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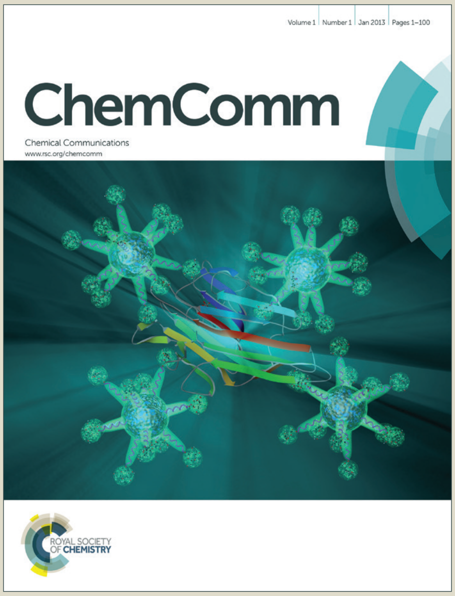

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Non-redox Metal Ions Promoted Oxygen Transfer by a Non-heme Manganese Catalyst

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This work demonstrates that non-redox metal ions as Lewis acid can sharply improve the oxygen transfer efficiency of a manganese(II) catalyst having non-heme ligand. In the absence of Lewis acid, oxidation of manganese(II) complex will generate the known di-μ-oxo-bridged dinuclear Mn_2(III,IV) core which is very sluggish for olefin epoxidation. Adding non-redox metal ions causes the dissociation of the dinuclear core, leading to sharply improve its oxygen transfer efficiency.

Non-redox metal ions have been realized to play significant roles in various oxidation processes as well as redox metal ions.[1,2] The well-known examples include that Ca^{2+} plays a significant role in water oxidation happening in Photosystem II.[2a] Many non-redox metal ions are frequently employed to modify the stability and reactivity of the oxide catalysts.[2b] Due to the complexity of biological and heterogeneous oxidations, clarifying the roles of those non-redox metal ions has been a long challenge, which has inspired alternative studies into investigating their roles in redox metal ion mediated homogeneous oxidations. Up to now, the available examples from stoichiometric oxidations have confirmed that adding non-redox metal ions like Mg^{2+}, Zn^{2+}, Sc^{3+}, and Al^{3+} would substantially accelerate the active metal oxo moieties, M^{n+}=O, including Collin's (TAML)Mn^{V}(O), Fukuzumi and Nam's nonheme Fe^{IV}(O) and Mn^{IV}(O), and Goldberg's (corrolazine)Mn^{V}(O) mediated electron transfer or hydrogen abstraction reactions.[3] Particularly, binding of Zn^{2+} to Goldberg's (corrolazine)Mn^{V}(O) will cause the valence tautomerization of the (corrolazine)Mn^{V}(O) to generate the Mn(IV) oxo corrolazine π radical intermediates, thus accelerate its rates in both hydrogen abstraction and electron transfer.[3a] Fukuzumi and Nam observed that the presence of Sc^{3+} would shift the oxygenation mechanism of sulfide oxidation by (N4PY)Fe^{IV}(O) or (N4PY)Mn^{IV}(O) from direct oxygen transfer to electron transfer.[3c,3d] Borovik also found that Ca^{2+} can promote dioxygen activation by their manganese(II) complexes.[4] In addition to Lewis acid metal ions, Lau found that BF_3 as Lewis acid could also improve alcohol oxidation by MnO_4^-, and BF_3 has been proposed to bind to the Mn^{VII}=O group.[5] Recently we observed that increasing the net charge of the active metal ion through protonation would substantially increase its reduction potential, thus accelerate its electron transfer rate,[6] which resembles the behaviour of binding Lewis acid to the active M^{n+}=O moieties (Brönsted acid vs Lewis acid). However, to the best of our knowledge, non-redox metal-ion-promoted oxygen transfer like olefin epoxidation by redox catalyst has never been reported, even though these Lewis acids have been known to catalyze olefin epoxidation independently.[7] Herein, we demonstrate the first example of that non-redox metal ions can sharply promote olefin epoxidation by redox active metal catalyst.

