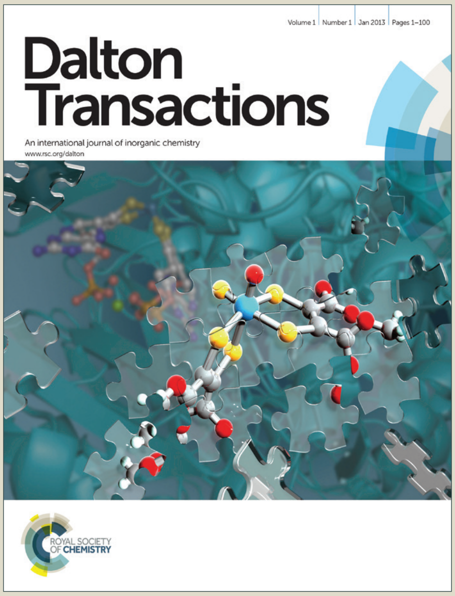
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Redox-inactive Metal Ions Promoted Catalytic Reactivity of Non-heme Manganese Complexes towards Oxygen Atom Transfer

Cholho Choe, Ling Yang, Zhanao Lv, Wanling Mo, Zhuqi Chen*, Guangxin Li* and Guochuan Yin*

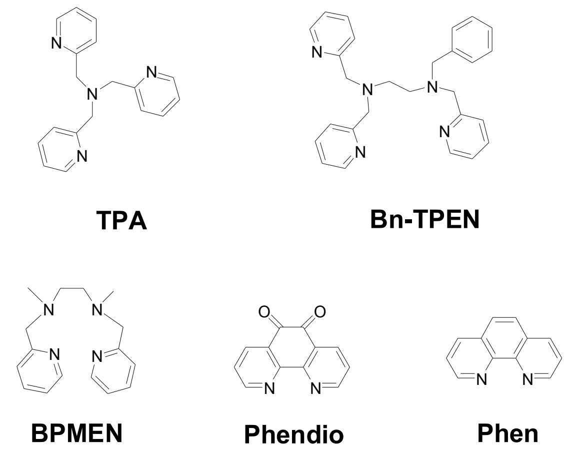
Redox-inactive metal ions can modulate the reactivity of the redox-active metal ions in a variety of biological and chemical oxidations. Many synthetic models have been developed to help addressing the elusive roles of these redox-inactive metal ions. Using a non-heme manganese(II) complex as model, the influence of redox-inactive metal ions as Lewis acid on its catalytic efficiency in oxygen atom transfer was investigated. In the absence of redox-inactive metal ions, manganese(II) catalyst is very sluggish, for example, in cyclooctene epoxidation, providing only 9.9% conversion with 4.1% yield of epoxide. However, adding 2 equiv. of Al^{3+} to the manganese(II) catalyst sharply improves the epoxidation up to 97.8% conversion with 91.4% yield of epoxide. EPR studies of the manganese(II) catalyst in the presence of oxidant reveal a 16-line hyperfine structure centered at g=2.0, clearly indicating the formation of a mixed valent di-μ-oxo-bridged diamond core, Mn^{III}-(μ-O)$_2$-Mn^{IV}. The presence of Lewis acid like Al^{3+} causes the dissociation of this diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core to form monomeric manganese(IV) species which is responsible for improved epoxidation efficiency. This promotional effect has also been observed in other manganese complexes bearing various non-heme ligands. The findings presented here have provided 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, and it may also provide clues to understand the mechanism of methane monooxygenase which has a similar diiron diamond core as the intermediate.

Introduction

Redox-inactive metal ions are critical components in many biological redox enzymes, and the oxygen-evolving complex (OEC) of photosystem II (PSII) in cyanobacteria and plants is the most well-known example in which redox-inactive Ca^{2+} acts as an essential cofactor in Mn_4CaO_5 cluster.[1] Also in the copper-zinc superoxide dismutases (CuZnSOD1), zinc has been proposed to play the significant role on the thermostability and activity of the metalloenzyme.[2,3] To clarify related oxidation mechanisms, many inorganic models bearing synthetic ligands have been explored, however, the exact roles of these redox-inactive metal ions still remain elusive. In addition to biological oxidations, redox-inactive metal ions are also frequently employed to improve the stability and/or to modulate the reactivity of transition metal catalysts in heterogeneous oxidations.[4] Thereof, addressing the functional roles of these redox-inactive metal ions is of great importance and has attracted much attention in both biological and chemical communities. Different from the complicated biological and heterogeneous systems, homogeneous system can offer simpler models to help understanding how these redox-inactive metal ions participate in the oxidation events and affect the reactivity properties of redox-active metal ions. Using different synthetic models, it has been found that binding of redox-inactive metal ions to the high valent metal-oxo moieties can modulate their oxidative reactivity, and this binding was even evidenced with the X-ray crystal structure of Sc^{3+}-bound $[(TMC)Fe^{IV}(O)]^{2+}$ complex determined by Fukuzumi and Nam.[5] It should be noted that the oxidation state assignment of the iron in this species has recently been challenged.[6] Nam and Fukuzumi reported that Lewis acid like Sc^{3+} can substantially accelerate the electron transfer rate from a series of one-electron reductants to a nonheme oxoiron(IV), Fe^{IV}(N4Py)(O),[7] and similar acceleration effect was also observed in oxidative dimerization and N-demethylation of N,N-dimethylaniline.[8] In particular, Goldberg found that Zn^{2+} may interact with the $Mn^{V}{\equiv}O$ group in their (corrolazine)Mn^{V}(O) complex, and cause the valence tautomerization of the (corrolazine)$Mn^V(O)$ to generate the Mn(IV) oxo corrolazine π radical intermediates, thus accelerate its rate in both hydrogen abstraction and electron transfer.[9] For BF_3 as Lewis acid, Lau also even found that it can dramatically improve the oxidation of alkanes and arylalkanes by $KMnO_4$ through BF_3 binding to the Mn^{VII}=O group.[10] Notably, Borovik observed that Ca^{2+} can promote dioxygen activation by their manganese(II) complexes, and the formation of heterobimetallic Ca^{II}-(μ-OH)-Mn^{III} complex was confirmed by X-ray diffraction.[11] The dioxygen activation triggered by redox-inactive metal ions was also observed by Que, Nam and Fukuzumi with Fe(TMC) complex.[12,13]

Above discoveries clearly reveal that the presence of Lewis acid can modulate the redox behaviors of the active metal ions at high oxidation state through its bridge or ligation with the metal oxo functional groups. However, the examples to demonstrate Lewis-acid-accelerated oxidations are still limited, and in most cases, only accelerated electron transfer rates were observed. Although Sc^{3+} accelerated sulfide oxygenation with Fe^{IV}(N4Py)(O) was even observed by Nam and Fukuzumi, the oxidation proceeds by switching of mechanism from direct oxygen transfer to metal-ion-coupled electron transfer.[14] Similarly, binding Sc^{3+} to a mononuclear non-heme Mn(IV) oxo complex also accelerates sulfoxidation, however, the rate of hydrogen atom abstraction was obviously decelerated, which was rationalized as the steric hindrance raised by Sc^{3+} binding to the Mn(IV) oxo moiety.[15,16] Collins also found that redox-inactive metal ions does not improve olefin epoxidation by their (TAML)Mn^V(O) analogue but accelerate triphenylphosphine oxygenation.[17] Due to the fact that examples reporting Lewis-acid-accelerated oxidation are mostly limited to electron transfer, one may concern that to which extent the Lewis acid could improve the efficiency of traditional oxidations. Moreover, most of these reported examples are based on stoichiometric oxidations, while the examples on Lewis-acid-accelerated catalytic oxidation are still seldom, which is more analogous to the biological and chemical oxidations catalyzed by enzymes and redox catalysts.

In our works to investigate the oxidative relationships of active metal oxo and hydroxo moieties, we observed that increasing the net charge of the active metal species by binding Brönsted acid (M^{n+}=O vs. $M^{(n+1)+}$-OH) can accelerate its electron transfer rate because of the increased redox potential.[18] This finding resembles the acceleration effect caused by binding Lewis acid to the active M^{n+}=O moieties as described above. Inspired by these, we found that the presence of redox-inactive metal ions like Al^{3+} can accelerate sulfide oxidation catalyzed by a manganese complex having cross-bridged cyclam ligand, and benzene hydroxylation with dioxygen by Pd^{II}(bpym) catalyst (bpym: 2,2'-pyrimidine).[19,20] Moreover, the presence of Ca^{2+} and Cl^- can synergistically affect the redox potentials of the manganese complexes, thus modulate their reactivity in oxidations,[21] which may provide new clues to understand their roles in oxygen evolution in Photosystem II. However, due to that the active functional group in the above mentioned manganese catalyst is a Mn^{IV}-OH moiety rather than Mn^{IV}=O, the catalytic olefin epoxidation was not improved by adding Lewis acid. Recently, we communicated the first example of that mixed valent di-μ-oxo-bridged diamond Mn^{III}-$(\mu\text{-}O)_2$-Mn^{IV} core, which is sluggish in oxygen atom transfer, can be dissociated by redox-inactive metal ions, leading to sharp improvement in olefin epoxidation.[22] Herein, we report this remarkable promotional effect with manganese catalysts bearing different ligands, and the epoxidation mechanism has been discussed in details. We hope these findings can provide a new strategy for exploring the catalytic functions of those redox metal complexes which generally form sluggish dimers under oxidative conditions. We also hope it may provide new clues to understand the mechanism of MMO (Methane Monooxygenase) which has a similar diamond $[Fe_2(\mu\text{-}O)_2]$ core.



