Catalytic mono-oxygenation reactions using mono- and bi-nuclear ruthenium amide complexes as the homogeneous catalysts

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Abstract

Mono-nuclear amide complexes, their substituted complexes and bi-nuclear amide complexes of ruthenium, reported earlier by us, have been used as catalysts for the epoxidation of olefins. The complexes exhibit low to moderate catalytic activity. The electronic spectra and electrochemical study of the catalyst does not show any change on the addition of PhIO, ruling out the involvement of the metal-oxo intermediate and hence the oxygen rebound mechanism. The catalytic reaction has been explained on the basis of lewis acid behaviour of the ruthenium centre in these complexes.
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1. Introduction

Cytochrome P-450 enzymes are a group of mono-oxygenese enzymes that oxygenate a wide variety of organic substrates. Mimicking the cytochrome P-450, various metal complexes have been used as catalysts for the mono-oxygenation of the organic substrates using a mono-oxygen-atom donor oxidants like PhIO, *t*-BuOOH, etc. Groves and McClusky [1] proposed the oxygen rebound mechanism according to which, the mono-oxygenation reaction proceeds through the formation of a metal-oxo intermediate. The efficiency of a metal complex, as the catalyst for the oxygenation of hydrocarbon substrates, is dependent on the nature of the metal ion, its oxidation state and the nature of the ligands coordinated to the metal centre [2–4]. A large number of ruthenium complexes have been studied as catalysts for the mono-oxygenation reaction of the hydrocarbon substrates [5,6].

With the aim to develop new catalysts for the oxygenation of the hydrocarbon substrates and to correlate the structure and catalytic activity of the complexes, various mono- and bi-nuclear ruthenium complexes of amide ligands have been used as catalysts for the epoxidation of the olefin using PhIO as the oxidant. Herein, we report the catalytic activity of a series of ruthenium complexes and the pathway of the catalytic oxidation. The amide ligands used for the preparation of the ruthenium complexes bear different substituents at suitable positions. The electron donating or electron withdrawing nature of the substituents provide different electron density at the ruthenium centre in these complexes and should affect their catalytic activity. The complexes obtained by the substitution of two monodentate ligands by a bidentate π-acidic ligand alters the electron density at the metal centre

and hence should affect the catalytic activity of the complexes. In these substituted complexes, the ruthenium centre exists in either +2 or +3 oxidation states, depending on the nature and mode of coordination of different ligands bound to the ruthenium centre. The oxidation state of the ruthenium centre should affect the catalytic activity of the complexes. Further, the complexes, which have been synthesised with non-coordinated donor atom bearing ligand should exhibit the effect of the presence of the non-coordinated donor atom in the ligand on the catalytic activity of the complexes. The study of the catalytic activity of the bi-nuclear ruthenium complexes should help to understand the mutual effect of the two centres on their catalytic activity.

2. Experimental

2.1. Physical measurements

The gas chromatographic analysis were carried out on a Shimadzu GC 14B instrument, equipped with a oracle-3 computing integrator, using 10% SC30 with 1% QF on chromosorb column (2 m) and purified nitrogen as the carrier gas. Electronic spectra were recorded on a Shimadzu 240 UV–VIS spectrophotometer. Electrochemical measurements were made using the 174A polarographic analyser, a universal programmer, an X–Y recorder, a platinum working electrode, a platinum wire auxiliary electrode and Ag/AgNO$_3$ reference electrode. All electrochemical measurements were performed under dinitrogen atmosphere. Ferrocene was used as an internal standard, all the potentials being quoted versus the ferrocene–ferrocenium couple. Supporting electrolyte used was tetraethylammonium perchlorate (TEAP) [7]. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer using dry acetonitrile as the solvent.

2.2. Materials

Iodosyl benzene was prepared by a reported method [8]. The olefinic substrates norbornylene, cis-cyclooctene and the corresponding oxidation products, norbornylene oxide, cis-cyclooctene oxide, were obtained from Aldrich and were used as received.

