间位苯基桥联的锰(Ⅲ)双咔咯的合成、表征及催化氧化性质

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摘要：通过间苯二甲醛与 5-氟苯基二吡咯甲烷反应合成了一种新的间位苯基桥联的双咔咯 **1**，并利用锰盐与自由咔咯反应制备了其锰的金属配合物 **2**。采用紫外、质谱、核磁、XPS 等手段对化合物进行了表征。以苯乙烯为底物考察了锰双咔咯 **2** 的催化氧化性质，探讨了时间、溶剂、氧源、轴向配体对催化反应的影响。结果表明以亚碘酰苯和间氯过氧苯甲酸为氧源时催化的主要产物为环氧苯乙烷，而以双氧水和叔丁基过氧化氢为氧源时则主要产物为苯甲醛；在极性溶剂中的催化氧化产率较高。轴向配体对催化氧化有促进作用，不同轴向配体对催化反应产率提高的顺序是：1-甲基咪唑>吡啶>咪唑。

关键词：双咔咯；锰；催化氧化；苯乙烯；轴向配体

Synthesis, Characterization and Catalytic Oxidation Activity of a Phenyl Bridged Dimanganese(Ⅲ) Biscorrole

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Abstract: A *m*-phenyl bridged biscorrole **1** was synthesized by reaction of 1, 3-phthalaldehyde with 5-pentafluorophenyl dipyrromethane. The free base biscorrole was converted into its corresponding manganese complex **2** on reaction with a manganese salt. These compounds were characterized by UV-Vis, MS, NMR and XPS. The catalytic oxidation of manganese biscorrole complex **2** was investigated by using styrene as the substrate. The influence of reaction time, solvents, oxidants and axial ligands on the catalytic reaction was also examined. The results reveal that styrene epoxide is the major product when iodosylbenzene or *m*-chloroperoxybenzoic acid is used as the oxidant, while benzaldehyde is the major product when hydrogen peroxide or *tert*-butyl hydroperoxide is used as the oxidant. The percentage conversion is higher in polar solvents. The significant effect of axial ligand on the rate of catalytic oxidation is observed in the following order: 1-methylimidazole>pyridine>imidazole.

Key words: biscorrole; manganese; catalytic oxidation; styrene; axial ligand

　　Corrole chemistry has been one of the most active branch of contemporary porphyrin researches in the past decade [1-3]. Corrole macrocyclic derivatives have potential applications in photodynamic therapy (PDT)[4], solar cells [5] and catalysis[6]. Biscorrole is a kind of dimeric macrocycle containing two corrole chromophores, which may form a larger conjugated system as compared to the monomeric corrole. Electronic interactions between the two chromophores in biscorrole are responsible for their unique fluorescence [7], near-infrared (NIR) transitions[8] and nonlinear optical (NLO) behavior [9]. Biscorrole

manganese or cobalt complexes have variable oxidation states and thus can be used in specific redox reactions [10-11]. It has also been reported that biscorrole metal complexes have the ability to catalyze the efficient electroreduction of oxygen to water or hydrogen peroxide[12-14], and have potential applications in fuel cells and batteries which use dioxygen as the reducible agent[15]. Various reports also emphasize the catalytic epoxidation of styrene by metal complexes[16] especially metalloporphyrins[17] and metallocorroles[18].

Biscorrole may be mainly classified into three types according to the mode of linkage: β, β-linked dimer[19-22], *meso-meso* linked[9] and central metal-metal bonded dimer [23], as well as dimers covalently linked by various spacers such as phenyl[24-25], anthracenyl, biphenylenyl, dibenzothiophenyl, dibenzofuranyl and dimethylxanthenyl[26]. Phenyl bridged biscorrole is of great interest because the two chromophores do not

