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SYNTHESIS, REDOX PROPERTIES AND REACTIVITIES OF RUTHENIUM(II) COMPLEXES OF 1,1′-BIISOQUINOLINE (BIQN) AND X-RAY CRYSTAL STRUCTURE OF [Ru^{II}(terpy)(BIQN)(Cl)]ClO_4 (terpy = 2,2′:6′,2″-TERPYRIDINE)

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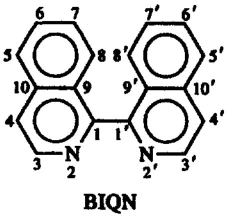
Abstract—The syntheses of the complexes [Ru^{II}(terpy)(BIQN)Cl]ClO_4 (**1**) and [Ru^{II}(terpy)(BIQN)(OH_2)](ClO_4)$_2$ (**2**) are described. The structure of **1** has been established by X-ray crystallography. The dihedral angle between the two isoquinoline rings is 37.4°. In aqueous solution, [Ru^{II}(terpy)(BIQN)(OH_2)](ClO_4)$_2$ shows two reversible/quasi-reversible oxidation couples assigned to the oxidation of ruthenium(II) to ruthenium(III) and ruthenium(III) to ruthenium(IV). [Ru^{II}(terpy)(BIQN)(OH_2)](ClO_4)$_2$ is an active catalyst for the oxidation of alkenes by PhIO.

2,2′-Bipyridine and its substituted derivatives are useful ligands for the generation of highly oxidizing Ru=O complexes.[1,2] Studies by Meyer and Che and their coworkers revealed that the E^0 and reactivities of [Ru^{IV}(terpy)(L—L)O]$^{2+}$, (terpy = 2,2′,6′,2″-terpyridine, L—L = substituted 2,2′-bipyridines) are affected by substituents on the 2,2′-bipyridine ring.[1b,2d] With 6,6′-dichloro-2,2′-bipyridine, which has an electron withdrawing substituent, it has been possible to prepare a relative robust and active ruthenium catalyst for alkane oxidation by *tert*-butylhydroperoxide.[2d,3]

We are interested in the coordination chemistry of 1,1′-biisoquinoline,[4,5] a ligand which has the combined structural features of 2,2′-bipyridine and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP). Regardless of the numerous studies on binaphthylic ligands and their metal complexes in asymmetric organic synthesis,[6] related studies on BIQN and its derivatives are sparse. The title ligand, because of its robust nature towards oxidative degradation and its potential C_2 chirality, may be useful in the design of new Ru=O catalyst for organic oxidation. Herein is described the synthesis, molecular structure and reactivities of some ruthenium(II) complexes of BIQN. The [Ru(terpy)(BIQN)(H_2O)]$^{2+}$ complex has been found to catalyse alkene epoxidation by PhIO.



BIQN

EXPERIMENTAL

Materials

$RuCl_3 \cdot 3H_2O$ (Johnson Matthey) was used as received. Trifluoroacetic acid (99%, Aldrich) was

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purified by distillation under nitrogen. Silver(I) trifluoromethanesulphonate and silver(I) perchlorate were dried *in vacuo*. Water was twice distilled from $KMnO_4$. Isocarbostiril (98%, Aldrich) was used as received. Other common reagents were analytical grade. Iodosylbenzene was prepared by alkaline hydrolysis of iodosylbenzene diacetate (98%, Aldrich). $Ru(terpy)Cl_3$[7] and 1,1′-biisoquinoline[4] were prepared by literature methods.

Syntheses

$[Ru^{II}(terpy)(BIQN)Cl]ClO_4$ (**1**). A mixture of $Ru(terpy)Cl_3$ (0.2 g), BIQN (0.2 g), lithium chloride (0.1 g) and triethylamine (1 cm^3) in aqueous ethanol (75% ethanol/water 25% v/v, 200 cm^3) was refluxed for 4 h. The solution was filtered after cooling to room temperature. The volume of the filtrate was reduced to *ca* 15 cm^3, and the complex was deposited as a deep purple solid which was collected on a frit and washed with distilled water (10 cm^3). The perchlorate salt was obtained by the metathesis reaction of $[Ru^{II}(terpy)(BIQN)Cl]Cl$ with $LiClO_4$ in an acetone solution. The product was recrystallized by slow diffusion of diethyl ether into acetonitrile solution (yield ≈ 85%). $RuC_{33}N_5H_{23}Cl_2O_4 \cdot MeCN$, Found: C, 54.5, H, 3.2, N, 11.1. Calc.: C, 54.8, H, 3.4, N, 10.9%. UV–visible [in MeCN, λ_{max}/nm (ε_{max}/$dm^3\ mol^{-1}\ cm^{-1}$)]: 273 (23,000), 316 (29,000), 370 (10,000), 543 (9900).

