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# Further Observations on Water Oxidation Catalyzed by Mononuclear Ru(II) Complexes

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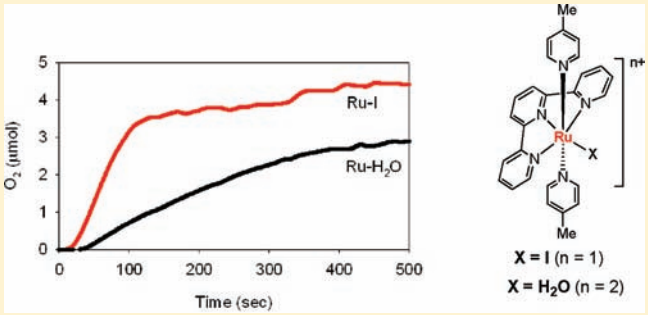
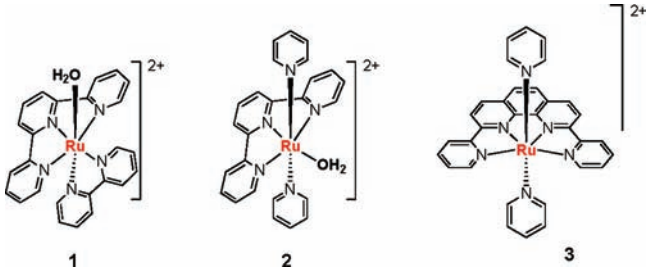
Supporting Information

**ABSTRACT:** A family of 28 mononuclear Ru(II) complexes have been prepared and characterized by $^1$H NMR, electronic absorption, and cyclic voltammetry. These complexes are studied as catalysts for water oxidation. All the catalysts possess one tridentate ligand, closely related to 2,2′;6,2″-terpyridine (tpy) and may be divided into two basic types. In the type-**1** catalyst, the three remaining coordination sites are occupied by a bidentate closely related to 2,2′-bipyridine (bpy) and a monodentate halogen (Br, Cl, or I) or water molecule. In the type-**2** catalyst, the three remaining coordination sites are occupied by two axial 4-picoline molecules and an equatorial halogen or water. In general the type-**2** catalysts are more reactive than the type-**1**. The type-**2** iodo-catalyst shows first-order behavior and, unlike the bromo- and chloro-catalysts, does not require water−halogen exchange to show good activity. The importance of steric strain and hindrance around the metal center is examined. The introduction of three *t*-butyl groups at the 4, 4′, and 4″ positions of tpy sometimes improves catalyst activity, but the effect does not appear to be additive.




## INTRODUCTION

The holy grail of solar energy research is the efficient execution of artificial photosynthesis.[1] The critical component of a successful photosynthetic system will be a catalyst that can effectively utilize the energy of solar radiation to implement the chemistry involved in the decomposition of water into its elements. Such an artificial system can be envisaged to consist of redox catalysts to effect both the oxidation and reduction of water and a chromophore that will provide a charge separated species with sufficient potential to activate the catalysts. Recently considerable progress has been made in the development of effective electroactive metal-based catalysts for water oxidation.[2] Both dinuclear[3] and, somewhat surprisingly, mononuclear[4,5] Ru(II) polypyridine catalysts have received the greatest attention.




We have discovered three general classes of mononuclear Ru(II) catalyst that show good activity in water oxidation (**1**−**3**).[4a,6] All three classes demand at least tridentate coordination of one of the polypyridine ligands and complex **3** utilizes a tetradentate ligand. It is interesting to note that **2** has the water molecule bound in the equatorial plane of the 2,2′;6,2″-terpyridine (tpy) ligand while **1** has the water held orthogonal to this plane. For **3**, there is no water molecule coordinated to the metal center.

When the catalyst is exposed to an aqueous solution containing a large excess of a strong sacrificial oxidant such as Ce(IV), oxygen is evolved vigorously. Substituents on the bpy and tpy ligands influence both the turnover number (TON) and the rate of this process, and considerable discussion has been directed toward understanding the mechanism of the reaction.[7] A key, and almost unavoidable feature, of these mononuclear catalysts is the necessary attack of water on the oxygen of an electrophilic Ru═O species. The events surrounding this key step are somewhat less clear and are the subject of continued discussion. In this study we will examine the behavior of 28 closely related mononuclear Ru(II) complexes (Scheme 1) as water oxidation catalysts. Their structures will involve a monodentate ligand, water or halide, in an axial or equatorial site, analogous to the general structures **1** and **2**. Tetradentate catalysts related to structure **3** will be presented in an upcoming publication.

## SYNTHESIS AND CHARACTERIZATION

The Ru(II) complexes were prepared by adaptations of well-described procedures.[8] The [Ru(NNN)$Cl_3$] reagent was

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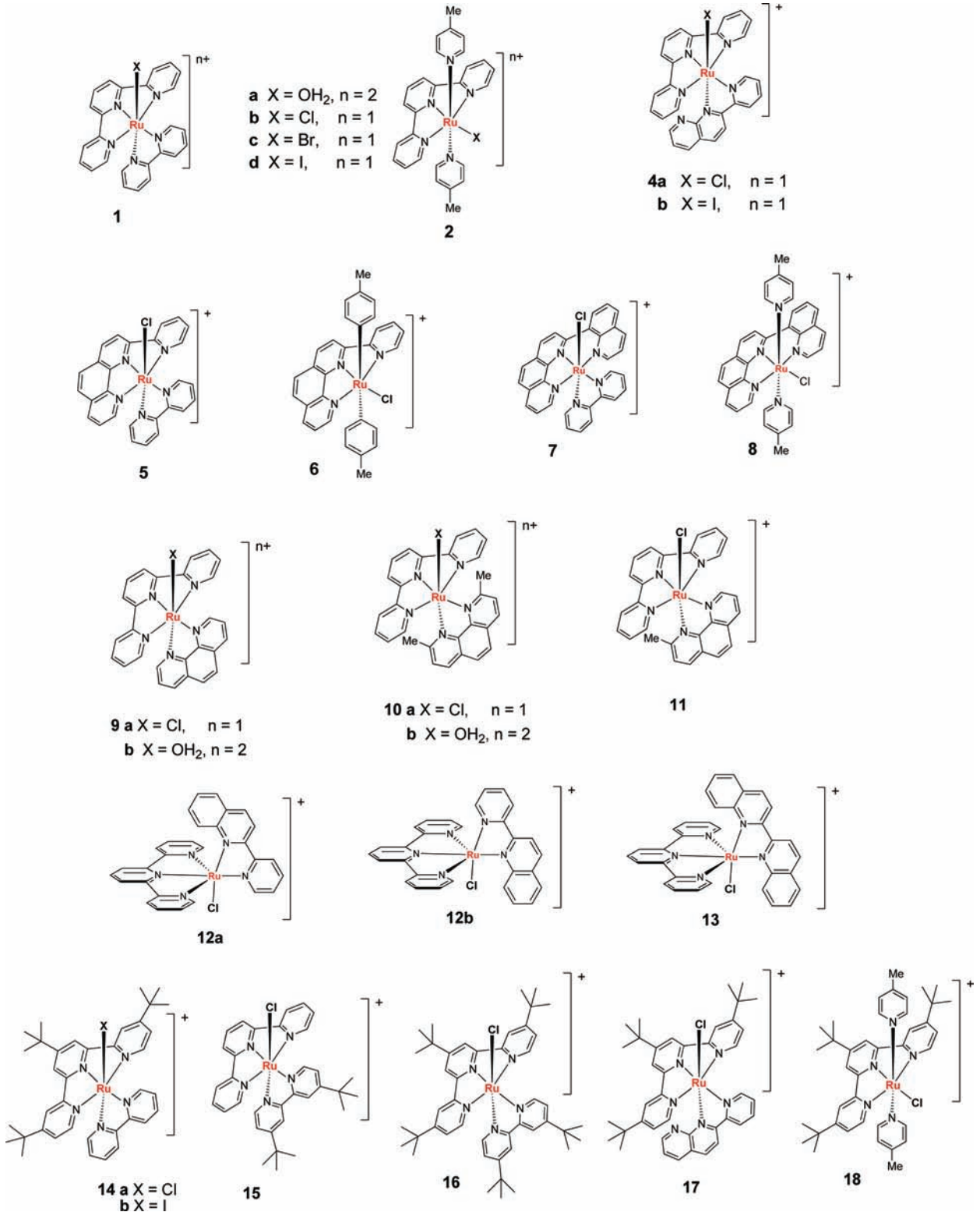
**Scheme 1. Structures of Mononuclear Ru(II) Catalysts**




prepared by treating the appropriate NNN tridentate ligand with exactly 1 equiv of $[RuCl_3{\cdot}3H_2O]$. The resulting $[Ru(NNN)Cl_3]$ is paramagnetic and thus difficult to characterize. It was used directly in a second step that involved treatment with 1 equiv of the NN bidentate ligand followed by precipitation with $NH_4(PF_6)$ to provide the type-**1** $[Ru(NNN)(NN)Cl](PF_6)$ complex directly. The chloride could be replaced by water by using Ag(I) to assist in departure of the chloride or by simply heating the chloride complex in triflic acid for two days. Bromide or iodide could be substituted for chloride by treatment with KBr or KI in refluxing aqueous acetone (Scheme 2). The bromide complex **1c** could alternatively be prepared from $[RuBr_3{-}3H_2O]$ by first treatment with tpy to afford $[Ru(tpy)Br_3]$ which was not isolated but rather reacted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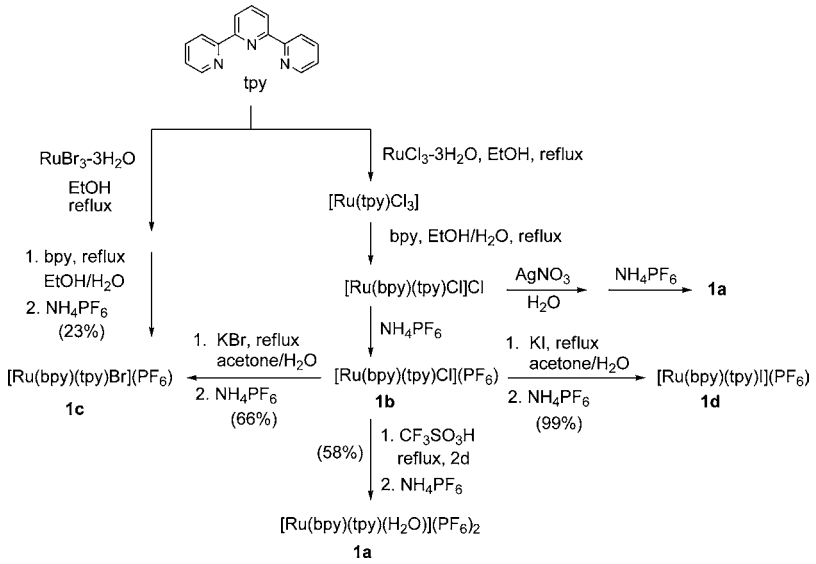
**Scheme 2. Preparation of $[Ru(tpy)(bpy)X]^+$ Catalysts**




