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Synthesis and Characterization of Oxoruthenium(IV) Complexes That Utilize a 2,2′-Biquinoline Ligand

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Novel oxoruthenium(IV) complexes of the form $[(bpy)(biq)(O)(PR_3)Ru^{IV}](ClO_4)_2$ (where bpy = 2,2′-bipyridine, biq = 2,2′-biquinoline, and PR_3 = a tertiary phosphine ligand) have been generated through the oxidation of the analogous aquoruthenium(II) species. Characterization of the oxoruthenium(IV), aquoruthenium(II), and chlororuthenium(II) complexes was accomplished through the following methods: IR spectroscopy, cyclic voltammetry, constant-potential coulometry, and UV–visible spectroscopy. The chlororuthenium(II) complex was also characterized by ^{13}C NMR spectroscopy. Aqueous cyclic voltammetric measurements of the aquoruthenium(II) and oxoruthenium(IV) complexes are consistent with a mechanism involving two concomitant one-electron, one-proton transfers: $Ru^{IV}(O)/Ru^{III}(OH)/Ru^{II}(OH_2)$. The oxoruthenium(IV) complexes act as oxidants toward organic substrates, where the 2,2′-biquinoline ligand has a clear effect on the kinetics of substrate oxidation.

Introduction

There has been much current interest in the synthesis and reactivity of oxoruthenium(IV) and dioxoruthenium(VI) complexes, with a focus on the role of the ligands in the control of the redox properties of the ruthenium centers.[1-5] The ligands utilized in conjunction with the ruthenium centers include 2,2′-bipyridine,[1,2a] tetraaza macrocycles,[2b,3] and porphyrin ligands,[4] where the ligands induce a variety of redox chemistries by the ruthenium center. Recently, we reported the synthesis of the first example of an oxoruthenium(IV) complex that utilizes a tertiary phosphine ligand.[5a] Phosphine ligands markedly affect both the physical properties[5b] and the reactivity[5c-f] of the oxoruthenium(IV) centers, resulting in the first example of hydrophobic selectivity in the oxidation of alcohols[5c,d] and the generation of a ruthenium catalyst which drives the aerobic oxidation of olefins.[5f]

In addition, a great deal of interest has been shown in the use of 2,2′-biquinoline as a ligand in combination with a ruthenium center.[6-17] In particular, Belser and von Zelewsky,[9,10] as well as Thummel,[13] have generated a number of complexes of the types $[Ru^{II}(biq)_3]^{2+}$, $[Ru^{II}(biq)_2(N\text{-}N)]^{2+}$, and $[Ru^{II}(biq)(N\text{-}N)_2]^{2+}$, where biq = 2,2′-biquinoline and N-N = 2,2′-bipyridine or a related ligand.[18] Interest in the use of 2,2′-biquinoline in place of 2,2′-bipyridine stems from the differing electronic properties between the two ligands,[6-12] as well as the increased steric demands of the 2,2′-biquinoline ligand relative to those of the 2,2′-bipyridine ligand.[13] Notably, the vast majority of the ruthenium complexes that utilize 2,2′-biquinoline contain ruthenium(II), with $[Ru^{III}(biq)(Cl)_2]^+$ as one of the few examples of a (biquinoline)ruthenium(III) complex.[16]

Due to the different electronic properties and increased steric demands of 2,2′-biquinoline relative to those of 2,2′-bipyridine, it was anticipated that oxoruthenium(IV) complexes which utilize a biquinoline ligand should display spectral and redox properties which differ from those of the analogous bipyridine complexes. Thus, we report here the synthesis and characterization of the first ruthenium(IV) complexes that contain a 2,2′-biquinoline ligand, namely (bipyridine)(biquinoline)oxo(phosphine)ruthenium(IV) perchlorate. In addition, the effect of the biquinoline ligand on the physical properties and reactivities of the (biquinoline)oxoruthenium(IV) complexes are also discussed.

Experimental Section

$RuCl_3{\cdot}3H_2O$ and $AgClO_4$ were purchased from Johnson Matthey Inc. 2,2′-Bipyridine (bpy) was obtained from Aldrich Chemical Co., and 2,2′-biquinoline (biq) was purchased from Lancaster Synthesis Ltd. Phosphine ligands were purchased from Aldrich Chemical Co. or Strem Chemical. These compounds were used as received. All aqueous reactions used house distilled water, which was passed through Barnstead HN combination (No. D8922) and HN organic removal (No. D8904) purification cartridges before use. Triethylamine was obtained from the Eastman Kodak Co. and was distilled over NaOH. The ceric perchlorate

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(18) Abbreviations used in this text incude biq = 2,2′-biquinoline and bpy = 2,2′-bipyridine.

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solution (0.5 N in 6 N perchloric acid) was obtained from G. F. Smith Chemical Co. All other materials were of reagent quality and were used without further purification.

Elemental analyses were performed by Atlantic Microlabs (Atlanta, GA). Infrared spectra were recorded with a Perkin-Elmer 1430 ratio recording infrared spectrophotometer, using Nujol mulls on NaCl plates, or on a Mattson Cygnus 100 FT-infrared spectrophotometer equipped with a Hewlett-Packard HP 7475A plotter, using diffuse-refractance techniques, with the sample distributed in powdered KBr. ^{13}C NMR spectra were obtained with a JEOL FX90Q Fourier transform spectrometer using deuteriated chloroform as the solvent. Me_4Si was used as the standard for the ^{13}C NMR experiments. Electronic spectra were obtained by using quartz cells (Uvonic Cuvettes) with either a Perkin-Elmer Lambda 3 UV–vis spectrophotometer equipped with a Houston Instruments Model 164 recorder or a Bausch and Lomb Spectronic 2000 spectrophotometer equipped with a Houston Instrument Model 200 recorder. Aqueous spectra were obtained with a pH 2.0 $NaNO_3/HNO_3$ buffer, having an ionic strength of 0.06 M, while nonaqueous spectra were obtained with methylene chloride distilled over CaH_2. Beer's law was verified for all extinction coefficients by obtaining spectra at a minimum of two different concentrations.

Cyclic voltammetric measurements were obtained with an IBM EC/225 voltammetric analyzer, and the current–potential waves were recorded with a Houston Instruments Model 164 recorder. The cyclic voltammetric experiments were performed in three-electrode, one-compartment cells, with a platinum or glassy-carbon working electrode (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium calomel reference electrode (SSCE). Nonaqueous electrochemical measurements were performed with use of a 0.1 M solution of tetra-*n*-butylammonium tetrafluoroborate (n-Bu_4NBF_4, the supporting electrolyte) in distilled methylene chloride. The electrolyte was prepared and purified by using standard methods.[19] Aqueous electrochemical measurements were obtained at ionic strengths of 0.1 M, with the following buffer solutions: $HNO_3/NaNO_3$ (pH 2.0), potassium hydrogen phthalate (pH 4.0), Na_2HPO_4/KH_2PO_4 (pH 6.8), and borax (pH 9.0). Coulometric measurements were performed in pH 6.8 Na_2HPO_4/KH_2PO_4 buffer, with use of the IBM EC/225 voltammetric analyzer. The two-compartment fritted cell used for the coulometric experiments consisted of a reticulated-vitreous-carbon working electrode, a platinum common electrode, and a SSCE reference electrode.