$[Ru^{II}(terpy)(BIQN)(H_2O)](ClO_4)_2$ (**2**). A mixture of $[Ru^{II}(terpy)(BIQN)Cl]Cl$ (0.1 g) and silver(I) perchlorate (0.2 g) in aqueous acetone (75% acetone/25% water v/v, 25 cm^3) was refluxed for 1 h. The resulting solution was filtered to remove the insoluble AgCl. The volume of the red filtrate was reduced to *ca* 5 cm^3, and the mixture was cooled overnight in a refrigerator. The $[Ru^{II}(terpy)(BIQN)(H_2O)](ClO_4)_2$ complex was deposited as a dark-red microcrystalline solid (yield ≈ 70%). $RuC_{33}N_5H_{25}Cl_2O_9$. Found: C, 49.4, H, 3.2, N, 8.5. Calc.: C, 49.1, H, 3.1, N, 8.7%. UV–visible [in 0.1 M CF_3CO_2H, λ_{max}/nm (ε_{max}/$dm^3\ mol^{-1}\ cm^{-1}$)]: 272 (21,500), 315 (28,000), 380 (10,100), 532 (10,300).

Oxidation of alkene by iodosylbenzene catalysed by an aqua-ruthenium(II) complex

In a typical experiment, a mixture of alkene (0.1 g) and **2** (25 mg) in dichloromethane (10 cm^3) was stirred at room temperature. Iodosylbenzene (0.1 g) was added to the mixture, which was then stirred for 8–12 h. A blank containing the same amount of solvent, substrate and iodosylbenzene but without the metal catalyst was simultaneously stirred under the same condition. After addition of internal standard, the aliquot was analysed by gas–liquid chromatography, and the product yields were calculated based on the amount of iodobenzene formed.

Physical measurements

Elemental analyses of the complexes were performed by Butterworth Laboratories. Infrared spectra were recorded in Nujol mulls on a Nicolet 20SXC FT-IR spectrophotometer and electronic absorption spectra on a Milton Roy 3000 spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273 Potentiostat. For electrochemical measurements in aqueous solutions, the reference electrode was the saturated calomel electrode (SCE).

GLC analyses were done on a Hewlett–Packard model HP 5890 Series II Chromatograph equipped with a flame ionization detector. Quantification of gas chromatographic components were performed on a Hewlett–Packard HP 3393 Series II integrator. Capillary column model HP 17 (phenyl methyl crosslink) was used to analyse the oxidation products of styrene, cyclohexene, cyclooctene and norbornene. Identification of the oxidation products of *cis-*/*trans*-stilbene were performed by ^1H NMR spectroscopy on a Jeol 270 FT-NMR spectrometer with TMS as the internal standard. The singlet resonance for epoxide protons of *trans-* and *cis*-stilbene oxide are at 3.85 and 4.34 ppm respectively. Quantification of the oxidized products was done by comparing the singlet resonance for the methyl protons of *m*-toluic acid at 2.3 ppm.

X-Ray structure analysis

Complex **1**: MeCN, $C_{35}H_{26}N_6Cl_2O_4Ru$, $M = 766.6$, space group $P2_1/c$, $a = 15.825(5)$, $b = 16.960(4)$, $c = 12.198(2)$ Å, $\beta = 102.28(2)°$, $U = 3199(1)$ Å^3, $D_c = 1.59$ g cm^{-3}, $Z = 4$, $F(000) = 1552$, $\mu(Mo\text{-}K_\alpha) = 6.97$ cm^{-1}. The diffraction data (h, $\pm k$, $\pm l$; 5612 unique data) were measured at 24°C on a CAD-4 diffractometer (graphite-monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å) in the bisecting mode up to $2\theta_{max} = 50°$. Convergence for 4129 reflections ($|F_0| \geqslant 2.0\sigma|F_0|$) was reached at $R_F = 0.044$, $R_w = 0.035$ and $S = 2.85$. The final difference map showed residual extrema in the range -0.570 to $+0.700$ e Å^{-3}.

