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Polydentate Analogues of 8-Hydroxyquinoline and Their Complexes with Ruthenium

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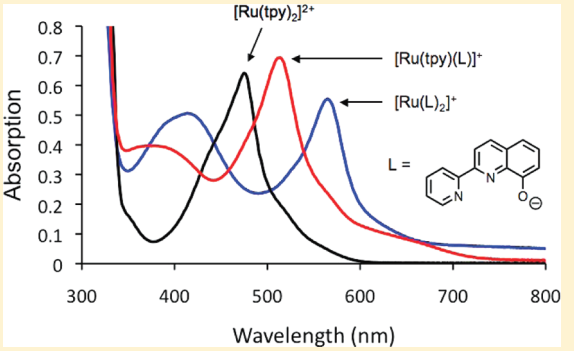
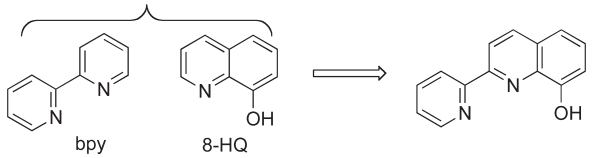
Supporting Information

ABSTRACT: Selective reduction of 2-nitro-3-methoxybenzaldehyde provides 2-amino-3-methoxybenzaldehyde that undergoes the Friedländer condensation with a variety of acetyl-substituted derivatives of pyridine and 1,10-phenanthroline. After cleavage of the methyl ether, the resulting polydentate analogues of 8-hydroxyquinoline are excellent ligands for ruthenium. The resulting oxidation state of the metal center depends on the anionic character of the ligands. The presence of two electron donating anionic ligands results in a Ru(III) complex as evidenced by paramagnetic NMR behavior. The electronic absorption and redox properties of the complexes were measured and found to be consistent with the anionic character of the 8-HQ moieties. A planar pentadentate ligand provides two Ru−O and two Ru−N bonds in the equatorial plane. An X-ray structure shows that the central pyridine of the ligand is oriented toward the metal but held at a distance of 2.44 Å.



INTRODUCTION

Out of seven potential quinolinols, only 8-hydroxyquinoline (8-HQ) can readily form a five-membered chelate complex with metal ions. The chelate compounds are stable and have been used in analytical chemistry for the separation and identification of metal ions as well as in spectrophotometric analysis and metal ion sensing.[1−5] Medicinal (antiseptic, disinfectant, bactericidal) and agricultural (pesticide, fungicidal) uses of 8-HQ have also been investigated.[1,5] In addition 8-HQ has also been explored as a potential anticancer drug.[6] The electroluminescent tris-(8-HQ)-aluminum complex plays a critical role in the development of organic light-emitting diodes (OLEDs)[7−10] that serve as buildings blocks for flat panel displays. Moreover, platinum complexes of 8-HQ have been used as redox photosensitizers in solar energy conversion.[11] Ditopic 8-HQ derivatives containing diaza-18-crown-6 ligands were studied as fluorophoric chemosensors as well as for selective metal ion extraction.[12,13] Tripodal ligands based on 8-HQ subunits have been shown to be strong chelators for Fe(III) over a wide range of pH.[14−17] However, binding of 8-HQ to Ru(II) has received only moderate attention.[18−30]



In this work we are interested in the incorporation of the 8-HQ subunit into polypyridine ligand systems. In structure, 8-HQ strongly resembles 1,10-phenanthroline (phen) where the hydroxyl group replaces a fused pyridine ring. Like phen, 8-HQ is rigid, planar, and fully conjugated. A major difference is that it generally binds to metals as its conjugate base, providing an anionic ligand with distinctly different electronic properties from the neutral phen.

The parent member of this new ligand series is 2-(pyrid-2′-yl)-8-hydroxyquinoline (**6b-H**), and several earlier reports of its synthesis have appeared.[31−35] These routes generally involve the multistep, low yield incorporation of a 2-halo group onto 8-HQ and then subsequent organometallic coupling with either 2-pyridylstannane or 2-pyridyl zinc bromide. We will show that commercially available 2-nitro-3-methoxybenzaldehyde (**1**) can be readily reduced to the corresponding aminoaldehyde that can then undergo a simple Friedländer condensation with appropriate acetyl pyridines to afford 8-methoxyquinoline derivatives that may be cleaved to provide polydentate analogues of 8-HQ. The tri-, tetra-, and pentadentate ligands **6b-H**, **7b-H**, and **8b-2H** are shown to afford interesting complexes with Ru(II).

Synthesis of Ligands. The prerequisite 2-amino-3-methoxybenzaldehyde (**2**) may be readily prepared in 87% yield by the reduction of 3-methoxy-2-nitrobenzaldehyde (**1**) with Fe powder in aqueous ethanol.

The Friedländer reaction was carried out by heating the aminoaldehyde **2** together with the precursor carbonyl compound in ethanolic KOH overnight. The 8-methoxyquinolines were purified by crystallization or chromatography on alumina, and they were readily characterized by their ^{1}H NMR spectra.

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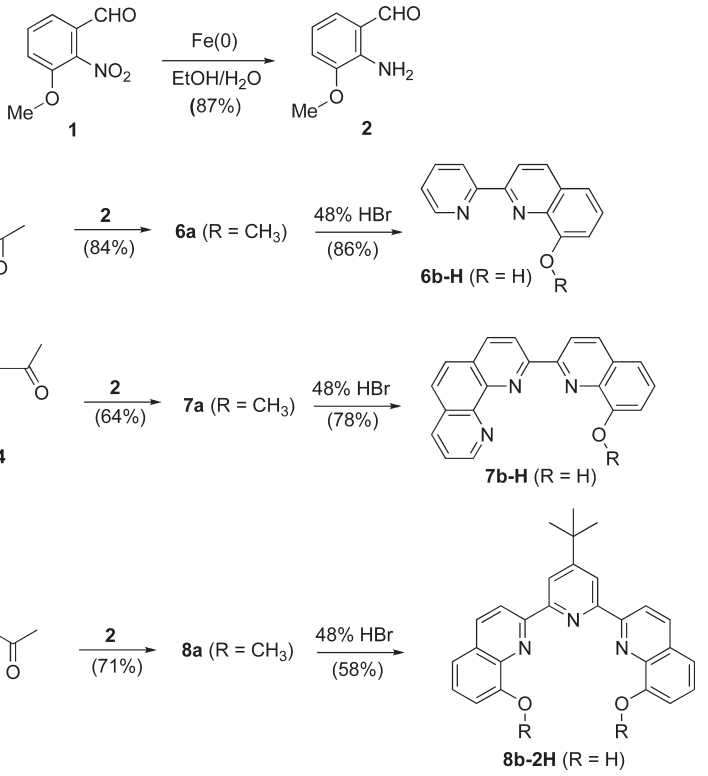
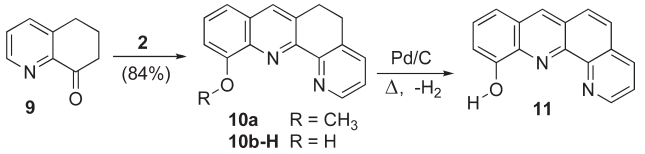
Scheme 1. Synthesis of the Ligands 6b-H−8b-H



Scheme 2. Synthesis of Ligand 11



These spectra were generally well resolved, and the independent spin systems could be easily identified by 2D techniques. The final ether cleavage to give the hydroxyquinoline ligands was accomplished by simply heating the methoxyquinolines in 48% HBr. We attempted to prepare **11**, which would be the planar, fully conjugated analogue of **6b-H** (Schemes 1 and 2). The Friedländer reaction of **2** with tetrahydro-8-quinolone **9** proceeded in 84% yield. During the ether cleavage step some dehydrogenation occurred providing a mixture of **10b-H** and **11** in a 20/1 ratio. Complete dehydrogenation in the presence of Pd/C was problematic so that a pure sample of **11** could not easily be obtained.

