



# Synthesis, crystal structures and catalytic abilities of new macrocyclic bis-pyridineamido Mn<sup>III</sup> and Fe<sup>III</sup> complexes

Li Yang<sup>a,b</sup>, Zhiqing Wu<sup>a</sup>, Lei Liang<sup>a</sup>, Xiangge Zhou<sup>a,\*</sup>

<sup>a</sup>Institute of Homogeneous Catalysis, College of Chemistry, Sichuan University, Chengdu 610064, China

<sup>b</sup>Department of Chemical Engineering, Yibin University, Yibin 640000, China

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## ABSTRACT

A new macrocyclic ligand H<sub>2</sub>L (H<sub>2</sub>L = 1,2-[bis(6'-pyridine-2'-carboxamido)-ethane]benzene) has been designed and synthesized by condensation of pyridine-carboxylic acid and diamine. Its Mn(III) and Fe(III) complexes, [Mn(L)Cl (DMF)] and [Fe(L)Cl], were prepared and respectively characterized by IR, UV-Vis, ESI-Mass, elemental analysis and X-ray single crystal diffraction. The catalytic abilities of them were examined, and up to 95% yield was achieved in epoxidation of styrene. The preliminary investigation of catalytic mechanism by manganese complex was carried out, suggesting the involvement of Mn(V) oxo species during catalysis.

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## 1. Introduction

Macrocyclic metal complexes have attracted considerable attention as biomimetic models due to their similarities to oxidation metalloenzymes found in biological systems [1,2]. There have been numerous reports on the catalytic oxidation of organic substrates by porphyrin complexes [3,4]. Meanwhile, development of other planar tetradentate ligands, such as Schiff base and amido ligands is highly desirable attributing to their facility in modification [5–12].

As one of amido ligands, bis-pyridineamide seems to be a good candidate for catalytic oxidation studies because of its stability to resist oxidation. The negative charges might be highly delocalized, which resembles the porphyrinato ligand to some extent as shown in Scheme 1. Both Che [13–15] and us [16] reported recently that bis-pyridineamide Mn(III)/Fe(III) complexes exhibited moderate to high catalytic abilities in epoxidation of alkenes.

On the other hand, the mechanism studies revealed the high-valent transition intermediates to be active oxidizing species formed in metal-catalyzed oxidation reactions [17–19]. The formation of metal-oxo species by porphyrin- or salen-complex with oxidant such as PhIO was also reported [20,21]. Aroused by the research of Collins and co-workers, who described the macrocyclic tetraamido ligands to be capable of stabilizing unusual high-valent transition metal ions such as cobalt(IV) and iron(IV) [22–24], here-

in is described the synthesis of novel macrocyclic bis-pyridineamido complexes with cheap and relatively nontoxic Mn(III) and Fe(III) ions [25], which exhibited higher catalytic abilities in epoxidation than the non-annular analogs. The preliminary investigation of the catalytic mechanism is also reported.

## 2. Results and discussion

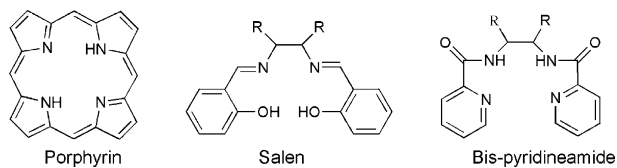
### 2.1. Synthesis of ligand and complexes

Ligand **5** and corresponding Mn(III) and Fe(III) complexes **6** and **7** were prepared starting from 2-methylpyridine as shown in Scheme 2. 2-Methylpyridine was reacted with *n*-butyllithium and 1,2-dibromoethane to give a coupled pyridine **1**. Peracid oxidation followed by treatment with *N,N*-dimethylcarbonyl chloride and trimethylsilyl cyanide gave dinitrile derivative **3**. After hydrolysis, dicarboxylic acid **4** was obtained and then condensed with diamine to give the ligand **5** with total yield of 31%. The manganese(III) and iron(III) complexes **6** and **7** were then obtained by the reaction of ligand **5** and corresponding metal ion in DMF.