behave independently and a profound electronic interactions exist between them in the dyads [25]. Paolesse et al [24] prepared a *m*-phenyl bridged biscorrole [1,3-Bis (2,3,7,8,12,13,17,18-octamethylcorrol-10-yl)benzene] which involved the synthesis of precursors of bisdipyrromethane and phenyl-linked a, c-biladiene. The final biscorrole product was obtained via the oxidation of phenyl-linked a, c-biladiene in methanolic solution using chloranil as the oxidant. Here, we report the facile preparation of a new *m*-phenyl bridged biscorrole and its manganese complex (scheme 1). The catalytic oxidation of styrene by *m*-phenyl bridged dimanganese (Ⅲ) biscorrole 2 was studied by using iodosylbenzene (PhIO), *m*-chloroperoxybenzoic acid (*m*-CPBA), hydrogen peroxide (H$_2$O$_2$) and *tert*-butyl hydroperoxide (TBHP) as the oxidant. The solvent and axial ligand effects were also investigated.

1, M=3H
2, M=Mn

3, M=3H
4, M=Mn
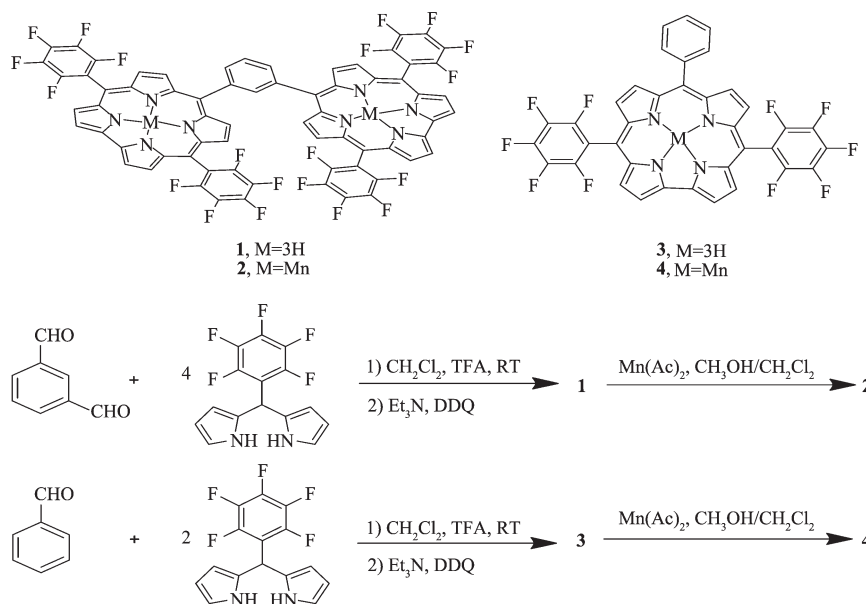
Scheme 1　Synthesis of free base corroles and their manganese complexes

1　Experimental

1.1　Materials and measurements

All the regents and solvents were of analytical grade and used without further purication. UV-Vis spectral measurements were taken on a U-3900H (Hitachi) spectrophotometer, and the MS spectra were

taken with fast atom bombardment mass spectrometry and time of flight mass spectrometry, and NMR spectra were taken on Bruker AVANCE Digital 400 MHz.

1.2　Synthesis

m-phenyl bridged biscorrole (**1**): 5-(pentafluorophenyl)dipyrromethane (425 mg, 1.36

mmol) and 1, 3-phthalaldehyde (45 mg, 0.34 mmol) were mixed in dichloromethane (DCM) (50 mL) and trifluoroacetic acid (35 μL) was also added. The mixture was stirred at room temperature for 5 h. Triethylamine (70 μL) was then added to quench the reaction, followed by adding 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (600 mg). The reaction mixture was stirred for another 1 h. DDQ was removed by flash chromatography on silica gel. The product was purified by column chromatography on silica gel with DCM/n-hexane (1:1, V/V) as eluent. (27 mg, Yield: 6%). UV-Vis (in toluene): λ_{max}/nm (absorbance), 413 (1.20), 439 (1.07), 568(0.24), 617(0.15); TOF-MS: m/z 1 334 (M$^+$, 100%); ^{1}H NMR (CDCl$_3$, 400 MHz): δ ppm, 8.18 (t, 1 H), 8.58 (m, 6 H), 8.83 (d, 4 H), 9.04 (s, 1 H), 9.12 (t, 8 H); ^{19}F NMR (in CDCl$_3$): δ ppm, −137.8 (dd, 8 F), −152.7 (dd, 4 F), −161.7 (t, 8 F).

