

Supporting Information
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HAA by the First {Mn(III)OH} Complex with All O-Donor Ligands

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Abstract: There is considerable interest in MnOH_x moieties, particularly in the stepwise changes in those O-H bonds in tandem with Mn oxidation state changes. The reactivity of aquo-derived ligands, {MOH_x}, is also heavily influenced by the electronic character of the other ligands. Despite the prevalence of oxygen coordination in biological systems, preparation of mononuclear Mn complexes of this type with all O-donors has yet to be described. Herein, we report several Mn complexes with perfluoropinacolate (pin^F)²⁻ including the first example of a crystallographically characterized mononuclear {Mn(III)OH} with all O-donors, K₂[Mn(OH)(pin^F)₂], **3**. Complex **3** is prepared via deprotonation of K[Mn(OH₂)(pin^F)₂], **1**, the *pK_a* of which is estimated to be 17.3 ± 0.3. Cyclic voltammetry reveals quasi-reversible redox behavior for both **1** and **3** with an unusually large Δ*E*_p, assigned to the Mn(III/II) couple. Using the Bordwell method, the bond dissociation free energy (BDFE) of the O-H bond in {Mn(II)-OH₂} is estimated to be 65 – 68 kcal mol⁻¹. Complex **3** abstracts H-atoms from 1,2-diphenylhydrazine and TEMPOH, the latter of which supports a PCET mechanism. Under basic conditions, the synthesis of **1** results in K₂[Mn(OAc)(pin^F)₂], **2**, proposed to result from the oxidation of Et₂O to EtOAc by a reactive Mn species, followed by ester hydrolysis. Complex **3** alone does not react with Et₂O, but addition of O₂ at low temperature effects the formation of a new chromophore proposed to be a Mn(IV) species. The related complexes K(18C6)[Mn(III)(pin^F)₂], **4**, and (Me₄N)₂[Mn(II)(pin^F)₂], **5**, have also been prepared and their properties discussed in relation to complexes **1-3**.

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Experimental Procedures

General – Reagents

Complexes **1**, **2**, and **4** were prepared in air under ambient conditions. The synthesis of **3** and **5** were performed in a N₂ filled dry box. The anhydrous solvents CH₂Cl₂, THF, Et₂O, and hexanes were dried in an alumina-based solvent purification system (SPS) under Ar and piped directly into a N₂-filled MBraun glovebox and stored over molecular sieves for 24 hours before use. Methyl tert-butyl ether (MTBE) was dried over CaSO₄ and distilled. Fluorobenzene was dried over P₂O₅ and distilled. Hexamethyldisiloxane (HMDSO) was distilled prior to use. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was obtained commercially and was recrystallized three times from hot EtOH prior to use. The diol form (H₂pin^F) of the perfluoropinacolate ligand was purchased from Oakwood Chemical and used as received. The potassium salt of perfluoropinacol, KHpin^F, was prepared by combining H₂pin^F and KO^tBu in a 1:1 ratio followed by crystallization from Et₂O. All other reagents were obtained commercially and used without any further purification. Solution phase magnetic susceptibilities were determined via the Evans method¹⁻³ with (Me₃Si)₂O or TMS as an internal reference. UV-vis spectra were collected with a Shimadzu UV-3600 spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc. (Norcross, Georgia).

Synthesis

K[Mn(H₂O)(pin^F)₂] **1**. Portions of H₂pin^F (0.427 mL, 2.3895 mmol) and KOH (0.1414 g, 2.5201 mmol) were combined in 5 mL H₂O and then added to a 5 mL solution of MnSO₄·H₂O (0.1946 g, 1.1513 mmol) affording an initially pink solution which darkened to deep red after stirring for 12 hours. The solvent was removed under vacuum and the product was extracted into Et₂O. Crystallization by layering 3 mL of this Et₂O solution under 3 mL hexanes at RT resulted in red, needle shaped, X-ray quality crystals (0.366 g, 36.6 %). Anal. Calcd. for MnC₁₂H₂F₂₄O₅K: C, 18.57; H, 0.26; F, 58.75 %. Found: C, 18.53; H, 0.37; F, 59.11 %. UV-vis (Et₂O) (λ_{max}, nm (ε_M, cm⁻¹M⁻¹)): 413 (259), 489 (293). Evans method (d₆-acetone): 4.34 μB

K₂[Mn(OAc)(pin^F)₂] **2**. A 5 mL aqueous solution of KOH (0.6910 g, 12.3151 mmol) and H₂pin^F (0.853 mL, 4.7734 mmol) was added to a 5 mL aqueous solution of MnSO₄·H₂O (0.4014 g, 2.3749 mmol) which caused immediate formation of an orange precipitate. The reaction was stirred for 12 h, after which time the solution had become dark red and cloudy. The mixture was filtered, affording a dark red filtrate. The solvent was removed under vacuum, then the product was extracted into 3 mL Et₂O, layered under 12 mL hexanes, and stored at 7 °C for 3 days resulting in purple, needle-shaped X-ray quality crystals (1.112 g, 58.6 %). Alternatively, **2** can be obtained by reacting **1** with KOAc in MeOH followed by crystallization from Et₂O. Anal. Calcd. for MnC₁₈H₁₃F₂₄O₇K₂: C, 23.24; H, 1.41; F, 40.01. Found: C, 23.49; H, 1.39; F, 48.74. UV-vis (Et₂O) (λ_{max}, nm (ε_M, cm⁻¹M⁻¹)): 516 (135), 440 (80). Evans method (d₆-acetone): 5.35 μB

