Novel Manganese Complex as an Efficient Catalyst for the Isobutyraldehyde-Mediated Epoxidation of Cyclic Alkenes with Dioxygen

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Abstract: The highly efficient oxidation of cyclic alkenes was realized using a novel manganese complex as catalyst and molecular oxygen as oxidant in the presence of isobutyraldehyde. The reaction of 2-pyridinecarboxylic acid with *p*-toluidine gave the corresponding amide in good yield. A manganese complex bearing this ligand was highly active in isobutyraldehyde-mediated epoxidation of cyclic alkenes using molecular oxygen as oxidant, and up to and over 99.9% conversion of the substrate and 99% yield of the epoxide were obtained for the epoxidation of norbornylene.

Keywords: cyclic alkene; dioxygen; epoxidation; manganese complex; N,O ligands

The catalytic epoxidation of alkenes with molecular oxygen is one of the most useful and elegant methods for the functionalization of olefinic substrates due to the low cost and environmentally friendly nature of the oxidant.[1] An important breakthrough in the epoxidation of alkenes was reported by Mukaiyama et al. using dioxygen as oxidant in the presence of aldehydes. Under mild conditions, epoxidation of cyclohexene and 1-methylcyclohexene gave the corresponding epoxides in 84% and 80% yields, respectively.[2] Epoxidation of cyclohexene by Corain et al.[3] and Thomas et al.[4] gave the corresponding epoxide in moderate yields.

In the course of developing efficient systems for the epoxidation of cyclic alkenes with dioxygen, we found that a ruthenium complex bearing a bidentate pyridinecarboxylic acid amide ligand gave over 90% yields for the epoxidation of cyclic alkenes such as cyclopentene or cyclohexene.[5] Compared to simple metal salt catalysts, pyridinecarboxamide complexes are more soluble in normal organic solvents, and reactions catalyzed by metal complexes proceed much faster than those catalyzed by simple metal salts. In the development of economic and environmentally friendly processes for the production of epoxides, using cheaper manganese complex instead of the more expensive ruthenium complex is of interest.[6]

Epoxidation of olefins has been realized using manganese complexes with various ligands such as porphyrin,[7] Schiff bases,[8] 2,2′-bipyridine,[9] pyridyl[10] or cyclic triamine[11] using iodosylbenzene, NaOCl, peracids, ozone and $NaIO_4$ as oxygen donors. These oxidants have limited potential industrial application because of their higher price, and/or pollution and safety concerns. There were few reports on the use of molecular oxygen as an oxidant with high yields.[2,12] Here, we report a highly effective catalyst system for the selective epoxidation of cyclic alkenes with molecular oxygen using a simple manganese catalyst $[Mn(HL)_2Cl_2]$ (**2**; where HL **1** the is N-4′-methylphenyl-2-pyridinecarboxamide ligand). Using complex **2** as catalyst, the epoxidation of norbornene by molecular oxygen at room temperature gave up to 99.0% yield of the desired product.

The ligand and the corresponding manganese complex were prepared according to the scheme shown in Figure 1 and were characterized by FTIR and elemental analysis.[13] The molecular structure of the complex was determined by single crystal X-ray diffraction. The ORTEP drawing shown in Figure 2 clearly reveals the binding of the metal centre to two pyridine nitrogens, two carbonyl oxygens and two Cl^- ions which electronically balance the bivalent Mn^{2+} ion. This differs from the coordination structure of the previously reported ruthenium complex which is coordinated by a deprotonated amide nitrogen as well as two chloride ions to satisfy the charge balance of the trivalent Ru^{3+} ion. In addition, not only the vibrational frequency of the carbonyl ($\nu_{C=O} = 1630\ cm^{-1}$) in the Mn complex is larger than

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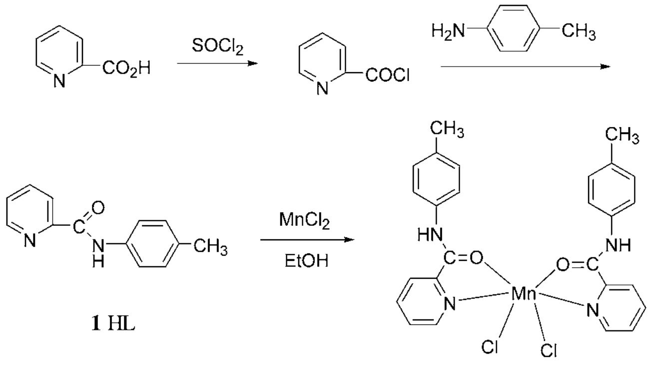


1 HL

2 *cis*-$[Mn(HL)_2Cl_2]$

Figure 1. Preparation of ligand **1** and its Mn complex **2**.

