A Redox-active Manganate(0) Dicarbene Metalloradical

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We report a rare redox-active Mn^0 metalloradical $[Mn(CO)_3(Ph_2B(^{tBu}NHC)_2)]^-$ (NHC = N-heterocyclic carbene) with countercations $[K([2.2.2]cryptand)]^+$, $[Na([2.2.2]cryptand)]^+$, or $[Li(DME)(12\text{-}crown\text{-}4)]^+$, all characterized via single crystal X-ray diffraction. Cyclic voltammograms reveal solvation-dependent $Mn^{I/0}$ redox potentials that are modeled using the Born equation.

There is ongoing interest in developing redox active transition metal complexes for applications in molecular electrocatalysis using Earth-abundant metals such as Ni, Fe, and Co.[1,2] An equally attractive metal is manganese and several groups have reported Mn^I complexes that are electrocatalytically active for CO_2 reduction to CO[3,4,5,6] and H^+ to H_2[7] via intermediates with a formal Mn^{-I} oxidation state. A key Mn^0 intermediate is typically proposed, however observing and chemically separating the mononuclear species has proven to be challenging because Mn^0 complexes readily dimerize to form a Mn—Mn bond, such as in $Mn_2(CO)_{10}$ and $[Mn(CO)_3(tmbp)]_2$[8] (tmbp = 4,4'5,5'-tetramethyl-2,2'biphosphinine). Likewise, $[Mn^I(CO)_3(bis\text{-}^{Me}NHC)Br]$[3] and $[Mn^I(CO)_3(bpy\text{-}^{t}Bu)Br]$[5] (NHC = *N*-heterocyclic carbene and bpy = bipyridine) suffer from an off-cycle dimerization pathway during the reduction CO_2 to CO in the presence of exogenous acid. In 2014, Kubiak and coworkers used 6,6'-dimesityl-2,2'-bipyridine (mesbpy) to increase the steric bulk of their $[Mn(CO)_3(bpyR)Br]$[6] framework, which prevented dimerization.

Despite the importance of Mn^0 intermediates in small molecule activation and electrocatalysis, only a few structurally characterized monomeric Mn^0 complexes have been published to date (Fig 1). Figueroa and coworkers reported that the incorporation of two sterically encumbering isocyanide ligands allows the formation of the monoradical $[Mn(CO)_3(CNAr^{Dipp2})_2]$,[9] an analogue to the unstable $[Mn(CO)_5]$ monoradical (Dipp = 2,6-diisopropylphenyl), demonstrating atom abstraction and radical scavenger reactivity. Deng and co-workers reported that the inclusion of NHC and alkene ligands gave rise to three-coordinate Mn^0 complexes [(NHC)Mn(dvtms)],[10] which are reactive towards H_2 and unsaturated C-C bonds to yield Mn^{II} dialkyl compounds. Furthermore, Tonzetich and coworkers showed that chemical reduction of the Mn^I pyrrole-based pincer complex, $[Mn(CO)_2(^{tBu}PNP)]$, yields the rare mononuclear low spin Mn^0 metalloradical, $[K][Mn(CO)_2(^{tBu}PNP)]$.[11] Cyclic voltammetry and treatment of $[K][Mn(CO)_2(^{tBu}PNP)]$ with $NO_{(g)}$ revealed a facile re-oxidation to the Mn^I precursor, demonstrating the robust nature of this $Mn^{I/0}$ redox couple ($E_{1/2}$ = -2.14 V vs. $Fc^{+/0}$, THF).

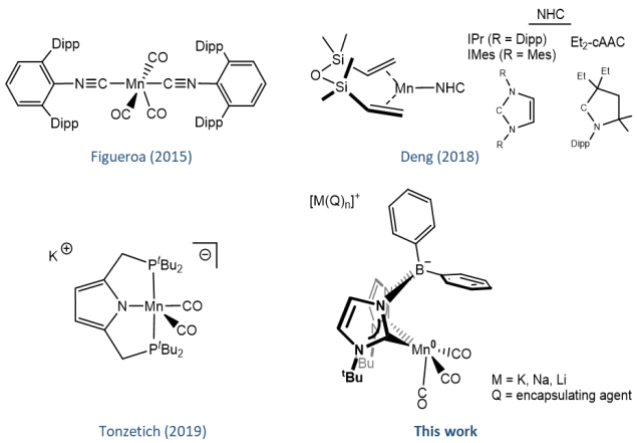
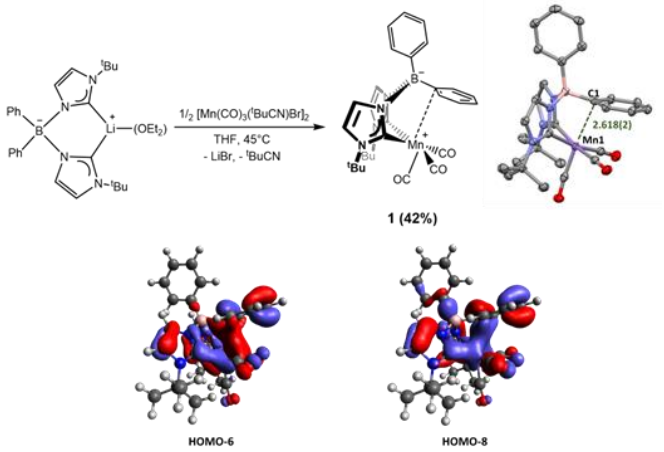