The kinetic experiments involving the oxidation of organic substrates were monitored spectrophotometrically, with use of the methods and instrumentation previously reported.[5d] The product determinations for the substrate oxidations were accomplished by using the techniques and instrumentation reported earlier.[5d–f]

Preparation of Starting Materials. (2,2′-Bipyridine)tetrachlororuthenium(IV), $[Ru^{IV}(bpy)(Cl)_4]$ (1). Complex **1** was prepared by using the method developed by Krause,[20] reduced to one-tenth the literature scale. The brown to black crystalline product was isolated by vacuum filtration, washed with water, and dried in vacuo at 50 °C for 24 h.

(2,2′-Bipyridine)(2,2′-biquinoline)dichlororuthenium(II) Dihydrate, $[Ru^{II}(bpy)(biq)(Cl)_2]\cdot 2H_2O$ (2). A 0.200-g (0.5-mmol) sample of complex **1** and 0.128 g (0.5 mmol, 1-equiv) of 2,2′-biquinoline were dissolved in 20 mL of N_2-deaerated absolute EtOH. A 0.060-g (0.6-mmol, 1.2 equiv) sample of Et_3N was then added to the solution. The mixture was heated at reflux under N_2 for 7 h, during which time the solution changed from black to blue-green. After the mixture was cooled, the solvent was completely removed with a rotary evaporator. The product was suspended in Et_2O and was collected by vacuum filtration. The gray-green product (**2**) was used without purification; yield 0.321 g (100%).

Bis(2,2′-biquinoline)dichlororuthenium(II) Dihydrate, $[Ru^{II}(biq)_2(Cl)_2]\cdot 2H_2O$ (3). Complex **3** was prepared by using a modification of the procedure for the synthesis of the corresponding bis(2,2′-bipyridine) analogue.[5b] A 0.990-g sample of $RuCl_3\cdot 3H_2O$ (3.8 mmol) was dissolved in 12 mL of *N,N*-dimethylformamide. A 2.036-g (7.9-mmol, 2.1-equiv) sample of 2,2′-biquinoline and 0.850 g (20 mmol, 5.3 equiv) of LiCl were then added to the solution, which was deaerated with N_2 for 5 min. The solution was heated at reflux for 6 h. The heating source was removed, and while the solution was still hot, 75 mL of acetone was added through the top of the condenser. The mixture was stirred at room temperature for an additional 0.5 h, after which time the blue-black microcrystalline solid was collected by vacuum filtration, washed with Et_2O, and air-dried. Complex **3** was used without purification; yield 1.600 g (58%).

Caution! All of the following complexes have perchlorate as the counterion. While we have used perchlorate as the counterion with a number of ruthenium(II) and ruthenium(IV) complexes without incident, perchlorate salts of metal complexes with organic ligands are potentially explosive. Care should be exercised when using a spatula or stirring rod to agitate any solid perchlorate. These complexes, as well as any other perchlorate salt, should be handled only in small quantities.[21,22]

Preparation of Chlororuthenium(II) Complexes. (2,2′-Bipyridine)(2,2′-biquinoline)chloro(trimethylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(bpy)(biq)(Cl)(PMe_3)](ClO_4)$ (4), (2,2′-Bipyridine)(2,2′-biquinoline)chloro(triethylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(bpy)(biq)(Cl)(PEt_3)](ClO_4)$ (5), (2,2′-Bipyridine)(2,2′-biquinoline)chloro(tri-*n*-propylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Pr)_3)](ClO_4)$ (6), (2,2′-Bipyridine)(2,2′-biquinoline)chloro(tri-*n*-butylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Bu)_3)](ClO_4)$ (7), and (2,2′-Bipyridine)(2,2′-biquinoline)chloro(triphenylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(bpy)(biq)(Cl)(PPh_3)](ClO_4)$ (8). In a typical reaction, 0.2–0.8 g (0.3–1.2 mmol) of complex **2** and 1 equiv (0.3–1.2 mmol) of the phosphine ligand were added to a N_2-deaerated 75% EtOH/25% H_2O solution (2.5 mg of complex/(mL of EtOH/H_2O)). The mixture was heated at reflux, under N_2, for 4–6 h. The solution was cooled and the volume was reduced to near-dryness by use of a rotary evaporator. H_2O was added to redissolve any solid, and the complex was precipitated as the perchlorate salt, by the addition of excess $NaClO_4$. The violet solids were collected by vacuum filtration, washed with a small amount of H_2O, and air-dried. Purification was undertaken by dissolution of the complex in acetone, followed by gravity filtration and titration of the filtrate into Et_2O. The recrystallized products, **4**–**8**, were collected by vacuum filtration, washed with Et_2O, and air-dried: yields ranged from 50 to 80% based on starting ruthenium.

Bis(2,2′-biquinoline)chloro(triethylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(biq)_2(Cl)(PEt_3)](ClO_4)$ (9). A 1.216-g (1.69-mmol) sample of complex **3** and 1.69 mmol of PEt_3 were added to 500 mL of a N_2-deaerated 75% EtOH/25% H_2O mixture. The mixture was heated at reflux, under N_2, for 4 h. After this time, the mixture was cooled, and the volume was reduced to near-dryness with the use of a rotary evaporator. The solid was redissolved in water and precipitated as the blue-violet perchlorate complex, by the addition of excess $NaClO_4$. Purification was achieved through column chromatography, by using a toluene-packed alumina column and eluting with an acetone/toluene solution (1:1 by volume). The desired product was eluted as a blue band, which was reprecipitated from Et_2O, forming dark blue crystals; yield 30% based on starting ruthenium.

Preparation of Aquoruthenium(II) Complexes. Aquo(2,2′-bipyridine)(2,2′-biquinoline)(trimethylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ (10), and Aquo(2,2′-bipyridine)(2,2′-biquinoline)(triethylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (11). A typical preparation involved 0.20 g of complex **4** or **5** and 1.5 equiv of $AgClO_4$ added to ca. 300 mL of H_2O. The solution was heated at reflux, under N_2, for 1 h. The solution changed color from deep purple to red-violet, accompanied by the formation of a white precipitate (AgCl). The solution was chilled in an ice bath to precipitate any unreacted starting compound and was then passed through a fine-fritted filter, to remove the AgCl. The product, **10** or **11**, was precipitated as the perchlorate salt, by the addition of excess $NaClO_4$. The red-violet crystals were collected by vacuum filtration, washed with cold water, and air-dried. The filtrate was chilled for several days, to obtain a second crop of crystals. Yields ranged between 50 and 80% based on starting ruthenium.

