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Supporting Information

A Redox-active Manganate(0) Dicarbene Metalloradical

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| General Comments | 2 |
|---|----|
| Syntheses | 3 |
| [Ph ₂ B(^{tBu} NHC) ₂ Mn(CO) ₃] (1) | 3 |
| [Mn ⁰][K(2.2.2)crypt] (2) | 4 |
| [Mnº][Na(2.2.2)crypt] (3) | 4 |
| [Mnº][Li(DME)(12-crown-4)] (4) | 4 |
| NMR Spectra | 5 |
| IR Spectroscopy | 7 |
| Electrochemistry | 7 |
| UV-vis Spectra | 10 |
| References | 11 |

General Comments

All reactions were carried out under an atmosphere of nitrogen using a standard glove box or Schlenk techniques unless stated otherwise. All reagents and solvents were stored in a nitrogen filled glove box prior to use. Acetonitrile (CH₃CN), dichloromethane (DCM), diethyl ether (Et₂O), tetrahydrofuran (THF), toluene and pentane were dried and degassed over activated alumina using an IT/Inert solvent purification system. Additionally, MeCN, DCM, Et₂O and toluene were dried over 20% w/v activated 3 Å molecular sieves.^[1] For chemical reduction, THF was dried again over 20% w/v activated 3 Å molecular sieves. Glassware was dried overnight at 140 °C and cooled under dynamic vacuum in a glove box antechamber. Glass fiber filters (1.5 μ m) were dried overnight at 140 °C and stored in a glovebox. Infrared spectra were recorded on a Thermo Nicolet FT-IR instrument by preparing a KBr pellet in the glove box. UVvis experiments were carried out using an Agilent Cary 100 spectrophotometer. Compounds $[Li(Ph_2B(^{tBu}NHC)_2 \bullet Et_2O]^{[2]} and [Mn(CO)_3(^{tBu}CN)Br]_2^{[3]} were prepared according to known procedures. The electrolyte$ $[^{n}Bu_{4}N][B(C_{6}F_{5})_{4}]$ was prepared by metathesis of an aqueous solution of $KB(C_{6}F_{5})_{4}$ and $[^{n}Bu_{4}N]Br$ dissolved in methanol, then recrystallized from fluorobenzene/pentane in a glove box prior to use. The commercially purchased electrolyte [nBu₄N][PF₆] (99+%) was recrystallized from fluorobenzene/pentane in a glovebox prior to use. All other reagents were purchased from commercial suppliers and used as received. Elemental analyses were obtained from Atlantic Microlabs (Norcross, GA) or the CENTC Elemental Analysis Facility at the University of Rochester. In the latter facility, microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their composition determined with a PerkinElmer 2400 Series II Analyzer. After multiple attempts on independently prepared samples of 2 and 3 sent to different facilities, EA analyses were consistently low in carbon and/or nitrogen. Using a combustion aid did not affect the outcome and we attribute this discrepancy to incomplete combustion due to the presence of the borate anion.^[4]

EPR Spectroscopy. Continuous-wave X-band EPR experiments were performed on a Bruker Elexsys580E EPR spectrometer using a standard TE102 resonator. EPR samples were anaerobically prepared at 1 mM Mn^o concentration in 2-MeTHF (a glass forming solvent), and after transferring into standard 4mm OD EPR quartz tubes the samples were air-tight sealed with rubber caps and immediately frozen in liquid nitrogen until use. All spectra were recorded at 77K using a liquid nitrogen finger quartz dewar. Typical EPR-settings were: microwave frequency, 9.534 GHz, microwave power 0.2 mW, and modulation amplitude 5 G. The EPR simulations were performed using EasySpin (http://www.easyspin.org/).^[5]

Electrochemistry. Cyclic voltammetry experiments were conducted under N₂ at 295 ± 3 K using a standard threeelectrode setup consisting of a PEEK-encased glassy carbon disc working electrode ($\emptyset = 1$ mm) and Type 2 graphite rod counter electrode ($\emptyset = 3$ mm). In acetonitrile, the Ag/AgCl pseudoreference electrode was stored in a glass compartment containing solvent and electrolyte and was separated from the bulk solution using a porous glass frit (Coralpor). In THF and MTBE, a bare silver wire was used as the pseudoreference electrode. The working electrode was polished with 0.25 µm diamond polishing paste and lapping oil in the glove box and thoroughly rinsed with the solvent used in the experiment. A Gamry Reference 1010B potentiostat and Gamry software were used for data collection and analysis. Samples contained either 0.1 M [$^{n}Bu_{4}N$][PF₆] (MeCN, THF) or 0.075 M [$^{n}Bu_{4}N$][B(C₆F₅)₄] (MTBE) as the electrolyte, organic solvent (3 mL), and 1.0 mM analyte. All CVs are referenced to the Cp₂Fe^{+/0} redox couple (0 V).