directly with bpy in aqueous ethanol to afford a modest yield of $[Ru(tpy)(bpy)Br]^+$ which was identical to the material prepared by halide exchange. Attempts to prepare the corresponding fluoride complex of **1** by treating the chloride complex **1b** with $NH_4F$ or NaF were unsuccessful as significant amounts of the corresponding hydroxide complex were always obtained, reflecting the fact that fluoride is a much weaker ligand for Ru(II).

The $[Ru(NNN)(pic)_2Cl](PF_6)$ complex was prepared by heating $[Ru(NNN)Cl_3]$ in 4-picoline (pic) as the solvent, followed by precipitation with $NH_4(PF_6)$. Water and halogen exchange was accomplished in a manner similar to that employed for the type-**1** complexes.

The complexes were characterized primarily by their $^1H$ NMR spectra. These types of polypyridine complexes exhibit several independent, well-resolved spin systems that make complete assignment using 2D-techniques relatively straightforward.[9] In the case of the type-**2** complexes, the axial picolines were equivalent and showed two widely separated pairs of doublets, the ortho proton coming at lower field and the meta proton at higher field. The presence of even trace amounts of an equatorial picoline was ruled out by NMR.

Events in the vicinity of the metal center for complexes of types **1** and **2** can be monitored with considerable sensitivity through chemical shift changes in H6 of NN (for type-**1**) or H6′ of NNN (for type-**2**). These protons are held in the vicinity of the monodentate ligand (halide or water) and experience a strong deshielding effect that is dependent on the size of the halide. For **1b**, the resonance of H6′ deshielded by the smaller chloride, appears at 10.33 ppm. This same proton is shifted to 10.51 ppm for the larger bromide and to 10.76 ppm for the largest iodide (Figure 1). There is no chloride or aquo (9.74 ppm) contaminant in either of the other two halide complexes. Interestingly, the H6 resonance is also affected. As the halide becomes larger, this proton is pushed more into the shielding face of the central ring of the orthogonal tpy ligand and the resonance consequently moves upfield from 7.58 to 7.44 ppm. For the series **2b−d**, the resonance of H6′ and H6″ is influenced by the water or halide ion bound to Ru(II) in the equatorial plane of the tpy ring. This resonance appears at 9.34, 9.55, and 9.84 ppm for the chloride, bromide, and iodide

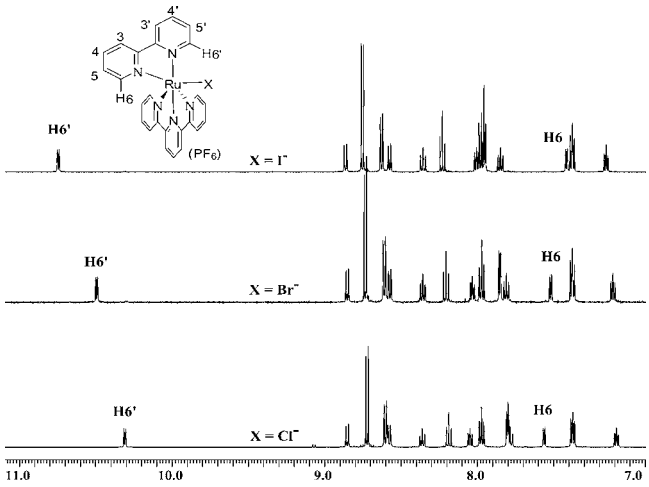



**Figure 1.** $^1H$ NMR spectra (500 MHz, acetone-$d_6$) of **1b−d** indicating variation of H6 and H6′.

complexes, respectively. These resonances are nearly 1 ppm higher field than for the corresponding $[Ru(bpy)(tpy)X]^+$ complexes. This difference reflects the fact that the tridentate chelation of tpy pulls H6 and H6″ on this ligand further away from the halide than for the H6′ proton on bpy in the $[Ru(bpy)(tpy)X]^+$ complexes.

We have measured the electronic absorption spectra for the complexes and found that they all show a long wavelength metal-to-ligand-charge transfer (MLCT) band in the range of 478−586 nm (Table 1). As recently reported by Endicott and co-workers, this electronic transition involves the promotion of an electron from a metal-based MO with predominant d character to a ligand-based MO located predominantly on the terpyridine ligand.[10] In this regard, we find the data to be quite self-consistent. For the complexes **1a−d** and **2a−d**, the aqua complexes **1a** and **2a** appear at higher energy (478 and 503 nm) than the analogous halide complexes (505−509 for **1b−d** and 547−551 for **2b−d**). The substitution of halide for water in these complexes results in an increase in the Ru d-orbital energy through $\pi$-donation from the halide, leading to the observed red shift.[11] The complexes **4a,b** and **17** all contain the


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**Table 1. Electronic Absorption[a] and Cyclic Voltammetric[c] Data for Ru Complexes**

| compound | $\lambda_{max}$ ($\varepsilon$) | $E^{ox}_{1/2}$ ($\Delta E$) | $E^{red}_{1/2}$ ($\Delta E$) |
|---|---|---|---|
| **1a** | 478 (6420) | 1.11 (85) | −1.31 (80), −1.61 (ir) |
| **1b** | 509 (10040) | 0.80 (73) | −1.39 (226), −1.60 (99) |
| **1c** | 505 (8880) | 0.83 (83) | −1.38 (204), 1.60 (74) |
| **1d** | 505 (9560) | 0.86 (89) | −1.39 (185), 1.64 (61) |
| **2a** | 503 (3840) | 0.90 (143) | −1.38 (ir) |
| **2b** | 551 (5820) | 0.75 (85) | −1.43 (85) |
| **2c** | 550 (4160) | 0.78 (97) | −1.42 (93) |
| **2d** | 547 (7820) | 0.79 (77) | −1.38 (77) |
| **4a** | 568 (10980) | 0.76 (86) | −1.13 (ir), −1.49 (ir) |
| **4b** | 564 (9740) | 0.76 (84) | −1.09 (132), −1.53 (ir) |
| **5** | 498 (10600)[b] | 0.83 (73) | −1.19 (225), −1.57 (81) |
| **6** | 486 (4040) | 0.71 (70) | −1.28 (77) |
| **7** | 490 (7740)[b] | 0.77 (123) | −1.38 (58) |
| **8** | 481 (7240) | 0.67 (76) | −1.38 (76), −1.89 (ir) |
| **9a** | 506 (11010) | 0.81 (101) | −1.38 (227), −1.59 (91) |
| **9b** | 484 (10720) | 1.08 (113) | −1.28 (ir) |
| **10a** | 523 (9810) | 0.83 (73) | −1.27 (175) |
| **10b** | 508 (6430) | 0.90 (88) | −1.11 (ir), −1.41(ir) |
| **11** | 506 (10110) | 0.85 (73) | −1.5 (ir) |
| **12a** | 532 (9340) | 0.67 (90) | −1.20 (166), −1.40 (82) |
| **12b** | 535 (9150) | 0.85 (75) | −1.21 (204), −1.43 (71) |
| **13** | 586 (11910) | 0.90 (87) | −1.06 (79), −1.38 (73) |
| **14a** | 508 (14840)[b] | 0.71 (108) | −1.46 (197), −1.61(86) |
| **14b** | 508 (11660)[b] | 0.76 (85) | −1.43 (167), −1.60 (84) |
| **15** | 506 (10760)[b] | 0.80 (70) | −1.46 (ir), −1.68 (ir) |
| **16** | 507 (9400)[b] | 0.66 (77) | −1.50 (240), −1.69 (60) |
| **17** | 573 (12500)[b] | 0.65 (79) | −1.18 (87) |
| **18** | 547 (6380) | 0.68 (78) | −1.51 (83) |

[a]Measured in acetone ($5.0 \times 10^{-5}$ M) at 20 °C; $\lambda$ in nanometers and $\varepsilon$ in liters per mole centimeter. [b]Measured in $CH_3CN$. [c]Measured with a glassy carbon electrode at 100 mV/s in $CH_3CN$ containing 0.1 M $NBu_4PF_6$ and $E_{1/2}$ reported in volts relative to SCE; $E_{1/2} = (E_{pa} + E_{pc})/2$ in volts, and $\Delta E = (E_{pa} - E_{pc})$ in millivolts; ir = irreversible.