Aquo(2,2′-bipyridine)(2,2′-biquinoline)(tri-*n*-propylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ (12), Aquo(2,2′-bipyridine)(2,2′-biquinoline)(tri-*n*-butylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Bu)_3)](ClO_4)_2$ (13), and Aquo(2,2′-bipyridine)(2,2′-biquinoline)(triphenylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(OH_2)(bpy)(biq)(PPh_3)](ClO_4)_2$ (14). A typical reaction required 0.2 g of a chloro complex, **6**, **7**, or **8**, and 1.5 equiv of $AgClO_4$. The $AgClO_4$ was added to 600 mL of near-boiling H_2O and allowed to dissolve. The chloro complex was slurried in H_2O and then added to the hot solution, where it dissolved after ca. 5–10 min. The reaction was heated at reflux for 0.75–1 h, during which time the solution underwent the same color change mentioned for complexes **10** and **11**, accompanied by the formation of AgCl. The solution was chilled in ice for 1 h, after which time it was passed through a fine-fritted filter. The product was isolated from the filtrate as the perchlorate salt, by the addition of excess $NaClO_4$, collected by vacuum filtration, washed with cold water, and air-dried. Complexes **12** and **13** were dark, red-violet

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solids, while complex **14** was a light brown solid. A second crop of crystals was isolated by chilling the filtrate for several days. Yields were 40–70% based on starting ruthenium.

Aquobis(2,2′-biquinoline)(triethylphosphine)ruthenium(II) Perchlorate, $[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (15). A 0.07-g sample of complex **9** (0.08 mmol) and 0.025 g (0.12 mmol, 1.5 equiv) of $AgClO_4$ were added to 200 mL of hot H_2O, by the method described for complexes **12–14**. The mixture was heated at reflux, under N_2, for 45 min. During the reaction time the solution changed from dark blue to violet, accompanied by the formation of AgCl. The solution was chilled in an ice bath and passed through a fine-fritted filter. The product, **15**, was precipitated as the perchlorate salt by the addition of excess $NaClO_4$. The light violet solid was collected by vacuum filtration, washed with cold H_2O, and air-dried. A second crop of crystals was obtained by chilling the filtrate for several days; yield 35% based on starting ruthenium.

Preparation of Oxoruthenium(IV) Complexes. (2,2′-Bipyridine)(2,2′-biquinoline)oxo(trimethylphosphine)ruthenium(IV) Perchlorate, $[Ru^{II}(bpy)(biq)(O)(PMe_3)](ClO_4)_2$ (16), and (2,2′-Bipyridine)(2,2′-biquinoline)oxo(triethylphosphine)ruthenium(IV) Perchlorate, $[Ru^{IV}(bpy)(biq)(O)(PEt_3)](ClO_4)_2$ (17). A typical preparation used 0.050 g of complex **10** or **11**, which was dissolved in 100 mL of H_2O. The solution was gravity-filtered to remove any undissolved material and then chilled in an ice bath for 10 min. A 15-fold excess of Ce(IV) solution (0.5 N in 6 N $HClO_4$) was added slowly (dropwise) to the rapidly stirred cold solution. The solution changed from red-violet to tan-brown, followed by precipitation of the product, **16** or **17**. The brown solid was collected by vacuum filtration, washed with cold H_2O, and air-dried: yields average between 40 and 60% based on the starting ruthenium.

(2,2′-Bipyridine)(2,2′-biquinoline)oxo(tri-*n*-propylphosphine)ruthenium(IV) Perchlorate, $[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Pr)_3)](ClO_4)_2$ (18), (2,2′-Bipyridine)(2,2′-biquinoline)oxo(tri-*n*-butylphosphine)ruthenium(IV) Perchlorate, $[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Bu)_3)](ClO_4)_2$ (19), and (2,2′-Bipyridine)(2,2′-biquinoline)oxo(triphenylphosphine)ruthenium(IV) Perchlorate, $[Ru^{IV}(bpy)(hiq)(O)(PPh_3)](ClO_4)_2$ (20). A typical preparation used 0.035 g of complex **12**, **13**, or **14**, dissolved in 125 mL of H_2O. The solution was gravity-filtered and kept at room temperature during the addition of the Ce(IV) (to avoid precipitation before the formation of the oxo complex was completed). A 15–equiv sample of Ce(IV) perchlorate, diluted to 0.003 M (1 mL of 0.1 N Ce(IV) solution in 35 mL of H_2O) was slowly added (dropwise) to the rapidly stirred solution. The solution changed from red-violet to tan-brown, followed by the precipitation of the brown product **18**, **19**, or **20**. The solid was collected by vacuum filtration, washed with cold H_2O, and air-dried; yields 30–50% based on the starting ruthenium.

Results and Discussion

Synthesis. The complexes $[Ru^{IV}(bpy)(biq)(O)(PR_3)](ClO_4)_2$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph; **16–20**) were prepared by utilizing the synthetic method

$$Ru^{II}(bpy)(biq)(Cl)_2 \xrightarrow{PR_3} [Ru^{II}(bpy)(biq)(Cl)(PR_3)]^+ \xrightarrow[H_2O]{Ag^+} [Ru^{II}(OH_2)(bpy)(biq)(PR_3)]^{2+} \xrightarrow{Ce(IV)} [Ru^{IV}(bpy)(biq)(O)(PR_3)]^{2+}$$

In this manner, the phosphine ligand was coordinated to a ruthenium(II) center, followed by the chemical oxidation of ruthenium(II) to ruthenium(IV), through the use of Ce(IV) as an oxidant. This route allows the phosphine to be coordinated prior to ruthenium oxidation, thus avoiding the oxidation of the tertiary phosphine ligand.

For the aquoruthenium(II) species (complexes **10–15**), as the hydrophobic nature of the tertiary phosphine ligands increased, the water solubility of the complex decreased. In a similar manner, all of the biquinoline complexes were less water soluble than their bipyridine analogues. Complexes **10–15** are stable in solution for weeks, while as solids, the complexes are stable for several months. The reactions forming the $Ru^{IV}(O)(bpy)(biq)(phosphine)$ complexes, **16–20**, were in general much less sensitive to the presence of excess Ce(IV) and excess perchlorate anion than the corresponding bis(bipyridine) complexes. The oxo(trimethylphosphine)ruthenium(IV) complex **16** is particularly stable, both in the solid state and in solution, remaining intact in aqueous solution for up to 12 h at room temperature.

The effect of the biquinoline ligand on the stability of the ruthenium complexes can be observed in several instances. First, (biquinoline)(bipyridine)oxo(phosphine)ruthenium(IV) complexes can be prepared and isolated for tri-*n*-propylphosphine and tri-*n*-butylphosphine ligands, while the bis(bipyridine) analogues of these complexes cannot be isolated as stable solids.[5b] Since the bis(bipyridine) analogues appear to decompose by a second-order, intermolecular mechanism, the increased steric hindrance of biquinoline relative to that of bipyridine may account for increased stability of the biquinoline complexes. Second, the resulting increase in the steric hindrance around the ruthenium center also greatly decreases the rate of conproportionation between the oxo(trimethylphosphine)ruthenium(IV) complex and the aquo(trimethylphosphine)ruthenium(II) complex, relative to that for the analogous bis(bipyridine)(trimethylphosphine)ruthenium complexes.

