Syntheses and Reactivities with Olefins of Ruthenium(IV) Oxo/Ruthenium(II)-Aqua Complexes that Contain 2,6-Bis(N-pyrazolylpyridine)

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The syntheses and reactivities with olefins of $[Ru^{II}(L_3)(L_2)OH_2]^{2+}$ $[L_3 = 2,6\text{-bis}(N\text{-pyrazolyl})\text{pyridine}(bpp)$, $2,6\text{-bis}(3,5\text{-dimethyl-}N\text{-pyrazolyl})\text{pyridine}$ (Me_4bpp); $L_2 = 2,2'\text{-bipyridine}(bpy)$, $4,4'\text{-dimethyl-}2,2'\text{-bipyridine}$ $(Me_2bpy)]$ are described. Their spectral and redox properties in aqueous solution were investigated. Evidence for each one electron redox process for the $Ru^{IV}\text{-}Ru^{III}$ and $Ru^{III}\text{-}Ru^{II}$ couples has been obtained. Oxidation of $[Ru^{II}(bpp)(bpy)OH_2]^{2+}$ with Ce^{IV} gave $[Ru^{IV}(bpp)(bpy)O]^{2+}$. The $Ru^{IV}=O$ complex is paramagnetic $(\mu_{eff} = 2.82)$ and the complexes $[Ru(L_3)(L_2)OH_2]^{2+}$ are robust catalysts for the oxidation of styrene, cyclohexene, and cyclooctene with cooxidant such as NaOCl. Product distributions and selectivities are discussed by varying the number of the substituted-methyl group in the ring.

Introduction

The chemistry of high-valent ruthenium-oxo complexes has received much attention recently due to the potential applications oxidation catalysts and as oxygen atom transfer agent.[1] The interest in studying these complexes stemed its origin from the postulation that high valent oxo-iron species is involved in the enzymatic reactions of cytochrome P-450 which is known to catalyze hydroxylation of unactivated C-H bonds under mild condition. Ruthenium, being in the same group as iron, is particularly interesting in studying owing to the wide applicability of its oxides such as RuO_4 in synthetic organic chemistry.[2] Many complexes containing Ru (IV)-oxo and Ru(VI)-dioxo moieties were reported and used as catalysts for the oxidation of a variety of organic compounds, including triphenylphosphine, dimethylsulfide, alcohols, phenols, olefins, and alkenes.[2-3]

The chemistry of ruthenium(IV) oxo complexes containing poly pyridine ligands, such as $[Ru(tpy)(bpy)O]^{2+}$ (tpy = 2,2' : 6', 2''-terpyridine, bpy = 2,2'-bipyridine) and $[Ru(bpy)_2(py)O]^{2+}$ (py = pyridine), has been extensively studied by Meyer and coworkers.[3] We have attempted to vary the structures of these complexes by replacing a tpy ligand with a pyrazole-substituted pyridine ligands such as bpp and Me_4bpp [bpp = 2,6-bis(N-pyrazolyl)pyridine; Me_4bpp = 2,6-bis(3,5-dimethyl-N-pyrazolyl) pyridine]. Investigations of transition metal complexes of the tridentate ligand such as terpyridine and substituted derivatives are severely limited by the tedious synthesis of this class of compounds. The resulting complexes are good structural and reactive mimics for the analogous terpyridine complexes, and being allowed for the systematic variation of the reactive properties of the complexes on the oxidation of olefin by varying the number of methyl groups on the ligand. We report here the syntheses and reactivities with olefins of ruthenium(IV)-oxo and ruthenium(II)-aqua complexes.

Experimental

Materials. $RuCl_3 \cdot 3H_2O$ was purchased from Aldrich chemical Co. Ligands (bpp, Me_4bpp) were prepared according to the literature method.[4] All reagents and solvents for synthesis and kinetic measurement were AR grade from Merck Co. and were used without further purification. All substrates were obtained from Aldrich Chemical Co.

