Inorg. Chem. **2005**, *44*, 8733–8739

[1,10]-Phenanthrolin-2-yl Ketones and Their Coordination Chemistry

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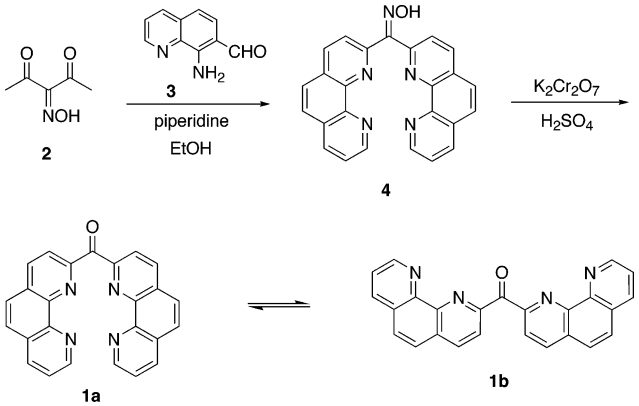
Received June 17, 2005

A synthetic protocol involving the Friedländer reaction of 8-amino-7-quinolinecarbaldehyde followed by potassium dichromate oxidation was applied to 2,3,4-pentanetrione-3-oxime and 1-(pyrid-2′-yl)propane-1,2-dione-1-oxime to provide the ligands di-(phenathrolin-2-yl)-methanone (**1**) and phenanthrolin-2-yl-pyrid-2-yl-methanone (**8**), respectively. Ligand **1** complexed as a planar tetradentate with Pd(II) to form [Pd(**1**)]$(BF_4)_2$ and with Ru(II) and two 4-substituted pyridines (4-R-py) to form [Ru(**1**)(4-R-py)$_2$]$(PF_6)_2$ where R = CF_3, CH_3, and Me_2N. With [Ru(bpy)$_2$Cl$_2$], the dinuclear complex [(bpy)$_2$Ru(**1**)Ru(bpy)$_2$]$(PF_6)_4$ was formed (bpy = 2,2′-bipyridine). Ligand **8** afforded the homoleptic Ru(II) complex [Ru(**8**)$_2$]$(PF_6)_2$, as well as the heteroleptic complex [Ru(**8**)(tpy)]$(PF_6)_2$ (tpy = 2,2′;6,2″-terpyridine). The ligands and complexes were characterized by their NMR and IR spectra, as well as an X-ray structure determination of [Ru(**1**)(4-CH_3-py)$_2$]$(PF_6)_2$. Electrochemical analysis indicated metal-based oxidation and ligand-based reduction that was consistent with results from electronic absorption spectra. The complexes [Ru(**1**)(4-R-py)$_2$]$(PF_6)_2$ were sensitive to the 4-substituent on the axial pyridine: electron donor groups facilitated the oxidation while electron-withdrawing groups impeded it.

The carbonyl group is an interesting linker in the construction of polypyridine ligand systems. The parent member of such a ligand family, di-(2-pyridyl)-ketone (DPK), is commercially available, and its complexation with a variety of metals has been studied.[1] The complex [Ru(DPK)(bpy)$_2$]$^{2+}$, where bpy = 2,2′-bipyridine, is well behaved and shows interesting reactivity of the carbonyl group.[2] Metal complexation increases the electrophilic character of the carbonyl, leading to the formation of a stable hydrate. In the hopes of examining an analogous system having higher denticity, we explored various routes to the preparation of ketones derived from 1,10-phenanthroline (phen).

The reaction of a 1,10-phenanthrolin-2-yl anion with an appropriate 2R-substituted phen (R = CN, CHO, or COCl) was problematic, and thus, we considered employing the Friedländer methodology which we have previously found quite useful for the preparation of various substituted phens.[3] In principle, the 2:1 reaction of 8-amino-7-quinolinecarbaldehyde (**3**) with 2,4-pentanedione might directly provide the diphen ketone **1**, except that the more highly activated central methylene of the diketone would direct the initial condensation to provide undesired 2-methyl-3-acetylphen as the intermediate.[4] This problem was solved by protecting the central methylene through formation of the oxime **2**. This oxime then reacted in a 2:1 fashion with the aminoaldehyde **3** to provide the bis-phen ketone oxime **4** that could be oxidatively cleaved to the ketone **1**.

The diphen ketone **1** may exist in three planar conformations, the anti, anti (**1a**), the syn, syn (**1b**), and an anti, syn



conformation. Conformation **1a** presents an interesting, well-organized tetradentate coordination environment, while

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(1) (a) Basu, A.; Saple, A. R.; Sapre, N. Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1797−1799. (b) Ishaq, M.; Bagklaf, A. O.; Al-Mouty, A.; Al-Doursry, M. *J. Chem. Soc. Pak.* **1992**, *14*, 115−117.

