (33H, Cy-C*H*), 0.06 (274, 6H, C*H*), -16.39 (491, 3H, C*H*). IR = 1659 cm^{-1} (C=N). ESI-MS m/z = 652.3525 for **4**. ESI-MS m/z = 654.3549 for **4-O^{18}.**,

Preparation of [N(afa^{Cy})$_3$MnO](OTf) (4) via Reduction of Nitrite. A 20 mL scintillation vial was charged with **4** (0.050 g, 0.054 mmol) and approximately 5 mL of acetonitrile. An equivalent of [^{n}Bu$_4$N][NO$_2$] (0.016 g, 0.056 mmol) was weighed by difference and added as a solid to the pale-yellow solution. Over the course of 24 hours at 40 °C, a gradual color change to red was noted. Volatiles were removed under reduced pressure, leaving a green solid. Following trituation with a diethylether and tetrahydrofuran mixture (1:1) to remove the byproduct, [^{n}Bu$_4$N][OTf], the product **4** was recrystallized from a concentrated acetonitrile solution via slow diffusion of diethyl ether. After removing residual solvents *in vaccuo*, the product, [N(afa^{Cy})$_3$MnO](OTf), was isolated as a green, crystalline powder in modest yields (0.027 g, 0.033 mmol, 61 %). Formation of the desired product was confirmed by ^{1}H NMR spectroscopy and X-ray diffraction.

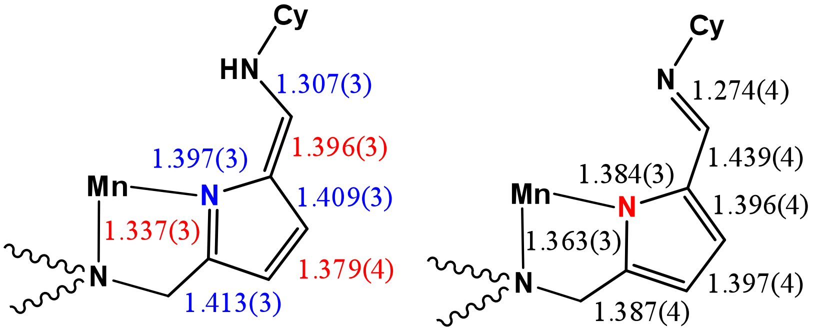

Chart S1. Bond length comparisons between complexes **1** (right) and **3** (left). Bond distances of the azafulvene substituent (**3**) listed in red denote contraction, while those in blue signify elongation from anionically coordinated pyrrole-imine (**1**) arm.

