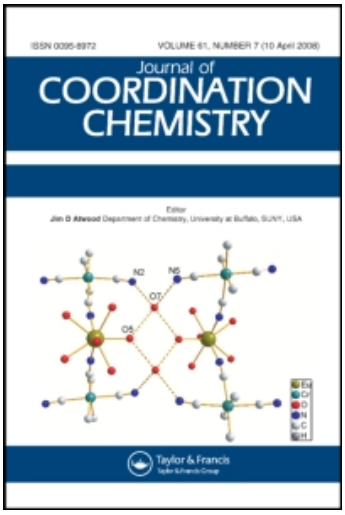

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RUTHENIUM (II) COMPLEXES IN CATALYTIC OXIDATION

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Ruthenium (II) complexes of the type $RuL(CO)_2Cl_2$, $[RuL(CO)_2L'_2]^{2+}$ and $[RuL(CO)_2Cl\ L']^+$ [L = bipyridine (bpy), phenanthroline (phen), biquinoline (biq) and L′ = pyridine (py), 4-chloropyridine (Cl-py), 4-methoxypyridine (MeO-py)] were synthesized from $[Ru(CO)_2Cl_2]_n$ and L, to produce the intermediate $RuL(CO)_2Cl_2$, followed by hydrolysis and reaction with L'. The catalytic activity of these complexes in epoxidation of olefins with iodosylbenzene under ambient conditions was investigated. A possible mechanism of these reactions, explaining the effects of the ligands on the reaction was explored. At least one carbonyl ligand remained bound to the metal through the reaction. The formation of an oxo intermediate was inferred from spectroscopic detection of bridged oxygen Ru—O—Ru and Ru=O species.

Keywords: Ruthenium; Carbonyl; Bipyridine; Phenantroline; Epoxidation

INTRODUCTION

Ruthenium complexes with nitrogen-based ligands have been intensively investigated in order to develop catalysts for organic oxidation processes and to simulate mechanism of bioorganic oxidation. This is because ruthenium complexes act as oxidation catalysts, often *via* ruthenium-oxo species, oxidizing alcohol or alkanes and epoxidizing alkenes [1]. Some examples of chiral induction in the epoxidation have been reported [2]. Substituted bipyridine ligands have been used to change the electronic and

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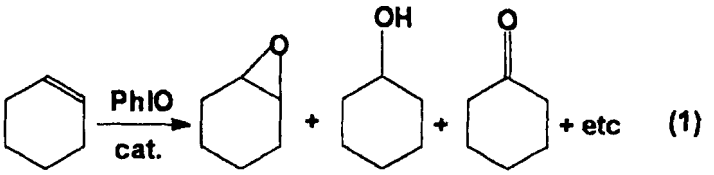
steric properties of Ru-complexes [3]. Groves and Quinn first examined the use of sterically bulky ruthenium (II) porphyrin complexes which catalyse aerobic oxidation of alkenes with high stereospecificity at room temperature [4]. It has been demonstrated that the sterically bulky *cis*-$[Ru^{II}(2,9\text{-}Me_2phen)_2(OH_2)_2]^{2+}$ complex (2,9-Me_2phen = 2,9-dimethyl-phenanthroline) mediates alkene epoxidation by dioxygen [5]. It is believed that a higher oxidation state ruthenium complex is generated under the oxidation conditions of reaction. Recent advances in the study of epoxidation of olefins by high-valent metal oxo-complexes have led to detailed suggestions about how these reactions occur. The mechanisms consider initial steps in which the key redox intermediate involves the formation of a) metalloxetanes, b) π-cation radicals, c) carbocations, d) carbon σ-radicals or, on the other side, concerted oxene insertion into the double bond [6]. When the oxidant is iodosylbenzene (Ph—I=O) other mechanisms are also possible [7]. One goes through a species Ru—O—I—Ph(Cl) which may be in equilibrium with Ru—O—I—$Ph^+ + Cl^-$. The I^{III} species reacts through an electrophilic attack on the olefin, before rearrangement and O—I bond cleavage. In this case no high valent metal oxo species is required, as the oxidant actually is I^{III}. In this manuscript the synthesis and catalytic activity of a series of Ru(II) complexes (Eq. **1**) in the epoxidation of olefins are reported.