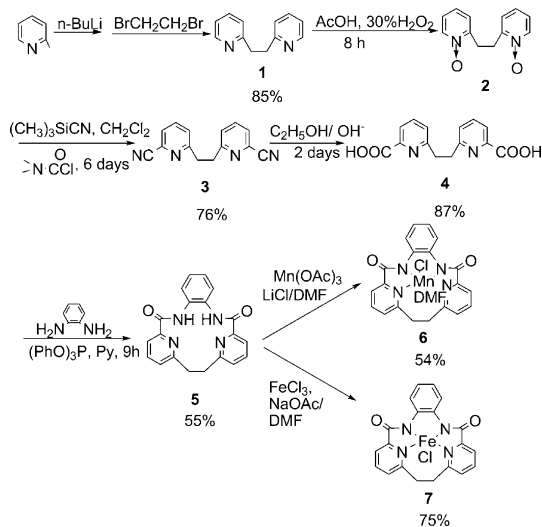
The new tetradentate ligand **5** and corresponding complexes **6** and **7** are in general air- and moisture-stable. All the complexes were characterized by MS, IR, UV-Vis, and elemental analysis, the single crystal structures of the compounds **5**, **6** and **7** have also been determined. The infrared spectra of the ligand and complexes displayed, in general, a large number of intense peaks in the range of 1600–600 cm<sup>-1</sup>. Disappearance of N–H stretching bands (3291 cm<sup>-1</sup>) in IR spectra supported the formation of Mn(III) and Fe(III) complexes.

\* Corresponding author. Tel./fax: +86 28 85412026.

E-mail address: [zhouxiangge@scu.edu.cn](mailto:zhouxiangge@scu.edu.cn) (X. Zhou).



Scheme 1. Some of usually used planar tetradentate ligands.



Scheme 2. Synthetic routine of ligand and complexes.

Table 1  
Selected bond lengths (Å), bond angles (°).

Ligand 5			
N(1)–C(1)	1.407(3)	N(1)–C(7)	1.350(3)
C(11)–C(12)	1.394(4)	C(14)–C(15)	1.491(4)
C(7)–N(1)–C(1)	129.9(2)	N(4)–C(20)–C(19)	112.9(3)
C(12)–C(13)–C(14)	113.6(2)	C(20)–N(4)–C(2)	127.6(3)
N(1)–C(7)–C(8)	111.1(2)	C(15)–C(14)–C(13)	114.0(3)
Complex 6			
Mn(1)–N(1)	1.947(3)	Mn(1)–N(3)	1.998(3)
Mn(1)–N(2)	1.943(2)	Mn(1)–N(4)	2.011(2)
Mn(1)–O(3)	2.428(3)	Mn(1)–O(3)	2.428(3)
Mn(1)–Cl(1)	2.4934(12)	N(1)–Mn(1)–N(4)	82.56(12)
N(1)–Mn(1)–N(2)	80.90(13)	N(2)–Mn(1)–N(4)	159.94(11)
N(1)–Mn(1)–N(3)	161.35(12)	N(3)–Mn(1)–N(4)	113.20(13)
N(2)–Mn(1)–N(3)	81.53(13)	N(2)–Mn(1)–O(3)	83.88(10)
N(1)–Mn(1)–O(3)	89.37(11)	N(4)–Mn(1)–Cl(1)	91.67(8)
N(3)–Mn(1)–O(3)	82.56(11)	N(3)–Mn(1)–Cl(1)	102.29(8)
N(4)–Mn(1)–O(3)	84.67(10)	N(3)–Mn(1)–Cl(1)	89.84(8)
N(1)–Mn(1)–Cl(1)	99.98(9)	O(3)–Mn(1)–Cl(1)	169.45(8)
Complex 7			
Fe(1)–N(1)	1.871(2)	Fe(1)–N(4)	1.889(2)
Fe(1)–N(2)	2.032(2)	Fe(1)–Cl(1)	2.3080(8)
Fe(1)–N(3)	2.016(2)	N(1)–Fe(1)–N(3)	161.28(10)
N(1)–Fe(1)–N(4)	82.38(10)	N(4)–Fe(1)–N(2)	155.32(10)
N(1)–Fe(1)–N(2)	82.39(10)	N(3)–Fe(1)–N(2)	107.69(10)
N(4)–Fe(1)–N(3)	82.51(9)	N(4)–Fe(1)–Cl(1)	108.32(8)
N(1)–Fe(1)–Cl(1)	101.67(8)	N(2)–Fe(1)–Cl(1)	93.71(7)
N(3)–Fe(1)–Cl(1)	93.53(7)		

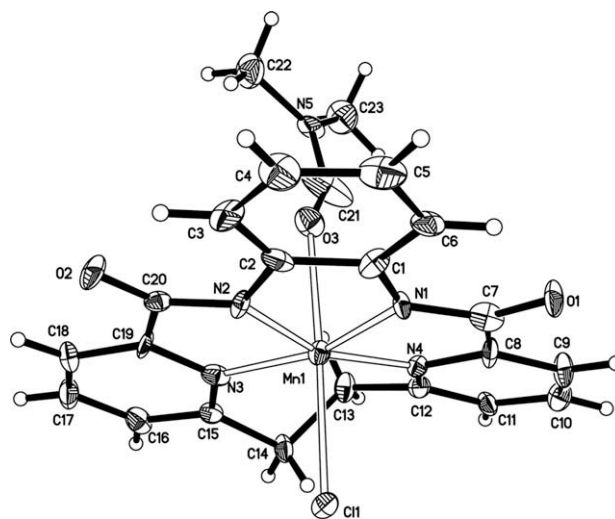


Fig. 2. Molecular structure of **6** with thermal ellipsoids set at 30% probability.