Ruthenium Complexes. Bhattacharya and co-workers[20−22] and Turro and co-workers[18,19] have examined Ru complexes of 8-HQ. They find that one, two, or three 8-Q ligands can be complexed to Ru(II) with the remaining coordination sites being occupied by one or two bpy (2,2′-bipyridine) or phen ligands. The complexes show increasingly long wavelength metal-to-ligand transfer (MLCT) absorptions as the number of 8-Q ligands increases. Similarly the oxidation potential of the complexes decreases due to stabilization of higher oxidation states of Ru resulting from the anionic nature of the quinolate ligand.

By treating ligands **6b-H**, **7b-H**, and **8b-2H** with an appropriate source of Ru(II), we have prepared complexes with all three ligands. When ligand **6b-H** is treated with $[Ru(tpy)Cl_3]$ (tpy = 2,2′;6.2″-terpyridine) in aqueous ethanol followed by precipitation with NH_4PF_6, the mixed ligand complex $[Ru(tpy)(\mathbf{6b})](PF_6)$ is formed in 48% yield (Scheme 3). The ^{1}H NMR spectrum in acetone-d_6 shows 15 well-resolved peaks, and the proton assignments were made by considering both 1D and 2D NMR. Due to the symmetry of the tpy ligand, we observe 5 peaks, each integrating for 2 protons, and a triplet at 8.23 ppm assigned to H4. The doublet at 7.85 ppm, integrating for 2 protons with a small coupling constant (5.1 Hz), is assigned to the protons H6 and H6″ of tpy due to their proximity to the nitrogen. The protons H5, H6, and H7 of the hydroxyquinoline moiety are shielded due to the anionic 8-oxide and appear at 6.95−6.39 ppm (Figure SI-10). Further proof of structure was provided by the positive ion MALDI-TOF mass spectrum that showed a pattern at m/z 556.28 identical to the simulated isotopic distribution for $[Ru(tpy)(\mathbf{6b})]^+$ (Figure SI-20).

If the same ligand **6b-H** is treated instead with 0.25 equiv of $[\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ in acetonitrile in the presence of 1 equiv of NaOH and KPF_6, a dark purple solution results that, after chromatography on alumina, provides a 53% yield of $[Ru(\mathbf{6b})_2](PF_6)$. The ^{1}H NMR spectrum of this material in CD_3OD shows several broad peaks characteristic of a Ru(III) complex (Figure 1, top). The addition of ascorbic acid reduces the Ru(III) to Ru(II), and the spectrum then shows typical diamagnetic behavior. Nine well resolved peaks are assigned to the protons of **6b** in the symmetric complex $[Ru(\mathbf{6b})_2]$ (Figure 1, bottom). The proton assignments were made by consideration of the 2D data. Due to the planar, cisoid conformation of **6b** required for

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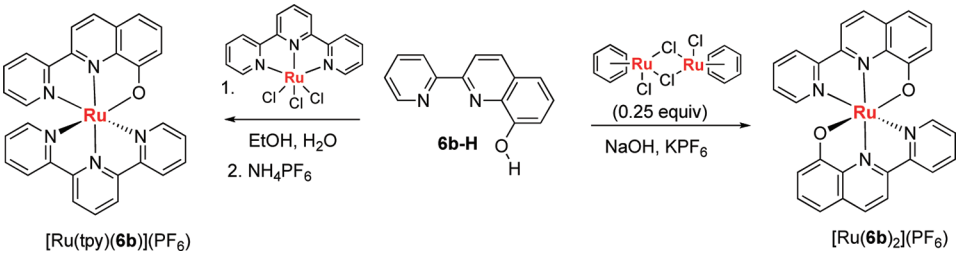
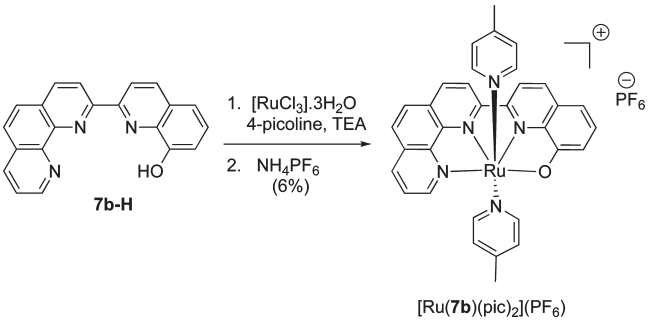
Scheme 3. Ru Complexes of Ligand 6b



tridentate coordination, the two 8-oxide functionalities must assume a *cis*-orientation in the homoleptic complex such that it will exist as a racemic mixture. The initial formation of the paramagnetic Ru(III) species could be explained by the two anionic ligands stabilizing the higher oxidation state of Ru(III). Further proof of structure was provided by the positive ion MALDI-TOF mass spectrum that showed a pattern at m/z 544.16 identical to the simulated isotopic distribution for $C_{28}H_{18}N_4O_2Ru$ expected for the cation $[Ru(\mathbf{6b})_2]^+$ (Figure SI-21).

In earlier work we have demonstrated that a tetradentate ligand such as 2,9-di(pyrid-2′-yl)-phen will coordinate with Ru(II) such that all four nitrogens bind to the metal in the equatorial plane. However, the closely related tetradentate ligand 2,2′-biphen, due to flexibility around the central 2,2′-single bond, can act as a bridging ligand and hence does not readily form a 1:1 complex with Ru(II).[36] The ligand **7b** has an arrangement of ligating centers similar to 2,2′-biphen and in its transoid conformation may also act as a bridging ligand, leading to oligomeric complexes. However, we find that when this ligand is treated with $RuCl_3$ and 4-picoline (pic) in the presence of triethylamine (TEA), followed by NH_4PF_6, a low (6%) yield is obtained of the mononuclear complex $[Ru(\mathbf{7b})(pic)_2](PF_6)$ (pic = 4-picoline).



The complex was characterized by its ^{1}H NMR in CD_3CN (Figure 2) where we observe 14 signals in the downfield region corresponding to the 12 protons of the equatorial anionic ligand **7b** and 8 protons of the two axial 4-picolines. The proton assignments were made by considering both 1D and 2D NMR. The two doublets at 7.96 and 6.83 ppm, each integrating for 4 protons, are assigned to the two axial 4-picolines. The protons H5′, H6′, and H7′ of the hydroxyquinoline moiety are shielded due to the anionic 8-oxide and appear at 7.07−6.53 ppm. Furthermore, the positive ion MALDI-TOF mass spectrum of $[Ru(\mathbf{7b})(pic)_2](PF_6)$ showed a pattern at m/z 610.43 $[M - PF_6]^+$ identical to the simulated isotopic distribution for $C_{33}H_{26}N_5ORu$ (m/z 610.12) (Figure SI-22).