The ruthenium atom was located from a Patterson map, and the coordinates of other non-hydrogen atoms were derived from successive Fourier difference syntheses. All non-hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms were included at idealized positions with a fixed isotropic thermal parameter. Selected bond distances and angles are given in Table 1.

RESULTS AND DISCUSSION

Synthesis, characterization and electrochemistry

There has been only one structural report on metal complexes of 1,1′-biisoquinoline in which the ligand adopts a η_2–μ_1 coordination mode. Previously, Dai and co-workers[5] reported the preparation and molecular structure of a dinuclear palladium(II) complex with BIQN acting as a bridging ligand. Presumably, the unfavourable steric repulsion between the H8 ad H8′ atoms of BIQN disfavours it from acting as a chelating bidentate ligand. Recently, the synthesis and molecular structure of $[Pt(BIQN)Cl_2]$ has been reported.[8] In this work, the preparation of $[Ru^{II}(terpy)(BIQN)Cl]Cl$ and $[Ru^{II}(terpy)(BIQN)(OH_2)]^{2+}$ followed the reported procedures for the respective syntheses of $[Ru^{II}(terpy)(L\wedge L)Cl]Cl$ and $[Ru^{II}(terpy)(L\wedge L)(H_2O)](ClO_4)_2$ where L^L = bipyridine and substituted bipyridine. In previous studies, Ru^{IV}-oxo complexes of polypyridines such as $[Ru^{IV}(terpy)(tmen)O]^{2+}$ (tmen = N,N,N′N′-tetramethyl-1,2-diaminoethane)[9] and $[Ru^{IV}(terpy)(6,6'\text{-}Cl_2\text{-}bpy)O]ClO_4$ (6,6′-Cl_2-bpy = 6,6′-dichloro-2,2′-bipyridine)[2d] were prepared by Ce^{IV} oxidation of the corresponding aqua-ruthenium(II) complexes in aqueous solution. Similar reaction of $[Ru^{II}(terpy)(BIQN)(H_2O)](ClO_4)_2$ with Ce^{IV} in water was tried. A yellowish green product, presumably $[Ru^{II}(terpy)(BIQN)O](ClO_4)_2$, was obtained. However, this species is not long lived enough for full characterization and therefore no further study has been made.

Figure 1 shows the UV–visible spectrum of **2** in 0.1 M trifluoroacetic acid. The broad and intense absorption at $\lambda_{max} = 550$ nm is attributed to metal-to-ligand charge-transfer transition, $d_\pi(Ru) \rightarrow p_{\pi^*}$(terpy)/BIQN). Complex **2** exhibits similar electrochemical behaviour as $[Ru^{II}(terpy)(tmen)(H_2O)]^{2+}$ [9] and $[Ru^{II}(terpy)(6,6'\text{-}Cl_2\text{-}bpy)(H_2O)]^{2+}$.[2d] A typical cyclic voltammogram of **2** in aqueous solution with edge-plane pyrolytic graphite as the working electrode is shown in Fig. 2. At pH = 1.1, a reversible couple (I) at 0.85 V vs SCE is observed, and it is assigned to Ru^{III}/Ru^{II}. The reversibility is based on the observed current ratio ($i_{pa}/i_{pc} \approx 1$) and the peak-to-peak separations ($\Delta E_p \approx 60$ mV), both of which are independent of scan rates (50–200 mV s^{-1}). An irreversible oxidation wave at 0.96 V vs SCE is also observed, and it becomes more reversible at higher pH. The E^0 values for both couples shift cathodically by about 60 mV per pH unit as shown by the Pourbaix plots given in Fig. 3. With reference to previous studies on other oxo-ruthenium(IV) systems, the following electrode reactions are suggested:

