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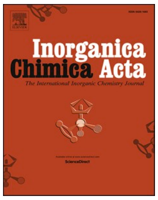

Research paper

Nonheme manganese(III) complexes for various olefin epoxidation: Synthesis, characterization and catalytic activity

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ABSTRACT

Three mononuclear imine-based non-heme manganese(III) complexes with tetradentate ligands which have two deprotonated phenolate moieties, ([(X$_2$saloph)Mn(OAc)(H$_2$O)], **1a** for X = Cl, **1b** for X = H, and **1c** for X = CH$_3$, saloph = *N,N-o*-phenylenebis(salicylidenaminato)), were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, ESI-Mass and elemental analysis. Mn^{III} complexes catalysed efficiently various olefin epoxidation reactions with *meta*-chloroperbenzoic acid (MCPBA) under the mild condition. Mn^{III} complexes **1a** and **1c** with the electron-withdrawing group -Cl and electron-donating group –CH$_3$ showed little substituent effect on the epoxidation reactions. Product analysis, Hammett study and competition experiments with *cis*- and *trans*-2-octene suggested that Mn^{IV} = O, Mn^{V} = O, and Mn^{III}-OOC(O)R species might be key oxidants in the epoxidation reaction under this catalytic system. In addition, the use of PPAA as a mechanistic probe demonstrated that Mn-acylperoxo intermediate (Mn^{III}-OOC(O)R) **2** generated from the reaction of peracid with manganese complexes underwent both the heterolysis and the homolysis to produce Mn^{V} = O (**3**) or Mn^{IV} = O species (**4**). Moreover, the Mn^{III}-OOC(O)R **2** species could react directly with the easy-to-oxidize substrate to give epoxide, whereas the species **2** might not be competent to the difficult-to-oxidize substrate for the epoxidation reaction.

1. Introduction

Developing catalysts which have high catalytic efficiency in olefin epoxidation reactions have been considered important because the epoxidation reactions have been used in a large field of the chemical industry [1]. The epoxidation products, epoxides, are well known as intermediates in the organic synthesis to produce perfumes, drugs, and so on [2]. Consequently, improving the efficiency of the epoxidation reaction with faster, cheaper, and more selective catalysts is meaningful and significant in organic synthesis and industry.

Cytochrome *P*-450, a family of heme enzymes, catalyzes diverse oxygenation reactions, including olefin epoxidation under environmentally favorable conditions [3]. Thus, modeling these enzymes has been paid attention to developing new olefin epoxidation catalysts with the first low-transition metals such as Fe, Mn, and Cu [3–5]. In particular, the Mn-containing complexes such as [Mn(salen)] and [Mn(porp)] have been well known as efficient catalysts toward olefin epoxidation (salen = N,*N*-bis(salicylidene)ethylenediamine, porp = porphyrin) [6,7]. For example, the homogeneous and heterogeneous Mn(salen) complexes showed an excellent catalytic reactivity in various olefin epoxidations [7–9]. Therefore, the number of salen metal complexes have been prepared and studied for several types of applications in bioinorganic and medicinal inorganic chemistry and drug developments [7–9]. We have previously reported the Mn^{III} complexes containing [Re$_4$Q$_4$(CN)$_{12}$]$^{4-}$ (Q = Te and Se) cluster which catalyzed rapidly epoxidation of various olefins under mild conditions [9]. However, they required a complicated and high-cost synthesis process. These results led us to develop new manganese complexes with simple, inexpensive, and efficient catalysis.

Herein, we demonstrate the synthesis, characterization, and catalytically efficient epoxidation reactions of Mn(saloph) complexes **1a**-**1c**. The Mn complexes showed an efficient catalytic reactivity for diverse olefin epoxidations with MCPBA as oxidant under mild conditions. Mn^{III} complexes **1a** and **1c** with the electron-deficient group –Cl and electron-rich group –CH$_3$ showed little electronic substituent effect on the epoxidation reactions. The mechanistic studies like product analysis, Hammett plots, the use of PPAA (peroxyphenylacetic acid) , and competition experiments with *cis*- and *trans*-2-octene led us to propose that Mn^{IV} = O, Mn^{V} = O, and Mn^{III}-OOC(O)R species might be key intermediates in the epoxidation reaction under this catalytic system.