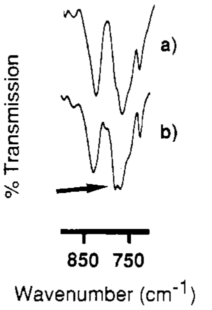

Figure 1. Diffuse-refractance FT-IR spectra of (a) $[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ and (b) $[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Pr)_3)](ClO_4)_2$ in powdered KBr. Arrow denotes Ru=O stretching frequency.

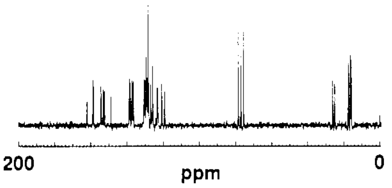

Figure 2. Proton-decoupled ^{13}C NMR spectrum of 0.11 M $[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Pr)_3)](ClO_4)$ in $CDCl_3$.

Analytical Data. Complexes **4–20** yielded satisfactory results for carbon and hydrogen elemental analyses, as either anhydrous or hydrated perchlorate salts. The analytical results are contained in Table X (supplementary material). Rigorous vacuum drying of these complexes resulted in decomposition, so drying was avoided.

IR Spectra. Infrared spectroscopy was used to establish the presence of the $Ru^{IV}=O$ moiety in the oxoruthenium(IV) complexes. Terminal $Ru^{IV}=O$ stretching frequencies typically occur in the region 785–890 cm^{-1}.[5b,23] The infrared spectra of all of the oxoruthenium(IV) complexes displayed an absorbance centered at 785 cm^{-1}, which is absent from the corresponding aquoruthenium(II) complexes. For a typical example of this spectral change, see Figure 1.

NMR Spectra. The number of absorbances in the proton-decoupled ^{13}C NMR spectra of the chlororuthenium(II) complexes suggest a specific geometry about the ruthenium center, where the bipyridine and biquinoline ligands occupy cis positions relative to each other (see Figure 2 and Table I). The NMR spectra for these complexes also display resonances corresponding to the carbon atoms of the coordinated phosphine ligands. Splittings of these resonances due to the coupling of the phosphorus atom to the carbon atoms of the tertiary phosphine ligands are noted in the spectra.

Cyclic Voltammetry. Cyclic voltammetric measurements on complexes **1–9** in a 0.1 M $n\text{-}Bu_4NBF_4$ solution of methylene chloride resulted in one reversible, well-behaved wave (representing the Ru(III)/Ru(II) redox couple) for all the complexes, in the range from 0 to +1.70 V vs SSCE (see Figure 3). Table II lists the results of these electrochemical experiments, showing the $E_{1/2}$ values, peak potential separations, and peak current ratios. A

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[23] Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1972**, 1449.

Table I. ^{13}C NMR Spectral Data for $[Ru^{II}(bpy)(biq)(Cl)(PR_3)](ClO_4)$ (Complexes **5**–**8**) in $CDCl_3$[a]

complex	bpy, biq[b]	PR_3
$[Ru^{II}(bpy)(biq)(Cl)(PEt_3)]^+$	161.9, 161.7, 158.7, 158.5, 154.2, 152.9, 152.3, 148.6, 138.5, 138.1, 137.1, 136.4, 130.5, 130.0, 129.1, 128.9, 128.2, 128.0, 126.8, 125.8, 123.2, 122.9, 120.6, 119.0	15.9, 14.8, 8.0, 7.8
$[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Pr)_3)]^+$	161.9, 158.6, 158.4, 154.2, 153.0, 152.2, 148.7, 138.5, 138.1, 137.1, 136.3, 130.5, 130.0, 129.2, 128.7, 128.2, 128.0, 126.8, 125.7, 123.2, 122.8, 120.6, 119.1	26.0, 24.9, 17.4, 17.2, 16.2, 15.7
$[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Bu)_3)]^+$	162.0, 158.7, 158.4, 154.3, 153.0, 152.2, 148.7, 138.6, 138.4, 138.2, 137.1, 136.3, 130.4, 130.0, 129.2, 128.8, 128.2, 128.0, 126.7, 125.6, 123.2, 122.8, 120.7, 119.1	25.6, 25.5, 24.4, 23.9, 23.4, 22.4, 13.2
$[Ru^{II}(bpy)(biq)(Cl)(PPh_3)]^+$	161.2, 159.5, 158.6, 158.4, 154.7, 152.5, 151.7, 148.8, 139.1, 138.4, 135.6, 136.2, 130.1, 131.4, 130.6, 129.3, 128.5, 128.1, 127.9, 127.6, 126.9, 125.5, 123.0, 122.4, 120.9, 119.3	136.1, 135.9, 133.8, 133.4, 129.8, 129.6

[a] Chemical shifts (ppm) are relative to Me_4Si internal standard. [b] Abbreviations: bpy = 2,2′-bipyridine; biq = 2,2′-biquinoline.

Table II. $E_{1/2}$ Potentials and ΔE_p Values in CH_2Cl_2[a] for $[Ru^{II}(bpy)(biq)(Cl)(PR_3)]^+$ and $[Ru^{II}(biq)_2(Cl)(PEt_3)]^+$ Complexes and Complexes **2** and **3**

complex	$E_{1/2}$, V vs SSCE	ΔE_p, V
$[Ru^{II}(bpy)(biq)(Cl)_2]\cdot 2H_2O$ (**2**)	+0.46	0.09
$[Ru^{II}(biq)_2(Cl)_2]\cdot 2H_2O$ (**3**)	+0.48	0.14
$[Ru^{II}(bpy)(biq)(Cl)(PMe_3)](ClO_4)$ (**4**)	+0.96	0.13
$[Ru^{II}(bpy)(biq)(Cl)(PEt_3)](ClO_4)$ (**5**)	+0.95	0.10
$[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Pr)_3)](ClO_4)$ (**6**)	+0.96	0.10
$[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Bu)_3)](ClO_4)$ (**7**)	+0.96	0.10
$[Ru^{II}(bpy)(biq)(Cl)(PPh_3)](ClO_4)$ (**8**)	+1.02	0.08
$[Ru^{II}(biq)_2(Cl)(PEt_3)](ClO_4)$ (**9**)	+1.08	0.13

[a] Key: ΔE_p = peak potential separation; $i_{p,c}/i_{p,a}$ = peak current ratio = 1.0 in all cases. Conditions: 0.1 M $n\text{-}Bu_4NBF_4$ in CH_2Cl_2; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s.

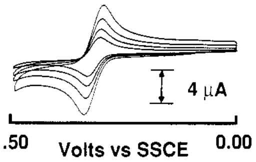

Figure 3. Cyclic voltammograms of $[Ru^{II}(bpy)(biq)(Cl)(PEt_3)](ClO_4)$ in CH_2Cl_2 with 0.1 M Bu_4NBF_4 supporting electrolyte and a platinum working electrode, at scan rates of 50, 100, 200, and 400 mV/s.