Mn(BPMEN)Cl_2 catalyst (BPMEN: N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine) was synthesized according to the literature.[8] Iodobenzene diacetate ($PhI(OAc)_2$) was employed as oxidant because of its good solubility in dichloromethane, and the epoxidation reactions were conducted in acetone/dichloromethane mixture (4:1, v/v) at 273 K. Using cyclooctene as substrate, the influences of non-redox metal ions on Mn(BPMEN)Cl_2 catalyzed epoxidation are summarized in Table 1. In the absence of non-redox metal ions, Mn(BPMEN)Cl_2 is very sluggish in catalyzing cyclooctene epoxidation. Only 7.6% of cyclooctene was converted with 6.4% yield of 1.2-epoxyoctane after 2 h. Adding 2 equiv. of Sc^{3+} sharply improves the olefin epoxidation efficiency, providing 100% conversion of cyclooctene with 94.4% yield of epoxide in 2 h. In the control experiment, Sc^{3+} alone is nearly inactive for epoxidation, providing only 4.6% conversion and 2.9% yield. Adding Al^{3+}, Y^{3+} or Yb^{3+} also achieves 100% conversion of substrate, but the yields of epoxide are relatively low, possibly due to the Lewis acid catalyzed ring-opening of epoxide. As evidence, cyclooctanediol was observed as the byproduct in GC-MS analysis (Fig. S1), and over dosage of lewis acid, for example Sc^{3+}, induced a lower yield of epoxide, possibly due to the Lewis acid catalyzed ring-opening of epoxide as displayed in Table S1. Adding one equiv. of NaOTf just slightly improves cyclooctene oxidation with 9.9% conversion and 6.0% yield of epoxide, suggesting that the acceleration effect cannot be attributed to the presence of OTf$^-$ anion. Adding Mg^{2+} and Ca^{2+} also substantially improves the epoxidation efficiency, giving 92.6% and 93.5% of conversion with 80.5% and 77.4% yield of epoxide, respectively. It is worth to emphasize that, in control experiments, all of these non-redox metal ions as catalyst alone demonstrate very poor catalytic activity as shown in the parentheses of Table 1. Although it has been frequently reported that, redox or non-redox metal ions serving as Lewis acid alone could efficiently catalyze olefin epoxidation in certain conditions,[7,9] here is apparently not the case. Clearly, there exists synergistic effect between Mn(BPMEN)Cl$_2$ and non-redox metal ions to achieve the highly efficient epoxidation, which has been further evidenced by catalytic kinetics (Fig. S2).

Table 1. Catalytic oxygenation of cyclooctene to 1,2-epoxyoctane by Mn(BPMEN)Cl$_2$ in the presence of non-redox metal ions as Lewis acid [a]

Additives	Conv. (%)	Yield (%)
-	7.6	6.4
Na$^+$	9.9 (3.8)	6.0 (3.7)
Mg^{2+}	92.6 (3.2)	80.5 (1.7)
Ca^{2+}	93.5 (8.9)	77.4 (1.9)
Ba^{2+}	31.8 (4.1)	26.7 (2.4)
Zn^{2+}	22.4 (5.0)	6.3 (2.3)
Sc^{3+}	100 (4.6)	94.4 (2.9)
Al^{3+}	100 (8.3)	79.7 (1.8)
Y^{3+}	100 (7.6)	78.9 (3.5)
Yb^{3+}	100 (5.7)	67.1 (2.0)

[a] Conditions: acetone/CH$_2$Cl$_2$ (4:1, v/v) 5 mL, cyclooctene 0.1 M, Mn(BPMEN)Cl$_2$ 1 mM, Lewis acid 2 mM, PhI(OAc)$_2$ 0.2 M, 273 K, 2 h. The data in parentheses represent control experiment with Lewis acids.