Scheme1 Molecular Structures of ligands studied in this work.

Experimental

Iodobenzene diacetate ($PhI(OAc)_2$), sodium trifluoromethanesulfonate (NaOTf), magnesium trifluoromethanesulfonate ($Mg(OTf)_2$), and scandium trifluoromethanesulfonate ($Sc(OTf)_3$) came from Aldrich. Barium trifluoromethanesulfonate ($Ba(OTf)_2$), calcium trifluoromethanesulfonate ($Ca(OTf)_2$), zinc trifluoromethanesulfonate ($Zn(OTf)_2$), aluminum trifluoromethanesulfonate ($Al(OTf)_3$), yttrium trifluoromethanesulfonate ($Y(OTf)_3$) and ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$) came from Aladdin. Olefins as well as epoxides were purchased from either Aldrich or Alfa Aesar. $H_2{}^{18}O$ (90% ^{18}O atom) came from Acros. Other organic compounds and organic solvent came from Shaoyuan or Shanghai Dibai. Tris(pyridin-2-ylmethyl)amine) (TPA) and N-benzyl-N,N',N''-tris(2-pyridylmethyl)-1,2-diaminoethane (Bn-TPEN) with their manganese complexes, $Mn(TPA)Cl_2$ and $Mn(Bn\text{-}TPEN)Cl_2$, were synthesized according to literatures.[23-25] N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine (BPMEN) and its complex, $Mn(BPMEN)Cl_2$, were synthesized according to our previous publication.[22] Phenantroline (Phen) was purchased from Aladdin. Phendio (1,10-phenanthroline-

5.6-dione) was synthesized according to the literature.[26] The structures of these ligands have been illustrated in Scheme 1. 1H-NMR data of ligands**:** TPA (CD_3CN): δ 8.48 (d, 3H), 7.69 (t, 3H), 7.60 (d, 3H), 7.17 (t, 3H), 3.81 (s, 6H).; Bn-TPEN ($CDCl_3$): δ 8.48(m, 2H), 7.58 (m, 3H), 7.45 (t, 3H), 7.19-7.32 (m, 5H), 7.12 (m, 3H), 3.77 (s, 4H), 3.72 (s, 2H), 3.59 (s, 2H), 2.74 (m, 4H).; Phendio ($CDCl_3$): δ 7.56(m, 2H), 8.41(m, 2H), 9.06 (m, 2H).; BPMEN ($CDCl_3$): δ 2.25 (s, 3H), 2.65 (s, 2H), 3.15 (s, 2H), 7.4 (m, 3H), 8.45 (d, H)

UV-Vis spectra were collected on Analytik jena, specord 205. GC-MS analysis was performed on Agilent7890A/5975C. FT-IR spectra were collected on Bruker VERTEX70. Electrochemical studies were performed on a CS Corrtest electrochemical workstation equipped with glassy carbon as both working and counter electrodes and saturated calomel as reference electrode. The redox potentials were measured under argon with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. EPR experiments were conducted at 130 K on Bruker A200, with Center Field of 3352.488 G, Frequency of 9.395 GHz, Power of 19.44 mW, Modulation Amplitude of 2.00 G and Receiver Gain of 1.00 × 10^3. ^{1}H-NMR spectra were collected on Bruker AV600(Avance III NMR spectrometer, 1H-frequency: 600.25 MHz)

Lewis-acid-promoted catalytic epoxidation by the manganese(II) complexes In a mixture solution of 4 mL of acetonitrile and 1 mL of CH_2Cl_2 containing 0.05 M olefin, 1 mM manganese(II) complexes and 2 mM Lewis acid, 0.5 mmol of $PhI(OAc)_2$ were added to initialize the reaction. The reaction mixture was stirred in an ice-water bath at 273 K, and the product analysis was performed by GC using the internal standard method (methyl benene or nitrobenzene as the internal standard). Control experiments using the manganese(II) complexes or Lewis acid alone as catalyst were carried out in parallel. Reactions were performed at least in triplicate, and the average data were used in discussion.

Lewis-acid-promoted catalytic epoxidation of *cis*- and *trans*-stilbene by the manganese(II) complexes In a mixture solution of 4 mL of acetonitrile and 1 mL of CH_2Cl_2 containing 0.05 M olefin, 1 mM manganese(II) complexes and 2 mM Lewis acid, 0.5 mmol of $PhI(OAc)_2$ were added to initialize the reaction. The reaction mixture was stirred in an ice-water bath at 273 K and the product analysis was performed by HPLC using the internal standard method (mesitylene as the internal standard). Control experiments using the manganese(II) complexes or Lewis acid alone as catalyst were carried out in parallel. Reactions were performed at least in triplicate, and the average data were used in discussion.

Lewis-acid-promoted catalytic epoxidation by the manganese(II) complexes in the presence of water In a mixture solution of 0.4 mL of acetonitrile, 0.1 mL of CH_2Cl_2 and various amount of H_2O containing 0.1 M olefin, 2 mM manganese(II) complexes, and 4 mM Lewis acid, 0.1 mmol of $PhI(OAc)_2$ were added to initialize the reaction. The reaction mixture was stirred in an ice-water bath at 273 K and the product analysis was performed by HPLC using the internal standard method. Control experiments using the manganese(II) complexes or Lewis acid alone as catalyst were carried out in parallel. Reactions were performed at least in triplicate, and the average data were used in discussion.

Lewis-acid-promoted catalytic epoxidation by the manganese(II) complexes in the presence of ^{18}O-water In a mixture solution of 0.4 mL of acetonitrile and 0.1 mL of CH_2Cl_2 containing 0.1 M *cis*-stilbene, 2 mM manganese(II) complexes, and 4 mM Lewis acid, 0.1 mL of $H_2{}^{18}O$ (90% ^{18}O enrichment as received) were added and stirred for 2 minutes, then 0.1 mmol of $PhI(OAc)_2$ were added to initialize the reaction. The reaction mixture was stirred in an ice-water bath at 273 K and the product analysis was performed by GC-MS using the procedure as those in normal epoxidation. The ^{18}O enrichments are calculated based on the peak abundances of ^{16}O- and ^{18}O-epoxide in GC-MS graphs as shown in supporting information.

Results and discussion

Adding redox-inactive metal ion as Lewis acid to promote olefin epoxidation with manganese catalysts was performed in acetonitrile/CH_2Cl_2 (4:1, v/v) using $PhI(OAc)_2$ as oxidant. $Mn(TPA)Cl_2$ (TPA = tris(pyridin-2-ylmethyl)amine) was first tested as catalyst which was synthesized according to the literature.[23] As shown in Table 1, without the addition of redox-inactive metal ions, $Mn(TPA)Cl_2$ is very sluggish in catalyzing cyclooctene epoxidation. After 3.5 h reaction at 273 K, only 9.9% of cyclooctene was converted with 4.1% yield of 1.2-epoxyoctane formation. When 2 equiv. of $Al(OTf)_3$ were added to the manganese catalyst in reaction solution, 97.8% conversion with 91.4% yield of epoxide could be achieved under the same conditions. In control experiment, $Al(OTf)_3$ alone as catalyst showed only 3.7% conversion and 1.7% yield. Apparently, Lewis acid alone has nearly no catalytic activity for olefin epoxidation in our case. Similarly, the addition of 2 equiv. of Sc^{3+} improved olefin epoxidation with 97.4% conversion and 91.0% yield, while Sc^{3+} alone gave only 4.3% conversion with 2.0% yield. In complimentary experiments using the mixture of $Al(OTf)_3$ and TPA ligand as catalyst, it also demonstrated very sluggish activity, providing only 4.4% of conversion with 2.3% yield of epoxide, thus excluded the possibility of that the synergistic effect originates from the potentially generated complex of Al^{3+} with ligand. Therefore, this greatly improved catalytic activity of the manganese complex by adding redox-inactive metal ions strongly supports that the synergistic effect occurs between the manganese catalyst and the Lewis acid in epoxidation.

This synergistic effect has also been observed by adding other redox-inactive metal ions. For examples, adding Y^{3+} or Yb^{3+} achieved 98.8% or 90.1% conversion of substrate, and the yield of epoxide was 84.4% or 81.2%, respectively. As shown in Table S1, the amount of redox-inactive metal ions can significantly affect the yield of epoxide. For example, adding 0.5 equiv. of Al^{3+} achieved 38.3% conversion with 21.9% yield, while adding 1.0 or 2.0 equiv. of Al^{3+} led to 77.2% or 91.4% yield, respectively. However, adding 4 equiv. of Al^{3+} demonstrated a decreased yield of 51.8%, while the conversion remained 98.7%. This decreased selectivity of epoxide can be attributed to the Lewis acid catalyzed ring-opening of epoxide. As evidence, 1,2-cyclooctanediol product has been detected by GC-MS (Figure S1).

