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Epoxidations Catalyzed by Manganese(V) Oxo and Imido Complexes: Role of the Oxidant−Mn−Oxo (Imido) Intermediate

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The manganese(V) oxo complex (TBP_8Cz)Mn^V(O) (**1**) is shown to catalyze the epoxidation of alkenes with a series of iodosylarenes (ArIO) as oxidants. Competition experiments reveal that the identity of ArIO influences the product ratios, implicating an unusual coordinated oxo−metal−ArIO intermediate (**1**-OIAr) as the active catalytic species. The isoelectronic manganese(V) imido complex (TBP_8Cz)Mn^V(NMes) (**2**) does not participate in NR transfer but does catalyze epoxidations with ArIO as the O-atom source, suggesting a mechanism similar to that seen for **1**. Direct evidence (ESIMS) is obtained for **1**-OIMes.

High-valent manganese and iron complexes have been implicated as key intermediates in catalytic atom- or group-transfer reactions for a number of synthetic and biological systems. For example, the metal-catalyzed transfer of an O atom is fundamental to a wide range of transformations, from asymmetric epoxidations, which rely on Mn−salen catalysts, to the selective hydroxylations carried out by the heme enzyme cytochrome P450. In these systems, a high-valent metal−oxo species is normally invoked as the intermediate that carries out the critical O-atom-transfer (OAT) step. Similarly, high-valent metal−nitrido and metal−imido species are thought to play key roles in metal-catalyzed N- or NR-group transfer.

In recent years, however, alternative mechanisms have been described for both porphyrin-[1] and non-heme-type[2] catalytic OAT reactions. These studies have implicated a metal−oxidant complex as the reactive intermediate (Scheme 1, pathway A) in lieu of a metal−oxo complex (pathway B). However, an alternative mechanistic hypothesis that had previously not been considered involves the coordination of the oxidant *after* the formation of the high-valent metal−oxo species (pathway C). We first proposed this mechanism in the course of studying catalytic OAT reactions with iodosylbenzene (PhIO) as the oxidant and the manganese(V) oxo complex (TBP_8Cz)Mn^V(O) [**1**; TBP_8Cz = octakis(4-*tert*-butylphenyl)corrolazinato; Chart 1] as the catalyst.[3] Metal-catalyzed oxidations involving hypervalent iodine reagents such as PhIO are widely used in organic synthesis and thus are of particular importance.[4]

Zdilla and Abu-Omar subsequently found that the same mechanism is operative in analogous catalytic aziridinations with manganese(V) imido complex (tpfc)Mn^V(NTs) [tpfc = tris(pentafluorophenyl)corrolato] as the catalyst.[5] Thus, we speculated that this mechanism may have broad implications for group-transfer reactions. Herein we show that pathway C is a general mechanism for catalytic epoxidations carried out by the manganese(V) oxo complex **1** and provide the first direct evidence for the ArIO−metal−oxo adduct. In addition,

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(6) For examples of mixed oxo/imido complexes that mediate OAT, see: (a) Ison, E. A.; Cessarich, J. E.; Travia, N. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 1167–1178. (b) Ramnauth, R.; Al-Juaid, S.; Motevalli, M.; Parkin, B. C.; Sullivan, A. C. *Inorg. Chem.* **2004**, *43*, 4072–4079.

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Scheme 1

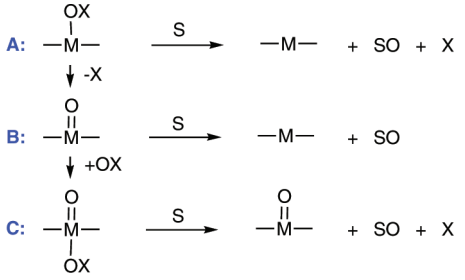
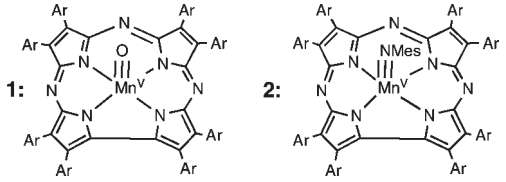


