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Donor Ligand Effect on the Nature of the Oxygenating Species in Mn^{III}(salen)-Catalyzed Epoxidation of Olefins: Experimental Evidence for Multiple Active Oxidants

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The stereoselectivity of olefin epoxidation catalyzed by Mn^{III}(salen)X (**1a**, X = Cl^-; **1b**, X = BF_4^-) complexes is examined in the presence of neutral donor ligands, employing various iodosylarenes (ArIO: PhIO, C_6F_5IO, and MesIO) as the oxygen atom source. The cis/trans ratios of stilbene oxides and the enantiomeric excesses of styrene oxide and 1,2-dihydronaphthalene oxide are found to be strongly dependent on the nature of the iodosylarenes under certain conditions. In other cases, olefin epoxidation is shown to proceed with essentially identical diastereoselectivities or enantioselectivities, regardless of the oxygen atom source used. We propose that a Mn^V-(salen)-oxo intermediate and a complex between the catalyst and the terminal oxidant competitively effect the epoxidation when the stereoselectivities are markedly dependent on the oxygen atom source. A single Mn^V(salen)-oxo species is considered to be the sole oxygenating intermediate when the terminal oxidants do not exert a notable influence on the product selectivities. Our results clearly demonstrate the existence of multiple oxidizing species and the conditions in which only a single oxygenating intermediate is involved. The axial donor ligands (both anionic ligands and neutral ligands) are shown to strongly influence both the identity and the reactivity of the oxygenating species.

Introduction

Transition-metal-catalyzed epoxidation is both synthetically useful and mechanistically intriguing.[1] Synthetic metalloporphyrins and manganese salen complexes are among the most efficient catalysts to effect epoxidation of unfunctionalized olefins with high selectivities.[2,3] A discrete high-valent metal-oxo species (either an $iron^{IV}$-oxo porphyrin radical cation complex or a $manganese^V$-oxo salen complex) has been proposed as the sole reactive intermediate and many experimental results have been successfully explained by the involvement of such a high-valent metal-oxo species.[4,5]

However, re-examination of the mechanisms of olefin epoxidation has raised interesting questions concerning the identity of the oxidizing species. In particular, the selectivity of the oxidation reactions catalyzed by metalloporphyrins has been shown in many cases to be strongly dependent on the oxygen atom source. For example, Nam et al. reported the selectivities are significantly dependent on the nature of the oxygen atom source (hydrogen peroxide, *tert*-butyl hydroperoxide, and *m*CPBA) in iron porphyrin-catalyzed competitive oxygenation reactions.[6] Similar dependence of selectivity on terminal peracids was also observed in the competitive oxidation of an alkane and an olefin catalyzed by a heme-thiolate complex, and electron-withdrawing para-substituents on the perbenzoic acids were shown to increase olefin epoxidation over alkane hydroxylation.[7] We also found

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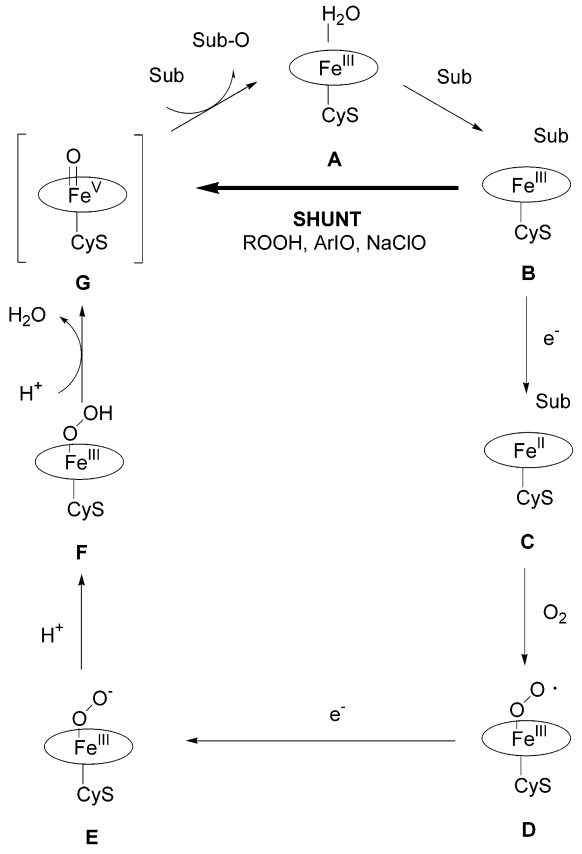
Scheme 1. Cytochrome P450 Reaction Cycle and the "Shunt Reaction"



small but statistically significant differences in the selectivities in competitive alkane hydroxylations and olefin expoxidations catalyzed by an electron-deficient iron porphyrin with different iodosylarenes.[8] If an iron-oxo intermediate is the only oxygenating species, it should mediate the reactions with identical selectivity regardless of its origin. The aforementioned results have prompted a new mechanistic proposal in which a complex between the catalyst and the terminal oxidant can effect the oxygenation in addition to the discrete iron-oxo porphyrin intermediate. Moreover, the existence of a complex between the catalyst and the terminal oxidant has been suggested in the iron porphyrin-catalyzed oxygenation of an organometallic compound, in which the discrete iron-oxo intermediate and the proposed complex were shown to furnish two distinct oxygenation products from the same substrate.[9]