Couple I

$$[Ru^{III}(terpy)(BIQN)(OH)]^{2+} + H^+ + e^- \rightleftharpoons [Ru^{II}(terpy)(BIQN)(OH_2)]^{2+} \quad (1)$$

Table 1. Selected bond distances (Å) and bond angles (°) of $[Ru^{II}(terpy)(BIQN)Cl]ClO_4$ (**1**)

Ru—Cl	2.420(1)
Ru—N(1)	2.072(4)
Ru—N(11)	2.029(4)
Ru—N(21)	2.075(4)
Ru—N(31)	1.952(4)
Ru—N(41)	2.050(4)
C(10)—C(20)	1.462(6)

Cl—Ru—N(1)	96.4(1)	N(11)—Ru—N(41)	86.9(2)
Cl—Ru—N(11)	173.0(1)	N(21)—Ru—N(31)	79.7(2)
Cl—Ru—N(21)	89.6(1)	N(21)—Ru—N(41)	159.6(2)
Cl—Ru—N(31)	85.3(1)	N(31)—Ru—N(41)	80.1(2)
Cl—Ru—N(41)	91.3(1)	Ru—N(1)—C(10)	116.0(3)
N(1)—Ru—N(11)	77.5(2)	N(1)—C(10)—C(20)	112.7(4)
N(1)—Ru—N(21)	97.6(2)	C(8)—C(9)—C(10)	124.0(4)
N(1)—Ru—N(31)	176.8(2)	C(18)—C(19)—C(20)	123.0(4)
N(1)—Ru—N(41)	102.6(2)	C(10)—C(20)—N(11)	113.5(4)
N(11)—Ru—N(21)	94.5(2)	C(10)—C(20)—C(19)	126.0(4)
N(11)—Ru—N(31)	101.0(2)		

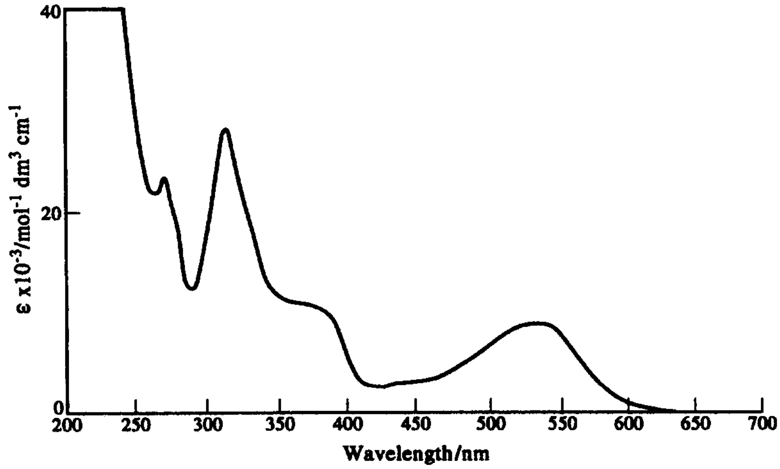


Fig. 1. UV–visible absorption spectrum of $[Ru(terpy)(BIQN)(OH_2)]^{2+}$ in 0.1 M CF_3CO_2H.

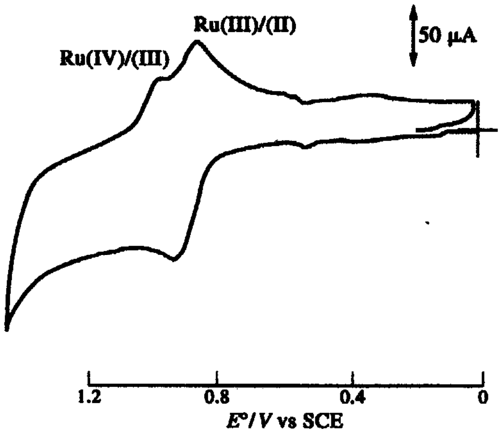


Fig. 2. Cyclic voltammogram of $[Ru(terpy)(BIQN)(OH_2)]^{2+}$ in 0.1 M CF_3CO_2H. Scan rate = 100 mV s^{-1}; working electrode, edge-plane pyrolytic graphite electrode.

