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Efficient Epoxidation of Electron-Deficient Olefins with a Cationic Manganese Complex

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The catalytic epoxidation of terminal and electron-deficient olefins remains a challenging task in organic chemistry. Few catalytic methods exist that are operationally efficient and readily scaled using simple oxidants. Recent reports have detailed several impressive catalytic systems for such olefins, but each system has limitations that include expensive catalysts, long reaction times, high catalyst loadings, or limited substrate scope.[1–10] Here we report a highly selective and efficient manganese complex, [Mn^{II}-(***R,R*-mcp**)]$^{2+}$ (Figure 1), that can rapidly (<5 min) epoxidize a wide range of olefins at room temperature with low catalyst loadings using 1.2 equiv of commercially available peracetic acid. The reactions are readily scaled from 5 mg to 25 g within minimal solvent, and the isolated yields are generally >85%.[11]
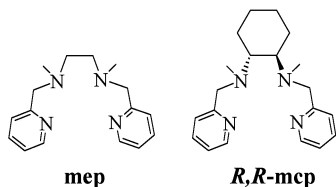

Figure 1. Tetradentate ligands **mep** and ***R,R*-mcp**.

The coordination geometries of the iron sites in heme and non-heme iron enzymes that epoxidize olefins provide inspiration for small-molecule catalyst design.[12–14] Notable in the non-heme iron area is the recent report of [Fe^{II}(**mep**)]$^{2+}$, that performs rapid, efficient epoxidations of terminal olefins using H$_2$O$_2$,[1] albeit with moderate catalyst loading (~3%) and somewhat capricious selectivity. Curiously, a near identical chiral variant, [Fe^{II}(***R,R*-mcp**)]$^{2+}$, is a poor epoxidation catalyst under similar conditions even though the iron centers in each complex are ligated in a *cis*-α coordination geometry.[15] The manganese analogues of these complexes, [Mn^{II}-(***R,R*-mcp**)(CF$_3$SO$_3$)$_2$] (**1**) and [Mn^{II}(**mep**)(CF$_3$SO$_3$)$_2$] (**2**), are effectively isostructural to the iron complexes with two *cis*-bound CF$_3$SO$_3^-$ anions completing the manganese octahedral coordination (Figure 1).[16] These labile-ligand *cis*-sites allow the formation of dimeric Mn^{II} and Mn^{III} complexes under aqueous conditions,[17–20] and such complexes are generally good H$_2$O$_2$ disproportionation catalysts. Indeed, the efficient H$_2$O$_2$ disproportionation by **1** and **2** precludes its use as an effective oxidant. However, other oxidants such as peracids, alkylperoxides, or iodosobenzene are effective oxidants with other manganese catalysts.[8,21–26] Particularly relevant is the epoxidation of terminal olefins with specialized Mn–porphyrin complexes and specially prepared peracetic acid.[27]

Commercially available peracetic is an inexpensive, readily available oxidant that is generally overlooked for epoxidation chemistry due to its strongly acidic composition (1% H$_2$SO$_4$).[28] Yet, peracetic acid is capable of epoxidizing terminal olefins without a catalyst at elevated temperatures (>60 °C) over hours. Such conditions often lead to significant amounts of epoxide ring-opened
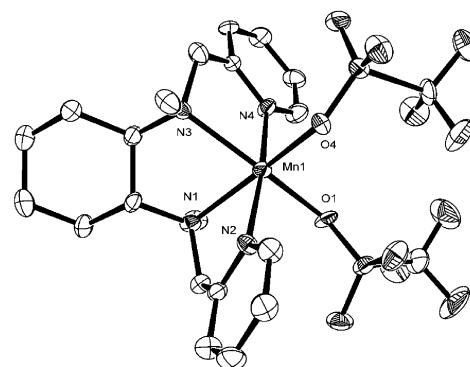

Figure 2. ORTEP drawing [Mn^{II}(***R,R*-mcp**)(CF$_3$SO$_3$)$_2$] (50% thermal ellipsoids). The average Mn−N and Mn−O distances are 2.25 and 2.17 Å, respectively. The N(2)−Mn(1)−N(4) angle is 172°.

products. Metal-based catalysts may potentially maximize the efficiency of this oxidant by minimizing unproductive chemistry.