(1)

EXPERIMENTAL

Materials

Commercial hydrated "$RuCl_3$" was purchased from Strem and the bpy, phen and biq ligands, as well as silver triflate from Aldrich. All solvents used were analytical grade and were distilled prior to use. Iodosylbenzene was prepared according to the literature procedure [8]. Although the Ru(II) complexes were stable in air, their synthesis was carried out under nitrogen.

The carbonyl derivative, $[Ru(CO)_2Cl_2]_n$ (**1**) was prepared by refluxing $RuCl_3$ in a solution of HCl/HCOOH 1/1 v/v, for 10 h. The yellow powder obtained shows the characteristic IR signals (Tab. II) Anal. Calcd. for $RuC_2O_2Cl_2$ (%): C, 10.53. Found: C, 10.85.

Synthesis of ***trans*-Cl-Ru(bpy)$(CO)_2Cl_2$ (2).** This procedure is a modification of a previously described method [3c]. 0.2 g (1.31 mmol) of **1** was dissolved in a mixture of ethanol/H_2O/CH_3CN 3/1/1 v/v. 0.206 g (1.31 mmol) of bpy was added and the reaction was refluxed for 3 h. The red mixture of the *cis*-and *trans*-isomers was separated by flash chromatography (silica gel, acetone/dichloromethane 1/1 v/v). The ***cis*-2** complex shows the carbonyl stretching modes at 2054 cm^{-1} and 1984 cm^{-1}. The *trans*-2 complex shows these bands at 2028 cm^{-1} and 1954 cm^{-1} Anal. Calcd. for $RuC_{12}N_2H_8O_2Cl_2$ (%): C, 37.52; N, 7.29. Found: C, 37.78; N, 7.31. Yield 67%. Mp = 283.4–284.0°C.

Synthesis of ***cis*-Cl-Ru(phen)$(CO)_2Cl_2$ (3).** This complex was prepared as previously reported for similar compounds [3c]. 0.32 g (1.40 mmol) of **1** was dissolved in a mixture of ethanol/H_2O 3/1 v/v. 0.255 g (1.4 mmol) of 1,10-phen was added and the reaction was refluxed for 4 h. The yellow precipitate of a mixture of the *cis*-and *trans*-isomers obtained after washing many times with ethanol was separated by flash chromatography (silica gel, acetone/dichloromethane 2/1 v/v). The ***cis*-3** complex shows the carbonyl stretching modes at 2049 cm^{-1} and 1986 cm^{-1}. The ***trans*-3** complex shows these bands at 2024 cm^{-1} and 1945 cm^{-1}. Yield 67% Anal. Calcd. for $RuC_{14}N_2H_8O_2Cl_2$ (%): C,41.19;N, 6.86. Found: C, 40.60; N, 6.66. Yield 67%. Mp = 300.1–301.0°C.

Synthesis of ***trans*-Ru(biq)$(CO)_2Cl_2$(4)** 0.3 g (1.31 mmol) of **1** was dissolved in a mixture of ethanol/H_2O 3/1 v/v. 0.335 g (1.31 mmol) of biq was added and the reaction was refluxed for three. The yellow precipitate of a mixture of the *cis*- and *trans*-isomers obtained after successive washing with ethanol was separated by flash chromatography (silica gel, acetone/dichloromethane 2/1 v/v). The ***cis*-4** complex shows the carbonyl stretching modes at 2049 cm^{-1} and 1978 cm^{-1}. The ***trans*-4** complex shows these bands at 2024 cm^{-1} and 1935 cm^{-1}. Anal. Calcd. for $RuC_{20}N_2H_{12}O_2Cl_2$ (%): C, 49.6; N, 5.78. Found: C, 50.41;N, 5.81. Yield for the mixture of the isomers is 67%. Mp = 254.1–255.0°C.

General synthesis of **Ru(L)$(CO)_2(CF_3SO_3)_2$** [L = bpy (**5**), phen (**6**) and biq (**7**)]0.4 mmol of compound **2,3** or **4** were dissolved in dichloromethane (15 mL) and a stoichiometric amount of $Ag(CF_3SO_3)$, dissolved in a minimum amount of methanol, was added. After stirring at 25°C for 5 h a white AgCl precipitate was separated by filtration. The solution was

evaporated to dryness. The product was recrystallized from dichloromethane/acetone.