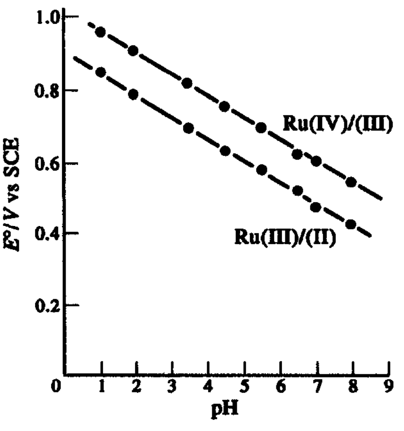


Fig. 3. Pourbaix diagram for the Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples of $[Ru(terpy)(BIQN)(OH_2)]^{2+}$ in aqueous solutions.

Couple II

$$[Ru^{IV}(terpy)(BIQN)O]^{2+} + H^{+} + e^{-} \rightleftharpoons [Ru^{III}(terpy)(BIQN)(OH)]^{2+}. \quad (2)$$

Interestingly, the E^0 values for both the $[Ru^{IV}(terpy)(BIQN)O]^{2+}/[Ru^{III}(terpy)(BIQN)(OH)]^{2+}$ and $[Ru^{IV}(terpy)(bpy)O]^{2+}/[Ru^{III}(terpy)(bpy)(OH)]^{2+}$[1b] couples are comparable despite the difference in structural feature between BIQN and bpy.

Structure of $[Ru^{II}(terpy)(BIQN)Cl]ClO_4$

Figure 4 shows a perspective view of the $[Ru^{II}(terpy)(BIQN)Cl]^{+}$ cation with atomic numbering. The coordination around ruthenium is a distorted octahedron with the terpy ligand in a meridional configuration. As in the case of $[Pt(BIQN)Cl_2]$,[8] the BIQN ligand adopts a η^2-μ_1 coordination mode. The measured dihedral angle of 37.4° between the two isoquinoline rings is close to the value of 37° found in the related $Pt(BIQN)Cl_2$.[8]

Catalytic oxidation of alkenes by iodosylbenzene

$[Ru^{II}(terpy)(BIQN)(H_2O)](ClO_4)_2$ has been found to mediate oxidation of alkenes by PhIO at room temperature. The results of catalytic oxidation of alkenes are summarized in Table 2. No significant oxidation was observed. Addition of PhIO to a mixture of **2** and alkene in dichloromethane did not cause any significant colour change, and at the end of every reaction $PhIO_2$ was obtained. Presumably, it was formed according to equation (3).

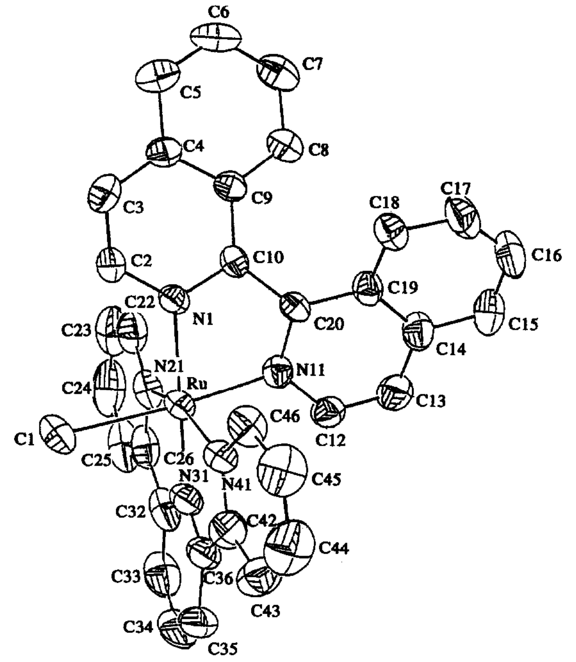


Fig. 4. A perspective view of the $[\mathrm{Ru(terpy)(BIQN)Cl}]^+$ cation.

$$2\,\mathrm{PhIO} \xrightarrow{[\mathrm{Ru^{II}(terpy)(BIQN)(H_2O)](ClO_4)_2}} \mathrm{PhIO_2} + \mathrm{PhI} \quad (3)$$

Oxidation of styrene gives styrene oxide and benzaldehyde in a ratio of approximately 2 : 1. Changing the solvent from dichloromethane to acetone increases the yield of benzaldehyde with the styrene oxide to benzaldehyde ratio becomes 1 : 1. No catalytic oxidation is observed when acetonitrile is used as solvent. This is not unexpected since acetonitrile is known to form a stable complex with ruthenium(II).

