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Ru(II) Complexes of Tetradentate Ligands Related to 2,9-Di(pyrid-2′-yl)-1,10-phenanthroline

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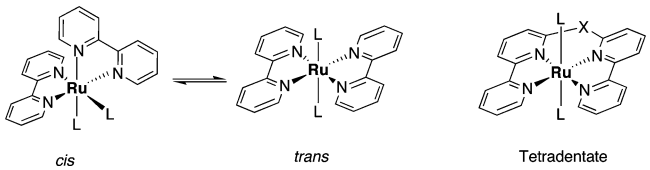
A series of 1,10-phenanthrolines were prepared having additional ligating substituents at the 2,9-positions. These substituents were either a 4-substituted pyrid-2-yl, quinolin-2-yl, 1,8-naphthyrid-2-yl, *N*-methyl imidazo-2-yl, or *N*-methyl benzimidazo-2-yl group. Additionally, 3,6-di-(pyrid-2′-yl)-dipyrido[3,2-*a*:2′,3′-*c*]phenazine was prepared. All but two of these ligands coordinated Ru(II) in a tetradentate equatorial fashion with two 4-methylpyridines bound in the axial sites. An X-ray structure analysis of the diimidazoyl system indicates considerable distortion from square planar geometry in the equatorial plane. Previously reported variations in the axial ligand for such complexes appear to have a stronger effect on the electronic absorption and redox properties of the system than similar changes in the equatorial ligand. In the presence of excess Ce(IV) as a sacrificial oxidant at pH 1, all the systems examined catalyze the decomposition of water to generate oxygen. Turnover numbers are modest, ranging from 146 to 416.

Introduction

The preparation and chemistry of heteroleptic complexes of Ru(II) involving bidentate ligands such as 2,2′-bipyridine (bpy) present some interesting stereochemical features. Complexes of the type $[Ru(bpy)_2L_2]^{2+}$ may exist in either a cis or trans geometry, with the former being strongly preferred because of less steric interaction between the two cis bpy ligands. However, there are potential features associated with a trans geometry which, in some cases, make this configuration more desirable. However, when complexes having the trans geometry can be prepared, they are prone toward photochemical or thermal conversion to the more stable cis form.[1]



The trans-to-cis interconversion can be avoided by connecting the subunits with a tether to the 6-position of the two adjacent bpys.[2] This same strategy has been employed in the preparation of tetradentate ligands involving 1,10-phenanthroline (phen) subunits.[3] Grätzel and co-workers have shown that the two bpys can be directly connected as in quaterpyridine, and equatorial binding with Ru(II) will occur if care is taken to avoid bridging through bis-bidentate behavior of the ligand.[4] We have recently discovered that an excellent method to avoid bridging by a tetradentate ligand is to incorporate a phen as the internal subunit thus avoiding conformational mobility around the central bond.[5] The

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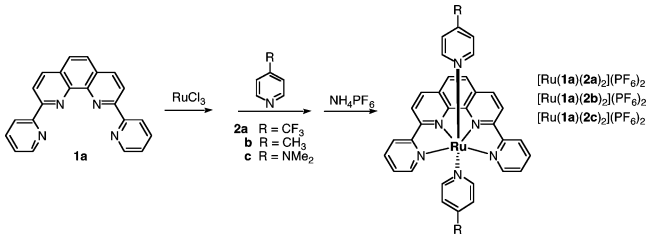
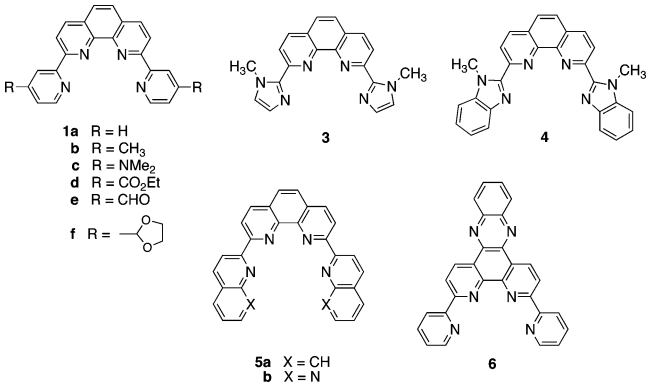
prototype example of such a system is 2,9-di(pyrid-2′-yl)-1,10-phenanthroline (**1a**), which readily binds Ru(II) in an equatorial tetradentate fashion. The two axial sites in complexes of **1a** may be occupied by a 4-substituted pyridine (**2a**−**c**), and the photophysical and electrochemical properties of these complexes are found to be quite sensitive to the nature of the 4-substituent. The more electron-donating this substituent, the better able the axial pyridine is to stabilize the Ru(III) state, as manifested by a lower oxidation potential (1.03 V for $[Ru(\mathbf{1a})(\mathbf{2c})_2](PF_6)_2$ vs 1.36 V for $[Ru(\mathbf{1a})(\mathbf{2a})_2](PF_6)_2$).[5] A similar effect is observed in the long-wavelength metal-to-ligand charge transfer (MLCT) absorption band that appears at lower energy for $[Ru(\mathbf{1a})(\mathbf{2c})_2](PF_6)_2$ (580 nm) than for $[Ru(\mathbf{1a})(\mathbf{2a})_2](PF_6)_2$ (516 nm).



In this paper we address modifications of the equatorial ligand and the effect of these changes on the photophysical and electrochemical properties of the corresponding Ru(II) complexes. The pyridyl rings at positions 2 and 9 of **1a** are modified by the introduction of a 4′-substituent (**1b**−**e**) or replaced by a 1-methyl-2-imidazoyl ring (**3**), a 1-methyl-2-benzimidazoyl ring (**4**), a 2-quinolinyl ring (**5a**), or a 2-[1,8]-naphthyridyl ring (**5b**). The central phen ring was also modified by conversion to a dipyridophenazine derivative (**6**).



In other recent work we have discovered that a family of mono- and dinuclear Ru(II) complexes having a tridentate equatorial ligand and two axial pyridine ligands (**2a**−**c**) are quite effective in the catalytic oxidation of water to produce dioxygen.[6] The complexes involving **2b** as the axial ligand showed the highest turnover number (TN). It therefore became of interest to examine the complexes derived from **1a**−**e** and **3**−**6**, having 4-methylpyridine (**2b**) as the axial ligand, for activity in this important water oxidation process.

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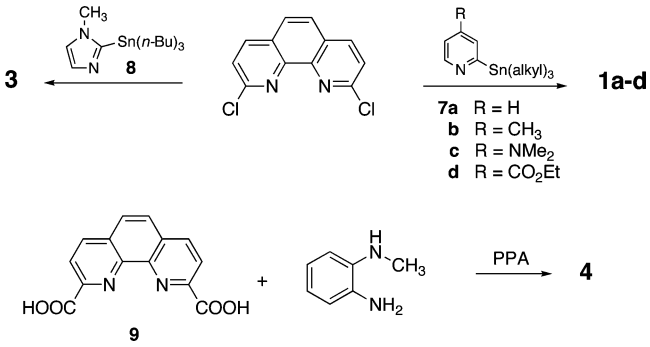
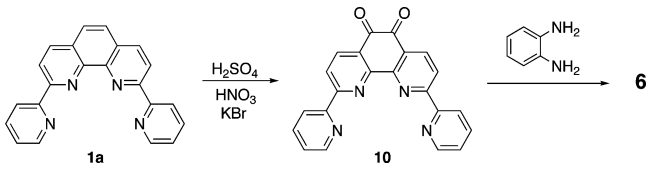
Results and Discussion

The 2,9-disubstituted phen ligands were prepared by an extension of the approach used to make the parent system **1a**. An appropriate 4-substituted pyridine derivative was converted to its tri-*n*-butylstannane derivative[7] **7b**−**d** and this was coupled to 2,9-dichlorophen[8] using Stille methodology to provide **1b**−**d**. The analogous *N*-methylimidazole derivative **3** was prepared by a similar coupling with 1-methyl-2-(tri-*n*-butylstannyl)imidazole[9] (**8**) while the benzimidazole analogue **4** was prepared by the polyphosphoric acid promoted condensation of *N*-methyl-1,2-phenylenediamine[10] with phen-2,9-dicarboxylic acid (**9**).[11]



The dipyridophenazine derivative **6** was prepared by condensation of the corresponding quinone **10** with *o*-phenylenediamine.[12] The quinone was derived in high yield from the oxidation of **1a** using a mixture of nitric acid, sulfuric acid, and KBr.[12] For phen itself, this oxidation can sometimes be problematic, but for the 2,9-di(pyrid-2′-yl) derivative it proceeded smoothly in 95% yield.