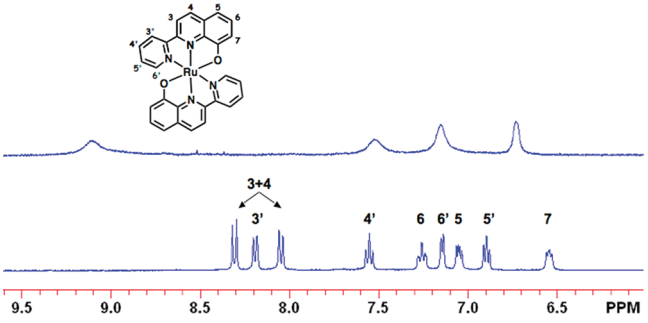


Figure 1. Downfield region of the 400 MHz ^{1}H NMR spectrum in CD_3OD of $[Ru(6b)_2]^+$ before (top) and $[Ru(6b)_2]$ after (bottom) the addition of ascorbic acid.

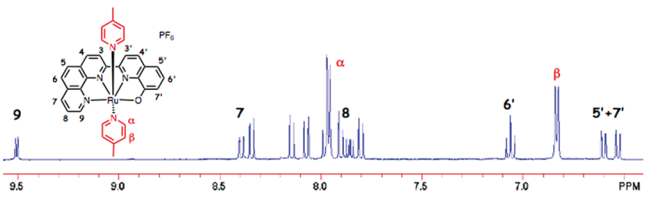


Figure 2. Downfield region of the 400 MHz ^{1}H NMR spectrum of $[Ru(\mathbf{7b})(pic)_2](PF_6)$ in CD_3CN.

The ligand **8b-2H** is potentially pentadentate, but with two σ-bonds connecting the two quinolines to the central pyridine, the molecule has considerable conformational freedom. This freedom could lead to some variety in the denticity of its binding to metal cations. In earlier work it has been demonstrated that the corresponding 2,6-di(quinolin-2′-yl)pyridine will bind Ru(II) as a tridentate.[37] After initial exposure to 1 equiv of NaOH, the ligand was treated with $[Ru(dmso)_4Cl_2]$ followed by an excess of 4-picoline. After the addition of NH_4PF_6, chromatography and recrystallization provided a black solid in 29% yield. ^{1}H NMR in acetone-d_6 showed only broad peaks characteristic of a paramagnetic Ru(III) species. Upon the addition of ascorbic acid and warming to 62 °C in CD_3OD, eight well resolved peaks were observed (Figure SI-13). Two four proton doublets were found at 8.02 and 6.83 ppm, matching very closely the two doublets for the 4-picoline protons found in $[Ru(\mathbf{7b})(pic)_2]PF_6$. Two doublets and a triplet appeared at 7.06−7.36 ppm for the protons H5′, H6′, and H7′ of the 8-oxyquinoline moiety. Further downfield was an AB quartet due to H3′ and H4′ and a sharp singlet at 8.34 ppm for the H3 proton on the central pyridine. It appears that the dianionic character of the ligand causes the metal to oxidize to

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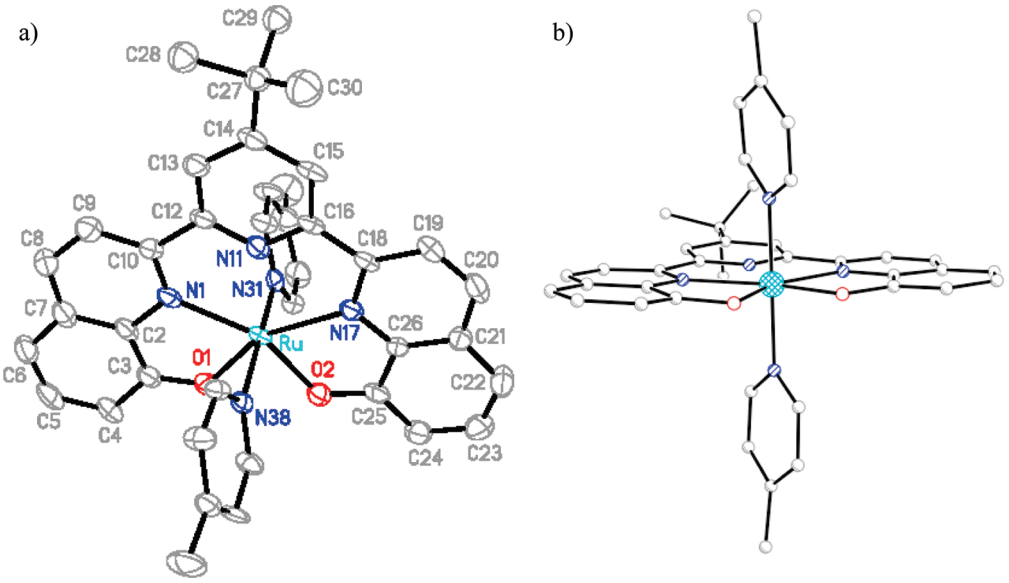
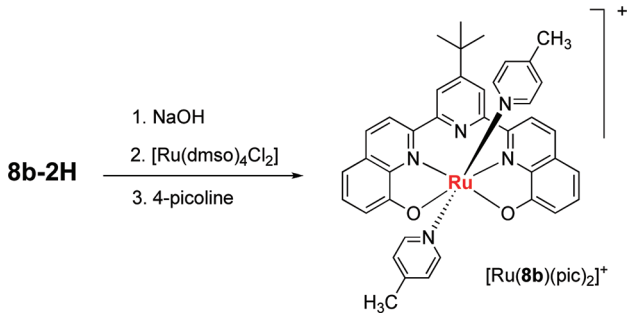


Figure 3. (a) Top view of the cation $[Ru(\mathbf{8b})(pic)_2]^+$ showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with H atoms omitted. (b) Side view of the cation.

Ru(III). The observation of only six aromatic resonances for **8b** indicates that the ligand is bound in a symmetric disposition. The presence of the necessary PF_6 counterion was verified by the appearance of a ^{19}F doublet at −74.80 ppm (J = 750 Hz). The MALDI-TOF mass spectral pattern at m/z 707.55 $[M - PF_6]^+$ was identical to the simulated isotopic distribution for $C_{39}H_{35}N_5O_2Ru$ (Figure SI-23). A complex analogous to $[Ru(\mathbf{8b})(pic)_2]PF_6$ was also prepared using 4-*t*-butylpyridine (tb-py) in place of 4-picoline.



