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Effect of Axial Ligands on Monooxygenation of Cyclohexane Catalyzed by A Dimanganese Schiff Base Complex

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There are many dimetalloenzymes in nature[1]. To mimic these enzymes, we synthesized a new dimanganese Schiff base complex — Bis [N,N'— ethylene — 2,2'—(phenylmethylene)-bis (3,4 — dimethylpyrrole — 5 — aldimino)] dimanganese Mn_2L (shown in Fig.1). Its structure was confirmed by IR, UV-Vis, ^{1}HNMR and elemental analysis. It can catalyze monooxygenation of cyclohexane with PhIO as an oxidant.

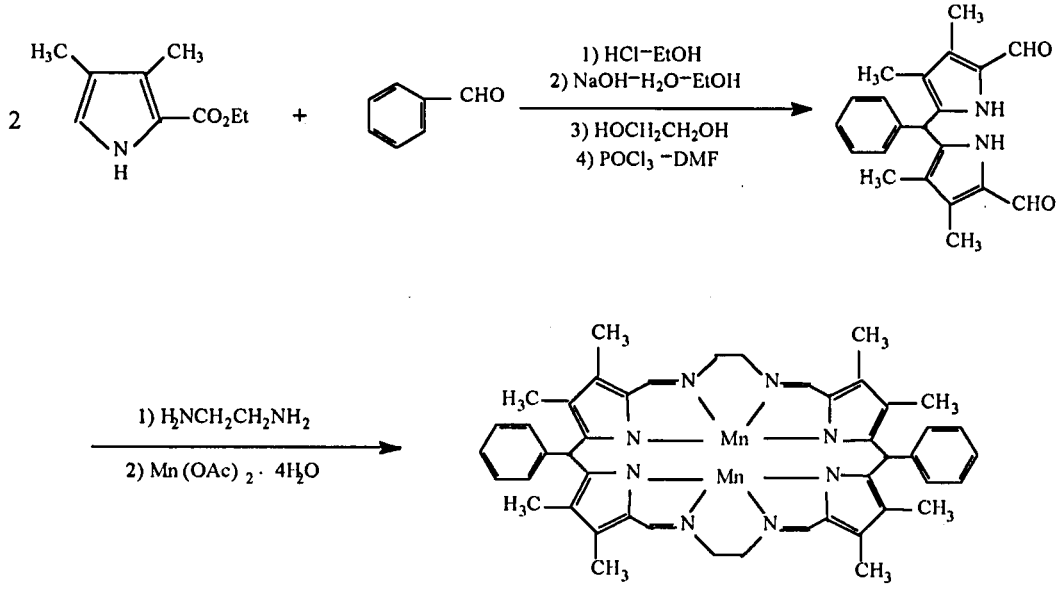
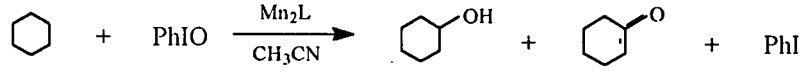


Fig. 1 Synthesis of the dimanganese complex Mn_2L



This paper reports the effect of some axial ligands on the reaction. The results are shown in Table 1 and Table 2.

Table 1. Rate constant k ($mol \cdot min^{-1}$) of cyclohexane monooxygenation affected by ligands[a]

Ligand	4 — methyl pyridine	3 — methyl pyridine	pyridine	2 — methyl pyridine	2,6 — dimethyl pyridine	nothing
pKa[2]	6.02	5.68	5.17	5.97	6.75	
$k \times 10^7$	17.29	14.99	13.48	12.69	9.109	8.162

a reaction conditions: 5mL of CH_3CN, 0.01mmol of internal standard, 0.5mL of cyclohexane, 0.005mmol of Mn_2L, 20mg of PhIO and 0.01mmol of axial ligand; 25 ℃; 10min.

Table 2. Yield (%)[b] of cyclohexane monooxygenation (4h)

Ligand	4 — methyl pyridine	3 — methyl pyridine	pyridine	2 — methyl pyridine	2,6 — dimethyl pyridine	nothing
Cyclohexanol	21.53	22.01	21.69	19.72	18.80	18.41
Cyclohexanone	18.49	16.09	15.14	13.07	11.47	10.02
Total yield	40.02	38.10	36.83	32.79	30.27	28.43

b Yield based on PhIO charged

(1) The reactions are zero order in kinetics, which are similar to the reactions catalyzed by enzymes.

(2) All of these axial ligands increase the reaction rate and the yield, because the coordination between an axial ligand and a manganese (II) may lower the activation energy of the reaction[3].

(3) The reaction rate and the yield increase with the increase of pKa of the axial ligand.

(4) Compared with pyridine, steric effect of methyl group in 2 — methylpyridine and 2,6 — dimethylpyridine decreases the reaction rate and the yield.

Reference

1. Jesie H., Brian M., Jane N.. J. Chem. Educ., 1991, 68: 59
2. Brown H. C., Mihm X. R.. J. Am. Chem. Soc., 1955, 77: 1723
3. Agarwal D. D., Bhatnagar R. P., Jain R.. J. Mol. Catal., 1990, 59: 385

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