Mn–N<sub>amide</sub> (1.945 Å) is shorter than that of Mn–N<sub>pyridine</sub> (2.00 Å). Both the Mn–Cl and Mn–O<sub>DMF</sub> distances are slightly longer than those of non-annular complexes such as H<sub>2</sub>bpc(1,2-bis(pyridine-2'-carboxamido)-4,5-dichloro-benzene) [26], H<sub>2</sub>bmcp(1,2-bis(4'-methylpyridine-2'-carboxamido)-4,5-dichlorobenzene) reported by us [27].

### 2.2.3. [Fe(L)Cl] (**7**)

A perspective view of compound **7** is depicted in Fig. 3. The selected bond distances and angles are listed in Table 1.

As shown in Fig. 3, complex **7** adopts a five-coordinated structure with two pyridine and two deprotonated amide N atoms in the equatorial plane, the axial position is occupied by the Cl<sup>−</sup> ion. Interestingly, dinuclear complexes were observed in the packing plot of complex **7**, crosslinked by the weak intermolecular Fe–O<sub>amide</sub> (3.011 Å) interactions compared with the normal Fe–O<sub>amide</sub> distance of about 2.0 Å. The Fe(III)–N<sub>pyridine</sub> distances of 2.016–

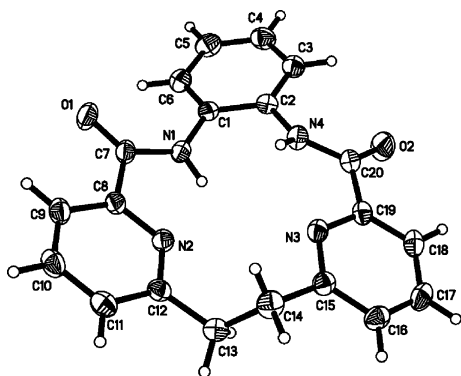


Fig. 1. Molecular structure of **5** with thermal ellipsoid set at 30% probability.

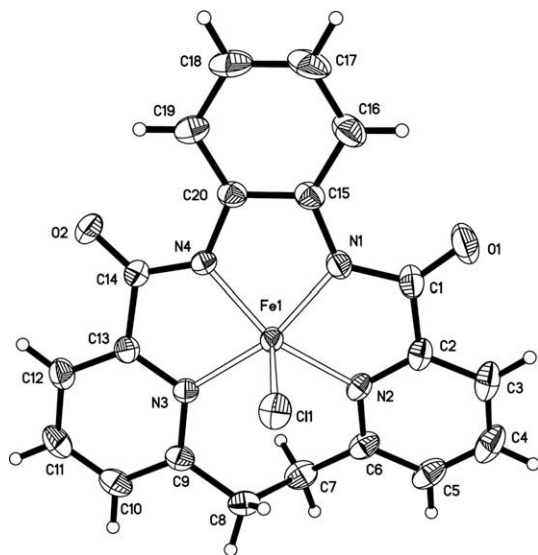


Fig. 3. Molecular structure of **7** with thermal ellipsoids set at 30% probability.

2.032 Å are comparable to those of 1.997–2.003 Å in the  $[\text{Fe}(\text{bpc})(1\text{-MeIm})_2]\text{ClO}_4$  [28], but considerably shorter than those of 2.170 and 2.174 Å in  $[\text{Fe}(\text{bbpc})\text{Cl}_2](\text{Et}_4\text{N})$  ( $\text{H}_2\text{bbpc} = 1,2\text{-bis}(4'\text{-}t\text{-butylpyridine-2'}\text{-carboxamido})\text{-4,5-dichlorobenzene}$ ) [29]. The  $\text{Fe}(\text{III})\text{-N}_{\text{amide}}$  distances are 1.872–1.889 Å. Similar values (1.895–1.927 Å) in the macrocyclic  $\text{Fe}(\text{IV})\text{-tetraamide}$  complex have also been reported [30]. The  $\text{Fe}(\text{III})\text{-Cl}$  distance of 2.308(1) Å was slightly shorter than those of 2.330 and 2.388 Å in  $[\text{Fe}(\text{bbpc})\text{Cl}_2](\text{Et}_4\text{N})$  [29].