Monocrystals of $Ru(\mathbf{8b})(pic)_2](PF_6)$ suitable for X-ray diffraction were obtained by slow evaporation of an acetone/toluene solution. The X-ray data confirm the NMR spectrum, indicating that ligand **8b** is bound in a symmetrical fashion to the central Ru(III) using both 8-HQ moieties. The ORTEP plot of the complex is shown in Figure 3, and selected bond lengths, bond angles, and torsion angles are collected in Table 1. An interesting geometrical situation is found in the disposition of **8b** around the metal. The two Ru−O bonds are both 2.03 Å, and the two axial Ru−N bonds involving the 4-picolines are typical at 2.10 Å. The interior Ru−N bonds involving N1 and N17 are quite long, averaging about 2.20 Å. These bond lengths can be compared to the four equatorial Ru−N bonds in $[Ru(dpp)(pic)_2]^{2+}$ [dpp = 2,9-di(pyrid-2′-yl)phen] where one observes two short interior Ru−N bonds at 1.94 Å and two long exterior ones at 2.17 Å. What is most intriguing is the central N11 of **8b** whose lone pair electrons are oriented toward the metal center. Due to constraints imposed by the four coordinative bonds between Ru and **8b**, N11 is held 2.44 Å from the metal center, a distance normally considered too long for effective binding. Orvig and co-workers have recently reported a similar pentadentate ONNNO ligand that does not use the central nitrogen in metal binding.[38] The two oxygens and two nitrogens that bind to Ru form a planar trapazoid with O−Ru−N angles that average 75.7°, O1−Ru−O2 at 78.3°, and N1−Ru−N17 at 130.3° for a total of 360.1° indicating a planar arrangement of all five atoms as illustrated in Figure 3b. The two 8-HQ moieties are pulled toward the metal center causing distortion of the trigonal carbons that form the C10−C12 and C16−C18 bonds.

Table 1. Selected Geometric Parameters for $[Ru(\mathbf{8b})(pic)_2](PF_6)$

Bond Lengths (Å)			
Ru−O2	2.030 (5)	Ru−N1	2.185 (6)
Ru−O1	2.031 (5)	Ru−N17	2.222 (6)
Ru−N38	2.097 (6)	Ru−N11	2.440 (6)
Ru−N31	2.100 (7)		
Bond Angles (deg)			
O1−Ru−N1	76.4 (2)	O2−Ru−N1	154.6 (2)
O2−Ru−N17	75.1 (2)	O1−Ru−N17	153.3 (2)
O1−Ru−O2	78.3 (2)	N11−C16−C18	111.4 (6)
N1−Ru−N17	130.3 (2)	N11−C12−C10	111.7 (6)
		C12−C10−N1	113.6 (6)
		C16−C18−N17	113.9 (6)
Dihedral Angles (deg)			
N11−C16−C18−N17	−3.5 (9)	N17−C26−C25-O2	3.4 (10)
N11−C12−C10−N1	2.3 (10)	N1−C2−C3-O1	−3.4 (11)
C25−O2−Ru−N17	2.6 (5)	C16−C18−N17-Ru	4.3 (9)
N1−Ru−O1−C3	−6.7 (5)	C12−C10−N1-Ru	−2.5 (10)

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Table 2. Electronic Absorption[a] and Cyclic Voltammetric[b] Data for Ru Complexes and Ligands

		cyclic voltammetric data[c]		
compd	λ_{abs}/nm ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})	Ru^{II}/Ru^{III}	Ru^{III}/Ru^{IV}	reduction
6b-H	264 (30), 280 (24), 314 (5)			
7b-H	290 (28), 327 (13), 337 (14)			
8b-2H	267 (93), 308 (27), 364 (7.4)			
$[Ru(tpy)_2](PF_6)_2$[c,d]	308 (54), 475 (13)	+1.38		−1.41(120), −1.67(200)
$[Ru(\mathbf{6b})(tpy)](PF_6)$ [c]	313 (46), 374 (8), 514 (14)	+0.54[ir]	+1.06[ir]	−1.44(83), −1.73(94)
$[Ru(\mathbf{6b})_2](PF_6)$[c]	302 (49), 414 (10), 565 (11)	+0.09(71)		−1.67[ir], −1.85[ir]
$[Ru(\mathbf{7b})(pic)_2](PF_6)$	346 (17), 481 (4.4), 609 (2)	+0.60[ir]		−1.17(124)
$[Ru(\mathbf{8b})(pic)_2](PF_6)$	342 (17), 450 (2.6), 556 (1.5)	−0.39(277)	+0.70[ir]	−1.57(90)
$[Ru(\mathbf{8b})(tb\text{-}py)_2](PF_6)$	341 (15), 454 (3.9)	−0.23(138)	0.51(352)	−1.54(135)

[a] Measured in CH_3CN (5×10^{-5} M) at room temp. [b] Recorded in CH_3CN (except $[Ru(\mathbf{6b})_2]^+$ in 9:1 CH_3CN/CH_3OH) containing 0.1 M NBu_4PF_6; $E_{1/2}$ in V vs SCE and ΔE in mV; scan rate = 100 mV/s; irreversible process (ir) estimated by differential peaks. [c] Electronic absorption data measured in CH_3OH (5×10^{-5} M) at room temp. [d] Cyclic voltammetric data from ref 39.

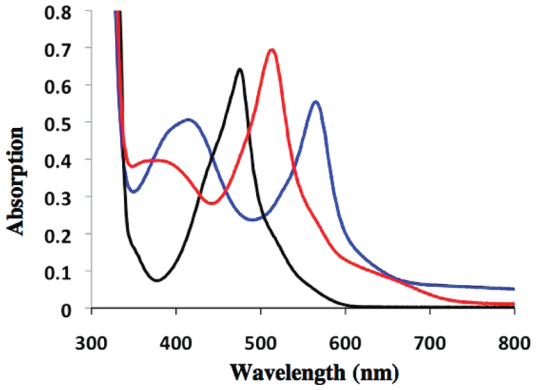

Figure 4. Long wavelength region of the electronic absorption spectra of $[Ru(tpy)_2](PF_6)_2$ (black), $[Ru(tpy)(\mathbf{6b})](PF_6)$ (red), and $[Ru(\mathbf{6b})_2](PF_6)$ (blue).

Ideally, the interior angles centered on these carbons should measure 120°, but in this complex, they are compressed to 111.4−113.9°.

Photophysical and Electrochemical Behavior. The electronic absorption maxima and extinction coefficients of the ligands and their Ru complexes are listed in Table 2 together with the electrochemical data for the Ru complexes. Due to its extended conjugation, the pentadentate ligand **8b-2H** shows a longer wavelength $\pi-\pi^*$ absorption at 364 nm than the tetradentate **7b-H** at 337 nm and tridentate **6b-H** at 314 nm. For the Ru complexes, relatively intense peaks in the region 302−346 nm are attributed to $\pi-\pi^*$ transitions of the ligands. A progressive red-shift in the lowest energy absorption band from 475 to 519 to 565 nm is observed as we substitute a tpy ligand in $[Ru(tpy)_2]^{2+}$ with one or two anionic tridentate ligands **6b** (Figure 4). This long wavelength band is normally associated with a metal-to-ligand charge transfer (MLCT) state in which an electron is promoted from a metal d-orbital to the π^*-orbital of the most electronegative ligand. The bathochromic shift is most likely due to increased electron donation from the ligand that serves to destabilize the metal-centered HOMO and raise its energy. This observation is reinforced by the dramatic increase in the first oxidation potential that is observed for this same series of complexes. It is also noteworthy that for the complexes involving ligand **6b** a higher energy component of the MLCT state is observed at 403 and 414 nm with stronger absorbance for the homoleptic complex $[Ru(\mathbf{6b})_2]^+$. For complexes involving the tetradentate **7b** or the pentadentate **8b** the situation is less clear and the longer wavelength absorbances are considerably less intense (Figure 5-SI).