Table 1. Catalytic epoxidation of cyclooctene to 1,2-epoxycyclooctane by $Mn(TPA)Cl_2$ catalyst in the presence of redox-inactive metal ions as Lewis acid

Additives	Mn(II) + L.A.		Only L.A.	
	Conv. (%)	Yield (%)	Conv. (%)	Yield (%)
-	9.9(0.2)	4.1(0.1)	2.4(0.1)	1.5(0.1)
Na^+ [a]	33.3(0.2)	24.7(0.6)	3.7(0.2)	0.8(0.1)
Mg^{2+}	46.2(1.2)	41.7(0.1)	4.5(0.3)	1.7(0.2)
Ba^{2+}	54.9(0.1)	48.8(0.7)	3.6(0.3)	2.0(0.1)
Ca^{2+}	60.1(0.4)	45.6(1.0)	3.9(0.1)	2.4(0.1)
Cu^{2+}	36.8(1.1)	34.1(0.2)	3.5(0.3)	1.5(0.3)
Zn^{2+}	66.6(0.8)	63.3(0.2)	5.0(0.4)	0.8(0.2)
Y^{3+}	98.8(0.8)	84.4(0.5)	4.2(0.1)	1.5(0.1)
Yb^{3+}	90.1(0.6)	81.2(0.2)	4.2(0.3)	0.7(0.2)
Al^{3+}	97.8(1.0)	91.4(0.3)	3.7(0.2)	1.7(0.1)
Sc^{3+}	97.4(0.4)	91.0(0.4)	4.3(0.3)	2.0(0.1)

Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 5 mL, cyclooctene 0.05 M, $Mn(TPA)Cl_2$ 1 mM, Lewis acid 2 mM, $PhI(OAc)_2$ 0.1 M, 273 K, 3.5 h. [a] 6 mM NaOTf was used in the reaction solution. Data in parentheses represent the deviations.

Meanwhile, redox-inactive metal ions with positive charge of 2+, such as Mg^{2+}, Ba^{2+}, Ca^{2+} and Zn^{2+}, shows relatively low promotional effect. For example, the addition of 2 equiv. of Ca^{2+} or Zn^{2+} provided the conversion of 60.1% or 66.6% with epoxide yield of 45.6% or 63.3%, respectively. Similarly, Ca^{2+} or Zn^{2+} alone provided only 3.9% or 5.0% conversion with 2.4% or 0.8% yield in control experiments, respectively. Adding 6 equiv. of NaOTf just slightly improved cyclooctene oxidation to 33.3% conversion with 24.7% yield of epoxide, much lower than that by adding $Al(OTf)_3$, revealing that the promotional effect cannot be attributed to the presence of OTf^- anion, because the concentration of OTf^- under this condition is identical to that of adding 2 equiv. of $Al(OTf)_3$. In addition, NaOTf alone under the same conditions gave only 3.7% conversion and 0.8% yield. It is worth to emphasize that, in control experiments, all of these non-redox metal ions alone as catalyst demonstrate very poor catalytic activity for epoxidation as shown in Table 1. Notably, above improved catalytic activity is generally dependent on Lewis acid strength, that is, metal ions with higher positive charge demonstrate better efficiency in promoting olefin epoxidation with manganese catalyst.

One may argue that this synergistic oxygen transfer originates from rapid reaction of Lewis acid with trace amounts of water to form metal-oxide/hydroxides, and liberate proton. Next, the oxo and hydroxide bridged complexes is simply destroyed through their protonation. To further rule out the influence of water/proton, epoxidation of cyclooctene was conducted using dehydrated solvent with Schlenk system in which the influence of even trace amount of water can be ruled out. In this case, epoxidation using $Mn(TPA)Cl_2$ as catalyst with $Al(OTf)_3$ as Lewis acid still showed efficient activity with 100 % conversion of substrate and 90.8 % yield of epoxide. Moreover, using protonic acid instead of Lewis acid ($Al(OTf)_3$) revealed very poor activity. For examples, 23.7% conversion with 5.9% yield was obtained by adding acetic acid, while for hydrochloric acid, the conversion was 28.1%, and the yield of epoxide was 10.5 % (Table S2). These data clearly indicate that the promotional effect by adding Lewis acid is not attributed to the protonation of trace amount of water.

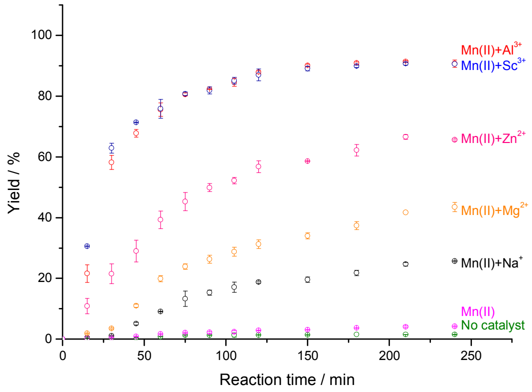
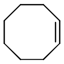
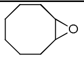
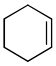
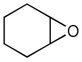
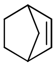
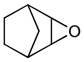
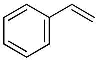
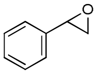
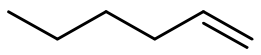
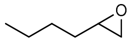
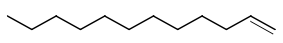
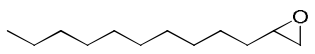


Figure 1. Lewis acid promoted epoxidation kinetics by $Mn(TPA)Cl_2$ catalyst. Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 5 mL, cyclooctene 0.05 M, $Mn(TPA)Cl_2$ 1 mM, Lewis acid 2 mM (6 mM in the case of NaOTf), $PhI(OAc)_2$ 0.1 M, 273 K, 3.5 h.

The catalytic kinetics further confirms the above-mentioned promotional effect of Lewis acid on the Mn(II) complexes mediated epoxidation (Figure 1). In the absence of Lewis acid, catalytic epoxidation of cyclooctene is apparently sluggish. Along the series of charge 1+, 2+, and 3+ of added redox-inactive metal ions, the formation of epoxide speeds up. These results are well consistent with the data in Table 1, supporting that adding redox-inactive metal ions with higher positive charge demonstrates better efficiency in promoting the epoxidation efficiency of the $Mn(TPA)Cl_2$ catalyst.

This synergistic oxygen atom transfer by adding redox-inactive metal ions was also observed in epoxidation of other cyclo-olefins and terminal linear olefins. In all of the investigated substrates, $Mn(TPA)Cl_2$ catalyst or Lewis acid alone showed sluggish activity for epoxidation. For example in Table 2, when cyclohexene was used as substrate, $Mn(TPA)Cl_2$ catalyst alone demonstrated sluggish activity in epoxidation, giving only 18.3 % conversion with 6.7 % yield of epoxide in 3.5 h. Under the identical conditions, addition of 2 equiv. of Al^{3+} generated high oxidation activity with 91.3% conversion and 69.0% yield of epoxide. In the case of norbornene, the conversion can be promoted from 11.1% to 84.3%, and the yield increased from 5.1% to 47.4% by adding Al^{3+}. Conversion of styrene was also promoted from 9.1% to 71.9%, and the yield of epoxystyrene increased to 45.1%. For these terminal linear olefins such as 1-hexene and 1-dodecene, the improved epoxidation efficiency with $Mn(TPA)Cl_2$ catalyst was also observed by adding redox-inactive metal ions. However, the required reaction time for electron-deficient linear olefins is much longer (8 h) than that of cyclo-olefins or electron-rich olefins (3.5 h), which leads to a lower selectivity because of Lewis-acid-catalyzed ring-opening of epoxide.

Table 2. $Al(OTf)_3$ promoted olefin epoxidations by $Mn(TPA)Cl_2$ catalyst

Substrate	Product	Mn(II) : Al^{3+}	Conv. %	Yield%
 cyclooctene	 1,2-epoxycyclooctane	0:0	2.4(0.1)	1.5(0.1)
		0:2	3.7(0.2)	1.7(0.1)
		1:0	9.9(0.2)	4.1(0.1)
		1:2	97.8(1.0)	91.4(0.3)
 cyclohexene	 1,2-epoxycyclohexane	0:0	3.8(0.6)	1.0(0.3)
		0:2	6.0(0.3)	2.5(0.5)
		1:0	18.3(0.6)	6.7(0.4)
		1:2	91.3(0.9)	69.0(0.2)
 norbornene	 epoxynorbornene	0:0	2.6(0.2)	1.4(0.2)
		0:2	3.5(0.4)	1.6(0.2)
		1:0	11.1(0.9)	5.1(0.2)
		1:2	84.3(0.7)	47.4(0.8)
 styrene	 epoxystyrene	0:0	3.7(0.3)	2.4(0.3)
		0:2	5.5(0.4)	1.9(0.2)
		1:0	9.1(0.4)	4.9(0.3)
		1:2	71.9(0.6)	45.1(0.6)
 1-hexene[a]	 1,2-epoxyhexene	0:0	3.1(0.2)	1.2(0.2)
		0:2	5.3(0.3)	1.5(0.1)
		1:0	9.3(0.4)	3.7(0.1)
		1:2	75.1(1.7)	51.7(0.6)
 1-dodecene	 1,2-epoxydodecene	0:0	3.8(0.1)	1.3(0.1)
		0:2	7.3(0.4)	1.7(0.1)
		1:0	13.5(1.3)	2.5(0.2)
		1:2	90.3(0.4)	45.1(1.9)

Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 5 mL, cyclooctene 0.05 M, $Mn(TPA)Cl_2$ 1 mM, $Al(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.1 M, 273 K, 3.5 h [a] reaction time, 8 h.The data in parentheses represent the deviations.