NMR Spectroscopy. NMR spectroscopic data were recorded on a Bruker Avance III HD 500 MHz spectrometer at 25°C. Spectra for ¹H and ¹³C were referenced to their respective residual protio solvent signal, ^[6] ¹¹B to external BF₃-OEt₂ and recorded in parts per million. Deuterated solvents were degassed via three freeze-pump-thaw cycles and dried over 10% w/v activated 3 Å molecular sieves in a nitrogen filled glove box. Solution magnetic susceptibilities were determined by Evans' method measurements in CD₃CN by dissolving a known concentration of analyte in a 5 mm OD NMR tube and inserting a flame sealed glass tube (1.7 mm OD) with pure CD₃CN and measuring the change in frequency for the residual protio signal.^[7]

X-Ray Crystallography. Single crystals were selected and mounted using Paratone onto a nylon fiber and cooled to the data collection temperature of 100(2) K with a stream of dry nitrogen gas. X-ray diffraction intensities were collected on a Rigaku XtaLAB Synergy-I diffractometer using CuK α (1.54178 Å) radiation with a HyPIX HPC detector. Structures were refined by full-matrix least squares based on F² with all reflections (SHELXTL V5.10; G. Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was applied. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center and is available free of charge through the CCDC online database.

Density Functional Theory. Calculations were performed with ORCA Version 4.0.1.2^[8] using a multi-level approach. All calculations include the SMD solvation model^[9] in acetonitrile or THF and D3 dispersion correction with Becke-Johnson damping and three-body correction (D3BJ ABC).^[10,11] Geometry optimization and numerical frequency calculations use the meta-GGA TPSS functional with the def2-TZVP^[12] basis set and def2/J^[13] auxiliary basis set (TPSS-D3(BJ)/def2-TZVP). Optimizations use a Grid5 integration grid and TightOpt convergence parameters. Full vibrational and thermochemical analyses were performed on optimized structures to obtain solvent-corrected free energies (G°) and enthalpies (H°) under standard state conditions. Optimized ground states have zero imaginary frequencies.

Syntheses [Ph₂B(^{tBu}NHC)₂Mn(CO)₃] (**1**)

In the glovebox, [Li(Ph₂B(^{tBu}NHC)₂•Et₂O] (167.7 mg, 0.34 mmol) was added to a vial and dissolved in THF (15 mL). A solution of [Mn(CO)₃(^{tBu}CN)Br]₂ (102.7 mg, 0.17 mmol) dissolved in THF (10 mL) was added dropwise to the vial and the mixture turned dark orange. The mixture was removed from the glovebox in a sealed flask and stirred at 45°C overnight to yield a bright red-orange solution. The solution was taken back into the box, filtered through a glass fiber filter and dried under vacuum to yield a crystalline dark red-brown powder. Diethyl ether (2 mL) was added to the residue followed by pentane (6 mL) to generate an oily brown residue on the bottom of the vial. The Et₂O/pentane solution was filtered through a glass fiber filter and dried under high vacuum to yield a red-brown powder. A DCM/pentane solution (1:4) mixture was added and after stirring for 15 mins a light-orange precipitate appears. The DCM/pentane solution was filtered through a glass fiber filter and was dried under high vacuum to yield 1 as a red-orange powder. Methanol (1 mL) was added to the red-orange powder and stirred for 10 min to remove any remaining LiBr. Then, the red-orange powder was washed on a 2 mL medium-pore filter frit with an additional 0.8 mL of MeOH, dried under vacuum, then dissolved using Et₂O (3 mL). The Et₂O solution was subsequently dried under vacuum to yield a red-orange powder (78 mg, 42%). Single crystals suitable for X-ray diffraction were grown via THF/pentane vapor diffusion. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.57 (1H, CH_{Ar}), 7.32 (2H, CH_{Ar}), 7.18 (3H, CH_{Ar}), 7.12 (2H, CH_{NHC}), 6.88 (4H; 2H, CH_{Ar} and 2H, CH_{NHC}), 6.76 (2H,CH_{Ar}), (1.77 (18H, ^tBu) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 191.2 (NCN), 140.8, 135.5, 133.7, 132.1, 128.4, 127.4, 127.3, 127.0, 123.3, 118.0, 57.7 ($C(CH_3)_3$), 31.9 $C(CH_3)_3$. Resonances for the CO ligands could not be observed. ¹¹B{¹H} NMR (160 MHz, CD₂Cl₂) δ -1.82 ppm. **IR** (KBr): 2010, 1928, 1881 cm⁻¹ (ν_{CO}). **UV-vis**: MeCN, $\epsilon_{\lambda max}$ (M⁻¹cm⁻¹): $\epsilon_{454} = 710 \pm 20$, $\epsilon_{349} = 350 \pm 10$; DCM, $\epsilon_{\lambda max}$ (M⁻¹cm⁻¹): ϵ_{455} = 890 ± 10, ϵ_{357} = 620 ± 40 Anal. calcd (%) for C₂₉H₃₂BMnN₄O₃: C: 63.29, H: 5.86, N: 10.18; Found C: 63.22, H: 6.05, N: 9.99.