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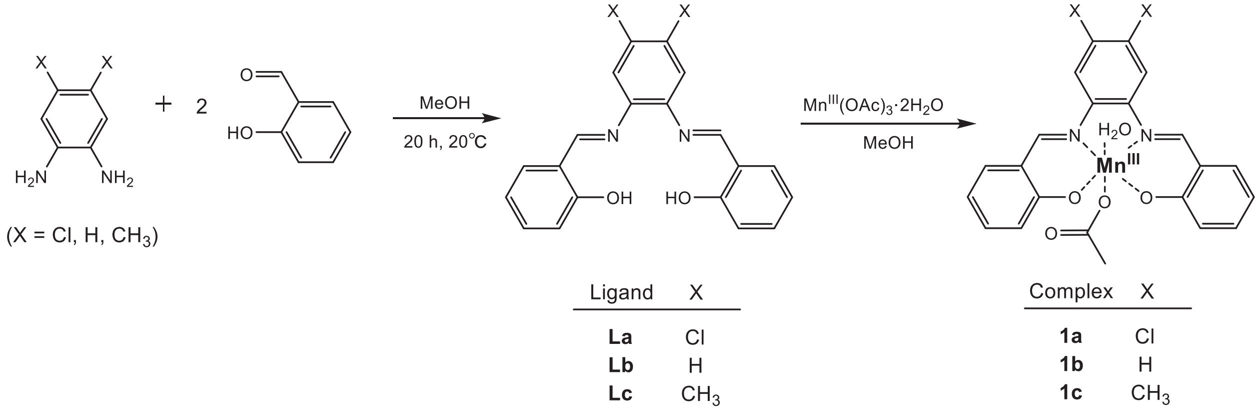


Scheme 1. Synthesis of ligands (**La**, **Lb**, and **Lc**) and Mn complexes (**1a**, **1b**, and **1c**).

However, the Mn^{III}-OOC(O)R species may not be competent to the difficult-to-oxidize substrate for the epoxidation reaction.

2. Experimental section

Epoxides, olefins, 2-cyclohexen-1-one, ethanol, 2-cyclohexen-1-ol, acetone, methanol, o-phenylenediamine, salicylaldehyde, benzaldehyde, acetonitrile, dichloromethane, $Mn(OAc)_3{\cdot}2H_2O$, MCPBA (65%), and dodecane were provided from Aldrich. PPAA (peroxyphenylacetic acid) was synthesized as reported in the literature [10a].

Product analyses for PPAA experiment and alkene epoxidation were achieved with a Perkin Elmer gas chromatograph with a 30 m capillary column (HP-FFAP or DB-5). Product analysis for *cis*-stilbene epoxidation were achieved with an Agilent 1100 series High-performance liquid chromatograph system (Agilent Technologies, USA) with a 5 μm, 4.6 mm X 150 mm Octadecyl column (Waters Corp., Milford, MA). ^1H and ^{13}C NMR spectra were gained on a Varian spectrometer. Elemental analyses were performed on a vario MICRO Cube analyzer. A single-quadrupole liquid chromatography detector (ACQUITY QDa) was used to collect ESI-MS spectra. UV/Visible spectra were provided with a Perkin Elmer spectrometer (Lambda 2S UV/Visible).

2.1. Preparation of X_2saloph ligands (**La** for X = Cl, **Lb** for X = H, **Lc** for X = CH_3)

Compound **Lb** was synthesized according to the literature methods (Scheme 1). [11–13] Benzene-1,2-diamine (108.1 mg, 1x10^{-3} mol) and 2-hydroxybenzaldehyde (268.7 mg, 2.2x10^{-3} mol) were dissolved in MeOH (5 mL). The solution was stirred for 20 h at 20 °C. Yellow powder was formed, filtered and washed with MeOH. ^1H NMR (DMSO-d_6): δ 12.93 (s, 2H), 8.94 (s, 2H) 7.68 (d, 2H) 7.45 (m, 6H), 6.97 (t, 4H) (Fig. S1 (a)). ^{13}C NMR (DMSO-d_6): δ 117.1 (2C), 119.5 (2C), 119.9 (2C), 120.2 (2C), 128.2 (2C), 132.9 (2C), 133.9 (2C), 142.7 (2C), 160.8 (2C), 164.5 (2C) (Fig. S1 (b)). ESI-MS: *m/z* calcd for $[\mathbf{Lb} + H^+]^+$: 317.13, found 317.07 (Fig. S1 (c)). Elements analysis calcd (%) for $C_{20}H_{16}N_2O_2$: C, 75.92; H, 5.11; N, 8.87. Found: C, 75.90; H, 5.59; N, 8.75.

A similar procedure was applied for **La** and **Lc.** [12] For **La**, ^1H NMR (DMSO-d_6): δ 12.53 (s, 2H), 8.98 (s, 2H) 7.80 (s, 2H) 7.67 (d, 2H), 7.42 (t, 2H), 6.98 (m, 4H) (Fig. S2 (a)). ^{13}C NMR (DMSO-d_6): δ 117.2 (2C), 119.7 (2C), 119.9 (2C), 121.7 (2C), 129.8 (2C), 132.9 (2C), 134.4 (2C), 142.8 (2C), 160.8 (2C), 165.6(2C) (Fig. S2 (b)). ESI-MS: *m/z* calcd for $[\mathbf{La} + H^+ + DMSO + MeOH]^+$: 495.09, found 495.53 (Fig. S2 (c)). Elements analysis calcd (%) for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.36; H, 3.66; N, 7.27. Found: C, 62.19; H, 3.77; N, 7.33. For **Lc**, ^1H NMR (DMSO-d_6): δ 13.08 (s, 2H), 8.93 (s, 2H) 7.65 (d, 2H) 7.40 (m, 2H), 7.30 (s, 2H), 6.98 (t, 4H), 2.30 (s, 6H) (Fig. S3 (a)). ^{13}C NMR (DMSO-d_6): δ 19.6 (2C), 117.1 (2C), 119.4 (2C), 119.9 (2C), 120.8 (2C), 132.8 (2C), 133.6 (2C), 136.6 (2C), 140.1 (2C), 160.8 (2C), 163.5 (2C) (Fig. S3 (b)). ESI-MS: *m/z* calcd for $[\mathbf{Lc} + H^+ + 2MeCN + H_2O]^+$: 445.23, found 445.08 (Fig. S3 (c)). Elements analysis calcd (%) for $C_{22}H_{20}N_2O_2$: C, 76.71; H, 5.84; N, 8.13. Found: C, 76.85; H, 5.93; N, 8.11.

