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A Bulky Bis-Pocket Manganese(V)−Oxo Corrole Complex: Observation of Oxygen Atom Transfer between Triply Bonded $Mn^V≡O$ and Alkene

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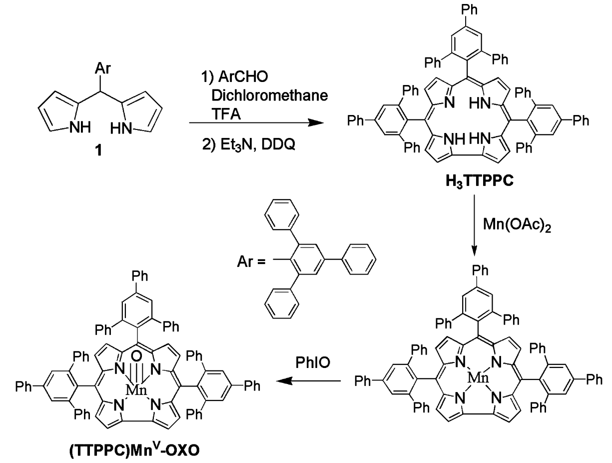
Reactive Mn−oxo species have been implicated as intermediates in the oxidation of water to oxygen in Photosystem II[1] as well as in certain catalases[2] and oxygen atom transfer (OAT) reactions.[3] While Mn-catalyzed oxidations of organic substrates[4] involving numerous Mn^{III}−oxo,[5a] Mn^{IV}−oxo,[5b,c] and Mn^V−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 Mn^V−oxo porphyrin,[6] which is one of the most studied Mn^V−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]

Mn^V−oxo complexes are an important mechanistic probe for OAT reactions in the catalytic oxidation of alkenes. However, the isolation and identification of OAT-active Mn^V−oxo complexes present a considerable challenge. On the one hand, reactive Mn^V−oxo species from salen,[4a] porphyrin,[4b] triazocyclononane,[9] and polyoxometalate[10] have only been observed as transient intermediates. On the other hand, Mn^V−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] Mn^V−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 Mn^V−oxo complex.[13] Kinetic studies implied that the (F_8TPFC)Mn^V−oxo complex was active for OAT to cyclooctene. Other studies also indicated that OAT from (TPFC)Mn^V−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_3TTPPC) and its Mn^V−oxo complex. Resonance Raman (RR) spectroscopy revealed a triply bonded $Mn^V≡O$ moiety. The reaction between (TTPPC)$Mn^V≡O$ and styrene yielded styrene epoxide, providing compelling evidence of OAT between the $Mn^V≡O$ corrole and the alkene.

H_3TTPPC was synthesized using the general procedure of Gryko[15] 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_2TTPPP)[16] could only be obtained in ∼1% yield. The remarkably higher yield obtained in the H_3TTPPC synthesis may be due to less peripheral steric hindrance without the methine C-20 in the corrole ring. The insertion of Mn into H_3TTPPC was achieved by heating with $Mn(OAc)_2 \cdot 4H_2O$ in DMF. Dark-green (TTPPC)Mn^{III} was obtained in 88% yield after purification by chromatography on basic alumina with diethyl ether as the eluent.

Scheme 1



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

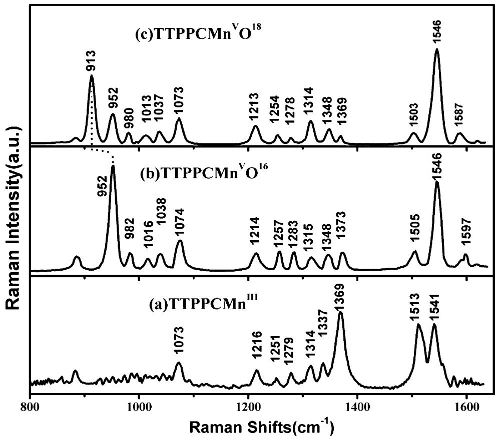


Figure 1. Resonance Raman spectra of (a) (TTPPC)Mn^{III}, (b) (TTPPC)MnO^{16}, and (c) its MnO^{18} isotopomer in ∼1.0 mM CH_2Cl_2 solution.