Chart 1



we report the first example, to our knowledge, of a manganese terminal imide complex that catalyzes not NR group transfer but OAT.[6]

Previously, it was shown conclusively through ^{18}O labeling that the terminal oxo ligand in **1** *does not transfer* to the substrate, remaining as a "spectator" oxo group, while the coordinated O atom of PhIO in the proposed intermediate $(TBP_8Cz)Mn^V(O)(OIPh)$ (**1**-OIPh) becomes incorporated in the oxidized product.[3] However, direct spectroscopic evidence for **1**-OIPh was lacking, and only one oxidant (PhIO) and one alkene substrate had been examined.

As seen previously for *cis*-stilbene,[3] the catalytic epoxidation of styrene with $(TBP_8Cz)Mn^{III}$ as the catalyst and PhIO proceeds smoothly, with a high selectivity for epoxide (**3**) over aldehyde (Scheme 2). Under these conditions, the Mn^{III} complex is rapidly (< 1 min) converted to **1**. The oxidant can be changed to the more reactive pentafluoroiodosylbenzene (PFIB), which yields **3** (42%) with a trace amount of aldehyde (4%). The isolated manganese(V) oxo complex **1** can also be added directly to the reaction as the catalyst. Utilizing **1** as the catalyst with PFIB as the oxidant and expanding the substrate scope to include cyclooctene results in 34% cyclooctene oxide (Scheme 2). These results point to the general scope of the catalytic epoxidations mediated by **1**/ArIO.

Competition experiments were next performed in which a 1:1 mixture of alkenes was reacted with different ArIO oxidants in CH_2Cl_2 at 23 °C. With limiting oxidant and excess substrate, the molar ratio of the products should reflect the inherent selectivity of the active catalytic species. If the active species is **1**-OIAr, as predicted for pathway C (Scheme 1), then the product ratio should depend on the identity of ArIO. Product analysis of the competition reaction between styrene and *cis*-stilbene (Table 1) shows that the ratio of epoxides is similar for PhIO and PFIB but different for MesIO.[7] This result is consistent with the steric encumbrance of ArIO having a dominant effect, as might be expected based on pathway C, providing good support for the proposed mechanism. However, it is not clear why an increase in stilbene oxide, the seemingly more sterically hindered product, is

Scheme 2

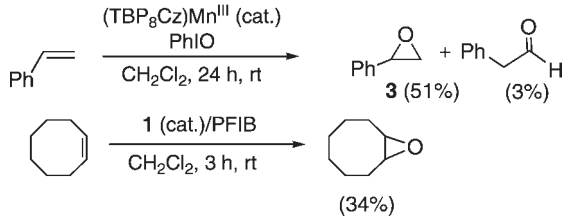
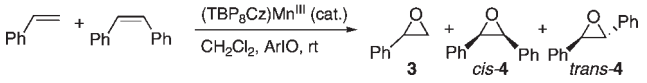


Table 1. Competitive Epoxidations of Styrene and *cis*-Stilbene with Different Oxidants[a]



ArIO	**3** (%)[b]	*cis*-**4** + *trans*-**4** (%)[b]	[**3**]/[*cis*-**4** + *trans*-**4**][c]
PhIO	26	19	1.39 ± 0.05
PFIB	17	12	1.41 ± 0.02
MesIO	24	22	1.05 ± 0.05

[a] Reaction conditions: $(TBP_8Cz)Mn^{III}$ (0.78 μmol), ArIO (48 μmol), styrene (280 μmol), and *cis*-stilbene (280 μmol). [b] Percent yields are determined by gas chromatography and based upon the amount of ArIO added. [c] Calculated from the ratio of the moles of the products determined by gas chromatography. Average of at least three runs.

observed for MesIO as compared to PhIO or PFIB. Similar findings have been obtained for both porphyrin and salen complexes, where product distributions are influenced by the nature of the oxidant but do not correlate with an obvious steric or electronic property.[1a,2d]