Table III. $E_{1/2}$ Potentials and ΔE_+ and $i_{p,c}/i_{p,a}$ Values for $[Ru^{II}(OH_2)(bpy)(biq)(PR_3)]^{2+}$ and $[Ru^{II}(OH_2)(biq)_2(PEt_3)]^{2+}$ Complexes in CH_2Cl_2[a]

complexes	$E_{1/2}$, V vs SSCE	ΔE_p, V	$i_{p,c}/i_{p,a}$
$[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ (**10**)	+1.30	0.16	0.5
$Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (**11**)	+1.24	0.17	0.4
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**12**)	+1.24	0.13	0.6
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**13**)	+1.20	0.19	0.6
$[Ru^{II}(OH_2)(bpy)(biq)(PPh_3)](ClO_4)_2$ (**14**)	+1.28	0.16	0.5
$[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (**15**)[b]	+1.24	0.09	0.5

[a] Key: ΔE_p = peak potential separation; $i_{p,c}/i_{p,a}$ = peak current ratio. Conditions: 0.1 M $n\text{-}Bu_4NBF_4$ in CH_2Cl_2; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s. [b] Irreversible at 100 mV/s; reported values are for 50 mV/s scan rate.

Table IV. $E_{1/2}$ Potentials and ΔE_p and $i_{p,c}/i_{p,a}$ Values for $[Ru^{II}(OH_2)(bpy)(biq)(PR_3)]^{2+}$ and $[Ru^{II}(OH_2)(biq)_2(PEt_3)]^{2+}$ Complexes in Aqueous Solution Buffered at pH 2.0[a]

complexes	$E_{1/2}$(Ru(III)/Ru(II)), V vs SSCE	ΔE_p, V	$i_{p,c}/i_{p,a}$
$[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ (**10**)	+0.75	0.06	1.0
$[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (**11**)	+0.76	0.10	0.8
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**12**)	+0.75	0.09	0.8
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**13**)	+0.75	0.10	0.8
$[Ru^{II}(OH_2)(bpy)(biq)(PPh_3)](ClO_4)_2$ (**14**)	+0.78	0.12	0.9
$[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (**15**)	+0.75	0.07	0.8

complexes[b]	$E_{1/2}$(Ru(IV)/Ru(III)), V vs SSCE	ΔE_p, V
$[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (**11**)	+0.92	0.06
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**12**)	+0.94	0.10
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**13**)	+0.96	0.11
$[Ru^{II}(OH_2)(bpy)(biq)(PPh_3)](ClO_4)_2$ (**14**)	+1.00	0.06
$[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (**15**)	+0.91	0.07

[a] Conditions: 0.1 M pH 2.0 nitrate buffer; glassy-carbon working electrode; SSCE reference electrode; scan rate 100 mV/s. The Ru(IV)/Ru(III) couple was not observed for complex **10** at this pH. A small cathodic wave was observed at +0.93 V but was irreversible. [b] $i_{p,c}/i_{p,a}$ = 1.0 in all cases.

comparison of the potentials for the two dichloride complexes **2** and **3** with that of $Ru^{II}(bpy)_2(Cl)_2$ shows that the replacement of one bipyridine with a biquinoline raises the $E_{1/2}$ value for the Ru(III)/Ru(II) couple by 50 mV, while the replacement of the second bipyridine raises the $E_{1/2}$ value by an additional 20 mV.

The effects on the potential of the Ru(III)/Ru(II) couple by substitution of a chloride ligand by a phosphine ligand reflect the trends observed for the bis(2,2′-bipyridine)chloro(phosphine)ruthenium(II) species.[5b] For example, the substitution of a tertiary phosphine ligand for a chloro ligand in $Ru^{II}(bpy)(biq)(Cl)_2$ resulted in an increase in the $E_{1/2}$ value for the Ru(III)/Ru(II) couple of approximately 500 mV for the trialkylphosphine (560 mV for the triarylphosphine), while the substitution of a triethylphosphine ligand for a chloro ligand in $Ru^{II}(biq)_2(Cl)_2$ resulted in an increase of the $E_{1/2}$ value for the Ru(III)/Ru(II) couple of approximately 600 mV.

The potentials for the Ru(III)/Ru(II) redox couple of the aquoruthenium(II) complexes **10**–**15** in CH_2Cl_2 are listed in Table III. The recorded waves of the aquoruthenium(II) complexes were at best quasi-reversible, as indicated by the large peak potential separations and low peak current ratios. This is typical behavior for aquoruthenium(II) complexes, which undergo proton/electron transfers, when the measurements are made in aprotic solvents.[5b]

The electrochemistry of the aquoruthenium(II) complexes was better behaved when the experiment was conducted in aqueous buffered solution. The redox potentials for complexes **10**–**15** were measured in 0.1 M, pH 2.0 nitrate buffer, to allow for direct comparison with the bis(bipyridine) analogues.[5b] The results obtained for the redox potentials are listed in Table IV and show that complexes **10**–**15** display the same behavior as the corresponding bis(bipyridine) complexes. The cyclic voltammograms displayed two waves: a quasi-reversible wave corresponding to the Ru(III)/Ru(II) redox couple and a second, quasi-reversible wave, with a smaller measured current, corresponding to the Ru(IV)/Ru(III) redox couple. Likewise, the cyclic voltammograms of the oxoruthenium(IV) complexes **16**–**20** displayed the

Table V. $E_{1/2}$ Values of Ru(III)/Ru(II) and Ru(IV)/Ru(III) as a Function of Solution pH for $[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (**10**), $[Ru^{IV}(bpy)(biq)(O)(PEt_3)](ClO_4)_2$ (**17**), and $[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (**15**)[a] and Regression Data for Linear Plots of $E_{1/2}$ vs pH

	$E_{1/2}$, V vs SSCE					
	10		**17**		**15**	
pH	Ru(III)/Ru(II)	Ru(IV)/Ru(III)	Ru(III)/Ru(II)	Ru(IV)/Ru(III)	Ru(III)/Ru(II)	Ru(IV)/Ru(III)
1.97	+0.76	+0.92	+0.71	+0.91	+0.75	+0.91
4.00	+0.62	+0.86	+0.62	+0.86	+0.65	+0.81
6.80	+0.48	+0.69	+0.45	+0.63	+0.45	+0.61
8.95	+0.36	+0.59	+0.32	+0.54	+0.35	+0.51
	m = −0.06 V/pH unit R^2 = 0.996	m = −0.05 V/pH unit R^2 = 0.987	m = −0.06 V/pH unit R^2 = 0.996	m = −0.06 V/pH unit R^2 = 0.996	m = −0.06 V/pH unit R^2 = 0.993	m = −0.06 V/pH unit R^2 = 0.993

[a] Conditions: glassy-carbon working electrode; SSCE reference electrode; scan rate 100 mV/s.

