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Ruthenium carbonyl complexes in catalytic epoxidation of olefins co-catalyzed by isobutyl-aldehyde

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The present work shows the catalytic activity of a series of carbonyl ruthenium complexes in the epoxidation of olefins co-catalyzed by isobutyl-aldehyde. The complexes display catalytic activity in the epoxidation of the cyclohexene with high selectivity. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: ruthenium complexes; olefin epoxidation; catalysis

INTRODUCTION

Ruthenium complexes containing nitrogen ligands as catalysts have shown good activity and selectivity in oxidation and epoxidation processes.[1–3] In these reactions, the catalysts often act via formation of ruthenium-oxo species.[4,5] Ruthenium compounds, especially those containing the amino group in their structure, in the presence of O_2[6,7] or H_2O_2[8,9] have proved to be useful catalysts for oxidation of organic substrates. Binuclear ruthenium complexes of the $[L_2Ru(OH_2)_2]O$ type, where L = 2,2′-bipyridine[10] or a ring-substituted analog,[11] display good catalytic capabilities in aqueous medium. In recent years, catalytic oxygen atom transfer reactions, mediated by transition metal complexes, have received considerable attention because of the possibility of designing chemical models for cytochrome P-450 and providing new chemical knowledge about the reactions in which these enzymes are involved.[12] The active species in these enzymatic reactions is thought to be a high-valency metal–oxo complex. An important goal in this research area has been to develop catalytic systems for selective oxidation of hydrocarbons.[13] Systems studied from this point of view include metal complexes of porphyrine,[14–16] Schiff bases[17,18] and nitrogen macrocycles.[19] Recently, a ruthenium complex containing the ligand *N*-2′-chlorophenyl-2-pyridine-carboxamide has been prepared. This compound generates a highly effective catalyst system for the selective epoxidation of cyclic alkenes.[20] Additionally ruthenium complexes containing the tetradentate square-planar ligand, 6,6′-bis(benzoylamino)-2,2′-bipyridine(H_2BABP) have been employed as catalysts for oxygen-transfer reactions.[21]

This paper presents a study of ruthenium complexes with polypyridyl ligands as catalysts for cyclohexene epoxidation. Single oxygen donors, iodosobenzene (PhIO) and tert-butyl hydroperoxide (t-BuOOH) were used as oxidants in order to compare their relative efficiencies in the reaction.

EXPERIMENTAL

All solvents used were analytical grade and distilled before being used. Tert-butyl hydroperoxide in water solution was obtained from Aldrich. Iodosobenzene was prepared according to a literature procedure.[22] Oxygen (99.99%) was obtained from AGA S.A. The carbonyl derivative $[Ru(CO)_2Cl_2]_n$ was prepared by refluxing $RuCl_3 \times 3H_2O$ in a solution of HCl–HCOOH (1 : 1 v/v) for 10 h. The complexes *cis*-carbonyl *cis*-chloro-$[Ru(phen)(CO)_2Cl_2]$ (**1**) (phen = 1,10-phenanthroline), [Ru(dpphen)(tbbpy)(CO)Cl] (**2**) (dpphen = 2,9-diphenyl-1,10-phenanthroline), *cis*-carbonyl *trans*-chloro-$[Ru(tbbpy)(CO)_2Cl_2]$ (**3**) (tbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine), *cis*-carbonyl *trans*-Cl-$[Ru(mbpy)(CO)_2Cl_2]$ (**4**) (mbpy = 6-methyl-4,4′-di-tert-butyl-2,2′-bipyridine), *cis*-carbonyl *trans*-Cl-$[Ru(dmbpy)(CO)_2Cl_2]$ (**5**), (dmbpy = 6,6′-dimethyl-4,4′-di-tert-butyl-2,2′-bipyridine), *cis*-carbonyl *trans*-chloro-$[Ru(dpbpy)(CO)_2Cl_2]$ (**6**) (dpbpy = 6,6′-diphenyl-4,4′-di-tert-butyl-2,2′-bipyridine) and *cis*-H_2O-*cis*-CO-$[Ru(dpphen)(CO)_2(H_2O)_2]$ (**7**) were synthesized according to previously published methods.[1–3,22,23]

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Physical measurements

IR and Raman spectra were recorded on a Bruker 66 V instrument. Gas chromatographic analysis was carried out with a Perkin Elmer 8500 P instrument with FID, using a Carbowax 20M column and nitrogen as carrier gas. The chromatographic analysis was performed under the following conditions: temperature program, oven temperature 90 °C; initial time 5 min; ramp 20 °C/min; final time 180 min. The retention times registered were: cyclohexene, $T_R = 2.8$ min; cyclohexene oxide, $T_R = 6.4$ min; cyclohexanone, $T_R = 7.8$ min; 2-cyclohexe-1-ol, $T_R = 8.5$ min; and cyclohexanol, $T_R = 9.5$ min.