K₂[Mn(OH)(pin^F)₂]:3 MTBE **3**:3 MTBE. In a N₂-filled glovebox a portion of **1** (0.1052 g, 0.136 mmol) was dissolved in 4 mL MTBE then KN(SiMe₃)₂ (0.0270 g, 0.135 mmol) was added in 1 mL MTBE. The color immediately changed from dark red to deep blue and the solution was stirred for 30 minutes. Removing the solvent under vacuum and trituration with hexanes afforded a blue powder. This powder was dissolved in 3 mL MTBE with drops of fluorobenzene and HMDSO then filtered through celite and layered with 5 mL of hexanes at RT giving blue X-ray quality crystals overnight (42.7 mg, 30.1%). Anal. Calcd. for **3** MnC₁₂HF₂₄O₅K₂: C, 17.70; H, 0.12; F, 56.00 Found: C, 17.94; H, 0.39; F, 49.95 Anal. Calcd. for **3**:2 MTBE

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MnC₂₂H₂₅F₂₄O₇K₂: C, 26.68; H, 2.54; F, 46.03 Found: C, 24.35; H, 2.08; F, 41.48 UV-vis (Et₂O) (λ_{max} , nm (ϵ_{M} , cm⁻¹M⁻¹)): 680 (170), 460 (95). Evans method (d₈-THF): 5.45 μB

Synthesis of K(18c6)[Mn(pin^F)₂] **4**. Portions of **1** (0.2022 g, 0.261 mmol) and 18-crown-6 ether (0.1041 g, 0.394 mmol) were combined in 10 mL CH₂Cl₂ resulting in a red solution. After concentrating to 3 mL under vacuum the solution was layered under 10 mL hexanes and stored at 7 °C overnight resulting in red needle. These crystals were collected on a frit and dried by airflow turning orange in the process. Crystallization from a second dry portion of CH₂Cl₂ gives orange X-ray quality blocks (178.8 mg, 67.2%). UV-vis (CH₂Cl₂) (λ_{max} , nm (ϵ_{M} , cm⁻¹M⁻¹)): 430 (117). Anal. Calcd. for MnC₂₄H₂₄F₂₄O₁₀K: C, 28.19; H, 2.37; F, 44.60. Found: C, 28.47; H, 2.52; F, 44.34. Evans method (CD₂Cl₂): 4.85 μB

Synthesis of (Me₄N)₂[Mn(pin^F)₂]-MeCN **5**. In a N₂-filled wet box a portion of MnSO₄ (0.103 g, 0.609 mmol) was added to a 20 mL vial and suspended in 5 mL of EtOH. To this solution H₂pin^F (0.406 g, 1.210 mmol) and Me₄NOH·5 H₂O (0.441 g, 2.430 mmol) were added sequentially in 2 mL EtOH each. The reaction was stirred for 92 hours then filtered through celite and dried to a white powder. Crystallization from a slow diffusion of Et₂O into a MeCN solution yielded X-ray quality crystals after 48 hours at -30° C (170mg, 32.2%). Evans method (d₃-Acetonitrile): 5.97 μB

In a N₂ filled dry box MnCl₂ (0.050 g, 0.400 mmol) was suspended in 5 mL THF then KHpin^F (0.300 g, 0.800 mmol) was added in 1 mL THF and stirred for 20 mins affording a colorless, hazy solution. A portion of KO^tBu (0.091 g, 0.810 mmol) was added in 1 mL THF and stirred for 30 mins resulting in a clear colorless solution with a colorless precipitate. This solution was dried, triturated with Et₂O and hexanes, then extracted into 5 mL MeCN and filtered through celite to remove KCl. To this MeCN solution Me₄NBr (0.600 g, 3.90 mmol) was added and stirred for 12 hours. Finally, this solution was filtered through celite to remove KBr and unreacted Me₄NBr, concentrated, and layered under Et₂O stored at -30 °C overnight affording colorless crystals overnight. (0.060 g, 16%) Anal. Calcd. For MnC₂₂H₂₇F₂₄N₃O₄: C, 29.1; H, 3.00; N, 4.63; F, 50.20. Found: C, 29.3; H, 3.05; N, 4.65; F, 48.9.

Single-Crystal X-ray Diffraction

Single crystals of **1**, **2**, **4**, and **5** were mounted on a Cryoloop with Paratone N oil, and X-ray diffraction studies were carried out on a Bruker Proteum-R with a CCD detector or a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). A single crystal of **3** was mounted on a Cryoloop with Paratone N oil, and diffraction studies were carried out on a Bruker D8 Venture CCD diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Data for all compounds were collected in a nitrogen gas stream at 100(2) K using ω and ϕ scans. The data for **1**, **2**, **4**, and **5** were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structures. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The data for **3** was integrated and scaled using the Bruker Apex 4 software and a solution was obtained using the Olex 2 software. The hydroxyl proton H(1) was located in the difference map. Its position was constrained relative to O(1) using the appropriate HFIX command and refined anisotropically by full-matrix least-squares.

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Electrochemistry

Cyclic voltammetry studies of **1** and **3** were performed in a N₂-filled glovebox with 5 mM anhydrous THF solutions of each complex and 250 mM of [NBu₄][PF₆] as the supporting electrolyte. A second electrochemical study was performed on a 2.5 mM solution of **1** in 60:40 CH₂Cl₂:Et₂O with 100 mM TBAPF₆ as a supporting electrolyte. All experiments used a standard three-electrode cell connected to an external CHI 630C potentiostat powered by a personal computer with CHI software. A glassy carbon working electrode (0.5 mm diameter) was employed with a Ag/AgNO₃ reference electrode and Pt wire counter electrode. The working electrode was rinsed and polished between experiments with polishing alumina and a fine grit pad. After all scans were complete, 0.5 mM of ferrocene (Fc) or CoCp*₂PF₆ was added to the same solution to be used to reference potentials.