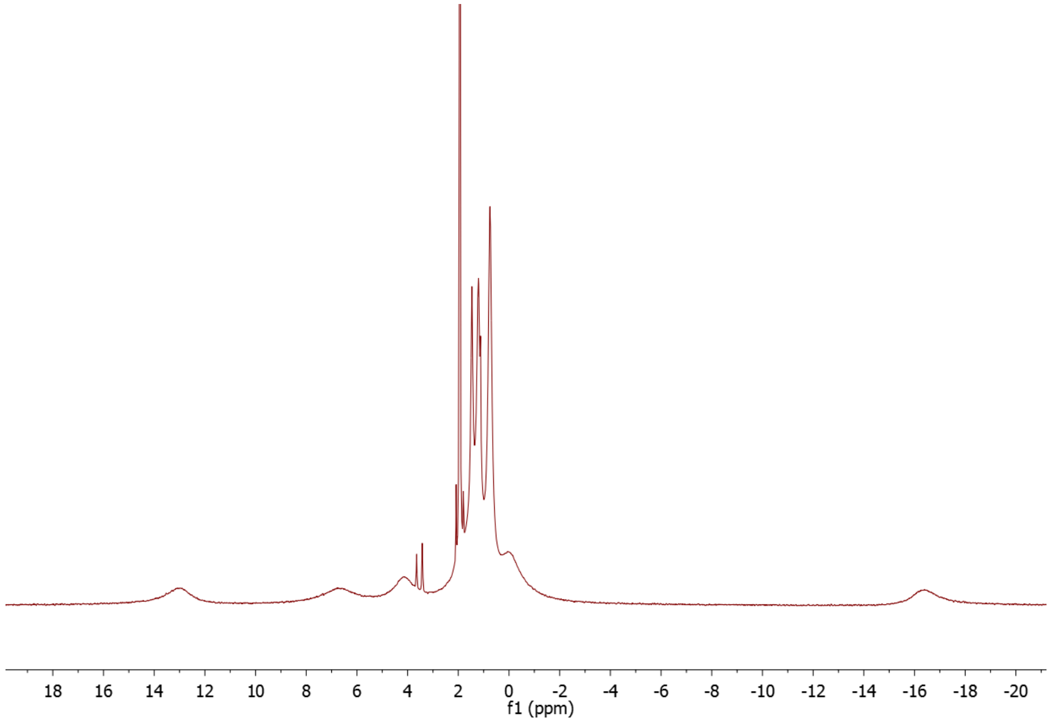

Figure S1. ^{1}H NMR Spectrum of [N(afa^{Cy})$_3$MnO](OTf) (**4**)

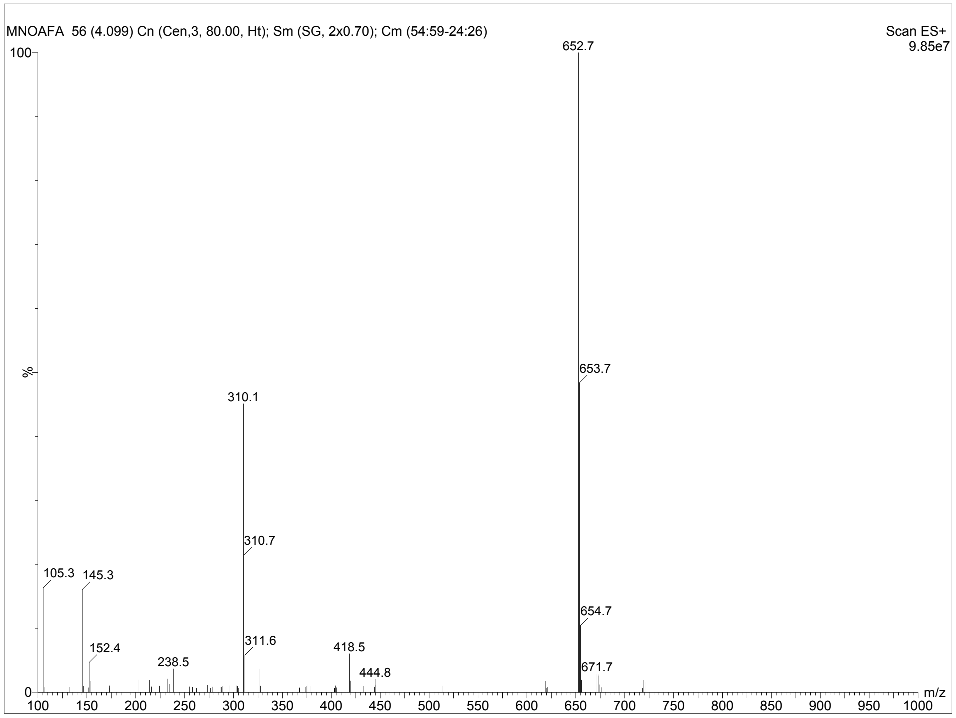

Figure S2. ESI-MS of [N(afa^{Cy})$_3$MnO](OTf) (**4**)