Intrumentation. The elemental analyses were carried out by a Carlo Erba Analyzer (Model 1106), UV-visible spectra were recorded on a Shimadzu UV-265 spectrophotometer. The ^{1}H-NMR spectra were obtained by an IBM AC-300 spectrometer. Magnetic susceptibility was determined by the Guoy method using $Hg[Co(SCN)_4]$ as calibrant. Cyclic voltammetry was conducted with a PAR model 175 universal programmer and model 173 potentiostat using an edge-plane pyrolytic graphite working electrode with a saturated calomel reference electrode (s.c.e.). Organic products were analyzed on a Varian 3300 gas chromatograph equipped with a flame ionization detector. Gas chromatographic column used included a 10% Carbowax with nitrogen as the carrier gas. Component identification was established by comparing the retention time with an authentic sample.

Catalytic oxidation of olefin. In a typical catalytic experiment, 0.02 mmol of ruthenium-aqua complex was dissolved in 10 m*l* of dichloromethane with 100-fold excess of olefin and 0.04 mmol of the phase transfer catalyst; benzyldimethyltetradecylammonium chloride (BDTAC). Ten milliliter of a NaOCl solution (Aldrich chemical Co.) and 10 m*l* of a HPO_4^{2-}/PO_4^{3-} phosphate buffer solution (pH 10.5) were layered over the dichloromethane. The reaction mixture was stirred vigorously at 25°C for 5 hr, with aliquots of the organic layer monitored by gas chromatography every 30 min. After 5 hr, the organic layer was extracted with ether to precipitate the metal complex. Ether and dichloromethane were removed under reduced pressure, and the remaining liquid was analyzed by gas chromatogaphy.

Ligand syntheses

2,6-Bis(N-pyrazolyl)pyridine (1a). A solution of 11.0 g of pyrazole (0.162 mol) in 200 m*l* of anhydrous 2-methoxyethyl ether was stirred with 6.0 g of potassium (0.153 mol) at 70°C until the metal was dissolved. To this solution was added 11.8 g (0.0496 mol) of 2,6-dibromopyridine in one portion. The resulting mixture was stirred at 110°C for 4 days. The solvent was removed on rotary evaporator. Water was

added, and the resulting white solid was collected by suction filtration. The compound was purified by dissolving it in methylene chloride, followed by adding methanol, and slowly removing the methylene chloride on a rotary evaporator. Yield 8 g (75%). mp. 136°C ; ^{1}H-NMR (CDCl$_3$) δ 6.48 (d, 2H), 7.75 (d, 2H), 7.75-7.95 (m, 3H), 8.55 (d, 2H).

2,6-Bis(3,5-dimethyl-N-pyrazolyl)pyridine (1b). The same procedure was taken with the one used for the preparation of (1a), the potassium salt of 3,5-dimethylpyrazole (15.5 g, 0.161 mol) and 11.8 g (0.0496 mol) of 2,6-dibromo-pyridine yielded 10.1 g (77%) of (1b). Recrystallization from methanol/water yielded white crystals. mp. 107°C , ^{1}H-NMR (CDCl$_3$) δ 2.30 (s, 6H), 2.53 (s, 6H), 5.99 (s, 2H), 7.55-7.95 (m, 3H), 8.55 (d, 2H).

Syntheses of Ruthenium Complexes

[Ru^{III}(bpp)Cl$_3$] (2a). To 125 m*l* of absolute ethanol in a 200 m*l* flask was added 263 mg of RuCl$_3$·3H$_2$O and 233 mg of bpp. The mixture was heated at reflux for 3 hr while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder which had appeared was filtered from the reddish yellow solution. The product was washed with absolute ethanol and ether and air-dried. Yield 85%. Calcd. for C$_{11}$H$_9$N$_5$Cl$_3$Ru: C, 31.54; H, 2.15; N, 16.73%. Found; C, 31.68; H, 2.03; N, 16.65%.

[Ru^{III}(Me$_4$bpp)Cl$_3$] (2b). The same procedure was utilized as in the previous preparation of [Ru(bpp)Cl$_3$] (2a), but the red brown precipitate appeared. Yield 80%. Calcd for C$_{15}$H$_{17}$N$_5$Cl$_3$Ru: C, 37.94; H, 3.58; N, 14.75%. Found; C, 37.54; H, 3.97; N, 15.04%.