The complexation of these ligands with Ru(II) involved three steps but could be carried out in a one-pot reaction. The equatorial ligand was combined with $[Ru(DMSO)_4Cl_2]$ in ethanol. After an hour of reflux, 4-methylpyridine (**2b**), triethylamine, and LiCl were added and reflux was continued for 24 h. The complex was finally precipitated as its hexafluorophosphate salt by the addition of NH_4PF_6. The

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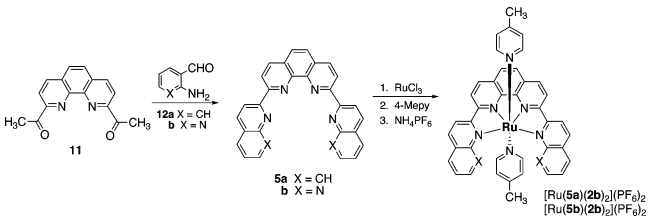
yield of the complex is influenced considerably by the nucleophilicity of the two distal azaaromatic rings. For ligand **1d**, with two electron-withdrawing 4-carboethoxy substituents, the complex $[Ru(\mathbf{1d})(\mathbf{2b})_2](PF_6)_2$ appeared to be unstable, so that a single pure product could not be obtained. It is likely that the electron-withdrawing 4-carboethoxy substituents cause the peripheral pyridines to become poorer nucleophiles, leading to complexes which are no longer tetradentate and, hence, unsymmetrical.

We attempted to resolve this problem by designing a tetradentate ligand with a 4-substituted pyridine where the electron-withdrawing group was protected and, hence, not deactivating. After complex formation, deprotection might lead to the desired tetradentate system. To this end, we oxidized **1b** with selenium dioxide in aqueous dioxane to obtain **1e** in 21% yield. The two aldehyde groups were then protected as ethylenedioxy derivatives by reaction with ethylene glycol in the presence of an acid catalyst, providing a 27% yield of **1f**. Using a sample of **1f** which was about 80% pure by ^{1}H NMR, we carried out a preliminary complexation with Ru(II) in hopes of forming $[Ru(\mathbf{1f})(\mathbf{2b})_2](PF_6)_2$; however, some hydrolysis of the acetal functions occurred, leading to a complex which again appeared not to be tetradentate. In a separate experiment, the direct coordination of **1e** with ruthenium did not occur in a tetradentate fashion.

Another way of introducing electronegativity into the two peripheral binding sites of the tetradentate ligand would be to employ azaaromatic rings other than pyridine. Initially, we attempted to prepare the 2-pyrimidyl analogue of **1a**, but the coupling reaction was unsuccessful. Instead, we elaborated the previously prepared 2,9-diacetyl-1,10-phenanthroline (**11**) through well-established Friedländer methodology to afford the di-(2′-quinolinyl) and di-(2′-[1′,8′]naphthyridinyl) derivatives **5a**,**b**.[13] These two ligands coordinate in the expected fashion with Ru(II) to provide the tetradentate complexes $[Ru(\mathbf{5a},\mathbf{b})(\mathbf{2b})_2](PF_6)_2$ in relatively low yields.



The complexes were readily characterized by their ^{1}H NMR spectra (Table S1). Due to 2-fold symmetry, the protons of the equatorial ligand were easily assigned. The H5, H6 singlet appeared in the narrow range of 8.45−8.62 ppm. The H6′ proton showed a characteristic small ortho-coupling constant (4.8−6.6 Hz). The H2 and H3 protons on the axial 4-methylpyridine gave a doublet of doublets having twice the intensity of the peaks from the equatorial ligand. If the Ru(II) had not been symmetrically bound by the equatorial ligand, the NMR spectrum would have been more

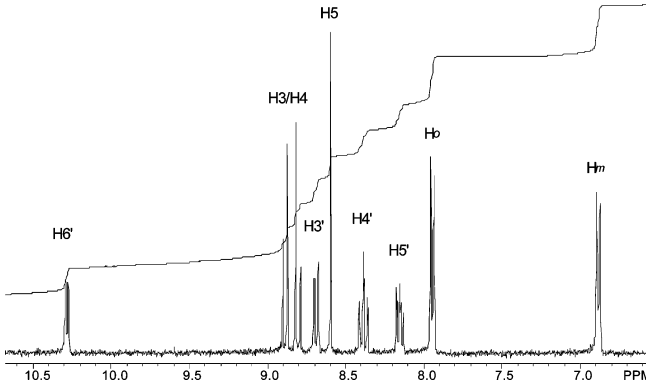
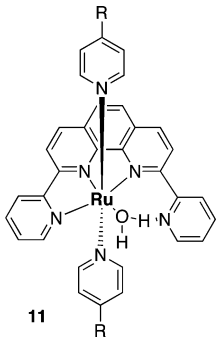


Figure 1. Downfield region of the 300 MHz ^{1}H NMR spectrum of $[Ru(\mathbf{1a})(\mathbf{2b})_2](PF_6)_2$ in acetone-d_6 at 25 °C. H_o and H_m are H2 and H3, respectively, on the ligand **2b**.

complex. Figure 1 illlustrates the 300 MHz ^{1}H NMR of $[Ru(\mathbf{1a})(\mathbf{2b})_2]^{2+}$ showing H6′ at 10.29 ppm, being strongly deshielded both by N1′ and the ring current effect of the opposing pyridyl group which has been pulled closer by complexation.

Our initial motive for preparing these systems was the expectation that the tetradentate ligands would only bind to Ru(II) in a tridentate fashion, leaving one of the pendant azaaromatic groups uncomplexed.[14] Our objective was to use this uncomplexed group as an internal photoactivated base to assist in the deprotonation of a water molecule bound in the equatorial plane as in structure **11**. We were surprised to find that the ligand was able to tolerate considerable



distortion to accommodate tetradentate binding. To make such binding even less favorable, we prepared the *N*-methylimidazole and *N*-methylbenzimidazole derivatives **3** and **4** where the 5-membered imidazole ring is expected to be even less conducive to tetradentate binding since it might require more distortion and an even longer coordinative bond. Nevertheless, both **3** and **4** formed well-organized tetradentate complexes. We carried out an X-ray crystal analysis to determine the structure of $[Ru(\mathbf{3})(\mathbf{2b})_2](PF_6)_2$. Table 1 lists some selected geometric features for the complex and Figure 2 shows two views of the cation.