2-(pyrid-2′-yl)-1,8-naphthyridine (pynap) ligand that is considerably more electronegative than bpy and hence the absorptions are shifted to lower energy (564, 568, and 573 nm). The complexes **5**−**11** all contain a 1,10-phenanthroline (phen) ligand and absorbances fall in the range of 481−523 nm. In comparing **1b** to its 2-pyridylphen analogue **5**, a shift from 509 to 498 nm is observed. Complexes **12a**,**b** are stereoisomers with almost identical absorbance maxima (532 and 535 nm) and intensities. Complex **13** contains the 2,2′-biquinoline ligand that is the most delocalized of the series and hence affords the most red-shifted absorbance (586 nm). Complexes **14**−**16** are all type-**1** complexes and have similar absorbances in the range 506−508 nm. Finally, complex **18** is a type-**2** complex and its absorbance at 547 nm is close to the value for the parent system **2b** (551 nm).

The redox potentials of the complexes were measured and the first oxidation and reduction potentials are recorded in Table 1. Oxidation of these complexes involves the removal of an electron from the HOMO which is a metal-based d-orbital and reduction involves the addition of an electron to the LUMO which is a ligand-based $\pi^*$-orbital on the most electronegative polypyridine ligand. Again the data is quite consistent with ligand structure. The aqua complex **1a** is 0.21 V more difficult to oxidize than the corresponding **2a** with this same difference reflected to a lesser extent in the analogous halide complexes **1b**−**d** and **2b**−**d**. Complex **9b** containing a phen in place of bpy shows an oxidation potential of 1.08 V that is very similar to **1b** at 1.11 V. Besides **9b**, the other phen containing complexes have oxidation potentials in the range of 0.67−0.90 V. The tri-*t*-butyl tpy ligand is a relatively good donor, and complexes containing this ligand are somewhat easier to oxidize (0.65−0.76 V).

There is less variation in the ligand-based reductions. For **1a**−**d** and **2a**−**d**, these fall in the narrow range of −1.31 to −1.43 V. Complexes with a pynap ligand are more easily reduced (−1.09 to −1.18 V) while those with a tri-*t*-butyl tpy, **14**−**16** and **18**, are more difficult to reduce (−1.43 to −1.51 V). In general, the aqua complexes (**1a**, **2a**, **9b**, and **10b**) are more easily reduced than the analogous chloro complexes.

## WATER OXIDATION

All the mononuclear Ru(II) complexes were evaluated for their activity as water oxidation catalysts. As their $PF_6$ complex, most of these complexes were more soluble in acetonitrile than water. The catalyst in 50 $\mu$L of acetonitrile was introduced into a solution containing 5000 equiv of ceric ammonium nitrate as a sacrificial oxidant. During the first 30 min of reaction, the initial rate of oxygen evolution was measured by a Clark electrode (YSI 5331) immersed in the solution. We also measured the turnover number (TON) by monitoring the headspace with a photosensitive Ocean Optics probe and by analyzing the same headspace gas after 24 h by GC. The results are tabulated in Table 2.

**Table 2. Water Oxidation Data for Ru Complexes**

| complex | $K_{obs} \times 10^{-4}$ $s^{-1}$ | TON (24 h) |
|---|---|---|
| **1a** | 190 | 270 |
| **1b** | 20 | 390 |
| **1c** | 150 | 450 |
| **1d** | 190 | 570 |
| **2a** | 370 | 300 |
| **2b** | 50 | 370 |
| **2c** | 40 | 140 |
| **2d** | 1610 | 378 |
| **4a** | 13 | 1170 |
| **4b** | 280 | 1135 |
| **5** | 0 | 0 |
| **6** | 230 | 350 |
| **7** | 0 | 0 |
| **8** | 80 | 152 |
| **9a** | 20 | 400 |
| **9b** | 280 | 450 |
| **10a** | 0 | 0 |
| **10b** | 50 | 60 |
| **11** | 80 | 155 |
| **12a** | 50 | 9 |
| **12b** | 10 | 66 |
| **13** | 0 | 0 |
| **14a** | 63 | 667 |
| **14b** | 790 | 701 |
| **15** | 33 | 218 |
| **16** | 3 | 94 |
| **17** | 20 | 274 |
| **18** | 40 | 310 |

For complexes of type-**1**, it has been suggested that initially water replaces the halide anion in the coordination sphere of


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the catalyst to provide the corresponding $[Ru(bpy)(tpy)(OH_2)]^{2+}$ species that is, in fact, the active catalyst. There are several observations, however, which lead to suspicion of this claim. First, the $[Ru(bpy)(tpy)Cl]^+$ complex is formed by the reaction of $[Ru(tpy)Cl_3]$ with bpy in aqueous alcohol in the presence of a 5-fold excess of LiCl. Preparation of the aqua complex normally requires refluxing in strongly acidic aqueous media or $Ag^+$ to irreversibly abstract the chloride anion.

In early work, Davies and Mullins used conductance and absorption measurements to support a claim that halide is rapidly replaced by water.[12] They go on to state that other nucleophiles such as pyridine will readily replace water. Collin and co-workers examined thermal ligand substitution reactions on a derivative of $[Ru(tpy)(phen)Cl]^+$ and found that acetonitrile replaced chloride in aqueous medium and that pyridine replaced acetonitrile.[13] In light of these observations, it appears that the nature of X in $[Ru(tpy)(bpy)X]^{n+}$ is highly dependent on the reaction medium. An additional concern is that when the Ru catalyst is added to Ce(IV), oxidation to Ru(III), or more likely Ru(IV), is instantaneous meaning that the chloride is now bound to a much more electrophilic Ru species. This Ru−Cl bond should be more difficult to break.

We used the sensitive H6 resonance of the type-**1** complexes to monitor the replacement of halide by water. Some recent work on this topic indicates that the chloride in **1b** is about 50% replaced by water in 3 h.[4c] We have reproduced this experiment, however adding LiCl to the NMR solution regenerated about 25% of **1b** (Supporting Information Figure S6). Hydration of **1c** was comparable to **1b**, with 50% replacement after 2.5 h. Hydration of **1d** was slower, requiring 4.3 h for 50% conversion (Supporting Information Figures S1−S3). Similar water exchange experiments for type-**2** complexes were complicated by poor water solubility of the complexes; however, we were able to measure exchange for **2b** where the half-life of the chloro-complex in water was about 30 min.

In the water oxidation experiments, $CH_3CN$ (50 $\mu$L) is used to introduce the catalyst as its $PF_6$ salt. This solvent is also an excellent ligand for Ru(II). We repeated the hydration experiments in $H_2O/CH_3CN$ (4:1). The main product was the acetonitrile complex with substitution more rapid for the chloro- and bromo-species than for the iodo-complex (Supporting Information Figures S4, S5). The aqua-complex is likely an intermediate since, in their report of an X-ray structure of **1d**, Petersen and co-workers state that the crystal was obtained from a toluene/$CH_3CN$ solution, indicating that this complex is stable to direct replacement of iodide by $CH_3CN$.[14]

The measurement of initial rates was somewhat complicated by the existence of a significant induction period (ca. ≥10 min) for several of the catalysts. This induction period led to the observation of deceptively low initial rates for complexes that eventually were reasonable catalysts. Note, for example, complexes **1b**, **4a**, **9a**, and **17** which have low initial rates but TON = 274−1170. Using 5000 equiv of Ce(IV) allowed for a maximum measured TON = 1250. TONs were typically measured after 24 h; however, some catalysts were still active at that time so that the final TON might have been greater than indicated in Table 2. Our method was not particularly sensitive to the measurement of a low TON, and thus, values less than 9 were considered to be 0.

The kinetic results for water oxidation catalyzed by **1a−d** are illustrated in Figure 2a−c where we observe behavior during the initial stage of reaction (a and b) and also over a 20 h

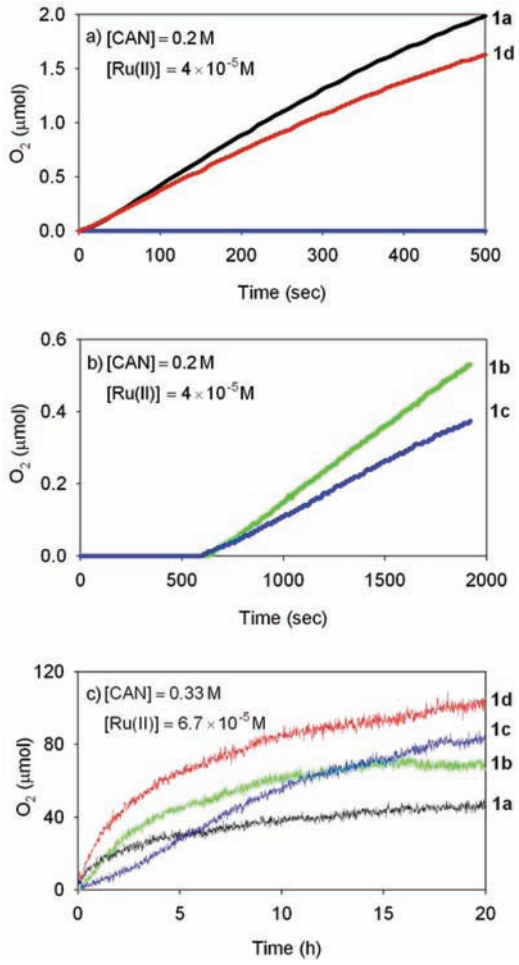


**Figure 2.** Oxygen generation as a function of time at 20 °C: (**1a**) black; (**1b**) green; (**1c**) blue; (**1d**) red. (a) **1a−d** first 500 s in $H_2O$, (b) **1b,c** first 2000 s in $H_2O$, (c) **1a−d** 20 h in $CF_3SO_3H$.

period (c). The initial rate data was measured with a Clark electrode immersed in the reaction mixture. In situations where an induction period is involved, this rate is more correctly referred to as a maximal rate. Over longer periods (2c), we used an Ocean Optics optical probe and verified end-point (TON) readings by GC analysis. From Figure 2b, it is evident that both the chloride and bromide complexes **1b,c** require an induction period of about 10 min. Both Berlinguette[4c] and Sakai[4b] attribute this behavior to the exchange of water for the chloride ligand to produce the "active" form of the catalyst. After this initial exchange period, both **1b** and **1c** appear to react in a manner not unlike the aqua-complex **1a**. The final TON for **1a** is, in fact somewhat less than for the bromide and chloride catalysts, but as Berlinguette has pointed out, these reactions are influenced strongly by small changes in conditions such as counterion, pH, and Ce(IV) concentration. What is unusual, however, is the behavior of the iodo catalyst **1d** that shows both the highest TON (570) and an initial rate that is comparable to the aqua-catalyst with essentially no induction period.