Anal. Calcd. for $RuC_{14}N_2H_8O_8F_6S_2$ (**5**) (%): C, 27.50; N, 4.57; S,10.49. Found: C, 26.91; N, 3.99; S, 8.30. Yield 55%. Anal. Calcd. for $RuC_{14}N_2H_8O_8F_6S_2$ (**6**) C, 30.24; N, 4.41; S, 10.09. Found: C, 29.11; N, 4.19; S, 9.72. Yield 57%. Anal. Calcd. for $RuC_{20}N_2H_{12}O_8F_6S_2$ (**7**) C, 37.13; N, 3.94; S, 9.02. Found: C, 36.69; N, 3.60; S, 7.58. Yield 69%.

Synthesis of **[Ru(bpy)(CO)$_2$(py)Cl]PF$_6$ (8)**. 0,2 g (0.5208 mmol) of **2** was suspended in water and 0.042 mL(0.5208 mmol) of freshly distilled pyridine was added. This mixture was refluxed until a yellow solution was formed. The solution was filtered and an excess of KPF_6 was added in order to precipitate the product, which was washed with water. Anal. Calcd. for $RuC_{17}N_3H_{13}O_2ClPF_6$ (%): C, 35.63; N, 7.34. Found: C, 35.23; N, 7.23. Yield 68%. Mp = 137.5–137.9

[Ru(bpy)(CO)$_2$(L')Cl]PF$_6$, with L' = 4-chloro-pyridine, (Cl-py) (**9**) and 4-methoxy-pyridine (MeO-py) (**10**) were prepared by similar procedures and recrystallized from dichloromethane. Anal. Calcd. for $RuC_{17}N_3H_{12}O_2Cl_2PF_6$ (**9**)(%): C, 33.63; N, 6.92. Found: C, 34.73; N, 6.65.Yield 62%. Mp = 135.1–135.9 Anal. Calcd. for $RuC_{18}N_3H_{15}O_3ClPF_6$ (**1O**)(%): C, 35.86; N, 6.97. Found: C 35.23; N, 6.97. Yield 63%. Mp = 139.3–140.2°C.

Synthesis of **[Ru(phen)(CO)$_2$(py)Cl]PF$_6$ (11)**. 0,2 g (0.4902 mmol) of **3** was suspended in water and 0.0395 mL (0.4902 mmol) of freshly distilled pyridine was added. This mixture was refluxed until a yellow solution formed. The solution was filtered and an excess of KPF_6 was added to precipitate the product, which was washed with water. Anal. Calcd. for $RuC_{19}N_3H_{13}O_2ClPF_6$(11)(%): C, 38.23; N, 7.04. Found C, 38.72; N, 6.60. Yield 62%. M.p. = 197.8–198.5°C.

[Ru(phen)(CO)$_2$(L')Cl]PF$_6$ with L' = 4-chloro-pyridine,(Cl-py) (**12**), 4-methoxy-pyridine (MeO-py) (**13**), 2-picoline (2Me-py) (**14**), 3-picoline (3Me-py) (**15**) and 4-picoline (4Me-py) (16) were prepared by a similar procedures and recrystallized from dichloromethane. Anal. Calcd. for $RuC_{19}N_3H_{13}O_2ClPF_6$(**12**) (%): C, 36.11; N, 6.66. Found: C, 35.89; N, 6.46 yield 67%. Mp = 197.8–198.5. Anal. Calcd. for $RuC_{19}N_3H_{12}O_3Cl_2PF_6$(**13**) (%): C, 38.32; N, 6.70. Found: C, 38.52; N, 6.46. Yield 63%. Mp = 199.5–202.1. Anal. Calcd. for $RuC_{20}N_3H_{15}O_2ClPF_6$ (**14**)(%): C, 39.30 ; N, 6.87. Found: C, 38.90; N, 6.47. Yield 78%. Mp = 201.3–202.1. Anal. Calcd. for $RuC_{20}N_3H_{15}O_2ClPF_6$(**15**)(%): C, 39.30; N, 6.87, Found: C, 38.70; N, 6.37. Yield 74%. Mp = 202.1–203.0. Anal. Calcd. for $RuC_{20}N_3H_{15}O_2ClPF_6$(**16**)(%): C, 39.30; N, 6.87, Found: C, 39.08; N, 6.68 yield 67%. Mp = 201.6–202.5°C.