The involvement of a second oxygenating species in metalloporphyrin-catalyzed oxygenation is reminiscent of recent findings in the oxygenation catalyzed by cytochrome P450 enzymes. For instance, studies of enzyme-catalyzed hydrocarbon oxygenation have shown that both an iron^{IV}-oxo porphyrin radical cation (**G** in Scheme 1) and a hydroperoxo-iron complex (**F** in Scheme 1) are competent to effect the oxygenation.[10,11] Furthermore, it has been proposed that particular mutations in wild enzymes interfere with the formation of the iron-oxo species from the iron-hydroperoxo intermediate and consequently alter the selectivities in competitive oxygenations.[12,13]

Elucidation of the nature of oxygenating species in manganese-salen-catalyzed epoxidation is particularly important and interesting since optically pure manganese-salen complexes have proven to be the most efficient catalysts for enantioselective epoxidation of unfunctionalized olefins.[3] In this paper, we demonstrate the dependence of stereoselectivity on terminal iodosylarenes in the manganese-salen-catalyzed epoxidation of olefins, and the participation of multiple active oxidants has been proposed to account for the experimental results. In a similar study of manganese-salen-catalyzed epoxidation of *cis*-stilbene, Adam et al. have also claimed the involvement of multiple active oxidants when the terminal oxidants are $TBAHSO_5$, NaOCl, and DMD (dimethyldioxirane).[14] In addition, we have systematically studied the influence of a wide variety of donor ligands (axial anionic ligands and exogenous neutral ligands) on the nature of the oxygenating species. Furthermore, we have found conditions in which a discrete manganese-oxo intermediate appears to be the sole epoxidizing species.

Results and Discussion

Epoxidations of olefins were carried out with manganese salen complexes (**1a**, X = Cl^-; **1b**, X = BF_4^-; **1c**, X = Br^-; **1d**, X = OAc^-) as the precatalysts; PhIO, C_6F_5IO, and MesIO as the oxygen atom source and Ph_3PO, PyNO, and 1-MeIm as the exogenous neutral donor ligands (Figure 1). Control experiments showed that *cis*-stilbene oxide did not isomerize to afford *trans*-stilbene oxide either under the reaction condition or during the separation. Chiral epoxides were also shown to be stable under the reaction conditions (except for the asymmetric epoxidations with **1b**, X = BF_4^-, in the absence of neutral donor ligands). Moreover, the product distributions remained constant and did not change with the degree of conversion (see Table S-1 in Supporting Information). Because of the insolubility of the iodosylarenes in common organic solvents, we did not attempt to determine the rate law.[15]

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(15) PhIO dissolves in methanol, but it is then converted into $PhI(OCH_3)_2$. (a) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563. (b) White, R. E. *Inorg. Chem.* **1987**, *26*, 3916. For an example of kinetic study of porphyrins-catalyzed epoxidation with PhIO in alcohol, see: Traylor, T. G.; Marsters, J. C., Jr.; Nakono, T.; Dunlap, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 5537−5539.

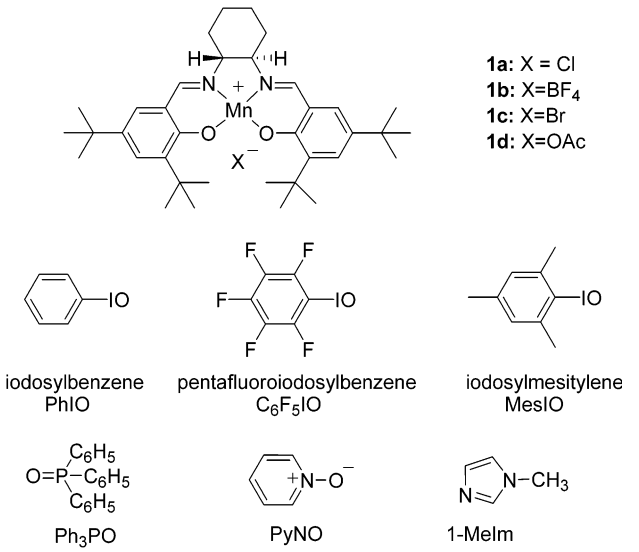

Figure 1. Structures of the catalysts, terminal oxidants, and donor ligands employed.