Procedure for catalytic studies

In a typical experiment, a known amount of catalytic complex (0.01 mmol) placed in an autoclave reactor (50 mL) together with isobutyl aldehyde (0.5 mL), cyclohexene (2.0 mmol) and molecular O_2 (1 atm) in 1,2-dichloroethane, was magnetically stirred at room temperature. Aliquots of solution (10 µL) were withdrawn at intervals of 2 h and analyzed by gas chromatography (GC). The procedure was modified replacing the isobutyl aldehyde and molecular O_2 by iodosobenzene or tert-butyl hydroperoxide as oxidizing agents and the reaction was carried out under nitrogen. The reaction was also followed by infrared and Raman spectroscopies.

RESULTS AND DISCUSSION

Epoxidation by ruthenium complexes

Analyses of the oxidation products show that cyclohexene gave selectively cyclohexene oxide. The reaction with oxygen and isobutyl aldehyde as oxidant agent showed good activities in cyclohexene oxide product formation. When the oxidation reactions were repeated with t-BuOOH and PhIO it was observed that the epoxidation rate was much slower than those found in the oxygen–isobutyl aldehyde systems.

The reaction rates defined as turnover frequency [TF = mol cyclohexene oxide/(mol Ru/h)] are summarized in Table 1. Iron complexes have been used as catalysts in the epoxidation of cyclohexene containing isobutyl aldehyde as co-catalyst.[24] The observed activities showed a value of TF = 15. The activities and selectivity found are lower than those reported by us in catalysis using carbonyl ruthenium (II) complexes.[1–3] All reactions gave cyclohexene oxide as the predominant product and product distributions were dependent on the identity of the individual metal complexes. The oxygen–isobutyl aldehyde system showed a very low activity when the catalyst was excluded (lower than 3% cyclohexene oxide). Nam *et al.*[24] have concluded that high-valency metal–oxo complexes are not required for the epoxidation reaction, because the acylperoxy radical generated *in situ* during the reaction of the dioxygen and aldehyde is the most probable epoxidizing agent. In this work we found dependence between epoxidation activity and the ruthenium complex identity.[1–3]

Mechanistic consideration

The radical process suggested for this catalytic reaction involves different mechanistic steps,[24] which are different from those observed in a classical epoxidation[1–3] (Scheme 1).

Oxidation mechanism of epoxidation using isobutyl aldehyde as co-catalyst

Scheme 1 shows the proposed mechanism for the epoxidation of olefins with the metallic systems used in this work, co-catalyzed by isobutyl aldehyde. In this mechanism, the metal plays two roles: (1) to activate the aldehyde as co-catalyst forming a radical species (RCO·) (steps 1 and 2); and (2) formation of the high valence oxo-metal species (step 4), responsible for the formation of epoxide of cyclohexene. Table 1 lists the activities found for the epoxidation of cyclohexene co-catalyzed by isobutyl aldehyde. The activities are better than those reported[4,5,24–26] for systems with tert-butyl hydroperoxide and iodosobenzene, showing high selectivity in epoxide formation. The isobutyl aldehyde catalyzes this reaction when the catalyst is excluded, but the activity does not surpass 3%. For this reason the activity was

Table 1. Effect of different oxidants on cyclohexene epoxidation by ruthenium complexes