Synthesis of **$[Ru(L)(CO)_2(H_2O)_2(CF_3SO_3)_2$** [L = bpy (**17**), phen (**18**) and biq (**19**)]. 0.5 mmol of $Ru(L)(CO)_2(CF_3SO_3)_2$ (**5**, **6** or **7**) was suspended in acetone/water 1:1 v/v. The solution was purged with nitrogen and then refluxed for 2 h. The solution changed from light yellow to red brown with precipitation of the complex, which was recrystallized from acetone. Anal. Calcd. for $RuC_{14}N_2H_{12}O_{10}F_6S_2$(**17**) (%): C, 25.96; N, 4.32; S 9.91. Found:C,26.30; N, 4.46; S 10. Yield 90% Anal. Calcd. for $RuC_{16}N_2H_{12}O_{10}F_6S_2$(**18**) (%): C, 28.61; N, 4.17, S 9.72. Found: C, 35.89; N, 6.46 55. Yield 92%. Anal. Calcd. for $RuC_{22}N_2H_{16}O_{10}F_6S_2$(**19**): C, 35.33; N, 3.94; S, 9.02. Found: C, 35.89; N, 3.56. Yield 87%.

Table I collects the molar conductivity in acetone of the complexes, showing the 1:1 or 1:2 nature of these electrolytes [9].

Epoxidation Reactions

Epoxidation reactions were carried out in a 25 mL batch reactor, provided with a septum in order to sample the reaction each hour. Cyclohexene (0.5 mmol) was epoxidized with iodosylbenzene (1.0 mmol) under nitrogen. The reactions were carried out in acetone/water 6 : 1 v/v at 25°C for 6 h and 24 h in the presence of 0.02 mmol of the ruthenium complex.

Test for the Oxo Ruthenium Complexes Obtained After the Oxidation Reactions

To $[Ru(phen)(py)(CO)_2Cl]PF_6$(0.01 mmol) in acetone/water 3/0.5 v/v, an excess of PhIO (0.05 mmol) was added. The mixture was stirred under N_2

TABLE I Molar conductivity of the complexes in acetone (10^{-3} M at 25°C) in Ohm^{-1} cm^2 mol^{-1}

Complex	Λ_m $Ohm^{-1}cm^2mol^{-1}$
$[Ru(bpy)(CO)_2(Cl\text{-}py)Cl]PF_6$	107.1
$[Ru(bpy)(CO)_2(MeO\text{-}py)Cl]PF_6$	99.8
$[Ru(bpy)(CO)_2pyCl]PF_6$	114.3
$[Ru(phen)(CO)_2(Cl\text{-}py)Cl]PF_6$	141.3
$[Ru(phen)(CO)_2(MeO\text{-}py)Cl]PF_6$	137.2
$[Ru(phen)(CO)_2pyCl]PF_6$	130.5
$[Ru(phen)(CO)_2(CF_3SO_3)_2$ *	195.3
$Ru(bpy)(CO)_2(CF_3SO_3)_2$ *	189.2
$Ru(biq)(CO)_2(CF_3SO_3)_2$	200.5
$[Ru(phen)(CO)_2(4Me\text{-}py)Cl]PF_6$	135.6
$[Ru(phen)(CO)_2(3Me\text{-}py)Cl]PF_6$	140.1
$[Ru(phen)(CO)_2(2Me\text{-}py)Cl]PF_6$	134.5
$[Ru(phen)_2(CO)Cl]PF_6$	120.5

*Solvation with the acetone produces the ionic complexes.

for 20 h until the solution became green. The undissolved PhIO was filtered out and an excess of KF_6 was added to precipitate the product which was exhaustively washed with acetone, dichloromethane and ether.