2.2. Preparation of the manganese complexes **1a-1c**

All complexes were prepared with the previously reported literature method [6,9,11,14]. They were synthesized by stirring the ligands (1x10^{-3} mol, **La** or **Lb** or **Lc**) and $Mn(III)(OAc)_3{\cdot}2H_2O$ (1x10^{-3} mol) in MeOH (5 mL) at 20 °C (Scheme 1) [6,9,11,14]. Brown powder was formed, filtered and washed with MeOH. For **1a**, ESI-MS: *m/z* calcd for $[\mathbf{1a} + H^+]^+$: 515.00, found 515.09 (Fig. S4(a)). Elements analysis calcd (%) for $C_{22}H_{19}MnN_2O_5$: C, 59.20; H, 4.29; N, 6.28. Found: C, 59.24; H, 3.90; N, 6.11. For **1b**, ESI-MS: *m/z* calcd for $[\mathbf{1b} + H^+ + 2MeCN]^+$: 529.13, found 528.93 (Fig. S4(b)). Elements analysis calcd (%) for $C_{22}H_{19}MnN_2O_5$: C, 51.29; H, 3.33; N, 5.44. Found: C, 51.83; H, 2.87; N, 5.46. For **1c**, ESI-MS: *m/z* calcd for $[\mathbf{1c} + H^+]^+$: 475.11, found 474.98 (Fig. S4(c)). Elements analysis calcd (%) for $C_{22}H_{17}Cl_2MnN_2O_5$: C, 60.76; H, 4.89; N, 5.91. Found: C, 60.74; H, 4.45; N, 5.69.

2.3. Olefin epoxidations by the manganese complexes **1a-1c** with MCPBA

MCPBA (1x10^{-4} mol) was delivered to a mixture of Mn complex (1x10^{-6} mol), substrate (3.5x10^{-5} mol) and solvent (1 mL, CH_2Cl_2/CH_3CN = 1:1), which was stirred for 10 min at 20 °C. Each reaction analyzed by GC was run at least three times. Dodecane was employed as an internal standard. *Cis*-stilbene epoxidation was analyzed by HPLC with ethyl benzoate as an internal standard.

2.4. Competitive epoxidations of styrene and para-substituted styrenes for Hammett plots

MCPBA (5x10^{-5} mol) was delivered to a mixture of styrene (2x10^{-5} mol) and *para*(X)-substituted styrene (2x10^{-5} mol, X = –Cl, –CN, and –OCH_3, –CH_3), Mn complex (1x10^{-6} mol) and solvent (1 mL, CH_2Cl_2/CH_3CN = 1:1), which was stirred for 10 min at 20 °C. The amounts of the styrenes before and after epoxidations were analyzed by GC. The relative reactivity was analyzed with the following equation: $k_x/k_y = \log(X_f/X_i)/\log(Y_f/Y_i)$ where Y_f and Y_i are the final and initial concentration of styrene and X_f and X_i are the final and initial concentration of *para*-substituted styrenes [15].

2.5. Determination of the O — O bond cleavage products from the epoxidation reactions of substrates by PPAA with Mn complexes

PPAA (3.5x10^{-5} mol) was delivered to a mixture of substrate (0–1.6x10^{-4} mol), Mn complex (1x10^{-6} mol), and solvent (1 mL, CH_2Cl_2/CH_3CN = 1:1), which was stirred for 10 min at 20 °C. Each reaction

Table 1
Olefin epoxidations by MCPBA with manganese catalysts **1a-1c** in CH_3CN/CH_2Cl_2 (1:1).[a, 14]