This synergistic oxygen atom transfer has also been observed in epoxidation of other olefins. Mn(BPMEN)Cl$_2$ catalyst alone is always very sluggish for olefin epoxidation, whereas Mn(BPMEN)Cl$_2$ plus Sc^{3+} (ratio 1:2) generates high epoxidation activity (Table 2). For example, oxidation of cyclohexene can provide 98.2% conversion with 74.9% yield of epoxide, and norbornylene gives 93.8% of conversion with 81.5% yield of epoxide. *cis*-Stilbene is a unique substrate which can provide extra mechanistic information. In active M^{n+}=O moieties mediated *cis*-stilbene epoxidation, the ratio of *cis* and *trans*-epoxide products is highly coordination environment dependent.[10] Here, the sluggish Mn(BPMEN)Cl$_2$ alone provides comparable *cis* and *trans*-epoxide (1.7% vs 1.4%). In contrast, the combination of Mn(BPMEN)Cl$_2$ with Sc^{3+} gives 52.1% yield of *cis*-epoxide with only 2.7% yield of *trans*-epoxide, and conversion is as high as 90.1%. Clearly, the active intermediate for epoxidation in the presence of Sc^{3+} is different from that of using Mn(BPMEN)Cl$_2$ alone. In the case of *trans*-stilbene, the combination of Mn(BPMEN)Cl$_2$ with Sc^{3+} provides 41.4% yield of *trans*-epoxide with 18.6% yield of benzaldehyde. Remarkably, there is no *cis*-stilbene epoxide formation.

The reaction data presented above have clearly revealed that there exists synergistic effect between Mn(BPMEN)Cl$_2$ catalyst and added non-redox metal ions in epoxidation. The evidence to display their interactions first comes from EPR studies (Fig. 1). When Mn(BPMEN)Cl$_2$ was oxidized by PhI(OAc)$_2$, a typical 16-line signal centered at g=2.0 and regularly spaced by 89 G was observed at 130 K, which is characteristic of the mixed valent di-μ-oxo-bridged dinuclear Mn$_2$(III,IV) core.[8,11] With the addition of Sc^{3+}, this 16-line signal disappeared over time (Fig. 1), clearly implicating a Sc^{3+} induced dissociation of the μ-oxo-bridged dinuclear structure. In literatures, dissociation of dimeric Mn$_2$(III,IV) core can be initialed by protonation of the bridged oxygen atom.[12] Herein, non-redox metal ion serves as Lewis acid may also interact with the bridged oxygen atom, thus weaken the Mn-O bond in the Mn$_2$(III,IV) core and induces the dissociation. In the present of Sc^{3+}, a 6-line hyperfine structure with A=92 G at g=1.9 was observed, indicating a high-spin mononuclear manganese(II) species[13] was generated possibly due to the instability of the activated high oxidation state manganese species by Sc^{3+}. As evidence, a similar 6-line hyperfine structure was directly observed by adding Sc^{3+} to Mn(BPMEN)Cl$_2$ (Fig. S3), which also indicates the formation of the Mn(II)/Sc^{3+} adduct. The lack of the direct EPR signal of similar Mn(IV)/Sc^{3+} adduct is possibly due to its short life time and/or its weakness compared with the strong signal of the Mn(II)/Sc^{3+} adduct. Although the accurate structure is still elusive, a plausible interaction between Mn(IV)=O and Sc^{3+} can be described as Mn(IV)=O•••Sc^{3+} for which similar structure of Fe(IV)=O•••Sc^{3+} has been illustrated in literature.[3e] On the other hand, the dissociation of dinuclear Mn$_2$(III,IV) core does not occur by adding Na(OTf) or Zn(OTf)$_2$ (Fig. S4), which is consistent with their poor synergistic effect in epoxidation.