Norbornene and cyclooctene are oxidized to *exo*-norbornene oxide and cyclooctene oxide respectively. *Endo*-norbornene oxide nor any rearranged products, norcamphor and 4-cyclohexene carboxyaldehyde, were not detected. Oxidation of *cis*-stilbene gives both *cis*-epoxide and *trans*-epoxide in a ratio of 3 : 1. With cyclohexene, the reaction proceeds predominantly via allylic oxidation to afford cyclohexenone (26%), yet a significant yield of cyclohexene oxide (12%) is found. This is in contrast to most stoichiometric oxidation of cyclohexene by monooxoruthenium(IV) where in most cases cyclohexenone and cyclohexenol are the only products.[2d,10]

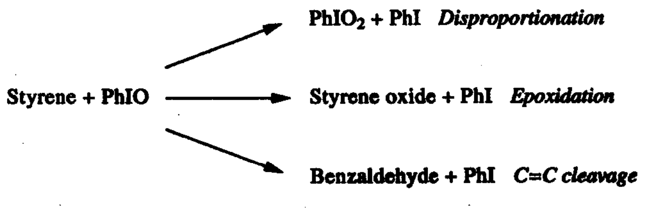
For each reaction studied, more than 85% of the ruthenium complex was recovered. The styrene oxide to benzaldehyde ratio is sensitive to the amount of the catalyst used. When the catalyst loading is 6.2 mg, the yields of benzaldehyde and styrene oxide based on the amount of PhI formed are 16% and 1.6% respectively. Thus the ratio of styrene oxide to benzaldehyde is 1 : 10, which is significantly different from that of 2 : 1 when the amount of catalyst is 25 mg.

Figure 5 shows the time course plot for the oxidation of styrene. The reaction is completed within 4–5 h and no induction period has been observed. The rate of formation of styrene oxide (k_s) and benzaldehyde (k_b) are 0.47 and 0.23 μmol min^{-1} respectively. The overall rate of consumption of PhIO (k_{total}), monitored by the formation of PhI, is 3.67 μmol min^{-1}. The k_s value is nearly twice that of k_b and this is in line with the styrene oxide to benzaldehyde ratio of 2 : 1 found after the reaction.

The rate of disproportionation of iodosylbenzene (k_{disp}) to $\mathrm{PhIO_2}$ and PhI is determined by stirring PhIO with **2** alone under similar reaction conditions, and is 3.0 μmol min^{-1}. The summation of k_s, k_b and k_{disp} is 3.7 μmol min^{-1}. This value is close to the value k_{total} of 3.67 μmol min^{-1} described above. This suggests that there would be no reaction pathway other than epoxidation, C═C cleavage and PhIO disproportionation (Scheme I).

General comment

There are several reports on the use of ruthenium catalysts for the oxidation of alkenes in literature. Groves and co-workers[11] reported that *trans*-dioxoruthenium(VI) of tetramesitylporphyrin is capable of catalysing aerobic epoxidation of alkenes. Several catalyst/oxidant systems such as $\mathrm{RuCl_3 \cdot 3H_2O/IO_4^-}$[12] and $\mathrm{Ru^{II}}$-phosphines/$\mathrm{OCl^-}$ or $\mathrm{IO_4^-}$ or PhIO also promote oxidative cleavage of



Scheme 1.

Table 2. Results of oxidation of alkenes by iodosylbenzene in CH_2Cl_2 catalysed by $[Ru^{II}(terpy)(BIQN)(H_2O)](ClO_4)_2$. Condition: Ru catalyst, 25 mg; alkene, 0.1g; PhIO, 0.1 g

Substrate	Solvent	Products (yield %)[a]
Norbornene	dichloromethane	*exo*-2,3-epoxynorbornane (36%)
cis-Cyclooctene	dichloromethane	*cis*-cyclooctene oxide (21%)
Cyclohexene	dichloromethane	cyclohexene oxide (12%) cyclohex-2-ol (9.7%) cyclohex-2-one (26.6%)
trans-Stilbene	dichloromethane	*trans*-stilbene oxide (28%) benzaldehyde (9%)
cis-Stilbene	dichloromethane	*cis*-stilbene oxide (11.5%) *trans*-stilbene oxide (3.9%) benzaldehyde (22.6%)
Styrene	dichloromethane	styrene oxide (26.7%) benzaldehyde (16.2%)
Styrene	acetone	styrene oxide (21%) benzaldehyde (19%)

[a] Products were identified and quantified by gas chromatography, and the yield is based on the amount of iodobenzene formed.