Entry	Substrate	Product	**1a**		**1b**		**1c**	
			Conversion [%][b]	Yield [%][b]	Conversion [%][b]	Yield [%][b]	Conversion [%][b]	Yield [%][b]
1	cyclopentene	epoxide	~100	84	~100	97	99	89
		2-cyclopentene-1-one		trace		trace		trace
2	cycloheptene	epoxide	~100	64	99	76	93	70
3	cyclooctene	epoxide	99	71	96	72	98	73
4	cyclohexene	epoxide	98	82	95	79	95	74
		2-cyclohexene-1-ol		3		3		3
		2-cyclohexene-1-one		2		3		2
5	1-hexene	epoxide	51	43	42	39	59	29
6	1-octene	epoxide	57	38	47	35	54	33
7	*cis*-2-hexene	*cis*-oxide	98	77	94	84	94	78
		trans-oxide		3		4		3
8	*trans*-2-hexene	*trans*-oxide	84.	62	77	66	77	61
9	*cis*-2-octene	*cis*-oxide	98	85	94	83	94	84
		trans-oxide		5		4		4
10	*trans*-2-octene	*trans*-oxide	67	65	62	52	64	54
11	styrene	epoxide	97	63	98	57	91	57
		benzaldehyde		6		6		5
		phenylacetaldehyde		20		18		16
12	*cis*-stilbene	*cis*-stilbene oxide	91	48	92	50	90	44
		trans-stilbene oxide		13		13		12
		benzaldehyde		13		15		12
		2-phenylacetophenone		8		8		8
13	*trans*-stilbene	*trans*-stilbene oxide	89	44	86	47	84	40
		benzaldehyde		11		11		9
		2-phenylacetophenone		4		5		4

[a] Reaction conditions: olefins ($3.5x10^{-5}$ mol), catalyst ($1x10^{-6}$ mol), MCPBA ($1x10^{-4}$ mol), and solvent (1 mL, CH_3CN/CH_2Cl_2 = 1:1). [b] Based on substrate.

analyzed by GC was run at least three times. Dodecane was employed as an internal standard.

2.6. *Competitive epoxidations of cis-2-octene and trans-2-octene by MCPBA with manganese complexes **1a-1c***

MCPBA ($4x10^{-5}$ mol) was delivered to a mixture of *cis*-2-octene (1-$8x10^{-5}$ mol) and *trans*-2-octene (1-$8x10^{-5}$ mol), Mn complex ($1x10^{-6}$ mol), and solvent (1 mL, CH_2Cl_2/CH_3CN = 1:1), which was stirred for 10 min at 20 °C. Each reaction analyzed by GC was run at least three times. Dodecane was employed as an internal standard.

2.7. *UV/Visible spectrophotometric studies*

UV/Visible spectrophotometric experiments were perform as follows. Solutions of **1a**, **1b**, and **1c** (1.0×10^{-5} mol) in CH_2Cl_2/CH_3CN (1:1, 3 mL) were transferred into 1 cm UV cell. Cyclohexene ($3.5x10^{-5}$ mol) and MCPBA ($1x10^{-4}$ mol) were then added into the UV cell, whereupon the spectral variations were monitored within 10 *sec* and further analyzed for 10 min.

3. Results and discussion

3.1. *Synthesis and characterization of manganese complexes **1a-1c***

Saloph ligand **Lb** was synthesized as reported in the literatures (Scheme 1) [11,12]. **La** having the electron-withdrawing group –Cl and **Lc** the electron-donating group $–CH_3$ were also synthesized with a similar method, and verified by ^1H and ^{13}C NMR, ESI-MS and elemental analysis. Manganese complexes **1a-1c** were prepared by the reaction of ligands **La-Lc** with $Mn(OAc)_3$, and characterized by ESI-MS and elemental analysis.

3.2. *Epoxidation reactions catalyzed by manganese complexes*

Catalytic epoxidation of dievrse alkenes by using MCPBA as oxidant with **1a**, **1b**, and **1c** as catalysts was performed. MCPBA was added to a mixture of olefin and manganese complex in 1 mL of CH_2Cl_2/CH_3CN (1:1). The reaction was complete for 1 min (Fig. S5). We certified that the direct oxidation of olefins by MCPBA was negligible under the conditions. UV/Visible experiments displayed that the Mn complexes **1a-1c** were sturdy enough during the catalytic epoxidations (Fig. S6). In Table 1 are summarized the epoxidation reactions. The epoxides were predominantly formed in the presence of **1b**. Cyclic alkenes of cyclopentene, cycloheptene and cyclooctene were epoxidized in good yields (72% – 97%, entries 1–3) with high conversions (96% – 100%). In the reaction containing cyclohexene (entry 4), cyclohexene oxide (79%) was mainly produced together with trace amounts of by-products, 2-cyclohexen-1-one (3%) and 2-cyclohexen-2-ol (3%). This result indicated that the radical-type oxidations were rarely involved in the epoxidation reactions [11,13]. The poor reactive terminal olefins, 1-hexene and 1-octene [15,16], showed low yields to 1-hexene