Generally, epoxidation of *cis*-stilbene can provide more mechanistic information than other olefins. In active $M^{n+}=O$ moieties mediated *cis*-stilbene epoxidation, the ratio of *cis* and *trans*-epoxide products is highly dependent on the reaction pathway as well as the coordination environments of the redox metal ions.[27-30] In some cases, the yields of *cis* and *trans*-epoxide are comparable, while in other cases, it provides dominant *cis*-epoxide. Here, $Mn(TPA)Cl_2$ alone as catalyst provided 5.9% *cis*-epoxide and 3.5% *trans*-epoxide when using *cis*-stilbene as substrate, and the ratio of substrate to $Mn(TPA)Cl_2$ does not affect the ratio of *cis/trans* in epoxide product (Table S3). In contrast, adding Al^{3+} can sharply improve the yield of *cis*-epoxide, whereas the yield of *trans*-epoxide remained unchanged. In the presence of 2 equiv. of Al^{3+}, $Mn(TPA)Cl_2$ catalyst gave 50.7% yield of *cis*-epoxide with only 5.8% yield of *trans*-epoxide (Table 3). Clearly, the active intermediate for epoxidation in the presence of Al^{3+} is different from that of using $Mn(TPA)Cl_2$ alone. In the case of *trans*-stilbene, the combination of $Mn(TPA)Cl_2$ with Al^{3+} provided 64.7% yield of *trans*-epoxide with 2.8% yield of benzaldehyde, while $Mn(TPA)Cl_2$ alone gave only 19.7% yield of *trans*-epoxide with 3.8% yield of benzaldehyde. Remarkably, there was no *cis*-stilbene epoxide formation.

Table 3. Stilbene epoxidations by $Mn(TPA)Cl_2$ catalyst promoted by different ratio of $Al(OTf)_3$

Substrate	Product	Mn(II):Al^{3+}			
		1:0	1:0.5	1:1	1:2
cis-stilbene	*cis*-epoxide	5.9 (0.1)	39.6 (0.7)	41.5 (2.0)	50.7 (0.2)
	trans-epoxide	3.5 (0.3)	2.8 (0.1)	3.6 (0.1)	5.8 (0.4)
	benzaldehyde	3.3 (0.2)	3.4 (0.3)	2.0 (0.3)	6.1 (0.6)
trans-stilbene	*cis*-epoxide	-	-	-	-
	trans-epoxide	19.7 (0.7)	43.5 (1.7)	44.6 (0.7)	64.7 (1.9)
	benzaldehyde	3.8 (0.4)	4.3 (0.6)	3.6 (0.2)	2.8 (0.4)

Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 5 mL, cyclooctene 0.1 M, $Mn(TPA)Cl_2$ 2 mM, $PhI(OAc)_2$ 0.1 M, 273 K, 8 h. The data in parentheses represent the deviations.

Interaction between high valent manganese species and redox-inactive metal ions. In literatures, the promotional effects of those redox-inactive metal ions are generally attributed to their linkages to the redox metal ions through the $M^{n+}=O$ functional group. Here, the reaction data presented above have clearly revealed that the synergistic effect exists between $Mn(TPA)Cl_2$ catalyst and redox-inactive metal ions in catalyzing olefin epoxidation, which is one of the rare examples that redox-inactive metal ions as Lewis acid can accelerate direct oxygen atom transfer.[22] The evidence to display their interaction first comes from EPR studies (Figure 2). In the absence of Lewis acid, a typical 16-line signal centered at g=2.0 and regularly spaced by about 84 G was observed at 130 K when $Mn(TPA)Cl_2$ was oxidized by $PhI(OAc)_2$ in acetonitrile/CH_2Cl_2 (4:1, v/v), accounting for the coupling of two non-equivalent ^{55}Mn nuclei (I=5/2).[22] This typical 16-line signal is highly characteristic of the mixed valent di-μ-oxo-bridged diamond core, Mn^{III}-(μ-O)$_2$-Mn^{IV}, which has been reported in chemical oxidation or electrochemical process of various manganese(II) complexes.[24,31-33] The 16-line signal spreads over a 1260 G range (first peak to last trough), which is highly consistent with the reported value of similar mixed-valent species in literature (1240 G).[24] On the other hand, this 16-line signal gradually disappeared with the addition of redox-inactive metal ions. As shown in Figure 2, at 10 minutes after adding $Al(OTf)_3$ to the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core, the 16-line hyperfine structure turns more irregular when compared with its initial EPR signal. Instead, after 30 minutes, a 6-line signal at g=1.9 with average spaced by 95 G was observed, while the 16-line hyperfine structure has almost vanished, indicating a high-spin mononuclear manganese(II) species was generated.[25,34,35] This change of EPR spectra clearly indicates an Al^{3+} induced dissociation of the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV}

core happens (Scheme 2, *vide infra*). Here, the generation of manganese(II) species is possibly related to the instability of the activated monomeric manganese(IV) species in the presence of Al^{3+}. As evidence, a similar 6-line hyperfine structure was directly observed for $Mn(TPA)Cl_2$ complex, and this structure remains unchanged by adding $Al(OTf)_3$, which simultaneously eliminates other influence of $Al(OTf)_3$ on the EPR signal of manganese complexes. The lack of the direct EPR signal of $Mn(IV)=O/Al^{3+}$ adduct is possibly related to its short life time and/or its weakness compared with the strong signal of the high-spin mononuclear manganese(II) species. It is worth to mention that, because the EPR signal of the Mn(II) species is so strong, even though the Mn(II) signal has been observed, it does not suggest that the Mn(IV) species have been completely reduced to the corresponding Mn(II) species. On the other hand, the dissociation of the diamond Mn^{III}-$(\mu\text{-}O)_2$-Mn^{IV} core does not happen by adding 3 equiv. of NaOTf (Figure S2), which is consistent with its poor synergistic effect in epoxidation. This result further confirms that the Lewis acid induced promotional effect is not attributed to the presence of OTf^- anion.

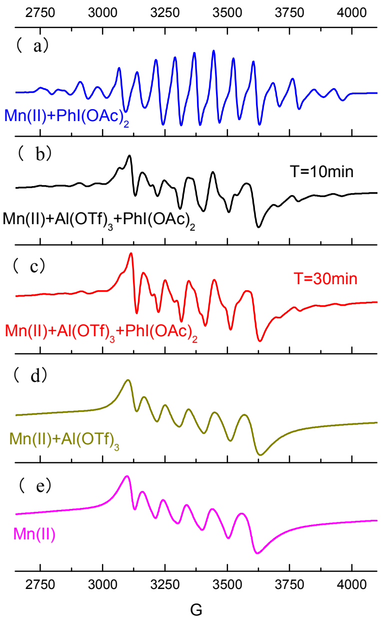


Figure 2. EPR spectra of (a) $Mn(TPA)Cl_2$ plus 5 equiv. of $PhI(OAc)_2$, (b) 10 minutes after adding 1 equiv. of Al^{3+} into (a), (c) 30 minutes after adding 1 equiv. of Al^{3+} into (a), (d) $Mn(TPA)Cl_2$ plus 1 equiv. of Al^{3+}, (e) $Mn(TPA)Cl_2$. Conditions: 5 mM $Mn(TPA)Cl_2$ in acetonitrile/CH_2Cl_2 (4:1, v/v) at 130 K.

Although the accurate structure is still elusive, one plausible interaction between Mn(IV) species and Al^{3+} can be described as formation of the $Mn(IV)=O{\bullet}{\bullet}{\bullet}Al^{3+}$ unit, and similar binding mode has been suggested in other Lewis-acid-accelerated oxidations by active metal oxo moieties in electron transfer, oxygenation and hydrogen abstraction.[7-9] Another alternative structure of the generated active intermediate is the form of $O=Mn^{IV}$-O-Al^{3+}. This hypothesis is similar of $O=Fe^{IV}$-O-Fe^{III} mode which is generated by disassembling of Fe^{III}-$(\mu\text{-}O)_2$-Fe^{IV}.[36,37] In literature, it has been reported that $O=Fe^{IV}$-O-Fe^{III} can cleave the C-H bond in 9,10-dihydroanthracene (DHA) over 10^6 fold faster, and transfer oxygen atom to diphenyl(pentafluorophenyl) phosphine over 10^3-fold faster than the corresponding diamond Fe^{III}-$(\mu\text{-}O)_2$-Fe^{IV} core.[36] The formation of a terminal iron(IV) oxo in open core has been proposed as the key factor for the activity enhancement. Here, similar dissociation of diamond Mn^{III}-$(\mu\text{-}O)_2$-Mn^{IV} core has been induced by the addition of Lewis acid, which improves oxygen transfer efficiency as observed in olefin epoxidation. Thereof, a similar open $O=Mn^{IV}$-O-Al^{3+} core can be alternatively proposed as the dissociation product from the diamond Mn^{III}-$(\mu\text{-}O)_2$-Mn^{IV} core. If it is correct, the improved activity in oxidation demonstrated here may provide clues to understand the reactivity of non-heme diiron enzymes, where the intermediate Q in MMO is proposed to have a diamond $[Fe_2(\mu\text{-}O)_2]$ core (*vide infra*).[38,39]