Results and Discussion

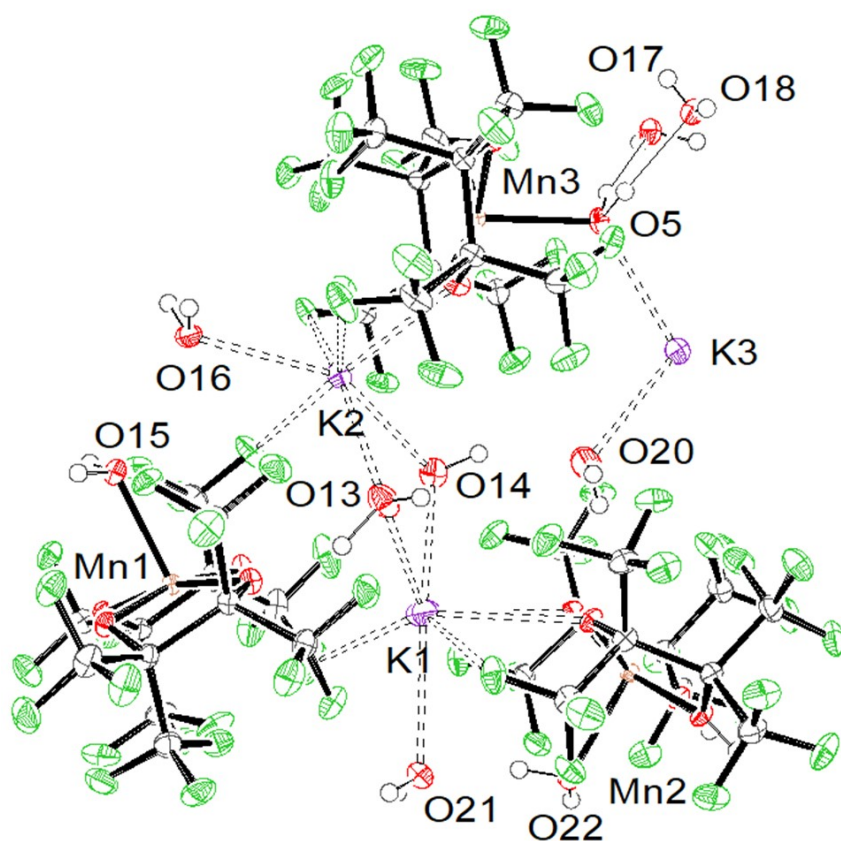


Figure S1. ORTEP of **1** with showing the three K[Mn(OH₂)(pin^f)₂] molecules and the seven H₂O molecules that make up the asymmetric unit.

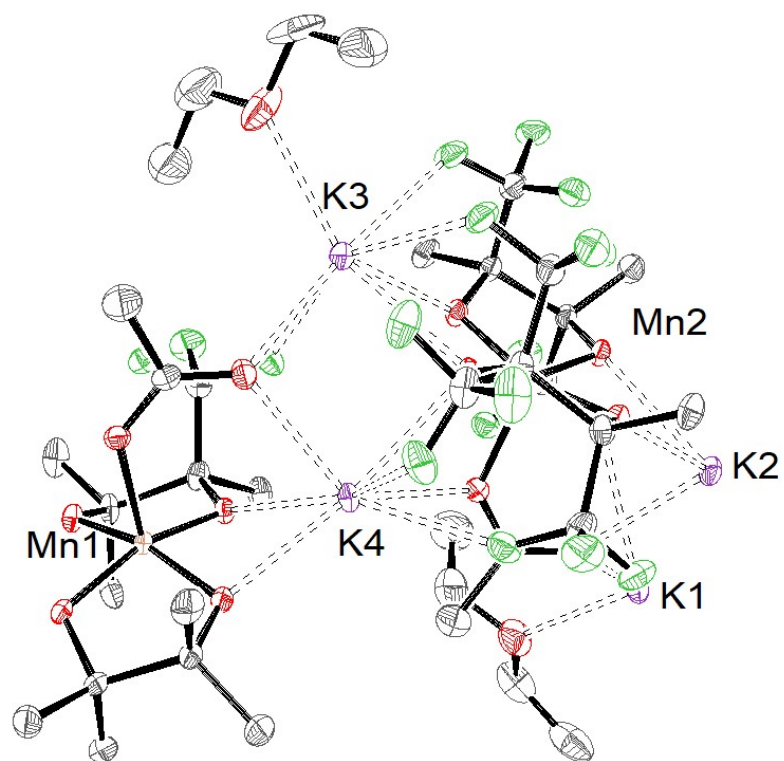


Figure S2. ORTEP of 2 with hydrogen atoms, and fluorine atoms not involved in K-F interactions removed for clarity.