Table VI. UV–Vis Spectral Data of $[Ru^{II}(bpy)(biq)(Cl)(PR_3)]^+$ and $[Ru^{II}(biq)_2(Cl)(PEt_3)]^+$ Complexes in CH_2Cl_2

complex	λ_{max}, nm ($10^{-3}\epsilon_{max}$, $M^{-1}\ cm^{-1}$)
$[Ru^{II}(bpy)(biq)(Cl)(PMe_3)](ClO_4)$ (**4**)	539 (7), 456 (2), 368 (sh), 341 (26), 292 (32), 268 (34)
$[Ru^{II}(bpy)(biq)(Cl)(PEt_3)](ClO_4)$ (**5**)	553 (7), 458 (2), 371 (sh), 344 (30), 294 (34), 267 (36)
$[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Pr)_3)](ClO_4)$ (**6**)	553 (8), 458 (2), 376 (sh), 344 (33), 295 (36), 268 (39)
$[Ru^{II}(bpy)(biq)(Cl)(P(n\text{-}Bu)_3)](ClO_4)$ (**7**)	553 (7), 458 (2), 372 (sh)8 346 (28), 296 (32), 270 (32)
$[Ru^{II}(bpy)(biq)(Cl)(PPh_3)](ClO_4)$ (**8**)	547 (7), 440 (3), 372 (sh), 346 (28), 290 (25), 267 (39)
$[Ru^{II}(biq)_2(Cl)(PEt_3)](ClO_4)$ (**9**)	661 (sh), 588 (9), 506 (5), 424 (5), 378 (sh), 341 (50), 302 (18), 290 (sh), 266 (82)

same two waves as the aquoruthenium(II) complexes **10–14**.

The electrochemical data suggest that the oxidation of complexes **10–14**, in aqueous media, proceeds via a two-electron, two-proton transfer:

$$[\mathrm{(biq)(L)(N\text{-}N)(O)Ru^{IV}}]^{2+} \xrightleftharpoons[-H^+,\ -e^-]{+H^+,\ +e^-} [\mathrm{(biq)(OH)(L)(N\text{-}N)Ru^{III}}]^{2+} \xrightleftharpoons[-H^+,\ -e^-]{+H^+,\ +e^-} [\mathrm{(OH_2)(biq)(L)(N\text{-}N)Ru^{II}}]^{2+}$$

aqueous buffer, N-N = bpy or biq, L = tertiary phosphine

When the $E_{1/2}$ values for both the Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples are plotted versus solution pH, over a range of 7 pH units, the observed slopes are in good agreement with the predicted Nernstian slope of −0.059 V/pH unit (see Table V for the data and results). These experiments were conducted with aqueous solutions of the aquo(triethylphosphine)ruthenium(II) complexes or the oxo(triethylphosphine)ruthenium(IV) complex.

Coulometry. Coulometric measurements were accomplished by exhaustive controlled-potential electrolysis on an aqueous solution of $[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)]^{2+}$ (cation of **11**) buffered at pH 6.8 (KH_2PO_4/Na_2HPO_4), and the products from the reaction were monitored by cyclic voltammetry and UV–visible spectroscopy. Holding the potential positive of the Ru(IV)/Ru(III) couple (+0.82 V versus SSCE) resulted in a value of n = 2.0. The cyclic voltammograms of the complex, both before and after electrolysis, were identical with those obtained for the chemically synthesized complexes. The electronic spectrum of the solution confirmed that the aquo/oxo conversion occurred as outlined above.

Electronic Spectroscopy. The biquinoline ligand dominates the electronic spectra of the complexes, effectively doubling the number of transitions observed for the analogous bis(bipyridine) complexes.

The spectral data for both $[Ru^{II}(bpy)(biq)(Cl)(PR_3)](ClO_4)$ and $[Ru^{II}(biq)_2(Cl)(PR_3)](ClO_4)$, complexes **4–9**, are presented in Table VI. The $[Ru^{II}(bpy)(biq)(Cl)(PR_3)](ClO_4)$ complexes **4–8** gave rise to a total of six absorbances in the region from 700 to 200 nm, two in the visible region, and four in the UV region. The wavelength of the lowest energy absorbance is directly influenced by the nature of the phosphine ligand coordinated to the metal center. This absorbance, ranging from 497 to 520 nm (varying according to the attached phosphine ligand), can be attributed to a $d\pi$(metal) → π^*(biq) metal to ligand charge-transfer (MLCT) transition, while the second absorbance in the visible region can be interpreted as a second MLCT band corresponding to a $d\pi \rightarrow \pi^*$(bpy) transition. The absorbances at 340 and 267 nm and the shoulder at 370 nm have all been assigned to $\pi \rightarrow \pi^*$(biq) transitions,[12] and the other absorbance at λ_{max} = 290 nm can be attributed to a $\pi \rightarrow \pi^*$(bpy) transition.[5b] The bis(2,2′-biquinoline)(chloro)(triethylphosphine)ruthenium(II) complex **9** gave rise to a spectrum that contained a total of nine absorbances. The absorbances at 588 and 506 nm correspond to $d\pi \rightarrow \pi^*$ MLCT transitions, while the absorbances at 378, 341, 302, and 266 nm correspond to $\pi \rightarrow \pi^*$(biq) electronic transitions.[12]

The spectra for the aquoruthenium(II) species, complexes **10–15**, were obtained both in CH_2Cl_2 (Table VII) and in H_2O, buffered at pH 2.0 (Table VIII), to determine if there were any significant solvent effects. The solvent had little effect on the energy levels for the transitions, but it did affect some of the extinction coefficients, especially the absorbances corresponding to the $\pi \rightarrow \pi^*$ transitions. A comparison of the spectra of the chlororuthenium(II) complexes with those of the corresponding aquoruthenium(II) complexes shows that in the aquoruthenium(II) complexes the two MLCT bands have shifted to higher energies, reflecting the increase in the redox potentials between the corresponding chloro/aquo pairs.[7]

The spectra for the $[Ru^{IV}(O)(bpy)(biq)(phosphine)]^{2+}$ complexes **16–20** were significantly different from those of the corresponding aquoruthenium(II) complexes, as evidenced by the data

Table VII. UV–Vis Spectral Data for $[Ru^{II}(OH_2)(bpy)(biq)(PR_3)]^{2+}$ and $[Ru^{II}(OH_2)(biq)_2(PEt_3)]^{2+}$ in CH_2Cl_2

complex	λ_{max}, nm ($10^{-3}\epsilon_{max}$, $M^{-1}\ cm^{-1}$)
$[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ (**10**)	507 (6), 419 (1), 374 (22), 355 (16), 326 (10), 290 (30), 268 (34)
$[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (**11**)	519 (7), 480 (sh), 424 (3), 375 (18), 355 (16), 327 (13), 292 (25), 270 (28)
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**12**)	519 (7), 483 (sh), 432 (3), 368 (18), 356 (18), 329 (18), 293 (32), 270 (30)
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**13**)	520 (5), 486 (sh), 428 (2), 375 (12), 358 (12), 331 (12), 293 (21), 271 (19)
$[Ru^{II}(OH_2)(bpy)(biq)(PPh_3)](ClO_4)_2$ (**14**)	491 (6), 418 (1), 373 (13), 356 (4), 310 (23), 268 (30)
$[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (**15**)	587 (sh), 525 (7), 473 (sh), 376 (8), 340 (38), 271 (39)