Olefin Epoxidation Catalyzed by Mn(salen)Cl and the Existence of Multiple Oxidants. As shown in Table 1 entries 1−3, the ratios of cis/trans epoxides are significantly influenced by the nature of the terminal oxidants when the reaction is catalyzed by manganese-salen complexes possessing coordinating axial anionic ligands (Cl^-, Br^-, and OAc^-) in CH_2Cl_2. For example, when the reaction is catalyzed by **1a** ($X = Cl^-$), the ratios of cis/trans epoxides range from 22:78 with PhIO to 47:53 with C_6F_5IO and 48:52 with MesIO (Table 1, entry 1). The diastereoselectivity is still appreciably dependent on the oxygen source in solvents other than CH_2Cl_2 (Table 1, entries 5−7). Moreover, upon the addition of neutral donor ligands such as Ph_3PO and PyNO, the diastereoselectivities still differ when different oxygen donors are used, although the specific cis/trans ratios and/or epoxide yields vary only to a limited extent (Table 1, entry 1 vs entry 8 and entry 1 vs entry 10).

It is also found that the enantioselectivity varies with different iodosylarenes in the asymmetric epoxidation of olefins catalyzed by optically pure **1a** ($X = Cl^-$). For instance, enantiomeric excesses of styrene oxide range from 23.5 ± 0.5 with PhIO to 30.5 ± 0.5 with C_6F_5IO (Table 2, entry 1). A similar difference (up to 11% ee) was observed in asymmetric epoxidation of 1,2-dihydronaphthalene (Table 3, entry 1). The presence of Ph_3PO does not exert a detectable influence in terms of enantioselectivity or yield (Table 2, entry 2, and Table 3, entry 2). The addition of PyNO moderately alters the enantioselectivity, but the selectivity still depends on the nature of the terminal oxidants (Table 2, entry 4, and Table 3, entry 4). In the asymmetric aziridination of olefins catalyzed by chiral (diimine)copper complexes, Jacobsen et al. observed the enantiomeric excess of the aziridines was almost identical when two different terminal tosyliminoiodoarenes were employed and they subsequently claimed that a Cu(diimine)-imido complex is the only reactive intermediate in the asymmetric aziridination of alkenes.[16] The asymmetric epoxidation of olefins catalyzed by optically pure **1a** ($X = Cl^-$) in this study is apparently different in that the nature of the terminal oxidants does exert an influence on the enantiomeric excesses. Dependence of enantioselectivity on terminal oxidants has also been reported in several cases in chiral metalloporphyrin-catalyzed olefin epoxidations.[17]

The pathway shown in Scheme 2a is the classic mechanism for epoxidation of olefins catalyzed by transition metal complexes. A putative metal-oxo species is formed by a "shunt reaction" from an exogenous oxygen donor.[18] The discrete high-valent metal-oxo intermediate should effect the reaction with identical selectivity, regardless of the nature of the oxygen atom source employed. The dependence of diastereoselectivity and enantioselectivity observed in the present study shows unambiguously that there is at least one other active epoxidizing intermediate in addition to the Mn^V-(salen)-oxo complex. A plausible mechanistic alternative is one in which the catalyst functions as a Lewis acid. Such a catalyst-terminal oxidant complex could deliver the oxygen atom directly to the substrate and bypass the metal-oxo intermediate if the formation of the metal-oxo species from the oxidant-catalyst adduct is relatively slow compared to the oxygen atom transfer to the substrate (Scheme 2b). We propose that the epoxidation catalyzed by **1a** ($X = Cl^-$) takes place via a bifurcated mechanism in which the manganese-oxo and a complex between the catalyst and the iodosylarene react competitively (Scheme 3). Since the complex between the catalyst and the oxygen donor is involved in one of the product-determining steps, the nature of the oxygen donors should exert an influence on the overall product selectivities. It is noteworthy that the iodoarenes that are released upon transfer of oxygen from iodine to the manganese-salen complex in this study may interact with the Mn(salen)-oxo intermediate via weak π-bond association, although the influence on the reactivity of the Mn(salen)-oxo species is probably insignificant. The formation of manganese porphyrin complexes that contain PhIO as the axial ligand has been reported.[19] Lewis acid activation of PhIO has precedent in epoxidation of olefins with iodosylbenzene catalyzed by non-redox-active metal (Zn and Al) complexes.[20] Furthermore, Nam and Que have recently demonstrated the formation of a porphyrin-PhIO complex by reacting an Fe^{VI}-(porphyrin)-oxo radical cation with iodobenzene.[21]

It is interesting that MesIO influences the selectivity to a similar extent to C_6F_5IO but is different from PhIO in olefin

