

# Tuning Electronic Structure To Control Manganese Nitride Activation

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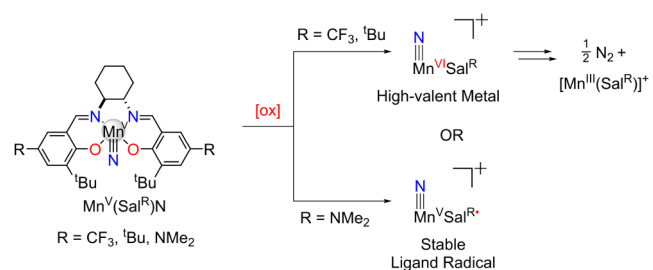
**S** Supporting Information

**ABSTRACT:** Investigation of a series of oxidized nitridomanganese(V) salen complexes with different para ring substituents ( $R = \text{CF}_3$ ,  $t\text{Bu}$ , and  $\text{NMe}_2$ ) demonstrates that nitride activation is dictated by remote ligand electronics. For  $R = \text{CF}_3$  and  $t\text{Bu}$ , oxidation affords a Mn(VI) species and nitride activation, with dinitrogen homocoupling accelerated by the more electron-withdrawing  $\text{CF}_3$  substituent. Employing an electron-donating substituent ( $R = \text{NMe}_2$ ) results in a localized ligand radical species that is resistant to N coupling of the nitrides and is stable in solution at both 195 and 298 K.

Transition metal complexes bearing terminal nitride ( $\text{N}^{3-}$ ) ligands are of significant interest because of the key role they may play in the nitrogen fixation process,<sup>1</sup> their importance in stoichiometric nitrene transfer reactions,<sup>2</sup> and their utility as catalysts.<sup>3</sup> In the context of industrial (and biological) nitrogen fixation,<sup>4</sup> there have been a number of important reports of Fe nitride complexes in oxidation states IV,<sup>5</sup> V,<sup>6</sup> and VI,<sup>7</sup> and their reactivities are well-documented.<sup>8</sup> In many cases the reactivity of terminal nitride complexes can be rationalized by the nucleophilicity (or electrophilicity) of the nitride ligand, which is determined by both the metal and the oxidation state as well as ancillary ligands.<sup>9</sup> Group 8 nitrides of Ru(VI) and Os(VI) react with a variety of nucleophiles<sup>10</sup> as a result of population of  $\text{M}\equiv\text{N} \pi^*$  antibonding orbitals in the transition state. In addition, reactive electrophilic group 9 terminal nitride complexes of Co,<sup>11</sup> Rh,<sup>12</sup> and Ir<sup>13</sup> have been reported, and a transient terminal nitride of Ni has recently been described.<sup>14</sup> In contrast to the reactivity of late metal nitrides, early metal nitrides are generally more stable and are often a product of  $\text{N}_2$  activation reactions.<sup>15</sup> In some cases, early transition metal nitrides react as nucleophiles.<sup>16</sup> Terminal nitrides of Mn(V) exhibit reactivity intermediate between their early and late transition metal analogues and have found utility as nitrene transfer reagents.<sup>2b</sup> Early work by Groves demonstrated nitrene transfer from a nitridomanganese(V) porphyrin complex to cyclooctene upon activation with trifluoroacetic anhydride (TFAA).<sup>17</sup> This reactivity was extended to nitridomanganese(V) salen complexes as a means of nitrene transfer to other electron-rich alkenes as well as silyl enol ethers.<sup>18</sup> Despite their synthetic utility, all examples require the addition of a Lewis acid such as TFAA or tosic anhydride, likely to activate the nitride by conversion to the corresponding imide before group transfer to the substrate.<sup>19</sup> Nitridomanganese(V) salen complexes have also been employed as reagents in the synthesis of other metal–nitrido fragments.<sup>20</sup> Herein, we investigate the oxidative activation of a series of Mn(V) nitrides in which the resulting reactivity is tuned by the

electronic properties of the ancillary ligand (Scheme 1). We employ the tetradentate salen ligand because of its facile and

**Scheme 1. Oxidation of Mn<sup>V</sup> Nitride Complexes To Afford High-Valent Metal or Ligand Radical Electronic Structures; Subsequent Homocoupling Affords  $\text{N}_2$  in the Case of the Mn<sup>VI</sup> Complexes**



highly modular synthesis, allowing for changes in the electron-donating ability of the ligand without altering the geometry at the metal center. More importantly, metal complexes of salen-type ligands have the potential for redox activity at either the ligand or the metal center upon one-electron oxidation,<sup>21</sup> permitting investigation of the resultant reactivity upon oxidation of either the metal or ligand in a series of nitridomanganese(V) complexes.