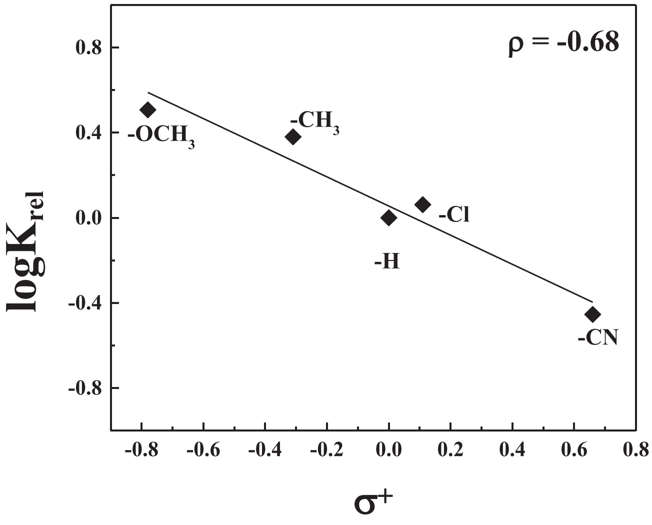
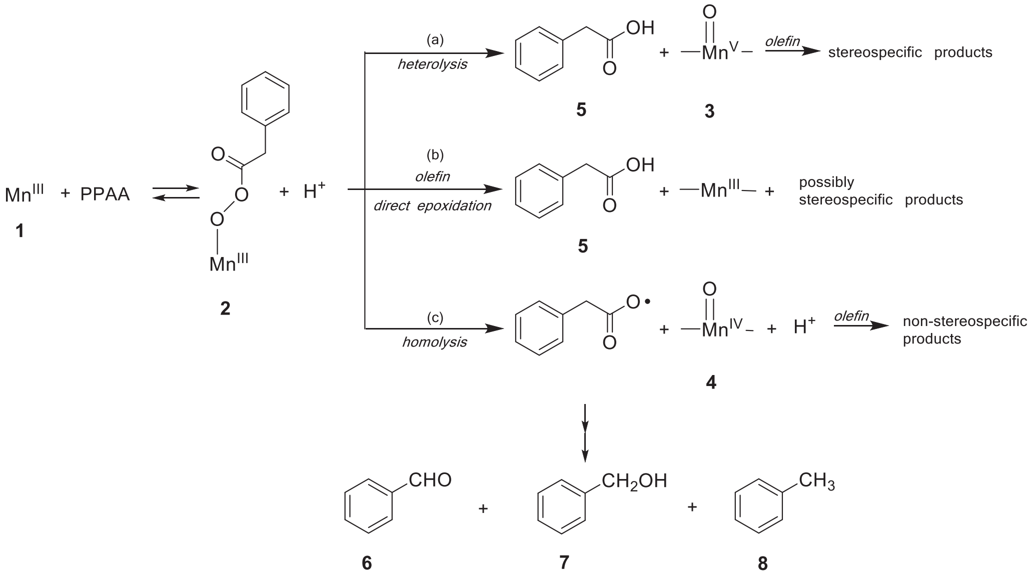


Fig. 1. Hammett plot for selective reactivity of styrene to *para*-substituted styrenes by catalyst **1a** with MCPBA.



Scheme 2. Possible mechanism for the production of the multiple active oxidants.

and 1-octene epoxides (39% and 35%, entries 5 and 6). *cis*-2-Hexene and *cis*-2-octene were epoxidized to *cis*-2-hexene oxide and *cis*-2-octene oxide (84% and 83%; entries 7 and 9) as well as a small amount of *trans*-2-hexene oxide and *trans*-2-octene oxide (4% and 4%). These outcomes suggested that the high stereochemical retentions were retained in this epoxidation reaction. *trans*-2-Hexene and *trans*-2-octene produced only *trans*-2-hexene oxide and *trans*-2-octene oxide (66% and 52%; entries 8 and 10). Styrene formed styrene oxide (57%; entry 11) with small amount of benzaldehyde (6%) and certain amounts of phenylacetaldehyde (18%). *cis*-Stilbene was epoxidized to *cis*-stilbene oxide (50%; entry 12) and *trans*-stilbene oxide (13%) together with some benzaldehyde (15%) and 2-phenylacetophenone (8%). However, *trans*-stilbene was only epoxidized to a *trans*-stilbene oxide (47%; entry 13) as a major product along with minor amounts of 2-phenylacetophenone (5%) and benzaldehyde (11%). Various products observed from these aromatic olefins indicated that either the peroxyl radical or oxomanganese(IV) is partially involved as the epoxidizing oxidant because they were proposed to carry out non-stereospecific or radical-induced epoxidations [11b,17,18].

On the other hand, complexes **1a** and **1c** showed similar results to **1b**, thus implying that the electron-deficient group –Cl and electron-rich group –CH_3 showed little effect on the epoxidation reactions.

3.3. *Competitive epoxidations of styrene and para-substituted styrenes for Hammett plots*

To figure out the electronic character of the reactive species in the epoxidation reaction, the substituent electronic effect with styrene and four different *para*-substituted styrenes was studied. The Hammett plots gave the ρ values of −0.68 for **1a** (Fig. 1), −0.66 for **1b** (Fig. S7(a)), and −0.80 for **1c** (Fig. S7(b)). The ρ values suggested that the reactive intermediates are electrophilic, and the reaction rate of the electron-rich styrenes is faster than those of electron-deficient ones.