Figure 1. Reported Mn^0 complexes in the literature and the novel Mn^0 dicarbene metalloradical. Dipp = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl, cAAC = cyclic alkylamino carbene. $[M(Q)_n]^+$ denotes counteraction M^+ and encapsulating agent Q.

We describe the synthesis of a rare five-coordinate manganate(0) tricarbonyl complex coordinated to a borate-bridged bis(NHC) ligand that exhibits medium-dependent redox behavior. Starting with a Mn^I precursor, the singly reduced Mn^0 species can be accessed via cyclic voltammetry or by using alkali metal sources to generate mononuclear manganates. X-ray crystallographic analysis confirms the molecular structure of these distorted trigonal bipyramidal complexes and the spectroscopic properties at Mn remain independent of the encapsulated counterion after crystallization ($[K(2,2,2\text{-crypt})]^+$ vs. $[Na(2,2,2\text{-crypt})]^+$ vs. $[Li(DME)(12\text{-crown-4})^+]$); (DME = 1,2-dimethoxyethane).

The Mn^I complex $[Ph_2B(^{tBu}NHC)_2Mn(CO)_3]$ (**1**) is synthesized from the lithium carbene $[Li(Ph_2B(^{tBu}NHC)_2 \bullet Et_2O]$[12] and half an equivalent of the bromide-bridged dimer $[Mn(CO)_3(^{tBu}CN)Br]_2$[13] with mild heating (Scheme 1, top). Formation of **1** is sensitive to the Mn source - using $MnBr(CO)_5$ was unsuccessful, mirroring observations made by Smith and co-workers for chelation of a borate-bridged tris(NHC) ligand to Mn.[13] Notably, washing the crude product with methanol is essential to remove all traces of LiBr from the product. After workup, red-orange **1** is obtained in 42% yield and was further characterized by single crystal X-ray diffraction (Scheme 1, right). The distance between the Mn atom and arene C_{ipso} atom above the metal center ($Mn\text{---}C_{ipso}$ = 2.618(2) Å) is significantly longer than the sum of the Mn—C and Mn—B covalent radii (2.12 and 2.23 Å, respectively)[14] but shorter than the sum of their van der Waals radii (3.75 and 3.85 Å, respectively).[15]

Computational analysis (DFT) reveals bonding interactions the between the *ipso* and *ortho* carbons of the arene π-system on the ligand, as portrayed in HOMO-6 and HOMO-8 (Scheme 1, bottom).This type of stabilizing interaction is expected because the coordinatively unsaturated Mn center would have only 16 valence e^- in the absence of overlap with the π-electron system of the aromatic ring. Solid-state IR spectroscopic data of **1** show CO stretches at 2010, 1928, and 1881 cm^{-1} which remain identical in solution-phase IR spectroscopy in both MeCN and DCM (Fig S4). Furthermore, UV-vis spectra in CH_2Cl_2 and CH_3CN only show minor differences in molar absorptivity (Fig S12,S13). The observed carbonyl stretches are significantly lower than $[Mn(CO)_3(^tBuCN)Br]_2$ (2025, 1936, and 1915 cm^{-1}) but similar to those found in the methylene-bridged dicarbene complex $[Mn(CO)_3(bis\text{-}^{Me}NHC)Br]$ (2004, 1912, and 1881 cm^{-1}).[3]



Scheme 1. Top: Synthesis of **1** and its molecular structure. Mn---C_{ipso} = 2.618(2) Å, 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Bottom: HOMO-6 and HOMO-8 of **1** (TPSS-D3(BJ)/def2-TZVP/CPCM(MeCN); isosurface value = 0.04; see the SI for additional details).