The electrochemical behavior of the Ru complexes of 8-HQ derivatives is highly dependent on the charge on the central metal atom that will strongly influence its ground state oxidation potential. Studies by two different groups on complexes of the type $[Ru(bpy)_{3-n}(8\text{-}HQ)_n]$ (n = 0−3) have demonstrated the effect of the anionic 8-HQ ligand on the redox properties of the system although there seem to be some discrepancies in the reported potentials.[18−22] There is considerable internal consistency to the results that we report in Table 2. For the series $[Ru(tpy)_{2-n}(\mathbf{6b})_n]$ (n = 0−2), we observe a steady decrease in the Ru^{II}/Ru^{III} oxidation potential from +1.38 V for $[Ru(tpy)_2]^{2+}$, to +0.54 V for $[Ru(tpy)(\mathbf{6b})]^+$, to 0.09 V for $[Ru(\mathbf{6b})_2]^+$ as the number of anionic **6b** ligands around Ru increases from 0 to 2. A second oxidation wave (Ru^{III}/Ru^{IV}) at +1.06 V is observed for $[Ru(tpy)(\mathbf{6b})]^+$. Due to solubility problems, the measurement for $[Ru(\mathbf{6b})_2]^+$ was made in 9:1 CH_3CN/MeOH. The near zero potential measured for $[Ru(\mathbf{6b})_2]^+$ indicates that this species might exist as either Ru(II) or Ru(III). From its paramagnetic NMR behavior we observe that the Ru(III) species is formed initially, but after reduction with ascorbic acid the resulting Ru(II) complex is stable for more than one month.

The tetradentate complex $[Ru(\mathbf{7b})(pic)_2]^+$ involves only one anionic ligand. Its Ru^{II}/Ru^{III} potential of +0.60 V matches well with the +0.54 V measured for $[Ru(tpy)(\mathbf{6b})]^+$. The pentadentate ligand **8b** presents two anionic 8-HQ moieties, and so, we would expect considerable stabilization of higher oxidation states. The first oxidation is the Ru^{III}/Ru^{IV} couple that we observe at +0.70 V. The first reduction is the Ru^{II}/Ru^{III} couple that occurs at the very low potential of −0.39 V. Changing the axial ligand from 4-picoline to the somewhat better donor 4-*t*-butylpyridine raises the Ru^{II}/Ru^{III} potential (−0.23 V) and lowers the Ru^{III}/Ru^{IV} potential (+0.51 V).

For the series $[Ru(tpy)_{2-n}(\mathbf{6b})_n]$ (n = 0−2), the reduction potential corresponds to the addition of an electron to the most electronegative ligand which is the tpy. For $[Ru(\mathbf{6b})_2]^+$ that contains only anionic ligands, we observe two irreversible waves at −1.67 and −1.85 V. The first reduction of the two complexes

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involving **8b** is consistent with adding an electron to the axial pyridine ligand.

It has been reported that mono- and dianionic ligands derived from bpy and phen as their Ru complexes can be used as catalysts for water oxidation.[40] It has been suggested that the lower oxidation potentials of these complexes might improve their performance in this regard. In line with our own work in this area,[41] we have examined appropriate Ru complexes derived from **6**−**8b**, but found only modest activity toward water oxidation. These studies will be reported in an upcoming publication.

CONCLUSIONS

A two-step Friedländer approach has been used to prepare a series of tri-, tetra-, and pentadentate analogues of 8-hydroxyquinoline. These ligands form stable complexes with Ru whose oxidation state depends on the overall anionic character of the 8-HQ analogue. Consistent behavior is observed both in the electronic absorption spectra and in the redox properties of these systems. A Ru(III) complex of the pentadentate ligand **8b** shows an unusual geometry in which the central pyridine on **8b** is oriented toward the metal but held at a distance that would normally preclude effective binding. Future work will reveal other coordination chemistry of this interesting family of ligands.

EXPERIMENTAL SECTION

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature, except for those of [Ru(**8b**)(pic)$_2$](PF$_6$) and [Ru(**8b**)(tb-py)$_2$](PF$_6$) that were recorded at 62 °C, on a JEOL ECX-400 spectrometer at 400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F, and on a JEOL ECA-500 spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C. The NMR data of [Ru(**6b**)$_2$](PF$_6$), [Ru(**8b**)(pic)$_2$](PF$_6$), and [Ru(**8b**)(tb-py)$_2$](PF$_6$) were collected in the presence of ascorbic acid. Chemical shifts are referenced to the residual solvent peak and were reported in parts per million (ppm), and the J values are ±0.5 Hz. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and were not corrected. Electronic absorption spectra were recorded with a Varian Cary 50 Bio UV−vis spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. Mass spectra were obtained on a Voyager-DE-STR MALDI-TOF mass spectrometer using α-cyano-4-hydroxycinnamic acid as 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}. CHN analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. All reagents and solvents were purchased from commercial sources and were used as received except 6,7-dihydroquinolin-8(5*H*)-one (**7**),[42] 4-*tert*-butyl-2,6-diacetylpyridine (**8**),[43] 2-acetyl-1,10-phenanthroline (**9**),[40c] and [Ru(tpy)Cl$_3$][44] that were prepared according to published procedures.

2-Amino-3-methoxybenzaldehyde (2). Iron powder (5.55 g, 99.3 mmol) and conc HCl (0.1 mL) were added to a solution of 3-methoxy-2-nitrobenzaldehyde (**11**, 1.80 g, 9.93 mmol) in EtOH/water (4/1, 40 mL), and the mixture was heated at reflux for 2 h. After cooling to room temperature, the solid was removed by filtration, and the filtrate was extracted with EtOAc. The combined organic phase was dried over MgSO$_4$ and concentrated. The residue was purified by chromatography on alumina, eluting with CH_2Cl_2 to afford **2** as a yellow oil (1.30 g, 87%). ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1H, CHO), 7.12 (dd, 1H, J = 8.4, 1.4 Hz), 6.88 (d, 1H, J = 7.3, 0.9 Hz), 6.68 (t, 1H, J = 7.8 Hz), 6.40 (s, 2H, NH$_2$), 4.11 (s, 3H, CH$_3$). Similar ^{1}H NMR ($CDCl_3$) values for **2** have been reported.[45]

8-Methoxy-2-(pyrid-2′-yl)quinoline (6a). To a mixture of **2** (1.30 g, 8.60 mmol) and 2-acetylpyridine (**3**, 0.96 mL, 8.60 mmol) in EtOH (80 mL) was added a solution of KOH (1.3 g) in EtOH (5 mL), and the mixture was heated at reflux for 15 h. The mixture was then cooled to room temperature, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, washed with water, dried over MgSO$_4$, and concentrated. Purification by chromatography on alumina and elution with CH_2Cl_2/MeOH (100:1) afforded **6a** as a light brown oil (1.71 g, 84%). ^{1}H NMR ($CDCl_3$): δ 8.71 (m, 2H), 8.59 (d, 1H, J = 8.7 Hz), 8.25 (d, 1H, J = 8.7 Hz), 7.85 (dt, 1H, J = 7.8, 1.8 Hz), 7.44 (AB, 2H, J = 8.2 Hz), 7.33 (m, 1H), 7.07 (dd, 1H, J = 7.3, 1.4 Hz), 4.11 (s, 3H, CH$_3$). Similar ^{1}H NMR ($CDCl_3$) values for **6a** have been reported.[34]