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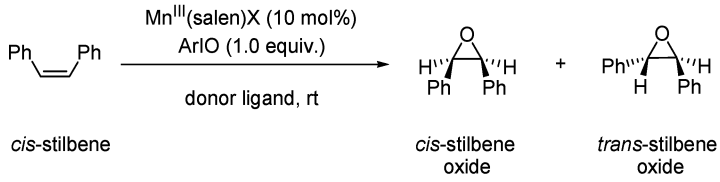
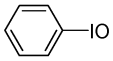
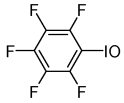
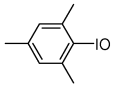
Table 1. Epoxidation of *cis*-Stilbene Catalyzed by Racemic Mn^{III}(salen)X

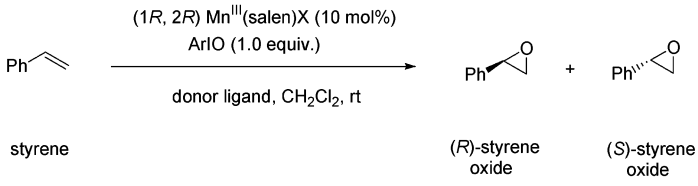


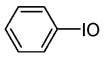
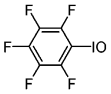
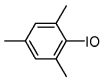
				cis/trans ratio[a] (yield[b])		
Entry	Catalyst	Solvent	Donor Ligand			
1	X=Cl	CH_2Cl_2	--	22±2:78 (48)	47±1:53 (52)	48±2:52 (70)
2	X=Br	CH_2Cl_2	--	18±2:82 (47)	41±2:59 (48)	50±3:50 (63)
3	X=OAc	CH_2Cl_2	--	19±1:81 (50)	36±1:64 (45)	32±1:68 (48)
4[c]	X=BF_4	CH_2Cl_2	--	80±2:20 (28)	83±3:17 (30)	77±2:23 (28)
5	X=Cl	benzene	--	37±1:63 (78)	50±3:50 (68)	39±2:61 (77)
6	X=Cl	CH_3CN	--	31±1:69 (42)	38±2:62 (40)	48±2:52 (46)
7	X=Cl	[Bmim][Br][d]	--	62±2:38 (37)	54±3:46 (34)	75±3:25 (33)
8	X=Cl	CH_2Cl_2	Ph_3PO	20±2:80 (49)	40±1:60 (58)	46±1:54 (67)
9	X=BF_4	CH_2Cl_2	Ph_3PO	73±2:27 (46)	81±2:19 (35)	80±2:20 (47)
10	X=Cl	CH_2Cl_2	PyNO	38±1:62 (60)	47±2:53 (57)	60±2:40 (68)
11	X=BF_4	CH_2Cl_2	PyNO	73±1:27 (71)	73±1:27 (65)	73±1:27 (69)
12[e]	X=Cl	CH_2Cl_2	1-MeIm	61±1:39 (22)	61±1:39 (20)	61±1:39 (20)
13[e]	X=BF_4	CH_2Cl_2	1-MeIm	61±1:39 (30)	61±1:39 (28)	61±1:39 (26)
14[e]	X=Br	CH_2Cl_2	1-MeIm	61±1:39 (34)	63±2:37 (20)	61±1:39 (41)

[a] The cis/trans ratios were determined by ^{1}H NMR analysis directly on the crude product mixture after the removal of the catalyst. All cis/trans ratios have been run three times and the error is also listed. [b] Yields are based on the terminal oxidants. [c] Oxides were not stable under the reaction conditions after 1 h. [d] The solvent is a mixture of 2.2 g of the ionic liquid and 5.0 mL of CH_2Cl_2. [e] 75 μmol or 15 mol % of 1-MeIm was used to maximize the yields of epoxides.

