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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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### Mononuclear Manganese(II)/4'-Ar-2,2':6',2"-Terpyridine Complexes: Synthesis, Characterization, and Olefins Oxidation Study

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## Mononuclear Manganese(II)/4'-Ar-2,2':6',2"–Terpyridine Complexes: Synthesis, Characterization, and Olefins Oxidation Study

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A series of mononuclear Mn(II)/terpyridine complexes were synthesized and characterized by elemental analysis, IR spectrum, and UV-vis spectrum. Catalytic activities of Mn(II)/4'-Ar-2,2':6',2"-terpyridine complexes were tested in the oxidation of cyclohexene or styrene in the presence of *tert*-butylhydroperoxide as oxidant. Significant catalytic effects of these complexes were observed in the oxidation of olefins, especially in the cyclo-oxidation of styrene.

Keywords: Mn(II) complex catalyst, tridentate chelate, TBHP, olefin oxidation

#### Introduction

The oxygen-evolving complex (OEC) of photosystem II (PS II) contains a  $\mu$ -oxo-bridged manganese tetramer, which can carry out the four-electron oxidation of water to O<sub>2</sub>.<sup>[1-3]</sup> [H<sub>2</sub>O(terpy)Mn( $\mu$ -O)<sub>2</sub>Mn(terpy)OH<sub>2</sub>]<sup>3+</sup> (terpy = 2,2':6',2"-terpyridine) has been reported to catalyze oxygen evolution from an oxidant (OCl<sup>-</sup> or HSO<sub>5</sub><sup>-</sup>) in aqueous solution.<sup>[4-6]</sup> Dioxygen transporting proteins existed in the hemocyanin and tyrosinase have important cores of tridentate-coordinated structure.<sup>[7,8]</sup> Thus, metal/tridentate-ligand complexes maybe have a great potential for catalytic oxidizability.<sup>[9,10]</sup>

Manganese complexes have been already applied in a lot of research fields,<sup>[11-14]</sup> but few mononuclear Mn/tridentate-ligand complexes could be found to be used in organic oxidative reaction. We synthesized a series of mononuclear Mn(II)/4'-Ar-2,2':6',2"-terpyridine complexes, and the catalytic activities of these complexes were explored in oxidative reactions, cyclohexene or styrene as substrate.

#### Experimental

#### **Reagents and instruments**

All chemicals of acceptable purity grade were purchased from the local market. The <sup>1</sup>H-NMR spectra was recorded on a WIPM-400(400MHz) in CDCl<sub>3</sub>-d<sub>1</sub> with tetramethylsilane as the internal standard. Vario Micro Cube of Germany elemental analyzer was used to collect microanalytical data (C, H, and N). FT-IR spectra of the samples were recorded on a NICOLET iS10 spectrophotometer using KBr pellets. The electronic spectra of complexes were recorded on a Perkin Elmer Lambda-35 spectrophotometer.

#### Synthesis of Ligand and Complex

4'-(4-nitrophenyl)-2,2':6',2"-terpyridine (L1), 4'-(4-chlorophenyl)-2,2':6',2"-terpyridine (L2), 4'-phenyl-2,2':6',2"-terpyridine (L3), 4'-(4-methylphenyl)-2,2':6',2"-terpyridine (L4), and 4'-(4-methoxylphenyl)-2,2':6',2"-terpyridine (L5) were synthesized according to the reported procedure.<sup>[15]</sup> Complexes (1–5) were precipitated after boiling the corresponding ligand with an equimolar amount of manganese (II) chloride for 3 h (Scheme 1).

Synthesis of complexes (1–5): MnCl<sub>2</sub>·4H<sub>2</sub>O (1 mmol) was dissolved in alcohol (10 mL), Ligand (1 mmol) was dissolved in CHCl<sub>3</sub> and was added dropwise to the above solution with stirring at room temperature in 1 h. Then the solution was refluxed for 4 h. The mixture was allowed to stay overnight at  $-10^{\circ}$ C, after which the precipitate was filtered off, washed with diethyl ether, and dried under vacuum. Complex 1 was obtained as a brown powder, yield 81%. IR (KBr,  $\nu/\text{cm}^{-1}$ ):

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Sch. 1. Synthesis of ligands and Mn(II) complexes.