2.3. Catalytic oxidation of olefins

All the reactions were carried out using the Schlenk tube technique, under dinitrogen atmosphere. A mixture of the ruthenium complex catalyst (0.01 mmol) in 1:4 (v/v) water–acetonitrile mixture and the internal standard, chlorobenzene, was deareated by passing oxygen free nitrogen gas for 5 min. Into this mixture the olefinic substrate (2.5 mmol) was added, followed by the addition of iodosyl benzene (0.5 mmol). The reaction mixture was stirred at room temperature. Two microlitres portion of aliquots were withdrawn from the reaction mixture, after each interval of 1 h, and was anaslysed by a gas chromatograph, using FID detector. After the fourth hour, no further increase in the yield of the oxidised product was found.

2.4. Result and discussion

1. The complexes obtained by the reaction of p-substituted N-phenylcarbamoyl derivatives with [Ru(dmso)$_4$Cl$_2$] in dry methanol have the following structure [9]:
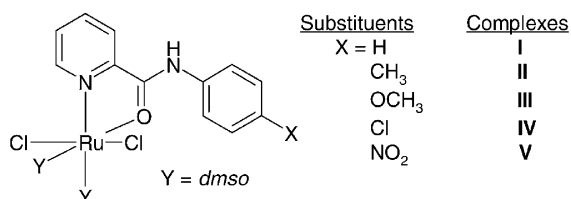
The yields of the catalytic reactions have been collected in Table 1.

Table 1
Catalytic epoxidation[a] of norbornylene and cis-cyclooctene using the complexes I–V

Catalyst	Epoxides and yields (%), turn over no.	
	Norbornylene epoxide	cis-Cyclooctene epoxide
I	25 (13)	7 (4)
II	26 (13)	13 (7)
III	25 (12)	14 (7)
IV	28 (14)	20 (10)
V	26 (13)	7 (4)

[a] Cat:PhIO:Olefine mol ratio = 1:50:250, Cat = 0.01 mmol, solvent used is aquo-acetonitrile 4:1 (v/v), yields are based on PhIO charged.
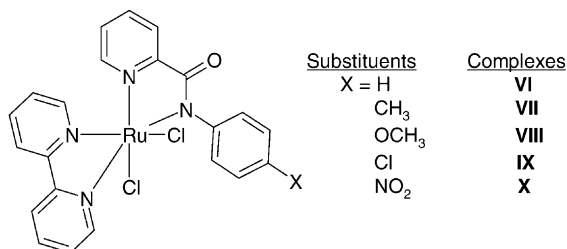
Table 2
Catalytic epoxidation[a] of norbornylene and *cis*-cyclooctene using the complexes VI–X

Catalyst	Epoxides and yields (%), turn over no.	
	Norbornylene-epoxide	*cis*-Cyclooctene-epoxide
VI	4 (2)	5 (3)
VII	5 (3)	5 (3)
VIII	4 (2)	6 (3)
IX	5 (3)	6 (3)
X	4 (2)	8 (4)

[a] Cat:PhIO:Olefine mol ratio = 1:50:250, Cat = 0.01 mmol, solvent used is aquo-acetonitrile 4:1 (v/v), yields are based on PhIO charged.

Table 3
Catalytic epoxidation[a] of norbornylene and *cis*-cyclooctene using the complexes XI–XV

Complexes	Epoxides and yields (%), turn over no.	
	Norbornylene-epoxide	*cis*-Cyclooctene-epoxide
XI	10 (5)	30 (15)
XII	13 (6)	11 (6)
XIII	11 (5)	10 (5)
XVI	9 (5)	15 (8)
XV	7 (4)	23 (11)

[a] Cat:PhIO:Olefine mol ratio = 1:50:250, Cat = 0.01 mmol, solvent used is aquo-acetonitrile 4:1 (v/v), yields are based on PhIO charged.