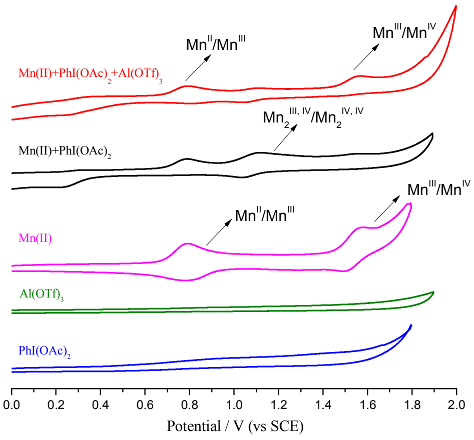


Figure 3 Cyclic voltammogram for $Mn(TPA)Cl_2$ in the presence/absence of $PhI(OAc)_2$ and $Al(OTf)_3$. Conditions: 5 mM $Mn(TPA)Cl_2$ in acetonitrile/CH_2Cl_2 (4:1,v/v), 5 equiv. of $PhI(OAc)_2$, 2 equiv. of $Al(OTf)_3$.

The dissociation of the diamond Mn^{III}-$(\mu\text{-}O)_2$-Mn^{IV} core has also been evidenced by electrochemical studies (Figure 3). $Mn^{II}(TPA)Cl_2$ alone revealed the Mn^{II}/Mn^{III} and Mn^{III}/Mn^{IV} couples of +0.79 V and +1.57 V (vs SCE) in acetonitrile/dichloromethane (4:1, v/v), respectively, which are similar to those potentials of $Mn(BPMEN)Cl_2$ in literature.[22] These electrochemical oxidation waves also indicate that TPA and BPMEN have similar electron donation ability and coordination structure around manganese(II) ions. *In situ* oxidizing of $Mn(TPA)Cl_2$ with $PhI(OAc)_2$ revealed a third redox couple at +1.12 V (vs SCE), which can be assigned to the couple of dinuclear core Mn_2(III,IV) to Mn_2(IV,IV) (it is +1.10 V *vs* SCE for $Mn(BPMEN)Cl_2$).[24] In the presence of Al^{3+}, this dinuclear redox couple almost vanished, indicating an Al^{3+} induced dissociation of the dinuclear core happens. Moreover, no electrochemical wave can be monitored when using $Al(OTf)_3$ or $PhI(OAc)_2$ alone in control experiments, indicating the above-mentioned redox couples were not contributed from Lewis acid or oxidant.

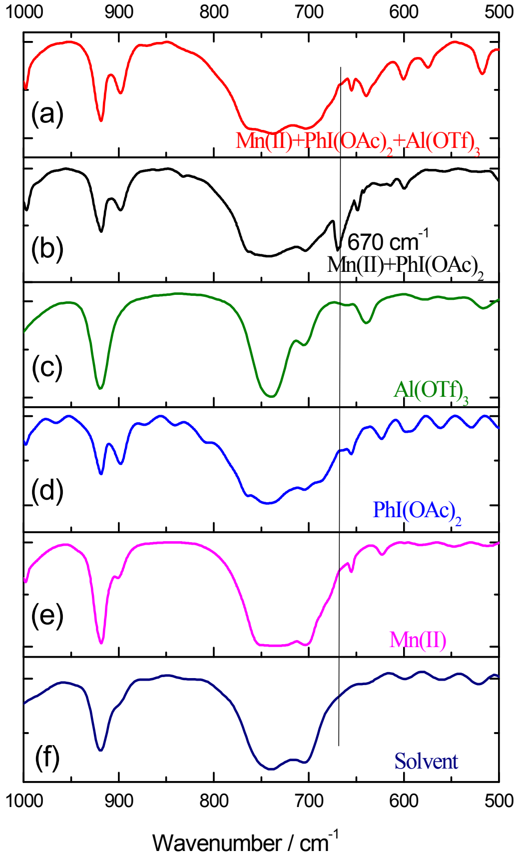


Figure 4. FT-IR spectra of manganese(II) complex in the presence/absence of PhI(OAc)$_2$ and Al(OTf)$_3$. Conditions: 5 mM Mn(TPA)Cl$_2$ in acetonitrile/CH$_2$Cl$_2$ (4:1, v/v), 5 equiv. of PhI(OAc)$_2$, 2 equiv. of Al(OTf)$_3$.

The FT-IR spectra also indicate the dissociation of the dinuclear Mn^{III}-(μ-O)$_2$-Mn^{IV} core by adding Al^{3+}. Both Mn(TPA)Cl$_2$ and PhI(OAc)$_2$ in acetonitrile/CH$_2$Cl$_2$ (4:1, v/v) gave a broad absorption band from 650 to 800 cm^{-1} and another sharp one around 920 cm^{-1}, which can be attributed to organic solvent (Figure 4f). The high valent diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core, generated by oxidation of the manganese(II) complex with PhI(OAc)$_2$, showed an obvious shoulder band around 670 cm^{-1} (Figure 4b). In literature, a diamond MnO$_2$Mn core, in which each manganese ion bears a tetradentate Schiff base ligand, gives rise to a prominent and characteristic IR absorption from 600 to 650 cm^{-1}.[40] In addition, a characteristic Mn^{IV}-O stretching mode of the diamond MnO$_2$Mn core with pyridyl-benzimidazole ligand is also located around 695 cm^{-1}, which has been believed as a useful reference probe for structural characterization of Mn containing active sites involving two oxo bridges.[41] Accordingly, in this work, the shoulder band at 670 cm^{-1} raised by oxidation of Mn(TPA)Cl$_2$ with PhI(OAc)$_2$ is consistent with those in literatures, indicating the formation of diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core (Fig. 4b), while vanishing of this band by adding Al^{3+} indicates the dissociation of the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core (Fig. 4a).

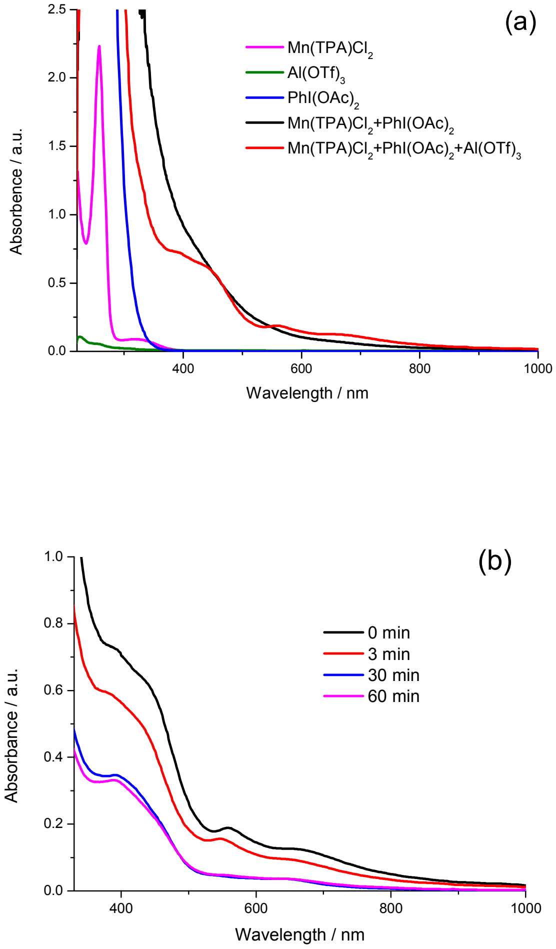


Figure 5. (a) UV-Vis spectra of the manganese complex, Al(OTf)$_3$ and PhI(OAc)$_2$. Conditions: 1 mM Mn(TPA)Cl$_2$ in acetonitrile/CH$_2$Cl$_2$ (4:1, v/v), 5 equiv. of PhI(OAc)$_2$, 2 equiv. of Al(OTf)$_3$. (b) UV-Vis spectra of (a) upon addition of 20 equiv. of cyclooctene.

The UV-Vis spectra provide further clue for the interaction of Al^{3+} with the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core. As shown in Figure 5, Mn^{II}(TPA)Cl$_2$ alone demonstrated a characteristic absorbance at 257 nm with ε value of 2230 M^{-1}cm^{-1}, which can be attributed to the absorbance of TPA ligand, while PhI(OAc)$_2$ alone gives no absorption band beyond 400 nm. With the addition of 5 equiv. of PhI(OAc)$_2$, a broad absorption band from 400 to 820 nm was observed, which is similar to the previous reported absorbance from diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core.[24] Adding 2 equiv. of Al(OTf)$_3$ generated a distinct UV-Vis absorbance, which contained a shoulder peak around 440 nm and two weak but nonetheless detectable peaks at 560 nm and 650 nm. This change in the absorption is consistent with those from EPR, FT-IR and electrochemistry, indicating a dissociation of the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core to form the active Mn(IV)=O/Al^{3+} adduct for epoxidation. As evidence, upon adding cyclooctene, the shoulder bands above 500 nm decayed gradually, and GC analysis confirmed the formation of epoxide. Similarly, adding Mg^{2+} or Zn^{2+} can also induce similar spectra changes as that by adding Al^{3+} (Figure S3), indicating a dissociation of diamond core has also been initialized by Mg^{2+} or Zn^{2+}.