3.4. *Product distribution of the O — O bond cleavage of PPAA with catalysts* ***1a-1c***

To demonstrate the O—O bond activation process of complexes **1a-**

Table 2
Yield of products generated from PPAA catalyzed by the manganese catalysts **1a**-**1c** in the absence and the presence of cyclohexene in a mixture of CH_2Cl_2/CH_3CN (1:1).[a, 14]

Entry	Catalyst	Cyclohexene[mM]	Heterolysis[b]	Homolysis[b]			Hetero (**5**)/Homo (**6** + **7** + **8**)	Oxidation products		
			5	**6**	**7**	**8**		oxide	-ol	-one
1	**1a**	0	57	22	2	–	**2.4** (70.4/29.6)	–	–	–
2		20	55	19	1	–	**2.8** (73.3/26.7)	45[d]	3[d]	2 [d]
3		40	81	19	1	–	**4.1** (80.2/19.8)	33[c]	2[c]	1 [c]
4		80	83	15	1	–	**5.2** (83.8/16.2)	51[c]	2[c]	2[c]
5		160	89	12	1	–	**6.9** (87.3/12.7)	77[c]	2[c]	2 [c]
6	**1b**	0	70	22	2	–	**2.9** (74.5/25.5)	–	–	–
7		20	66	20	1	–	**3.1** (75.9/24.1)	44[d]	3[d]	2[d]
8		40	58	15	1	–	**3.6** (78.4/21.6)	34[c]	2[c]	1 [c]
9		80	76	14	1	–	**5.1** (83.5/16.5)	46[c]	2[c]	2[c]
10		160	83	12	1	–	**6.4** (86.5/13.5)	60[c]	2[c]	2[c]
11	**1c**	0	62	20	2	–	**2.8** (73.8/26.2)	–	–	–
12		20	69	18	1	–	**3.6** (78.4/21.6)	22[d]	1[d]	1[d]
13		40	58	16	1	–	**3.4** (77.3/22.7)	32[c]	2[c]	1[c]
14		80	69	13	1	–	**4.9** (83.1/16.9)	35[c]	2[c]	2[c]
15		160	83	12	1	–	**6.4** (86.5/13.5)	52[c]	2[c]	2[c]

[a] Reaction conditions: substrate (0–0.16 mmol), catalyst ($1x10^{-6}$ mol), PPAA ($4x10^{-5}$ mol), and solvent (1 mL).
[b] Based on PPAA.
[c] Based on oxidant, PPAA; oxide, -ol, and -one indicate cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one, respectively.
[d] Based on cyclohexene.

Table 3

Yield of products generated from PPAA catalyzed by the manganese catalysts **1a**-**1c** in the absence and the presence of 1-octene in a mixture of CH_2Cl_2/CH_3CN (1:1).[a, 14]

Entry	Catalyst	1-Octene[mM]	Heterolysis[b]	Homolysis[b]			Hetero (**5**)/Homo (**6** + **7** + **8**)	Oxidation product
			5	**6**	**7**	**8**		1-octene oxide
1	**1a**	0	57	22	2	–	**2.4** (70.4/29.6)	–
2		20	75	27	3	–	**2.5** (71.4/28.6)	16[d]
3		40	76	26	3	–	**2.6** (72.4/27.6)	11[c]
4		80	67	26	3	–	**2.3** (69.8/30.2)	16[c]
5		160	70	25	3	–	**2.5** (71.4/28.6)	21[c]
6	**1b**	0	70	22	2	–	**2.9** (74.5/25.5)	–
7		20	72	23	2	–	**2.9** (74.2/25.8)	14[d]
8		40	73	28	3	–	**2.4** (70.2/29.8)	10[c]
9		80	75	22	2	–	**3.1** (75.8/24.2)	15[c]
10		160	73	22	2	–	**3.0** (75.3/24.7)	20[c]
11	**1c**	0	62	20	2	–	**2.8** (73.8/26.2)	–
12		20	66	19	3	–	**3.0** (75.0/25.0)	11[d]
13		40	58	19	2	–	**2.8** (73.4/26.6)	7[c]
14		80	68	18	2	–	**3.4** (77.3/22.7)	11[c]
15		160	65	17	2	–	**3.4** (77.4/22.6)	14[c]

[a] Reaction conditions: substrate (0–0.16 mmol), catalyst ($1x10^{-6}$ mol), PPAA ($4x10^{-5}$ mol), and solvent (1 mL).

[b] Based on PPAA.

[c] Based on oxidant, PPAA.

[d] Based on 1-octene.

Table 4

Competitive oxidations of *cis*-2-octene and *trans*-2-octene by the manganese catalysts **1a**-**1c** with MCPBA in a mixture of CH_2Cl_2/CH_3CN (1:1).[a, 14]