2-(Pyrid-2′-yl)-8-hydroxyquinoline (6b-H). A solution of **6a** (120 mg, 0.50 mmol) in HBr (48%, 25 mL) was heated at 120 °C for 16 h. The mixture was cooled to room temperature, and then cold water (200 mL) was added. The precipitate was collected, extracted with CH_2Cl_2, and washed with NaHCO$_3$ and water. The combined organic phase was dried over MgSO$_4$ and concentrated to afford **6b-H** as a white solid (88 mg, 86%): mp 128−130 °C (lit.[34] mp 119−121 °C). ^{1}H NMR ($CDCl_3$): δ 8.74 (d, 1H, J = 4.1 Hz), 8.60 (t, 2H, J = 8.7 Hz), 8.28 (d, 1H, J = 8.7 Hz), 8.27 (s, 1H, OH), 7.89 (dt, 1H, J = 7.8, 4.6 Hz), 7.47 (t, 1H, J = 7.8 Hz), 7.37 (m, 2H), 7.20 (dd, 1H, J = 8.2, 0.9 Hz). Similar ^{1}H NMR ($CDCl_3$) values for **6b-H** have been reported.[31] ^{13}C NMR ($CDCl_3$): δ 155.4, 153.8, 152.4, 149.2, 137.6, 136.9, 136.8, 128.5, 128.0, 124.1, 121.4, 119.6, 117.9, 110.3; IR 3391, 1590, 1504, 1482, 1452, 1229, 783 cm^{-1}. MS (MALDI-TOF): m/z 223.23 [M + H]$^+$, 222.08 calcd for C$_{14}$H$_{10}$N$_2$O.

2-(8′-Methoxyquinolin-2′-yl)-1,10-phenanthroline (7a). In the manner described for **6a**, **2** (606 mg, 4.01 mmol), 2-acetyl-1,10-phenanthroline (**4**, 823 mg, 3.97 mmol), and KOH (600 mg) in EtOH (50 mL) provided **7a** as a yellow solid after recrystallization from CH_2Cl_2 (865 mg, 64%): mp 212 °C (dec). ^{1}H NMR ($CDCl_3$): δ 9.26 (dd, 1H, J = 4.9, 1.8 Hz), 9.24 (d, 1H, J = 8.6 Hz), 9.16 (d, 1H, J = 8.0 Hz), 8.42 (d, 1H, J = 8.0 Hz), 8.35 (d, 1H, J = 8.6 Hz), 8.29 (dd, 1H, J = 8.0, 1.7 Hz), 7.85 (AB, 2H, J = 8.6 Hz), 7.66 (dd, 1H, J = 8.2, 4.6 Hz), 7.48 (m, 2H), 7.10 (dd, 1H, J = 7.7, 1.7 Hz), 4.16 (s, 3H, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 156.3, 155.7, 155.1, 150.6, 146.5, 145.7, 139.8, 137.0, 136.9, 136.3, 129.9, 129.1, 129.0, 127.3, 127.0, 126.7, 123.0, 121.8, 121.0, 119.8, 108.8, 56.3; IR 1548, 1489, 1461, 1255, 1109, 852, 755 cm^{-1}. MS (MALDI-TOF): m/z 338.39 [M + H]$^+$, 337.12 calcd for C$_{22}$H$_{15}$N$_3$O.

2′-(1,10-Phenanthrolin-2-yl)quinolin-8′-ol (7b-H). In the manner described for **6b-H**, **7a** (120 mg, 0.35 mmol) in HBr (48%, 25 mL) provided **7b-H** (90 mg, 78%) as an orange solid after recrystallization from EtOH/hexane: mp 184 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.93 (s, 1H, OH), 9.48 (d, 1H, J = 8.2 Hz), 9.18 (dd, 1H, J = 4.6, 1.8 Hz), 9.03 (d, 1H, J = 8.7 Hz), 8.66 (d, 1H, J = 8.7 Hz), 8.54 (d, 1H, J = 8.7 Hz), 8.52 (dd, 1H, J = 8.4, 1.8 Hz), 8.04 (AB, 2H, J = 8.7 Hz), 7.81 (dd, 1H, J = 8.4, 4.1 Hz), 7.48 (m, 2H), 7.16 (dd, 1H, J = 6.8, 4.3 Hz). ^{13}C NMR (DMSO-d_6): δ 155.3, 154.2, 153.9, 150.4, 145.9, 145.3, 138.4, 137.5, 137.4, 136.9, 129.4, 129.3, 129.2, 128.8, 127.7, 127.0, 123.8, 122.0, 119.9, 118.15, 112.2. IR 3394, 2923, 2854, 1502, 1444, 1108, 845, 749 cm^{-1}. MS (MALDI-TOF): m/z 324.07 [M + H]$^+$, 323.11 calcd for C$_{21}$H$_{13}$N$_3$O.

4-*t*-Butyl-2,6-di(8′-methoxy-quinolin-2′-yl)pyridine (8a). In the manner described for **6a**, **2** (527 mg, 3.48 mmol), 4-*t*-butyl-2,6-diacetylpyridine (**5**, 382 mg, 1.75 mmol), and KOH (550 mg) in EtOH (40 mL) provided **8a** as a beige solid (558 mg, 71%): mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.80 (dd, 2H, J = 6.9, 1.8 Hz), 8.79 (s, 2H), 8.20 (dd, 2H, J = 8.1, 2.8 Hz), 7.36 (m, 4H), 6.99 (m, 2H), 4.05 (s, 6H, CH$_3$), 1.53 (s, 9H, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 162.1, 155.8, 155.6, 139.8, 136.8, 129.5, 127.0, 120.2, 119.6, 119.4, 108.0, 56.2, 35.6, 30.9; IR 2957, 1603, 1503, 1262, 1097, 836, 747 cm^{-1}. MS (MALDI-TOF): m/z 450.38 [M + H]$^+$, 449.21 calcd for C$_{29}$H$_{27}$N$_3$O$_2$.

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4-*t*-Butyl-2,6-di(8′-hydroxy-quinolin-2′-yl)pyridine (8b-2H). In the manner described for **6b-H**, **8a** (558 mg, 1.24 mmol) in HBr (48%, 65 mL) provided **8b-2H** (300 mg, 58%) as a yellow solid: mp 260 °C. ^{1}H NMR ($CD_3OD/CDCl_3$): δ 8.73 (s, 2H), 8.62 (d, 2H, J = 8.7 Hz), 8.40 (d, 2H, J = 8.7 Hz), 7.45 (t, 2H, J = 8.2 Hz), 7.38 (d, 2H, J = 8.2 Hz), 7.16 (d, 2H, J = 8.7 Hz), 4.8 (br s, OH), 1.56 (s, 9H, CH_3). ^{13}C NMR ($CD_3OD/CDCl_3$): δ 164.3, 153.1, 152.1, 138.6, 136.6, 129.2, 128.6, 120.3, 119.3, 118.0, 112.0. IR 3500, 3415, 2959, 1610, 1243, 840, 761 cm^{-1}. MS (MALDI-TOF): m/z 422.10 $[M + H]^+$, 421.18 calcd for $C_{27}H_{23}N_3O_2$.