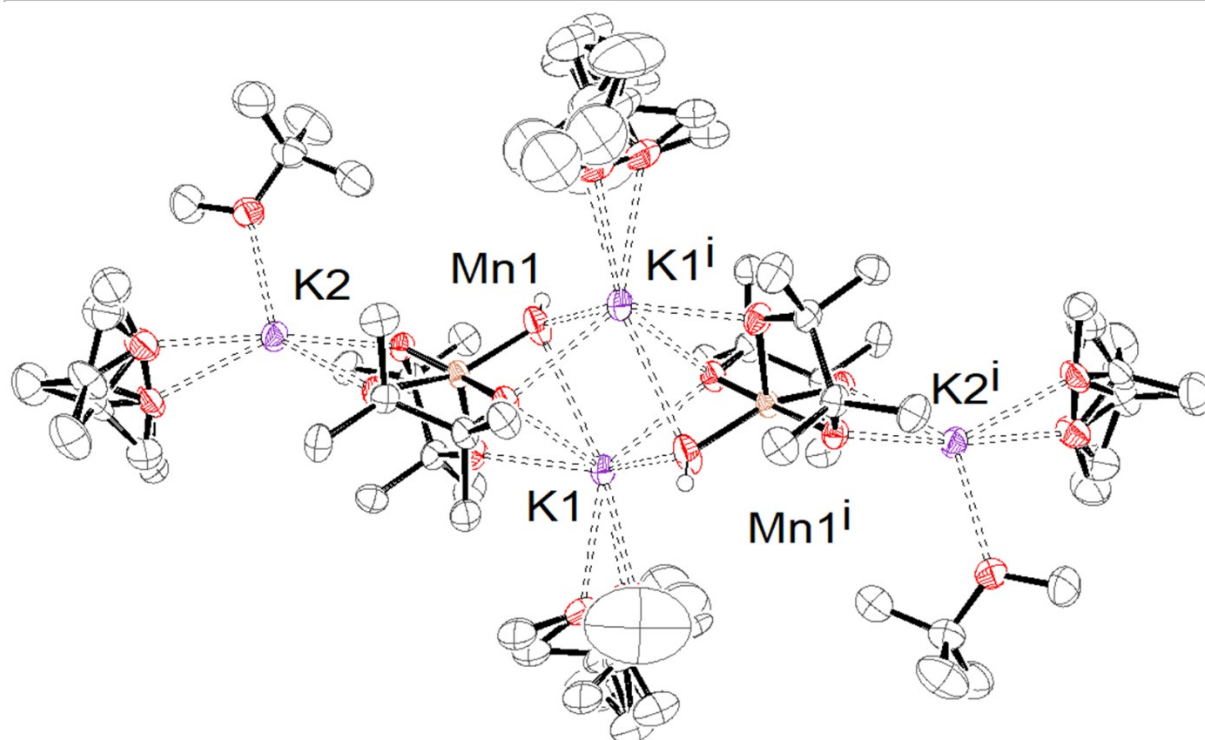


Figure S3. ORTEP of **3** with hydrogen and fluorine atoms omitted for clarity. Ellipsoids are shown at the 50% probability level.

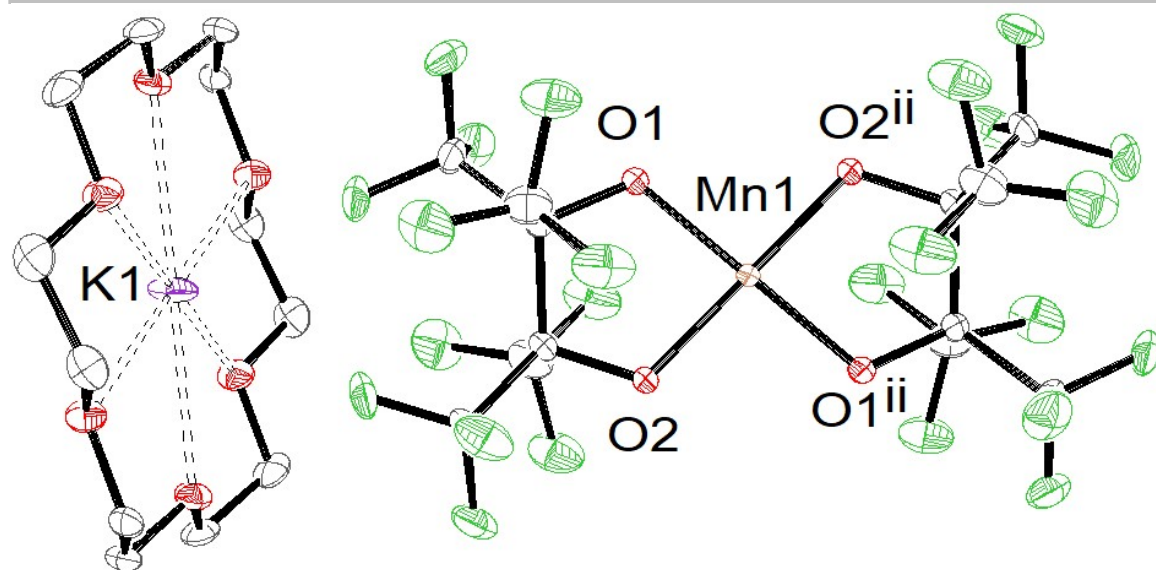


Figure S4. ORTEP of **4** with cation included. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at the 50% probability level.

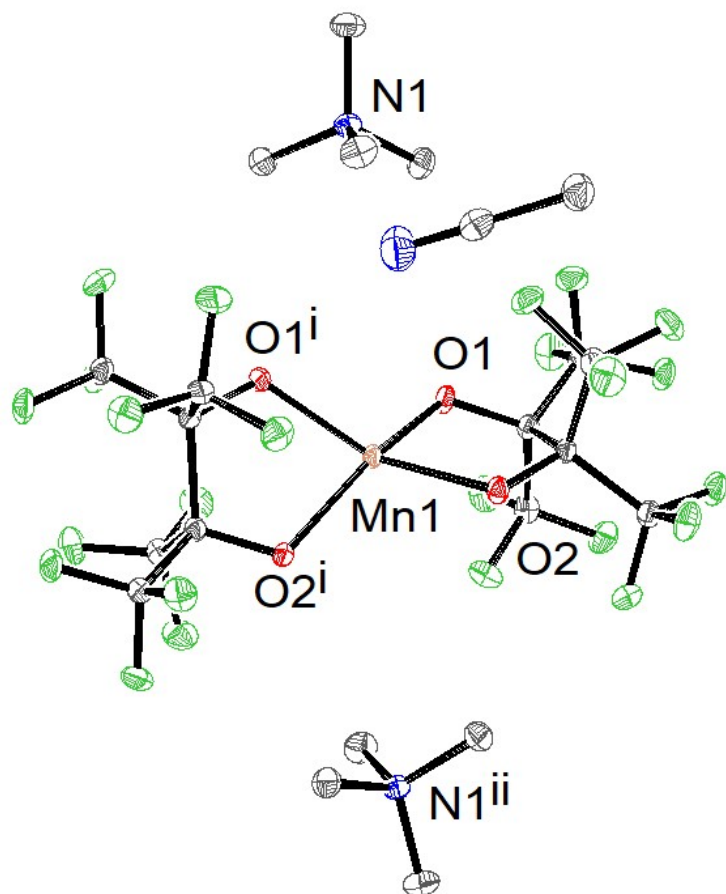


Figure S5. ORTEP of 5 with cations and solvent molecule included. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at the 50% probability level.