Table VIII. UV-Vis Spectral Data in H_2O[a]

complex	λ_{max}, nm ($10^{-3}\epsilon_{max}$, M^{-1} cm^{-1})
(a) $[Ru^{II}(OH_2)(bpy)(biq)(PR_3)]^{2+}$	
$[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ (**10**)	508 (6), 424 (1), 373 (18), 354 (15), 325 (sh), 296 (25), 268 (32)
$[Ru^{II}(OH_2)(bpy)(biq)(PEt_3)](ClO_4)_2$ (**11**)	519 (7), 428 (3), 373 (14), 354 (9), 335 (sh), 295 (30), 268 (32)
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**12**)	519 (7), 429 (3), 372 (15), 351 (12), 324 (sh), 293 (30), 268 (34)
$[Ru^{II}(OH_2)(bpy)(biq)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**13**)	524 (6), 430 (2), 373 (13), 356 (12), 338 (sh), 297 (22), 272 (30)
$[Ru^{II}(OH_2)(bpy)(biq)(PPh_3)](ClO_4)_2$ (**14**)	497 (6), 430 (2), 373 (15), 356 (8), 318 (sh), 293 (22), 266 (21)
$[Ru^{II}(OH_2)(biq)_2(PEt_3)](ClO_4)_2$ (**15**)	588 (sh), 522 (6), 472 (sh), 371 (10), 330 (18), 301 (sh), 266 (40)
(b) $[Ru^{IV}(bpy)(biq)(O)(PR_3)]^{2+}$	
$[Ru^{IV}(bpy)(biq)(O)(PMe_3)](ClO_4)_2$ (**16**)	428 (4), 372 (19), 360 (19), 299 (20), 268 (36)
$[Ru^{IV}(bpy)(biq)(O)(PEt_3)](ClO_4)_2$ (**17**)	428 (6), 369 (20), 356 (22), 295 (18), 267 (37)
$[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**18**)	430 (6), 372 (20), 357 (14), 293 (8), 268 (26)
$[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**19**)	431 (4), 372 (15), 357 (16), 293 (7), 268 (27)
$[Ru^{IV}(bpy)(biq)(O)(PPh_3)](ClO_4)_2$ (**20**)	435 (4), 376 (18), 361 (17), 298 (8), 270 (40)

[a] Buffered at pH 2.0; ϵ values in the UV region were corrected for the absorbance due to the buffer.

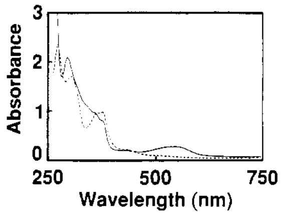

Figure 4. Electronic spectra of $[Ru^{IV}(bpy)(biq)(O)(PMe_3)](ClO_4)_2$ (4.4×10^{-5} M, dashed spectrum) and $[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ (4.4×10^{-5} M, solid spectrum) in pH 2.0, ionic strength 0.06, $NaNO_3/HNO_3$ aqueous buffer.

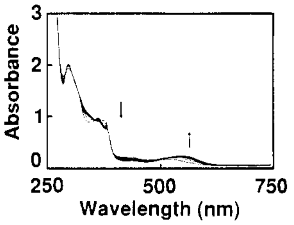

Figure 5. Electronic spectral changes observed during the reaction of 0.03 M benzyl alcohol solution with $[Ru^{IV}(bpy)(biq)(O)(PMe_3)](ClO_4)_2$ (4.4×10^{-5} M) in pH 2.0, ionic strength 0.06, $NaNO_3/HNO_3$ buffer. Spectra were recorded at 6-min intervals. The final spectrum, at t = 48 min, represents the quantitative reconversion to $[Ru^{II}(OH_2)(bpy)(biq)(PMe_3)](ClO_4)_2$ upon completion of the reaction.

listed in Table VIII. The oxoruthenium(IV) complexes are characterized by the absence of the absorbance corresponding to the lowest energy MLCT transition (see Figure 4), as well as a large decrease in the extinction coefficient for the absorbance at 290 nm ($\pi \rightarrow \pi^*$(bpy)) and an increase in the extinction coefficient for the absorbance at 355 nm ($\pi \rightarrow \pi^*$(biq)). There also are increases in the extinction coefficients for $d\pi \rightarrow \pi^*$(bpy) and for the $\pi \rightarrow \pi^*$(biq) transition, but the wavelengths for these transitions are essentially unchanged.

The differences between the spectra of the oxoruthenium(IV) complexes and the corresponding aquoruthenium(II) complexes allow the interconversion of the two complexes to be monitored spectrophotometrically. The reduction of the oxoruthenium(IV) to the aquoruthenium(II) complex proceeds via a reaction with an oxidizable organic substrate that yields spectral changes consistent with a direct conversion between the two species (see Figure 5).

Reactivity. All of the $[Ru^{IV}(O)(bpy)(biq)(phosphine)]^{2+}$ complexes are active oxidants toward a variety of organic substrates and display reactivity with cyclobutanol that is characteristic of two-electron oxidations.[24,25] The oxidation of substrates proceeds via a second-order reaction, first-order in oxidant and first-order in substrate. Table IX lists the second-order rate constants (M^{-1} s^{-1}) for reactions of the oxoruthenium(IV) oxidant with allyl and benzyl alcohols. The data demonstrate the biquinoline ligand effects on the rate of substrate oxidation. For example, the rates of substrate oxidation by the (biquinoline)oxoruthenium(IV) complexes were faster than the rates for the corresponding bis(bipyridine) complexes. This is consistent with previous hydrophobicity arguments, where the biquinoline is more hydrophobic than the bipyridine ligand.[5c,d]

Table IX. Second-Order Rate Constants for Alcohol (Substrate) Oxidation by $[Ru^{IV}(bpy)(biq)(O)(PR_3)]^{2+}$[a]

complex	solvent	substrate[b]	k, M^{-1} s^{-1}
$[Ru^{IV}(bpy)(biq)(O)(PMe_3)](ClO_4)_2$ (**16**)	CH_2Cl_2	allOH	$(1.31 \pm 0.12) \times 10^{-1}$
	H_2O	allOH	$(7.93 \pm 1.0) \times 10^{-2}$
	CH_2Cl_2	BzlOH	$(5.35 \pm 0.42) \times 10^{-1}$
	H_2O	BzlOH	$(6.62 \pm 0.42) \times 10^{-1}$
$[Ru^{IV}(bpy)(biq)(O)(PEt_3)](ClO_4)_2$ (**17**)	CH_2Cl_2	allOH	$(1.02 \pm 0.1) \times 10^{-1}$
	H_2O	allOH	$(4.05 \pm 0.29) \times 10^{-2}$
	CH_2Cl_2	BzlOH	$(3.22 \pm 0.12) \times 10^{-1}$
	H_2O	BzlOH	$(4.07 \pm 0.40) \times 10^{-2}$
$[Ru^{IV}(bpy)(biq)(O)(PPh_3)](ClO_4)_2$ (**20**)	CH_2Cl_2	allOH	$(1.79 \pm 0.28) \times 10^{-1}$
	H_2O	allOH	$(2.27 \pm 0.24) \times 10^{-1}$
	CH_2Cl_2	BzlOH	$(6.44 \pm 0.70) \times 10^{-1}$
	H_2O	BzlOH	2.23 ± 0.28
$[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Pr)_3)](ClO_4)_2$ (**18**)	H_2O	allOH	$(4.78 \pm 0.78) \times 10^{-3}$
$[Ru^{IV}(bpy)(biq)(O)(P(n\text{-}Bu)_3)](ClO_4)_2$ (**19**)	H_2O	allOH	$(4.08 \pm 0.17) \times 10^{-3}$

[a] Reactions were performed under pseudo-first-order Conditions, with an excess of alcohol present: see ref 5c,d for experimental details. [b] Abbreviations: allOH, allyl alcohol; BzlOH, benzyl alcohol.

