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# Highly efficient epoxidation of cyclic alkenes catalyzed by ruthenium complex

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**The epoxidation of cyclic alkenes with molecular oxygen was efficiently completed in excellent epoxide yield using a novel ruthenium complex as catalyst under mild reaction conditions.**

The selective oxidation of hydrocarbons using molecular oxygen as an oxidant is a highly attractive reaction because of the low cost and environmentally friendly nature of the oxidant.[1] In 1990, Mukaiyama *et al*. reported an important breakthrough in the epoxidation of olefins using dioxygen as oxidant under ambient conditions.[2] The process involved the use of β-diketonate complexes of $Ni^{2+}$, $Co^{2+}$, and $Fe^{3+}$ as catalysts and an aldehyde as an oxygen acceptor. The yield for 1,2-epoxycyclohexane reached 84% after carrying out the reaction for 13 hours. Corain *et al*. used a copper β-carbonylenolate catalyst and obtained similar conversion and epoxide selectivity after 20–30 hours of reaction.[3] Recently Thomas *et al*. described a selective epoxidation of cyclohexene, using Mn(III)- and Co(III)-containing molecular sieves as catalysts. The conversion and epoxide selectivity were 62% and 77%, respectively, after 8 hours of reaction at 50 °C.[4]

The epoxidations of other cyclic olefins were relatively less studied and the reported systems usually employed other oxidants such as $H_2O_2$,[5] urea hydrogen peroxide[6] or oxone[7] instead of molecular oxygen.[8]

In the pursuit of economical and environmentally friendly processes for the production of epoxides, the selective epoxidation of olefins with molecular oxygen is particularly desirable. In this communication we report a highly effective catalyst system for the selective epoxidation of cyclic alkenes with molecular oxygen using a new ruthenium catalyst, namely $Ru(HL)(L)Cl_2$ (where HL is a new ligand *N*-2′-chlorophenyl-2-pyridine-carboxamide and L is its corresponding anion). Using this complex as catalyst, the epoxidation of cyclic alkenes by molecular oxygen was usually completed within 3–9 hours with excellent conversion and selectivity (*e.g.* 99.9% conversion and 97.4% selectivity for the epoxidation of cyclooctene).

The ligand and catalyst were prepared as shown in Figure 1. The red-brownish Ru complex was characterized by FTIR.[9] The molecular structure of the complex with one molecule of ethanol in the crystal lattice was determined by single crystal X-ray diffraction† and the ORTEP drawing of it is shown in Figure 2.

The crystal structure revealed the deprotonation of the amide group of one of the coordinated ligands and the coordination of this anionic ligand (L) to the metal center through the binding of the negative amide nitrogen and the pyridine nitrogen. The negative amido ligand and two coordinated chloride ligands electronically balanced the trivalent $Ru^{3+}$ metal center, while the other ligand (HL) coordinated to $Ru^{3+}$ *via* a carbonyl oxygen and a pyridine nitrogen. Therefore, the vibrational frequency of the carbonyl (C=O) in the complex was lower than that in the free ligand. Characteristic hydroxyl (O–H) vibration frequency was also found due to the presence of hydroxyl of ethanol in the complex.

In our study of the epoxidation of cyclohexene with $O_2$ catalyzed by the Ru complex (entry 1–9 in Table 1), we discovered that the reaction proceeded with high conversion and high selectivity for the desired 1,2-epoxycyclohexane product by using a substrate-to-isobutyraldehyde molar ratio of 1 : 2 or 1 : 3 (entry 1–3). When the substrate/isobutyraldehyde molar ratio was 1 : 2, catalyst concentration had a notable effect on the result of the epoxidation (entry 4–7). The results indicated that the Ru complex was highly efficient in the catalytic reaction. High conversion was achieved even with a catalyst concentration as low as 0.22 mmol $L^{-1}$. A control experiment without catalyst (entry 8) indicated that the conversion was only 21.5%.

In the absence of isobutyraldehyde (entry 9), low conversion rate and low selectivity were observed and the major product was 2-cyclohexen-1-one besides the epoxide. These results were consistent with a previous suggestion that there were two possible types of active species in the reaction,[10] one of which produced the epoxide and the other induced the formation of allylic products 2-cyclohexen-1-ol and 2-cyclohexen-1-one. The presence of isobutyraldehyde in the reaction favored the

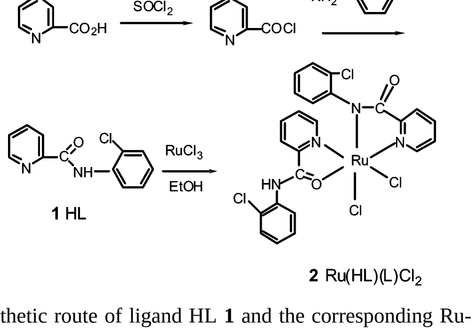

**Fig. 1** Synthetic route of ligand HL **1** and the corresponding Ru-complex **2**.

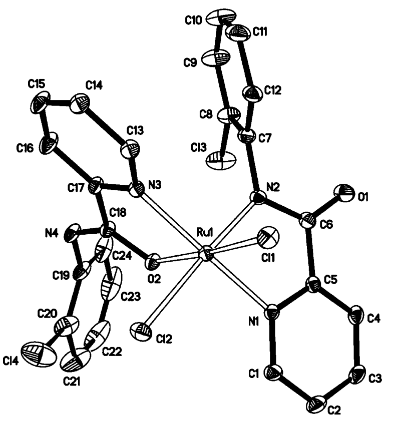

**Fig. 2** Molecular structure of complex **2** (thermal ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity).

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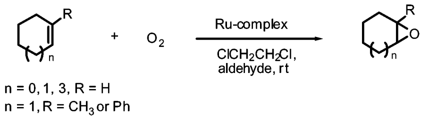
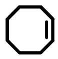
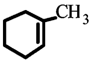
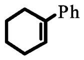
formation of the first type of active species and resulted in epoxide as a major product.