We evaluated the relative rates for water halogen exchange by monitoring the change in the downfield NMR signals of a $D_2O$ solution of the complexes **1b−d** (Supporting Information Figures S1−S3). This exchange is slowest for **1d** ($t_{1/2}$ = 260 min at 25 °C), as compared with $t_{1/2}$ = 200 and 150 min for **1b** and **1c**, respectively. We also carried out the same NMR


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exchange experiment using $D_2O/CH_3CN$ (4:1) as the solvent and found that $CH_3CN$ dominated the exchange process for all three halide complexes (Supporting Information Figure S4).

For the type-**2** catalysts the unusual behavior of the iodo-complex **2d** is even more apparent (Figure 3). The TONs for

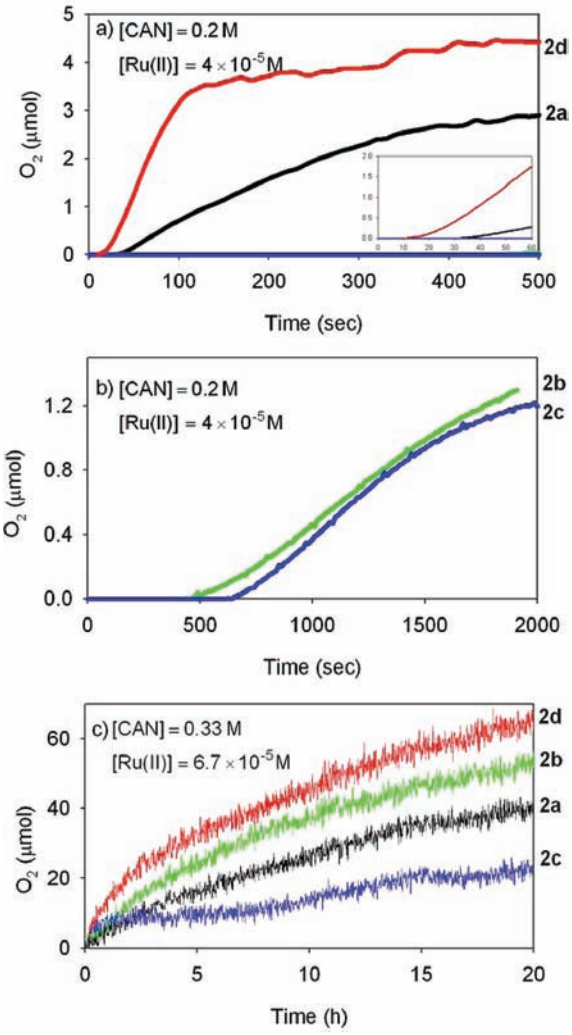


**Figure 3.** Oxygen generation as a function of time at 20 °C: (**2a**) black; (**2b**) green; (**2c**) blue; (**2d**) red. (a) **2a**–**d** first 500 s in $H_2O$, (b) **2b**,**c** first 2000 s in $H_2O$, (c) **2a**–**d** 20 h in $CF_3SO_3H$.

**2a**–**d** fall in the range 140–378, only slightly less than the type-**1** complexes (270–570), but, with the exception of **2b**, the initial rates for the **2** series are all higher and **2d** has a remarkably high rate of 0.16 $s^{-1}$. It is clear that for the first 2 min the iodide complex **2d** catalyzes considerably faster production of oxygen than the aqua-complex **2a** (a). After that point, the rates of **2a** and **2d** become more equivalent while the chloro- and bromo-complexes show essentially no activity until a 10–12 min induction period has elapsed (b). From that point on the rates of **2b** and **2c** remain relatively constant and these systems show reasonable TONs (140 and 370). Once again the iodo system **2d** gives the highest TON (378). For both the type-**1** and type-**2** bromide-catalysts, the kinetic behavior is less consistent than for the other members of the group.

Figure 4 shows the rate profiles for the evolution of oxygen during the first five minutes of reaction at various

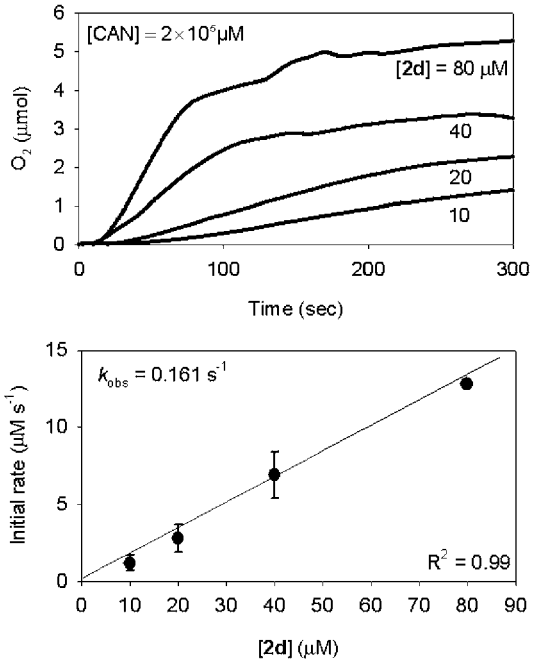


**Figure 4.** (top) Rate profiles for the production of oxygen using various concentrations of **2d** (10, 20, 40, 80 $\mu$M). (bottom) First-order plot of initial rate data for **2d**.

concentrations of the catalyst **2d**. When the initial rates are plotted against catalyst concentration, a straight line plot is obtained, indicating first order behavior for **2d**. Thus, unlike **2b** and **2c**, the iodo complex **2d** is not behaving as a precatalyst that requires initial water–halogen exchange. Rather **2d** is an active catalyst, and the actual role played by the iodide ligand remains open to question.

The complexes **4**–**18** belong to the family $[Ru(bpy)(tpy)X]^{n+}$ (type-**1**, $n$ = 1, 2) or the family $[Ru(tpy)(pic)_2X]^{n+}$ (type-**2**, $n$ = 1, 2). We have varied the structures of these systems in an attempt to evaluate steric and electronic features that might influence catalyst performance. From examination of complexes **1** and **2**, we have learned that the iodide complex (X = I) is particularly reactive. Therefore we examined the pynap complex **4a** that we had previously evaluated as being one of the most active catalysts (TON = 1170). We exchanged chloride for iodide to obtain **4b** and measured a significant initial rate of 0.028 $s^{-1}$ and an impressive TON of 1135. This activity is closely related to the stereochemistry of this complex, and in a separate communication, this issue has been examined in considerable detail.[15]

Complex **5** replaces the tpy in **1b** with the somewhat more delocalized and rigidified 2-pyridylphen. Surprisingly, this complex shows no activity as a water oxidation catalyst. Knowing that type-**2** complexes are more active, we then prepared the analogous 2-pyridylphen complex **6** and observed appreciable activity (TON = 350), further substantiating the observation of increased reactivity for type-**2** catalysts. In complex **7**, we modify the 2-pyridylphen ligand to a closely related 8-quinolinyl analogue. This species is a tridentate chelator that forms both 5- and 6-membered chelate rings with Ru(II). We reasoned that this less strained situation might lead to diminished reactivity, especially if expansion to a seven-coordinate intermediate was involved. Complex **7** shows no activity in water oxidation; however, its type-**2** analogue **8** does show modest reactivity (TON = 152).


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For all the halogen complexes under study, those that perform as active water oxidation catalysts must at some point accommodate a water molecule in the coordination sphere of the metal. Steric hindrance around the metal center could influence this water binding event. Thus we chose to examine complexes involving the ligands 2-methylphen (**11**) and 2,9-dimethylphen (**10a**,**b**) as well as the parent phen complex (**9a**,**b**). For **9a**,**b** the TONs are 400 and 450 for the chloro- and aqua complexes, respectively. The incorporation of two methyl groups near the metal center in **10a** inhibits all activity but if the chloro is first exchanged for water using Ag(I), modest activity (TON = 60) is observed. With just one methyl group on the side away from the Ru−Cl bond (**11**) activity increases with a TON = 155.

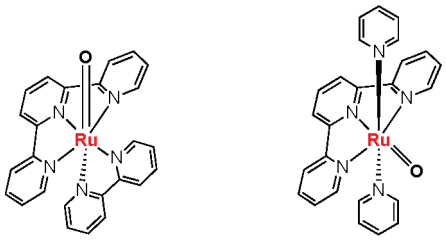
The replacement of a pynap with 2-(pyrid-2′-yl)quinoline (pq) increases steric crowding due to the positioning of H8 near the metal center. Treatment of $[Ru(tpy)Cl_3]$ with pq gave equal amounts of the two stereoisomers **12a** and **12b** which were separated by chromatography. Interestingly, the isomer with the quinoline moiety proximal to the chloride ligand **12b** was the more active one with a TON = 66 as compared to a TON = 9 for **12a**. The complex involving 2,2′-biquinoline as the bidentate ligand, as reported earlier, shows no activity.

We prepared complexes analogous to **1b** and **1d** using 4,4′,4″-tri-*t*-butyltpy as the tridentate ligand (**14a**,**b**). Both complexes showed enhanced activity in water oxidation and the iodo-complex gave an impressive initial rate of 0.079 $s^{-1}$. In complex **15** we put the *t*-butyl groups on the bpy ligand rather than the tpy but the TON dropped to 218. When we put *t*-butyl groups on both the bpy and tpy the activity falls even lower with TON = 94. Finally, we decided to combine the best bidentate ligand, pynap, with the best tridentate, tri-*t*-butyltpy, affording complex **17**. The activity was appreciable (TON = 274) but still less than **4a** (1170) or **14a** (667). Could the situation be improved by going to a type-2 complex? To answer this question we prepared **18** which showed modest activity (TON = 310) that was actually somewhat lower than the parent **2b** (TON = 370).