[Ru^{II}(bpp)(bpy)Cl] ClO$_4$ (3a). This compound was prepared by heating 132 mg (3.00 mmol) of (2a), 500 mg (3.00 mmol) of bipyridine, and 127 mg (30.0 mmol) of LiCl at reflux for 1 hr in 270 m*l* of ethanol/water (3 : 1) under a N$_2$ atmosphere. After 1 hr. the solution was cooled and the volume reduced to ea. 80 m*l*. Saturated NaClO$_4$ was then added and the solution chilled. The resulting reddish microcrystalline solid was filtered off, washed with ice-cold water, then ether, and air-dried *in vacuo*. Yield 65%. Calcd. for C$_{21}$H$_{17}$N$_7$Cl$_2$O$_4$Ru: C, 41.79; H, 2.82; N, 16.25%. Found; C, 41.68; H, 3.03; N, 15.85%. ^{1}H-NMR (D$_2$O) δ 6.75 (t, 2H), 7.01 (t, 1H), 7.35 (t, 1H), 7.48 (d, 2H), 7.76 (t, 1H), 7.99 (t, 1H), 8.23 (d, 2H), 8.34-8.51 (m, 3H), 8.67 (d, 1H), 8.92 (d, 2H), 9.62 (d, 1H) UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 266 (9.2), 288 (18), 450 (3.6).

[Ru^{II}(bpp)(Me$_2$bpy)Cl]ClO$_4$ (3b). This compound was prepared by following the procedure for the isolation of (3a). Yield 63%. Calcd. for C$_{23}$H$_{21}$N$_7$Cl$_2$O$_4$Ru: C, 43.74; H, 3.33; N, 15.53%. Found; C, 43.38; H, 3.07; N, 15.65%. ^{1}H-NMR (CD$_3$OD) δ 2.50 (s, 3H), 2.76 (s, 3H), 6.65 (t, 2H), 6.67 (d, 1H), 7.17 (t, 3H), 7.72 (d, 1H), 8.06 (d, 2H), 8.15-8.44 (m, 3H), 8.67 (s, 2H), 9.99 (d, 1H). UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 268 (17), 286 (22), 444 (4.2).

[Ru^{II}(Me$_4$bpy)(bpp)Cl]ClO$_4$ (3c). This compound was prepared by following the procedure for the isolation of (3a). Yield 75%. Calcd. for C$_{25}$H$_{25}$N$_7$Cl$_2$O$_4$Ru: C, 45.53; H, 3.79; N, 14.87%. Found: C, 45.97; H, 3.54; N, 15.21%. ^{1}H-NMR (CD$_3$CN) δ 1.48 (s, 6H), 2.86 (s, 6H), 6.19 (s, 2H), 7.47 (t, 1H), 7.58 (d, 2H), 7.68 (t, 1H), 7.91 (t, 1H), 8.00 (m, 3H), 8.40 (d, 1H), 8.68 (d, 1H), 9.78 (d, 1H). UV-visible spectrum

in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^{-3}·mol^{-1} cm^{-1}); 267 (16), 292 (10), 305 (9.3), 396 (3.8).

[Ru^{II}(Me$_4$bpp)(Me$_2$bpy)Cl]ClO$_4$ (3d). This compound was prepared by following the procedure for the isolation of (3a). Yield 58%. Calcd. for C$_{27}$H$_{29}$N$_7$Cl$_2$O$_4$Ru: C, 47.16; H, 4.22; N, 14.27%. Found; C, 47.58; H, 4.03; N, 14.65%. ^{1}H-NMR (CD$_3$CN) δ 1.50 (s, 6H), 2.44 (s, 3H), 2.70 (s, 3H), 2.87 (s, 6H), 6.10 (s, 2H), 7.03 (d, 1H), 7.51 (d, 1H), 7.73 (d, 1H), 8.00 (d, 2H), 8.23-8.34 (m, 2H), 8.44 (s, 1H), 9.58 (d, 1H). UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 268 (17), 286 (15), 429 (4.3).