The structure of the equatorial ligand **3** shows considerable distortion in order to accommodate tetradentate binding. In this respect, it closely resembles the equatorial ligand **1a** in the previously determined[5] structure of $[Ru(\mathbf{1a})(\mathbf{2b})_2]^{2+}$. The

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Table 1. Selected Geometric Parameters for $[Ru(\mathbf{3})(\mathbf{2b})_2](PF_6)_2$

	Bond Lengths (Å)		
Ru−N1	2.138(5)	C5−C6	1.459(9)
Ru−N20	2.145(5)	C15−C16	1.459(9)
Ru−N21	1.951	C10−C11	1.371(10)
Ru−N24	1.961(5)	C22−C23	1.420(8)
Ru−N27	2.099(5)		
Ru−N34	2.088(5)		
	Bond Angles (deg)		
N20−Ru−N21	76.13(19)	C8−C9−C10	128.9(6)
N21−Ru−N24	82.3(2)	C11−C12−C13	128.5(6)
N1−Ru−N24	76.41(20)		
N1−Ru−N20	125.03(19)		
N27−Ru−N34	172.96(18)		
N21−C15−C16	108.0(5)	N24−C6−C5	107.5(5)
C14−C15−C16	133.2(6)	C5−C6−C7	133.5(6)
N20−C16−C15	118.8(5)	N1−C5−C6	119.7(5)
C15−C16−N17	130.9(6)	N4−C5−C6	130.8(6)
	Dihedral Angles (deg)		
N20−C16−C15−N21	−3.5(8)	N1−C5−C6−N24	−4.1(7)
C14−C15−C16−N17	−5.2(12)	N4−C5−C6−C7	−6.4(11)

internal Ru−N bonds are compressed to 1.95−1.96 Å, while the outer Ru−N bonds are stretched to about 2.14 Å. These distortions result in a more "trapezoidal" rather than square planar arrangement around the central Ru. The external N1−Ru−N20 angle is 125.1°, nearly identical to the 125.6° measured for the complex of **1a**. The phenanthroline portion of the ligand is bowed as evidenced by the C8−C9−C10 and C11−C12−C13 angles, which average 128.7°. There is a slight dihedral twist between the phenanthroline and *N*-methylimidazole rings which averages about 4.8°. Interestingly, both angles have the same sign, indicating that they have the same direction of twist. The bonds from Ru to the two axial 4-methylpyridine ligands are 2.09 and 2.10 Å, which is closer to the normal Ru−N bond length. The angle along this axis is about 173°, which is again similar to the 170° measured for the complex of **1a**. The complexes appear to be quite robust and we saw no evidence for dissociation of either the axial or equatorial ligand over time.

The electronic absorption spectra of the complexes were measured in acetone at room temperature, and the results are recorded in Table 2. With the exception of $[Ru(\mathbf{6})(\mathbf{2b})_2](PF_6)_2$, these spectra all appear somewhat similar (Figure 3). In the region of 332−353 nm, a strong band appears which may be attributed to $\pi-\pi^*$ absorptions associated with the equatorial ligands. In the long-wavelength region, there is a broad absorption band showing some vibrational fine structure. The lowest energy component is generally the most intense and is found in the range of 536−605 nm. This band is attributed to a MLCT transition involving the tetradentate equatorial ligand as the charge acceptor. There is a relatively weak component in the range of 405−426 nm, and it is tempting to assign this to charge transfer involving the axial 4-methylpyridine which remains invariant throughout the series. Figure 3 illustrates the long-wavelength region for the complexes involving **1a**, **1c**, **3**, and **4**. The spectrum for $[Ru(\mathbf{1c})(\mathbf{2b})_2]^{2+}$ where the peripheral substituent is the strongly donating dimethylamino group is only slightly red-shifted from the spectrum of the parent system $[Ru(\mathbf{1a})(\mathbf{2b})_2]^{2+}$. The same comparison can be made for *N*-methylbenzimidazole vs *N*-methylimidazole as the peripheral

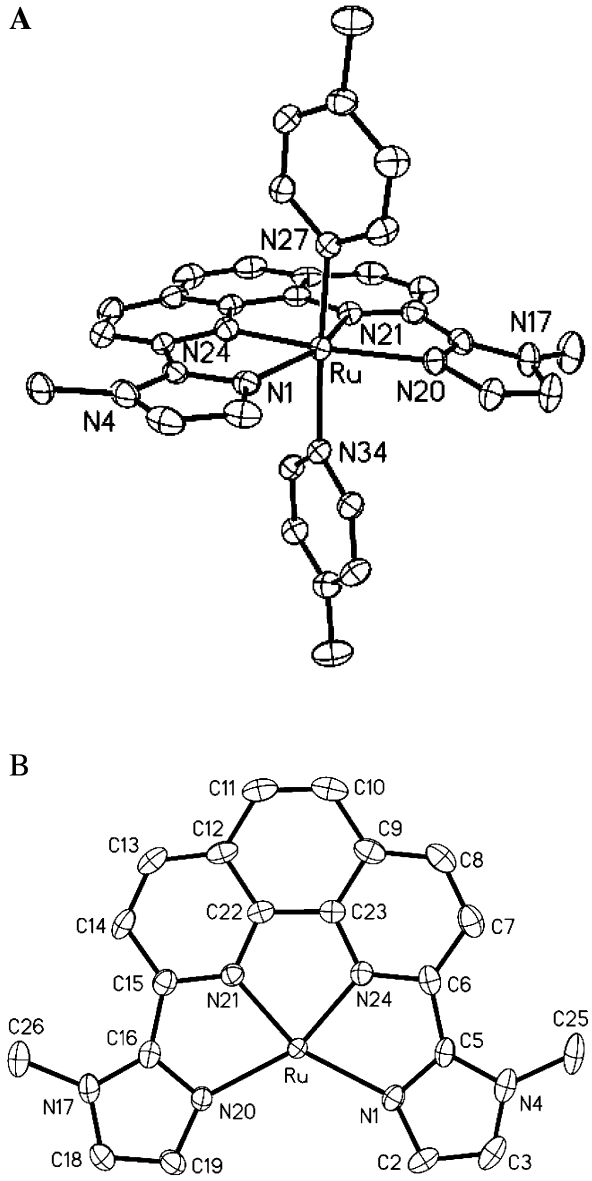

Figure 2. Side (A) and top (B) views of the X-ray crystal structure of the cation of $[Ru(\mathbf{3})(\mathbf{2b})_2](PF_6)_2$, showing the numbering pattern for the X-ray discussion.

binding group. The more delocalized benzimidazole causes a small but consistent (11−24 nm or 539−994 cm^{-1}) red-shift of the four observed components of the MLCT band.

In our earlier study of the complexes $[Ru(\mathbf{1a})(\mathbf{2a}-\mathbf{c})_2](PF_6)_2$, we noted that the energy of the MLCT band was quite sensitive to the nature of the axial ligand. Variations in the equatorial ligand appear to have less of an effect, possibly due to the fact that the Ru−N bonds to the peripheral pyridines or imidazoles are highly distorted and do not encourage strong interaction of these ligand sites with the metal d orbitals. Figure 4 illustrates the effect of benzo- and pyrido-annelation on the peripheral pyridine ring. The long-wavelength band red-shifts 29 nm (892 cm^{-1}) for the quinolinyl system and an additional 34 nm (984 cm^{-1}) for the 1,8-naphthyridyl system. The complex $[Ru(\mathbf{6})(\mathbf{2b})_2]^{2+}$ involves an equatorial ligand in which the central phen ring of **1a** has been elaborated to a dipyridophenazine (dppz). Although the main absorption band at 541 nm remains almost