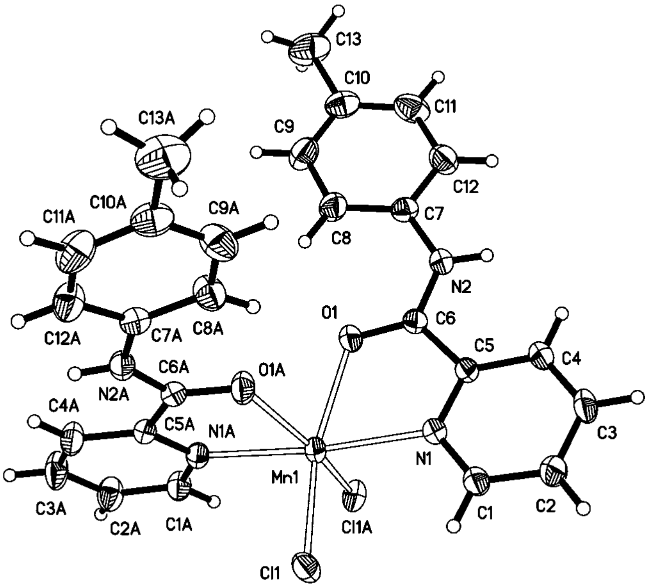


Figure 2. Molecular structure of complex **2** (thermal ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity).

that ($\nu_{C=O} = 1615\ cm^{-1}$) in the Ru complex, but also the bond lengths (2.239–2.458 Å) of the coordination atoms N, O or Cl to Mn in the Mn complex are longer than the corresponding bond lengths (2.001–2.363 Å) in the Ru complex. Moreover, the M–Cl bond lengths are always the longest in the three types of coordination bonds whether in the Mn complex (2.458 Å) or in the Ru complex (2.315 and 2.363 Å). The M–Cl bonds are expected to be cleaved in the process of catalytic epoxidation. The two *cis*-positioned Cl^- ions in crystal **2**, which resemble their counterparts in the ruthenium complex, are expected to facilitate the attack of reactants or formation of active intermediates.

In the investigation of the epoxidation of cyclohexene catalyzed by the Mn complex **2** we found that the turnover frequency was high at ambient temperature and reached 328 mol/mol catalyst·h in the first hour (Table 1). When the reaction was carried out at 0 °C (Table 1, entry 4), the epoxidation was too slow to be useful and afforded only 42.5% conversion after 13 hours of reaction. At 35 °C, 99.9% conversion was achieved in 12 hours (entry 5), but the epoxide selectivity decreased from 92.4% to 84.5%. These results indicated that the reaction temperature was a key factor that significantly influenced both the conversion and selectivity of the epoxidation. These results are consistent with a chain reaction mechanism involving free radicals.[1a]

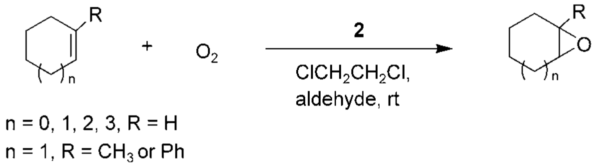
In the absence of isobutyraldehyde (entry 6), only 1.8% conversion with 23.1% selectivity for epoxide was observed. 2-Cyclohexen-1-one was found to be the main product (70.2%). The presence of isobutyraldehyde clearly favoured the formation of epoxide instead of allylic products.[14] A control experiment without catalyst (entry 7) gave only 37.3% conversion after 13 hours. This result, coupled with the fact that the catalytic activity of the simple manganese salt was very low (entry 8), suggested that the Mn complex with a better solubility in the reaction medium can play a more important role on the catalytic activity and selectivity in the epoxidation.

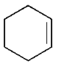
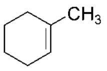
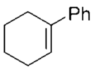
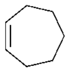
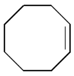
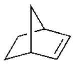
The epoxidations of other cyclic alkenes (entries 12–17) were successful and > 99% conversions with excellent selectivity were achieved in all cases tested. The epoxidation of norbornene gave up to 99% selectivity for the desired epoxide. It is noteworthy that the epoxide selectivities for cyclopentene, 1-methylcyclohexene and 1-phenylcyclohexene were all higher than those obtained using a previously reported Ru catalyst.[5] It seems that the same *cis*-conformation of both the Mn and the Ru complexes facilitated the attack of substrates and exhibited high catalytic activity.

Both the temperature effect and the fact that the addition of a radical-trapping compound stopped the epoxidation (entry 9) suggested that the reaction might involve free radical intermediates.[15,16] In addition, in those cases where the dioxygen source was changed to air instead of molecular oxygen (entries 10 and 11), the conversion decreased significantly. It is possible that the dioxygen concentration influenced the rate of the formation of the acylperoxy radical, which was a rate-determining step[17] in the catalytic cycle of the epoxidations of alkenes. These results are consistent with the speculations proposed by Haber,[15] Valentine,[16] and Nolte[17] using prophyrin, cyclam or β-diketonate complexes of metal as catalyst. The role of the metal complex in the catalytic process is still under investigation.