1554 (-NO<sub>2</sub> str.), 1610 (C=N str.), C=C-H (3019 str.). UVvis [H<sub>2</sub>O,  $\lambda$ /nm]: 230, 284, 302. Anal. Calcd. for C<sub>21</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>Mn: C, 52.52; H, 2.94; N, 11.67%. Found: C, 52.81; H, 3.18; N, 11.87%.

Complexes (2–5) were prepared in similar way with the corresponding ligands and were obtained as yellow powders.

Complex **2**, yield 82%. IR (KBr,  $\nu/cm^{-1}$ ): 1567, 1479 (C=C str.), 1607 (C=N str.), 3065 (C=C-H str.). UV-vis [H<sub>2</sub>O,  $\lambda/nm$ ]: 249, 281, 316. Anal. Calcd. for C<sub>21</sub>H<sub>14</sub>N<sub>3</sub>Cl<sub>3</sub>Mn: C, 53.70; H, 3.00; N, 8.95%. Found: C, 53.99; H, 2.81; N, 9.02%.

Complex **3**, yield 77%. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 1616 (C=C str.), 1600 (C=N str.), 3055 (C=C—H str.). UV-vis [H<sub>2</sub>O,  $\lambda/\text{nm}$ ]: 246, 267, 286. Anal. Calcd. for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>Cl<sub>2</sub>Mn: C, 57.95; H, 3.47; N, 9.66%. Found (%): C, 57.47; H, 3.29; N, 9.58%.

Complex 4, yield 82%. IR (KBr,  $\nu/cm^{-1}$ ): 1426(-CH<sub>3</sub> str.), 1544, 1473 (C=C str.), 1659 (C=N str.), 3058 (C=C-H str.). UV-vis [H<sub>2</sub>O,  $\lambda/nm$ ]: 226, 289, 312. Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>Cl<sub>2</sub>Mn: C, 58.82; H, 3.81; N, 9.35%. Found: C, 59.02; H, 3.72; N, 9.44%.

Complex 5, yield 81%. IR (KBr,  $\nu/cm^{-1}$ ): 1427(-CH<sub>3</sub> str.), 1553 (C=C str.), 1599 (C=N str.), 1471, 1545 (C=C-H str.). UV-vis [H<sub>2</sub>O,  $\lambda/nm$ ]: 230, 285, 308. Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>OCl<sub>2</sub>Mn: C, 56.80; H, 3.68; N, 9.03%. Found: C, 56.29; H, 3.58; N, 8.79%.

#### General Procedure for Oxidation of Substrate

Substrate, TBHP and metal complex were introduced in the 50 mL two-necked round-bottomed flask placed in an appropriate temperature controlled by water bath under vigorous stirring. After oxidation, the reaction mixture was passed quickly through a short pad of silica gel and reaction solvent was used as eluent. The solution was placed in a GC sample vial, then a quantitative of internal standard (*p*-xylene) was added for quantitative analysis by GC (Agilent 6810 chromatograph, Agilent DB-5ms capillary column 0.25 mm  $\times$  30 m  $\times$  0.25  $\mu$ m, FID detector).

#### **Results and Discussion**

#### Liquid Phase Reaction Oxidation of Cyclohexene

In order to test the catalytic performance of the impact of different substituent group to the catalyst, five types of mononuclear Mn(II)/terpyridine complex were investigated in the oxidation of cyclohexene. The results showed that the main oxidation products of the cyclohexene were 2-cyclohexene-1one, 2-cyclohexene-1-ol, and cyclohexene epoxide (Scheme 2).

#### Effect of different oxidant

The effect of different oxidants on the catalytic activity of mononuclear Mn(II)/terpyridine complex in the oxidation of styrene was studied. We chose different oxidant such as TBHP (65%), H<sub>2</sub>O<sub>2</sub> (30%), molecular oxygen, and air in the oxidation of cyclohexene. The catalysis results were summarized in Table 1. In the case of TBHP, the reaction showed the highest conversion ratio.