C=C bonds.[13] We have also reported that an aquaruthenium(II) complex such as $[Ru^{II}(terpy)(6,6'\text{-}Cl_2\text{-}bpy)(H_2O)]^{2+}$ [2d] (6,6'-Cl_2-bpy = 6,6'-dichloro-2,2'-bipyridine) catalyses oxidation of alkenes by *tert*-butylhydroperoxide.

It has been our long term goal to develop a catalytic oxidation cycle via a non-porphyrin ruthenium-oxo intermediate (Scheme 2). Based on the result of electrochemical studies, the $[Ru^{IV}(terpy)(BIQN)(O)]^{2+}$ complex, if generated, should be a competent oxidant. However, in the present study, $[Ru^{IV}(terpy)(BIQN)(O)]^{2+}$ should not be the sole reactive intermediate. Here, oxidation of *cis*-stilbene is non-stereospecific. This is quite incompatible with that found in the stoichiometric oxidation of *cis*-stilbene by most $Ru^{IV}{=}O$ complexes of polypyridines where in most cases *cis*-stilbene oxide is the major product. This marked discrepancy cannot justify an oxo-ruthenium(IV) intermediate alone.

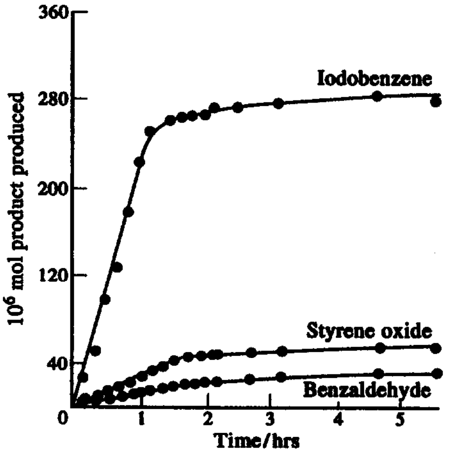
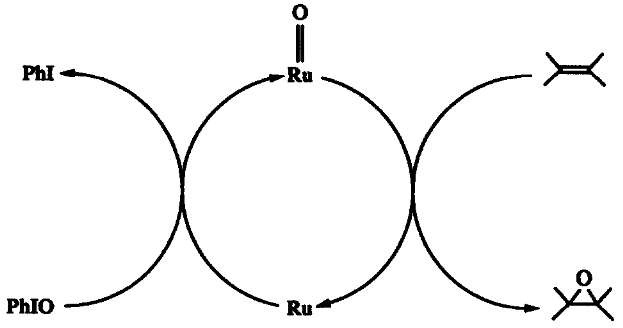


Fig. 5. Plots of the amount of organic products versus time for the oxidation of styrene by PhIO in dichloromethane with $[Ru(terpy)(BIQN)(OH_2)](ClO_4)_2$ as catalyst.



Scheme 2.

Epoxidation by PhIO is not necessarily initiated by a redox-active metal complex. Valentine and coworkers[14] showed that some non-redox active metal salts can also catalyse alkene epoxidation by iodosylbenzene. The catalytic ability was explained on the basis of the Lewis acidity of the metal ion. It has been suggested that oxidation could be initiated through coordination of PhIO to a metal ion.

Here we found a Ru^{II}-aqua complex of 1,1′-biisoquinoline, which can mediate alkene epoxidation by PhIO. Because of the potential C_2 chirality of the chelating BIQN, it may be of interest to prepare optically active ruthenium(II)–BIQN complexes. However, attempts to resolve the [Ru(terpy)(BIQN)(H_2O)]$^{2+}$ complex have so far been unsuccessful.

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