### 2.3. Electrochemistry

Complexes **6** and **7** were furthermore characterized by electrochemical study. The typical cyclic voltammograms recorded in DMF with a glassy carbon working electrode are illustrated in Fig. 4. The  $E_{1/2}$  and peak-to-peak separation ( $\Delta E_p$ ) values of **6** were  $-0.17\text{ V}$  (vs. SCE) and 80 mV, indicating a reversible one-electron redox process ( $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ ), which is in accordance with the  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$  couple of non-annular complexes  $[\text{Mn}(\text{bpc})\text{X}]$  ( $\text{X} = \text{Cl}, \text{N}_3, \text{NCS}$ ) ( $\text{H}_2\text{bpc} = 1,2\text{-bis}(2'\text{-carboxamido})\text{-4,5-dichlorobenzene}$ ) [31]. Compared with **6**, the cyclic voltammogram of **7** shows the

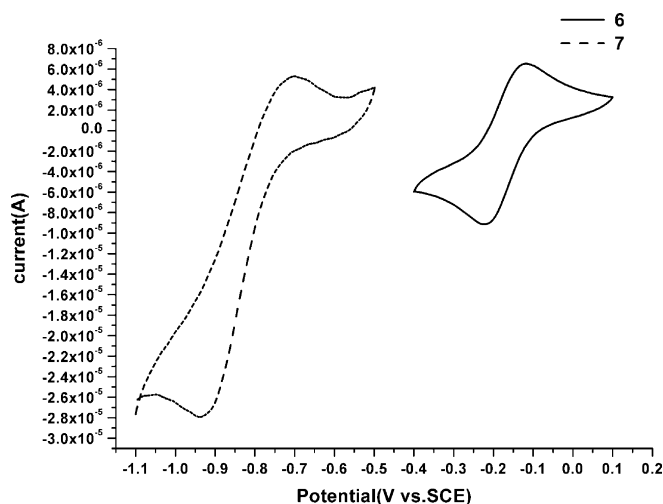


Fig. 4. Cyclic voltammograms of a  $1.0 \times 10^{-3}\text{ M}$  solution of **6** and **7** in anhydrous DMF (0.1 M TBAP) at a glassy-carbon electrode (298 K), SCE at a reference electrode with a scan rate of  $200\text{ mV S}^{-1}$ .

separation of 139 mV between them ( $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$ ), indicating a pseudo-reversible one-electron redox ( $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ ) and  $E_{1/2}[E_{\text{pa}} + E_{\text{pc}}/2]$  is equal to  $-0.82\text{ mV}$  (vs. SCE).

### 2.4. Catalytic epoxidation

The catalytic activities of complexes **6** and **7** were examined in the epoxidation of styrene with oxidants such as PhIO, NaClO or  $\text{H}_2\text{O}_2$  as shown in Scheme 3.

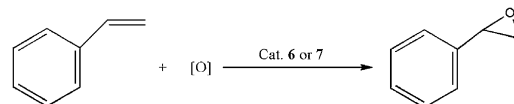
In general, among these oxidants, PhIO showed to be beneficial to the catalysis, while the other two oxidants  $\text{H}_2\text{O}_2$  and NaClO resulted in less than 15% yields in all cases under the reaction conditions. The results of catalytic epoxidation of styrene by **6** and **7** with PhIO were listed in Table 2. It is observed that the yield increased considerably within the first 3 h during reaction. After that, the yields increased slightly, which results from the appearance of the oxidative-cleavage product, namely benzaldehyde. Similar with our previous study [16], central metal plays an important role, and  $\text{Mn}(\text{III})$  complex exhibited much higher catalytic ability and selectivity than  $\text{Fe}(\text{III})$  analogue (entries 1 and 11, or 3 and 13, Table 2). The same rule could also be observed in salen and porphyrin systems [32–34]. It is presumed that the easier formation of high-valent Mn complex resulted in the higher catalytic ability than Fe analogue during reaction [35].

Variation of the amount of catalyst was also studied. When 1%, 2%, 5%, 7% or 10% catalyst **6** was applied, styrene oxide was obtained in the yields 88%, 90%, 94%, 94% or 95%, respectively. It suggested that more catalyst than 5% was not necessary. Solvent, on the other hand, exhibited significant influence on the results, here acetonitrile (entries 1–3, Table 2) was chosen as the best. Polar aprotic solvent seemed to be beneficial for the catalysis by  $\text{Mn}(\text{III})$  complex **6**, while changing solvent seemed to be less effective on the activity of **7** (entries 11–13, Table 2). Increasing the reaction temperature resulted in the decline of yield (entries 3 and 10, Table 2).

