

A Bulky Bis-Pocket Manganese(V)–Oxo Corrole Complex: Observation of Oxygen Atom Transfer between Triply Bonded $\text{Mn}^{\text{V}}\equiv\text{O}$ and Alkene

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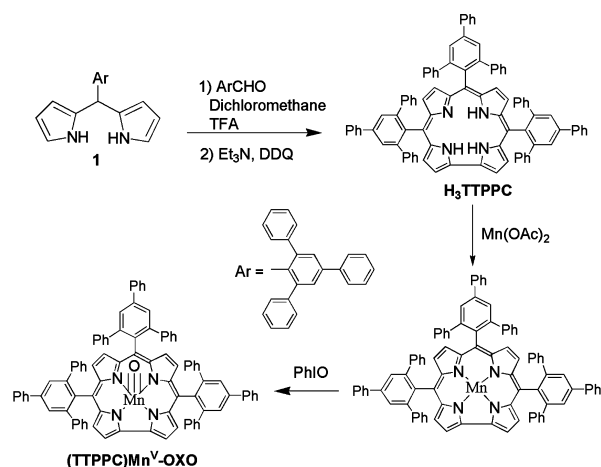
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Reactive Mn–oxo species have been implicated as intermediates in the oxidation of water to oxygen in Photosystem II¹ as well as in certain catalases² and oxygen atom transfer (OAT) reactions.³ While Mn-catalyzed oxidations of organic substrates⁴ involving numerous $\text{Mn}^{\text{III}}\text{--oxo}$,^{5a} $\text{Mn}^{\text{IV}}\text{--oxo}$,^{5b,c} and $\text{Mn}^{\text{V}}\text{--oxo}$ ^{5d,e} complexes have been extensively studied, the factors controlling the reactivity of Mn–oxo complexes are not completely understood, and the current literature on Mn–oxo chemistry is not without controversy. An example is $\text{Mn}^{\text{V}}\text{--oxo}$ porphyrin,⁶ which is one of the most studied $\text{Mn}^{\text{V}}\text{--oxo}$ systems but exhibits a wide range of reactivity in OAT reactions.^{4b,5e,7} Recently, a definitive characterization of the inert *trans*-dioxo Mn(V) porphyrins has greatly enhanced our understanding of the structure and properties of Mn–oxo complexes.⁸

$\text{Mn}^{\text{V}}\text{--oxo}$ complexes are an important mechanistic probe for OAT reactions in the catalytic oxidation of alkenes. However, the isolation and identification of OAT-active $\text{Mn}^{\text{V}}\text{--oxo}$ complexes present a considerable challenge. On the one hand, reactive $\text{Mn}^{\text{V}}\text{--oxo}$ species from salen,^{4a} porphyrin,^{4b} triazacyclononane,⁹ and polyoxometalate¹⁰ have only been observed as transient intermediates. On the other hand, $\text{Mn}^{\text{V}}\text{--oxo}$ species from tetraamide macrocycles^{11a,b} and corrolazine^{11c} are too stable to attack the olefinic double bond. Corrole is a trianionic ligand bearing a close resemblance to porphyrin. Manganese corrole is an effective oxidation catalyst, and its reactivity can be remarkably enhanced by electron-withdrawing groups.^{12a,b} $\text{Mn}^{\text{V}}\text{--oxo}$ corrole was first prepared with 5,10,15-tris(pentafluorophenyl)corrole (TPFC) and showed a low reactivity.^{12a} We previously prepared a perfluorinated 2,3,7,8,12,13,17,18-octafluoro-5,10,15-tris(pentafluorophenyl)corrole (F_8TPFC) and its $\text{Mn}^{\text{V}}\text{--oxo}$ complex.¹³ Kinetic studies implied that the (F_8TPFC) $\text{Mn}^{\text{V}}\text{--oxo}$ complex was active for OAT to cyclooctene. Other studies also indicated that OAT from (TPFC) $\text{Mn}^{\text{V}}\text{--oxo}$ to styrene may be greatly enhanced by N-base ligation.¹⁴ We herein report the synthesis of a highly bulky 5,10,15-tris(2,4,6-triphenylphenyl)corrole (H_3TPPC) and its $\text{Mn}^{\text{V}}\text{--oxo}$ complex. Resonance Raman (RR) spectroscopy revealed a triply bonded $\text{Mn}^{\text{V}}\equiv\text{O}$ moiety. The reaction between (TPPC) $\text{Mn}^{\text{V}}\equiv\text{O}$ and styrene yielded styrene epoxide, providing compelling evidence of OAT between the $\text{Mn}^{\text{V}}\equiv\text{O}$ corrole and the alkene.