[Mn⁰][K(2.2.2)crypt] (2)

In the glovebox, **1** (34.9 mg, 0.063 mmol) and [2.2.2]cryptand (26.2 mg, 0.070 mmol) were added to a vial with THF (5 mL). Solid KC₈ (9.4 mg, 0.070 mmol) was added to the orange solution and the mixture instantly turned a dark forest-green and was stirred for 2 h. The dark-green solution was filtered through a glass fiber filter and dried under vacuum to yield a dark forest-green crystalline powder. The powder was suspended in pentane and stirred for 15 min. The liquid was decanted and the solid was dried under vacuum to yield the crude product as a dark forest-green powder (42 mg, 68%). Single crystals suitable for X-ray diffraction were grown via slow evaporation of **2** dissolved in diethyl ether. To purify the crystalline powder, crystals are grown from THF/ether vapor diffusion. ¹H NMR (500 MHz, CD₃DN): δ 3.56 (s, 12H, [K(crypt)]⁺), 3.51 (t, 12H, [K(crypt)]⁺), 2.52 (t, 12H, [K(crypt)]⁺) ppm. ¹¹B{¹H} NMR (160 MHz, CD₃CN) no signal. IR (KBr): 1908, 1808, 1765 cm⁻¹ (v_{CO}). μ_{eff} (Evans', CD₃CN) 2.06 μ_{B} . UV-vis (MeCN, $\varepsilon_{\lambda max}$ (M⁻¹cm⁻¹)): $\varepsilon_{669} = 220 \pm 10$, $\varepsilon_{360} = 1000 \pm 100$), Anal. calcd (%) for C₄₇H₆₈BKMnN₆O₉: C: 58.44, H: 7.10, N: 8.70; Found C: 55.43, H: 7.02, N: 7.73.

[Mn⁰][Na(2.2.2)crypt] (3)

Sodium naphthalenide (NaNap) was prepared in the glovebox by adding naphthalene (6 mg, 0.05 mmol) to a vial containing a large excess of Na⁰ chunks, followed by addition of THF (1 mL). The mixture turned dark green and was stirred for 30 min. The resulting solution was filtered through a glass fiber filter and added dropwise to an orange solution of **1** (22 mg, 0.04 mmol) and [2.2.2]cryptand (18 mg, 0.05 mmol) dissolved in THF (2 mL). The resulting dark-green solution was stirred for 2 h, filtered through a glass fiber filter, and dried under high vacuum to yield a dark green oily residue. An ether/pentane solution (1:1) mixture was added and after scraping the oily residue a green powder was obtained (24 mg, 63%). Single crystals suitable for X-ray diffraction were grown via vapor diffusion of pentane into a THF solution containing **3**. ¹**H NMR** (500 MHz, C₆D₆): δ (br), 3.06 (br, 12H, Na(crypt)), 3.01 (br, 12H, Na(crypt)), 2.03 (br, 12H, Na(crypt)), 1.55 (br) ppm. ¹¹B{¹H} NMR (160 MHz, C₆D₆) no signal. IR (KBr): 1908, 1801, 1771 cm⁻¹ (v_{C0}). μ_{eff} (Evans', CD₃CN) 2.49 μ_{B} . Anal. calcd (%) for C₄₇H₆₈BNaMnN₆O₉: C: 59.43, H: 7.22, N: 8.85; Found C: 58.6, H: 7.04, N: 7.77.

[Mn⁰][Li(DME)(12-crown-4)] (4)

Lithium naphthalene (LiNap) was prepared in the glovebox by adding naphthalene (6.4 mg, 0.05 mmol) to a vial containing a large excess of Li⁰ chunks, followed by addition of THF (1 mL). The mixture turned dark green and stirred for 30 min to yield a dark purple solution. The resulting solution was filtered through a glass fiber filter and added dropwise to a solution of **1** (23 mg, 0.04 mmol) and 12-crown-4 (17.8 μ L, 0.11 mmol) dissolved in THF (1.5 mL). The resulting dark-green solution was stirred for 2 h, filtered through a glass fiber filter, and dried under high vacuum to yield a dark green oily residue. Pentane (2 mL) was added and after scraping the oily residue a forest-green powder was obtained after decanting the solvent and drying under vacuum. Crude yield: (27.6 mg, 73% based on 2 equiv. 12-crown-4 coordinated to Li⁺). Due to the high sensitivity of **4** the product was not purified any further. Single crystals suitable for X-ray diffraction were grown via vapor diffusion of pentane into a dimethoxyethane (DME) solution with formation of the countercation [Li⁺(DME)(12-crown-4)]⁺. The crystalline product slowly decomposes in paratone oil at room temperature and crystal samples were kept on a bed of dry ice prior to mounting on the X-ray diffractometer.