Measurements

UV-Vis spectra were obtained in a quartz cell at room temperature on a UNICAM UV/Vis spectrometer UV3. Molar extinction coefficients were calculated from a least square linear regression of absorbance data at different concentrations. Elemental analyses were done by the Pharmacy School of the University of Chile. Molar conductivities were determined for 1 mF solutions of the complexes in acetone at 25°C using a W.T.W. microprocessor conductivity meter. Infrared spectra were carried out with KBr or polyethylene discs, using a Bruker IFS-66 V Fourier-transform spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ on a 300 MHz Bruker Avance DRX spectrometer. Gas chromatographic analyses of the samples from oxidation reactions were conducted by using a Perkin Elmer Sigma 3 with flame ionization detector and a SP-1000 column. High purity grade nitrogen was used as carrier gas. Identification of components was established by comparing the retention time with the authentic samples. Quantification of the individual gas chromatographic components was performed by an internal standard method employing a E. Nelson 1022 Integrator and using heptane or toluene as internal standard.

RESULTS

Complexes of the type $[RuL(CO)_2L'Cl]PF_6$ (Fig. 1) were obtained by hydrolysis of the $RuL(CO)_2Cl_2$ complexes and reaction with the pyridine ligand. The yellow complexes were stable in air and showed the

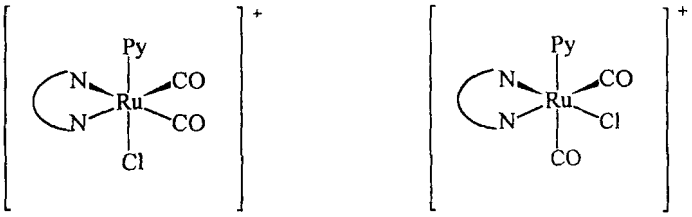


FIGURE 1 Complexes $[Ru(bpy)(CO)_2pyCl]^+$ (A) and $[Ru(phen)(CO)_2pyCl]^+$ (B).

characteristic IR for a *trans*-complex. ^1H NMR spectra showed the characteristic resonances of the coordinated ligands.

The Ru(II) complexes $RuL(CO)_2(CF_3SO_3)_2$ were obtained from $RuL(CO)_2Cl_2$ by substitution of the chloride ions by silver triflate in dichloromethane. They were stable yellow products, but the lability of the triflate ligand was evidenced in more coordinating solvents, giving cationic complexes in acetone (see Tab. I).

The variety of ligands used changes the electron density on the ruthenium atom as shown by the CO stretching mode, displayed in Table II. In fact the ν(CO) correlate with the Hammet parameters of the H, Cl and CH_3O substituents. A linear relationship between ν(CO) and σ_p is shown in Figure 2. This relationship can be explained by the electron donating ability of the methoxy group, which gives electron density to the metal, enhancing the π backbonding $Ru \rightarrow \pi^*(CO)$, leading to a decrease of ν(CO). In contrast, an electron-releasing group such as Cl withdraws electron density from the metal, decreasing the $Ru \rightarrow \pi^*(CO)$ backbonding, leading to an increase of the ν(CO). When iodosylbenzene was added to acetone/water solution of the complexes (in the presence or absence of the cyclohexene), a shift in color was observed from yellow to brown, which slowly changed to green after 14 h. At this time all the iodosylbenzene was consumed, as the characteristic band in the UV-Vis at 560 nm was not found [10]. The IR spectra of the solid isolated from these reactions showed a band at

TABLE II IR data in the CO stretching mode for the complexes

	Complex	ν *CO* cm^{-1}
1	$Ru(CO)_2Cl_2$	2066, 1995, 1945
2	$Ru(bpy)(CO)_2Cl_2$	2056, 1997
3	$Ru(phen)(CO)_2Cl_2$	2028, 1957
4	$Ru(biq)(CO)_2Cl_2$*	2050, 2021, 1979,1935
5	$Ru(bpy)(CO)_2(CF_3SO_3)_2$	2082, 2019
6	$Ru(phen)(CO)_2(CF_3SO_3)_2$	2097, 2037
7	$Ru(biq)(CO)_2(CF_3SO_3)_2$	2091, 2036
8	$[Ru(bpy)(CO)_2(py)Cl]PF_6$	2082, 2021
9	$[Ru(bpy)(CO)_2(Cl\text{-}py)Cl]PF_6$	2089, 2025
10	$[Ru(bpy)(CO)_2(MeO\text{-}py)Cl]PF_6$	2066, 1996
11	$[Ru(phen)(CO)_2(py)Cl]PF_6$	2081, 2019
12	$[Ru(phen)(CO)_2(Cl\text{-}py)Cl]PF_6$	2083, 2020
13	$[Ru(phen)(CO)_2(MeO\text{-}py)Cl]PF_6$	2076, 1998
14	$[Ru(phen)(CO)_2(2Me\text{-}py)Cl]PF_6$	2080, 2021
15	$[Ru(phen)(CO)_2(3Me\text{-}py)Cl]PF_6$	2076, 2015
16	$[Ru(phen)(CO)_2(4Me\text{-}py)Cl]PF_6$	2085, 2023
17	$Ru(bpy)(CO)_2(H_2O)_2(CF_3SO_3)_2$	2084, 2025
18	$Ru(phen)(CO)_2(H_2O)_2(CF_3SO_3)_2$	2095, 2035
19	$Ru(biq)(CO)_2(H_2O)_2(CF_3SO_3)_2$	20912027