H_3TPPC was synthesized using the general procedure of Gryko¹⁵ in an isolated yield of 6.5% (Scheme 1). Interestingly, the corresponding bis-pocket 5,10,15,20-tetra(2,4,6-triphenylphenyl)porphyrin (H_2TPPP)¹⁶ could only be obtained in ~1% yield. The remarkably higher yield obtained in the H_3TPPC synthesis may be due to less peripheral steric hindrance without the methine C-20 in the corrole ring. The insertion of Mn into H_3TPPC was

Scheme 1



achieved by heating with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in DMF. Dark-green (TPPC) Mn^{III} was obtained in 88% yield after purification by chromatography on basic alumina with diethyl ether as the eluent.

Treatment of (TPPC) Mn^{III} with PhIO in CH_2Cl_2 resulted in the formation of (TPPC) $\text{Mn}^{\text{V}}\text{O}$. Flash chromatography on basic alumina afforded purified (TPPC) $\text{Mn}^{\text{V}}\text{O}$. It is a diamagnetic complex with a low-spin d^2 Mn ion as indicated by its highly resolved ^1H NMR spectrum (Figure S5 in the Supporting Information). The ^{18}O -labeled isotopologue (TPPC) $\text{Mn}^{\text{V}}\text{O}^{18}$ was prepared by the same procedure using PhIO¹⁸ as the oxidant,¹⁷ and the nature of (TPPC) $\text{Mn}^{\text{V}}\text{O}$ was characterized by RR spectroscopy (Figure 1). Excitation at 413.1 nm in resonance with the Soret band led to

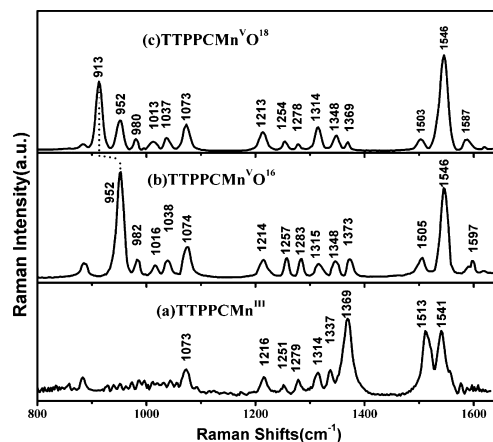


Figure 1. Resonance Raman spectra of (a) (TPPC) Mn^{III} , (b) (TPPC) $\text{Mn}^{\text{V}}\text{O}^{16}$, and (c) its $\text{Mn}^{\text{V}}\text{O}^{18}$ isotopomer in ~1.0 mM CH_2Cl_2 solution.

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the appearance of a strongly enhanced Raman peak at 952 cm^{-1} (Figure 1b). This peak was assigned to the stretching vibration of the $\text{Mn}^{\text{V}}\text{--O}$ unit, as it shifted to 913 cm^{-1} with ^{18}O substitution (Figure 1c). The observed isotopic shift of 39 cm^{-1} is in close agreement with that calculated for an isolated $\text{Mn}\text{--O}$ diatomic oscillator (42 cm^{-1}). The calculated force constant for the 952 cm^{-1} mode is $6.61\text{ mdyn/\AA}$. This force constant is consistent with that calculated for triply bonded $\text{Mn}^{\text{V}}\text{=O}$ in $\text{Mn}^{\text{V}}\text{--oxo}$ corrolazine (for which $\nu_{\text{Mn=O}} = 979\text{ cm}^{-1}$),^{11c} indicating a triply bonded $\text{Mn}^{\text{V}}\text{=O}$ in $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$. Notably, RR-identified triply bonded $\text{Mn}^{\text{V}}\text{=O}$ complexes are rare.¹¹ The observed $\text{Mn}^{\text{V}}\text{=O}$ stretching frequency of $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ is significantly higher than that of doubly bonded $\text{Mn}^{\text{V}}\text{=O}$ porphyrin species such as dioxo $\text{O}=\text{Mn}^{\text{V}}\text{=O}$ ($\nu_{\text{Mn=O}} = 741\text{--}743\text{ cm}^{-1}$),⁸ and $(\text{OH})\text{Mn}^{\text{V}}\text{=O}$ ($\nu_{\text{Mn=O}} = 791\text{ cm}^{-1}$).¹⁸

At $25\text{ }^{\circ}\text{C}$, the half-life of $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ in CH_2Cl_2 is $\sim 7\text{ h}$. In the presence of excess amounts of styrene substrate, a significant acceleration of the decay of $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ occurred (Figure 2), indicating direct reaction with styrene. At the end of the reaction, $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ returned to the $(\text{TPPC})\text{Mn}^{\text{III}}$ complex. The reaction yielded styrene oxide, as detected by GC–MS. That OAT occurred between $(\text{TPPC})\text{Mn}^{\text{V}}\text{=O}$ and styrene was further confirmed by the stoichiometric reaction between $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ ¹⁸ and styrene, which afforded ^{18}O -styrene oxide (see the Supporting Information).