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Table S1. Selected bond lengths (Å) and angles (°) for complexes 1-3

	1 Mn(1)	1 Mn(2)	1 Mn(3)	2 Mn(1)	2 Mn(2)	3
Mn-O _e	2.168(3)	2.160(3)	2.215(3)	2.094(2)	2.086(2)	1.857(3)
Mn-O _a	1.890(3)	1.886(3)	1.893(3)	1.889(2)	1.891(2)	1.912(3)
Mn-O _b	1.893(3)	1.891(3)	1.885(3)	1.923(2)	1.926(2)	1.935(3)
Mn-O _c	1.888(3)	1.890(3)	1.884(3)	1.879(2)	1.896(2)	1.920(3)
Mn-O _d	1.883(3)	1.898(3)	1.883(3)	1.898(2)	1.887(2)	2.059(3)
O _a -Mn-O _e	103.83(12)	88.63(12)	88.98(12)	97.97(10)	97.81(10)	84.79(13)
O _b -Mn-O _e	90.64(11)	102.16(12)	107.14(12)	92.07(10)	92.29(10)	150.72(15)
O _c -Mn-O _e	89.68(11)	103.81(12)	90.80(11)	99.74(10)	98.26(10)	101.25(13)
O _d -Mn-O _e	103.48(12)	93.12(12)	102.02(12)	106.34(10)	107.44(10)	98.75(15)
O _a -Mn-O _b	84.67(12)	84.81(12)	84.68(12)	94.34(11)	94.24(10)	84.70(13)
O _b -Mn-O _d	165.84(12)	164.50(13)	163.70(12)	161.56(10)	160.25(11)	109.80(12)
O _c -Mn-O _d	84.55(12)	84.35(12)	84.37(12)	92.27(10)	92.53(10)	101.25(13)
O _a -Mn-O _c	166.47(13)	167.16(13)	167.06(12)	162.21(11)	163.84(11)	171.99(12)
O _a -Mn-O _d	92.88(12)	98.29(12)	97.78(12)	84.30(10)	84.28(10)	103.90(12)
O _b -Mn-O _c	94.57(12)	89.43(12)	89.77(12)	83.41(10)	83.42(10)	82.26(11)
τ ₅	0.01	0.04	0.06	0.01	0.06	0.35

Table S2. Selected bond lengths (Å) and angles (°) for complexes 4 and 5.

	4	5
Mn-O _a	1.8588(15)	2.0400(10)
Mn-O _b	1.8588(15)	2.0400(10)
Mn-O _c	1.8574(14)	2.0447(11)
Mn-O _d	1.8574(14)	2.0448(11)
O _a -Mn-O _b	85.50(6)	105.01(6)
O _b -Mn-O _a	94.50(6)	149.54(4)
O _c -Mn-O _d	85.50(6)	81.27(4)
O _a -Mn-O _c	94.50(6)	81.27(4)
O _a -Mn-O _d	180.0	149.54(4)
O _b -Mn-O _c	180.0	108.62(6)
τ ₄	0.0	0.43

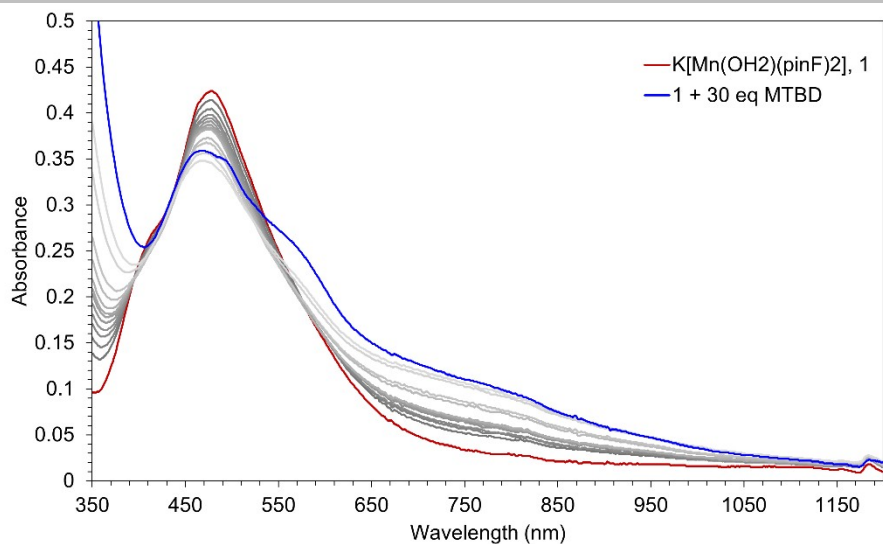


Figure S6. UV-vis spectra for the titration of **1** (red) with MTBD. Addition of one equivalent of 30 eq. MTBD results in only partial conversion to **3**.