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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 Mn^{V}−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 Mn−O diatomic oscillator (42 cm^{-1}). The calculated force constant for the 952 cm^{-1} mode is 6.61 mdyn/Å. This force constant is consistent with that calculated for triply bonded Mn^{V}≡O in Mn^{V}−oxo corrolazine (for which $\nu_{\mathrm{Mn}\equiv\mathrm{O}} = 979$ cm^{-1}),[11c] indicating a triply bonded Mn^{V}≡O in (TTPPC)Mn^{V}O. Notably, RR-identified triply bonded Mn^{V}≡O complexes are rare.[11] The observed Mn^{V}≡O stretching frequency of (TTPPC)Mn^{V}O is significantly higher than that of doubly bonded Mn^{V}=O porphyrin species such as dioxo O=Mn^{V}=O ($\nu_{\mathrm{Mn=O}}$ = 741−743 cm^{-1}),[8] and (OH)Mn^{V}=O ($\nu_{\mathrm{Mn=O}}$ = 791 cm^{-1}).[18]

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

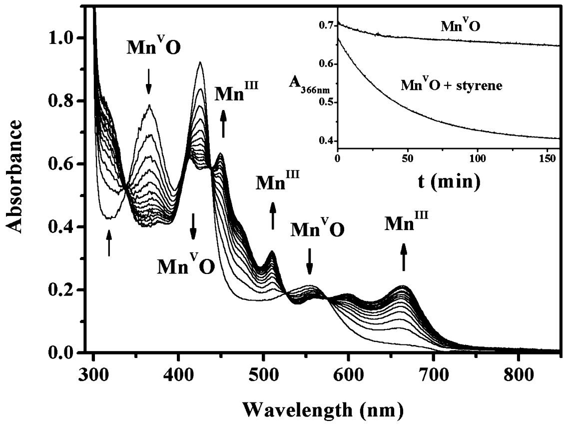

Figure 2. UV−vis spectral changes of (TTPPC)Mn^{V}O in the presence of excess styrene in CH_2Cl_2 (scan interval = 20 min). Inset: absorbance decay of (TTPPC)Mn^{V}O monitored at $\lambda = 366$ nm; the pseudo-first-order rate constant is 3.8×10^{-4} s^{-1} (25 ± 0.1 °C).

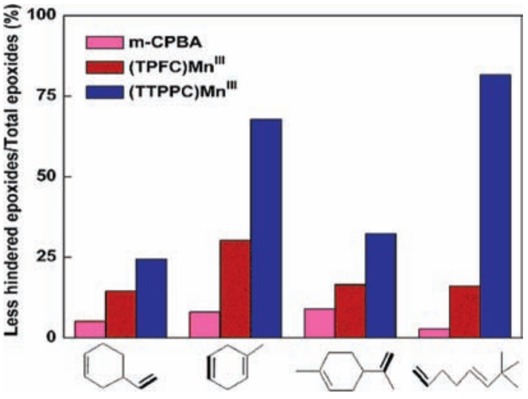

Figure 3. Percentage of less-substituted epoxides (formed at the darkened C=C bonds) produced by epoxidation of dienes using *m*-CPBA (magenta), PhIO−(TPFC)Mn^{III} (red), and PhIO−(TTPPC)Mn^{III} (blue).

Shape-selective catalytic epoxidation of nonconjugated dienes using (TTPPC)Mn^{III}/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*-CPBA as a stoichiometric oxidant (Figure 3), where the more-substituted, electron-rich double bonds are preferably oxidized. The bulky bis-pocket (TTPPC)Mn^{III}−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 (TPFC)Mn^{III} toward steric crowdedness. The regioselectivty toward 1-methyl-1,2,4,5-cyclohexadiene and 7,7-dimethyl-1,2,5,6-octadiene displayed by (TTPPC)Mn^{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 Mn^{V}≡O moiety and an alkene substrate. This is also the first RR spectroscopic identification of Mn(V)−oxo corrole. From this work and previously demonstrated electronic effects,[12,13] it is now clear that the corrole Mn−oxo system possesses a wide range of reactivity rivaling that of the established porphyrin system. Further study of applications of Mn−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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