Up to this point we have based our assessment of "activity" mainly on comparison of TONs which is primarily a thermodynamic characteristic, reflecting the stability of the catalyst toward eventual deactivation. Presumably such deactivation occurs by oxidative decomposition of the organic ligands. Considering the initial rates compiled for the first 10 min of reaction, the chloride and bromide complexes show low values due primarily to relatively long induction periods before oxygen evolution begins. In contrast, the aqua complexes, **1a**, **2a**, and **9b** show appreciable initial rates while the iodo complexes **1d**, **2d**, **4b**, and **14b** are particularly impressive with rates ranging from 0.019−0.161 $s^{-1}$. The one exception is the aqua complex **10b** that shows a low initial rate. However, this system also has a relatively low TON = 60.

## CONCLUSIONS

This structure−activity study for mononuclear Ru(II) based water oxidation catalysts has uncovered several important features of the reaction. First, complexes of the type-2 ($[RuNNN(pic)_2X]^{n+}$) often are more active than the type-1 ($[Ru(NNN)(NN)X]^{n+}$). If one assumes that the basic geometry of the complex is preserved through the steps leading to oxidative decomposition of the Ru-bound water molecule, then two different types of Ru=O intermediates (**19** and **20**) must be involved. The mechanistic implications that underlie the reactivity of these two types of intermediates are beyond the scope of this paper but provide food for thought on the mechanism of the process.




**19** **20**

Although it seems likely that the bromo- and chloro-complexes involve water−halogen exchange as an initial step leading to the active water oxidation catalyst, the possible slow water−iodide exchange combined with the unusually high initial rates for these iodo-systems suggests a different pathway. It is hard to rationalize how the iodo-complexes can react faster than the aqua complexes if they are merely a precursor to such complexes. The possible retention of iodide in the reactive catalyst then becomes a possibility, and the seven coordinate intermediate that we have suggested in earlier work[4a] begins to look more attractive. The critical experiment would be to definitively isolate an iodocatalyst *after* it has run through several cycles, and we are currently pursuing this challenging objective.

The unusual reactivity observed for the tri-*t*-butyltpy containing systems is intriguing but apparently somewhat haphazard and certainly not additive (complex **17**). One can imagine rationales based on steric effects, solubility changes, and inductive effects, and we continue in our evaluation of complexes involving this interesting ligand.

## EXPERIMENTAL SECTION

**Synthesis.** All solvents were reagent grade and used as supplied. $[RuCl_3{-}3H_2O]$ was obtained from Pressure Chemical Co. The $[Ru(tpy)Cl_3]$ was prepared according to a reported procedure.[16]

The ligands 2-(pyrid-2′-yl)-1,10-phenanthroline,[17] 2-(pyrid-2′-yl)-1,8-naphthyridine,[18] 2-(quinol-2′-yl)-1,10-phenanthroline,[19] 2-methyl-1,10-phenanthroline,[20] 2-(pyrid-2′-yl)quinoline,[21] and 4,4′-di-*t*-butylbpy[22] were prepared according to reported procedures. All other ligands were obtained from commercial sources. The complexes **4a**, **9a**, and **13** have been reported previously.[4a] Other complexes were prepared by one of the two general methods outlined below or by halide exchange on the corresponding chloride complex. The yield and $^1H$ NMR data for each complex is included below and the actual spectrum is given in the Supporting Information (SI).

*General Procedure for* $[Ru(NN)(NNN)X]^{n+}$ *Complexes.* The appropriate tridentate ligand NNN was heated for several hours at reflux with exactly 1 equiv of $RuCl_3{-}3H_2O$ in $H_2O$-EtOH (1:1). The brown $[Ru(NNN)Cl_3]$ intermediate was isolated by filtration and then treated directly with 1.1 equiv of the bidentate NN ligand, heating at reflux for several hours in $H_2O$−EtOH (1:1). After cooling, $NH_4PF_6$ (excess) was added to precipitate the complex that was collected by vacuum filtration, dried, and purified by chromatography on alumina.

*General Procedure for* $[Ru(NNN)(pic)_2X]^{n+}$ *Complexes.* The appropriate tridentate ligand NNN was heated for several hours at reflux with exactly 1 equiv of $RuCl_3{-}3H_2O$ in $H_2O$−EtOH (1:1). The brown $[Ru(NNN)Cl_3]$ intermediate was isolated by filtration and then heated in 3 mL of picoline at reflux for several hours. After cooling, $NH_4PF_6$ (excess) was added to precipitate the complex that was collected by vacuum filtration, dried, and purified by chromatography on alumina.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*Complex* ***1a*** *($(SO_3CF_3)_2$).* A mixture of [Ru(tpy)(bpy)Cl]Cl (31.0 mg, 0.055 mmol), aqueous $CF_3SO_3H$ solution (pH = 1.0, 1.30 g), and acetone (1 mL) was heated in an open round-bottom flask at 50 °C overnight to give a solid residue. Recrystalliztion of the residue from acetone (0.5 mL) and water (1 mL) afforded dark crystals (29.5 mg, 66%): $^1$H NMR (acetone-$d_6$ + $D_2O$) $\delta$ 9.74 (d, $J$ = 5.74 Hz, 1H), 8.93 (d, $J$ = 8.02 Hz, 1H), 8.84 (d, $J$ = 8.02 Hz, 2H), 8.70 (d, $J$ = 8.02 Hz, 2H), 8.60 (d, $J$ = 8.02 Hz, 1H), 8.45 (dt, $J$ = 1.72, 8.02 Hz, 1H), 8.34 (t, $J$ = 8.02 Hz, 1H), 8.16 (ddd, $J$ = 1.15, 5.73, 8.02 Hz, 1H), 8.08 (dt, $J$ = 1.72, 8.31 Hz, 2H), 7.94 (d, $J$ = 5.73 Hz, 2H), 7.81 (dt, $J$ = 1.15, 8.02 Hz, 1H), 7.56 (d, $J$ = 5.15 Hz, 1H), 7.47 (ddd, $J$ = 1.15, 5.65, 7.66 Hz, 2H), 7.12 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 1H). MS $m/z$ 510.2 $[M - 2SO_3CF_3]^+$.

*Complex* ***1b*** *($PF_6$).* The complex was prepared by a published[2] procedure: $^1$H NMR (acetone-$d_6$) $\delta$ 10.33 (d, $J$ = 5.73 Hz, 1H), 8.87 (d, $J$ = 8.02 Hz, 1H), 8.74 (d, $J$ = 8.02 Hz, 2H), 8.62 (d, $J$ = 8.02 Hz, 2H), 8.59 (d, $J$ = 8.02 Hz, 1H), 8.38 (dt, $J$ = 1.72, 8.02 Hz, 1H), 8.20 (t, $J$ = 8.31 Hz, 1H), 8.06 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 1H), 7.99 (dt, $J$ = 1.72, 8.31 Hz, 2H), 7.82 (d, $J$ = 4.01 Hz, 2H), 7.79 (dt, $J$ = 1.15, 8.02 Hz, 1H), 7.58 (d, $J$ = 5.73 Hz, 1H), 7.39 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 2H), 7.11 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 1H).

*Complex* ***1c*** *($PF_6$). Method A.* A mixture of [Ru(tpy)(bpy)-Cl]($PF_6$) (100 mg, 0.149 mmol) and KBr (600 mg, mmol) in acetone (10 mL) and water (5 mL) was refluxed overnight. $NH_4PF_6$ in a minimum amount of water was added, cooled to room temperature, and the precipitate was collected, washed with water, and dried to afford a brown powder (90 mg). Chromatography on silica gel eluting with acetone to produced first a dark red fraction that was collected. The solvent was evaporated to give [Ru(tpy)(bpy)Br]($PF_6$) as brown solid (71 mg, 66%): $^1$H NMR (acetone-$d_6$) $\delta$ 10.51 (dd, $J$ = 1.15, 5.73 Hz, 1H), 8.87 (d, $J$ = 8.02 Hz, 1H), 8.75 (d, $J$ = 8.02 Hz, 2H), 8.27 (d, $J$ = 8.02 Hz, 2H), 8.59 (d, $J$ = 8.02 Hz, 1H), 8.37 (dt, $J$ = 1.72, 8.16 Hz, 1H), 8.22 (t, $J$ = 8.31 Hz, 1H), 8.05 (ddd, $J$ = 1.72, 5.73, 7.45 Hz, 1H), 7.99 (dt, $J$ = 1.72, 8.02 Hz, 2H), 7.87 (d, $J$ = 5.15 Hz, 2H), 7.83 (dt, $J$ = 1.15, 7.45 Hz, 1H), 7.53 (d, $J$ = 5.73 Hz, 1H), 7.39 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 2H), 7.13 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 1H). MS $m/z$ 570.2 $[M\text{-}PF_6]^+$.

*Method B.* A mixture of $RuBr_3$ (83 mg, 0.24 mmol), EtOH (10 mL), and MeOH (10 mL) was heated to reflux, followed by the addition of an ethanol solution of tpy (60 mg, 0.26 mmol). The reaction continued for 3 h, then bpy (40 mg, 0.26 mmol), triethylamine (6 drops), and $H_2O$ (3 mL) were added. The mixture was refluxed overnight, filtered through a short pad of Celite, and the filtrate was evaporated. The residue was washed with acetone to give a brown powder (150 mg). Column chromatography on alumina using acetone–MeOH (10:1) and $NH_4PF_6$ afforded the product (40 mg, 23%). The spectral properties of this product were identical to those of the material prepared by method A.