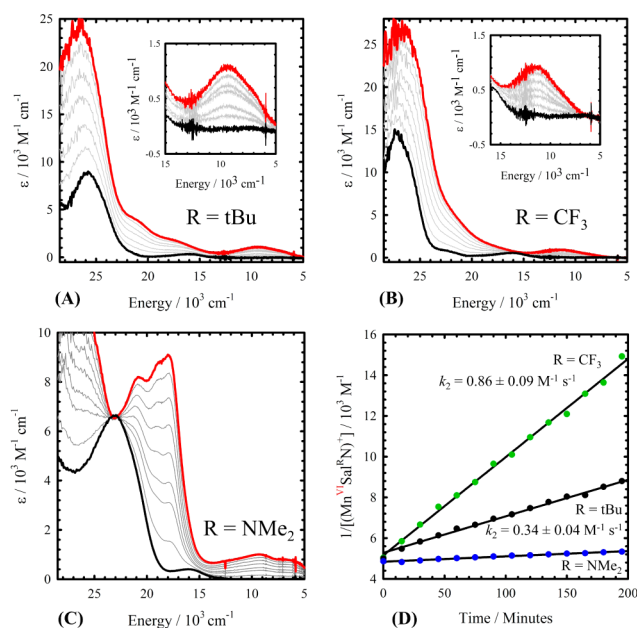
Of the three nitridomanganese(V) salen complexes studied herein,  $\text{Mn}(\text{Sal}^{t\text{Bu}})\text{N}$  and  $\text{Mn}(\text{Sal}^{\text{CF}_3})\text{N}$  were prepared from the corresponding Mn chloride complexes using  $\text{NH}_4\text{OH}$  as described by Carreira and co-workers.<sup>18d</sup> While  $\text{Mn}(\text{Sal}^{\text{NMe}_2})\text{N}$  could also be prepared in this manner, photolysis of the precursor azido complex afforded  $\text{Mn}(\text{Sal}^{\text{NMe}_2})\text{N}$  in higher yield. All three complexes are isolated as microcrystalline solids with diamagnetic  $d^2$  ground states, as expected for Mn(V) nitrides in tetragonal ligand fields.<sup>22</sup> The solid-state structures of the two new nitridomanganese(V) complexes  $\text{Mn}(\text{Sal}^{\text{CF}_3})\text{N}$  and  $\text{Mn}(\text{Sal}^{\text{NMe}_2})\text{N}$  are depicted in Figures S1 and S2, while the solid-state structure of  $\text{Mn}(\text{Sal}^{t\text{Bu}})\text{N}$  was previously reported by Jørgensen.<sup>23</sup> Cyclic voltammetry (CV) experiments on the three complexes revealed an oxidation process that was tunable by ca. 480 mV and correlates well with the respective Hammett parameters of the para substituents (Figure S3).<sup>21b,24</sup> Analysis of the scan-rate dependence suggested an EC process for both the  $t\text{Bu}$  and  $\text{CF}_3$  derivatives, while the  $\text{NMe}_2$  redox couple remained quasi-reversible at all scan rates investigated (Figures S4 and S5). The relatively low oxidation potentials of the three complexes allowed for their one-electron oxidation with  $\text{AgSbF}_6$ .<sup>25</sup>

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Oxidation of a green solution of  $\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}$  at 298 K resulted in an immediate color change to orange-brown, and characterization of the recrystallized product showed quantitative formation of the high-spin Mn(III) complex  $[\text{Mn}(\text{Sal}^{\text{tBu}})]\text{[SbF}_6\text{]}^-$  (Figures S7 and S8). This result suggested that oxidation of  $\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}$  resulted in rapid loss of the nitride ligand to afford the crystallographically characterized  $[\text{Mn}(\text{Sal}^{\text{tBu}})]\text{[SbF}_6\text{]}^-$  product. Lau has extensively studied the N–N homocoupling reactivity of various complexes of Ru(VI), Os(VI), and Mn(V) with Schiff base ligands.<sup>26</sup> While both Ru(VI) and Os(VI) complexes undergo N–N coupling reactions in the presence of N-heterocyclic ligands,<sup>10h,27</sup> Mn nitrides have not been observed to couple  $\text{N}_2$  directly.<sup>28</sup> Additional examples of dinitrogen coupling reactions from transition metal nitrides include Fe(IV/V) complexes,<sup>5b,29</sup> an open-shell Ir complex and its analogous Rh complex,<sup>12,13</sup> as well as Os and Mo complexes.<sup>30</sup>