Entry	Catalyst	Substrate	Concentration [mM]	Product yield (%)		Ratio of *cis*- to *trans*-oxide
				cis-oxide	*trans*-oxide	
1	**1a**	*cis-/trans*-2-octene	10 / 10	32 [b]	18 [b]	**1.78** (64.0/36.0)
2			20 / 20	25 [b]	12 [b]	**2.08** (67.6/32.4)
3			40 / 40	34 [c]	16 [c]	**2.13** (68.0/32.0)
4			80 / 80	41 [c]	18 [c]	**2.28** (69.5/30.5)
5	**1b**	*cis-/trans*-2-octene	10 / 10	30 [b]	15 [b]	**2.00** (66.7/33.3)
6			20 / 20	26 [b]	10 [b]	**2.60** (72.2/27.8)
7			40 / 40	33 [c]	12 [c]	**2.75** (73.3/26.7)
8			80 / 80	38 [c]	13 [c]	**2.92** (74.5/25.5)
9	**1c**	*cis-/trans*-2-octene	10 / 10	36 [b]	17 [b]	**2.12** (67.9/32.1)
10			20 / 20	25 [b]	11 [b]	**2.27** (69.4/31.6)
11			40 / 40	38 [c]	14 [c]	**2.71** (73.1/26.9)
12			80 / 80	44 [c]	15 [c]	**2.93** (74.6/25.4)

[a] Reaction conditions: substrate ($1\text{-}8x10^{-5}$ mol), catalyst ($1x10^{-6}$ mol), MCPBA ($3.5x10^{-5}$ mol), and solvent (1 mL).

[b] Based on substrate. [c] Based on MCPBA.

1c, PPAA was employed as a mechanistic probe, because it could determine the O—O bond cleavage mode from degradation products (Scheme 2) [6,19]. When the O—O bond of the Mn-acylperoxo species **2** is cleaved heterolytically, it produces phenylacetic acid (PAA (**5**), pathway (a)). The homolytic cleavage of the O—O bond produces an acyloxyl radical, which decomposes to benzaldehyde (**6**), benzyl alcohol (**7**), and toluene (**8**) with a rapid β-scission (pathway (c)). The direct oxidation reaction of the Mn-acylperoxo species and substrate produces PAA and influences the O—O bond cleavage pattern (pathway (b)).

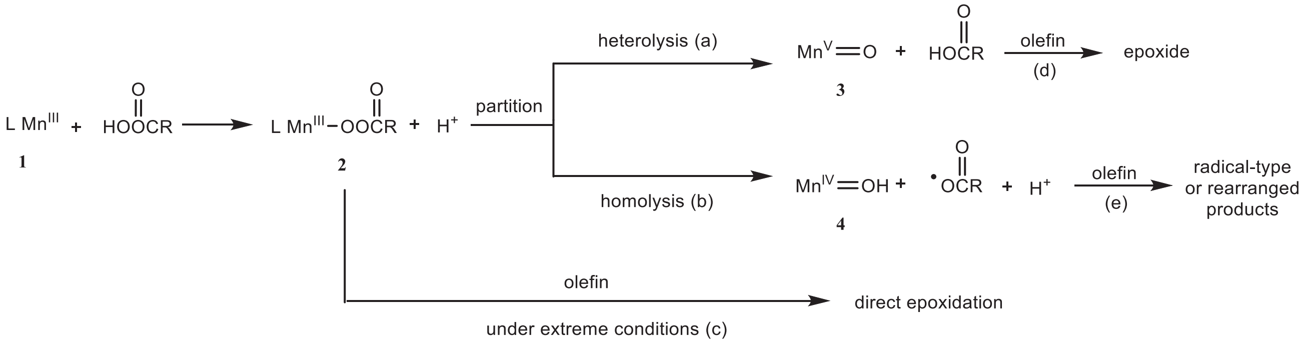
A control experiment by **1a** with PPAA was performed without substrate (Table 2, entry 1). The heterolysis product, PAA, and the homolysis products, benzyl alcohol, benzaldehyde, and toluene, were formed in a ratio of 2.4. This result indicated that the heterolysis (70.4%) and the homolysis (29.6%) of the O—O bond of Mn^{III}-OOC(O)R intermediate **2** occurred simultaneously to afford high-valent $Mn^{V} = O$ (**3**) and $Mn^{IV} = O$ (**4**).

To comprehend the concentration dependence on the ratio variation of heterolysis to homolysis of the O—O bond, we increased the amount of cyclohexene, known as easy-to-oxidize substrate, and monitored the ratio variation of heterolysis to homolysis (entries 2–5) [5,11a,19]. If the Mn^{III}-OOC(O)R **2** directly contributes to the epoxidation reaction, the ratio of heterolysis to homolysis would increase with the increase of the substrate concentration [19c]. The ratio of the heterolysis to homolysis changed from 2.4 to 6.9 with the increase of the cyclohexene concentration (entries 1–5). Similar outcomes were obtained for **1b** and **1c** (entries 6–15). These results suggested that the Mn^{III}-OOC(O)R (**2**) might also be a possible active oxidant in the epoxidation, as formerly proposed for [Mn(bpc)]-, [Mn(salen)]-, and Re_4 cluster-supported Mn complex-catalyzed epoxidations (bpc = 4,5-dichloro-1,2-bis(2-pyridine-2-carboxamido)benzene) [5,7,10].

We changed the substrate from cyclohexene to 1-octene which is known as difficult-to-oxidize alkene to examine the cleavage pattern of the O—O bond on the kind of substrate (Table 3) [19c]. The distribution of the heterolysis and the homolysis was virtually identical, irrespective to the change of 1-octene concentration. These results led us to propose that the Mn^{III}-OOC(O)R would not be active in the epoxidation of difficult-to-oxidize alkene, 1-octene.