[Mn^{II}(**mep**)(CF$_3$SO$_3$)$_2$] (**2**) and commercially available peracetic acid create a powerful epoxidation agent in MeCN at ambient temperatures. Terminal olefins are rapidly and efficiently epoxidized (vinyl cyclohexane; 1.2 equiv of CH$_3$CO$_3$H, <5 min, >90%), but complete conversion generally requires 5 mol % catalyst loading. Control experiments, including one that shows that simple manganese salts are ineffective as catalysts under these conditions, suggested that catalyst degradation was the limiting factor with **2**.

[Mn^{II}(***R,R*-mcp**)(CF$_3$SO$_3$)$_2$] (**1**) is a more kinetically and thermodynamically stable complex under oxidative, acidic conditions (Figure 2).[29] Under conditions described above, **1** efficiently epoxidizes vinyl cyclohexane with 0.1 mol % of catalyst at a rate greater than 250 turnovers min^{-1} (Scheme 1) at ambient temperatures.[30] This catalyst also rapidly epoxidizes electron-rich di- and trisubstituted olefins in addition to the electron-poor olefins of allyl acetate, methacrylate, and 2-cyclohexen-1-one.[31,32] The more electron-deficient olefins (entries 9, 10, 11, 15, Table 1) require slight adjustments of the reaction conditions; a slight increase in either the catalyst loading or the amount of peracetic acid is generally sufficient to achieve high conversion and yields.

Scheme 1. Epoxidation of Olefins with **1**
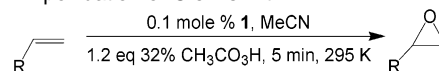
As with many oxidation catalysts, the nature of the active oxidant is difficult to assess. The addition of 3 equiv of peracetic acid to a 1 mM solution of high-spin **1** (μ_{eff} = 5.6 μ_B)[33] in MeCN induces a slight color change from pale-tan to a light-brown at 238 K, but neither the broad isotropic g = 2.0 Mn^{II} EPR signal (77 K) nor the magnetic susceptibility of this mixture is significantly altered from a solution of pure **1**. Under these lower-temperature conditions, epoxidation of cyclooctene efficiently occurs. Together, the data

Table 1. Epoxidations Catalyzed by **1** with CH$_3$CO$_3$H[a]

	alkene	mol % **1**	oxidant (equiv)	GC yield[b]	isolated yield[c]
1	cyclooctene	0.1	1.2	99 (1)	90 (4)[d]
2	cyclohexene	0.1	1.2	98 (2)	85 (2)
3	1-methyl-cyclohexene	0.1	2	92 (3)	
4	*cis*-2-heptene	0.1	1.2	99 (1)[e]	
5	*trans*-2-heptene	0.1	1.2	99 (1)[f]	
6	2-methyl-1-pentene	0.1	1.2	97 (1)	
7	1-heptene	0.1	1.2	95 (3)	89 (3)
8	vinyl cyclohexane	0.1	1.2	99 (1)	90 (2)
9	allyl acetate	0.1	2	89 (3)	
10	methyl methacrylate	0.2	1.2	98 (1)	86 (6)
11	2-cyclohexen-1-one	0.5	1.2	97 (4)	88 (2)
12	ethyl sorbate[g]	0.1	1.2	94 (4)[h]	
13	*cis*-β-methylstyrene	1.0	1.2	90 (1)	
14	*trans*-β-methylstyrene	1.0	1.2	97 (1)	
15a	*R*-(−)-carvone	0.5	3	98 (1)[i]	88 (2)[i]
15b	*R*-(−)-carvone	0.5	1	97 (2)[j]	91 (2)[j]

[a] Olefin (0.5 M in CH$_3$CN), 32% CH$_3$CO$_3$H in acetic acid/water, 25 °C, 5 min. [b] Yields determined by GC versus internal standard, average of three runs. Conversion for all substrates is >95%. The numbers in parentheses represent a standard deviation of a minimum of three experiments. [c] Isolated yields, 1-g scale. [d] 0.25-mol scale, 88% yield. [e] 98% *cis*-epoxide, 2% *trans*-epoxide. [f] 97% *trans*-epoxide, 3% *cis*-epoxide. [g] *trans,trans*-CH$_3$CH$_2$=CH$_2$CH$_2$=CH$_2$−CO$_2$CH$_2$CH$_3$. [h] 4:1 mixture of 4,5-monoepoxide and 2,3-monoepoxide. [i] 0 °C diepoxide product, 20% de. [j] −20 °C, *R*-carvone 8,9-monoepoxide, 15% de.

suggests the resting form of the catalyst is Mn^{II} and that the optical changes are associated with catalyst decomposition. A Lewis-acid assisted oxidation is possible, but [Zn^{II}(***R,R*-mcp**)]$^{2+}$, a redox-innocent complex, is unable to epoxidize olefins under identical conditions. Thus, a higher-valent manganese species is suggested.