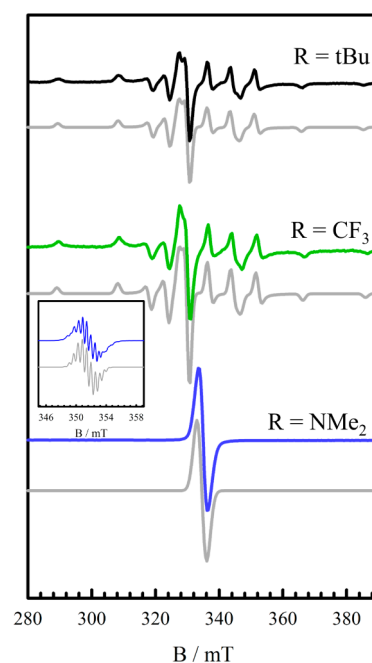
We next endeavored to characterize the oxidized species at low temperature in order to further understand the observed reactivity.  $\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}$  can be cleanly oxidized at 195 K using an aminium radical chemical oxidant,  $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3]^+\text{[SbF}_6\text{]}^-$ ,<sup>25</sup> to afford a species with an electronic structure that differs from those of the starting material and decay product (Figure 1A). Upon oxidation, the formation of a low-



**Figure 1.** (A–C) Oxidation titration data for  $\text{Mn}(\text{Sal}^{\text{R}})\text{N}$  (black) to the corresponding one-electron-oxidized species (red). Intermediate gray lines were measured during the oxidation titrations with  $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3]^+\text{[SbF}_6\text{]}^-$ . Insets: enhanced views of the low-energy bands for  $\text{R} = \text{tBu}$  and  $\text{CF}_3$ . (D) Representative kinetic decay data for the three complexes ( $\text{R} = \text{tBu}$  and  $\text{CF}_3$ , 195 K;  $\text{R} = \text{NMe}_2$ , 298 K). Conditions:  $\text{CH}_2\text{Cl}_2$ , 0.2 mM complex.

intensity band is observed at  $9300\text{ cm}^{-1}$  ( $\epsilon = 1100\text{ M}^{-1}\text{ cm}^{-1}$ ). Time-dependent density functional theory (TD-DFT) analysis predicts the low-energy band to have ligand-to-metal charge transfer (LMCT) character (Figure S9).

A sample of the oxidized species  $[\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}]^+$  was then analyzed by electron paramagnetic resonance (EPR) spectroscopy at 100 K. The EPR spectrum of  $[\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}]^+$  shows that the oxidation is metal-based, affording a Mn(VI) species (Figure 2). The spectrum displays a typical axial splitting pattern for a  $d^1$  metal ion ( $d_{xy}^1$  ground state) with hyperfine coupling to a single



**Figure 2.** X-band EPR spectra of  $[\text{Mn}(\text{Sal}^{\text{R}})\text{N}]^+$  recorded in frozen  $\text{CH}_2\text{Cl}_2$  at 0.4 mM: (top)  $\text{R} = \text{tBu}$ ; (middle)  $\text{R} = \text{CF}_3$ ; (bottom)  $\text{R} = \text{NMe}_2$ . Gray lines represent simulations of the experimental data. Inset: room-temperature spectrum of  $\text{R} = \text{NMe}_2$ . Conditions: frequency = 9.38 GHz; power = 2.0 mW; modulation frequency = 100 kHz; modulation amplitude = 0.6 mT;  $T = 100\text{ K}$ .

$^{55}\text{Mn}$  ( $I = 5/2$ ) nucleus ( $A_{zz} = 533\text{ MHz}$ ,  $A_{xx} = A_{yy} = 182\text{ MHz}$ ). These values are in close agreement with those for two Mn(VI) complexes previously reported by Wieghardt and co-workers.<sup>31</sup>