[Ru^{II}(bpp)(bpy)OH$_2$](ClO$_4$)$_2$ (4a). This compound was prepared by dissolving 330 mg (0.47 mmol) of (3a) and 207 mg (1.00 mmol) of AgClO$_4$ in 50 m*l* of acetone/water (3 : 1) and heating at reflux for 30 min. After the precipitated AgCl was filtered off, the volume of the resulting solution was reduced to 15 m*l* and 5 m*l* of saturated NaClO$_4$ added. The resulting precipitate was filtered off, washed with a little ice-cold water, and dried *in vacuo*. Yield 65%. Calcd. for C$_{21}$H$_{19}$N$_7$Cl$_2$O$_9$Ru: C, 36.80; H, 2.77; N, 14.31%. Found: C, 36.58; H, 2.96; N, 14.14%. ^{1}H-NMR (CD$_3$OD) δ 6.77 (t, 2H), 7.06 (t, 1H), 7.33 (t, 1H), 7.53 (d, 2H), 7.77 (t, 1H), 8.00 (t, 1H), 8.34 (m, 3H), 8.46 (d, 2H), 8.74 (d, 1H), 9.12 (d, 2H), 9.53 (d, 1H). UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 269 (18), 282 (19), 302 (16), 412 (6.2).

[Ru^{II}(bpp)(Me$_2$bpy)OH$_2$](ClO$_4$)$_2$ (4b). This compound was prepared by following the procedure for the isolation of (4a). Yield 74%. Calcd. for C$_{23}$H$_{23}$N$_7$Cl$_2$O$_9$Ru: C, 38.71; H, 3.23; N, 13.75%. Found; C, 38.68; H, 3.03; N, 13.85%. ^{1}H-NMR (CD$_3$CN) δ 2.42 (s, 3H), 2.79 (s, 3H), 6.75 (t, 2H), 6.89 (d, 1H), 7.17 (t, 3H), 7.49 (d, 1H), 8.06 (d, 2H), 8.29-8.51 (m, 3H), 9.09 (t, 2H), 9.33 (d, 1H). UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 260 (18), 282 (18), 306 (15), 425 (4.6).

[Ru^{II}(Me$_4$bpp)(bpy)OH$_2$](ClO$_4$)$_2$ (4c). This compound was prepared by following the procedure for the isolation of (4a). Yield 75%. Calcd. for C$_{25}$H$_{27}$N$_7$Cl$_2$O$_9$Ru: C, 40.49; H, 3.64; N, 13.23%. Found: C, 40.04; H, 3.50; N, 13.03%. ^{1}H-NMR (CD$_3$CN) δ 1.18 (s, 6H), 2.86 (s, 6H), 6.19 (s, 2H), 7.17 (t, 1H), 7.36 (d, 1H), 7.85 (t, 2H), 8.00 (m, 3H), 8.26 (t, 1H), 8.35 (d, 1H), 8.58 (d, 1H), 9.78 (d, 1H). UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 268 (22), 286 (17), 308 (14), 426 (3.9).

[Ru^{II}(Me$_4$bpp)(Me$_2$bpy)OH$_2$](ClO$_4$)$_2$ (4d). This compound was prepared by following the procedure for the isolation of (4a). Yield 56%. Calcd. for C$_{27}$H$_{31}$N$_7$Cl$_2$O$_9$Ru: C, 42.13; H, 4.03; N, 12.74%. Found; C, 42.58; H, 4.33; N, 12.85%. ^{1}H-NMR (CD$_3$CN) δ 1.59 (s, 6H), 2.50 (s, 3H), 2.76 (s, 3H), 2.93 (s, 6H), 6.26 (s, 2H), 7.07 (d, 1H), 7.22 (d, 1H), 7.77 (d, 1H), 8.06 (d, 2H), 8.29-8.37 (m, 2H), 8.51 (d, 1H), 9.64 (d, 1H). UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 268 (18), 283 (15), 309 (12), 423 (5.8).