Table 2. Electronic Absorption,[a] Cyclic Voltammetric,[b] and Turnover Number Data for Ru(II) Complexes

complexes	absorbance λ_{max}, nm (log ϵ)	$E_{1/2}^{ox}(\Delta E)$	$E_{1/2}^{red}(\Delta E)$		TN
[Ru(**1a**)(**2b**)$_2$](PF$_6$)$_2$	336(4.45), 405(3.54), 451(3.40), 487(3.57), 542(3.75)	1.24(86)	−1.04(97)	−1.53^{ir}	416
[Ru(**1b**)(**2b**)$_2$](PF$_6$)$_2$	336(4.50), 407(3.57), 457(3.45), 485(3.64), 540(3.79)	1.20(76)	−1.08(67)	−1.66^{ir}	403
[Ru(**1c**)(**2b**)$_2$](PF$_6$)$_2$	332(4.47), 423(3.73), 460(sh, 3.67), 488(3.83), 547(3.88), 592(sh, 3.58)	0.94(97)	−1.22(82)	−1.62(85)	186
[Ru(**3**)(**2b**)$_2$](PF$_6$)$_2$	345(4.60), 405(3.47), 446(3.52), 471(3.76), 536(3.78)	1.06(103)	−1.22(103)	−1.85^{ir}	281
[Ru(**4**)(**2b**)$_2$](PF$_6$)$_2$	353(4.61), 422(3.64), 457(3.56), 491(3.64), 560(3.81)	1.21(116)	−1.01(82)	−1.57(84)	384
[Ru(**5a**)(**2b**)$_2$](PF$_6$)$_2$	347(4.45), 424(sh, 3.48), 464(sh, 3.29), 535(sh, 3.43), 571(3.66), 620(sh, 3.32)	1.38(110)	−0.87(113)	−1.43(111), −1.90^{ir}	146
[Ru(**5b**)(**2b**)$_2$](PF$_6$)$_2$	348(4.47), 426(3.58), 470(sh, 3.24), 565(sh, 3.40), 605(3.59), 660(sh, 3.12)	1.35^{ir}	−0.77(74)	−1.29(84) −1.69(112)	213
[Ru(**6**)(**2b**)$_2$](PF$_6$)$_2$	335(4.61), 462(3.72), 541(3.75), 578(sh, 3.64), 690(sh, 2.46)	1.29(90)	−0.83(86)	−1.21(176) −1.72^{ir}	396

[a] Measured in acetone (5×10^{-5} M) at room temperature. [b] Recorded in CH_3CN 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 estimated by differential peaks.

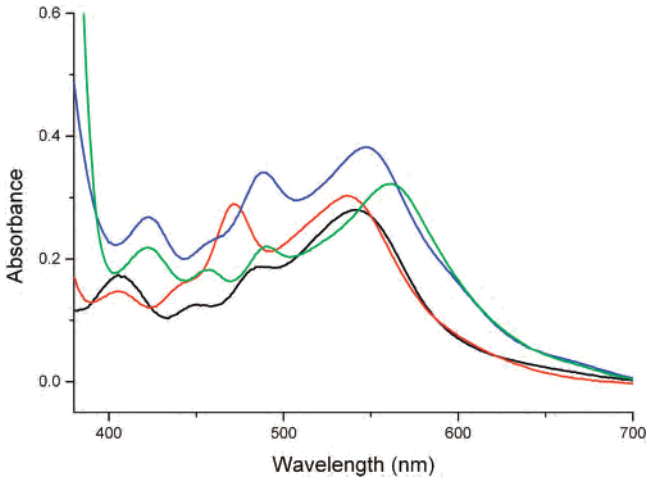

Figure 3. Electronic absorption spectra of [Ru(L)(**2b**)$_2$](PF$_6$)$_2$ in acetone (5×10^{-5} M): L = **1a** (black), **1c** (blue), **3** (red), **4** (green).

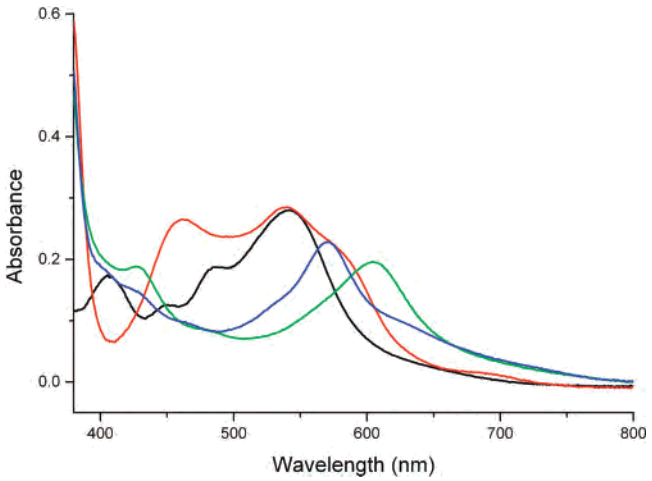

Figure 4. Electronic absorption spectra of [Ru(L)(**2b**)$_2$](PF$_6$)$_2$ in acetone (5×10^{-5} M): L = **1a** (black), **5a** (blue), **5b** (green), **6** (red).

unchanged from the parent complex [Ru(**1a**)(**2b**)$_2$]$^{2+}$, this band is significantly broadened to span almost 200 nm. Interestingly, a weak absorption at 690 nm is also observed for the dppz complex (Figure 4). At room temperature in acetone solution, none of the tetradentate complexes showed appreciable emission. The strain inherent in three fused chelate rings in the equatorial plane leads to a lowering of the energy of the ligand field states which then provides a facile pathway for the nonradiative decay of the excited state.

Also recorded in Table 2 are the redox potentials for the complexes as measured by cyclic voltammetry in acetonitrile solution. These results are consistent with the electron-donating abilities of the 4-substituent on the distal pyridines of the equatorial ligand. The oxidation potential decreases along the series [Ru(**1a**−**c**)(**2b**)$_2$]$^{2+}$ as this substituent changes from hydrogen to methyl to dimethylamino. The better donor group helps to stabilize the Ru(II/III) couple. At the same time, the reduction potential, which is ligand-based, decreases as the peripheral pyridine becomes a poorer acceptor. In both cases the change is most apparent for the strongly donating dimethylamino group. For the *N*-methylimidazoyl vs the *N*-methylbenzimidazoyl substituent, the reverse trend is evidenced with the more delocalized benzimidazole, leading to both a more positive oxidation and reduction potential. The quinoline and 1,8-naphthyridine substituents are the most electronegative, so that their complexes show the most positive oxidation and reduction potentials. When increased electronegativity and delocalization are instead localized on the central ring of the equatorial ligand, as in the dppz-containing complex, similarly increased redox potentials are observed.

The stability associated with complexes such as [Ru(bpy)$_3$]$^{2+}$ is largely due to the chelate ring effect. By joining together two monodentate pyridine ligands through a 2,2′-bond, one alleviates possible intramolecular steric interactions between these pyridines and also benefits from the chelate effect whereby each ligand is joined to the metal by two bonds rather than just one. In potential photocatalytic applications, however, it may become important for a substrate to enter the coordination sphere of the metal, and thus, these stabilizing effects could, in fact, prove detrimental to catalytic activity. The systems under consideration in this study are somewhat unusual in that they combine a strongly chelated tetradentate polypyridine with two simple monodentate pyridines. If complexation of a substrate to the

ruthenium center is important, one could imagine this complexation occurring either through replacement of an axial pyridine or by the decomplexation of a distal ring of the tetradentate ligand. It should be noted that in complexes such as $[Ru(\mathbf{3})(\mathbf{2b})_2](PF_6)_2$ the outer Ru−N bonds to **3** are unusually long and thus might be easily broken. For these reasons, we thought it might be of interest to test the activity of this series of complexes as catalysts for water oxidation.

The complexes were tested for catalytic activity in water oxidation by adding an acetonitrile solution (50 μL) of the catalyst (0.004 M) to 3 mL of an aqueous CF_3SO_3H solution (pH 1.0) containing a 5000× excess of ceric ammonium nitrate at 24 °C.[15] After the mixture stirred for 48 h, the amount of generated oxygen was measured by GC and the catalyst TN was calculated. These results are included in Table 2. All the tetradentate complexes showed modest activity in water oxidation, and in this regard, they do not differ much from the three mononuclear Ru systems which we reported earlier.[6] A less active system is $[Ru(\mathbf{1c})(\mathbf{2b})_2](PF_6)_2$, having the dimethylamino substituent, which again is in accord with the lower activity observed when this substituent is at the 4-position of the monodentate ligand. It should be remembered, however, that at pH 1 the dimethylamino group is most likely protonated, causing it to function inductively as an electron-withdrawing group.