In addition, the increased steric size of the 2,2′-biquinoline ligand relative to that of the 2,2′-bipyridine ligand has a significant effect on the rate of conproportionation between oxoruthenium(IV) and aquoruthenium(II) complexes. The increased steric bulk of the biquinoline ligand decreases the rate of conproportionation of complex **16**, to the point where the oxidation of organic substrates by (biquinoline)(bipyridine)(oxo)(trimethylphosphine)ruthenium(IV) (cation of **16**) proceeds with well-defined, measurable kinetics, without the formation of the (biquinoline)(bipyridine)hydroxo(trimethylphosphine)ruthenium(III) complex. This is in contrast to the marked conproportionation displayed by the analogous bis(bipyridine) complex.[5b]

Conclusion

The chemistry of ruthenium(II) complexes that employ polypyridyl and tertiary phosphine ligands has been utilized in the preparation of the first oxoruthenium(IV) complexes that contain a 2,2′-biquinoline ligand. These complexes display electrochemical and spectrochemical properties that demonstrate the effects of the biquinoline ligand. In addition, these (biquinoline)oxo-

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ruthenium(IV) complexes oxidize organic substrates faster than the analogous bis(bipyridine) complexes, with fewer side reactions. The increased hydrophobic character of the biquinoline ligand, relative to that of bipyridine, enhances the rate of oxidation of hydrophobic substrates in aqueous solution. In addition, side reactions such as conproportionation are decreased, presumably through the increased steric bulk of the biquinoline ligand, relative to that of bipyridine. Thus, in the design of substrate oxidants, it is important to differentiate between hydrophobic and steric ligand effects, where it is possible to enhance reactivity and minimize side reactions.

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Supplementary Material Available: Table X, listing carbon and hydrogen elemental analysis data for the synthesized complexes (1 page). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Acid-Catalyzed Aquation and Base Hydrolysis of Nitropentacyanoferrate(III) in Aqueous Solution. Evidence for a Pseudo-Zero-Order Hydrolysis Process

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The title reactions were studied spectrophotometrically and kinetically in the pH ranges 0.3–2.0 and 11–13.7, respectively. For the acid-catalyzed aquation, a dependence of the observed rate constant on the square of the acid concentration was found. A mechanism consisting of acid-catalyzed aquation of a protonated nitro complex is proposed to account for these observations and the kinetic parameters (ΔH^*, ΔS^*, and ΔV^*). Base hydrolysis was found to be catalyzed by iron(II) species and exhibits pseudo-zero-order kinetics. In the presence of $Fe^{II}(CN)_5NO_2^{4-}$ as catalyst, aquation of this complex is the rate-determining step of the process, followed by a rapid ligand-exchange reaction between the Fe(II) and Fe(III) species. The observed mechanistic results are discussed in reference to related systems reported in the literature.

Introduction

Substitution reactions of pentacyanoiron(II/III) follow the overall reaction (1) and have received considerable attention from both a kinetic and a thermodynamic point of view.[1-11] Most of

$$Fe(CN)_5X + Y \rightleftharpoons Fe(CN)_5Y + X \qquad (1)$$

the studies were performed on the iron(II) complexes and only a few[10-14] on the less reactive and more stable iron(III) species. Noteworthy is the fact that some of the latter reactions are catalyzed by traces of $Fe^{II}(CN)_5X^{n-}$ complexes.[11] We recently studied the substitution reactions of $Fe(CN)_5NO_2^{3-}$ [15] and found the complex to be relatively stable in aqueous solutions in the range $5 \le pH \le 10$. In more acidic medium, acid-catalyzed aquation occurs and the reaction product is $Fe(CN)_5H_2O^{2-}$. In basic medium (pH >10), hydrolysis to $Fe(CN)_5OH^{3-}$ occurs and the rate of the process depends on [OH⁻]. These reported observations were of preliminary nature, and in this paper we report a detailed kinetic analysis of numerous rate parameters, viz. [H⁺], [OH⁻], [Fe(II) species], temperature, and pressure, in order to reveal the intimate nature of the substitution mechanisms.

Experimental Section

Potassium nitropentacyanoferrate(III), $K_3[Fe(CN)_5NO_2]$, was prepared as described before,[15] and its purity was checked by elemental analyses and IR and UV–vis spectroscopy. Solutions containing $Fe(CN)_5NO_2^{4-}$ were prepared by dissolving $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ in 0.2 M NaOH. Conversion of the nitrosyl complex to the nitro species (for which $\epsilon = 3000$ M^{-1} cm^{-1} at 400 nm) was observed by monitoring spectral changes. Solutions of HCl and NaOH were used to adjust the pH in acidic and basic media, respectively, and buffers were not employed to avoid further complications. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

The acid-catalyzed aquation of $Fe(CN)_5NO_2^{3-}$ was monitored at 555 nm by using a Shimadzu UV-250 spectrophotometer for the slow reactions and a Durrum D110 stopped-flow spectrophotometer for the fast reactions (pH <2). The latter instrument was connected to a Tektronix 5111A oscilloscope for visual display of the reaction trace and an Apple

Table I. Rate and Activation Parameters for the Acid-Catalyzed Aquation of $Fe(CN)_5NO_2^{3-}$ in Aqueous Solution[a]

temp, °C	pH	k_{obsd},[b] s^{-1}	k,[c] M^{-1} s^{-1}	K,[c] M^{-1}
17	2.0	5.60×10^{-4}	7.5 ± 1.9	0.75 ± 0.21
	1.0	5.30×10^{-2}		
	0.6	0.317		
	0.3	0.910		
25	2.0	1.41×10^{-3}	12.9 ± 1.9	1.11 ± 0.17
	1.3	3.55×10^{-2}		
	1.0	0.124		
	0.70	0.445		
	0.60	0.700		
	0.46	1.29		
	0.40	1.60		
	0.35	1.89		
	0.30	2.10		
32	2.0	2.10×10^{-3}	17.4 ± 2.6	1.22 ± 0.26
	1.0	0.182		
	0.6	1.10		
	0.3	3.30		
40	2.0	4.56×10^{-3}	31.2 ± 2.0	1.48 ± 0.10
	1.0	0.410		
	0.6	2.10		
	0.3	6.41		
ΔH^*, kJ mol^{-1}			43 ± 3	
ΔS^*, J K^{-1} mol^{-1}			−80 ± 10	

[a] Conditions: [Fe(III)] = 1×10^{-3} M; ionic strength 0.5 M ($LiClO_4$). [b] Mean value of at least five kinetic runs. [c] Calculated according to eq 4—see Discussion.

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