[Ru^{IV}(bpp)(bpy)O](ClO$_4$)$_2$ (5). The complex [Ru(bpp)(bpy)H$_2$O](ClO$_4$)$_2$ (0.5 g) was dissolved in a minimum amount of hot water and then add to a solution of [NH$_4$]$_2$[Ce(NO$_3$)$_6$] (2 g, 10 m*l*). After a few minutes excess of NaClO$_4$ was added to precipitate a greenish yellow solid which was filtered off, washed with ice-cold water, and dried *in vacuo*. Yield 40%. Calcd. for C$_{21}$H$_{17}$N$_7$Cl$_2$O$_9$Ru: C, 36.90; H, 2.49; N, 14.35%. Found: C, 36.58; H, 2.96; N, 14.14%. UV-visible spectrum in acetonitrile $-\lambda_{max}$/nm (10^{-3} ε$_{max}$/dm^3·mol^{-1} cm^{-1}); 262
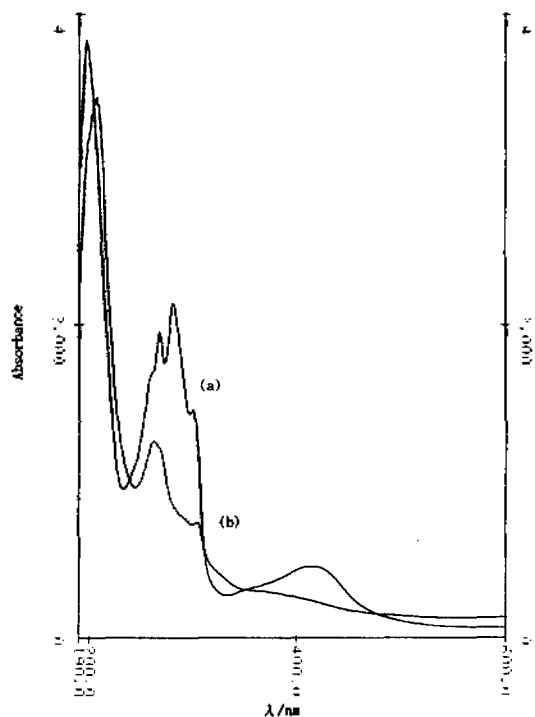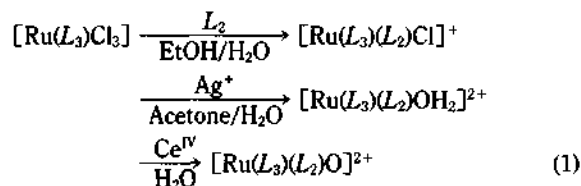
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Figure 1. UV-visible spectra of (a) [Ru(bpp)(bpy)OH₂](ClO₄)₂ and (b) [Ru(bpp)(bpy)(O)](ClO₄)₂ in acetonitrile.

(4.5), 306 (1.8). $\mu_{eff}=2.82$ (Solid sample, Guoy method)

Results and Discussion

Syntheses and spectroscopic properties. The tridentate ligands (bpp, Me₄bpp) were previously reported by Jameson and co-workers.[4] The syntheses of $[Ru(L_3)(L_2)OH_2]^{2+}$ followed Meyer's procedure such as (1) for the tpy analogue, using [Ru(tpy)Cl₃] as the starting material. The metal complexes were characterized by elemental (C, H, N) analysis, spectra (UV-vis and ¹H-NMR) and magnetic moment measurement.

$$[Ru(L_3)Cl_3] \xrightarrow[\text{EtOH/H}_2\text{O}]{L_2} [Ru(L_3)(L_2)Cl]^+$$

$$\xrightarrow[\text{Acetone/H}_2\text{O}]{\text{Ag}^+} [Ru(L_3)(L_2)OH_2]^{2+}$$

$$\xrightarrow[\text{H}_2\text{O}]{\text{Ce}^{IV}} [Ru(L_3)(L_2)O]^{2+} \qquad (1)$$