2. The complexes VI–X were obtained by the substitution of the coordinated dmso molecules of the complexes I–V with 2,2′-bipyridine (bpy) in dimethylformamide as the solvent. The complexes are having the following structure [10]:

Substituents	Complexes
X = H	**VI**
CH$_3$	**VII**
OCH$_3$	**VIII**
Cl	**IX**
NO$_2$	**X**

The yields of the catalytic reactions have been collected in Table 2.

3. The complex [Ru(L$_6$)(PPh$_3$)$_2$Cl$_2$], XI, where L$_6$ = 2-(*N*-(2-pyridyl)carbamoyl)pyridine, and the complexes, XII – XV, obtained as the products of the reaction of XI with the bidentate chelating ligands (L′) bpy, 1,10-phenanthroline (phen),
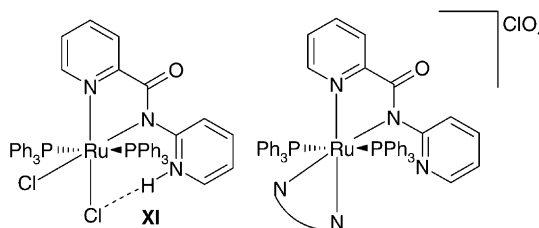
[Ru(L$_6$)(L′)(PPh$_3$)$_2$]ClO$_4$. The structure [11] of these complexes are given below:

The yields of the catalytic reactions have been collected in Table 3.

4. The complexes [Ru(L$_7$)(dmso)$_2$Cl$_2$], XVI, where L$_7$ = 2-(*N*-(2-hydroxyphenyl)carbamoyl)pyridine, was obtained by reacting L$_7$ and [Ru(dmso)$_4$Cl$_2$] in 1:1 molar proportion and XVII & XVIII were obtained by the substitution of the two coordinated dmso molecules in XVI by bpy and 1,10-phenanthroline (phen), respectively. These complexes are having the following structure [12]:

N N	Complexes
bpy	**XVII**
phen	**XVIII**
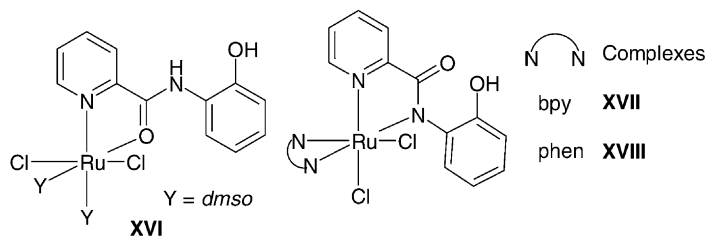
1,2-diaminoethane (en) and 2-(2-aminoethyl)pyridine (amepy), are having general formula
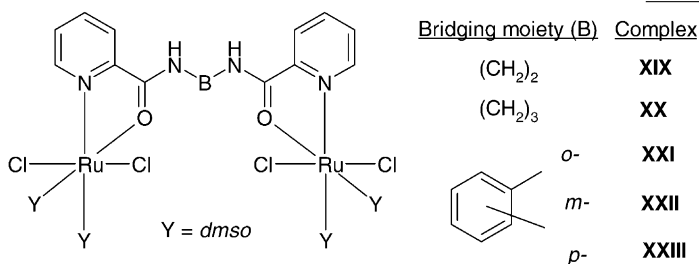
The yields of the catalytic reactions have been collected in Table 4.

Table 4
Catalytic epoxidation[a] of norbornylene and *cis*-cyclooctene using
the complexes XVI–XVIII

Complexes	Epoxides and yields (%), turn over no.	
	Norbornylene-epoxide	*cis*-Cyclooctene-epoxide
XVI	5 (3)	4 (2)
XVII	4 (2)	4 (2)
XVIII	4 (2)	4 (2)

[a] Cat:PhIO:Olefine mol ratio = 1:50:250, Cat = 0.01 mmol,
solvent used is aquo-acetonitrile 4:1 (v/v), yields are based on
PhIO charged.

5. The bi-nuclear complexes, XIX–XXIII, having the
   following structure [13] also have been used as
   catalysts:

Bridging moiety (B)	Complex
$(CH_2)_2$	**XIX**
$(CH_2)_3$	**XX**
o-	**XXI**
m-	**XXII**
p-	**XXIII**

The yields of the catalytic reactions have been col-
lected in Table 5.