**Cis* and *trans* mixture.

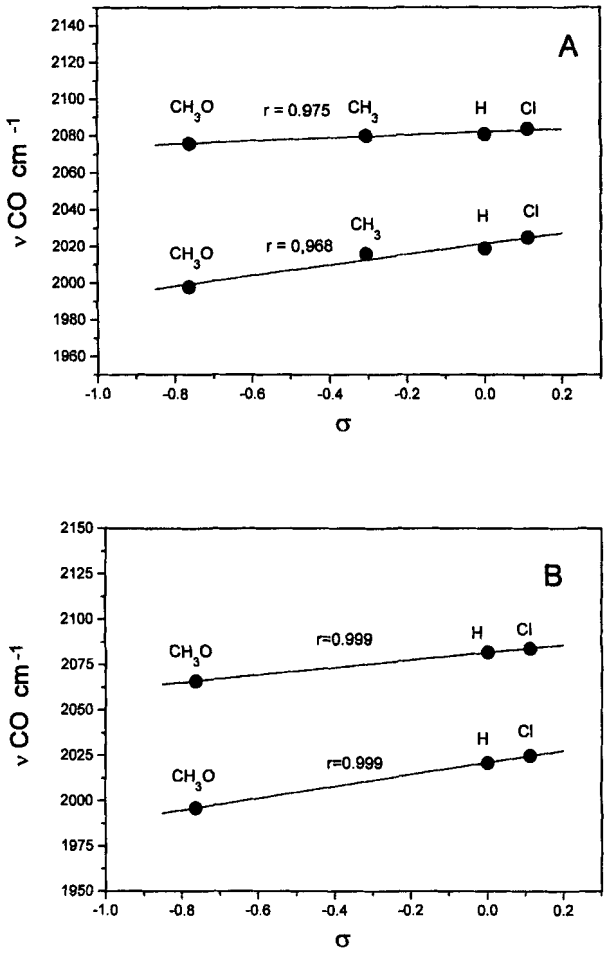


FIGURE 2 Hammet plot of ν CO and σ_p. The *para* substituent X in the pyridine ligand is Cl, CH_3 or CH_3O. **A**: $[Ru(phen)(CO)_2(p\text{-}Xpy)Cl]^+$; **B**: $[Ru(bpy)(CO)_2(p\text{-}Xpy)Cl]^+$

760.6 cm^{-1}, which was not present in the precursor complex, that may belong to a Ru=O stretching mode [11]. In addition this product shows a band in 1960 cm^{-1}, which is characteristic of a mono carbonyl complex. Figure 3 shows the absorption at 689 nm that this complex displays, which is very close to those reported for similar Ru μ-oxo complexes [10, 12]. As Table III shows, no other absorptions are expected in this region of the spectra. Elemental analysis of this complex is consistent with the proposed formula $[(bpy)(CO)pyClRu]_2O$. These types of μ-oxo ruthenium complexes are generally considered catalytically inactive [10, 13].