More importantly, the novel designed macrocyclic  $\text{Mn}(\text{III})$  complex showed much higher catalytic activity under similar conditions than the non-annular analogue. For example, **6** gave the yield of 94% in  $\text{CH}_3\text{CN}$  (entry 3, Table 2), while only 69% was achieved by non-annular analogue  $[\text{Mn}(\text{bpc})\text{Cl}(\text{DMF})]$  [15]. Thus, the best result 95% yield could be obtained under the optimized conditions by catalyst **6**, which is comparable with about 90% by Mn-porphyrin complex (2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl) porphyrinato manganese chloride) [36], and much higher than 79% by Salen complex [37]. The other two substrates cyclohexene and indene were also tried by this catalytic system with moderate to high yields 72% and 85%, respectively.

### 2.5. Catalytic mechanism study

The preliminary investigation in the mechanism of catalytic epoxidation was then carried out with complex **6**. The reaction between **6** and PhIO was monitored. During the reaction, the color of solution slowly changed from brown to dark green, which was consistent with  $\text{Mn}(\text{V})$  porphyrin-oxo or nonporphyrin macrocyclic tetraamido-oxo complexes [38,39]. The appearance of two new peaks around 340 and 380 nm in UV–Vis spectrum is quite similar



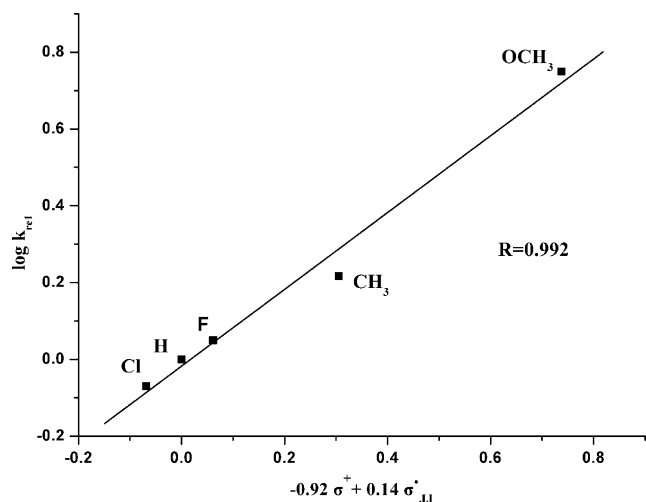
Scheme 3. Catalytic epoxidation of styrene by catalyst **6** or **7**.

**Table 2**  
Epoxidation of styrene with PhIO catalyzed by complex **6** and **7**.<sup>a</sup>

Entry	Cat	T (h)	T (°C)	Dosage (mol%)	Solvent	Conversion (%) <sup>b</sup>	Yield (%) <sup>b</sup>
1	<b>6</b>	8	25	5	CH <sub>2</sub> Cl <sub>2</sub>	86	78
2	<b>6</b>	8	25	5	ClCH <sub>2</sub> CH <sub>2</sub> Cl	85	74
3	<b>6</b>	8	25	5	CH <sub>3</sub> CN	95	94
4	<b>6</b>	8	25	1	CH <sub>3</sub> CN	90	88
5	<b>6</b>	8	25	2	CH <sub>3</sub> CN	90	90
6	<b>6</b>	8	25	7	CH <sub>3</sub> CN	94	94
7	<b>6</b>	8	25	10	CH <sub>3</sub> CN	97	95
8	<b>6</b>	16	−10	5	CH <sub>3</sub> CN	95	95
9	<b>6</b>	12	0	5	CH <sub>3</sub> CN	95	94
10	<b>6</b>	5	40	5	CH <sub>3</sub> CN	88	85
11	<b>7</b>	8	25	5	CH <sub>2</sub> Cl <sub>2</sub>	78	37
12	<b>7</b>	8	25	5	ClCH <sub>2</sub> CH <sub>2</sub> Cl	75	32
13	<b>7</b>	8	25	5	CH <sub>3</sub> CN	80	39

<sup>a</sup> Reactions were performed by using catalyst, substrate (0.5 mmol) and PhIO (0.1 mmol) in 5 mL solvent.

<sup>b</sup> Determined by GC based on PhIO used.



**Fig. 5.** Plot of  $\log k_{rel}$  vs.  $(\sigma^+, \sigma_J)$  for the epoxidation of substituted styrenes  $p$ -YC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> (Y = MeO, Me, F, Cl) by PhIO catalyzed by [Mn(L)(DMF)Cl]. The  $R$  value for the multiple regressions is indicated.

to Mn(V)=O corrole species [40]. The electrospray ionization mass spectrum of the mixture of **6** and PhIO in CH<sub>2</sub>Cl<sub>2</sub> further confirms the existence of [O=Mn<sup>V</sup>(L)]<sup>+</sup>(H<sub>2</sub>L = **5**) with the peak at  $m/z$  413. Presumably, the color conversion from brown to dark green proceeds simultaneously with the formation of metal-oxo species.