The yields of the catalytic oxygenation reactions
were found to be moderate for the complexes I–V,
XI–XV and XIX–XXIII, while the yields for the com-
plexes VI–X and XVI–XVIII, are poor.

Table 5
Catalytic epoxidation[a] of norbornylene and *cis*-cyclooctene using
the complexes XIX–XXIII

Catalyst	Epoxides and yields (%), turn over no.	
	Norbornylene-epoxide	*cis*-Cyclooctene-epoxide
XIX	14 (7)	15 (8)
XX	9 (5)	4 (2)
XXI	24 (12)	19 (10)
XXII	9 (5)	18 (9)
XXIII	38 (19)	35 (18)

[a] Cat:PhIO:Olefine mol ratio = 1:50:250, Cat = 0.01 mmol,
solvent used is aquo-acetonitrile 4:1 (v/v), yields are based on
PhIO charged.

To find out the path way of the catalytic reaction,
electronic spectral studies and cyclic voltammetric
studies were carried out under catalytic reaction con-
ditions. Electronic spectra of the complexes, in 1:4
(v/v) aqueous-acetonitrile, in presence and absence
of PhIO and the olefins, are identical, indicating that
all the chromophores, which are responsible for the
different absorptions in the UV–VIS region of the
complexes, are retained under the catalytic reaction
conditions. Further, the cyclic voltammogram of the
complexes, in presence and absence of PhIO and
the olefins, are also identical, indicating that no new
redox active species is generated under the catalytic
reaction condition.

The ruthenium(II) or the ruthenium(III) centres in
the complexes, used as the catalyst for the epoxi-
dation reaction, may form either ruthenium(IV)-oxo
or ruthenium(V)-oxo intermediates, respectively, if
the catalytic reactions proceed via the oxygen re-
bound mechanism. In the IR spectra, the absorption
due to the ruthenium(IV)-oxo stretching appears
at 792 cm^{-1} for *trans*-[Ru^{IV}(trpy)(bpy)O][ClO$_4$]$_2$
[14] (trpy is 2,2':6',2''-terpyridine), at 815 cm^{-1} for
trans-[Ru^{IV}(14-TMC)O(Cl)][ClO$_4$] [15] (14-TMC
is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetrade-
cane) and at 860 cm^{-1} for *trans*-[Ru^{IV}(15-TMC)(O)$_2$]
[ClO$_4$]$_2$ [15] (15-TMC is 1,4,8,12-tetramethyl-1,4,8,
12-tetraazacyclopentadecane), and the absorp-
tion due to the ruthenium(V)-oxo stretching in
trans-[Ru^{V}(14-TMC)(O)$_2$][ClO$_4$] appears in the
840–860 cm^{-1} region [16]. To detect the formation
of the ruthenium(IV)-oxo or ruthenium(V)-oxo in-
termediates from the ruthenium(II) or ruthenium(III)
complexes, respectively, under the catalytic reaction
condition, IR spectra of the complexes were recorded
in acetonitrile solution in the presence of PhIO. The
IR spectra of the complexes in acetonitrile solution, in
the presence of PhIO, were found to be identical to that

of the parent complexes, indicating that the formation of the ruthenium(IV)-oxo or ruthenium(V)-oxo intermediates does not take place during the catalytic reaction. Thus it is concluded that the catalytic reactions do not take place via the oxygen rebound mechanism.

The metal complexes, where the metal ions do not have stable higher oxidation states, e.g. Cu(II) complexes [17,18], have been shown to catalyse epoxidation reaction. An amide complex of Fe(III), with 1,2-bis(pyridine-2-carboxamido)benzene (bpb), $[Et_3NH][Fe(bpb)Cl_2]$ has been shown to catalyse the epoxidation of olefins, though the involvement of the metal-oxo intermediate, for the catalytic epoxidation by this Fe(III) complex, could not be traced [19].