Table 2. Sc(OTf)$_3$ promoted olefin epoxidations by Mn(BPMEN)Cl$_2$ catalyst [a]

Substrate	Time (h)	Product	Conv. (%)	Yield (%)
cyclooctene	2	epoxide	100 (7.6)	94.4 (6.4)
cyclohexene	3		98.2 (14.9)	74.9 (6.5)
norborylene	1		93.8 (10.7)	81.5 (10.1)
1-hexene	13.5		85.3 (19.9)	69.5 (3.6)
1-dodecene	11.5		76.2 (13.0)	70.8 (2.2)
trans-stilbene	6	*cis*-epoxide	97.5 (17.5)	0 (0)
		trans-epoxide		41.4 (10.8)
		benzaldehyde		18.6 (6.4)
cis-stilbene	4	*cis*-epoxide	90.1 (7.9)	52.1 (1.7)
		trans-epoxide		2.7 (1.4)
		benzaldehyde		18.7 (3.7)

[a] Conditions: acetone/CH$_2$Cl$_2$ (4:1, v/v) 5 mL, olefin 0.1 M, Mn(BPMEN)Cl$_2$ 1 mM, Sc(OTf)$_3$ 2 mM, PhI(OAc)$_2$ 0.2 M, 273 K. The data in parentheses represent control experiments with Mn(BPMEN)Cl$_2$.

Further evidence of the dissociation of dinuclear Mn$_2$(III,IV) core comes from electrochemical studies (Fig. S5).

Mn^{II}(BPMEN)Cl$_2$ alone reveals the Mn^{III}/Mn^{II} and Mn^{IV}/Mn^{III} couples of +0.76 V and +1.56 V (vs SCE) in acetone/dichloromethane (4:1, v/v), respectively, similar to those in literature.[8a] In situ oxidizing of Mn(BPMEN)Cl$_2$ with PhI(OAc)$_2$ revealed a third redox couple at +1.10 V (vs SCE), which can be assigned to the couple of dinuclear core Mn$_2$(III,IV) to Mn$_2$(IV,IV) (it is +1.12 V vs SCE in literature[8a]). However, in the presence of Sc^{3+}, this dinuclear redox couple disappeared, indicating a Sc^{3+} induced dissociation of the dinuclear core happens. This dissociation event is also indicated by the fact that the IR absorption band at 686 cm^{-1}, given rise by the Mn(μ-O)$_2$Mn diamond,[14] vanishes with the addition of Sc^{3+}(Fig. S6).

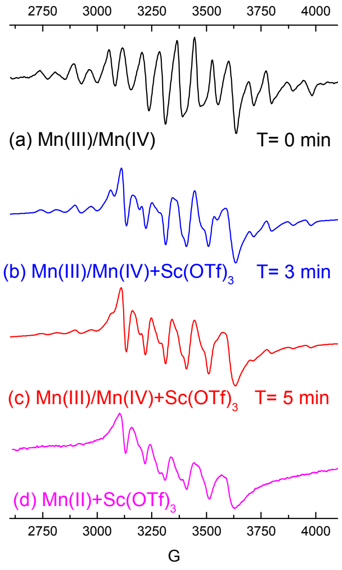
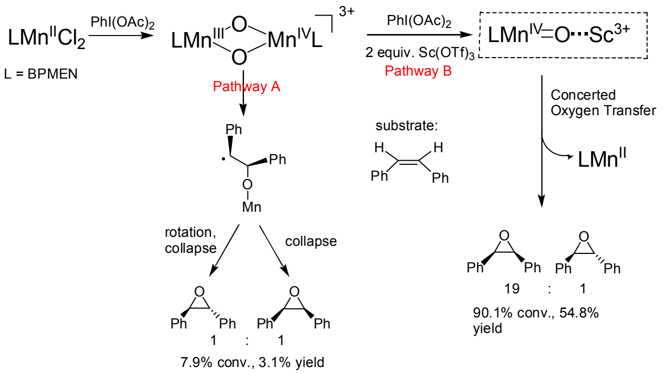


Figure 1. EPR spectra of (a) Mn(BPMEN)Cl$_2$ plus 5 equiv. PhI(OAc)$_2$, (b) 3 min after adding 1 equiv. Sc^{3+} into (a), (c) 5 min after adding 1 equiv. Sc^{3+} into (a), (d) Mn(BPMEN)Cl$_2$ plus 1 equiv. Sc^{3+}. Conditions: 5 mM Mn(BPMEN)Cl$_2$ in acetone/CH$_2$Cl$_2$ (4:1, v/v) at 130 K.