#### Effect of different solvent

In the catalytic oxidation of cyclohexene, acetonitrile, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), CH<sub>2</sub>Cl<sub>2</sub>, and CH<sub>2</sub>ClCH<sub>2</sub>Cl were used as solvent. As shown in Table 2, the highest conversion was obtained in presence of acetonitrile. It was observed that the catalytic activity of the Mn(II) complex decreased in the order: acetonitrile > CH<sub>2</sub>ClCH<sub>2</sub>Cl > DMF > THF > CH<sub>2</sub>Cl<sub>2</sub> at 50°C. Then, all experiments will be performed in acetonitrile.

#### Effect of reaction temperature

Effect of temperature on the oxidation of cyclohexene as a function of time has been plotted in Figure 1. A series of experiments were carried out in order to test the temperature effect at different temperatures of 35, 60, 70, and  $80^{\circ}$ C. As shown in Figure 1, the best conversion ratio was observed at  $80^{\circ}$ C. Diminishing conversion ratios were generated when the reaction temperatures were lower than  $80^{\circ}$ C.

#### Effect of the amount of catalyst

The effect of the amount of catalyst on the oxidation of cyclohexene as a function of time is illustrated in Figure 2. The data revealed that the conversion of cyclohexene decreased with the increase of the catalyst amount from 0.5 to 2 mol%. 88% conversion of cyclohexene was observed after 6 h at 80°C using 0.5 mol% of catalyst **3**. An increase of the amount of catalyst would obtain a lower conversion of cyclohexene from the Figure 2. The possible reason is that the decomposition of TBHP which resulted from the excess Mn(II) complex.



Sch. 2. Oxidation of cyclohexene by Mn(II) complex.

	D	roduct select	i vita	
hexene oxidation <sup>a</sup>				
Table 1. Effect of various o	oxidant to	o conversion	ratio o	of cyclo-



<sup>a</sup>Cyclohexene 5 mmol, oxidant 10 mmol, complex **3** 1 mol%, acetonitrile 10 mL, 6 h, 50°C.

<sup>b</sup>Determined by GC.

<sup>c</sup>Others: 1,2-cyclohexanediol and 2,3-epoxy-1-cyclohexanone.

#### Effect of amount of oxidant

The effect of the substrate/oxidant molar ratio on the oxidation of cyclohexene is illustrated in Figure 3. Different substrate/oxidant molar ratios (1:0.5, 1:1, 1:1.5, and 1:2) were tested. When the molar ratio of substrate/oxidant increased from 1:0.5 to 1:2, the conversion ratio of cyclohexene changed significantly from 56% up to 90% after 6 h.

# Effect of different Mn(II) complexes in the oxidation of cyclohexene

Under the optimized catalytic condition, five mononuclear Mn(II)/terpyridine complexes were tested in the oxidation of cyclohexene. All catalytic data were presented in Table 3 .

It is very clear that the Mn(II) complex do have the powerful influence for oxidation of cyclohexene. A very poor conversion ratio of cyclohexene was observed without any catalysts, which was only 26%. It can be seen that the ligand play a significant role to the catalytic properties of the



**Fig. 1.** Effect of the temperature on the oxidation of cyclohexene. Reaction condition: cyclohexene 5 mmol, TBHP 10 mmol, Mn (II) complex 3 0.5 mol%, acetonitrile 10 mL.



**Fig. 2.** Effect of the amount of oxidant on the oxidation of cyclohexene. Reaction condition: cyclohexene 5 mmol, TBHP 10 mmol, acetonitrile 10 mL, 80°C.

complexes. The best conversion ratio of cyclohexene pertains to Catalyst 1 (90%) and the lowest belongs to Catalyst 2 (79%). A low conversion ratio of the Catalyst 2 is due to its poor solubility in acetonitrile. Results indicated that 4'-(4-nitrophenyl)-2,2':6',2"-terpyridine had best catalytic effect for cyclohexene oxidation than those containing the electron-donating group.