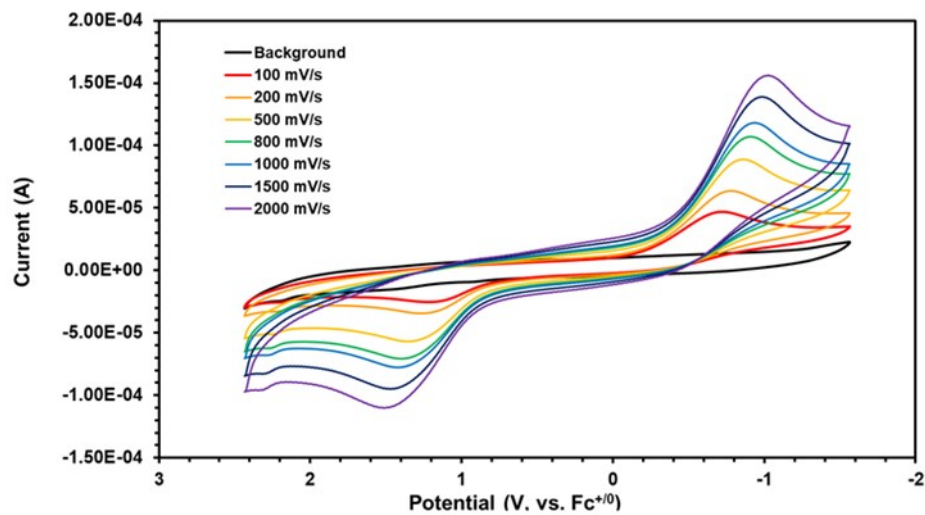


Figure S7. Cyclic voltammograms of 5 mM **1** in THF/250 mM TBAPF₆ recorded over a range of scan rates from 100-2000 Vs⁻¹. Recorded using a glassy carbon working electrode, Pt(s) counter electrode and a AgNO₃/Ag reference electrode. Referenced to Fc⁺⁰ using an internal standard (Figure S8).

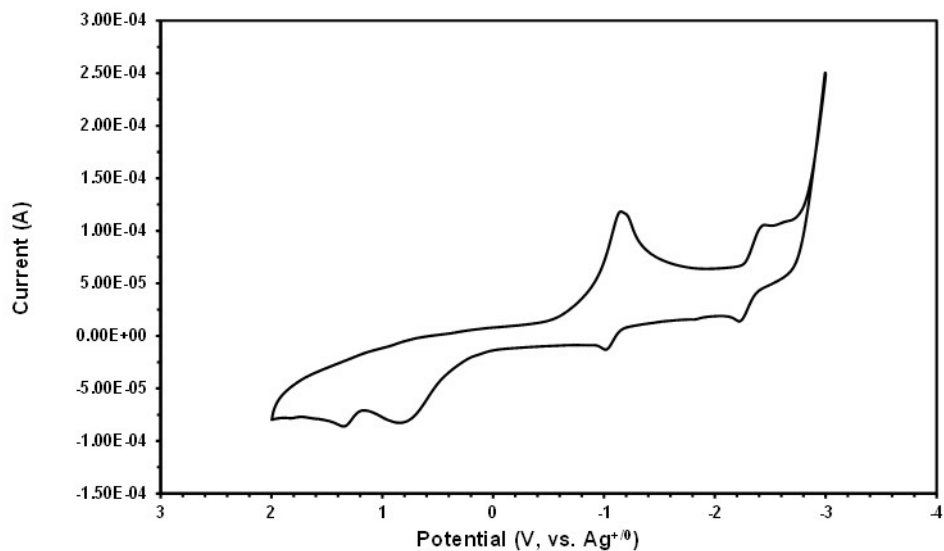


Figure S8. Voltammogram of 5 mM **1** in THF/250 mM TBAPF₆ with [CoCp*₂]PF₆ added as an internal reference. The Co(III/II) couple can be seen at -2.345 V (vs. Ag^{+/0}). This potential was used to standardize using a known potential of for CoCp*₂ of -1.94 V vs Fc^{+/0}.