Epoxidation Mechanism. It is generally accepted that versatile active M^{n+}=O species can conduct oxygen atom transfer reaction like epoxidation, and the key evidence to support this comes from ^{18}O isotope labelling experiments. In Groves' studies, Mn^V(TMPyP)(O) species can exchange its oxo functional group with ^{18}O-water to form Mn^V(TMPyP)(^{18}O). Next, it was identified that ^{18}O can be subsequently incorporated into olefin, forming the ^{18}O-epoxide product, thus the Mn^V=O moiety was established as the active intermediate in olefin epoxidation.[42] Here, incorporation of ^{18}O into epoxide from ^{18}O-water was also observed in Mn(TPA)Cl_2 catalyzed epoxidation of *cis*-stilbene (Figure S4). Importantly, the abundance of ^{18}O in epoxide is highly Al^{3+}-dependent. In the absence of Al^{3+}, the yields of *cis*- and *trans*-epoxide were 5.9% and 3.5% (Table 3), in which the abundances of ^{18}O were 89.2% and 81.0%, respectively (Table 4). Along with increasing the dosage of Al^{3+}, the yield of *cis*-epoxide sharply increased up to 50.7%, whereas the abundance of ^{18}O in *cis*-epoxide decreased down to 66.1%. This decrease of the ^{18}O enrichment can be attributed to the fact that with the addition of Al^{3+}, the generated Mn(IV)=O/Al^{3+} adduct is highly active for epoxidation, which reacts with olefin much faster than its exchange with ^{18}O-water, otherwise Al^{3+} has delayed the ^{18}O exchange between the Mn(IV)=O/Al^{3+} adduct and ^{18}O-water (*vide infra*).

Table 4. Isotopic labelling experiments using $H_2{}^{18}O$ for the catalytic oxidation of *cis*-stilbene

Substrate	Product	The abundance of ^{18}O (%)			
		1:0[a]	1:0.5[a]	1:1[a]	1:2[a]
cis-stilbene	^{18}O-labelled *cis*-epoxide	89.2	68.6	67.5	66.1
	^{18}O-labelled *trans*-epoxide	81.0	65.0	63.9	65.5

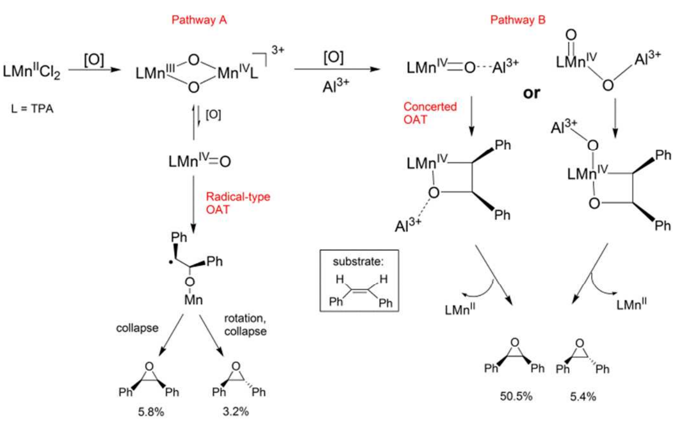
Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 0.5 mL, *cis*-stilbene 0.1 M, Mn(TPA)Cl_2 2 mM, PhI(OAc)$_2$ 0.2 M, $H_2{}^{18}O$ 0.05 mL, 273 K, 8 h. [a] The ratio of Mn(II):Al^{3+} as catalyst.

One may argue that, in literature, some manganese complexes and redox-inactive metal ions have been reported to serve as Lewis acid to assist olefin epoxidation with oxidant in which the valence of metal ions does not change.[43-48] Here, we still prefer that it is manganese oxo moiety that delivers the oxygen atom to olefin to form epoxide due to several reasons: 1) control experiments using either Mn(TPA)Cl_2 or redox-inactive metal ions alone as catalyst provided very limited olefin conversion and epoxide formation, supporting none of them can serve as Lewis acid to achieve efficient epoxidation; 2) in UV-Vis studies, the weak but nontheless absorption bands beyond 500 nm can be observed by adding Al^{3+} to the manganese(II) complex in the presence of PhI(OAc)$_2$, and it decays with the addition of cyclooctene, supporting that this band is a signal of high valent manganese intermediate, proposed as Mn(IV)=O/Al^{3+} adduct, responsible for epoxidation (*vide supra*); 3) it has been reported that epoxidation of *cis*-stilbene by Lewis acid pathway with PhIO can yield *trans*-stilbene as product in addition to cis-epoxide,[43] however, this isomerization was not observed here; 4) in using iodosylbenzene analog as oxidant, Lewis-acid-assisted oxygen transfer, in which the valence of metal ion does not change, was commonly observed with PhIO;[43,49,50] here, using PhIO for cyclooctane epoxidation gave only 27.1% conversion with 23.3% yield of epoxide (Table S5), much lower than that of using PhI(OAc)$_2$. Accordingly, the generation of the active intermediate, Mn(IV)=O/Al^{3+} adduct, does not proceed by oxidation of manganese(II) catalyst with potentially *in situ* generated PhIO, but with PhI(OAc)$_2$ directly.

In active M^{n+}=O moieties mediated olefin epoxidation, it has been reported that there exist at least two distinct reaction pathways:[27,51] 1) olefin attacking on the M^{n+}=O moiety through one electron oxidation to generate an olefinic C=C π bond broken radical intermediate, followed by collapse or rotation-collapse process which in turn provides the mixture of *cis* and *trans* epoxides, known as the radical-type oxygen atom transfer;[28,52] 2) 2+2 cycloaddition of the M^{n+}=O moiety with olefin to generate a metallaoxetane intermediate, followed by its subsequent breakdown to form epoxide, which remains the stereo-structure of olefin, known as the concerted oxygen atom transfer pathway.[53-55] It is worth to mention that, in concerted oxygen atom transfer process, the exact transition state is still elusive. The three-member ring transition state, generated by the oxygen atom of the M^{n+}=O moiety attacking on the olefinic double bond, has also been proposed.[56]

Here, in the absence of Al^{3+}, the sluggish Mn(TPA)Cl_2 alone provides comparable yields of *cis*- and *trans*-epoxide in each case (Table S3), indicating the occurrence of an olefinic C=C π bond broken radical intermediate (pathway A in Scheme 2). The sluggish activity of the manganese(II) catalyst alone is related to the formation of the dominant diamond core structure which is believed to be much less active than the corresponding M^{n+}=O moieties.[39,55] As shown in Table 4, the high enrichment of ^{18}O in epoxide indicates that, here, the manganese species responsible for epoxidation can rapidly exchange oxygen with ^{18}O-water, which eliminates the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core serving epoxidation. As described in literature, a feasible coordination site on the manganese intermediate is essential for ^{18}O exchange with ^{18}O-water, in which binding of ^{18}O-water followed by protonation on the M^{n+}=^{16}O moiety and simultaneous deprotonation on ^{18}O generates the ^{18}O-labelled M^{n+}=^{18}O species.[57] In the case of di-μ-oxo bridged Mn dimer, coordination of water at the vacated sites is also essential for the μ-oxo exchange happens.[58] Apparently, our well-characterized diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core, in which both manganese ions are coordination saturated in diamond core, cannot offer feasible oxygen exchange with ^{18}O-water to achieve a high enrichment of ^{18}O in epoxide. Accordingly, the high enrichment of ^{18}O in epoxide products (89.2 % in *cis*-

epoxide and 81.0 % in *trans*-epoxide, Table 4) suggests that there exist certain active species other than diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core responsible for epoxidation. In literature, the equilibrium between the dimeric core and monomeric metal oxo moiety has been reported.[32] Accordingly, similar minor free Mn^{IV}=O moiety may exist in the reaction solution when Mn(TPA)Cl_2 alone is employed as catalyst, and it is responsible for epoxidation. Due to its low concentration, the catalytic efficiency of Mn(TPA)Cl_2 is poor.



Scheme 2. Proposed mechanism of redox-inactive Al^{3+} promoted epoxidation by Mn(TPA)Cl_2 catalyst.

In the case of adding Al^{3+}, the yield of *cis*-epoxide (50.7%) was sharply improved, whereas the yield of *trans*-epoxide remains unchanged (5.8%) (it is worth to mention that again, Al^{3+} alone is very sluggish for epoxidation as demonstrated in Table 1). Clearly, the presence of Al^{3+} has shifted the epoxidation from the radical-type oxygen atom transfer (pathway A) to the concerted oxygen atom transfer, which leads to the high stereoselectivity of *cis*-epoxide (pathway B). This switch in epoxidation mechanism can be attributed to the formation of a plausible Mn(IV)=O/Al^{3+} adduct through Lewis acid induced dissociation of the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core as evidenced by EPR and others. Then, the Mn(IV)=O/Al^{3+} adduct mediates the concerted oxygen atom transfer, which provides the stereo-structure maintained epoxide product with sharply improved yield.