*Complex* ***1d*** *($PF_6$).* A mixture of [Ru(tpy)(bpy)Cl]($PF_6$) (26.6 mg, 0.040 mmol) and KI (200 mg, 1.20 mmol) in acetone (3 mL) and water (4 mL) was refluxed overnight. $NH_4PF_6$ (160 mg) was added and the precipitate was collected while it was hot, washed with water, and dried to afford [Ru(tpy)(bpy)I]($PF_6$) as a brown powder (30 mg, 100%): $^1$H NMR (acetone-$d_6$) $\delta$ 10.76 (d, $J$ = 5.73 Hz, 1H), 8.88 (d, $J$ = 8.02 Hz, 1H), 8.77 (d, $J$ = 8.02 Hz, 2H), 8.64 (d, $J$ = 8.02 Hz, 2H), 8.59 (d, $J$ = 8.02 Hz, 1H), 8.37 (dt, $J$ = 1.72, 7.59 Hz, 1H), 8.25 (t, $J$ = 8.02 Hz, 1H), 8.02 (ddd, $J$ = 1.15, 5.73, 7.45 Hz, 1H), 7.99 (dt, $J$ = 1.72, 7.16 Hz, 2H), 7.97 (dd, $J$ = 1.44, 5.44 Hz, 2H), 7.87 (dt, $J$ = 1.8, 8.1 Hz, 1H), 7.44 (m, 3H), 7.17 (ddd, $J$ = 1.8, 5.7, 7.8 Hz, 1H). MS $m/z$ 618.2 $[M - PF_6]^+$.

*Complex* ***2b***[23] *($PF_6$).* A mixture of 4-picoline (10 mL), [Ru(tpy)-$Cl_3$] (79 mg, 0.181 mmol), and triethylamine (0.3 mL) was heated at 100 °C for 13 h. After cooling, hexane (10 mL) was added to the reaction mixture. The precipitate was collected and washed with hexane (20 mL) to remove unreacted 4-picoline. The residue was dissolved in water (5 mL) to which was added $NH_4PF_4$ (100 mg) in water (3 mL). The resulting solid was collected, washed with water (5 mL), and dried under vacuum. Chromatography on silica gel and eluting with $CH_2Cl_2$/acetone (1:1) followed by recrystallization from $CH_2Cl_2$/hexane afforded **2b** as a dark brown solid (80 mg, 63%): $^1$H NMR (acetone-$d_6$): $\delta$ 9.34 (d, 2H, $J$ = 6.30 Hz), 8.65 (d, 2H, $J$ = 8.02 Hz), 8.61 (d, 2H, $J$ = 8.02 Hz), 8.17 (td, 2H, $J$ = 9.16, 1.72 Hz), 8.02 (t, 1H, $J$ = 8.02 Hz), 7.95 (d, 4H, $J$ = 6.30 Hz), 7.89 (td, 4H, $J$ = 5.73, 1.72 Hz), 6.89 (d, 4H, $J$ = 5.73 Hz), 2.16 (s, 6H, $CH_3$).

*Complex* ***2a***[23] *($PF_6)_2$.* A mixture of **2b** as its chloride salt (50 mg, 0.085 mmol) and $AgBF_4$ (165 mg, 0.85 mmol) in acetone/water (1:1, 10 mL) was heated at reflux overnight. The resulting mixture was filtered through Celite to remove AgCl. The filtrate was evaporated and $NH_4PF_4$ (60 mg) in water (2 mL) was added. Chromatography on alumina, eluting with $CH_2Cl_2$/acetone (1:1) followed by recrystallization from $CH_2Cl_2$/$Et_2O$ afforded **2a** as a dark solid (55 mg, 81%): $^1$H NMR (acetone-$d_6$): $\delta$ 9.21 (d, 2H, $J$ = 5.15 Hz), 8.67 (d, 2H, $J$ = 8.02 Hz), 8.65 (d, 2H, $J$ = 7.45 Hz), 8.24 (td, 2H, $J$ = 8.02, 1.15 Hz), 8.06 (t, 1H, $J$ = 8.02 Hz), 7.90 (td, 2H, $J$ = 6.30, 1.15 Hz), 7.83 (d, 4H, $J$ = 6.30 Hz), 7.02 (d, 4H, $J$ = 6.30 Hz), 2.18 (s, 6H, $CH_3$).

*Complex* ***2c*** *(Br).* A mixture of **2b** as its chloride salt (50 mg, 0.085 mmol) and KBr (100 mg, 0.85 mmol) in acetone/water (1:1, 10 mL) was heated at reflux for 48 h. Chromatography on alumina, eluting with $CH_2Cl_2$/acetone (1:1) followed by recrystallization from $CH_2Cl_2$/$Et_2O$ afforded **2c** as a dark solid (40 mg, 70%): $^1$H NMR (acetone-$d_6$): $\delta$ 9.55 (dd, 2H, $J$ = 5.84, 1.72 Hz), 8.64 (d, 2H, $J$ = 8.59 Hz), 8.62 (d, 2H, $J$ = 9.16 Hz), 8.20 (td, 2H, $J$ = 6.30, 1.72 Hz), 8.07 (t, 1H, $J$ = 8.02 Hz), 7.96 (d, 4H, $J$ = 6.30 Hz), 7.92 (td, 2H, $J$ = 6.30, 1.15 Hz), 6.88 (d, 4H, $J$ = 6.30 Hz), 2.16 (s, 6H, $CH_3$). Anal. Calcd. for $RuC_{27}H_{25}N_5Br_2{\cdot}C_3H_6O$: C, 42.91; H, 2.98; N, 8.34. Found: C, 43.48; H, 2.65; N, 8.90.

*Complex* ***2d*** *(I).* A mixture of **2b** as its chloride salt (125 mg, 0.226 mmol) and KI (375 mg, 2.26 mmol) in EtOH/$CH_2Cl_2$ (1:1, 25 mL) was heated at 80 °C for 24 h. Chromatography on alumina, eluting with $CH_2Cl_2$/acetone (1:1) followed by recrystallization from $CH_2Cl_2$/$Et_2O$ afforded **2d** as a violet solid (135 mg, 77%): $^1$H NMR (acetone-$d_6$): $\delta$ 9.84 (d, 2H, $J$ = 6 0.3 Hz), 8.64 (d, 2H, $J$ = 8.02 Hz), 8.62 (d, 2H, $J$ = 8.02 Hz), 8.19 (td, 2H, $J$ = 7.45, 1.72 Hz), 8.09 (t, 1H, $J$ = 8.02 Hz), 7.96 (dd, 4H, $J$ = 6.30, 1.15 Hz), 7.92 (td, 2H, $J$ = 5.73, 1.15 Hz), 6.83 (d, 4H, $J$ = 6.3 Hz), 2.13 (s, 6H, $CH_3$). Anal. Calcd. for $RuC_{27}H_{25}N_5I_2{\cdot}H_2O$: C, 40.86; H, 3.40; N, 8.83. Found: C, 40.26; H, 2.77; N, 8.78.

*Complex* ***4b*** *($PF_6)_2$.* A mixture of complex **4a** (22.4 mg, 0.0366 mmol), water (2 mL), acetone (2 mL), and KI (105 mg, 0.63 mmol) was treated in the same manner as described for **1d** to provide **4b** (22.5 mg, 77%): $^1$H NMR (acetone-$d_6$) $\delta$ 11.07 (d, $J$ = 5.50 Hz, 1H), 9.15 (d, $J$ = 8.24 Hz, 1H), 8.77 (d, $J$ = 8.70 Hz, 1H), 8.70 (d, $J$ = 7.79 Hz, 2H), 8.50 (t, $J$ = 6.55 Hz, 3H), 8.43 (dt, $J$ = 1.37, 8.24 Hz, 1H), 8.32 (d, $J$ = 2.05, 8.01 Hz, 1H), 8.22 (dd, $J$ = 2.29, 4.12 Hz, 1H), 8.20 (d, $J$ = 8.24 Hz, 1H), 8.06 (ddd, $J$ = 1.37, 6.34, 7.67 Hz, 1H), 7.87 (d, $J$ = 4.58 Hz, 2H), 7.85 (dd, $J$ = 1.60, 8.70 Hz, 2H), 7.46 (dd, $J$ = 4.35, 8.01 Hz, 1H), 7.26 (ddd, $J$ = 1.37, 5.72, 7.33 Hz, 2H). MS $m/z$ 669.25 $[M - PF_6]^+$.

The following complexes were prepared by one of the general procedures given above. The metal-bound choride could be replaced by water by using $AgNO_3$ or $AgBF_4$ to assist in departure of the chloride. The NMR spectra of the purified complexes are given as Supporting Information Figures S9–S36.

*Complex* ***5*** *($PF_6$) (70%).* $^1$H NMR (acetone-$d_6$): $\delta$ 10.42 (d, 1H, $J$ = 5.73 Hz), 8.99 (d, 1H, $J$ = 9.16 Hz), 8.92 (d, 1H, $J$ = 8.02 Hz), 8.77 (d, 1H, $J$ = 8.02 Hz), 8.72 (d, 1H, $J$ = 9.16 Hz), 8.63 (d, 1H, $J$ = 8.02 Hz), 8.56 (d, 1H, $J$ = 8.02, 1.15 Hz), 8.43 (td, 1H, $J$ = 8.02, 1.72 Hz), 8.42 (d, 1H, $J$ = 9.16 Hz), 8.18 (dd, 1H, $J$ = 5.15, 1.15 Hz), 8.12 (td, 1H, $J$ = 7.45, 1.72 Hz), 8.06 (td, 1H, $J$ = 8.02, 1.72 Hz), 8.00 (d, 1H, $J$ = 5.73 Hz), 7.78 (td, 1H, $J$ = 8.02, 1.15 Hz), 7.70 (d, 1H, $J$ = 5.15 Hz), 7.68 (d, 1H, $J$ = 5.15 Hz), 7.48 (d, 1H, $J$ = 5.73 Hz), 7.45 (td, 1H, $J$ = 7.45, 1.15 Hz), 6.97 (td, 1H, $J$ = 7.45, 1.15 Hz). MS $m/z$ 550.25 $[M - PF_6]^+$.