In summary, a series of 2,9-disubstituted derivatives of 1,10-phenanthroline has been prepared and studied as tetradentate ligands for Ru(II). Due to the preorganization inherent in the central phenanthroline ring, these ligands bind readily in an equatorial fashion to the metal center with two monodentate pyridines occupying the axial sites on the complex. The complexes are distorted and strained but nonetheless quite stable. Substitution on the equatorial ligand does do not have as strong or well-defined influence on the properties of the system as the same substituent on the axial monodentate pyridines. All these systems are moderately active in water oxidation, but the mechanism by which this process occurs is not clear at this time.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 and 75 MHz, respectively, and the chemical shifts were referenced to the residual solvent peak. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer. Infrared spectra were taken on a Thermo Nicolet AVATAR 370 FT-IR spectrometer. Mass spectra were obtained on an Applied Biosystems Voyager-DE STR MALDI-TOF mass spectrometer. Cyclic voltammetric (CV) measurements were carried out with a BAS Epsilon Electroanalytical System using a one-compartment cell equipped with a glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a Pt wire as the auxiliary electrode. An acetonitrile solution of n-$Bu_4N(PF_6)$ (0.1 M) in a tube with a porous glass frit on one end was used between the SCE electrode and the sample solution. Melting points are uncorrected, and CHN analyses were performed by QTI, Whitehouse, NJ. The 2-(tri-*n*-butylstannyl)-pyridine,[7] 2,9-dichloro-1,10-phenanthroline,[8] 1,10-phenanthroline-2,9-dicarboxylic acid,[11] 2,9-di-(1′,8′-naphthyrid-2′-yl)-1,10-phenanthroline (**5b**),[13] and $[Ru(\mathbf{1a})(\mathbf{2b})_2](PF_6)_2$[5] were prepared according to literature procedures.

TNs were measured in the following manner. To a 10 mL one-neck round-bottom flask, $Ce(NH_4)_2(NO_3)_6$ (550 mg, 1 mmol) and 3 mL of $CF_3SO_3H_{(aq)}$ (adjusted to pH 1) were added and magnetically stirred to give a homogeneous solution. The complex (2.0×10^{-4} mmol) dissolved in CH_3CN (50 μL) was injected into the solution through a rubber septum, and the mixture was stirred at room temperature for 48 h. The oxygen content in the headspace of the flask was measured using a Gow-Mac Series 400 thermal conductivity GC with a 6 ft × 1/8 in. 5 Å molecular sieve column operating at 70 °C and 20 mL/min Ar.

4-Methyl-2-(tri-*n*-butylstannyl)pyridine (7b). A solution of *n*-butyllithium in hexanes (2.5 M, 12.0 mL) was added dropwise to a solution of 2-bromo-4-picoline (5.16 g, 0.030 mol) in dry THF (40 mL) cooled to −78 °C under Ar. After 30 min, Bu_3SnCl (9.76 g, 0.030 mol) was added slowly to give a dark solution which was stirred at −78 °C for 1 h. The solution was allowed to warm to room temperature and concentrated. The residue was Kugelrohr-distilled (0.2 mm, 160 °C) and further purified by chromatography on alumina eluting with petroleum ether to obtain **7b** as a pale yellow oil (7.15 g, 62%): ^{1}H NMR ($CDCl_3$) δ 8.58 (d, J = 5.4 Hz, 1H), 7.21 (d, J = 0.6 Hz, 1H), 6.94 (dd, J = 5.1 Hz, 0.9 Hz, 1H), 2.29 (s, 3H), 1.6−1.5 (m, 6H), 1.4−1.2 (m, 6H), 1.1 (m, 6H), 0.87 (t, J = 7.5 Hz, 9H).

4-Dimethlyamino-2-(tri-*n*-butylstannyl)pyridine (7c). A solution of *n*-butyllithium in hexanes (2.5 M, 40.0 mL, 0.10 mol) was added dropwise to a solution of 2-dimethylamino ethanol (4.27 g, 0.048 mol) in dry THF (60 mL) cooled to −5 °C under Ar. After 30 min of stirring at 0 °C, 4-dimethylamino pyridine (3.05 g, 0.025 mol) was added at once as a solid. After 1 h of stirring at 0 °C, the reaction mixture was cooled to −78 °C. A solution of Bu_3SnCl (16.3 g, 0.050 mol) in dry THF (70 mL) was added dropwise over 40 min, and the reaction was allowed to warm to room temperature and concentrated. The residue was Kugelrohr-distilled (0.15 mm, 170−180 °C) and further purified by chromatography on alumina eluting with petroleum ether to yield **7c** as a yellow oil (10.3 g, 100%): ^{1}H NMR ($CDCl_3$) δ 8.33 (d, J = 5.7 Hz, 1H), 6.64 (d, J = 3.0 Hz, 1H), 6.37 (dd, J = 5.4 Hz, 2.7 Hz, 1H), 2.96 (s, 3H), 1.54 (m, 6H), 1.32 (m, 6H), 1.07 (m, 6H), 0.89 (m, 9H).

4-Ethoxycarbonyl-2-(trimethylstannyl)pyridine (7d). A mixture of 2-bromo-4-ethoxycarbonylpyridine (1.15 g, 5.0 mmol), hexamethylditin (1.64 g, 5.0 mmol), and $[Pd(PPh_3)_4]$ (0.35 g, 0.30 mmol) in toluene was flushed with Ar and refluxed for 2.5 h under Ar. The solvent was evaporated and the residue was purified on alumina, eluting with petroleum ether and then petroleum ether/EtOAc (20:1), to yield **7d** (0.72 g, 46%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 8.91 (d, J = 4.8 Hz, 1H), 7.98 (d, J = 1.8 Hz, 1H), 7.68 (dd, J = 4.8, 1.5 Hz, 1H), 4.41 (q, J = 6.9 Hz, 2H), 1.41 (t, J = 6.9 Hz, 3H), 0.38 (s, 9H).

2-Tri-*n*-butylstannyl-1-methylimidazole (8). To a solution of 1-methylimidazole (4.11 g, 0.050 mol) in dry THF (60 mL) cooled to −15 °C was added a solution of *n*-butyllithium in hexanes (2.5 M, 22.0 mL) over a period of 1.5 h under Ar. The solution was stirred at −10 °C for 2 h, and then a solution of Bu_3SnCl (16.3 g, 0.050 mol) in dry ether (60 mL) was added over a 1.5 h period. The mixture was allowed to warm to ambient temperature and concentrated. The product was isolated by Kugelrohr distillation (0.2 mm, 160−180 °C) to yield **8** as a colorless oil (16.77 g,

(15) (a) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029−30. (b) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855−3864. (c) Sens, C.; Romero, I.; Rodriguez, M.; Llobet, A.; Parella, T.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2004**, *126*, 7798−7799.

90%): ^{1}H NMR ($CDCl_3$) δ 7.17 (d, J = 0.9 Hz, 1H), 6.98 (d, J = 0.9 Hz, 1H), 3.65 (s, 3H), 1.51 (m, 6H), 1.29 (m, 6H), 1.15 (m, 6H), 0.85 (t, J = 6.9 Hz, 9H).