	Turnover frequency		
Complexes	Ox (PhIO)[a]	Ox (t-BuOOH)[b]	Ox (O_2)[c]
cis-Cl-*cis*-CORu(phen)$(CO)_2Cl_2$ (1)	3.3	7.0	31
[Ru(dpphen)(bpy)(CO)Cl]PF_6 (2)	No activity	5.0	29
trans-Cl-*cis*-CORu(bpy)$(CO)_2Cl_2$ (3)	1.0	3.0	23
trans-Cl-*cis*-CO-Ru(mbpy)$(CO)_2Cl_2$ (4)	1.0	3.5	25
trans-Cl-*cis*-CO-Ru(dmbpy)$(CO)_2Cl_2$ (5)	1.6	3.0	20
trans-Cl-*cis*-CO-Ru(dpbpy)$(CO)_2Cl_2$ (6)	2.0	3.0	23
cis-H_2O-*cis*-CO-Ru(dpphen)$(CO)_2(H_2O)_2]Cl_2$ (7)	2.0	1.5	40

[a] Catalyst, 0.01 mmol; cyclohexene, 2.0 mmol; PhIO, 2.5 mmol; dichloromethane, 5 mL.
[b] Catalyst, 0.01 mmol; cyclohexene, 2.0 mmol; t-BuOOH, 0.5 mmol; PhIO, 2.5 mmol; dichloromethane, 5 mL.
[c] Catalyst, 0.01 mmol; cyclohexene, 2.0 mmol; oxygen, 1 atm; isobutyl aldehyde, 0.5 mL; dichloromethane, 5 mL.

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\begin{array}{lclcl l l}
\text{L-M}^{n+} & + & \text{RCHO} & \longrightarrow & \text{L-M}^{(n-1)+} + \text{RCO}^{\cdot} + \text{H}^{+} & & \text{Step 1} \\
\text{RCO}^{\cdot} & + & \text{O}_2 & \longrightarrow & \text{RCO}_3^{\cdot} & & \text{Step 2} \\
\text{RCO}_3^{\cdot} & + & \text{RCHO} & \longrightarrow & \text{RCO}_3\text{H} + \text{RCO}^{\cdot} & & \text{Step 3} \\
\text{L-M}^{n+} & + & \text{RCO}_3\text{H} & \longrightarrow & \text{L-M}^{(n+2)}=\text{O} + \text{RCO}_2\text{H} & & \text{Step 4} \\
\text{Olefin} & + & \text{L-M}^{(n+2)}=\text{O} & \longrightarrow & \text{L-M}^{n+} + \text{Product(O)} & & \text{Step 5}
\end{array}
$$

Scheme 1.

standardized previously (mmol of cyclohexene oxide—mmol of cyclohexene produced when the catalyst is excluded). The observed activities in all systems shown in Table 1 were over 30%, with the formation of small amounts of cyclohexenol, cyclohexenone and 2-cyclohexe-1-ol as by-products.

The analysis of those steps where the metal is involved showed that opposite effects were developed by the polypyridine ligand: thus in step 1, increasing the donate capacity of the ligands disfavored RCO$^\bullet$ species formation, consequently affecting the formation of species like RCO_3H and decreasing activity.

Step 4 is strongly helped by the presence of polypyridine ligands with high donating capacity, which can be appreciated by the formation of an oxometal. The oxometal formation is the key step for the generation of the epoxide from cyclohexene, which is in accord with classic epoxidations.

From the results obtained, it is possible to observe that complexes with phenanthroline as ligands provide better results than those with 2,2′-bipyridine and the results are even better when the complex used is cationic. A correlation between activity and pyridine substitution was not found for the series of 2,2′-bipyridine complexes. This can be the consequence of the fact that step 4 of the proposed mechanism is not the determining step for the reaction rate. However, both steps 1 and 4 play an important role in the speed control of the reaction, which can explain the results.

For the *cis*-CO-[Ru(dpphen)$(CO)_2(H_2O)_2](ClO_4)_2$ system an appreciable difference with the other complexes was observed which can be explained by the cationic nature and the presence of water ligand that facilitates the oxometal formation in step 4 of the mechanism.

The formation of the oxometal has been studied by Yamada[27] and Meyer.[28,29] They report the oxidation of the ruthenium complexes with polypyridyl ligand obtaining different ruthenium oxo species. Characterization by Raman and electronic spectroscopy show bands centered at 780 and 818 cm^{-1} and in the 400–600 nm range, respectively. These bands have been assigned to different Ru = O stretching modes. A solution of the catalytic system formed by ruthenium complexes with O_2 and isobutyl aldehyde shows a series of signals in the 700–800 cm^{-1} range in Raman spectroscopy and a strong band centered at 688 nm in electronic spectroscopy (Figure 2). This confirms the oxidation of the ruthenium complexes in oxo-ruthenium species after addition of the isobutylaldehyde in presence of oxygen. This information also suggests a mechanism which implies the formation of an oxo-metal species similar to that found in the oxidation of olefins.