m-phenyl bridged dimanganese(Ⅲ) biscorrole (**2**): A mixture of m-phenyl bridged biscorrole (20 mg, 15 mol) in DCM (1 mL) and manganese acetate tetrahydrate (73.5 mg, 300 mol) in methanol (50 mL) was refluxed for 3 h. The reaction was monitored by TLC and UV-Vis spectroscopy. The solvent was then removed under vacuum. Reaction residue was dissolved in 25 mL dichloromethane and washed with saturated sodium chloride solution for 3 times. The crude product was obtained after removing dichloromethane by distillation in vacuum. Purified product was obtained by chromatography on silica gel with DCM as the eluent (17.9 mg, Yield: 83%). UV-Vis (in toluene): λ_{max}/nm (absorbance), 415 (1.35), 422 (1.31), 491 (0.67), 584 (0.45), 632 (0.44); TOF-MS: m/z 1438 (M$^+$, 100%).

5,15-bis(pentafluorophenyl)-10-(phenyl)corrole (**3**): 5-(pentafluorophenyl)dipyrromethane (670 mg, 2.14 mmol) and benzaldehyde (130 mg, 1.07 mmol) were mixed in DCM (50 mL) and trifluoroacetic acid (6 μL) was also added. The mixture was stirred at room temperature for 5 h. Triethylamine (12 μL) was then added to quench the reaction, followed by the addition of DDQ (800 mg). The reaction mixture was stirred for another 1 h. DDQ was removed by flash chromatography on silica gel. The product was purified by column chromatography on silica gel with DCM/n-hexane (1/3, V/V) as the eluent. (86.8 mg, Yield: 11%). UV-Vis (in toluene): λ_{max}/nm (absorbance), 415 (1.20), 562 (0.20), 615 (0.12); FAB-MS: m/z 706 (M$^+$, 100%); ^{1}H NMR (CDCl$_3$, 400 MHz): δ, 9.11 (d, 2 H), 8.69 (s, 4 H) , 8.56 (d, 2 H), 8.16 (m, 2 H), 7.75 (m, 3 H); ^{19}F NMR (in CDCl$_3$): δ, −138.3 (2d, 4 F), −153.2 (t, 2 F), −162.1 (m, 4 F).

5,15-bis(pentafluorophenyl)-10-(phenyl)manganese(Ⅲ) corrole (**4**): **4** was prepared according to the reported method [27]. UV-Vis (in toluene): λ_{max}/nm (absorbance), 400 (0.99), 490 (0.36), 585 (0.33), 630 (0.31); FAB-MS: m/z 758.3 (M$^+$, 100%).

1.3 Catalytic oxidation

Catalytic reactions were carried out at ambient conditions in a small test tube. 1 μmol of complex **2** or 2 μmol of complex **4**, 100 μmol of the oxidant and 1 000 μmol of styrene were dissolved in 2 mL of solvent. After an appropriate reaction time, chlorobenzene (Internal standard,10 μmol·L^{-1}) was added to this reaction mixture. The injection volume of the filtrated reaction mixture was 1.0 μL and the products were confirmed by the retention time using standard samples under the same GC conditions, equipped with HP-5 capillary column (30.0 m×320 μm×0.25 μm).