To probe the nature of the intermediates formed in the rate-limiting step during the catalytic epoxidation by **6**, the substitution effect was examined by measuring the rates ( $k_{rel}$ ) of substituted styrenes  $para$ -YC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> (Y = MeO, Me, F, H, Cl) relative to that of styrene, which revealed that electron-donating substituents promote the epoxidation process. A dual-parameter ( $\sigma^+$ ,  $\sigma_J$ ) fitting of  $\log(k_X/k_H)$ , as established by Jiang [41], through multiple regression gave rise to good linearity ( $R = 0.992$ ) with  $\rho^+$  and  $\rho_J$  values of  $-0.92$  and  $0.14$ , respectively (Fig. 5), suggesting that polar effects are dominant during catalysis.

Although it is difficult to delineate the accurate mechanism, on the basis of our studies as well as references, it is suggested the catalysis by **6** might include the Mn(V)=O species during reaction.

### 3. Conclusion

Synthesis, structures and catalytic abilities in epoxidation of olefins by novel macrocyclic bis-pyridineamido Mn(III) and Fe(III) complexes have been reported. Higher catalytic abilities were

observed than the reported planar non-annular complexes. The preliminary studies of catalytic mechanism indicated the catalysis by **6** might include Mn(V)=O species. A series of asymmetric catalysis assay by corresponding analogs are currently in progress in our laboratory.

## 4. Experimental

### 4.1. Materials and reagents

THF was dried over sodium benzophenone ketyl and distilled under N<sub>2</sub> before use. Methanol was dried over magnesium methoxide and distilled before use. Olefins were purchased from Aldrich or Lancaster and purified by standard procedures before use [42]. All other chemicals were obtained commercially and used as received. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate with sodium hydroxide solution [43]. Sodium cyanide was dried in vacuum at 120 °C. 1,2-Bis(2'-pyridyl)-ethane (**1**) was synthesized according to the literature procedures [44]. Unless otherwise indicated, standard Schlenk techniques were used during all syntheses to avoid exposure to dioxygen or water.

### 4.2. Instrumentation/analytical procedures

All melting points were measured by a micro-melting apparatus and uncorrected. Ultraviolet-Visible (UV-Vis) spectra were recorded on a HP 8453 spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AV-400 (400 or 100 MHz) spectrometer. Chemical shifts were measured relative to tetramethylsilane as the internal reference. Gas chromatography (GC) measurements were carried out on an Agilent 6890 series chromatograph equipped with a flame ionization detector. Mass spectra data were recorded on a Finnigan MAT 4510 spectrometer. Elemental analysis were performed on a Carlo Erba 1106 instrument. IR spectra were performed on a NEXUS-670 FT-IR spectrophotometer in the 4000–400 cm<sup>−1</sup> region using KBr disks. Cyclic voltammetry of all complexes was performed with a Autolab-Pgstat 302 electrochemical analyzer, using a three-electrode system on conjunction with a purged dinitrogen gas inlet and outlet. A saturated calomel reference electrode, a glassy carbon working electrode and a platinum auxiliary electrode were used in this three-electrode measurement. The complex was at  $1.0 \times 10^{-3}$  M concentration with tetrabutylammonium perchlorate (TBAP) (0.1 M) as the support electrolyte in DMF solution. All solutions were purged with N<sub>2</sub> prior to analysis.

#### 4.3. Synthesis of coupling pyridine bis(*N*-oxide) (**2**)

The method was similar with the literature procedure [45]. After removal of solvent, a slightly yellow solid was obtained without further purification or characterization.

#### 4.4. Synthesis of 1,2-bis(2-(6'-cyanopyridyl)-ethane) (**3**)

Prepared by the modified method of Fife [46]. The solution of coupling pyridine bis(*N*-oxide) **2** (8.6 g, 0.04 mol) in anhydrous dichloromethane (150 mL) was added trimethylsilyl cyanide (8 g, 0.081 mol) at room temperature. Dimethylcarbonyl chloride (8.7 mL, 0.08 mol) in dichloromethane (50 mL) was then added dropwise with stirring over 30 min. The mixture was kept stirring at room temperature for 6 days. A solution of 20% aqueous potassium carbonate (80 mL) was added. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane (2 × 100 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, and concentrated in vacuo to obtain the crude product. The off-white pure product was obtained by washing with ethanol and dried in vacuo (7.1 g, 76%). M.p. 162.5–164 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.34 (s, 4H, -PyCH<sub>2</sub>CH<sub>2</sub>Py-), 7.41 (d, *J* = 8.0 Hz, 2H, H<sub>Py</sub>), 7.35 (d, *J* = 7.6 Hz, 2H, H<sub>Py</sub>), 7.73 (t, *J* = 7.6 Hz, 2H, H<sub>Py</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 36.30, 117.42, 126.23, 127.02, 133.26, 137.23, 162.62.