In summary, a new manganese(II) complex **2** was prepared and its molecular structure was determined by X-ray diffraction. Using this complex as catalyst and molecular oxygen as oxidant in the presence of isobutyraldehyde, the epoxidation of cyclic alkenes was efficiently accomplished under mild conditions. The Mn complex **2**

Table 1. Epoxidation of cyclic alkenes catalyzed by complex **2**.[a]



Entry	Substrate	Reaction Time [h]	Conv. [%]	Selectivity [%]	
				Epoxide[b]	Others
1		1	59.6	92.2	7.8
2		2.5	68.7	91.5	8.5
3		13	97.7	91.0	9.0
4[c]		13	42.5	92.4	7.6
5[d]		12	99.9	84.5	15.5
6[e]		13	1.8	23.1	76.9[f]
7[g]		13	37.3	86.2	13.8
8[h]		13	43.5	80.6	19.4
9[i]		13	18.4	88.5	11.5
10[j]		13	2.7	23.0	77.0
11[k]		13	86.1	83.8	16.2
12[l]		13	41.7	90.9	9.1
13		13	99.5	93.6	6.4
14		12	$\geq$99.9	93.4[m]	6.6
15		12	$\geq$99.9	84.6[m]	15.4
16		12	$\geq$99.9	89.7[m]	10.3
17		12	$\geq$99.9	98.0	2.7
18		11	$\geq$99.9	99.0[m]	1.0

[a] The reactions were carried out at room temperature under the following conditions: substrate = 0.44 M; catalyst = 0.80 mM; isobutyraldehyde = 0.88 M; O_2 = 1 atm; 2 mL of $ClCH_2CH_2Cl$.

[b] Epoxides were identified by using authentic samples for comparison.

[c] At 0 °C.

[d] At 35 °C.

[e] No aldehyde.

[f] Main by-product was 2-cyclohexen-1-one.

[g] No catalyst.

[h] Catalyst was 2.2 mM of $MnCl_2 \cdot 4\,H_2O$.

[i] Catalyst was 1.6 mM of ligand.

[j] 8.0 mM of radical trapping compound 2,6-di-*tert*-butyl-4-methylphenol was added to the reaction system.

[k] 3 atm of air instead of pure O_2 was used.

[l] 1 atm of air instead of pure O_2 was used.

[m] Epoxides were identified by GC (HP 5890 or 4890, column AT-1 30 m × 0.25 mm) and GC-MS (HP G1800C).

showed a better selectivity for epoxides than the previously reported Ru complex.

Experimental Section

All chemicals and solvents used were of regent grade and were used without further purification unless stated otherwise. Tetrahydrofuran was distilled from sodium.

Preparation of 1

The ligand was prepared by a previously reported method.[18]

Preparation of 2

The ligand **1** (0.322 g, 1.52 mmol) was dissolved in EtOH (5 mL) and to it was added manganese dichloride (0.180 g, 0.76 mmol) dissolved in EtOH (2 mL). The mixture was stirred at 50 °C for 0.5 h. The precipitate was filtered, washed with ethanol, and air-dried to give **2** as a yellow powder, yield: 0.361 g (88%).

Single crystals suitable for data collection were obtained by slow evaporation of the solvent from an ethanol saturated solution at room temperature.

Crystal Data for Complex 2

$C_{26}H_{24}Cl_2MnN_4O_2$, M = 550.33, orthorhombic, $a = 13.388(2)$, $b = 9.5559(17)$, $c = 19.716(4)$ Å, U = 2522.3(8) Å^3, $T = 294$ K, space group *Pbcn*, $Z = 4$, λ (Mo-Kα) = 0.767 mm^{-1}, 15931 reflections collection, 2915 independent reflections (Rint = 0.0402). The final R indices [$I > 2\sigma$ (I)]: R1 = 0.0351, wR2 = 0.1040, R indices (all data): R1 = 0.0545, wR2 = 0.1193. The crystal information file of the complex has been deposited at the Cambridge Crystallographic Data Centre with a deposition number CCDC 221760. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[13] The yields for **1** and **2** were 65% and 88%, respectively. The IR spectra show characteristic bands for **1** at 3336 cm^{-1} (ν_{N-H}), 1677 cm^{-1} ($\nu_{C=O}$) and **2** at 3270 cm^{-1} (ν_{N-H}), 1630 cm^{-1} ($\nu_{C=O}$); anal. calcd for **1**: C 73.56, H 5.70, N 13.20; found: C 72.77, H 5.54, N 12.99; anal. calcd for **2**: C 56.74, H 4.40, N 10.18; found: C 55.84, H 4.28, N 9.42.

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