2,9-Di-(pyrid-2′-yl)-1,10-phenanthroline (1a). A mixture of 2,9-dichloro-1,10-phenanthroline (2.49 g, 10 mmol), 2-(tri-*n*-butylstannyl)pyridine (11.07 g, 30 mmol), and [$Pd(PPh_3)_4$] (1.4 g, 1.2 mmol) in toluene (15 mL) was refluxed under Ar for 48 h. After evaporation of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2 and filtered, and the filtrate was precipitated with hexanes. The precipitate was collected and washed with hexanes and ether to afford **1a** as beige crystals (2.80 g). The mother liquor was evaporated and the residue was chromatographed on alumina, eluting with hexanes and then CH_2Cl_2, to obtain additional **1a** (0.24 g, total yield 91%). Further purification was afforded by recrystallization from CH_2Cl_2-hexanes, mp 212−215 °C (lit[5] mp 205−206 °C): ^{1}H NMR ($CDCl_3$) δ 9.12 (d, J = 7.5 Hz, 2H), 8.93 (d, J = 8.4 Hz, 2H), 8.82 (dd, J = 4.8, 0.6 Hz, 2H), 8.45 (d, J = 8.4 Hz, 2H), 8.07 (dt, J = 8.1, 1.5 Hz, 2H), 7.89 (s, 2H), 7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 156.2, 155.9, 149.0, 145.7, 137.1, 129.1, 126.7, 124.2, 122.7, 122.2, 120.6.

2,9-Di-(4′-methylpyrid-2′-yl)-1,10-phenanthroline (1b). A mixture of 2,9-dichloro-1,10-phenanthroline (498 mg, 2.0 mmol), **7b** (3.07 g, 8.0 mmol), and [$Pd(PPh_3)_4$] (0.23 g, 0.2 mmol) in toluene (20 mL) was heated at reflux for 24 h under Ar. The solvent was removed under vacuum and the residue was purified by chromatography on alumina, eluting with hexanes and then CH_2Cl_2, to afford **1b** as a white powder (535 mg, 74%), mp 222−223 °C: ^{1}H NMR ($CDCl_3$) δ 9.02 (d, J = 0.9 Hz, 2H), 8.90 (d, J = 8.7 Hz, 2H), 8.66 (d, J = 5.1 Hz, 2H), 8.43 (d, J = 8.4 Hz, 2H), 7.89 (s, 2H), 7.28 (dd, J = 5.1, 1.2 Hz, 2H), 2.60 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 155.8, 155.7, 148.8, 148.2, 145.5, 137.2, 129.1, 126.7, 125.3, 123.2, 120.6, 53.4. Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.54; H, 5.01; N, 15.46. Found: C, 79.26; H, 4.82; N, 15.42.

2,9-Di-(4′-dimethylaminopyrid-2′-yl)-1,10-phenanthroline (1c). In the manner described for **1b**, a mixture of 2,9-dichloro-1,10-phenanthroline (125 mg, 0.5 mmol), **7b** (0.82 g, 2.0 mmol), and [$Pd(PPh_3)_2$]Cl_2 (35 mg, 0.05 mmol) in toluene (20 mL) was heated at reflux for 24 h under Ar. Chromatography on alumina, eluting with CH_2Cl_2 followed by CH_2Cl_2/CH_3OH (50:1), afforded a yellow solid which was recrystallized from CH_2Cl_2/hexanes (1:10) to give **1c** as a white powder (105 mg, 50%), mp >270 °C (dec): ^{1}H NMR ($CDCl_3$) δ 8.82 (d, J = 8.4 Hz, 2H), 8.44 (d, J = 5.7 Hz, 2H), 8.38 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 3.0 Hz, 2H), 7.84 (s, 2H), 6.63 (dd, J = 5.7, 3.0 Hz, 2H), 3.20 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 157.0, 156.3, 155.4, 149.1, 145.7, 137.0, 129.1, 126.7, 121.5, 107.0, 105.1, 39.5. Anal. Calcd for $C_{26}H_{24}N_6 \cdot 0.5H_2O$: C, 72.70; H, 5.88; N, 19.57 Found: C, 72.81; H, 5.38; N, 19.39.

2,9-Di-(4′-ethoxycarbonylpyrid-2′-yl)-1,10-phenanthroline (1d). In the manner described for **1b**, a mixture of 2,9-dichloro-1,10-phenanthroline (125 mg, 0.5 mmol), **7d** (0.63 g, 2.0 mmol), and [$Pd(PPh_3)_4$] (60 mg, 0.05 mmol) in toluene (10 mL) was flushed with Ar and heated at reflux for 24 h. Chromatography on alumina, eluting with CH_2Cl_2 followed by CH_2Cl_2/CH_3OH (200:1), afforded **1d** as a white powder (171 mg, 71%), mp 213−214 °C: ^{1}H NMR ($CDCl_3$) δ 9.50 (d, J = 1.5 Hz, 2H), 8.91 (d, J = 4.8 Hz, 2H), 8.84 (d, J = 8.4 Hz, 2H), 8.43 (d, J = 8.1 Hz, 2H), 7.96 (dd, J = 4.8, 1.8 Hz, 2H), 7.89 (s, 2H), 4.51 (q, J = 6.9 Hz, 2H), 1.41 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.3, 157.5, 155.6, 149.8, 145.8, 139.1, 137.3, 129.3, 127.0, 123.2, 121.7, 121.2, 61.8, 14.3. Anal. Calcd for $C_{28}H_{22}N_4O_4$: C, 70.28; H, 4.64; N, 11.71. Found: C, 70.39; H, 4.53; N, 11.32.

2,9-Di-(4′-formylpyrid-2′-yl)-1,10-phenanthroline (1e). To a solution of SeO_2 in 1,4-dioxane (3 mL) and water (0.1 mL) at 60 °C was added a solution of 2,9-di-(4′-methylpyrid-2′-yl)-1,10-phenanthroline (**1b**, 106 mg, 0.29 mmol) in 1,4-dioxane (3 mL) dropwise, producing some white precipitate which disappeared shortly. The mixture was refluxed for 24 h, giving a light yellow solution along with some dark gray precipitate. The 1,4-dioxane was evaporated and the residue was chromatographed on alumina, eluting with CH_2Cl_2/MeOH (5%). The first fraction gave 24 mg (21%) of a colorless solid, mp 254−255 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.45 (s, 2 H), 9.60 (d, J = 1.5 Hz, 2 H), 8.97 (d, J = 4.8 Hz, 2 H), 8.84 (d, J = 8.1 Hz, 2 H), 8.40 (d, J = 8.1 Hz, 2 H), 7.86 (s, 2 H), 7.80 (dd, J = 1.5, 5.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 157.9, 154.6, 150.4, 145.4, 142.7, 137.3, 129.4, 127.0, 121.9, 121.6, 120.4; FTIR (cm^{-1}) 1698 ($\upsilon_{C=O}$).

2,9-Di-(*N*-methylimidazo-2′-yl)-1,10-phenanthroline (3). A mixture of 2,9-dichloro-1,10-phenanthroline (233 mg, 0.94 mmol), **8** (1.11 g, 3.0 mmol), and [$Pd(PPh_3)_4$] (0.12 g, 0.1 mmol) in dry toluene (15 mL) was heated at reflux for 12 h under Ar. The precipitate was collected and washed with hexanes and ether to afford **3** as black crystals (271 mg, 85%), mp 200−201 °C: ^{1}H NMR ($CDCl_3$) δ 8.57 (d, J = 8.7 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H), 7.79 (s, 2H), 7.24 (s, 2H), 7.09 (s, 2H), 4.50 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.4, 145.3, 145.2, 136.7, 128.8, 128.1, 126.5, 124.6, 122.7, 36.2. Recrystallization from CH_2Cl_2/hexanes gave a pure sample. Anal. Calcd for $C_{20}H_{16}N_6 \cdot 0.5H_2O$: C, 68.75; H, 4.90; N, 24.05. Found: C, 68.99; H, 4.39; N, 24.10.