11-Methoxy-5,6-dihydrobenzo[*b*][1,10]phenanthroline (10a). In the manner described for **6a**, **2** (459 mg, 3.03 mmol), 6,7-dihydroquinolin-8(5*H*)-one (**9**, 447 mg, 3.03 mmol), and KOH (450 mg) in EtOH (30 mL) provided **10a** as a beige solid (673 mg, 84%): mp 96−98 °C. ^{1}H NMR ($CDCl_3$): δ 8.74 (d, 1H, J = 4.6 Hz), 7.89 (s, 1H), 7.51 (d, 1H, J = 7.3 Hz), 7.38 (t, 1H, J = 7.8 Hz), 7.26 (d, 1H, J = 7.8 Hz), 7.18 (dd, 1H, J = 7.8, 4.6 Hz), 6.93 (d, 1H, J = 7.8 Hz), 4.01 (s, 3H, CH_3), 2.09 (m, 2H, CH_2), 2.98 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 156.1, 151.8, 151.0, 149.3, 139.9, 136.0, 135.4, 134.9, 134.1, 132.1, 129.4, 127.3, 127.1, 123.8, 118.6, 106.9, 55.7. MS (MALDI-TOF): m/z 263.12 $[M + H]^+$, 262.11 calcd for $C_{17}H_{14}N_2O$.

11-Hydroxy-5,6-dihydrobenzo[*b*][1,10]phenanthroline (10b-H). In the manner described for **6b-H**, **10a** (150 mg, 0.45 mmol) in HBr (48%, 30 mL) provided a white solid as a mixture of **10b-H** and **11** in a 20/1 ratio (123 mg, 85%). Data follow for **10b-H**. ^{1}H NMR ($CDCl_3$): δ 9.10 (dd, 1H, J = 5.7, 1.7 Hz), 8.80 (d, 1H, J = 3.9 Hz), 8.09 (dd, 1H, J = 8.6, 1.7 Hz), 7.99 (s, 1H), 7.59 (d, 1H, J = 7.5 Hz), 7.41 (dd, 1H, J = 8.0, 4.0 Hz), 7.28 (dd, 1H, J = 9.7, 4.6 Hz), 3.17 (m, 2H, CH_2), 3.04 (m, 2H, CH_2). Data for **11** follow. ^{1}H NMR ($CDCl_3$): δ 9.34 (dd, 1H, J = 5.7, 2.8 Hz), 9.23 (d, 1H, J = 3.8 Hz), 8.78 (s, 1H), 8.39 (dd, 1H, J = 8.6, 1.7 Hz), 8.21 (d, 1H, J = 7.5, 3.7 Hz), 7.72−7.86 (AB, 2H, J = 9.1 Hz), 7.67 (dd, 1H, J = 8.0, 4.6 Hz), 7.54 (dd, 1H, J = 8.0, 4.0 Hz).

[Ru(6b)$_2$](PF$_6$). Under argon and shielded from light by aluminum foil, a suspension of $[\eta^6$-$C_6H_6)RuCl(\mu$-$Cl)]_2$ (31 mg, 0.125 mmol), **6b-H** (55 mg, 0.25 mmol), NaOH (10 mg, 0.25 mmol), and KPF_6 (90 mg, 0.49 mmol) in dry MeCN (6 mL) was stirred at 50 °C for 16 h. The resulting purple suspension was filtered through a plug of Al_2O_3 using CH_2Cl_2/MeOH (90/10) as the eluant. The dark purple fraction was collected and concentrated, and the residue was precipitated by the addition of *n*-hexane to provide $[Ru(\mathbf{6b})]_2$ as a purple solid (37 mg, 53%). ^{1}H NMR (CD_3OD, ascorbic acid): δ 8.30 (d, 1H, J = 9.1 Hz, H_3 or H_4), 8.19 (d, 1H, J = 8.2 Hz, $H_{6'}$), 8.05 (d, 1H, J = 9.1 Hz, H_3 or H_4), 7.55 (t, 1H, J = 7.9 Hz, $H_{5'}$), 7.27 (dt, 1H, J = 7.8, 3.9 Hz, H_6), 7.14 (d, 1H, J = 5.5 Hz, $H_{3'}$), 7.05 (dd, 1H, J = 7.8, 4.6 Hz, H_5), 6.90 (t, 1H, J = 6.4 Hz, $H_{4'}$), 6.55 (dd, 1H, J = 9.6, 4.6 Hz, H_7). MS (MALDI-TOF): m/z 544.16 $[M - PF_6]^+$, 544.05 calcd for $C_{28}H_{18}N_4O_2Ru$. Anal. Calcd for $C_{28}H_{18}F_6N_4O_2PRu \cdot 2H_2O$: C, 46.60; H, 3.03; N, 7.73. Found: C, 46.46; H, 2.71; N, 7.29.

[Ru(6b)(tpy)](PF$_6$). A mixture of **2-H** (48 mg, 0.21 mmol), $[Ru(tpy)Cl_3]$ (95 mg, 0.21 mmol), and Et_3N (0.2 mL) in EtOH/H_2O (2:1, 30 mL) was refluxed for 90 min, and then the solvent was evaporated. NH_4PF_6 (100 mg, 0.8 mmol) was added, and the dark red solid was collected, washed with water, and purified by chromatography on alumina. The column was eluted first with CH_2Cl_2, and the complex was recovered by eluting with acetone. Recrystallization from acetone/hexane affords $[Ru(\mathbf{6b})(tpy)](PF_6)$ as a red solid (73 mg, 48%): mp > 285 °C. ^{1}H NMR (acetone-d_6): δ 8.72 (d, 2H, J = 8.0 Hz), 8.56 (d, 2H, J = 8.0 Hz), 8.37 (AB, 2H, J = 9.1 Hz), 8.23 (m, 2H), 7.97 (dt, 2H, J = 9.1, 1.7 Hz), 7.84 (d, 2H, J = 5.1 Hz), 7.70 (dt, 1H, J = 8.0, 1.7 Hz), 7.35 (m, 3H), 7.10 (d, 1H, J = 8.0 Hz), 6.94 (d 1H, J = 5.15 Hz), 6.87 (dt, 1H, J = 6.9, 1.1 Hz), 6.40 (d, 1H, J = 8.0). MS (MALDI-TOF): m/z 556.28 $[M - PF_6]^+$, 556.07 calcd for $C_{29}H_{20}N_5ORu$. Anal. Calcd for $C_{29}H_{20}F_6N_5OPRu \cdot H_2O$: C, 48.47; H, 3.06; N, 9.74. Found: C, 48.60; H, 2.90; N, 9.12.