Despite being able to characterize the reactive Mn(VI) intermediate, we observed slow decay of this species at 195 K ( $t_{1/2} = 4\text{ h}$  at 0.2 mM). The decay was fit to a second-order process ( $k_2 = 0.34 \pm 0.04\text{ M}^{-1}\text{ s}^{-1}$ ; Figure S10), in line with a reaction mechanism that involves coupling of two molecules of  $[\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}]^+$  to produce  $\text{N}_2$  and two molecules of  $[\text{Mn}(\text{Sal}^{\text{tBu}})]\text{[SbF}_6\text{]}^-$ . In order to confirm that the mechanism for nitride loss involves an intermolecular reaction between two molecules of  $[\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}]^+$ , we prepared the 50%  $^{15}\text{N}$ -labeled complex and performed GC–MS measurements to monitor the gas evolved after oxidation of  $\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}$ . Although it was difficult to eliminate atmospheric  $^{14}\text{N}^{14}\text{N}$  from the instrument, we detected  $^{14}\text{N}^{15}\text{N}$  and  $^{15}\text{N}^{15}\text{N}$  in a 2:1 ratio, as expected for an intermolecular reaction mechanism involving two molecules of 50%  $^{15}\text{N}$ -labeled  $\text{Mn}(\text{Sal}^{\text{tBu}})\text{N}$  (Table S3 and Figure S11).

We next investigated activation of the two additional Mn(V) nitride complexes with salen para substituents of contrasting electron-donating abilities ( $\text{CF}_3$  and  $\text{NMe}_2$ ). Oxidation of  $\text{Mn}(\text{Sal}^{\text{CF}_3})\text{N}$  at 195 K resulted in the appearance of similar spectral features as for the tBu derivative, with the low-energy band at slightly higher energy ( $11\,600\text{ cm}^{-1}$ ). As expected, EPR analysis confirmed that oxidation of the  $\text{CF}_3$  derivative resulted in metal-based oxidation to Mn(VI), with nearly identical simulation parameters as for the tBu derivative (Table 1).  $[\text{Mn}(\text{Sal}^{\text{CF}_3})\text{N}]^+$  also decays at low temperature following a second-order decay model (Figures 1D and S12). The rate constant ( $k_2 = 0.86 \pm 0.09\text{ M}^{-1}\text{ s}^{-1}$ ) is approximately 2.5 times larger in comparison with the tBu derivative, which can be attributed to the change in auxiliary ligand electronics (vide infra).  $^{15}\text{N}$  isotopic labeling of the nitride again suggests an

**Table 1. EPR Simulation Parameters for the Three Oxidized Complexes<sup>a</sup>**

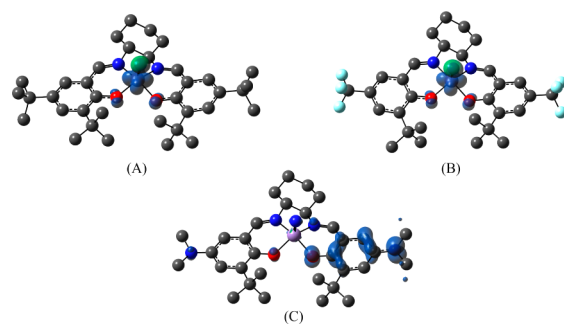
	$g_{zz}$	$g_{xx} = g_{yy}$	$A_{zz}$	$A_{xx} = A_{yy}$
R = tBu	1.985	1.995	533	181
R = CF <sub>3</sub>	1.984	1.995	540	187
R = NMe <sub>2</sub> (100 K)	2.003			
R = NMe <sub>2</sub> (298 K)	2.003		$A_{N1} = 13.5$ ; $6 \times A_{H11} = 16.7$ ; $A_{H12} = 2.8$ ; $A_{H13} = 0.8$ ; $A_{Mn} = 4.2$	

<sup>a</sup>Hyperfine values (A) are in MHz.

intermolecular reaction mechanism for the CF<sub>3</sub> derivative (Table S4 and Figure S13).