In our previous communication,[22] the interaction between Mn(IV) species and Al^{3+} was described as Mn(IV)=O•••Al^{3+} for which a similar, though controversial, structure has been illustrated in literature.[7-9] In this case, a metallaoxetane intermediate can be generated by 2+2 cycloaddition of Mn(IV)=O•••Al^{3+} with olefin as shown in Scheme 2. Because of the Lewis acidity of Al^{3+}, Mn-O bond in this metallaoxetane intermediate is weakened and oxygen atom can be easily transferred to the substrate, which remarkably increases the epoxidation efficiency (Table 2). Also this hypothesis has rationalized the fact that redox-inactive metal ions with higher positive charge demonstrate better efficiency in promoting the Mn(II) complex catalyzed epoxidation (Table 1), in which higher Lewis acidity may lead to a more stretched Mn-O bond thus facilitate the oxygen atom transfer. In the case of ^{18}O labelling experiments, the decreased ^{18}O enrichment in epoxide can be attributed to the presence of Al^{3+} which delays the ^{18}O exchange between the Mn^{IV}=O•••Al^{3+} species and ^{18}O-water (Table 4).

Alternatively, another form of Mn(IV)=O/Al^{3+} adduct, O=Mn^{IV}-O-Al^{3+}, may be generated when the diamond Mn^{III}-(μ-O)$_2$-Mn^{IV} core structure is disassembled in the presence of redox-inactive metal ions and excess oxidant. Similarly, a metallaoxetane intermediate can also be formed by 2+2 cycloaddition of O=Mn^{IV}-O-Al^{3+} and olefin, as shown in Scheme 2. In this case, the dramatically increased epoxidation efficiency can be attributed to two main factors: (1) generation of a highly active Mn^{IV}=O species by dissociation of sluggish di-μ-oxo-bridged species with Al^{3+}; and (2) the linkage of Al^{3+} through μ-O-bridge with manganese(IV) species, not via directly bound to the oxygen atom which will be delivered to olefin, increases the net charge of the manganese(IV) intermediate, thus improves the oxygen transfer capability of the Mn^{IV}=O moiety in epoxidation. Apparently this hypothesis is also consistent with the fact that redox-inactive metal ions with higher positive charge demonstrate better efficiency in promoting the epoxidation efficiency of the Mn(II) complex (see Table 1). In this case, ^{18}O exchange is also delayed because binding of Al^{3+} to form O=Mn^{IV}-O-Al^{3+} prevents the coordination of ^{18}O-water onto the manganese(IV) ion. Complimentarily, the concerted oxygen transfer from the O=Mn^{IV} functional group in the O=Mn^{IV}-O-Al^{3+} unit to the substrate, which is not illustrated in Scheme 2, may happen without the formation of a metallaoxetane as described in literature.[56]

The plausible O=Mn^{IV}-O-Al^{3+} species demonstrated here recalls the reported O=Fe^{IV}-O-Fe^{III} species from the geometric and electronic structural point of view. In literature, the formation of a terminal Fe^{IV}=O unit in open core was also proposed as the main factor that contributes the enhancement of reactivity towards C-H bond cleavage and oxygen atom transfer reactions.[36] This phenomenon can be extended to help understanding the catalytic mechanism of MMO which has a diamond Fe^{III}-(μ-O)$_2$-Fe^{IV} core as the key active Q intermediate. If it is correct, the second iron in MMO enzymes may enhance the hydrogen abstraction capability of the Fe^{IV}=O from the robust methane through the dissociation of diamond Fe^{III}-(μ-O)$_2$-Fe^{IV} core to form more active O=Fe^{IV}-O-Fe^{III} structure as well as the plausible O=Mn^{IV}-O-Al^{3+} species here. In view of this point, this work may provide new clues in understanding the catalytic mechanism of methane monooxygenase and identifying the real reactive species in catalytic cycle.

The stability and reactivity of high valent transition metal clusters having μ-oxo bridge have attracted much attention over the past decades, however, the formation of di-μ-oxo-bridged core from the M^{n+}=O moieties also greatly reduce its oxidative activity.[39,55] Apparently our results have illustrated a novel strategy to explore the catalytic reactivity of a variety of redox metal complexes which form inactive clusters under oxidation conditions. To further testify this strategy, manganese complexes with different ligands are employed as catalyst for the epoxidation of cyclooctene (Table 5). Due to the formation of the binuclear diamond core structure under oxidative conditions as reported in literature,[59] these manganese complexes alone are very sluggish in olefin epoxidation as well as Mn(TPA)Cl_2 complex. For example, Mn(Bn-TPEN)Cl_2 alone as catalyst only gave 18.5% conversion and 8.7% yield in epoxidation of cyclooctene. Remarkably, the addition of Lewis acid sharply promoted conversion up to 95.3% with 88.9% yield of epoxide. This acceleration has been observed in each case, which further supports the effectiveness of our strategy. That is, *in situ* dissociating of these sluggish dimeric cores to generate the active intermediates by simply adding redox-inactive metal ions can provide a convenient protocol to explore their applications in versatile oxidation processes.

Table 5. Catalytic epoxidation of cyclooctene by Mn(II) complexes bearing different ligands

Ligands	Al(OTf)$_3$ mM	Conv. %	Yield %
TPA	0	9.9(0.2)	4.1(0.1)
	2	97.8(1.0)	91.4(0.3)
Bn-TPEN	0	18.5(0.8)	8.7(0.3)
	2	95.3(0.3)	88.9(0.1)
Phen[a]	0	11.0(0.8)	5.8(0.5)
	2	76.3(1.1)	67.4(0.3)
Phendio[a]	0	14.1(0.6)	6.9(0.5)
	2	86.3(1.7)	72.5(0.8)
BPMEN	0	10.3(2.0)	2.8(1.0)
	2	99.5(0.5)	79.3(0.4)

Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 0.5 mL, cyclooctene 0.05 M, Mn(II) complex 1 mM, 3.5 h, 273 K. The data in parentheses represent the deviations. [a] Pre-mixing $MnCl_2$ with ligand to in-situ generate the catalyst for epoxidation.

Conclusions

We have illustrated an early example that redox-inactive metal ions can sharply improve the oxygen atom transfer efficiency of redox metal catalysts like olefin epoxidation, which represents another important enzymatic and chemical oxidative process. Disclosed by various spectroscopies, oxidation of Mn(TPA)Cl_2 with PhI$(OAc)_2$ dominantly generated a mixed valent di-μ-oxo-bridged diamond core as Mn^{III}-$(\mu\text{-}O)_2$-Mn^{IV} which is very sluggish for olefin epoxidation. Dissociation of this diamond core is indicated in the presence of redox-inactive metal ions to form a plausible $Mn^{IV}{=}O{\cdots}Al^{3+}$ or $O{=}Mn^{IV}\text{-}O\text{-}Al^{3+}$ moiety which is highly active for epoxidation. Notably, the presence of Al^{3+} has shifted the epoxidation mechanism from radical-type oxygen atom transfer to concerted oxygen atom transfer. Our results have illustrated a novel strategy to explore the catalytic reactivity of a variety of redox metal complexes which form inactive clusters under oxidative conditions. Moreover, studies demonstrated here may also provide new clues to understand the catalytic mechanism of methane monooxygenase.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No 21303063 and 21273086). The GC-MS analysis was performed in the Analytical and Testing Center of Huazhong University of Science and Technology. Mr. Hong Yi was appreciated sincerely for EPR analysis in Wuhan University.

Notes and references

School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology. Key Laboratory for Large-Format Battery Materials and System, Ministry of Education. Luoyu Road 1037, Wuhan 430074, PR China. E-mail: zqchen@hust.edu.cn, ligxabc@163.com, gyin@hust.edu.cn.