#### 4.5. Synthesis of 1,2-bis(2-(6'-carboxypyridyl)-ethane) (**4**)

A solution of **3** (2.34 g, 0.01 mol) in 70 mL hot ethanol was added 70 mL 3 N sodium hydroxide. The mixture was kept at 85 °C for 3 days. The pH was adjusted to ca. 3–4 by 6 N HCl. A white precipitate was formed and collected by filtration, washed with water and dried in vacuo to give product 2.36 g (87%); m.p. 212 °C. <sup>1</sup>H NMR (400 MHz, DMSO): δ = 3.23 (s, 4H, -PyCH<sub>2</sub>CH<sub>2</sub>Py-), 7.53 (m, 2H, H<sub>Py</sub>), 7.87 (m, 4H, H<sub>Py</sub>); <sup>13</sup>C NMR (100 MHz, DMSO): δ = 36.66, 122.29, 126.27, 137.68, 147.74, 160.73, 166.22. MS (EI): *m/z* = 272[M<sup>+</sup>]. Elemental Anal. Calc. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 61.76; H, 4.44; N, 10.29. Found: C, 61.52; H, 4.76; N, 10.10%.

#### 4.6. Synthesis of 1,2-bis(6'-pyridine-2'-carboxamido)-ethane]benzene (**5**)

The ligand was prepared according to the similar method with modification [47]. A solution of the acid **4** 1.36 g (5 mmol) in 50 mL dry pyridine was slowly added to a solution of 0.54 g (5 mmol) *o*-phenylenediamine in 15 mL pyridine. After heating the solution to 50 °C, 2.61 mL (10 mmol) triphenylphosphite was added dropwise with continuous stirring. The temperature was then raised and kept at 100 °C for 9 h, the mixture was cooled down. After removal of pyridine under reduced pressure, the resulting brown oil was dissolved in dichloromethane, washed with water and sodium bicarbonate solution, and then dried over magnesium sulphate. After filtration and removal of solvent, the residue was washed with ethanol and dried in vacuo to afford off-white pure product 0.94 g (yield 55%). Crystals suitable for X-ray diffraction were grown *via* slow evaporation of a solution of the ligand in xylene/pyridine. m.p. 218–219 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.22 (s, 4H, -PyCH<sub>2</sub>CH<sub>2</sub>Py-), 7.20 (m, 2H, H<sub>benzene</sub>), 7.31 (d, *J* = 7.6 Hz, 2H, H<sub>Py</sub>), 7.77 (t, *J* = 8.0 Hz, 2H, H<sub>Py</sub>), 8.04 (d, *J* = 7.6 Hz, 2H, H<sub>Py</sub>), 8.19 (m, 2H, H<sub>benzene</sub>), 10.72 (s, 2H, H<sub>amide</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 35.00, 118.66, 121.03, 124.00, 125.10, 127.44, 137.41, 148.31, 160.11, 161.39. Selected IR data (KBr, cm<sup>-1</sup>): ν = 3291(N–H), 1700, 1674 (C=O), 1585 (C–N), 1566, 1319, 1296, 1223, 1078, 764.

MS (EI): *m/z* = 344[M<sup>+</sup>]. Elemental Anal. Calc. for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>: C, 69.76; H, 4.65; N, 16.28. Found: C, 69.42; H, 4.78; N, 16.15%.

#### 4.7. Synthesis of [Mn(L)Cl(DMF)] (**6**)

Two hundred and three milligrams ligand **5** (0.6 mmol) was dissolved in 50 mL hot DMF. 55 mg LiCl (1.3 mmol) and 160 mg Mn(OAc)<sub>3</sub> · 2H<sub>2</sub>O (0.6 mmol) were then added. The solution was heated at 80 °C for 30 min. After removal of solvent under vacuum, the brown solid product was obtained after recrystallization from DMF/methanol. Yield: 170 mg (54%). Dark brown needles of **6** suitable for X-ray analysis were grown by diffusion of diethyl ether into a DMF solution of the complex. Selected IR data (KBr, cm<sup>-1</sup>): ν = 1640 (C=O), 1598 (C–N), 1571, 1355, 1282, 1141, 1032, 1081, 759. Elemental Anal. Calc. for C<sub>23</sub>H<sub>21</sub>ClN<sub>5</sub>O<sub>3</sub>Mn: C, 54.61; H, 4.18; N, 13.85. Found: C, 54.45; H, 4.34; N, 13.83%. MS (FAB): 397.3 ([Mn(L)]<sup>+</sup>).