NMR Spectra



Figure S1 – ¹H NMR spectrum of **1** (500 MHz, CD₂Cl₂, 25 °C).



Figure S3 – Background corrected $^{11}B\{^{1}H\}$ NMR spectrum of 1 (160 MHz, CD₂Cl₂, 25 °C).

IR Spectroscopy







Figure S5 – Left: CVs of **1** (1.0 mM) at various scan rates (50 – 1000 mV/s) in MeCN with 0.1 M [ⁿBu₄N][PF₆] under an N₂ atmosphere. $E_{1/2}$ values at -1.75 V vs. Fc^{+/0}). Right: Plot of the peak current as a function of $\upsilon^{\frac{1}{2}}$.



Figure S6 – Left: CVs of **1** (1.0 mM) at various scan rates (50 – 100 mV/s) in a 0.1 M [$^{n}Bu_{4}N$][PF₆] electrolyte in 75:25 MeCN:THF under an N₂ atmosphere. E_{1/2} values at -1.79 V vs Fc^{+/0}. Right: Plot of the peak current as a function of $u^{\frac{1}{2}}$.



Figure S7 – Left: CVs of **1** (1.0 mM) at various scan rates (50 – 100 mV/s) in a 0.1 M [$^{n}Bu_{4}N$][PF₆] electrolyte in 50:50 MeCN:THF under an N₂ atmosphere. E_{1/2} values at -1.83 V vs Fc^{+/0}. Right: Plot of the peak current as a function of $U^{\frac{1}{2}}$.



Figure S8 – Left: CVs of **1** (1.0 mM) at various scan rates (50 – 100 mV/s) in a 0.1 M [ⁿBu₄N][PF₆] electrolyte in 25:75 MeCN:THF under an N₂ atmosphere. $E_{1/2}$ values at -1.88 V vs. Fc^{+/0}. Right: Plot of the peak current as a function of $u^{\frac{1}{2}}$.



Figure S9 – Left: CVs of **1** (1.0 mM) at various scan rates (50 – 1000 mV/s) in a 0.1 M [$^{n}Bu_{4}N$][PF₆] electrolyte in THF under an N₂ atmosphere. E_{1/2} values at -1.94 vs. Fc^{+/0}. Right: Plot of the peak current as a function of $u^{\frac{1}{2}}$.



Figure S10 – Left: CVs of **1** (1.0 mM) at various scan rates (25 – 100 mV/s) in MTBE with ~ 0.75 M [ⁿBu₄N][B(C₆F₅)₄] under an N₂ atmosphere. $E_{1/2}$ values at -2.09 vs. Fc^{+/0}). Right: Plot of the peak current as a function of $\upsilon^{\frac{1}{2}}$.



Figure S11. Cyclic voltammograms of 1 with varying MeCN:THF ratios: 100:0 (brown), 75:25 (red), 50:50 (yellow), 25:75 (green) and 0:100 (blue). In all cases, CVs were conducted under N_2 with 1 mM analyte and 0.1 M [nBu_4N][PF₆] at a scan rate of 0.1 V/s.

UV-vis Spectra



Figure S12 – Left: UV-visible spectra of **1** in MeCN. Right: Plot of **1** vs. absorbance at λ_{max} = 454 nm and λ_{max} = 349 nm.



Figure S13 – Left: UV-visible spectra of **1** in DCM. Right: Plot of **1** vs. absorbance at λ_{max} = 455 nm and λ_{max} = 357 nm.



Figure S14 – Left: UV-visible spectra of **2** in MeCN. Right: Plot of **2** vs. absorbance at λ_{max} = 669 nm and λ_{max} = 360 nm.



Figure S15. Overlay of UV-visible spectra of **1** (CH₃CN, $\varepsilon_{\lambda max}$ (M⁻¹cm⁻¹): ε_{454} = 710 ± 20, ε_{349} = 350 ± 10) and **2** (CH₃CN, $\varepsilon_{\lambda max}$ (M⁻¹cm⁻¹): ε_{669} = 220 ± 10, ε_{360} = 1000 ± 100) to illustrate wavelength shifts.

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