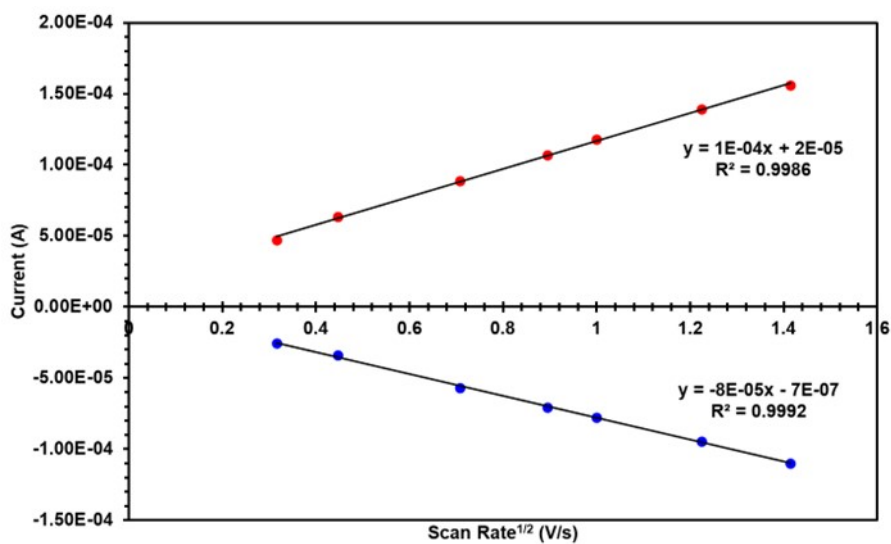
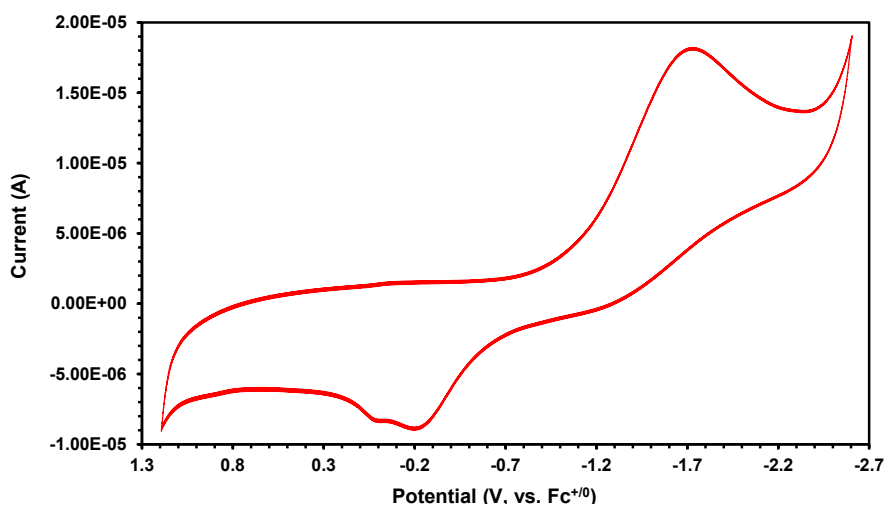
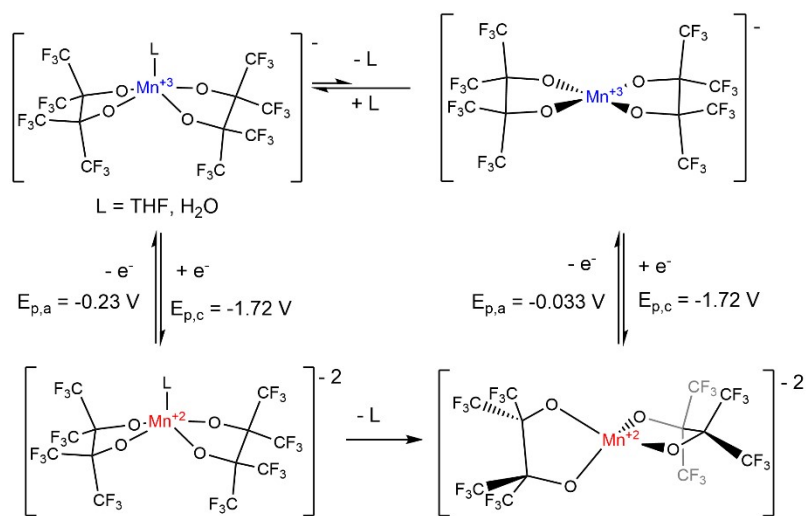


Figure S9. Randles-Sevcik plot for the cyclic voltammetry of **1** shown in Figure S7.



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Figure S10. Cyclic voltammogram of 2.5 mM **1** in 60:40 CH₂Cl₂:Et₂O with 100 mM TBAPF₆ as a supporting electrolyte. Recorded at 100 mVs⁻¹ using a glassy carbon working electrode, Pt(s) counter electrode, and a AgNO₃/Ag reference electrode. Potentials are referenced to Fc^{+/0} using an internal standard.



Scheme S11. Depiction of the chemical changes experienced by **1** under the cyclic voltammetry conditions.

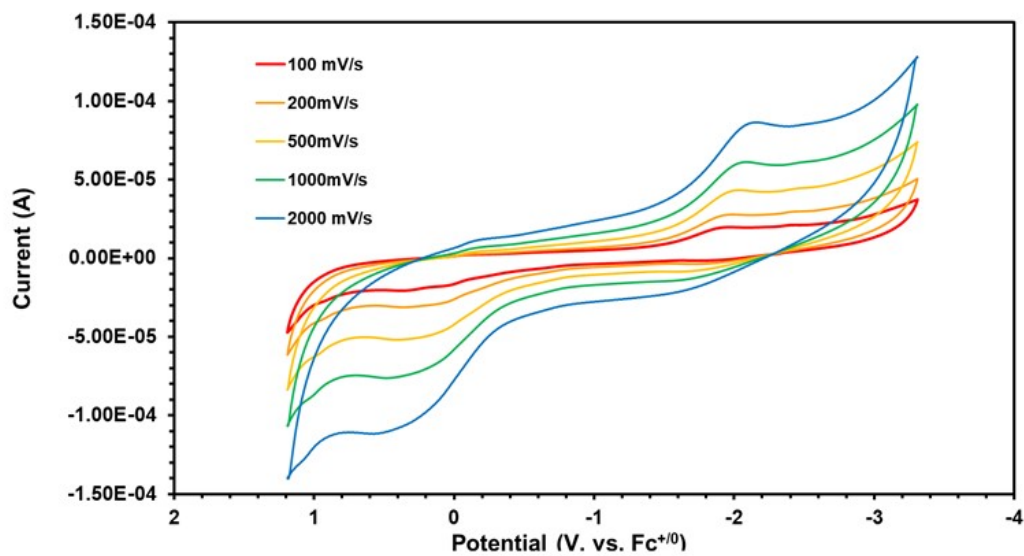


Figure S12. Cyclic voltammograms of 5 mM **3** in THF/250 mM TBAPF₆ recorded over a range of scan rates from 100-2000 Vs⁻¹. Recorded using a glassy carbon working electrode, Pt(s) counter electrode and a AgNO₃/Ag reference electrode Referenced to Fc⁺⁰ using an internal standard (Figure S12).