2　Results and discussion

The free base biscorrole **1** was prepared by condensation reactions of corresponding aldehyde and pyrrole following the reported acid-catalyzed one-pot procedures [28-30] (Scheme 1). The free base biscorrole was converted to manganese(Ⅲ) complexes by refluxing with manganese acetate in dichloromethane-methanol mixture [31]. Corrole monomer **3** and its manganese(Ⅲ) complex were also prepared as reference. The target compounds were characterized by UV-Vis, ^{1}H NMR, ^{19}F NMR, XPS and MS spectroscopy. Free-base corroles **1** and **3** (Fig.1) show typical absorption spectra of corroles, having sharp Soret-band near 400 nm and Q-band in the region between 520~650 nm. The biscorrole **1** exhibits a split Soret-band due to the excitation coupling interaction between the two
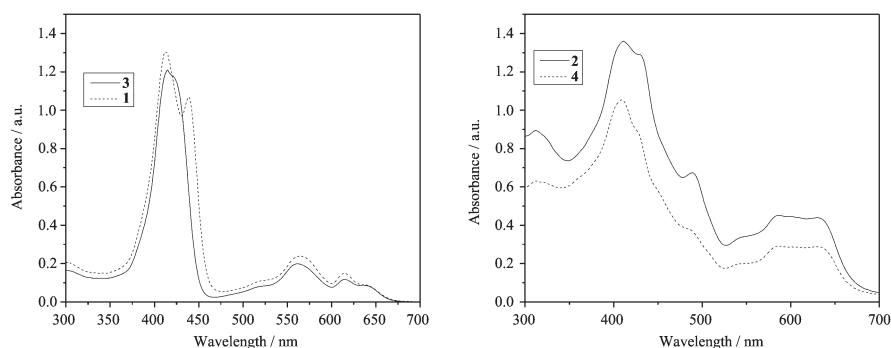
Fig.1　UV-Vis spectra of free base corroles (**1**, **3**) and their manganese complexes (**2**, **4**)
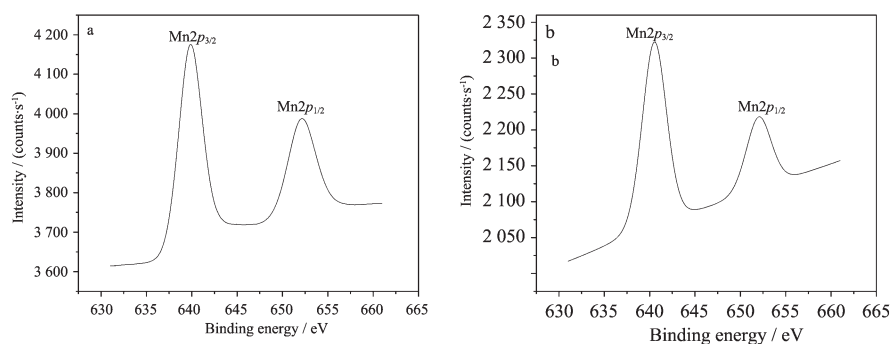
Fig.2　X-ray photoelectron spectra of Mn2p region of **2** (a) and **4** (b)

chromophoric units [25]. The UV-Vis spectra of corresponding manganese corroles **2** and **4** (Fig.1) exhibit typical MLCT band around 480 nm and are sensitive to the nature of the solvent and axial ligand [1,30]. The valence of manganese in complex **2** and **4** was confirmed by X-ray photoelectron spectroscopy (XPS) as shown in Fig.2. The XPS of **2** (Mn2$p_{3/2}$: Binding energy (BE) =639.9 eV; Mn2$p_{1/2}$, BE=652.15 eV) and **4** (Fig.2 Mn2$p_{3/2}$: Binding energy (BE)=640.55 eV; Mn2$p_{1/2}$, BE=652.1 eV) is in close agreement with the +3 oxidation state of the Mn[32].

The catalytic oxidation activity of manganese corrole complexes **2** and **4** was investigated by using styrene as substrate. It is found that the catalytic oxidation products of styrene by **2** and **4** are benzaldehyde, phenylacetaldyhyde and styrene

epoxide (Scheme 2).