The spectral features of the $[Ru(L_3)(L_2)OH_2]^{2+}$ complexes include an intense visible absorption band assigned to a metal-to-ligand dπ(Ru)→π*(bpy) charge transfer (MLCT) transition, a charge transfer band centered at $\lambda_{max}=420$ nm, and a very intense band at 280 nm assigned to π→π* ligand localized transitions of bpy which are characteristic of related comlexes. As determined by spectrophotometry,[5] the pK_a value of $[Ru(L_3)(L_2)OH_2]^{2+}$ was found to be 9.5± 0.2. The corresponding value of $[Ru^{II}(tpy)(bpy)OH_2]^{2+}$ is 9.7.[6] The lower pK_a values of $[Ru(L_3)(L_2)OH_2]^{2+}$ can be rationalized by the stronger σ-donor strength of the pyrazole-substituted ligand.

Oxidation of $[Ru^{II}(bpp)(bpy)OH_2]^{2+}$ by Ce^{IV} gave [Ru^{IV}(bpp)(bpy)O]^{2+}, isolated as a greenish-yellow ClO₄⁻ salts. With the addition of Ce(IV), the visible absorption peak at
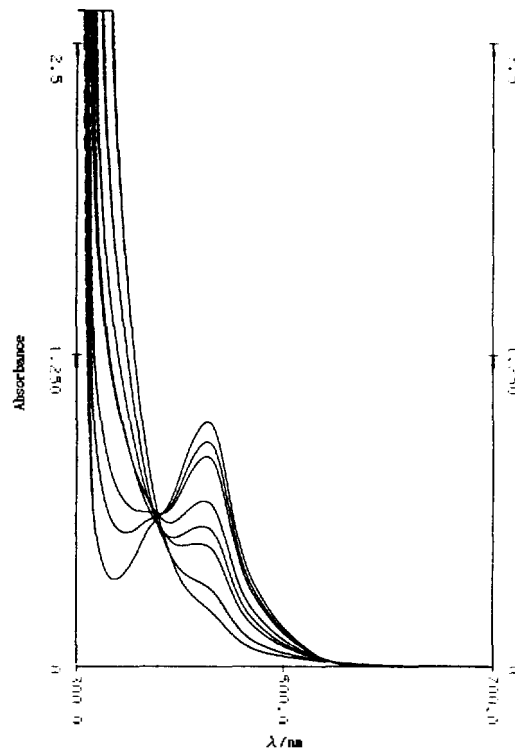

Figure 2. Spectrophotometric titration of $[Ru(bpp)(bpy)OH_2]^{2+}$ by Ce(IV). The solutions contained initially 1.56×10^{-5} M Ru(II) and the following stoichiometric equivalents of Ce(IV): 0.00 (top spectrum), 0.10, 0.20, 0.40, 0.60, 0.70, 0.90, and 0.99. Conditions: room temperature, in 0.962 M HClO₄/0.038 M NaClO₄.

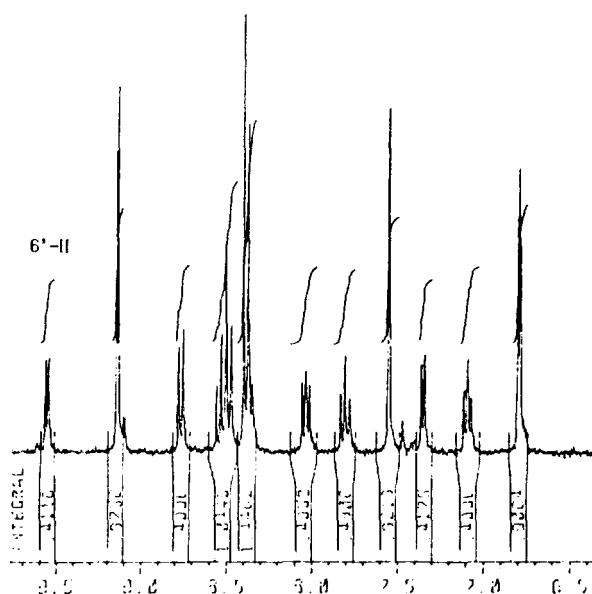**Figure 3.** ¹H-NMR spectrum of [Ru(bpp)(bpy)OH₂](ClO₄)₂ in CD₃-OD.