Zdilla and Abu-Omar have shown that the manganese(V) imido complex $(tpfc)Mn^V(NTs)$ catalyzes the aziridination of styrene through a coordinated oxidant intermediate $(tpfc)Mn^V(NTs)(ArINTs^*)$.[5] We speculated that a suitable manganese(V) imido complex might be able to promote the *epoxidation* of an alkene via a coordinated ArIO intermediate. The corrolazine complex $(TBP_8Cz)Mn^V(NMes)$ (**2**; Chart 1) is a rare example of a stable, isolable Mn^V terminal imide and shows no direct reactivity toward alkenes.[8] Thus, **2** was an ideal candidate for this study. We were pleased to find that the stoichiometric reaction of **2**−PFIB−cyclooctene (1:1:1 molar ratio) in CD_2Cl_2 at 23 °C over 24 h produced cyclooctene oxide (23%). Analysis by ^1H NMR spectroscopy showed that diamagnetic **2** remained intact at the end of the reaction, and quantitation by UV−vis [λ_{max} (ε) 419 (3.60×10^4 M^{-1} cm^{-1}), 659 (9.29×10^3 M^{-1} cm^{-1})/nm] revealed an 86% recovery for **2**. The majority of cyclooctene oxide (19%) is formed within 1 h, at which point the recovery of **2** is nearly quantitative (≥95%). If excess substrate (20−40 equiv) is employed, the yield of epoxide (50−68%) increases dramatically, and there is no loss of **2** (98−103% by UV−vis). We conclude that **2** mediates OAT through a reactive intermediate that is intercepted by substrate until the substrate becomes diminished, at which point **2** begins to degrade.

With the manganese(V) imido complex employed as the catalyst (**2**:PFIB:cyclooctene = 1:25:250 molar ratio), the oxide is formed in 34% (9 turnovers), similar to catalysis with **1**. The proposed catalytic mechanism is shown in Scheme 3, in which a coordinated oxidant−Mn−imido intermediate is

(7) The [*cis*-**4**]/[*trans*-**4**] ratio also varies with the identity of the oxidant (see the Supporting Information).

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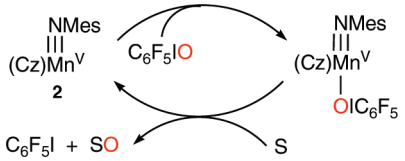
Scheme 3



the active epoxidizing agent. We considered the possibility that **2** was being hydrolyzed to **1** to a small extent by exogenous H_2O, allowing **1** to serve as the catalyst. However, stirring **2** in a mixture of $CH_2Cl_2-H_2O$ (1:1, v/v) for 24 h did not produce any **1** as monitored by UV−vis. Even the addition of the strong H^+ donor trifluoroacetic acid to this mixture failed to convert **2** to **1**. Examining the stability of **2** under catalytic conditions [**2**−PFIB (1:25) or **2**−PFIB−H_2O (1:25:excess) in CH_2Cl_2] revealed only the decay of **2** (Figure S3 in the Supporting Information), which likely occurs in the absence of substrate from overoxidation by PFIB. These results rule out **1** as the active catalyst during the manganese(V) imido-mediated epoxidations.

As a further test of the mechanism in Scheme 3, we added Lewis bases as potential donors that could compete for the binding site trans to the imido group. The addition of MeOH as the cosolvent [$CH_2Cl_2-CH_3OH$ (3:1, v/v)] to **2**−PFIB−cyclooctene lowers the catalytic yield of cyclooctene oxide to 17%, consistent with MeOH inhibiting the reaction through binding to the open site on the metal. Similarly, the addition of either excess Bu_4NCl or 1-methylimidazole (1-MeIm; 25 equiv) causes a decrease in the epoxide yield (23% and 24%, respectively).[9] Finally, the addition of $H_2{}^{18}O$ to **2**−PFIB−cyclooctene under catalytic conditions gives ^{18}O-cyclooctene oxide (79% isotopic enrichment). The incorporation of ^{18}O into metal-bound PhIO adducts from $H_2{}^{18}O$ is well-precedented.[1c,d,3,10] Taken together, all of the data indicate that **2** functions as a catalyst for the epoxidation of alkenes and provide strong evidence for (TBP$_8$Cz)Mn^V(NMes)(OI-C_6F_5) as the active epoxidizing agent.