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10.1021/ic050996k CCC: $30.25
Published on Web 10/27/2005

conformation **1b** provides two bi- or tridentate sites depending on possible coordination through the carbonyl oxygen.[5]

Treatment of **1** with $[Pd(CH_3CN)_4](BF_4)_2$ provided an 82% yield of the 1:1 complex $[Pd(\mathbf{1a})](BF_4)_2$ which was characterized by its simple and symmetric NMR spectrum. Coordination of **1** with Ru(II) may occur through conformation **1a** leading to a tetradentate complex in which **1a** occupies the equatorial plane and two 4-substituted pyridines are introduced as axial ligands. The yields are modest, 14−17%, and again the NMR is quite characteristic, especially indicating the axial ligands which exhibit an AA′BB′ pattern accounting for eight protons. When the ligand **1** is treated with $[Ru(bpy)_2Cl_2]$, only bidentate complexation is possible and the ligand thus behaves as a bis-bidentate, incorporating two metals in a yield of 49%. The two metal centers are stereogenic so that the complex exists as a mixture of meso- and ΔΔ, ΛΛ-forms. As a consequence of the lack of symmetry, the ^{1}H NMR is too complicated for a meaningful interpretation.

A tridentate species intermediate in structure between DPK and **1** would be 1,10-phenanthrolin-2-yl pyrid-2-yl ketone (**8**). This material could be prepared in a manner similar to

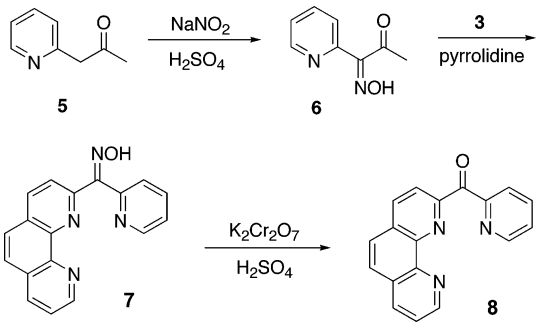


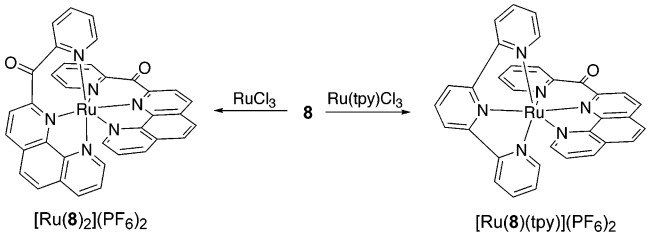
Table 1. Selected Geometric Data for $[Ru(\mathbf{1a})(4\text{-}CH_3\text{-}py)_2](PF_6)_2$[a]

bond lengths (Å)			
Ru−N1	2.109(6)	Ru−N31	2.110(6)
Ru−N12	2.027(6)	Ru−N38	2.097(6)
Ru−N17	2.015(7)	C15−O16	1.229(10)
Ru−N28	2.108(6)		
bond angles (deg)			
N1−Ru−N12	80.0(2)	N1−Ru−N38	87.8(2)
N17−Ru−N28	80.2(3)	N12−Ru−N38	88.9(2)
N12−Ru−N17	92.9(3)	C11−C15−C18	126.6(7)
N1−Ru−N28	106.8(2)	C11−C15−O16	116.2(8)
N31−Ru−N38	177.1(2)	C18−C15−O16	117.2(8)
torsion angles (deg)			
N17−C18−C15−O16	−163.5(8)	N12−C11−C15−O16	165.0(7)
distances (Å)			
N12−N17	2.929	N1−N28	3.385

[a] Atom numbering scheme given in Figure 1.

1. A previous report described a two-step photochemical route which afforded oxime **6** in 12% yield.[6] We prepare this same species in 65% yield from pyrid-2-yl acetone[7] by treatment with sodium nitrite in sulfuric acid. The oxime reacted with **3** in the presence of pyrrolidine to afford the oxime **7** that was oxidatively cleaved in 53% yield to the desired ketone, **8**.

The ligand **8** coordinates with Ru(II) in a tridentate fashion using its three nitrogens. Upon treatment with $RuCl_3$, it forms a homoleptic 2:1 complex in 78% yield. Due to the unsymmetrical nature of the ligand **8**, the complex is chiral and is formed as a racemic mixture. An achiral heteroleptic complex was also prepared in 42% yield by the treatment of **8** with $[Ru(tpy)Cl_3]$.