#### Liquid Phase Reaction Oxidation of Styrene

The catalytic abilities of Mn(II) complexes were also examined in the oxidation of aromatic olefin, styrene used as a model substrate. The experiments showed that the main oxidation products of the styrene were benzaldehyde, styrene cyclo-oxide, and 1-phenylethane-1,2-ethanediol (Scheme 3).

As shown in Table 4, Mn(II) complexes have played a very important role on the oxidation of styrene. Only 32% of styrene was oxygenated without any Mn(II) complexes. The

 

 Table 2. Effect of various solvent to conversion ratio of cyclohexene oxidation<sup>a</sup>

 Product selectivity

Solvent			Product selectivity			
	Conv. (%) <sup>b</sup>	OH	o		Other <sup>c</sup>	
Acetonitrile	58	7	47	12	34	
DMF	26	15	11	66	8	
THF	18	10	48	40	2	
CH <sub>2</sub> ClCH <sub>2</sub> Cl	30	19	27	27	27	
$CH_2Cl_2$	15	24	30	27	19	

<sup>a</sup>Cyclohexene 5 mmol, TBHP 10 mmol, complex 3 1 mol%, solvent 10 mL, 6 h, 50°C.

<sup>b</sup>Determined by GC.

<sup>c</sup>Others: 1,2-cyclohexanediol and 2,3-epoxy-1-cyclohexanone.



Sch. 3. Oxidation of styrene by Mn(II) complex.



**Fig. 3.** Effect of the amount of oxidant on the oxidation of cyclohexene. Reaction condition: cyclohexene 5 mmol, Mn(II) complex **3** 0.5 mol%, acetonitrile 10 mL, 80°C.

 Table 3. Effect of different Mn(II) complexes on conversion ratio

 of cyclohexene oxidation<sup>a</sup>

		Product selectivity			
Complex used	Conv. (%) <sup>b</sup>	OH	o		Others <sup>c</sup>
	26	9	31	60	
Complex 1	90	5	38	51	6
Complex 2	79	4	36	52	8
Complex 3	88	4	34	55	7
Complex 4	89	10	20	58	12
Complex 5	80	7	31	55	8

<sup>a</sup>Cyclohexene 5 mmol, TBHP 10 mmol, Mn(II) complex 0.5 mol%, acetonitrile 10 mL, 6 h, 80°C.

<sup>b</sup>Determined by GC.

<sup>c</sup>Others: 1,2-cyclohexanediol and 2,3-epoxy-1-cyclohexanone.

 Table 4. Effect of various Mn(II) complexes to conversion of styrene oxidation<sup>a</sup>

Complex used		Product selectivity			
	Conv. (%) <sup>b</sup>	СНО	C o	OH OH	
Complex 1	94	2	92	6	
Complex 2	77	2	94	4	
Complex 3	93	1	95	4	
Complex 4	93	1	94	5	
Complex 5	85	1	96	3	
_ ^	32	72	23	5	

<sup>a</sup>Styrene 5 mmol, TBHP 10 mmol, Mn(II) complexes 0.5 mol%, acetonitrile 10 mL, 12 h, 80°C.

<sup>b</sup>Determined by GC.

conversion ratio of styrene was increased up to 77–94% when 0.5 mol% Mn(II) complex was added. The selectivity of styrene cyclo-oxide was also improved from 23% up to 96%, at the same time. Complex 1 has best catalytic effect than the others. The results were similar with those in previous reports<sup>[16–18]</sup> in which the withdrawing electron group would have active influence on the catalytic oxidation. The introduction of nitro substituents, possessing electroaccepting abilities into terpyridine, makes the center metal strongly electron deficient. The electron deficient center metal would preferably coordinated with TBHP.

#### Conclusions

Five mononuclear Mn(II)/4'-Ar-2,2':6',2"-terpyridine complexes were synthesized and applied in the catalytic oxidations of cyclohexene or styrene. All these Mn(II) complexes exhibited good catalytic activities for oxidation of olefins when TBHP was used as oxidant, especially for the reaction of styrene. For the cyclo-oxidation of styrene, a conversion ratio up to 94% and selectivity up to 96% were observed after 12 h at 80°C when Mn(II) complexes were used as catalyst. Moreover, the catalytic oxidation system is safe, clean, and operationally simple.

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