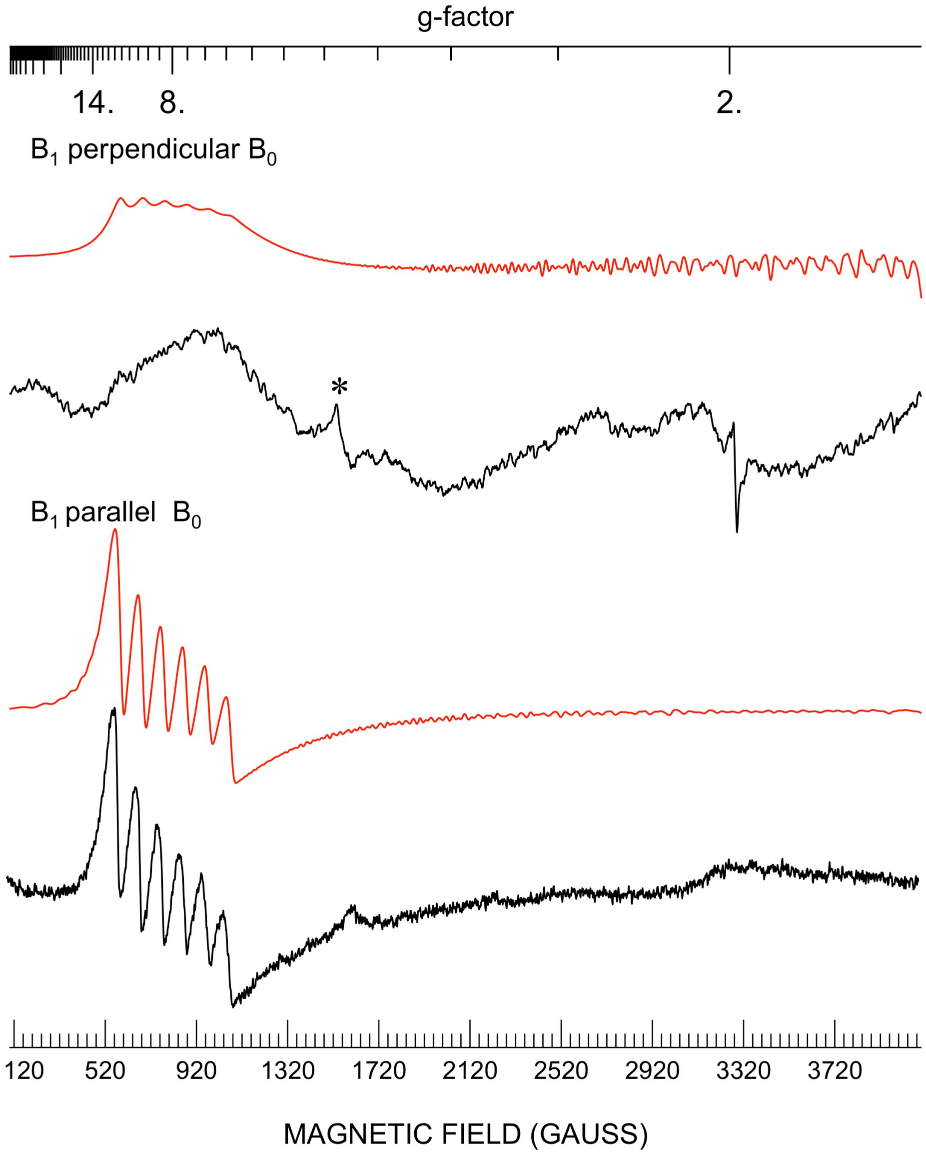

Figure S3. EPR Spectrum (X Band, Perpendicular Mode (top, simulation red, experimental black) Parallel Mode (bottom, simulation red, experimental black) of **4** (4K) (5 mM solution of **4** in a 1:1 dichloromethane/toluene mixture). The microwave frequency = 9.1008 GHz; receiver gain = 6.40E+3; modulation amplitude = 20.00G; Power = 10.00dB. The experimental data is shown in green and simulated spectrum in black g = 1.95 (E/D = .09). * denotes signal due to cavity background.