Thus for complex catalysed epoxidation reaction, where the formation of the metal-oxo intermediate could not be traced, an alternative pathway has been suggested. In this pathway the lewis acid activity of the metal centre, in the presence of the mono-oxygen-atom donor oxidant, PhIO, is held responsible for the catalytic activity. The metal complex, bearing at least one dissociable mono-dentate anionic ligand, reacts with PhIO to form an adduct (A) (in the reaction). This reactive species transfers its oxygen atom to the olefin and thereby the metal complex is regenerated, completing the catalytic cycle. In the mono-oxygenation reactions using PhIO as the oxidant and manganese porphyrin complex as the catalyst a product analogous to (A_1) (in the reaction) has been characterised spectroscopically [19].
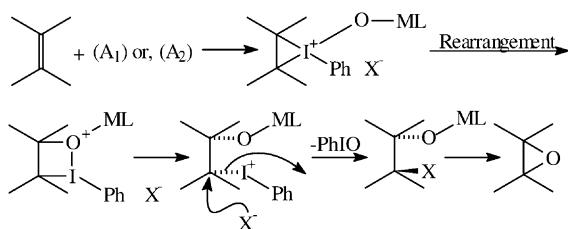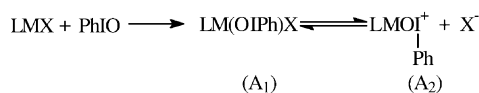
As the catalytic reactions, involving ruthenium complex catalysts, indicate no oxo-cation formation, it is assumed, that the catalytic reactions involve the above mentioned lewis acid mechanism.

A comparison of the catalytic activity of the complexes I–V and VI–X shows, that the complexes, bearing the coordinated dmso ligands, show better catalytic activity compared to the same in the complexes, where the coordinated dmso ligands are substituted by the strong π-acidic chelating ligand bpy. In the light of the above mentioned mechanism, it appears that the formation of the intermediate species (A) may be difficult for the latter class of complexes. This may be because in the latter class of complexes, the ruthenium centre is in +3 oxidation state, while in the former one it is +2. Further in the latter class of complexes the strong π-acidic nature of the bpy ligand pulls the electron density towards itself due to the π-back bonding, thereby increasing the formal positive charge over the ruthenium(III) centre. The combined effect of these two factors makes the Ru–Cl bond stronger, and hence difficult to dissociate. Thus, the formation of the intermediate (A) in the oxygenation reaction is retarded and hence the catalytic activity of the bpy substituted complexes is lowered.

In case of the complexes XVI, XVII and XVIII, the yields of the catalytic reactions are low, for both the types of complexes, containing coordinated dmso molecules or the complexes, where the coordinated dmso molecules are substituted by the strong π-acidic chelating ligands bpy and phen. Thus the low yields of the catalytic reactions may be attributed to the amide ligand L_7, present in these complexes. The amide ligand L_7 contains a non-coordinated phenolic hydroxyl group. The steric effect, exerted by this non-coordinated phenolic hydroxyl group, may make the approach of the PhIO towards the ruthenium centre difficult and hence the formation of the intermediate (A) is inhibited, resulting in lowering of the catalytic activity.

For most of the catalytic reaction, the catalytic activity of the bi-nuclear ruthenium(II) complexes XIX–XXIII are found to be less than the mono-nuclear complexes I–V. The poor catalytic activity of the bi-nuclear complexes may be attributed to the steric effect created by the second metal centre towards the interaction of the first metal centre with PhIO and the substrate in the bi-nuclear complexes, leading to the lowering of the catalytic activity of the ruthenium centre.

Moderate catalytic activity has been found for the complexes XI–XV. All of these complexes contain triphenylphosphine (PPh_3) as a secondary ligand. The coordinated PPh_3 ligand is known to undergo

oxidation under the catalytic reaction condition [20]. The moderate catalytic activity of the complexes XI–XV has been attributed to the oxidation of the coordinated PPh_3 ligands in these complexes, leading to the disintegration of the catalysts.

Acknowledgements

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