412 nm decreases in intensity with the occurence of isosbestic point at 382 nm. As found for the bpy analogue, the optical spectrum of Ru^{IV}=O in the visible region is featureless with the complete absence of the metal-to-ligand charge transfer bands at 412 nm. As expected for a d^4 metal-oxo system.[7] $[Ru(bpp)(bpy)O]^{2+}$ is paramagnetic with a measured
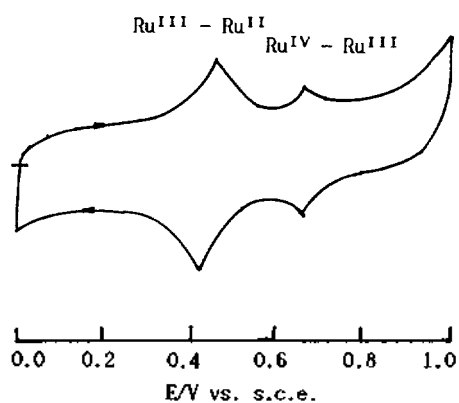
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Figure 4. Cyclic voltammogram of [Ru(bpp)(bpy)OH$_2$](ClO$_4$)$_2$ in aqueous solution buffered at pH 5.6 (0.2 mol dm^{-3} acetic acid −0.2 mol dm^{-3} sodium acetate) with an edge-plane pyrolytic graphite working electrode at scan rate 50 mVs^{-1}.
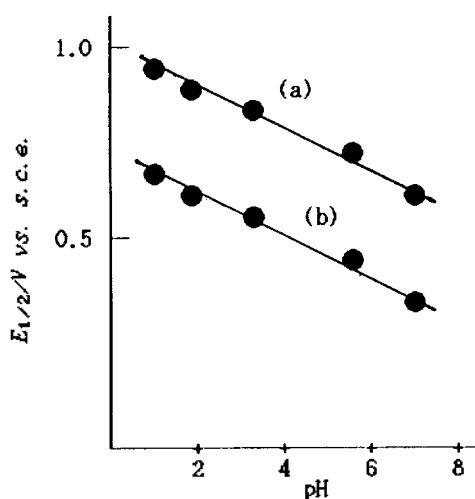

Figure 5. Plot of $E_{1/2}$ versus pH for the couples (a) Ru^{IV}-Ru^{III} and (b) Ru^{III}-Ru^{II} of the [Ru(bpp)(bpy)OH$_2$]$^{2+}$.

Table 1. $E_{1/2}$ potentials for [Ru^{II}(L_3)(L_2)OH$_2$]$^{2+}$ complexes in aqueous solution buffered at pH 5.6

Complex		pH*	$E_{1/2}$ (V vs. SSCE)	
L_3	L_2		Ru^{III}/Ru^{II}	Ru^{IV}/Ru^{III}
bpp	bpy	9.5	0.44	0.62
bpp	Me$_2$bpy	9.7	0.46	0.66
Me$_4$bpp	bpy	9.6	0.45	0.64
Me$_4$bpp	Me$_2$bpy	9.8	0.48	0.67

*pH values of [Ru(L_3)(L_2)OH$_2$]$^{2+}$ complexes obtained spectrophotometrically.

μ$_{eff}$ of 2.82 close to the spin-only value for two unpaired electrons.

^{1}H-NMR spectroscopies was utilized to determine the ligand arrangement about the ruthenium(II) center for [Ru(L_3)(L_2)Cl] ClO$_4$ and [Ru(L_3)(L_2)OH$_2$](ClO$_4$)$_2$. As assigned to in the caption for Figure 3, in complexes of the type [Ru(L_3)(L_2)X]$^{2+}$ (X=H$_2$O, Cl$^-$), the chemical shift of the protons of the bipyridine ring, which is oriented along the Ru-L bond axis, is shifted to upfield because of its presence in the shielding region of the pyridine ring currents. But the 6′-proton is nearest to the ligand X, and its chemical shift is sensitive to the nature of X. Because the 6′-proton is out of the pyridine ring current, it is shifted to downfield.