*Complex* ***6*** *($PF_6$) (53%).* $^1$H NMR ($CDCl_3$): $\delta$ 9.47 (dd, 1H, $J$ = 5.15, 1.15 Hz), 9.27 (dd, 1H, $J$ = 5.73, 1.15 Hz), 8.97 (d, 1H, $J$ = 8.59 Hz), 8.80 (d, 1H, $J$ = 8.02), 8.41 (d, 1H, $J$ = 8.59 Hz), 8.37 (d, 1H, $J$ = 8.59 Hz), 8.15 (d, 1H, $J$ = 8.86), 8.11 (td, 1H, $J$ = 8.02, 1.72 Hz), 8.02 (d, 1H, $J$ = 9.16 Hz), 7.91 (dd, 1H, $J$ = 8.18, 5.11 Hz), 7.72 (d, 4H, $J$ =


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6.87 Hz), 7.63 (td, 1H, $J$ = 6.30, 1.15 Hz), 6.68 (d, 4H, $J$ = 6.30, 1.15 Hz), 2.09 (s, 6H). MS $m/z$ 580.44 $[M - PF_6]^+$.

*Complex* ***7*** *($PF_6$) (50%).* $^1$H NMR ($CD_3CN$): $\delta$ 10.24 (d, 1H, $J$ = 5.15 Hz), 8.90 (d, 1H, $J$ = 7.45 Hz), 8.82 (d, 1H, $J$ = 9.16 Hz), 8.75 (d, 1H, $J$ = 9.16 Hz), 8.70 (dd, 1H, $J$ = 5.15, 1.15 Hz), 8.51 (d, 1H, $J$ = 8.59 Hz), 8.42 (dd, 1H, $J$ = 8.02, 1.15 Hz), 8.31 (dd, 1H, $J$ = 8.02, 1.15 Hz), 8.28 (dd, 1H, $J$ = 8.59, 2.86 Hz), 8.21 (dd, 1H, $J$ = 8.02, 1.72 Hz), 8.15 (dd, 1H, $J$ = 8.59, 2.29 Hz), 8.03 (td, 1H, $J$ = 6.87, 1.15 Hz), 7.98 (t, 1H, $J$ = 7.45 Hz), 7.76 (d, 1H, $J$ = 5.73 Hz), 7.57 (d, 1H, $J$ = 5.15 Hz), 7.55 (d, 1H, $J$ = 5.15 Hz), 7.53 (d, 1H, $J$ = 6.30 Hz), 7.50 (td, 1H, $J$ = 7.45, 1.72 Hz), 7.26 (d, 1H, $J$ = 5.15 Hz), 7.24 (d, 1H, $J$ = 5.73 Hz), 6.69 (td, 1H, $J$ = 5.73, 1.15 Hz).

*Complex* ***8*** *(Cl) (41%).* $^1$H NMR (acetone-$d_6$): $\delta$ 10.61 (dd, 1H, $J$ = 5.73, 1.72 Hz), 10.16 (dd, 1H, $J$ = 5.73, 1.72 Hz), 8.91 (d, 1H, $J$ = 9.16 Hz), 8.84 (d, 1H, $J$ = 8.02 Hz), 8.74 (m, 3H), 8.43 (dd, 1H, $J$ = 8.02, 1.72 Hz), 8.30 (AB quartet, 2H), 8.19 (dd, 1H, $J$ = 9.16, 5.73 Hz), 7.95 (t, 1H, $J$ = 8.02 Hz), 7.78 (dd, 1H, $J$ = 9.16, 5.73 Hz), 7.73 (d, 4H, 6.87 Hz), 6.68 (d, 4H, 6.30 Hz), 2.05 (s, 6H). Anal. Calcd. for $RuC_{33}H_{27}N_5Cl_2{\cdot}4H_2O$: C, 53.73; H, 4.78; N, 9.49. Found: C, 54.13; H, 4.51; N, 9.45.

*Complex* ***9a*** *($PF_6$) (15%).*[8] $^1$H NMR (acetone-$d_6$): $\delta$ 10.55 (dd, 1H, $J$ = 5.50, 1.37 Hz), 8.99 (dd, 1H, $J$ = 8.24, 1.37 Hz), 8.79 (d, 2H, 8.24 Hz), 8.64 (d, 2H, $J$ = 7.79 Hz), 8.46 (dt, 2H, $J$ = 8.70, 2.75 Hz), 8.40 (td, 1H, $J$ = 8.24, 1.37 Hz), 8.26 (m, 2H), 7.96 (m, 3H), 7.66 (dt, 2H, $J$ = 5.50, 0.92 Hz), 7.47 (dd, 1H, $J$ = 7.79, 5.50 Hz), 7.26 (td, 2H, $J$ = 7.33, 1.83 Hz).

*Complex* ***9b*** *($PF_6$)$_2$ (76%).*[24] $^1$H NMR (acetone-$d_6$): $\delta$ 10.11 (d, 1H, $J$ = 5.50 Hz), 9.07 (d, 1H, $J$ = 7.33 Hz), 8.89 (d, 2H, 8.70 Hz), 8.72 (d, 2H, $J$ = 8.24), 8.53 (dd, 1H, $J$ = 8.70, 4.58 Hz), 8.44 (m, 3H), 8.26 (d, 1H, $J$ = 8.24 Hz), 8.06 (td, 2H, $J$ = 7.33, 1.83 Hz), 7.95 (dd, 1H, $J$ = 6.87, 1.37 Hz), 7.85 (d, 2H, $J$ = 5.95 Hz), 7.48 (dd, 1H, $J$ = 9.16, 5.04 Hz), 7.34 (td, 2H, $J$ = 6.87, 2.06 Hz).

*Complex* ***10a*** *($PF_6$) (34%).*[25] $^1$H NMR (acetone-$d_6$): $\delta$ 8.81 (d, 1H, $J$ = 8.24 Hz), 8.70 (d, 2H, $J$ = 7.79 Hz), 8.60 (d, 2H, $J$ = 7.79 Hz), 8.30 (d, 1H, $J$ = 9.16 Hz), 8.25 (d, 1H, $J$ = 9.16 Hz), 8.17 (m, 2H), 8.08 (d, 1H, $J$ = 9.62 Hz), 7.99 (td, 2H, $J$ = 9.16, 2.13 Hz), 7.88 (d, 2H, $J$ = 7.33 Hz), 7.34 (td, 2H, $J$ = 5.50, 2.29 Hz), 7.30 (d, 1H, $J$ = 9.16 Hz), 3.60 (s, 3H), 1.86 (s, 3H).

*Complex* ***10b*** *($PF_6$)$_2$ (83%).*[25] $^1$H NMR (acetone-$d_6$): $\delta$ 8.87 (d, 1H, $J$ = 8.24 Hz), 8.81 (d, 2H, $J$ = 8.24 Hz), 8.67 (d, 2H, $J$ = 8.24 Hz), 8.32 (m, 2H), 8.28 (d, 1H, $J$ = 8.24 Hz), 8.24 (d, 1H, $J$ = 9.16 Hz), 8.07 (m, 3H), 7.92 (d, 2H, $J$ = 5.50 Hz), 7.40 (td, 2H, $J$ = 6.41, 1.83 Hz), 7.33 (d, 1H, $J$ = 9.62 Hz), 3.31 (s, 3H), 1.94 (s, 3H).

*Complex* ***11*** *($PF_6$) (38%).* $^1$H NMR (acetone-$d_6$): $\delta$ 10.65 (dd, 1H, $J$ = 5.04, 1.37 Hz), 8.96 (dd, 1H, $J$ = 8.70, 0.92 Hz), 8.79 (d, 2H, $J$ = 8.24 Hz), 8.65 (d, 2H, $J$ = 8.70 Hz), 8.41 (dd, 2H, $J$ = 9.16, 0.45 Hz), 8.34 (dd, 1H, $J$ = 8.24, 5.04 Hz), 8.24 (d, 1H, $J$ = 8.70 Hz), 8.20 (t, 1H, $J$ = 7.79 Hz), 7.97 (td, 2H, $J$ = 8.24, 1.83 Hz), 7.61 (d, 2H, $J$ = 6.41 Hz), 7.44 (d, 1H, $J$ = 8.24 Hz), 7.26 (td, 2H, $J$ = 7.33, 1.83 Hz), 2.02 (s, 3H). MS $m/z$ 564.12 $[M - PF_6]^+$.