Electronic Supplementary Information (ESI) available: Experimental details of catalytic epoxidation, GC-MS graphs, EPR spectra are available in supporting information. See DOI: 10.1039/c000000x/

1. I. Rivalta, G. W. Brudvig and V. S. Batista, *Curr. Opin. Chem. Biol.*, 2012, **16**, 11.
2. S. V. Seetharaman, D. D. Winkler, A. B. Taylor, X. H. Cao, L. J. Whitson, P. A. Doucette, J. S. Valentine, V. Schirf, B. Demeler, M. C. Carroll, V. C. Culotta and P. J. Hart, *Biochemistry*, 2010, **49**, 5714.
3. J. S. Valentine, P. A. Doucette and S. Zittin Potter, *Annu. Rev. Biochem*, 2005, **74**, 563.
4. R. K. Grasselli, *Top Catal*, 2002, **21**, 79.
5. S. Fukuzumi, Y. Morimoto, H. Kotani, P. Naumov, Y.-M. Lee and W. Nam, *Nat. Chem.*, 2010, **2**, 756.
6. J. Prakash, G. T. Rohde, K. K. Meier, A. J. Jasniewski, K. M. Van Heuvelen, E. Münck and L. Que, *J. Am. Chem. Soc.*, 2015, **137**, 3478.
7. Y. Morimoto, H. Kotani, J. Park, Y.-M. Lee, W. Nam and S. Fukuzumi, *J. Am. Chem. Soc.*, 2010, **133**, 403.
8. J. Park, Y. Morimoto, Y. M. Lee, Y. You, W. Nam and S. Fukuzumi, *Inorg. Chem.*, 2011, **50**, 11612.
9. P. Leeladee, R. A. Baglia, K. A. Prokop, R. Latifi, S. P. de Visser and D. P. Goldberg, *J. Am. Chem. Soc.*, 2012, **134**, 10397.
10. W. W. Y. Lam, S.-M. Yiu, J. M. N. Lee, S. K. Y. Yau, H.-K. Kwong, T.-C. Lau, D. Liu and Z. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 2851.
11. Y. J. Park, J. W. Ziller and A. S. Borovik, *J. Am. Chem. Soc.*, 2011, **133**, 9258.
12. F. Li, K. M. Van Heuvelen, K. K. Meier, E. Münck and L. Que, *J. Am. Chem. Soc.*, 2013, **135**, 10198.
13. Y. Nishida, Y. M. Lee, W. Nam and S. Fukuzumi, *J. Am. Chem. Soc.*, 2014, **136**, 8042.
14. J. Park, Y. Morimoto, Y. M. Lee, W. Nam and S. Fukuzumi, *J. Am. Chem. Soc.*, 2011, **133**, 5236.
15. J. Chen, Y. M. Lee, K. M. Davis, X. Wu, M. S. Seo, K. B. Cho, H. Yoon, Y. J. Park, S. Fukuzumi, Y. N. Pushkar and W. Nam, *J. Am. Chem. Soc.*, 2013, **135**, 6388.
16. H. Yoon, Y.-M. Lee, X. Wu, K.-B. Cho, R. Sarangi, W. Nam and S. Fukuzumi, *J. Am. Chem. Soc.*, 2013, **135**, 9186.
17. C. G. Miller, S. W. Gordon-Wylie, C. P. Horwitz, S. A. Strazisar, D. K. Peraino, G. R. Clark, S. T. Weintraub and T. J. Collins, *J. Am. Chem. Soc.*, 1998, **120**, 11540.
18. G. Yin, *Acc. Chem. Res.*, 2013, **46**, 483.

19. L. Dong, Y. Wang, Y. Lv, Z. Chen, F. Mei, H. Xiong and G. Yin, *Inorg. Chem.*, 2013, **52**, 5418.
20. H. Guo, Z. Chen, F. Mei, D. Zhu, H. Xiong and G. Yin, *Chem.-Asian J.*, 2013, **8**, 888.
21. Z. Zhang, K. L. Coats, Z. Chen, T. J. Hubin and G. Yin, *Inorg. Chem.*, 2014, **53**, 11937.
22. Z. Chen, L. Yang, C. Choe, Z. Lv and G. Yin, *Chem. Commun.*, 2015, **51**, 1874.
23. B. K. Shin, Y. Kim, M. Kim and J. Han, *Polyhedron*, 2007, **26**, 4557.
24. C. Hureau, G. Blondin, M. F. Charlot, C. Philouze, M. Nierlich, M. Cesario and E. Anxolabehere-Mallart, *Inorg. Chem.*, 2005, **44**, 3669.
25. X. Wu, M. S. Seo, K. M. Davis, Y. M. Lee, J. Chen, K. B. Cho, Y. N. Pushkar and W. Nam, *J. Am. Chem. Soc.*, 2011, **133**, 20088.
26. G. Conte, A. J. Bortoluzzi and H. Gallardo, *Synthesis*, 2006, 3945.
27. R. D. Arasasingham, G. X. He and T. C. Bruice, *J. Am. Chem. Soc.*, 1993, **115**, 7985.
28. W. Adam, K. J. Roschmann, C. R. Saha-Möller and D. Seebach, *J. Am. Chem. Soc.*, 2002, **124**, 5068.
29. R. V. Ottenbacher, D. G. Samsonenko, E. P. Talsi and K. P. Bryliakov, *Acs Catal.*, 2014, **4**, 1599.
30. S. E. Park, W. J. Song, Y. O. Ryu, M. H. Lim, R. Song, K. M. Kim and W. Nam, *J. Inorg. Biochem.*, 2005, **99**, 424.
31. C. Hureau, E. Anxolabehere-Mallart, G. Blondin, E. Riviere and M. Nierlich, *Eur. J. Inorg. Chem.*, 2005, 4808.
32. C. Hureau, L. Sabater, E. Anxolabehere-Mallart, M. Nierlich, M. F. Charlot, F. Gonnet, E. Riviere and G. Blondin, *Chem.-Eur J*, 2004, **10**, 1998.
33. S. D. Hicks, D. Kim, S. L. Xiong, G. A. Medyedey, J. Caruthers, S. Hong, W. Nam and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2014, **136**, 3680.
34. J. Kliava and J. Purans, *J. Magn. Reson.*, 1980, **40**, 33.
35. M. V. Golynskiy, W. A. Gunderson, M. P. Hendrich and S. M. Cohen, *Biochemistry*, 2006, **45**, 15359.
36. G. Q. Xue, R. De Hont, E. Munck and L. Que, *Nat. Chem*, 2010, **2**, 400.
37. H. Zheng, S. J. Yoo, E. Munck and L. Que, *J. Am. Chem. Soc.*, 2000, **122**, 3789.
38. S. Friedle, E. Reisner and S. J. Lippard, *Chem. Soc. Rev.*, 2010, **39**, 2768.
39. G. Q. Xue, D. Wang, R. De Hont, A. T. Fiedler, X. P. Shan, E. Munckt and L. Que, *P. Natl. Acad. Sci. USA*, 2007, **104**, 20713.
40. L. J. Boucher and C. G. Coe, *Inorg. Chem.*, 1975, **14**, 1289.
41. B. C. Dave and R. S. Czernuszewicz, *Inorg. Chim. Acta*, 1994, **227**, 33.
42. J. T. Groves, J. B. Lee and S. S. Marla, *J. Am. Chem. Soc.*, 1997, **119**, 6269.
43. Y. H. Yang, F. Diederich and J. S. Valentine, *J. Am. Chem. Soc.*, 1991, **113**, 7195.
44. S. Y. Tosaki, R. Tsuji, T. Ohshima and M. Shibasaki, *J. Am. Chem. Soc.*, 2005, **127**, 2147.
45. S. H. Wang, B. S. Mandimutsira, R. Todd, B. Ramdhanie, J. P. Fox and D. P. Goldberg, *J. Am. Chem. Soc.*, 2003, **126**, 18.
46. J. P. Collman, L. Zeng and J. I. Brauman, *Inorg. Chem.*, 2004, **43**, 2672.
47. G. Yin, J. M. McCormick, M. Buchalova, A. M. Danby, K. Rodgers, V. W. Day, K. Smith, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper and D. H. Busch, *Inorg. Chem.*, 2006, **45**, 8052.
48. G. Yin, M. Buchalova, A. M. Danby, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper and D. H. Busch, *J. Am. Chem. Soc.*, 2005, **127**, 17170.
49. W. Nam and J. S. Valentine, *J. Am. Chem. Soc.*, 1993, **115**, 1772.
50. T. Niwa and M. Nakada, *J. Am. Chem. Soc.*, 2012, **134**, 13538.
51. N. S. Finney, P. J. Pospisil, S. Chang, M. Palucki, R. G. Konsler, K. B. Hansen and E. N. Jacobsen, *Angew. Chem. Int. Edit.*, 1997, **36**, 1720.
52. M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Guler, T. Ishida and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 948.
53. J. P. Collman, J. I. Brauman, B. Meunier, T. Hayashi, T. Kodadek and S. A. Raybuck, *J. Am. Chem. Soc.*, 1985, **107**, 2000.
54. E. N. Jacobsen, W. Zhang, A. R. Muci, J. R. Ecker and L. Deng, *J. Am. Chem. Soc.*, 1991, **113**, 7063.
55. E. M. McGarrigle and D. G. Gilheany, *Chem. Rev.*, 2005, **105**, 1563.
56. L. Kurti, M. M. Blewett and E. J. Corey, *Org. Lett.*, 2009, **11**, 4592.
57. J. Bernadou, A.-S. Fabiano, A. Robert and B. Meunier, *J. Am. Chem. Soc.*, 1994, **116**, 9375.
58. R. Tagore, R. H. Crabtree and G. W. Brudvig, *Inorg. Chem.*, 2007, **46**, 2193.
59. E. M. Mcgarrigle and D. G. Giheany, *Chem. Rev.*, 2005, **105**, 1563.

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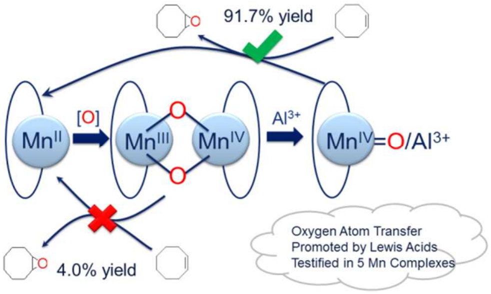

Oxygenation efficiency of manganese catalyst can be sharply improved by Lewis acid which causes the dissociation of diamond Mn_2(III,IV) core.