In isotopically labelling experiments using H$_2$^{18}O, it was found that the abundance of ^{18}O in *cis*-epoxide is highly Sc^{3+} dependent, whereas it remains roughly constant in *trans*-epoxide. Without Sc^{3+}, the abundance of ^{18}O in *cis*-epoxide is 75.7%, and it decreases along with the increase of added Sc^{3+} to the catalytic solution. Decreased ^{18}O abundance in epoxide by adding Sc^{3+} can be attributed to that Sc^{3+} delays the ^{18}O exchange between the Mn(IV)=O•••Sc^{3+} species and ^{18}O-water, and/or the Mn(IV)=O•••Sc^{3+} is highly active for epoxidation which is faster than its exchange with ^{18}O-water.

In literature, olefin epoxidation can occur by either a Lewis acid metal ions mediated process,[7,9] in which the valence of metal ion does not change, or by an direct oxygen atom transfer process involving an active M^{n+}=O moities that delivers the oxygen atom to olefin.[15] In M^{n+}=O moieties mediated epoxidation, it has been reported at least two distinct pathways: 1) direct olefin attacking at the oxo group to generate an olefinic C=C π bond broken intermediate, followed by collapse or rotation-collapse process which in turn provides the mixture of *cis* and *trans* epoxides;[15b,c] 2) concerted oxygen atom transfer from M^{n+}=O to olefin which remains the stereo-structure of olefin.[15d,e] To provide further insights into the mechanism, epoxidation of *cis*-stilbene has been investigated in details here. In the absence of Sc^{3+}, Mn(BPMEN)Cl$_2$ has only minor catalytic activity, and provides comparable *cis* and *trans* epoxides in each case (Table S2), suggesting the occurrence of an olefinic C=C π bond broken intermediate followed by collapse or rotation-collapse process (Scheme 1, pathway A). Adding Sc^{3+} can sharply improve the yield of *cis*-epoxide, whereas the yield of *trans*-epoxide remains unchanged. For example, adding one equiv. of Sc^{3+} gives 41.7% yield of *cis*-epoxide with 88.7% of conversion, whereas the yield of *trans*-epoxide is only 2.8% (it is worth to mention again that, Sc^{3+} alone is very sluggish for epoxidation, see Table 1 and S3). Clearly, the presence of Sc^{3+} has shifted the epoxidation from a C=C π broken process (pathway A) to a concerted oxygen transfer process (pathway B), which gives the high stereo-selectivity of *cis*-epoxide. This mechanism switch in epoxidation can be attributed to the formation of a Mn(IV)=O•••Sc^{3+} species as described above. The sluggish activity of Mn(BPMEN)Cl$_2$ alone can be attributed to the formation of the dimer which prevents the efficient transferring of oxygen to olefin. In literatures, it has been reported that formation of di-μ-oxo-bridged core from M^{n+}=O moieties would greatly reduce its oxidative activity.[11b,16] Here, *our findings provide a promising strategy to explore the catalytic reactivity of some di-μ-oxo-bridged complexes by adding non-redox metal ions to in situ dissociate those dimeric cores.*



Scheme 1. Proposed mechanism of Lewis acid promoted epoxidation by Mn(BPMEN)Cl$_2$ catalyst.

In conclusion, we have illustrated the first example that non-redox metal ion can sharply improve the oxygen atom transfer efficiency of a redox metal catalyst in olefin epoxidation, thus confirm that non-redox metal ions can not only promote the electron transfer of an active M^{n+}=O intermediate, but also sharply improve their oxygen atom transfer which represents another important enzymatic and chemical oxidative process. Meanwhile, it also demonstrates a novel strategy to explore the catalytic reactivity of some redox metal complexes which would form inactive clusters under oxidation conditions.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details of catalytic epoxidation, EPR spectra, cyclic voltammogram, UV-Vis spectra as well as FTIR spectra of Mn(BPMEN)Cl_2 plus Sc$(OTf)_3$ are available in supporting information. See DOI: 10.1039/c000000x/

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