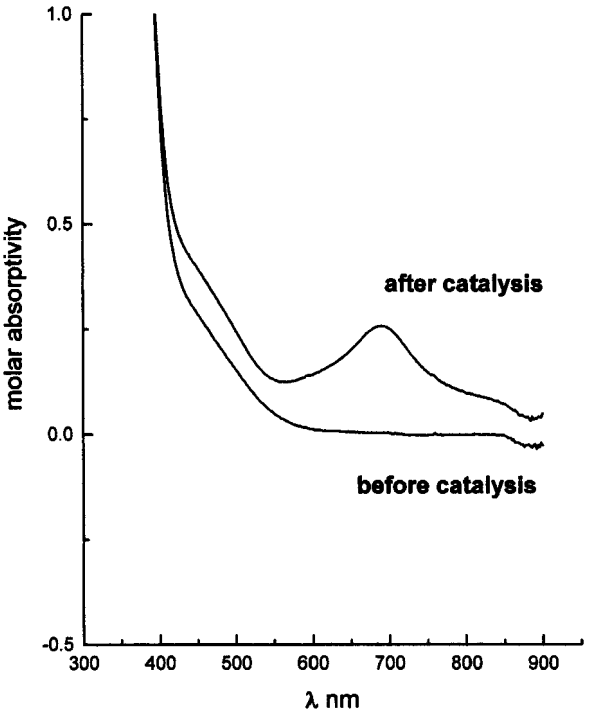


FIGURE 3 UV-Vis spectrum of $[Ru(bpy)(CO)_2Clpy]^+$ and the same complex oxidized by PhIO in acetone/water.

TABLE III Electronic absorption band maxima of the complexes in acetone

Complex	$\lambda_{max}nm(\varepsilon_{max} \times 10^{-3}, M^{-1}cm^{-1})$
$[Ru(bpy)(CO)_2pyCl]PF_6$	448(0.12); 348 (2.4) sh; 316 (19) 304 (18); 248(22); 218 (26)
$[Ru.(bpy)(CO)_2(MeO\text{-}py)Cl]PF_6$	447 (0.11); 348 (2.3) sh; 316 (18) 304 (17); 249(21); 218 (25)
$[Ru(bpy)(CO)_2(Cl\text{-}py)Cl]PF_6$	444 (0.2); 344 (2.1) sh; 316 (14) 304 (14); 248(17); 220 (22)
$[Ru(phen)(CO)_2pyCl]PF_6$	459 (0.30); 365 (2.8); 278 (38); 226 (40)
$[Ru(phen)(CO)_2(MeO\text{-}py)Cl]PF_6$	458(0.42); 367 (3.0); 278 (37); 226 (37.)
$[Ru(phen)(CO)_2(Cl\text{-}py)Cl]PF_6$	460 (0.26); 366(2.9); 278(36); 226 (43.)
$[Ru(phen)(Co)_2(4Me\text{-}pyCl]PF_6$	455 (0.50); 364 (2.7); 278 (41); 226 (31)

Moderate activity with high selectivity to cyclohexene oxide formation is observed in the oxidation reactions of cyclohexene in presence of these complexes, as is displayed in Tables IV and V. The complexes with bpy show activity and selectivity dependent on the substituent in the pyridine ligand: the more basic is the ligand the larger the activity and selectivity observed. In complexes with phen this trend is less evident.

TABLE IV Catalytic activity of 2,2 bipyridine complexes in the epoxidation of cyclohexene ($5 * 10^{-4}$ M) by iodosylbenzene, in acetone/H_2O (3 mL/0,5 mL), $2 * 10^{-3}$ M in complex, at 20°C, under a N_2 atmosphere, 24 hours

	Complex	*Cyclohexene* (%)	*Cyclohexene oxide* (%)	*Cyclohexanone* (%)	*Cyclohexanol* (%)
9	$[Ru(bpy)(CO)_2(Cl\text{-}py)Cl\text{-}py]PF_6$	62.0	34.5	1.4	2.2
8	$[Ru(bpy)(CO)_2pyCl]PF_6$	58.1	37.5	1.7	2.7
10	$[Ru(bpy)(CO)_2(MeO\text{-}py)Cl]PF_6$	53.3	42.3	2.3	2.1
17	$Ru(bpy)(CO)_2(H_2O)_2(CF_3SO_3)_2$	77.0	6.2	1.1	16.2
	$Ru(bpy)_2Cl_2$	78.1	5.9	0.0	0.0