Cyclic voltammograms (CVs) of **1** were conducted under N_2 to examine its solution phase electrochemical activity. CVs in anhydrous MeCN and THF reveal redox events at $E_{1/2}$ = -1.75 V and $E_{1/2}$ = -1.94 V vs. $Fc^{+/0}$, respectively (Fig 2). The anodic shift on going from MeCN to a different solvent can be estimated using a modified Born equation[17,18] where $\Delta\Delta G°$ is expressed in kcal/mol, z is the ionic charge (-1), ε is the dielectric constant (ε_{THF} = 7.43, ε_{MeCN} = 35.7),[19] r_{eff} is the effective spherical ionic radius in Å, and 166 is a grouping of all other constants (eq 1). The r_{eff} is estimated to be 5.3 Å based on distances measured from X-Ray structural data for the Mn^0 anion (see below).

$$\Delta\Delta G°(Solv - MeCN) = 166\frac{z^2}{r_{eff}}\left(\frac{1}{\varepsilon_{solv}} - \frac{1}{\varepsilon_{MeCN}}\right) \quad (1)$$

Using eq. 1, we estimate $\Delta\Delta G°$(THF-MeCN) = -3.3 kcal/mol, or $\Delta E°$ = 0.15 V, which is in excellent agreement with the observed potential difference of 0.19 V in Figure 2. In addition, CV experiments with varying THF:MeCN ratios show a gradual shift in redox potential between these two extremes (Fig S11). To further validate this interpretation, CVs of **1** in methyl *tert*-butyl ether (MTBE) saturated with $[^nBu_4N][B(C_6F_5)_4]$[20] reveal that $E_{1/2}$ = -2.09 V vs. $Fc^{+/0}$. Assuming that $\varepsilon_{MTBE} \cong \varepsilon_{Et2O}$ (4.24),[19] $\Delta\Delta G°$(MTBE-MeCN) = -6.5 kcal/mol and $\Delta E°$ = 0.28 V which also agrees with experiment ($\Delta E°$ = 0.34 V). Therefore, **1** becomes more reducing as the dielectric constant decreases due to poorer solvent stabilization of the electrogenerated anion at the solution-electrode interface.

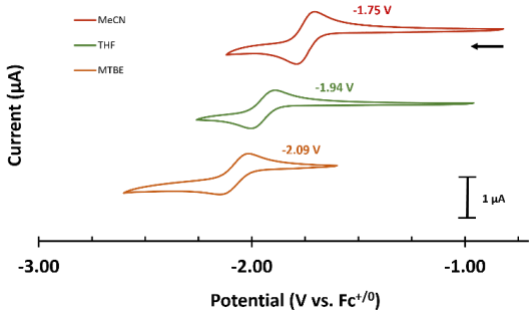
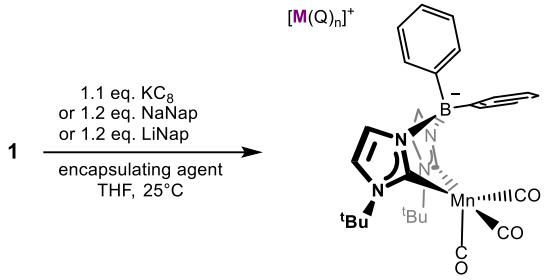


Figure 3. Cyclic voltammogram of **1** under three different conditions: MeCN, 0.1 M $[^nBu_4N][PF_6]$ (red); THF, 0.1 M $[^nBu_4N][PF_6]$ (green); MTBE, 0.075 M $[^nBu_4N][B(C_6F_5)_4]$ (orange). In all cases, CVs were conducted under N_2 with 1 mM analyte at a scan rate of 0.1 V/s.

We sought to chemically reduce **1** by screening its reactivity with alkali metals. Red-orange **1** can be reacted with a slight excess of KC_8, NaNap, or LiNap (Nap = Naphthalenide) in THF at 25°C to afford dark forest-green solutions. The addition of (2,2,2)cryptand or 12-crown-4 yielded the crystalline green salts [K(2,2,2-crypt)][$Ph_2B(^{tBu}NHC)_2Mn(CO)_3$] (**2**), [Na(2,2,2-crypt)][$Ph_2B(^{tBu}NHC)_2Mn(CO)_3$] (**3**), and [Li(DME)(12-crown-4)][$Ph_2B(^{tBu}NHC)_2Mn(CO)_3$] (**4**; Scheme 2).