Infrared analysis of the catalytic solution showed a peak centered at 1940 cm^{-1}, indicating that the catalytic active species is a monocarbonyl one (Figure 1). After some time the signal for the carbonyl group at 1940 cm^{-1} in the infrared spectrum is weakened, probably due to the fact that one or all of carbonyl groups from the precursor complex are oxidized into carbon dioxide in the reaction medium, generating one coordination vacancy in the substrate which finally can be occupied by oxygen to generate the Ru=O species. Gas chromatographic analysis of the gas phase showed CO_2

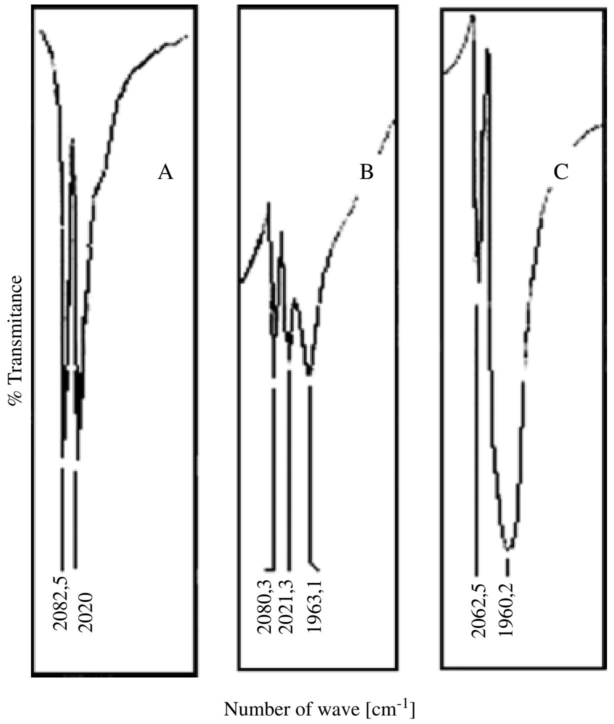

Figure 1. ν_{CO} stretching registered for the *cis*-H_2O-*cis*-CO-Ru(dpphen)$(CO)_2(H_2O)_2]Cl_2$ system in the catalytic reaction at (a) $t = 0$ min; (b) $t = 10$ min; (c) $t = 30$ min.

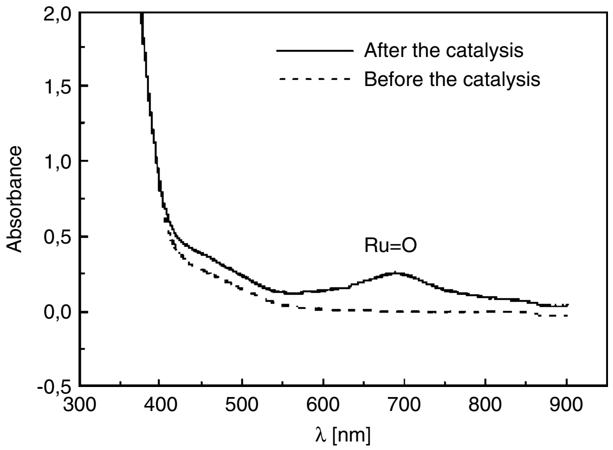

Figure 2. UV–visible spectrum of *cis*-H_2O-*cis*-CO-Ru(dpphen)$(CO)_2(H_2O)_2]Cl_2$ complex (a) before catalytic reaction and (b) after catalytic reaction.

presence. Confirmation for Ru=O species formation comes from the fact that the peak at 1960 cm^{-1} disappears completely after some time of reaction (Figure 1), which is consistent with the electronic spectrum of the solution which shows a typical band around 689 nm (Figure 2) reported for Ru=O complexes.[1–3,27–29] These results show that there is a clear dependency between the catalytic activity and the identity of the catalyst compound. The spectroscopical evidence obtained in this work allowed us to conclude that the activity follows a mechanism via oxometal formation.

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