*Complexes* ***12a,b*** *(Cl).* A mixture of 2-(pyrid-2′-yl)-quinoline (160 mg, 0.78 mmol) and $[Ru(tpy)Cl_3]$ (255 mg, 0.58 mmol) in EtOH (15 mL), $H_2O$ (5 mL), and $NEt_3$ was refluxed for 2 d. The volatile solvents were evaporated and the residue chromatographed on silica gel eluting with acetone. The first acetone−MeOH (6:1) fraction (65 mg) was discarded. The second fraction (231 mg, 65%), obtained by eluting the column with acetone−MeOH−$H_2O$ (30:5:1) was identified as **11a**: $^1$H NMR (DMSO-$d_6$) $\delta$ 10.26 (d, $J$ = 4.58 Hz, 1H), 9.20 (d, $J$ = 8.24 Hz, 1H), 8.88 (d, $J$ = 8.24 Hz, 2H), 8.83 (d, $J$ = 9.16 Hz, 1H), 8.67 (d, $J$ = 8.24 Hz, 2H), 8.45 (m, 2H), 8.27 (t, $J$ = 7.79 Hz, 1H), 8.05 (ddd, $J$ = 1.37, 5.72, 7.56 Hz, 1H), 7.92 (m, 3H), 7.59 (dd, $J$ = 0.92, 5.50 Hz, 2H), 7.45 (d, $J$ = 1.15, 6.87, 8.01 Hz, 1H), 7.31 (ddd, $J$ = 1.37, 5.50, 7.33 Hz, 2H), 7.23 (ddd, $J$ = 1.83, 7.11, 8.93 Hz, 1H), 7.03 (d, $J$ = 8.70 Hz, 1H); MS $m/z$ 576.27 ($M^+$). Eluting the column further provided **11b** (117 mg, 33%): $^1$H NMR (DMSO-$d_6$) $\delta$ 10.24 (m, 1H), 8.92 (s, 2H), 8.80 (d, $J$ = 7.79 Hz, 2H), 8.76 (d, $J$ = 7.79 Hz, 1H), 8.68 (d, $J$ = 7.79 Hz, 2H), 8.34 (m, 1H), 8.26 (t, $J$ = 7.79 Hz, 1H), 7.98 (t, $J$ = 1.83, 7.79 Hz, 2H), 7.88 (m, 2H), 7.81 (dt, $J$ = 1.37, 7.79 Hz, 1H), 7.63 (d, $J$ = 5.04 Hz, 2H), 7.45 (d, $J$ = 5.04 Hz, 1H), 7.32 (ddd, $J$ = 1.37, 5.79, 7.56 Hz, 2H), 7.14 (ddd, $J$ = 1.37, 5.79, 7.56 Hz, 1H); MS $m/z$ 576.33 ($M^+$).

*Complex* ***14a*** *($PF_6$)*[22a] *(80%).* $^1$H NMR (acetone-$d_6$): $\delta$ 10.33 (d, 1H, $J$ = 5.15 Hz), 9.03 (d, 1H, $J$ = 7.45 Hz), 8.96 (s, 2H), 8.83 (d, 2H, $J$ = 1.72), 8.77 (d, 1H, $J$ = 8.02 Hz), 8.35 (td, 1H, $J$ = 7.45, 1.72 Hz), 8.03 (td, 1H, $J$ = 5.73, 1.15 Hz), 7.79 (td, 1H, $J$ = 7.45, 1.15 Hz), 7.66 (d, 2H, $J$ = 5.73 Hz), 7.55 (d, 1H, $J$ = 5.73 Hz), 7.37 (dd, 2H, $J$ = 5.73, 1.72 Hz), 7.09 (td, 1H, $J$ = 6.30, 1.72 Hz), 1.64 (s, 9H), 1.37 (s, 18H).

*Complex* ***14b*** *($PF_6$)*[22b] *(98%).* $^1$H NMR (acetone-$d_6$): $\delta$ 10.79 (dd, 1H, $J$ = 5.95 Hz and $J$ = 0.92 Hz), 8.89 (d, 1H, $J$ = 7.79 Hz), 8.87 (s, 2H), 8.75 (d, 2H, $J$ = 1.83), 8.61 (d, 1H, $J$ = 8.70 Hz), 8.36 (td, 1H, $J$ = 8.70, 1.83 Hz), 8.01 (td, 1H, $J$ = 7.33, 1.83 Hz), 7.86 (td, 1H, $J$ = 8.70, 1.37 Hz), 7.82 (d, 2H, $J$ = 5.95 Hz), 7.39 (m, 2H), 7.15 (td, 2H, $J$ = 7.33, 0.92 Hz), 1.63 (s, 9H), 1.36 (s, 18H). Anal. Calcd. for $RuC_{37}H_{43}N_5F_6IP{\cdot}H_2O{\cdot}CH_2Cl_2$: C, 44.15; H, 4.58; N, 6.78. Found: C, 43.70; H, 4.26; N, 6.58.

*Complex* ***15*** *($PF_6$) (63%).* $^1$H NMR (acetone-$d_6$): $\delta$ 10.22 (d, 1H, $J$ = 6.87 Hz), 8.93 (d, 1H, $J$ = 2.29 Hz), 8.74 (d, 2H, $J$ = 7.45 Hz), 8.67 (d, 1H, $J$ = 1.72 Hz), 8.62 (d, 2H, $J$ = 8.02), 8.19 (t, 1H, $J$ = 7.45 Hz), 8.11 (dd, 1H, $J$ = 5.73, 2.29 Hz), 7.99 (td, 2H, $J$ = 8.59, 1.72 Hz), 7.81 (dd, 2H, $J$ = 5.73, 2.29 Hz), 7.40 (d, 2H, $J$ = 6.30 Hz), 7.39 (dd, 1H, $J$ = 6.30, 1.15 Hz), 7.11 (dd, 1H, $J$ = 6.30, 2.29 Hz), 1.60 (s, 9H), 1.24 (s, 9H). MS $m/z$ 638.52 $[M - PF_6]^+$.

*Complex* ***16*** *($PF_6$) (50%).* $^1$H NMR ($CD_3CN$): $\delta$ 10.05 (d, 1H, $J$ = 6.30 Hz), 8.55 (dd, 1H, $J$ = 6.87, 2.86 Hz), 8.54 (s, 2H), 8.41 (d, 2H, $J$ = 2.29), 8.29 (d, 1H, $J$ = 2.29 Hz), 7.94 (dd, 1H, $J$ = 6.30, 1.72 Hz), 7.53 (d, 2H, $J$ = 5.73 Hz), 7.28 (dd, 2H, $J$ = 6.30, 2.29 Hz), 7.14 (d, 1H, $J$ = 6.30 Hz), 6.96 (dd, 1H, $J$ = 6.30, 2.29 Hz), 1.66 (s, 9H), 1.59 (s, 9H), 1.36 (s, 18H), 1.25 (s, 9H). MS $m/z$ 806.70 $[M - PF_6]^+$.

*Complex* ***17*** *($PF_6$) (32%).* $^1$H NMR ($CD_3CN$): $\delta$ 10.49 (d, 1H, $J$ = 5.95 Hz), 8.83 (d, 1H, $J$ = 8.24 Hz), 8.53 (s, 2H), 8.45 (d, 1H, $J$ = 8.70), 8.31 (d, 2H, $J$ = 2.29 Hz), 8.28 (td, 1H, $J$ = 8.70, 2.29 Hz), 8.18 (d, 1H, $J$ = 8.70), 8.15 (dd, 1H, $J$ = 8.70, 2.29 Hz), 8.07 (dd, 1H, $J$ = 4.58, 1.83 Hz), 7.96 (td, 1H, $J$ = 6.87, 1.37 Hz), 7.43 (d, 2H, $J$ = 5.95 Hz), 7.35 (dd, 1H, $J$ = 7.79, 4.58 Hz), 7.15 (dd, 2H, $J$ = 5.95, 1.83 Hz), 1.71 (s, 9H), 1.29 (s, 18H). MS $m/z$ 745.46 $[M - PF_6]^+$.

*Complex* ***18*** *(Cl) (50%).* $^1$H NMR (acetone-$d_6$): $\delta$ 9.18 (d, 2H, $J$ = 6.30 Hz), 8.90 (s, 2H), 8.86 (d, 2H, $J$ = 2.86 Hz), 7.96 (d, 4H, $J$ = 6.30 Hz), 7.86 (dd, 2H, $J$ = 6.30, 2.29 Hz), 6.86 (d, 4H, $J$ = 6.30 Hz), 2.15 (s, 6H), 1.55 (s, 9H), 1.45 (s, 18H). Anal. Calcd. for $RuC_{39}H_{49}N_5Cl_2{\cdot}CH_2Cl_2$: C, 56.87; H, 6.09; N, 8.29. Found: C, 56.87; H, 5.98; N, 7.87.

**Measurements.** The NMR spectra were recorded on a JEOL ECA-500 or ECX-400 spectrometer operating at 500/400 MHz for $^1$H. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak. Electronic absorption spectra were recorded with a VARIAN Cary-50 Bio spectrophotometer and were corrected for the background spectrum of the solvent. MALDI-TOF mass spectra were obtained on an Applied Biosystems Voyager DE STR-4160 spectrometer using $\alpha$-cyano-4-hydroxycinnamic acid as the matrix. Electrochemical measurements were carried out using a BAS Epsilon electroanalytical system. Cyclic voltammetry (CV) experiments were performed at room temperature in a one-compartment cell equipped with a glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a platinum wire as the auxiliary electrode in $CH_3CN$ containing ($n$-butyl)$_4$N($PF_6$) (0.1 M) at a scan rate of 100 mV s$^{-1}$.

*Oxygen Evolution.* A 2-necked flask, fitted with a septum cap and a YSI 5331 oxygen probe connected to a YSI 5300A biological oxygen monitor, is charged with $[Ce(NO_3)_6](NH_4)_2$ (550 mg, 1 mmol) and water (5 mL). Before each experiment a fresh Teflon membrane was installed over the YSI probe tip and the probe was calibrated in oxygen-free ($N_2$ purge) and oxygen saturated ($O_2$ purge) water. The calibration was adjusted to give a reading of 19 ± 1% $O_2$ for air saturated water. The Ce(IV) solution was purged with $N_2$ to provide an oxygen-free solution and then the Ru(II) catalyst ($5 \times 10^{-5}$ to $8 \times 10^{-4}$ mmol) in acetonitrile (50 $\mu$L) was introduced by syringe through the septum cap. The program "Bytewedge" (Fog Software, Inc., fogsoft.com) gave an $O_2$ reading every 10 s for up to 30 min. The initial rates of oxygen evolution ($\mu$M s$^{-1}$) were calculated from the

plot of oxygen evolution as a function of time. The initial rate constants ($s^{-1}$) were estimated from the slope of the plot of the initial rate of oxygen evolution ($\mu M\ s^{-1}$) as a function of the concentration of the catalyst ($\mu M$).

The turnover number (TON) was determined using an Ocean Optics (FOXY-OR125-G) oxygen sensor and the 24 h end point reading verified by a GC measurement according to a procedure that has been previously described.[4a]

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1H$ NMR spectra for all Ru(II) complexes presented in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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