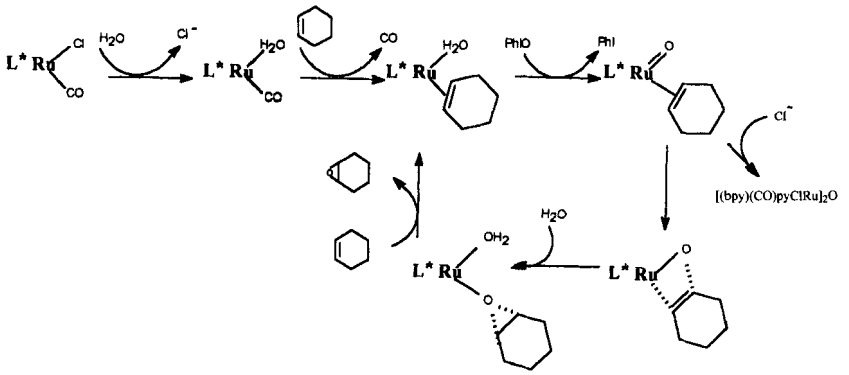
TABLE V Catalytic activity of 1,10 phenanthroline complexes in the epoxidation of cyclohexene by iodosylbenzene in acetone/H_2O (3 mL/0.5 mL), $2 * 10^{-3}$ M in complex at 20°C, under a N_2 atmosphere, 24 hours

	Complex	*Cyclohexene* (%)	*Ciclohexene oxide* (%)	*Ciclohexanone* (%)	*Ciclohexanol* (%)
12	$[Ru(phen)(CO)_2(Cl\text{-}py)Cl]PF_6$	43.8	40,5	1,6	4.2
11	$[Ru(phen)(CO)_2(py)Cl]PF_6$	43.5	39.5	1,7	2,7
14	$[Ru(phen)(CO)_2(2Me\text{-}py)Cl]PF_6$	68.5	30.5	0.0	1.0
15	$[Ru(phen)(CO)_2(3Me\text{-}py)Cl]PF_6$	68.2	31.1	0.1	0.6
16	$[Ru(phen)(CO)_2(4Me\text{-}py)Cl]PF_6$	26.9	32.4	0.0	0.8
13	$[Ru(phen)(CO)_2(MeO\text{-}py)Cl]PF_6$	51.2	45,3	1,4	1,1
18	$Ru(phen)(CO)_2(H_2O)_2(CF_3SO_3)_2$	71.7	7,4	0,7	20,2
	$[Ru(phen)(CO)\{P(MeOPh)_3\}Cl_2]PF_6$	82.6	7.6	0.0	0.8
	$[Ru(phen)_2(CO)Cl]PF_6$	79.5	4.5	0.0	0.0

DISCUSSION

The experimental evidence suggests the formation of an oxo complex during the catalytic cycle. Hydrolysis of the chloride ligand and oxidation of the complex by iodosylbenzene may generate it. This oxo complex may decompose during the reaction to the reported inactive μ-oxo Ru—O—Ru complex detected as one of the final products. The surprising stability of the carbonyl ruthenium bond was shown by its FT-IR absorption, after the ruthenium complex reacted with an excess of the oxidant. This band is characteristic of a mono carbonyl derivative and its stability may be attributed to the large sigma donor capacity of the other ligands bonded to the ruthenium ion. On the other hand, Table IV shows the importance of this ligand for the catalytic activity, as the complex $Ru(bpy)_2Cl_2$, which does not have carbonyl ligand, shows very low catalytic activity. The liberated CO ligand in the catalytic cycle probably is substituted by cyclohexene (its concentration is 25 times that of the catalyst), allowing a proximity interaction with the oxo ligand. In this step decomposition to a dimeric oxo bridged ruthenium complex may occur.

The derivatives of bpy show that oxidation of the Ru(II) to Ru(IV) oxo complex may be a slow step in the mechanism, as more basic ligands facilitate oxidation. This is also in accord with the slowest rate observed for complex **17** (which has no py derivative as ligand) and $Ru(bpy)_2Cl_2$ (which has no labile carbonyl ligands to allow coordination of the olefin substrate). On the other hand, the phen derivatives are less sensitive to the basicity of the pyridine ligand as phen itself is basic enough to support the oxidation of



SCHEME 1 Proposed catalytic cycle for the epoxidation of cyclohexene by PhIO in the presence of L*Ru(CO)Cl (L* = L(CO)L', see text for the meaning of L and L').

the metal. The low activity of the $[Ru(phen)_2(CO)Cl]PF_6$ shows the adverse effect of a bulky ligand in this reaction.

A possible mechanism for this reaction is represented in Scheme 1.

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