Table S1. EPR Parameters for complex **4** determined by simulation.

Compound	**4**
E/D	0.09
g_{eff}	7.9
g_z	1.95
$^{Mn}A_z$ /(MHz)	262

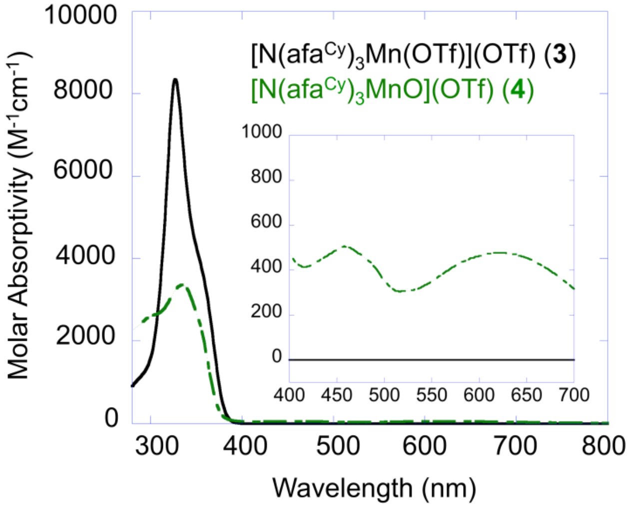

Figure S4. Electronic absorption spectrum of **3** and **4** in MeCN at ambient temperature.

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[1] Riedel, P. J.; Arulsamy, N.; Mehn, M. P. *Inorg. Chem. Commun.* **2011**, *14*, 734.

[2] Matson, E. M.; Bertke, J. A.; Fout, A. R. *Inorg. Chem.* **2014**, *53*, 4450.

[3] Nilges, M. J.; Matteson, K.; Belford, R. L. SIMPOW6: a software package for simulation of ESP powder-type spectra. In *ESR Spectroscopy in Membrane Biophysics, Biological Magentic Resonance;* Hemmings, M.A., Berlinger, L. Eds; Springer, New York, 2007.

Table S2. Crystallographic Parameters for complexes **1**-**4**.

	[N(pi^{Cy})$_3$Mn(OH$_2$)][K(THF)$_3$] (**1**) **c29das**	[N(afa^{Cy})$_2$(pi^{Cy})Mn(OH)] (**2**) **cc54cas**	[N(afa^{Cy})Mn(OTf)](OTf) (**3**) **cm90cas**	[N(afa^{Cy})MnO](OTf) (**4**) **cd73f2as**
Empirical formula	C48 H74 K Mn N7 O4	C40 H59 Mn N7 O2	C38 H51 F6 Mn N7 O6 S2	C37 H51 Mn N7 O4 F3 S
Formula weight	907.18	724.88	934.93	801.84
Temperature	174(2) K	183(2) K	171(2) K	223(2)
Wavelength	0.71073	1.54178	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	P 21/c	P 21/c	P 21 21 21	P -1
Unit cell dimensions	a = 23.141(3) b = 9.7932(14) c = 22.661(3) α = 90 β = 105.9139(18) γ = 90	a = 9.7762(4) b = 9.2337(4) c = 42.2828(18) α = 90 β = 90.193(3) γ = 90	a = 10.6932(11) b = 16.2784(17) c = 27.670(3) α = 90 β = 90 γ = 90	a = 13.1912(13) b = 13.5415(14) c = 23.494(2) α = 93.278(3) β = 103.037(3) γ = 104.963(3)
Volume	4938.7(12)	3816.9(3)	4816.5(9)	3920.1(7)
Z	4	4	4	4
Reflections collected	9058	6616	10654	13948
Independent reflections	6725	5758	10080	8844
Goodness-of-fit on F2	1.028	1.040	1.018	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0493 wR2 = 0.1338	R1 = 0.0370 wR2 = 0.0964	R1 = 0.0268 wR2 = 0.0693	R1 = 0.0973 wR2 =0.2761