The $[Ru(\mathbf{1a})(4\text{-}CH_3\text{-}py)_2](PF_6)_2$ complex was further characterized by a single-crystal X-ray analysis, selected geometric data are collected in Table 1, and an ORTEP drawing

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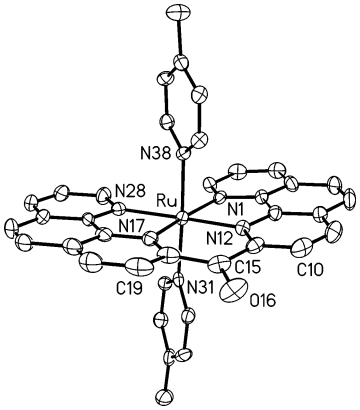

Figure 1. ORTEP drawing of the cation of $[Ru(\mathbf{1a})(4\text{-}CH_3\text{-}py)_2](PF_6)_2$ with atom numbering scheme.

of the cation is given in Figure 1. The ruthenium is not equidistant from the four nitrogens of ligand **1**. It lies closer (2.02 and 2.03 Å) to the interior nitrogens N12 and N17 as compared with the exterior N1 and N28 (2.11 Å). If one assumes the axial Ru−N bonds to be approximately normal (2.10 and 2.11 Å), then the bonds to N12 and N17 are unusually short.

The N−Ru−N bite angles involving a single phen (80.0 and 80.2°) are close to the expected angle of about 80° for Ru-phen complexes.[8] The two N−Ru−N angles involving both phen rings (92.9 and 106.8°) differ considerably, indicating that the ligand is more open at the end opposite the carbonyl group. This splaying of the ligand is further evidenced upon comparing the nonbonded distances N12−N17 (2.93 Å) and N1−N28 (3.38 Å). Another indicator of this same effect is the carbonyl group. The C11−C15−C18 angle is larger (126.6°) than the trigonal sp^2 angle. The sum of angles around C15 is exactly 360°, indicating that C11, C15, C18, and O16 all lie in the same plane. However, the torsion angles N12−C11−C15−O16 (165.0°) and N17−C18−C15−O16 (163.5°) deviate an average of 15.8° from 180°, showing that the carbonyl group lies outside the approximate equatorial plane by this amount.

The axial ligands are almost linearly disposed where N31−Ru−N38 is 177.1°. Although one could imagine that the possible steric interference between C28−H and C2−H could lead to a slight helicity of the ligand, this interaction is instead relieved by a small puckering effect so that the four N(phen)-Ru−N38 angles average about 89.1° while the four N(phen)-Ru−N31 angles are larger at an average of 91.0°.

The electronic absorption spectra of the ligands and their Ru(II) complexes have been measured, and the data are collected in Table 2. Ligand **1**, having a more delocalized π system, shows a slightly lower-energy $\pi-\pi^*$ absorption than ligand **8**. In considering the tetradentate complexes, three regions are observed in their electronic absorption spectra (Figure 2). At higher energy, each complex exhibits four bands between 232 and 352 nm which may be associated with $\pi-\pi^*$ absorptions of the associated ligands. In the region of 415−464 nm appear bands attributed to metal-to-ligand charge transfer (MLCT) transitions. These bands involve the promotion of an electron from a metal d orbital to a π^* orbital of **1**. The energy of this transition is sensitive to the electron-donating ability of the axial pyridine ligand. The stronger donor, 4-NMe_2-py ($\lambda_{max} = 464$ nm), destabilizes the d level more than the weaker donor, 4-CF_3-py ($\lambda_{max} = 415$ nm), with the 4-Me-py being intermediate in behavior ($\lambda_{max} = 437$ nm). At lower energy, a weak band is observed which may be assigned to a d−d transition (Figure 2, inset). These bands are even more sensitive to the electronic nature of the axial pyridine ligands. The electron-withdrawing 4-CF_3-py gives a band at 603 nm; the electron-donating 4-NMe_2-py gives a band at 735 nm; and the intermediate 4-Me-py gives a band at 649 nm. The dinuclear complex $[(bpy)_2Ru(\mathbf{1})Ru(bpy)_2](PF_6)_4$ shows strong $\pi-\pi^*$ bands at 284 and 344 nm, as well as a relatively strong MLCT absorption at 436 nm. All the complexes of ligand **1**, mono- and dinuclear, were nonemissive at room temperature in acetonitrile.

The absorption properties of the complexes of **8** are consistent with the structures of the ligands. The homoleptic complex $[Ru(\mathbf{8})_2](PF_6)_2$ shows the simpler spectrum with four higher-energy $\pi-\pi^*$ absorptions attributable to ligand **8**. The MLCT occurs at relatively low energy (549 nm). For the heteroleptic complex $[Ru(\mathbf{8})(tpy)](PF_6)_2$, seven bands are reported in the $\pi-\pi^*$ region in agreement with the two different ligands complexed with Ru(II). In the MLCT region, two bands are observed. The lower-energy band at 536 nm is associated with charge transfer into the more electronegative ligand **8** while the higher energy band at 451 nm corresponds to MLCT into the terpyridine ligand.