3.5. *Competition experiments of cis- and trans-2-octene by catalysts **1a**-**1c***

To further understand the electronic property of the reactive



Scheme 3. Possible mechanism for the production of the active oxidants from the reaction of the manganese complexes with peracids.

oxidants involved in the olefin epoxidation, competition experiments with *cis*- and *trans*-2-octene were conducted (Table 4). The ratio of *cis*- to *trans*-2-octene oxides was increased as the concentration of substrates increased (from 1.78 to 2.28 for complex **1a**; entries 1–4). **1b** and **1c** showed a little bigger change with the increasing amounts of substrates (entries 5–12). These outcomes indicated that the Mn^{III}-OOC(O)R **2** would prefer to react with *cis*- olefins over *trans*-olefins owing to the steric hindrance between **2** and *trans*-type substrate. Thus, we could demonstrate that the species **2** might be somewhat involved in the epoxidation reactions with easy-to-oxidize olefin [20].

3.6. *Mechanism study*

The most reasonable mechanism for the formation of the active intermediates responsible for epoxidation reaction with Mn complexes is proposed in Scheme 3. Peracid reacts with manganese complexes to produce a Mn-acylperoxo intermediate (Mn^{III}-OOC(O)R **2**), which undergoes both the heterolysis and the homolysis to afford $Mn^{V} = O$ (**3**) or $Mn^{IV} = O$ (**4**) in aprotic solvent ($CH_3CN/CH_2Cl_2 = 1:1$). The $Mn^{V} = O$ intermediate might carry out the olefin epoxidation with high stereospecificity, whereas the $Mn^{IV} = O$ complex might cause radical-type oxidation including the production of allylic oxidation by-products and loss of stereospecificity [6,10,13]. In addition, the Mn^{III}-OOC(O)R **2** species could react directly with the easy-to-oxidize substrate to give epoxide, whereas the species **2** might not be competent to the difficult-to-oxidize substrate for the epoxidation reaction [4a,10,20]. On the other hand, to observe the proposed active intermediates like Mn^{III}-OOC(O)R, $Mn^{V} = O$ and $Mn^{IV} = O$, the spectroscopic instruments such as low-temp UV–Vis spectroscopy (-40 °C) and ESI mass spectrometry (0 °C) were applied. However, they were not observed under our test conditions.

4. Conclusion

We prepared the Mn^{III} complexes **1a**, **1b**, and **1c**, which showed efficient various olefin epoxidation reactions with MCPBA as peracid oxidant under mild conditions. Mn^{III} complexes **1a** and **1c** with the electron-deficient group –Cl and electron-rich group $–CH_3$ showed little substituent effect on the epoxidation reactions. The Hammett study suggested that the active oxidants involved in the olefin epoxidation reaction are electrophilic. The use of PPAA as a mechanistic probe demonstrated that peracid reacts with manganese complexes to produce an initial Mn-acylperoxo intermediate (Mn^{III}-OOC(O)R), which undergoes both the heterolysis and the homolysis to afford $Mn^{V} = O$ or $Mn^{IV} = O$. In addition, the Mn^{III}-OOC(O)R **2** species could react directly with the easy-to-oxidize substrate to give epoxide, whereas the species **2** might not be competent to the difficult-to-oxidize substrate for the epoxidation reaction. Competition experiments with *cis*- and *trans*-2-octene showed that the ratios of *cis*- to *trans*-2-octene oxides were increased as the concentration of substrates increased. This observation further proved that the species **2** might be somewhat involved in the epoxidation reactions with easy-to-oxidize olefin. Taken all together, Mn^{III}-OOC(O)R, $Mn^{IV} = O$, and $Mn^{V} = O$ species might be key intermediates in olefin epoxidation reaction under this catalytic system. However, the species **2** might not be competent to the difficult-to-oxidize substrate for the epoxidation reaction. Future studies will concentrate on attempts to understand the physical properties of the active oxidants.

CRediT authorship contribution statement

Sojeong Lee: Conceptualization, Investigation, Validation, Visualization, Writing-Origianl draft. **Soyoung Park:** Investigation, Validation. **Myoung Mi Lee:** Investigation, Validation. **Jiyoung Lee:** Investigation, Validation. **Cheal Kim:** Supervision, Writing-review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120306.

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[14] The similar results of Tables 1-4, which were obtained under the slightly different conditions, were previously presented in MS degree by M. M. Lee (the third author of this manuscript); Hydrocarbon Oxidations and Transesterification by Using Heterogeneous Catalysts and Homogeneous Catalysts, MS degree (Seoul National University of Science and Technology), 2016. However, the Mn complexes 1a-1c were not characterized at that time. In this study, we clearly characterized the Mn complexes by 1H NMR, 13C NMR, ESI-MS and elemental analysis. Then, we reexamined the catalytic epoxidation reactions (Tables 1-4) with Mn complexes and presented the results herein.

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