epoxidation catalyzed by **1a** (X = Cl^-) (Table 1, entries 1, 3, and 8; Table 2, entries 1 and 2; Table 3, entries 1, 2, and 4). For example, in asymmetric epoxidation of 1,2-dihydronaphthalene, the enantioselectivity is 67.0 ± 1.0 with MesIO. This result is close to that obtained with C_6F_5IO (69.0 ± 1.0) while significantly different from that with PhIO (58.0 ± 0.5). PhIO should have a similar oxidizing potential as MesIO, so the oxidizing potential alone would suggest that PhIO and MesIO should have a similar influence on the selectivity. The dependence of selectivity on the nature of terminal oxidant may be the result of a combined effect of the redox potential of the iodosylarenes and the electronic and steric properties of the aryl groups on the iodosylarenes. In a similar study of Mn(salen)Cl-catalyzed epoxidation of *cis*-stilbene by Adam et al., a single mangense(V)-oxo intermediate has been proposed to be the sole active oxidant when PhIO and C_6F_5IO were employed, and the dependence of diastereoselectivity on the nature of two iodosylarenes (cis/trans: PhIO 29:71; C_6F_5IO 47:53) has been attributed to the oxidation of the axial anionic ligand Cl^-, converting it into another terminal oxidant ClO^-, which would give a cis/trans ratio of 75:25.[14b] However, the cis/trans ratio found with MesIO in this study (48 ± 2:52) is much closer to that of C_6F_5IO (47 ± 2:53). Since MesIO should have an oxidizing potential similar to PhIO, this observation contradicts the hypothesis that oxidation of Cl^- to ClO^- is responsible for the selectivity observed with C_6F_5IO. Adam et al. observed that C_6F_5IO dissolves in a CH_2Cl_2 solution of TEBACl to give a homogeneous solution, whereas PhIO remains as suspension in the CH_2Cl_2 solution of TEBACl. They used this observation to argue that C_6F_5IO can oxidize Cl^- while PhIO cannot. However, our control experiments show that C_6F_5IO can also dissolve in a CH_2Cl_2 solution of TBAF to afford a yellowish homogeneous solution (see Supporting Information). Since it is unlikely that the fluoride anion of TBAF can be further oxidized, the disappearance

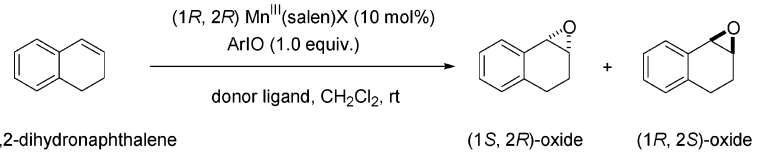
Table 2. Asymmetric Epoxidation of Styrene with Mn^{III}(salen)X in CH_2Cl_2

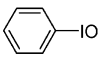
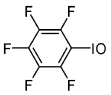
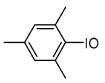


			epoxide ee[a] (yield)[b]		
Entry	Catalyst	Donor Ligand			
1	X=Cl	--	23.5±0.5 (90)	30.5±0.5 (85)	31.5±0.5 (85)
2	X=Cl	Ph_3PO	23.0±0.5 (85)	27.5±0.5 (90)	31.0±0.5 (90)
3[c]	X=BF_4	Ph_3PO	40.0±1.0 (85)	42.0±1.0 (81)	41.0±1.0 (78)
4	X=Cl	PyNO	26.0±0.5 (87)	29.5±0.5 (87)	34.0±0.5 (89)
5	X=BF_4	PyNO	39.0±0.5 (90)	39.0±0.5 (88)	39.0±0.5 (85)
6	X=Cl	1-MeIm	37.0±1.0 (65)	36.5±0.5 (60)	37.0±0.5 (68)
7	X=BF_4	1-MeIm	37.0±0.5 (82)	37.0±0.5 (85)	37.0±0.5 (80)

[a] The enantiomeric excesses were determined by chiral GC analysis directly on the crude product mixture after passing through a short silica gel column. All enantiomeric excesses have been obtained three times and the error is also listed. [b] Yields are based on the terminal oxidants. [c] 0.50 mmol or 1.0 equiv of Ph_3PO was used.

Table 3. Epoxidation of 1,2-Dihydronaphthalene with Mn^{III}(salen)X in CH_2Cl_2



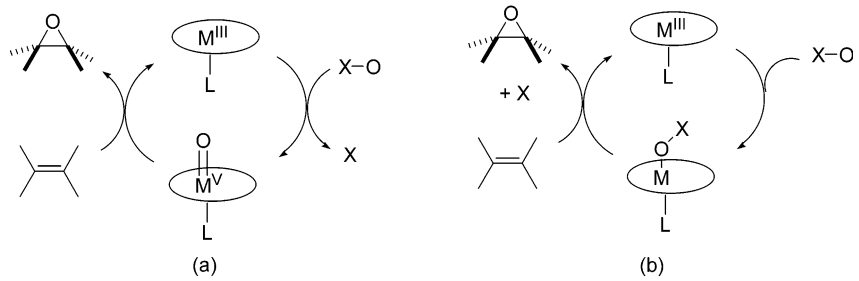
			epoxide ee[a] (yield[b])		
Entry	Catalyst	Donor Ligand			
1	X=Cl	--	58.0±0.5 (51)	69.0±1.0 (50)	67.0±1.0 (61)
2	X=Cl	Ph_3PO	59.0±1.0 (51)	69.5 ±0.5 (46)	66.5±1.0 (55)
3	X=BF_4	Ph_3PO	74.0±0.5 (57)	74.0±0.5 (63)	74.5±0.5 (61)
4	X=Cl	PyNO	65.5±0.5 (57)	72.0±0.5 (65)	72.5±0.5 (72)
5	X=BF_4	PyNO	79.0±0.5 (63)	79.0±0.5 (66)	79.0±0.5 (70)
6	X=Cl	1-MeIm	66.0±0.5 (70)	66.0±0.5 (72)	66.0±0.5 (70)
7	X=BF_4	1-MeIm	68.0±0.5 (60)	68.0±0.5 (68)	68.0±0.5 (67)