In order to test the suitable reaction time for the catalytic oxidation, catalytic reaction was firstly carried out in toluene using PhIO as oxidant. Table 1 summarizes the effect of time on the catalytic oxidation of styrene. In all cases, styrene epoxide is the main product. The total conversion of catalyst **2** increases sharply within 90 min, and only an increase of ~10% is observed from 90~210 min time scale. The total conversion reaches 97% in 210 min. As for monomer catalyst **4**, the conversion increases quickly within 60 min, and reaches 76% in 90 min. Nearly no increase in conversion could be observed from 90~210 min. This phenomenon can be easily seen from conversion vs. time plot (Fig.3). It is clear that after 60 min, the increase in the conversion yield for **4** is
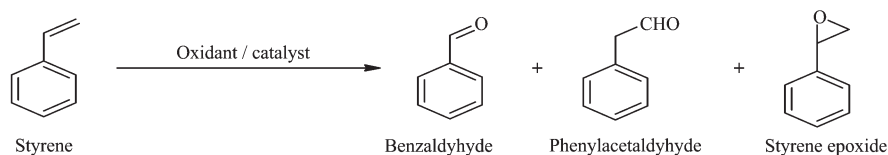

Scheme 2　Catalytic oxidation of Styrene by manganese corroles **2** and **4**

Table 1　Effect of reaction time on the catalytic oxidation of styrene[a]

Time / min	Catalyst	Yield / %[b]			
		Conversion / %	Benzaldehyde	Phenylacetaldehyde	Styrene epoxide
30	**2**	3.8	5.6	18.6	28.0
	4	3.2	8.7	23.2	35.1
60	**2**	7.6	10.8	40.3	58.7
	4	7.6	10.7	53.4	71.7
90	**2**	12.8	15.5	57.9	86.2
	4	9.9	14.7	51.7	76.3
150	**2**	15.7	16.4	59.4	91.5
	4	10.5	14.4	50.5	75.4
210	**2**	16.8	17.0	63.2	97.0
	4	8.8	11.6	54.5	74.9

[a]Reaction conditions: 1.0 μmol **2** or 2.0 μmol **4**, 0.1 mmol of PhIO, 1.0 mmol styrene in 2 mL neutral toluene at room temperature. [b]Yield is based on the amount of oxidant used.

very slow. In order to proceed the reaction under the same conditions and having comparability, we choose 30 min reaction time for further catalytic studies.

Axial ligand has prominent effect on the catalytic activity of manganese corrole complexes[33]. Here, the effect of different axial-ligands on the catalytic
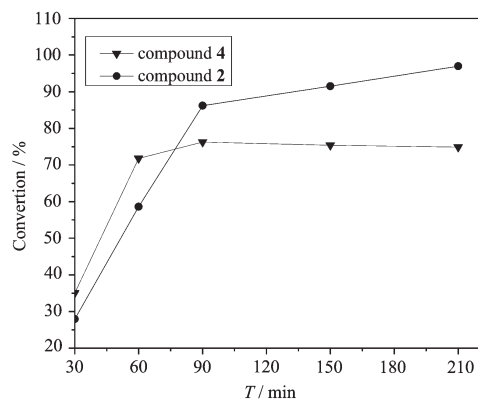

Fig.3　Conversion vs. time plot for catalytic oxidation of styrene by **2** and **4**

oxidation was also investigated in toluene using PhIO as the oxidant and the results are summarized in Table 2. Three ligands differing in their coordinating ability were used that can bind with manganese corroles in a 1:1 ratio[34]. The conversion follows the order: 1-methylimidazole >pyridine >imidazole. While the binding tendency of these *three* ligands are in the order: 1-methylimidazole >imidazole >pyridine [35], the results suggest that catalytic oxidation in the presence of axial ligands may involve some other factors.