2,9-Di-(*N*-methylbenzimidazo-2′-yl)-1,10-phenanthroline (4). A mixture of 1,10-phenanthroline-2,9-dicarboxylic acid (536 mg, 2.0 mmol) and *N*-methyl-1,2-phenylenediamine (732 mg, 6.0 mmol) was mechanically stirred in PPA (5 mL) at 180 °C for 1.5 h. Additional *N*-methyl-1,2-phenylenediamine (244 mg, 2.0 mmol) was added, and the mixture was stirred at 180 °C for another 2 h. The dark red melt was added to ice water (50 mL) with strong stirring. The precipitate was collected and stirred in hot Na_2CO_3 solution (10%, 30 mL) for 1 h. After cooling, the precipitate was collected, washed with water, and dried in air. It was purified by chromatography on alumina, eluting with CH_2Cl_2 and then CH_2Cl_2/CH_3OH (100:1), to yield **4** as a white solid (446 mg, 51%), mp 295−296 °C: ^{1}H NMR ($CDCl_3$) δ 8.82 (d, J = 8.1 Hz, 2H), 8.44 (d, J = 8.7 Hz, 2H), 7.92 (s, 2H), 7.90 (s, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.40 (m, 4H), 4.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.5, 150.2, 145.3, 142.7, 137.4, 137.0, 128.8, 127.2, 124.3, 123.8, 122.9, 120.3, 110.1, 32.9. Anal. Calcd for $C_{28}H_{20}N_6 \cdot 0.25H_2O$: C, 75.57; H, 4.65; N, 18.89. Found: C, 75.57; H, 4.48; N, 18.98.

2,9-Di-(quinolin-2′-yl)-1,10-phenanthroline (5a). A suspension of 2,9-diacetyl-1,10-phenanthroline (102 mg, 0.38 mmol), 2-aminobenzaldehyde (150 mg, 1.24 mmol), KOH (100 mg), and EtOH (15 mL) was refluxed for 40 h. The yellow precipitate was collected, washed with ethanol, and air-dried to afford 105 mg (64%) of the product, mp 275−277 °C: ^{1}H NMR ($CDCl_3$) δ 9.35 (d, J = 8.7 Hz, 2 H), 9.20 (d, J = 8.7 Hz, 2 H), 8.51 (t, J = 8.4 Hz, 4 H), 8.30 (d, J = 7.8 Hz, 2 H), 7.96 (d, J = 9.9 Hz, 2 H), 7.94 (s, 2 H), 7.80 (dt, J = 0.6, 6.9 Hz, 2 H), 7.63 (dt, J = 1.2, 7.5 Hz, 2 H). Anal. Calcd for $C_{30}H_{18}N_4 \cdot 0.6$ KOH: C, 76.97; H, 4.04; N, 11.97. Found: C, 76.96; H, 3.97; N, 11.80.

2,9-Di-(pyrid-2′-yl)-1,10-phenanthroline-5,6-dione (10). A mixture of 2,9-di-(pyrid-2′-yl)-1,10-phenanthroline (668 mg, 2.0 mmol) and KBr (2.38 g, 20 mmol) was placed in an ice/salt bath. Ice-cold concd H_2SO_4 (8 mL) was added dropwise, and then ice-cold concd HNO_3 (4 mL) was added slowly. The resulting solution was heated at 85 °C for 2 h and then was poured into ice (150 g). The yellow precipitate was collected, washed with saturated aqueous $NaHCO_3$ and water, and dried in air to give **10** (625 mg, 86%) as a yellow powder, mp >300 °C: ^{1}H NMR ($CDCl_3$) δ 8.82 (d, J = 8.1 Hz,

2H), 8.74 (d, $J = 3.6$ Hz, 2H), 8.58 (d, $J = 8.4$ Hz, 2H), 8.15 (d, $J = 8.1$ Hz, 2H), 7.93 (dt, $J = 7.8$, 2.1 Hz, 2H), 7.41 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 189.0, 163.3, 161.2, 154.7, 149.3, 137.1, 132.4, 130.1, 124.8, 122.8, 122.3.

3,6-Di-(pyrid-2′-yl)-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (6). A mixture of 2,9-di-(pyrid-2′-yl)-1,10-phenanthroline-5,6-dione (**10**, 364 mg, 1.0 mmol) and *o*-phenylenediamine (324 mg, 3.0 mmol) in ethanol (20 mL) was refluxed for 3 h. The mixture was cooled and the precipitate was collected, washed with ethanol, acetone, and dried in air to yield **6** (425 mg, 97%) as a yellow powder, mp >300 °C: ^{1}H NMR ($CDCl_3$) δ 9.79 (d, $J = 8.7$ Hz, 2H), 9.10 (d, $J = 7.8$ Hz, 2H), 9.02 (d, $J = 8.4$ Hz, 2H), 8.84 (d, $J = 4.2$ Hz, 2H), 8.39 (q, $J = 3.6$ Hz, 2H), 8.08 (dt, $J = 8.1$, 1.8 Hz, 2H), 7.94 (q, $J = 3.3$ Hz, 2H), 7.48 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 157.8, 155.7, 149.1, 147.7, 142.5, 141.2, 137.2, 134.8, 130.6, 129.6, 127.8, 124.5, 122.3, 121.4. Anal. Calcd for $C_{28}H_{16}N_6 \cdot 1/3CHCl_3$: C, 71.51; H, 3.46; N, 17.66. Found: C, 71.51; H, 3.53; N, 17.83.

[Ru(1b)(2b)$_2$](PF$_6$)$_2$. A mixture of [Ru(DMSO)$_4$Cl$_2$] (53 mg, 0.11 mmol) and **1b** (36.2 mg, 0.10 mmol) in absolute ethanol (15 mL) was refluxed for 1 h under Ar. Water (6 mL), **2b** (0.5 mL, 5.1 mmol), triethylamine (0.3 mL), and LiCl (5 mg) were introduced. The mixture was further refluxed for 24 h, generating a purple-brown solution which was concentrated, treated with water, and filtered. To the filtrate was added NH_4PF_6 (163 mg, 1 mmol) to give a dark precipitate, which was collected. After chromatography on alumina, eluting with acetone, a purple-brown solid (91 mg, 97%) was obtained: ^{1}H NMR (acetone-d_6) δ 10.05 (d, $J = 5.4$ Hz, 2H), 8.84 (d, $J = 9.0$ Hz, 2H), 8.77 (d, $J = 8.4$ Hz, 2H), 8.57 (s, 2H), 8.54 (s, 2H), 7.96 (d, $J = 5.7$ Hz, 2H), 7.90 (d, $J = 6.9$ Hz, 4H), 6.88 (d, $J = 6.0$ Hz, 4H), 2.87 (s, 6H), 2.66 (s, 6H). Anal. Calcd for $C_{36}H_{32}N_6F_{12}P_2Ru$: C, 46.01; H, 3.43; N, 8.94. Found: C, 45.97; H, 3.08; N, 8.90.

[Ru(1c)(2b)$_2$](PF$_6$)$_2$. The same procedure as described for [Ru(**1b**)(**2b**)$_2$](PF$_6$)$_2$ was followed using **1c** (42.0 mg, 0.10 mmol), [Ru(DMSO)$_4$Cl$_2$] (53 mg, 0.11 mmol), and **2b** (0.5 mL, 5.1 mmol) to afford a purple-brown solid (88 mg, 88%): ^{1}H NMR (acetone-d_6) δ 9.55 (d, $J = 6.6$ Hz, 2H), 8.86 (d, $J = 9.0$ Hz, 2H), 8.66 (d, $J = 8.4$ Hz, 2H), 8.50 (s, 2H), 7.81 (d, $J = 3.0$ Hz, 2H), 7.77 (d, $J = 5.7$ Hz, 4H), 7.14 (dd, $J = 6.6$, 3.3 Hz, 2H), 6.87 (d, $J = 5.7$ Hz, 4H), 3.28 (s, 12H), 2.88 (s, 6H). Anal. Calcd for $C_{38}H_{38}N_8F_{12}P_2Ru$: C, 45.74; H, 3.85; N, 11.23. Found: C, 45.77; H, 3.90; N, 10.71.