Cyclic voltammetry. The electrochemistry of ruthenium-aqua or oxo complexes is very similar to that for its bpy analogue which exhibit a dependence on the nature of the electrode surface. With basal-plane pyrolytic graphite as the working electrode, the cyclic voltammograms of (4a) and (5) in aqueous solutions are identical and consist of two waves; a reversible wave corresponding to the Ru^{III}-Ru^{II} couple and a second, quasi-reversible wave, with a smaller measured current, corresponding to the Ru^{IV}-Ru^{III} couple (Figure 4).
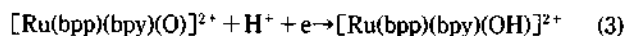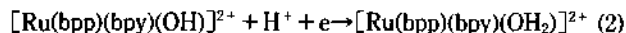
At pH 5.6, these couple occur at 0.44 and 0.62 V vs. s.c.e.

Table 2. Catalytic oxidation of olefins by [Ru(L_3)(L_2)OH$_2$]$^{2+}$/NaOCl at pH 10.5^a.

Complex (L_3) (L_2)	Olefins	Conversion (%)	Product distribution^b			Selectivity (%)
			A	B	C	
(bpp) (bpy)	styrene	57	32	20	5	56
	cyclohexene	36	12	24		
	cyclooctene	26	18	8		69
(bpp) (Me$_2$pby)	styrene	48	19	27	2	40
	cyclohexene	35	16	19		
	cyclooctene	21	14	7		67
(Me$_4$bpp) (bpy)	styrene	63	29	30	4	46
	cyclohexene	38	14	24		
	cyclooctene	29	18	11		62
(Me$_4$bpp) (Me$_2$bpy)	styrene	50	18	26	6	36
	cyclohexene	34	13	21		
	cyclooctene	23	16	7		70

^{a}Conditions as described in the Experimental section. reaction time 5 hr. ^{b}Styrene (A=epoxide, B=benzaldehyde, C=phenylacetaldehyde), Cyclohexene (A=cyclohexanone, B=cyclohexanol), Cyclooctene (A=cyclooctene oxide, B=cyclooctenol)

(Table 1), respectively; both couples shift 55 mV per pH unit over the range pH 1-7 (Figure 5) suggesting that the redox processes involve one-electron, one-proton transfers [Eqs. (2) and (3)].

$$[Ru(bpp)(bpy)(OH)]^{2+} + H^+ + e \rightarrow [Ru(bpp)(bpy)(OH_2)]^{2+} \quad (2)$$

$$[Ru(bpp)(bpy)(O)]^{2+} + H^+ + e \rightarrow [Ru(bpp)(bpy)(OH)]^{2+} \quad (3)$$

Catalytic oxidation of olefins. Recently ruthenium catalyzed oxidation of alkanes with *tert*-butyl hydroperoxide has been reported using cis-$[Ru^{II}L_2(OH_2)_2]^{2+}$ complexes as catalysts (L = substituted 2,2'-bpy or 1,10-phen).[8] The efficiencies of these catalysts have prompted us to initiate similar investigations on $[Ru(L_3)(L_2)OH_2]^{2+}$. The results are summarized in Table 2.

The ruthenium complex was found to be a highly active catalyst for olefin. No oxidation product was detected in the absence of the catalyst. The discovery of the catalyst after the oxidation reactions was studied by UV-visible spectroscopy. The catalytic reactions was usually complete within 5 hr. A high percentage of PhCHO as a product of the NaOCl-catalyzed oxidation of styrene has been found under similar conditions based on RuO_4 or $RuCl_3 \cdot nH_2O$.[9] We cannot account for the change in product distribution and the appearance of PhCHO under catalytic condition. Even though OCl^- oxidation of the aqua complexes leads to $Ru^{IV}=O$ in water, the actual state of the catalyst in the catalytic runs was unknown. Under catalytic conditions in the hypochlorite oxidations a pathway leading to oxidative olefin bond cleavage, occurs in competition with epoxidation or, perhaps, by further oxidation of bound epoxide.

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