The effect of solvent on the catalytic oxidation reaction of styrene by manganese corroles is summarized in Table 3, and shows significant differences in the product yield in different solvents. Among the tested solvents, acetonitrile is the best solvent where the conversion efficiency reaches 76.7% and 64.6% for **2** and **4**, respectively, in 30 min. The conversion yield in different solvents follows the order:

Table 2　Effect of axial ligand on the catalytic oxidation of styrene[a]

Axial ligand	Catalyst	Yield / %[b]			Conversion / %
		Benzaldehyde	Phenylacetaldehy	Styrene epoxide	
1-methylimidazole	**2**	6.1	6.4	22.4	34.9
	4	4.6	7.4	26.6	38.6
Pyridine	**2**	4.9	7.1	20.4	32.4
	4	4.2	9.1	24.2	37.5
Imidazole	**2**	1.4	2.6	8.2	12.2
	4	2.4	4.2	10.2	16.8

[a]Reaction conditions: 1.0 μmol **2** or 2.0 μmol **4**, 25 μmol of axial ligand, 0.1 mmol of PhIO, 1.0 mmol styrene in 2 mL toluene at room temperature; reaction time: 30 min. [b]Yield is based on the amount of oxidant used.

Table 3 Effect of solvent on the catalytic oxidation of styrene[a]

Solvent	Catalyst	Yield / %[b]			Conversion / %
		Benzaldehyde	Phenylacetaldehyde	Styrene epoxide	
Hexane	**2**	0.6	2.8	7.2	10.6
	4	0.8	4.8	8.7	14.3
Toluene	**2**	3.8	5.6	18.6	28.0
	4	3.2	8.7	23.2	35.1
DCM	**2**	4.3	19.8	48.4	72.5
	4	1.6	18.6	33.7	53.9
Acetonitrile	**2**	2.4	21.8	52.6	76.8
	4	1.6	22.4	40.6	64.6

[a]Reaction conditions: 1.0 μmol **2** or 2.0 μmol **4**, 0.1 mmol of PhIO, 1.0 mmol styrene in 2 mL solvent at room temperature; reaction time: 30 min. [b]Yield is based on the amount of oxidant used

hexane <toluene <dichloromethane <acetonitrile. Based on the solvents polarity[36], it may be suggested that the higher polarity solvent will favor the catalytic oxidation by manganese(Ⅲ) corroles.

The effect of different oxidants on the catalytic oxidation of styrene by **2** and **4** was also investigated and the results are shown in Fig.4. Acetonitrile is chosen as the solvent due to its higher conversion efficiency (Table 3). When H_2O_2 is used for styrene oxidation, benzaldehyde could only be significantly observed, while styrene epoxide and phenylacetaldehyde are negligible. TBHP oxidant also gives benzaldehyde as the major product, but the conversion yield increases sharply. The formation of benzaldehyde as the major product may involve a free radical reaction [37-39]. Scheme 3 shows the plausible catalytic cycle for the conversion of styrene to