[Ru(3)(2b)$_2$](PF$_6$)$_2$. The same procedure as described for [Ru(**1b**)(**2b**)$_2$](PF$_6$)$_2$ was followed using **3** (34.0 mg, 0.10 mmol), [Ru(DMSO)$_4$Cl$_2$] (53 mg, 0.11 mmol), and **2b** (0.5 mL, 5.1 mmol) in absolute ethanol (15 mL). The crude product was purified by chromatography on alumina eluting with acetone to afford a purple solid (73 mg, 80%): ^{1}H NMR (acetone-d_6) δ 8.63 (d, $J = 8.1$ Hz, 2H), 8.61 (d, $J = 9.0$ Hz, 2H), 8.45 (s, 2H), 8.34 (d, $J = 1.8$ Hz, 2H), 7.81 (d, $J = 3.6$ Hz, 2H), 7.80 (d, $J = 5.7$ Hz, 4H), 6.86 (d, $J = 5.7$ Hz, 4H), 4.38 (s, 6H), 2. 87 (s, 6H). Recrystallization from acetone/water gave purple-brown crystals. Anal. Calcd for $C_{32}H_{30}N_8F_{12}P_2Ru$: C, 41.88; H, 3.30; N, 12.21. Found: C, 42.03; H, 3.03; N, 12.03.

[Ru(4)(2b)$_2$](PF$_6$)$_2$. The same procedure as described for [Ru(**1b**)(**2b**)$_2$](PF$_6$)$_2$ was followed using **4** (22.0 mg, 0.050 mmol), [Ru(DMSO)$_4$Cl$_2$] (25 mg, 0.052 mmol), and **2b** (0.3 mL, 3.1 mmol) to afford a purple-brown solid (18 mg, 35%): ^{1}H NMR (acetone-d_6) δ 9.11 (d, $J = 8.7$ Hz, 2H), 9.06 (d, $J = 8.4$ Hz, 2H), 8.82 (d, $J = 8.7$ Hz, 2H), 8.62 (s, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.96 (t, $J = 7.5$ Hz, 2H), 7.83 (t, $J = 7.5$ Hz, 2H), 7.73 (d, $J = 6.0$ Hz, 4H), 6.69 (d, $J = 6.0$ Hz, 4H), 4.67 (s, 6H), 2.82 (s, 6H). Anal. Calcd for $C_{40}H_{34}N_8F_{12}P_2Ru$: C, 47.20; H, 3.37; N, 11.01. Found: C, 47.54; H, 3.14; N, 10.72.

[Ru(5a)(2b)$_2$](PF$_6$)$_2$. A mixture of 2,9-di-(quinolin-2′-yl)-1,10-phenanthroline (20 mg, 0.046 mmol), $RuCl_3 \cdot 3H_2O$ (16 mg, 0.61 mmol), and ethylene glycol (3 mL) was refluxed in a microwave (3×6 min). To the reaction mixture were added water (5 mL), Et_3N (0.3 mL), EtOH (5 mL), LiCl (20 mg), and 4-methylpyridine (0.5 mL). The mixture was refluxed overnight. Water (5 mL) and NH_4PF_6 (196 mg, 1.2 mmol) were added in that order to give a precipitate, which was collected and washed with water. Column chromatography on alumina, eluting with acetone and CH_2Cl_2 gave a purple fraction. Evaporation of the solvents afforded a reddish solid (6.2 mg, 13%): ^{1}H NMR (acetone-d_6) 9.27 (d, $J = 8.1$ Hz, 2 H), 9.20 (t, $J = 9.0$ Hz, 4 H), 9.08 (d, $J = 8.7$ Hz, 2 H), 8.86 (d, $J = 9.0$ Hz, 2 H), 8.54 (s, 2 H), 8.42 (dd, $J = 1.8$, 8.4 Hz, 2 H), 8.04 (dt, $J = 0.9$, 7.8 Hz, 2 H), 7.93(dt, $J = 1.5$, 8.4 Hz, 2 H), 7.39 (dd, $J = 1.2$, 5.7 Hz, 4 H), 6.69 (d, $J = 6.3$ Hz, 4 H), 1.95 (s, 6 H); MS: m/z 1070 $(M + C_3H_6O)^+$.

[Ru(5b)(2b)$_2$](PF$_6$)$_2$. A mixture of 2,9-di-(1′,8′-naphthyrid-2′-yl)-1,10-phenanthroline (54.6 mg, 0.125 mmol), $RuCl_3 \cdot 3H_2O$ (32 mg, 0.122 mmol), EtOH (30 mL), and MeOH (4 mL) was refluxed for 2 h before the addition of water (5 mL), Et_3N (0.3 mL), and 4-methylpyridine (1.0 mL). The mixture was further refluxed for 40 h. The solvents were evaporated, and water (5 mL) was added. The addition of aqueous KPF_6 (satd) produced a precipitate which was collected and washed with water. Column chromatography on alumina, eluting with acetone and acetone/KPF_6, gave a green fraction. Evaporation of the solvent afforded a green solid (8.3 mg, 7%): ^{1}H NMR (acetone-d_6) 9.99 (dd, $J = 1.8$, 3.9 Hz, 2 H), 9.36 (d, $J = 8.7$ Hz, 2 H), 9.07 (d, $J = 8.1$ Hz, 2 H), 8.92 (d, $J = 8.4$ Hz, 4 H), 8.83 (dd, $J = 2.1$, 4.8 Hz, 2 H), 8.71 (s, 2 H), 8.27 (d, $J = 6.6$ Hz, 4 H), 8.20 (dd, $J = 4.5$, 8.1 Hz, 2 H), 6.62 (d, $J = 6.0$ Hz, 2 H), 1.92 (s, 6H); MS: m/z 1075 $(M + C_3H_6O)^+$.

[Ru(6)(2b)$_2$](PF$_6$)$_2$. The same procedure as described for [Ru(**1b**)(**2b**)$_2$](PF$_6$)$_2$ was followed using **6** (43.6 mg, 0.10 mmol), [Ru(DMSO)$_4$Cl$_2$] (53 mg, 0.11 mmol), and **2b** (0.5 mL, 5.1 mmol) to afford a purple-brown solid (33 mg, 33%): ^{1}H NMR (acetone-d_6) 10.32 (d, $J = 5.7$ Hz, 2H), 9.55 (d, $J = 9.0$ Hz, 2H), 9.07 (d, $J = 8.7$ Hz, 2H), 8.76 (d, $J = 7.8$ Hz, 2H), 8.60 (q, $J = 3.3$ Hz, 2H), 8.42 (dt, $J = 8.7$, 1.5 Hz, 2H), 8.30 (q, $J = 3.3$ Hz, 4H), 8.21 (d, $J = 4.8$ Hz, 4H), 8.18 (m, 2H), 6.89 (d, $J = 5.4$ Hz, 2H). Anal. Calcd for $C_{40}H_{30}N_8F_{12}P_2Ru \cdot 1/3DMSO$: C, 46.98; H, 3.10; N, 10. 78. Found: C, 46.98; H, 2.73; N, 10.47.

X-ray Determination of [Ru(3)(2b)$_2$](PF$_6$)$_2$. 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 30 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 pathlength 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 3480 reflections having $I > 10\sigma(I)$, and these, along with other information pertinent to data collection and refinement, are listed in Table S2. The Laue symmetry was determined to be -1, and the space group was shown to be either $P1$ or $P\bar{1}$. Both independent anions were found to be disordered, and this was treated by refinement of ideal rigid bodies at each of the major orientations, having occupancy factors based on comparison of their average isotropic displacement parameters.

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Supporting Information Available: ^{1}H NMR data for tetradentate ligands and their Ru(II) complexes, data collection and processing parameters for [Ru(**3**)(**2b**)$_2$](PF$_6$)$_2$, and X-ray crystallographic data for [Ru(**3**)(**2b**)$_2$](PF$_6$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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