#### 4.8. Synthesis of [Fe(L)Cl] (**7**)

One hundred and thirty-two milligrams ligand **5** (0.38 mmol) and sodium acetate (0.08 g, 0.76 mmol) were added to 20 mL CH<sub>3</sub>OH solution of FeCl<sub>3</sub> · 6H<sub>2</sub>O (244 mg, 0.9 mmol). The color of the mixture turned into green immediately. After the mixture was refluxed for 3 h, the dark green crystals were collected by filtration, washed with methanol, and dried under vacuum (123 mg, yield 75%). Crystals suitable for X-ray diffraction were grown *via* diffusion of Et<sub>2</sub>O into a DMF solution of the complex. Selected IR data (KBr, cm<sup>-1</sup>): ν = 1629 (C=O), 1602 (C–N), 1572, 1346, 1287, 1142, 1083, 1081, 762. Elemental Anal. Calc. for C<sub>20</sub>H<sub>14</sub>ClN<sub>4</sub>O<sub>2</sub>Fe: C, 55.39; H, 3.25; N, 12.92. Found: C, 55.61; H, 3.15; N, 13.00%. MS (FAB): 398.3 ([Fe(L)]<sup>+</sup>).

#### 4.9. General procedure for catalytic epoxidation of styrene

Iron(III) or manganese(III) complex, PhIO (0.1 mmol) and styrene (0.5 mmol) in solvent (5 mL) were stirred at room temperature for 8 h. After filtration, the residue was determined by GC with 1,4-dichlorobenzene as internal standard and the yields were calculated based on PhIO used.

#### 4.10. General procedure for the competition experiments [48,49]

A 10 mL round bottom flask was charged with styrene (52.6 mg, 0.5 mmol), *p*-substituted styrene (0.5 mmol), 1,4-dichlorobenzene (0.5 mmol, internal standard), complex **6** (12.3 mg, 0.025 mmol), PhIO (0.5 mmol) and acetonitrile (2.0 mL) under nitrogen. The reaction mixture was stirred for 8 h at room temperature. After filtration, conversion of each olefin was determined by GC analysis.

#### 4.11. Crystallography

Diffraction data for **5**, **6**, and **7** were collected at 296 K on a Bruker SMART 1000 system. Mo Kα (0.71073 Å) radiation was used, and the data were corrected for absorption. A solution was provided by direct method with SHELXS-97, refined by full-matrix least-squares on *F*<sup>2</sup> using SHELXL-97 and analyzed with PLATON [50]. All non-H atoms were refined with anisotropic thermal parameters. Aryl and alkyl H atoms were included at estimated positions using a riding model. Crystal and refinement data are summarized in Table 3. In these three crystal structures, the crystal sample of **6** is very small (0.18 × 0.06 × 0.06 mm<sup>3</sup>), its diffraction intensity are very weak. Some of atoms have errors on anisotropic parameters and less weight, its Flack parameter is –0.03(3).

**Table 3**  
Crystallographic data.

	5	6	7
Empirical Formula	C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> · 1/2 (C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> )	MnCl(HCONMe <sub>2</sub> )(C <sub>20</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )	Fe(Cl)(C <sub>20</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> )
<i>M</i>	397.45	505.84	433.65
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	8.9987(2)	8.6974(7)	11.8532(2)
<i>b</i> (Å)	16.1908(4)	8.3283(6)	8.20280(1)
<i>c</i> (Å)	12.8798(3)	15.1408(11)	19.3507(3)
<i>R</i> (°)	90	90	90
	90.359(2)	91.194(4)	106.8890(1)
	90	90	90
<i>V</i> (Å <sup>3</sup> )	1876.50(8)	1096.48(14)	1800.31(5)
<i>Z</i>	4	2	4
<i>T</i> (K)	296(2)	296(2)	296(2)
<i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.407	1.532	1.600
Number of data	13 641	9779	24 687
Number of unique data	4272	4253	4142
Number of parameters	272	298	253
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.092	0.761	1.011
<i>R</i> (int)	0.0696	0.1225	0.0406
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0717, 0.1912	0.0489, 0.0694	0.0397, 0.1192
<i>R</i> indices (all data) <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.1613, 0.2415	0.1772, 0.0951	0.0515, 0.1263

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## Appendix A. Supplementary material

CCDC 208392, 208393, 208394 contain the supplementary crystallographic data for **5**, **6**, and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.019.

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