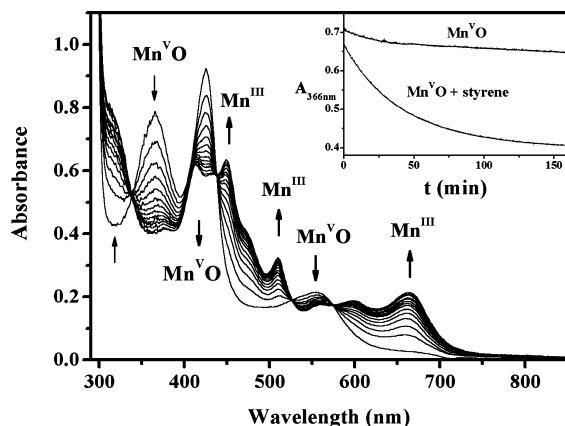


Figure 2. UV–vis spectral changes of $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ in the presence of excess styrene in CH_2Cl_2 (scan interval = 20 min). Inset: absorbance decay of $(\text{TPPC})\text{Mn}^{\text{V}}\text{O}$ monitored at $\lambda = 366\text{ nm}$; the pseudo-first-order rate constant is $3.8 \times 10^{-4}\text{ s}^{-1}$ ($25 \pm 0.1\text{ }^{\circ}\text{C}$).

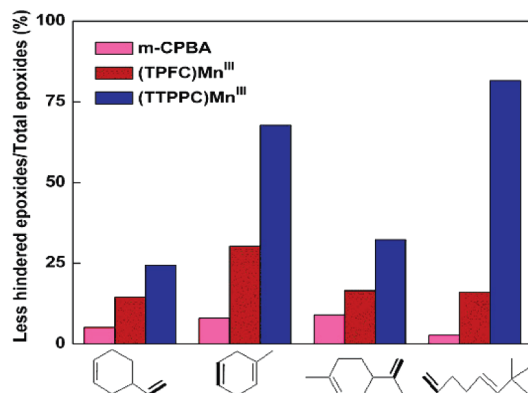


Figure 3. Percentage of less-substituted epoxides (formed at the darkened $\text{C}=\text{C}$ bonds) produced by epoxidation of dienes using $m\text{-CPBA}$ (magenta), $\text{PhIO}\text{--}(\text{TPFC})\text{Mn}^{\text{III}}$ (red), and $\text{PhIO}\text{--}(\text{TPPC})\text{Mn}^{\text{III}}$ (blue).

Shape-selective catalytic epoxidation of nonconjugated dienes using $(\text{TPPC})\text{Mn}^{\text{III}}/\text{PhIO}$ was also examined in the presence of

N -methylimidazole as the axial ligand. A 10:1 alkene/oxidant ratio was employed in order to suppress double epoxidation. The regioselectivity for the epoxidation was compared with results obtained using $m\text{-CPBA}$ as a stoichiometric oxidant (Figure 3), where the more-substituted, electron-rich double bonds are preferably oxidized. The bulky bis-pocket $(\text{TPPC})\text{Mn}^{\text{III}}\text{--PhIO}$ system showed a significantly higher selectivity toward the less-substituted but more accessible double bond. It is not surprising that the bis-pocket corrole is more sensitive than the flat corrole $(\text{TPFC})\text{Mn}^{\text{III}}$ toward steric crowdedness. The regioselectivity toward 1-methyl-1,2,4,5-cyclohexadiene and 7,7-dimethyl-1,2,5,6-octadiene displayed by $(\text{TPPC})\text{Mn}^{\text{III}}$ compared favorably with those reported for encumbered Mn porphyrins.¹⁹

In conclusion, this study has presented for the first time direct evidence of OAT between a corrole $\text{Mn}^{\text{V}}\text{=O}$ moiety and an alkene substrate. This is also the first RR spectroscopic identification of $\text{Mn}(\text{V})\text{--oxo}$ corrole. From this work and previously demonstrated electronic effects,^{12,13} it is now clear that the corrole $\text{Mn}\text{--oxo}$ system possesses a wide range of reactivity rivaling that of the established porphyrin system. Further study of applications of $\text{Mn}\text{--corrole}$ in molecular catalysis is underway.

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Supporting Information Available: Synthesis, selected characterization data, and epoxidation and RR experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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