[Ru(7b)(pic)$_2$](PF$_6$). A mixture of **7b-H** (40 mg, 0.125 mmol) and $RuCl_3 \cdot 3H_2O$ (32.6 mg, 0.125 mmol) in EtOH (20 mL) was refluxed for 30 min, and then Et_3N (0.2 mL) was added and the reflux continued for 90 min. Water (7 mL), 4-picoline (0.4 mL), and LiCl (10 mg) were added to the dark solution, and the mixture was refluxed for 16 h. NH_4PF_6 (60 mg, 0.5 mmol) was added, and the mixture was concentrated to about 5 mL. The precipitate was collected, washed with water, and purified by chromatography on alumina. The column was eluted first with CH_2Cl_2 to remove the impurities, and the complex was recovered by eluting with CH_2Cl_2/acetone (1:1) (6 mg, 6%): mp > 260 °C. ^{1}H NMR (CD_3CN): δ 9.50 (dd, 1H, J = 5.4, 1.1 Hz, H_9), 8.38 (dd, 1H, J = 8.7, 0.9 Hz, H_7), 8.34 (d, 1H, J = 8.2 Hz), 8.14 (d, 1H, J = 8.7 Hz), 8.07 (d, 1H, J = 8.7 Hz) 7.98 (d, 1H, J = 9.1 Hz), 7.96 (d, 4H, J = 6.4 Hz, H_{pic}, 7.90 (d, 1H, J = 9.1 Hz), 7.86 (dd, 1H, J = 8.2, 5.0 Hz, H_8), 7.80 (d, 1H, J = 9.1 Hz), 7.07 (t, 1H, J = 7.8 Hz, $H_{6'}$), 6.83 (d, 4H, J = 6.4 Hz, H_{pic}), 6.60 (d, 1H, J = 7.8 Hz, $H_{5'}$), 6.53 (d, 1H, J = 8.2 Hz, $H_{7'}$), 2.07 (s, 6H, CH_3). MS (MALDI-TOF): m/z 610.29 $[M - PF_6]^+$, 424.20 $[M - PF_6 - 2\ pic]^+$, 610.12 calcd for $C_{33}H_{26}N_5ORu$. Anal. Calcd for $C_{33}H_{26}F_6N_5OPRu \cdot HPF_6$: C, 43.94; H, 3.01; N, 7.76. Found: C, 44.78; H, 3.25; N, 7.60.

[Ru(8b)(pic)$_2$](PF$_6$). A mixture of **8b-2H** (65 mg, 0.15 mmol) and NaOH (6 mg, 0.15 mmol) in EtOH (7 mL) was stirred at 50 °C for 10 min. $[Ru(dmso)_4Cl_2]$ (74.6 mg, 0.15 mmol) was added, and the mixture was refluxed for 2 h. Then, 4-picoline (0.5 mL), LiCl (10 mg), and Et_3N (0.1 mL) were added, and the reflux was continued for 6 h. The solution was concentrated, NH_4PF_6 (100 mg, 0.8 mmol) was added, and the resulting black solid was collected, washed with water, and purified by chromatography on alumina, eluting first with CH_2Cl_2 followed by acetone and acetonitrile. Recrystallization from acetone/hexane afforded $[Ru(\mathbf{8b})(pic)_2](PF_6)$ as a black solid (38 mg, 29%): mp > 285 °C. ^{1}H NMR (CD_3OD, ascorbic acid): δ 8.34 (s, 2H), 8.26 (d, 2H, J = 9.7 Hz, $H_{3'}$), 8.16 (d, 2H, J = 8.7 Hz, $H_{4'}$), 8.03 (d, 4H, J = 6.9 Hz, H_{Pic}), 7.36 (t, 2H, J = 8.2 Hz, $H_{6'}$), 7.14 (d, 2H, J = 8.2 Hz, $H_{5'}$), 7.06 (d, 2H, J = 8.2 Hz, $H_{7'}$), 6.83 (d, 4H, J = 6.8 Hz, H_{pic}), 2.06 (s, 6H, CH_3), 1.58 (s, 9H, CH_3). ^{19}F NMR (CD_3OD): δ −74.80 (d, J = 750 Hz). MS (MALDI-TOF): m/z 707.55 $[M - PF_6]^+$, 521.39 $[M - PF_6 - 2\ pic]^+$, 707.12 calcd for $C_{39}H_{35}N_5O_2Ru$.

[Ru(8b)(tb-py)$_2$](PF$_6$). In the manner described for $[Ru(\mathbf{8b})(pic)_2](PF_6)$, a mixture of **8b-2H** (65 mg, 0.15 mmol), NaOH (6 mg, 0.15 mmol), $[Ru(dmso)_4Cl_2]$ (74.6 mg, 0.15 mmol), 4-*t*-butylpyridine (0.75 mL), LiCl (10 mg), Et_3N (0.1 mL), and NH_4PF_6 (100 mg, 0.8 mmol) afforded a black solid that was purified by chromatography on alumina, eluting first with CH_2Cl_2 followed by acetone and acetonitrile. Recrystallization from acetone/hexane afforded $[Ru(\mathbf{8b})(tb\text{-}py)_2](PF_6)$ as a black solid (22 mg, 16%): mp > 285 °C. ^{1}H NMR (CD_3OD, ascorbic acid): δ 8.39 (s, 2H), 8.32 (d, 2H, J = 9.15 Hz, $H_{3'}$), 8.12 (d, 2H, J = 8.6 Hz, $H_{4'}$), 8.08 (d, 4H, J = 6.3 Hz, $H_{tb\text{-}py}$), 7.38 (t, 2H, J = 7.45 Hz, $H_{6'}$), 7.21 (d, 2H, J = 8.6 Hz, $H_{5'}$), 7.04 (m, 2H), 7.03 (d, 4H, J = 6.3 Hz, $H_{tb\text{-}py}$), 1.59 (s, 9H, CH_3), 1.04 (s, 18H, CH_3). MS (MALDI-TOF): m/z 521.39 $[M - PF_6 - 2\ tb\text{-}py]^+$, 521.07 calcd for $C_{27}H_{21}N_3O_2Ru$. Anal. Calcd for $C_{45}H_{47}F_6N_5O_2PRu \cdot 3H_2O$: C, 54.60; H, 5.35; N, 7.07. Found: C, 54.47; H, 4.77; N, 6.57.

X-ray Determination of [Ru(8b)(pic)$_2$](PF$_6$)·C$_3$H$_6$O·0.5C$_7$H$_8$. All measurements were made with a Siemens SMART platform diffractometer equipped with a 4K CCD APEX II detector. A hemisphere of data (1271 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30% in ω and an exposure time of 40 s/frame. The data were integrated using the Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A ψ scan absorption correction was applied on the basis of the entire data set. Redundant reflections were averaged. Final cell constants were refined using 2912 reflections having $I > 10\sigma(I)$, and these, along with other information pertinent to

data collection and refinement, are listed in Table S-1. The Laue symmetry was determined to be −1, and the space group was shown to be either $P1$ or $P\bar{1}$. The asymmetric unit consists of one cation and one molecule of acetone solvent in general positions, two half-molecules of PF_6^- on inversion centers, and one-half molecule of toluene solvent on an inversion center. The *t*-butyl group of the cation and the toluene solvent molecule are both disordered over two different positions. One of the PF_6 anions is heavily disordered, and the acetone is so massively disordered that only 80% of the total electron density could be located. Ideal rigid body models were used to refine most of the disordered moieties, with population factors estimated by comparison of isotropic displacement parameters. The acetone solvent site is presumed to be fully occupied for all calculations.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data for $[Ru(\mathbf{8b})(pic)_2](PF_6)\cdot C_3H_6O\cdot 0.5C_7H_8$ (CIF file and Table S1). ^1H and ^{13}C NMR spectra for ligands **6b**, **7b**, and **8b** and their Ru complexes. MALDI-TOF MS and simulated MS for Ru complexes. Electronic absorption spectra for Ru complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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