Scheme 2. Syntheses of **2**, **3**, and **4**.

Complexes **2**, **3** and **4** have been characterized by single crystal X-ray diffraction and exhibit very similar structural features at the manganate center (Fig 4). The Mn---C_{ipso} distance increases by approximately 0.860 Å (**2**), 0.765 Å (**3**), and 0.637 Å (**4**) when compared to **1** due to increased electronic repulsion between the metalloradical and ligand (Table 1). Furthermore, there is a weak interaction between the carbonyl oxygen (OB) and potassium (K2) atoms of **2** (2.963(4) Å; Fig 4) whereas for **3** and **4** there are no interactions between the encapsulated cation and CO ligands. A solid-state CO---$[K(2.2.2)crypt]^+$ interaction has been previously observed in a tricarbonylrhenium-bound quinoxaline salt (CO---K = 2.900(5) Å) but in the analogous manganese salt no interaction was observed.[21] A similar interaction was also observed when metallic rubidium was used as the reductant in the presence of (2.2.2)crypt to give an interatomic CO---Rb distance of 3.126(2) Å between the terminal oxygen atom and rubidium cation.[21]

Solid-state IR spectra of **2**, **3**, and **4** reveal nearly identical CO stretching frequencies that are all shifted 100-120 cm^{-1} lower than **1**, confirming the strong π backdonation effects upon reduction and that the counterion has little influence on the electronic structure at Mn (Table 1). UV-vis spectroscopy of **2** reveals a strong absorption maximum at 360 nm (ε_{360} = 1000 ± 100 $M^{-1}cm^{-1}$), complementary to its perceived green colour (Fig S14).

Table 1. Selected bond distance comparisons and IR carbonyl stretches observed.

Complex	C≡O bond distance (Å)	Mn---C_{ipso} (Å)	C≡O stretches (cm^{-1})
1	1.150(3), 1.151(3), 1.161(3)	2.618(2)	2010,1928, 1881
2	1.166(5), 1.179(5), 1.174(6)	3.478(5)	1908,1808, 1765
3	1.168(5), 1.166(5), 1.174(5)	3.383(3)	1908,1801, 1771
4	1.165(6), 1.165(6), 1.165(6)	3.255(4)	1905,1801, 1764

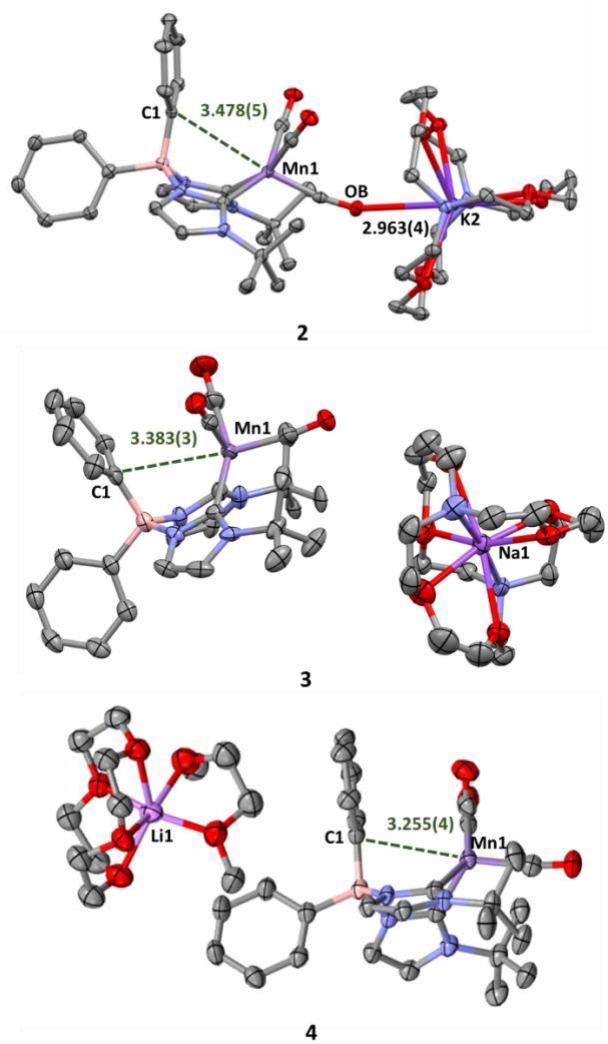


Figure 4. Molecular structures of **2**, **3**, and **4** with 50% probability ellipsoids; H atoms omitted for clarity. Cocrystallized solvent and additional molecules in the asymmetric unit of **4** are also omitted for clarity.