Intermolecular competition experiments with several pairs of olefin substrates at low substrate conversion support an electrophilic oxidant; the more electron-rich olefins are epoxidized at faster rates, e.g. allyl acetate < vinyl cyclohexane < cyclooctene (1:15:120). The prominent chemoselectivity of porphyrin or salen metal−oxo oxidants for *cis*-olefins over *trans*-olefins is not observed for **1**; *cis*-2-heptene is preferentially oxidized to *trans*-2-heptene in a 3:1 ratio while *cis*-β-methylstyrene and *trans*-β-methylstyrene are epoxidized in a 1:1 ratio. A slight loss of the original olefin stereochemistry in the epoxide products (∼3%) suggests either a short-lived radical intermediate or the presence of more than one oxidant in the solution.

Regioselective epoxidation of polyolefins (entries 12 and 15) further supports an electrophilic oxidant with **1**. Ethyl sorbate yields a 4:1 mixture of the 4,5- and 2,3-monoepoxide, respectively. High regioselectivity is possible if the olefin groups are electronically distinct, and the reaction temperature is reduced. The terminal olefin of *R*-carvone is selectively epoxidized at −20 °C in 15 min with 1 equiv of peracetic acid (Scheme 2). Three equivalents of oxidant at 0 °C gives the diepoxide of *R*-carvone in high yield. In both cases, only a modest diastereoselectivity (de) of the terminal olefin epoxidation is observed (∼20%).

Scheme 2. Epoxidation of *R*-(−)-Carvone
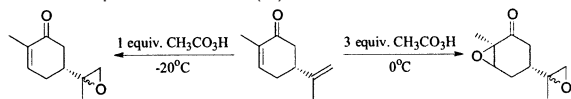
This system provides an operationally simple and rapid way to epoxidize a wide scope of olefins using low catalyst loadings. Mechanistic studies as well as comparative studies of the iron

analogues are in progress to understand the nature of the active oxidant and improve on the low observed enantio- and diastereoselectivities.[34]

Supporting Information Available: Experimental procedures for the synthesis of **1** and **2**, and for the epoxidation of olefins with **2** (PDF). Crystallographic data of **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal Data for **1**: a pale brown rectangular plate from acetonitrile/ether; monoclinic *P*2$_1$, *a* = 9.1024(5) Å, *b* = 9.7740(6) Å, *c* = 16.2918(8) Å, β= 101.871(2), *V* = 1418.4(1) Å^3, 2230 reflections (4° < 2θ < 49.42°), R(Rw) = 0.045(0.108). Crystal Data for **2**: a colorless rhombic crystal from acetonitrile/ether; orthorhombic *Pbca*, *a* = 9.4259(6) Å, *b* = 17.4826(9) Å, *c* = 30.462(2) Å, *V* = 5019.6(4) Å^3, 3401 reflections (4° < 2θ < 43.94°), R(Rw) = 0.036 (0.095).
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(27) The peracetic acid used in ref 24 is prepared to be sulfuric acid and H$_2$O$_2$ free.
(28) Peracetic acid solutions are generally prepared from H$_2$O$_2$ and HOAc using 1% sulfuric acid catalyst.
(29) The formation constant for [Mn^{II}CDTA]$^{2-}$ is ∼4 orders of magnitude larger than [Mn^{II}EDTA]$^{2-}$. CDTA = *trans*-cyclohexyl-1,2-diamine tetraacetic acid.
(30) The observed ee's are small. At room temperature **1**/CH$_3$CO$_3$H only gives a 10% ee for vinyl cyclohexane. [Mn^{II}(**6-methyl-*R,R*-mcp**)](CF$_3$SO$_3$)$_2$ shows no reactivity under these conditions.
(31) This system does not exclusively provide the epoxide product for sensitive olefins such as styrene, ethyl acrylate, or α-pinene.
(32) The dependence of the epoxidation reaction on the counterion is minimal. Both the CF$_3$SO$_3^-$ and CH$_3$CO$_2^-$ complexes have identical reactivity. However, the chloride complex provides only 25% conversion of vinyl cyclohexane under the same conditions and time. Consequently, the catalyst can be formed in situ by combining the available Mn(OAc)$_2$ salt and ***R,R*-mcp**. In addition, these reactions can be run in an identical manner when glacial acetic acid is used as the solvent.
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