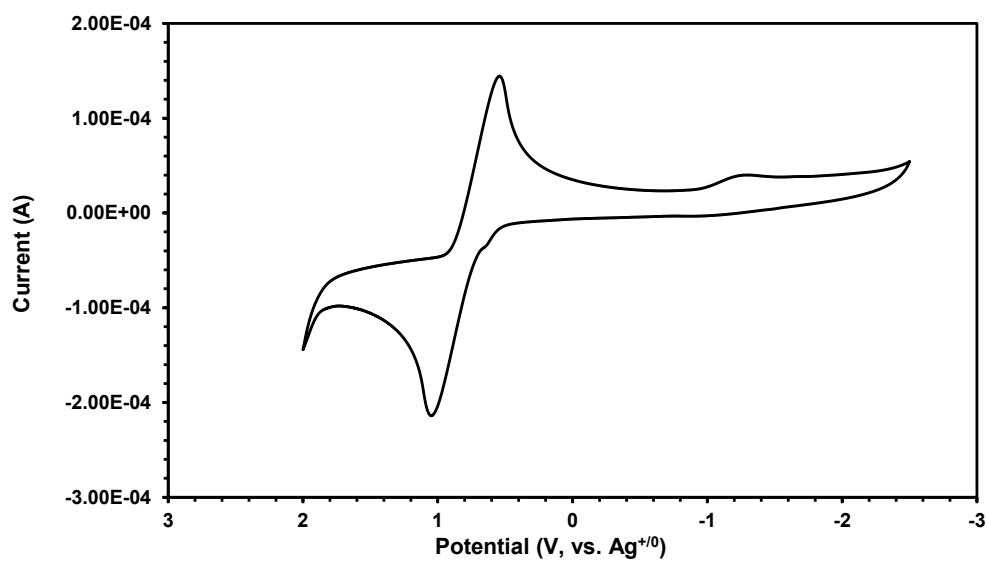


Figure S13. Voltammogram of 5 mM **3** in THF/250 mM TBAPF₆ with FeCp₂ added as an internal reference. The Fe(III/II) couple can be seen at +0.809 V (vs. Ag⁺⁰).

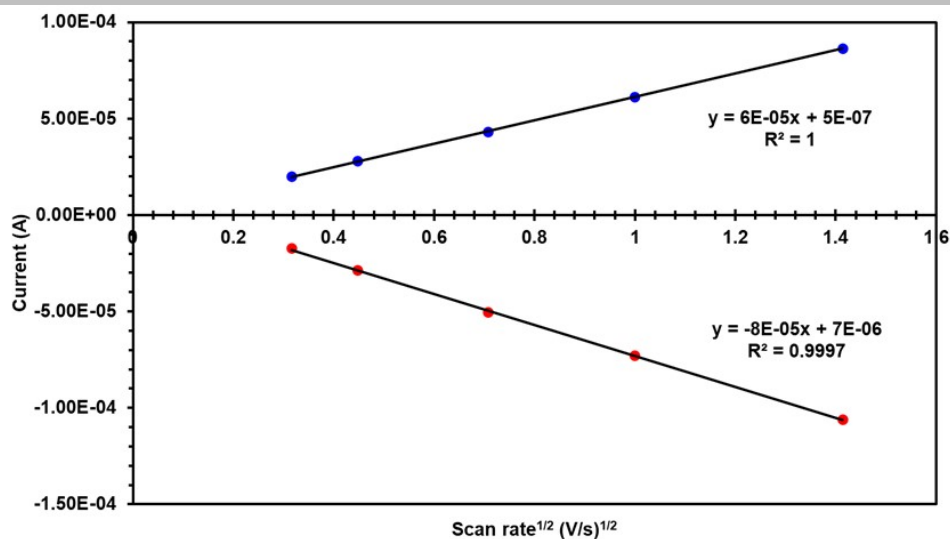


Figure S14. Randles-Sevcik plot for the cyclic voltammetry of **3** shown in Figure S11.

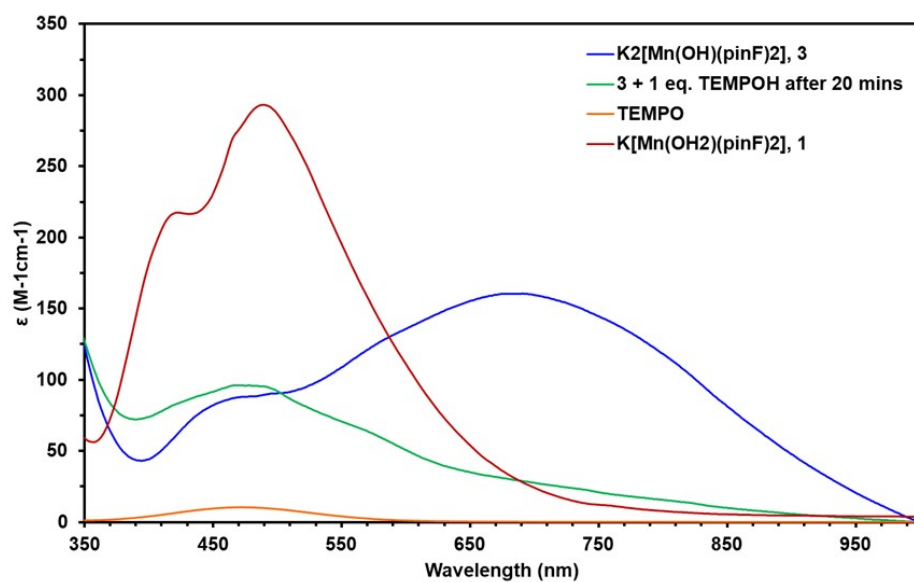


Figure S15. UV-vis spectra of a 2 mM Et₂O solution of **3** before (blue) and after (green) the addition of one equivalent of TEMPOH. The spectrum of **1** (red) and the TEMPO radical (orange) are included for comparison.

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Author Contributions

Shawn M. Moore – Data curation, investigation, analysis, and primary authorship

Jennifer L. Steele – Investigation and analysis

Ellen M. Laaker – Investigation

Arnold L. Rheingold – X-ray crystallography

Linda H. Doerrer – funding acquisition, project administration, authorship, and validation.

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