Solution-phase magnetic susceptibility of **2** (2.06 μ_B, Evans' method)[22] confirms the presence of one unpaired electron (S = ½). The electron paramagnetic resonance (EPR) spectrum of **2** (Fig 5, left) demonstrates a rhombic symmetry with the simulation parameters g = [2.018, 2.023, 1.998] and $A(^{55}Mn)$ = ± [212, 149, 126] MHz. One g-factor component g_z = 1.998 is close to a free electron g-factor while two other components $g_{x,y}$ are slightly larger, as expected for $3d^7$ Mn^0 in a strong square-pyramidal ligand field with the unpaired spin residing on the $3d_{z2}$ orbital.[23,24] The EPR parameters of **2** are noticeably different from other reported square-pyramidal Mn^0 complexes, like $Mn(CO)_5$ ($g_\perp$ = 2.038, $g_\parallel$ = 2.000; $A(^{55}Mn)$ = [$A_\perp$ = -94, $A_\parallel$ = 185] MHz)[25] and [$((n\text{-}Bu)_3P)_2$-$Mn(CO)_3$] ($g_\perp$ = 2.036, $g_\parallel$ = 2.007; $A(^{55}Mn)$ = [$A_\perp$ = -114, $A_\parallel$ = 164] MHz),[23] reflecting a different ligand field strength and coordination symmetry of the dicarbene ligand in **2** as compared to the CO and phosphine ligands in the above examples. Furthermore, a high hyperfine anisotropy, as observed in **2** and the above examples, is a signature feature of a Mn^0 redox state, distinguishing it from the Mn^{II} redox state with a low hyperfine anisotropy. The pronounced rhombicity of both g and $A(^{55}Mn)$ in **2** indicates a low symmetry coordination geometry (C_{2v} or lower), promoting a sizeable admixture of $3d_{x2-y2}$ to the dominant $3d_{z2}$ population.[24] The DFT-calculated spin density for **2** (Fig 5, right) supports the predominately $3d_{z2}$ metal-based radical character of the Mn^0 centre.

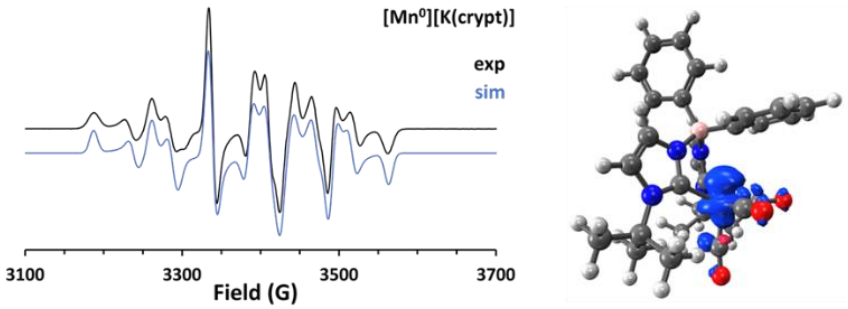


Figure 5. Left: X-band EPR spectrum of **2** (77 K, 2-MeTHF glass): experiment (black) and stimulation (blue). Right: Computed spin density plot of the Mn^0 radical anion $\mathbf{2}^-$ at the TPSS-D3(BJ)/def-TZVP/CPCM(THF) level of theory, revealing predominantly $3d_{z2}$ spin localization (blue) consistent with the EPR data.

In summary, new anionic Mn^0 complexes have been chemically synthesized from a redox-active Mn^I precursor using the chemical reductants KC_8, NaNap, or LiNap. All compounds have been structurally authenticated by single crystal X-ray diffraction and characterized by various spectroscopic methods to evaluate their structural and electronic properties. The arene ring of the borate-bridged bis(*N*-heterocyclic carbene) ligand plays an important role in stabilizing the Mn^I centre. The solvent-dependent redox behaviour can be rationalized using the Born equation, showing that media with a lower dielectric constant destabilize the manganate anion in solution. Upon $1e^-$ reduction, an increase in Mn^0---C_{ipso} distance by 0.6–0.9 Å is observed and the low spin (S = ½) Mn^0 complexes exhibit metal-based radical character, as confirmed by EPR spectroscopy and DFT calculations. The stoichiometric and electrocatalytic reactivity of this novel metalloradical complex with small molecules is ongoing.

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