[a] The enantiomeric excesses were determined by chiral GC analysis directly on the crude product mixture after passing through a short silica gel column. All enantiomeric excesses have been obtained three times and the error is also listed. [b] Yields are based on the terminal oxidants.

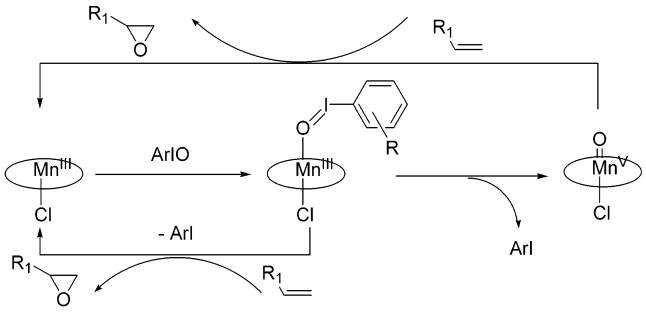
of C_6F_5IO does not necessarily mean that oxidation of the anion has taken place.

Epoxidation Catalyzed by Mn(salen)BF_4 and the Involvement of a Single Mn^V(salen)-oxo Species. Epoxidation of *cis*-stilbene catalyzed by **1b** (X = BF_4^-) in CH_2Cl_2 affords mainly *cis*-stilbene oxide (77−83%) and this diastereoselectivity is nearly independent of the terminal oxidants employed (Table 1, entry 4). The epoxides in the asymmetric epoxidation of styrene and 1,2-dihydronaphthalene catalyzed by **1b** (X = BF_4^-) undergo further decomposition. The independence of stereoselectivity when the catalyst has a poorly ligating anionic ligand (**1b**: X = BF_4^-) implies a discrete Mn^V(salen)-oxo intermediate is the sole epoxidizing species in these cases since only a single common oxygenating species can mediate the reactions with identical selectivities. It is worth mentioning that the stereoselectivity

Scheme 2. Two Possible Reaction Pathways in the Transition-Metal-Catalyzed Epoxidation of Olefins



Scheme 3. Bifurcated Mechanism in Epoxidation of Olefins-Catalyzed Manganese-Salen Complexes



is strongly dependent on the nature of the terminal iodosylarene when the catalyst processes anionic coordinated axial ligands (Cl^-, Br^-, and OAc^-) in CH_2Cl_2 (Table 1, entries 1−3), where the catalyst-iodosylarene adduct is speculated to effect the epoxidation in addition to the Mn^V(salen)-oxo intermediate. Nam et al. suggested the involvement of multiple oxidants in porphyrins-catalyzed epoxidation studies to explain the counterion effect.[22] A similar counterion effect found in manganese-salen-catalyzed epoxidation has been rationalized in terms of *two-state-reactivity* model supported by computational studies.[14a] Since more *trans*-stilbene oxide is produced than *cis*-stilbene oxide when the catalyst is **1a** ($X = Cl^-$) and the opposite product distribution is found when the catalyst is **1b** ($X = BF_4^-$), we suggested that the catalyst-iodosylarene adduct produces mainly *trans*-stilbene oxide from *cis*-stilbene while the Mn^V(salen)-oxo epoxidizes *cis*-stilbene more stereospecifically.

The addition of a neutral donor ligand in the epoxidation catalyzed by **1b** ($X = BF_4^-$) has a pronounced effect on the selectivity. For example, virtually identical cis/trans ratios are obtained when the epoxidation is catalyzed by **1b** ($X = BF_4^-$) in the presence of either Ph_3PO or PyNO (Table 1, entries 9 and 11). The cis/trans ratio is 73 ± 1:27 with all three iodosylarenes in the presence of PyNO (Table 1, entry 11). When the reaction is catalyzed by optically pure **1b** ($X = BF_4^-$), the addition of a donor ligand such as Ph_3PO or PyNO causes the reaction to proceed with constant enantiomeric excesses regardless of the nature of the terminal iodosylarenes (Table 2, entries 3 and 5; Table 3, entries 3 and 5). The poorly coordinated counterion BF_4^- may be replaced by the neutral donor ligand and a single six-coordinated Mn^V(salen)-oxo intermediate with the donor ligand occupying the sixth coordination site is the most probable candidate as the sole oxygenating species. Recent MS-ESI studies have shown the existence of such oxidizing species.[23] Donor ligands are reported to lengthen and weaken the metal−oxygen bond in the metal-oxo species by donating electron density into the M−O antibonding orbital, which may account for the improved reactivity observed in this study.[24]