benzaldehyde in the presence of TBHP oxidant. The tert-butyl hydroperoxide is known to undergo a cleavage of the peroxide O-O bond on coordination to the central metal, and forms tert-butyl oxygen radical[38]. The tert-butyl oxygen radical then initiates a free radical reaction with styrene which is propagated by the involvement of molecular oxygen, leading to the formation of benzaldehyde as the major product[39]. In contrast, when using m-CPBA as the oxidant, the products are styrene epoxide, phenylacetaldyhyde and benzaldehyde. The monomer catalyst **4** exhibits a little higher conversion and selectivity for styrene epoxide. However, both **2** and **4** give styrene epoxide as the major product in case of PhIO as the oxidant, which also exhibits higher selectivity for the epoxidation of styrene than m-CPBA. The different behavior of PhIO and m-CPBA oxidants can be explained in terms of
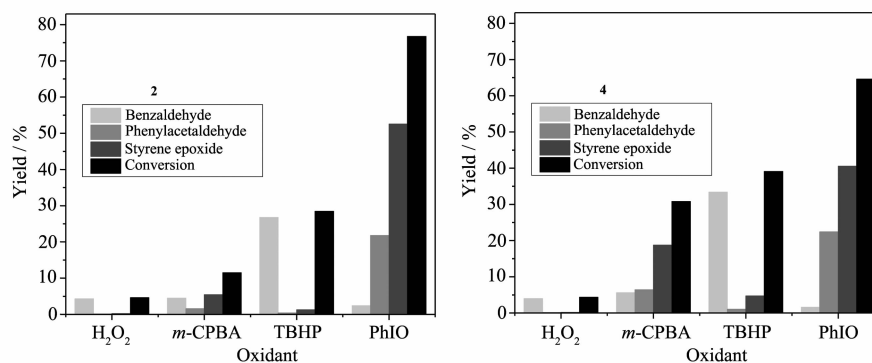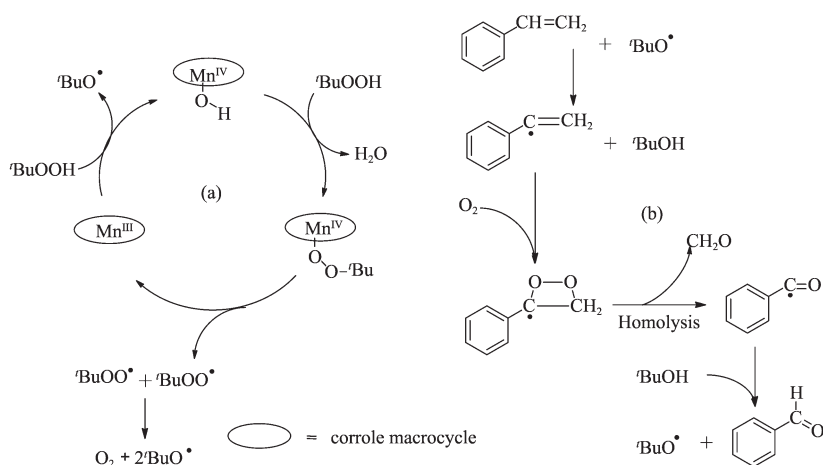

Fig.4　Bar-graph showing the effect of different oxidants on the styrene oxidation by **2** and **4** (Reaction conditions: 1.0 μmol **2** or 2.0 μmol **4**, 0.1 mmol of oxidant, 1.0 mmol styrene in 2 mL acetonitrile at room temperature; reaction time: 30 min. Yield based on the amount of oxidant used.)

Scheme 3　Plausible mechanism for manganese corroles catalyzed conversion of styrene into benzaldehyde in the presence of *tert*-butyl hydroperoxide; (a) Generation of dioxygen and *tert*-butyl oxygen radical, and (b) their subsequent reaction with styrene to produce benzaldehyde

the possible formation of the high-valent (oxo) manganese (V) species $(Mn^V \equiv O)$ as intermediates, which may cause insertion of oxygen into the carbon-carbon double bond of styrene (Scheme 4) to form styrene epoxide [40]. While the observed benzaldehyde product may also be formed via free radical pathway[1], and the phenylacetaldehyde can also be obtained through oxidation of styrene epoxide. These observations indicate that the products distribution of the catalytic oxidation of styrene by manganese corrole is correlated with the nature of the oxidant u sed.
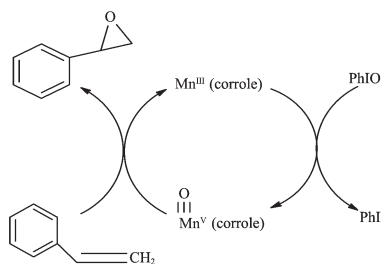
Scheme 4　Plausible mechanism for the main product of catalytic oxidation of styrene into styrene epoxide by manganese corrole using PhIO

3　Conclusions

　　m-phenyl bridge d dimanganese (Ⅲ) biscorrole **2** and its monomeric analogue **4** were synthesized and characterized by spectroscopic techniques. The catalytic activity of manganese complexes **2** and **4** were investigated against styrene as the substrate under various reaction conditions. The experimental data reveal that **2** exhibits comparable catalytic behavior to its monomer counterpart **4**. Acetonitrile is the best solvent, and PhIO is more suitable oxidant for the catalytic oxidation of styrene to styrene epoxide. The use of TBHP as the oxidant, however, gives benzaldehyde as the major product. The influence of the axial ligand follows the order: 1-methylimidazole> pyridine>imidazole.

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