In the epoxidations of different cyclic alkenes (entry 10–13), most substrates except 1-phenylcyclohexene gave > 99.9% conversion and excellent selectivity. The highest selectivity for cyclooctene reached 97.4%. The epoxidation of 1-phenylcyclohexene did not give high selectivity, probably due to the large spatial hindrance of the phenyl group attached to the double bond.

Although the mechanism of the catalytic reaction and the role of the metal complex are still not clear, it is reasonable to speculate a mechanism involving radical species, with the metal complex acting as an initiator of the reaction as well as a catalyst for the epoxidation. When a radical trapping compound such as 2,6-di-tert-butyl-4-methylphenol was added to the reaction mixture, the epoxidation was stopped. This result is consistent with those of Haber,[11] Valentine,[12] and Nolte[13] using porphyrin, cyclam or β-diketonate complexes of metal as catalyst. Further study on the mechanism of the reaction is in progress.

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



| Entry | Substrate | Reaction time (h) | Conv. (%) | Selectivity (%) | |
|---|---|---|---|---|---|
| | | | | Epoxide[b] | Others |
| 1 [c] | | 3 | 95.0 | 84.0 | 16.0 |
| 2 [d] | | 3 | 99.5 | 87.0 | 13.0 |
| 3 [e] | | 3 | 99.7 | 88.1 | 11.9 |
| 4 [f] | | 4.0 | 95.7 | 85.1 | 14.9 |
| 5 [g] |  | 3.5 | 97.3 | 88.1 | 11.9 |
| 6 [h] | | 3.5 | > 99.9 | 90.1 | 9.9 |
| 7 [i] | | 2.5 | > 99.9 | 85.1 | 14.9 [j] |
| 8 [k] | | 3.0 | 21.5 | 68.7 | 31.3 |
| 9 [l] | | 3.0 | 3.4 | 45.8 | 54.2 [j] |
| 10 |  | 3 | > 99.9 | 90.1 | 9.9 |
| 11 |  | 9 | > 99.9 | 97.4 | 2.6 |
| 12 [m] |  | 6 | > 99.9 | 90.2 [n] | 9.8 |
| 13 |  | 7 | > 99.9 | 78.0 [n] | 22.0 |

[a] The reactions were carried out at room temperature under the following conditions: substrate = 0.93 M; catalyst = 0.88 mM; isobutyraldehyde = 1.85 M; $O_2$ = 1 atm; 4mL $ClCH_2CH_2Cl$ solvent. [b] Epoxides were identified by using authentic samples for comparison. [c] Molar ratio of alkene to isobutyraldehyde was 1:1. [d] Molar ratio of alkene to isobutyraldehyde was 1:2. [e] Molar ratio of alkene to isobutyraldehyde was 1:3. [f] Catalyst concentration was 0.22 mM. [g] Catalyst concentration was 0.44 mM. [h] Catalyst concentration was 0.88 mM. [i] Catalyst concentration was 1.76 mM. [j] Main by-product was 2-cyclohexen-1-one. [k] No catalyst. [l] No aldehyde. [m] n-butyraldehyde was used. [n] The epoxides were identified by GC (HP 5890 or 4890, column AT-1 30m × 0.25 mm) and GC-MS (HP G1800C).

In conclusion, we have prepared a novel ruthenium complex $Ru(HL)(L)Cl_2$ and its molecular structure has been determined by X-ray diffraction. When cyclic alkenes were oxidized with molecular oxygen using this complex as catalyst, the epoxidation was highly efficiently completed giving up to 97.4% yield of the desired epoxides.

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## Notes and references

† Crystal data for the complex **2**: $RuC_{24}H_{17}C_{l4}N_4O_2.C_2H_5OH$, M = 699.87, monoclinic, $a$ = 16.706(2), $b$ = 13.6138(17), $c$ = 15.7145(19) Å, $U$ = 3219.7(7) Å$^3$, $T$ = 294 K, space group $P21/c$, $Z$ = 4, μ(Mo–Kα) = 0.854 mm$^{-1}$, 21105 reflections collected, 7350 independent reflections ($R_{\text{int}}$ = 0.0629). The final $R$ indices [$I > 2\sigma(I)$]: $R1$ = 0.0506, $wR2$ = 0.1287, $R$ indices (all data): $R1$ = 0.1021, $wR2$ = 0.1561. CCDC 183350. See http://www.rsc.org/suppdata/cc/b2/b212899c/ for crystallographic data in .cif or other electronic format.

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