Epoxidation in the Presence of 1-Methylimidazole. When **1a** ($X = Cl^-$) is used as the catalyst in the presence of 1-MeIm, the cis/trans ratios are essentially identical regardless of the iodosylarenes employed (Table 1, entry 12). This is contrary to the cases with Ph_3PO and PyNO, in which the diastereoselectivity is still dependent on the terminal oxidants. A similar lack of dependence on the terminal oxidant is also observed when the reaction is catalyzed by **1b** ($X = BF_4^-$) in the presence of 1-MeIm (Table 1, entry 13). Moreover, the cis/trans ratio in the case of **1a** ($X = Cl^-$) is the same as the ratio in the case of **1b** ($X = BF_4^-$) (61 ± 1:39 with **1a** vs 61 ± 1:39 with **1b**). The reaction catalyzed by **1c** ($X = Br^-$) also gives a ratio of 61 ± 2:39 (Table 1, entry 14). In addition, optically pure **1a** ($X = Cl^-$) effects asymmetric olefin epoxidation with the same stereoselectivity in the presence of 1-MeIm, which is almost identical to the selectivity found in the case of optically pure **1b** ($X = BF_4^-$) in the presence of 1-MeIm (Table 2, entry 6 vs entry 7; Table 3, entry 6 vs entry 7).

The results indicate that a common active species, presumably a Mn^V(salen)-oxo intermediate with 1-MeIm coordinated to the sixth coordination site, is the active species in these cases. This implies that when the reaction is catalyzed by **1a** ($X = Cl^-$), 1-MeIm replaces Cl^- and a discrete oxo intermediate containing 1-MeIm is formed. In the presence of 1-MeIm, the same metal-oxo intermediate is apparently formed in the epoxidation catalyzed by **1a** ($X = Cl^-$) and **1b** ($X = BF_4^-$). Similar *N*-methylimidazole effects have been observed in other salen and metalloporphyrin-catalyzed olefin epoxidation.[25,26]

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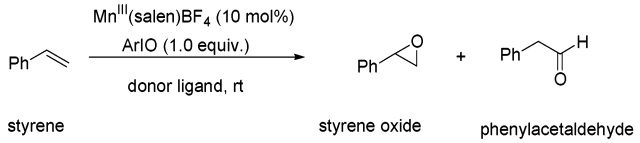
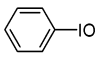
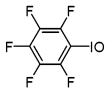
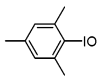
Table 4. Formation of Phenylacetaldehyde in Epoxidation of Styrene Catalyzed by $Mn^{III}(salen)BF_4$ in the Presence of Donor Ligands



styrene | styrene oxide | phenylacetaldehyde

			epoxide/aldehyde[a]		
Entry	Catalyst	Donor Ligand			
1	X= BF_4	Ph_3PO	5.6±0.2	5.0±0.2	4.8±0.2
2	X=BF_4	PyNO	30±1	30±1	30±1

[a] The epoxide/aldehyde ratios were determined by GC analysis directly on the crude product mixture after passing through a short silica gel column. All ratios have been obtained twice and the error is also listed.

Influence of Donor Ligands on the Reactivity of Metal-oxo Species. In the asymmetric epoxidation of styrene, phenylacetaldehyde is also found in the product mixture in addition to styrene oxide. Control experiments show that styrene oxide does not undergo isomerization before the reaction reaches completion. Therefore, phenylacetaldehyde is a primary oxygenation product from styrene. As shown in Table 4, entries 1 and 2, the selectivity does not depend on the nature of the terminal oxidants. Moreover, the epoxide/aldehyde ratio in the presence of Ph_3PO differs from the ratio in the presence of PyNO, suggesting that the reactivity of the Mn^V(salen)-oxo intermediate can be altered by a coordinated neutral donor ligand.

Conclusion

In summary, our results unambiguously demonstrate the existence of at least one other epoxidizing species in addition to the discrete Mn^V(salen)-oxo species in olefin epoxidation catalyzed by manganese-salen complexes under certain conditions. A complex between the catalyst and the terminal iodosylarene is proposed to account for the dependence of selectivity on the nature of the terminal oxygen donors. The bifurcated mechanism proposed in this study (Scheme 3) is reminiscent of the mechanism proposed by Katsuki et al. in a manganese-salen-catalyzed sulfimidation reaction.[27] Neutral donor ligands have been widely employed in porphyrin and salen-catalyzed epoxidation reactions to enhance turnover rates and product selectivities.[28,29] Our results show that they can strongly influence the nature of active oxidant(s) and the reactivity of the Mn^V(salen)-oxo intermediate. Furthermore, our results show the conditions in which only a single Mn^V(salen)-oxo intermediate is involved.