We next installed an electron-donating NMe<sub>2</sub> group at the para position of the salen ligand. Examination of the CV spectrum of Mn(Sal<sup>NMe2</sup>)N does not suggest an EC process on the basis of an evaluation of the scan-rate dependence (Figure S4). Low-temperature oxidation results in unique vis-NIR spectral features in comparison with the tBu and CF<sub>3</sub> derivatives. Two broad, low-energy transitions at 6500 cm<sup>-1</sup> (800 M<sup>-1</sup> cm<sup>-1</sup>) and 9500 cm<sup>-1</sup> (1000 M<sup>-1</sup> cm<sup>-1</sup>) are present in the spectrum as well as an envelope of transitions between 15 000 and 22 000 cm<sup>-1</sup> (Figure 1C). TD-DFT reveals these transitions to be largely ligand-based, and their absence in the spectra of the previous derivatives suggests a change in electronic structure. Indeed, collection of the EPR spectrum in frozen CH<sub>2</sub>Cl<sub>2</sub> revealed that the locus of oxidation for [Mn(Sal<sup>NMe2</sup>)N]<sup>•+</sup> is ligand-based, exhibiting an isotropic ligand radical signal centered at  $g = 2.003$  (Figure 2). This demonstrates that sufficiently electron-donating para substituents are capable of reordering the relative energies of redox-active orbitals such that oxidation is no longer metal-centered but rather is ligand-centered in this derivative. In addition, unlike the tBu and CF<sub>3</sub> derivatives, the oxidized NMe<sub>2</sub> derivative is resistant to homocoupling, as the oxidized complex is stable at 195 K and decays only minimally over a 48 h period at 298 K (Figures 1D and S14). The Mn≡N stretching band at 1045 cm<sup>-1</sup> persists after oxidation with AgSbF<sub>6</sub> at room temperature. Furthermore, the decay at 298 K is not well modeled by second-order kinetics, suggesting that the instability of the oxidized complex is due to a mechanism other than N coupling.<sup>32</sup> Unfortunately, we were unable to isolate X-ray-quality crystals of the oxidized complex. In a recent report, van der Vlugt and co-workers described the participation of a redox-active ligand in the formation of a Ru trimer with bridging nitrido ligands,<sup>33</sup> highlighting the alternative reactivity pathways that redox-active ligands may impose on transition metal nitrido complexes. We aimed to investigate the degree of radical localization for [Mn(Sal<sup>NMe2</sup>)N]<sup>•+</sup> via EPR analysis at 298 K (Figure 2 inset). The EPR spectrum was simulated by considering significant hyperfine interactions to one NMe<sub>2</sub> group with smaller hyperfine couplings to Mn and two phenoxyl protons (Table 1). Thus, the EPR pattern at 298 K provides experimental verification of a localized ligand radical electronic structure for [Mn(Sal<sup>NMe2</sup>)N]<sup>•+</sup>.

Theoretical calculations on the oxidized species match the experimental findings, predicting a Mn(VI) ( $d_{xy}$ ) ground state for R = CF<sub>3</sub> and tBu and the formation of a localized ligand radical for R = NMe<sub>2</sub> (Figures 3 and S17). Natural bond order (NBO) analysis is consistent with a covalent Mn≡N triple bond in the oxidized forms (Tables S7 and S8), with the Mayer bond orders decreasing slightly in the order NMe<sub>2</sub> > tBu > CF<sub>3</sub> (2.868, 2.732, 2.730). The negative spin density localized on the nitride in R = tBu (-0.20) and R = CF<sub>3</sub> (-0.24) can be rationalized by



**Figure 3.** Spin density plots for the three oxidized complexes: (A) [Mn(Sal<sup>tBu</sup>)N]<sup>•+</sup>; (B) [Mn(Sal<sup>CF3</sup>)N]<sup>•+</sup>; (C) [Mn(Sal<sup>NMe2</sup>)N]<sup>•+</sup>. See the Supporting Information for details.

considering the Mn–N bond as a combination of Mn(VI)≡N<sup>3-</sup> ( $S_{Mn} = 1/2$ ) and Mn(V)=N<sup>•</sup> ( $S_N = 1/2$ ) resonance forms (Figure 3).<sup>6a,29,34</sup> A nitridyl radical resonance form, which could be slightly favored for R = CF<sub>3</sub>, provides further support for a radical coupling pathway to produce N<sub>2</sub> in this study.

This study provides key insight into the role of ligand electronics in the nitride activation process, with the nitride precursors readily synthesized from oxidative conditions in the presence of NH<sub>4</sub>OH. Further efforts are needed to model the reaction pathway and assess the possibility of accessing and activating NH<sub>3</sub> adducts of electron-deficient Mn–salen systems for H<sub>2</sub> generation as well as the potential for these systems to activate C–H bonds through radical reaction pathways.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b09576.

Full experimental details, X-ray structures, CV and DPV data, full triplicate kinetics analysis, DFT assignment of the low-energy UV–vis–NIR bands, GC–MS headspace analysis, NBO analysis, and optimized DFT coordinates for neutral and oxidized complexes (PDF)

Crystallographic data for Mn(Sal<sup>NMe2</sup>)N, Mn(Sal<sup>CF3</sup>)N, and [MnSal<sup>tBu</sup>][SbF<sub>6</sub>] (CIF)

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### Notes

The authors declare no competing financial interest.

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