No UV−vis spectral change is seen upon the addition of ArIO to **1** or **2**. However, negligible changes to the optical spectra of both Mn^V(O)(corrole) and Fe^{IV}(O)(porph$^{\bullet+}$) complexes have been observed upon the coordination of axial ligands.[11] Direct evidence for the intermediate in pathway C was obtained by electrospray ionization mass spectrometry (ESIMS). Rapid injection of freshly prepared mixtures of **1** and MesIO (2.5 equiv) gives rise to a prominent peak at a mass-to-charge ratio (m/z) of 1711.2 (calcd m/z 1711.8),

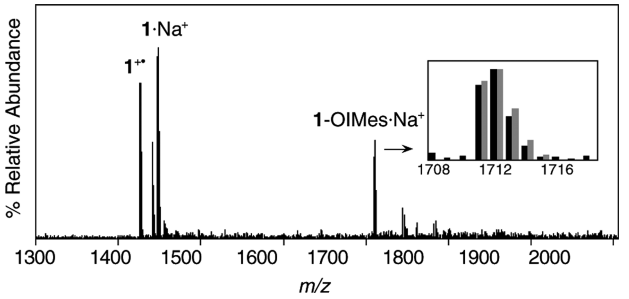


Figure 1. ESIMS of **1**-OIMes·Na$^+$. The inset shows observed (black) and theoretical (gray) isotope distribution patterns.

corresponding to **1**-OIMes·Na$^+$ (Figure 1).[12] The isotope pattern firmly establishes the composition of **1**-OIMes·Na$^+$ (inset, Figure 1). A cluster centered at m/z 1449.8 is assigned to **1**·Na$^+$ (calcd m/z 1449.8). Another cluster near m/z 1427.0 corresponds to **1**$^{\bullet+}$ (calcd m/z 1426.8). Structural characterization of **1**-OIMes·Na$^+$ was obtained by collision-induced dissociation tandem ESIMS/MS (Figure S4 in the Supporting Information). The ion at m/z 1711.2 dissociates cleanly to give a single fragment ion at m/z 1449.8, corresponding to a loss of MesIO. This fragmentation is consistent with the OIMes group being axially ligated to **1**.

In conclusion, we have demonstrated that **1** functions as a general catalyst for the selective epoxidation of alkenes with a range of ArIO oxidants. It was also shown that the isoelectronic manganese(V) imido complex **2** is capable of mediating alkene epoxidation, but not aziridination, under conditions similar to those of **1**. These reactions most likely proceed through an unusual oxidant−metal−oxo/imido intermediate as the active catalytic species. The first direct evidence for one of these intermediates has been obtained by ESIMS. The mechanism in pathway C may have broad significance for both porphyrin- and non-heme-type oxidations. Although heme enzymes are less likely to proceed through pathway C because of the proximal ligand, this work strengthens the notion that coordinated metal−oxidant adducts may be viable alternatives to the generally accepted metal−oxo intermediates.

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Supporting Information Available: Experimental details, Table S1, and UV−vis and ESIMS/MS spectra (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

(9) No UV−vis change is seen for **2** upon the addition of Cl^- or 1-MeIm, and thus binding affinities could not be obtained. However, laser-desorption mass spectrometry data provide direct evidence that isoelectronic **1** does bind Lewis bases (e.g., F^-, CN^-). Prokop, K.; Goldberg, D. P. Unpublished results.

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(12) Alkali−metal cation adducts are commonly observed in ESIMS. See: (a) Wang, H. Y.; Yim, W. L.; Klüner, T.; Metzger, J. O. *Chem.—Eur. J.* **2009**, *15*, 10948–10959. (b) O'Toole, M. G.; Kreso, M.; Kozlowski, P. M.; Mashuta, M. S.; Grapperhaus, C. A. *J. Biol. Inorg. Chem.* **2008**, *13*, 1219–1230. (c) Colton, R.; D'Agostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *14*, 79–106.