Recent computational results have suggested a two-state reactivity of the discrete iron^{IV}-oxo porphyrin radical cation (compound I), and it has been proposed that this two-state reactivity of the same oxidant is sometimes masked as two distinct active oxidants.[30] Nonetheless, other computational studies have revealed the existence of only one spin state for such an iron-oxo compound.[31] Therefore, the two-state reactivity should be interpreted with caution and further experimental results are needed to justify the computational results. It is noteworthy that recent kinetic isotope studies by Newcomb et al. have shown results that are consistent with the two-oxidant theory and contradictory to the two-state reactivity model.[32]

Experimental Section

Materials. All reagents were purchased from Aldrich and were used as supplied unless otherwise noted. CH_2Cl_2 and CH_3CN were distilled under N_2 from CaH_2. Benzene was distilled under N_2 from sodium/benzophenone. *cis*-Stilbene, *trans*-stilbene, 1,2-dihydronaphthalene, styrene, *cis*-stilbene oxide, and *trans*-stilbene oxide were stored at −20 °C and their purities were checked by ^{1}NMR spectroscopy or GC. Donor ligands triphenylphosphine oxide (Ph_3PO), pyridine *N*-oxide (PyNO), and 1-methylimidazole (1-MeIm) were used as received. Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodobenzene diacetate.[33]Pentafluoroiodosylbenzene (C_6F_5IO) was prepared in two steps from pentafluoroiodobenzene.[34] Iodosylmesitylene (MesIO) was prepared in three steps from mesitylene.[35] The purities of all iodosylarenes were determined to be greater than 98% by iodometric titrations.[36] All iodosylarenes were all stored at −20 °C. H_2salen and Mn^{III}(salen)Cl (**1a**) were synthesized from literature procedures.[37] $Mn^{III}(salen)BF_4$ (**1b**) was prepared from the corresponding chloride compound (**1a**) with $AgBF_4$.

Instruments. NMR spectra were recorded on a Varian XL-400 spectrometer in the solvent specified, referenced to the residual proton signals. Enantiomeric excesses were determined on a Hewlett-Packard 6850 gas chromatograph equipped with a Cyclodex-β chiral capillary column (0.26 mm × 30 m, i.d., 0.25 μm, J&W Scientific). Yields of the epoxides were determined by the peak area ratios of the epoxides relative to the internal standard. Elemental analyses were obtained from Midwest Microlab, Indianapolis, IN.

General Procedure for Olefin Epoxidation. Mn^{III}(salen)X (50 μmol or 10 mol %), an olefin substrate (0.50 mmol in epoxidation

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of *cis*-stilbene and 2.50 mmol in asymmetric epoxidation) and the neutral donor ligand specified (0.25 mmol or 50 mol % unless otherwise noted) were dissolved in 5.0 mL of freshly distilled specified solvent (CH_2Cl_2, CH_3CN, or benzene). With stirring and under a N_2 flow, an iodosylarene (0.50 mmol) was added portionwise. The reaction mixture was then stirred at room temperature. In the epoxidation of *cis*-stilbene, the solvent was removed under reduced pressure after the reaction was completed and the residue was loaded on a short silica gel column and eluted with ethyl acetate/hexane (200 mL, v/v = 1:3). The solvents were removed under reduced pressure and 25.0 μL of 1,1,2,2-tetrachloroethane was added to the residue as the internal standard. The solution was subsequently analyzed by ^{1}H NMR spectroscopy. In the asymmetric epoxidation, 50 μL of 1,3-dichlorobenzene was added as the internal standard at the beginning of the reaction. An aliquot (ca. 50 μL) was taken from the reaction mixture periodically and passed through a pad of short silica gel (ca. 50 mg) and eluted with 0.5 mL of ethyl acetate/hexane (v/v = 1:3). The elute was then collected and injected into GC for analysis.

Abbreviations. Mn(salen)Cl = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-*trans*-1,2-cyclohexanediminatomanganese(III) chloride; ArIO = iodosylarene; PhIO = iodosylbenzene; C_6F_5IO = pentafluoroiodosylbenzene; MesIO = iodosylmesitylene; Ph_3PO = triphenylphosphine oxide; PyNO = pyridine *N*-oxide; 1-MeIm = 1-methylimidazole; TEBACl = triethylbenzylammonium chloride; TBAF = tetrabutylammonium fluoride; [Bmim][Br] = 1-butyl-3-methylimidazolium bromide.

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Supporting Information Available: Experimental details and data of control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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