When the two complexes of ligand **8** were excited at 532 nm, where the MLCT portions of their absorption spectra intersect, they both showed weak emission. The emission for the homoleptic complex $[Ru(\mathbf{8})_2](PF_6)_2$ appeared at 772 nm ($\Phi = 1.77 \times 10^{-4}$), while that of the heteroleptic complex $[Ru(\mathbf{8})(tpy)](PF_6)_2$ appeared at 796 nm ($\Phi = 1.30 \times 10^{-4}$). For comparison, we measured the emission of $[Ru(\mathbf{9})_2](PF_6)_2$ where **9** = 2-(2′-pyridyl)-1,10-phenanthroline.[9] When excited at 525 nm, where it had the same absorbance as the complexes of **8**, this model complex showed only very weak emissions at 620 and 662 nm ($\Phi = 1.56 \times 10^{-5}$). The increased emission intensity for the complexes of **8** as compared with **9** is associated with longer excited-state lifetimes due to less strain in the ligand field. In turn, this diminished strain is due to incorporation of the carbonyl group that expands one chelate ring from five atoms to six. Consistent with this interpretation, emission from the homoleptic complex is stronger than that from the heteroleptic one. In a separate study, we are examining the effects of six-membered ring chelation in greater detail for a variety of related Ru(II) complexes.[10]

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(10) Work in progress.

Table 2. Electronic and Infrared Absorption Data for **1** and **8** and Their Ru(II) Complexes[a]

compound	λ_{max} (log ϵ)[b]	$\nu_{C=O}$ (cm^{-1})
1	268 (4.57), 279 (4.57)	1674
8	277 (4.38)	1666
[Ru(**1**)(4-CF_3-py)$_2$](PF_6)$_2$	233 (4.68), 262 (4.52), 296 (4.34), 352 (4.32), 415 (3.98), 449 (sh, 3.88), 603 (3.24)	1660
[Ru(**1**)(4-CH_3-py)$_2$](PF_6)$_2$	232 (4.76), 260 (4.63), 300 (4.48), 325 (4.34), 437 (4.01), 463 (4.00), 649 (3.30)	1654
[Ru(**1**)(4-NMe_2-py)$_2$](PF_6)$_2$	235 (4.67), 259 (4.73), 302 (4.67), 350 (4.05), 464 (3.94), 735 (3.31)	1625
[Ru(**8**)$_2$](PF_6)$_2$	247 (4.68), 284 (4.65), 304 (4.51), 338 (4.33), 549 (3.75)	1662
[Ru(**8**)(tpy)](PF_6)$_2$	219 (4.70), 242 (4.57), 272 (4.55), 281 (4.57), 305 (4.63), 331 (4.37), 382 (3.86), 451 (3.96), 536 (3.70)	1652
[(bpy)$_2$Ru(**1**)Ru(bpy)$_2$](PF_6)$_4$	284 (5.09), 344(4.26), 436 (4.32)	1605

[a] Wavelength reported in nanometers. [b] 2×10^{-5} M in CH_3CN at 25 °C.

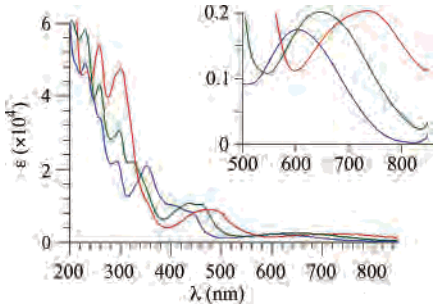

Figure 2. Long-wavelength region of the electronic absorption spectra of [Ru(**1**)(4-R-py)$_2$](PF_6)$_2$ in CH_3CN (2.0×10^{-5} M); R = CF_3 (blue), CH_3 (green), NMe_2 (red). Inset recorded at 2×10^{-4} M.

The infrared carbonyl stretching frequencies are also consistent with ligand structure. The more delocalized ligand **8** shows an expected lower-frequency C=O stretch as compared with **1**. The series of tetradentate complexes shows a trend toward lower frequency as the axial ligand becomes a better donor, implying a lower C−O bond order along the series. The dinuclear complex [(bpy)$_2$Ru(**1**)Ru(bpy)$_2$](PF_6)$_4$ shows a remarkably low frequency absorption which may be partially explained by the steric bulk of the two [(phen)-Ru(bpy)$_2$] fragments joined by the carbonyl group. These bulky substituents may distort the sp^2 nature of the carbonyl, leading to a lower C−O bond order. The difference in the stretching frequency of the two complexes of **8** is less easily explained.

The redox potentials of the ligands and complexes were measured in CH_3CN, and the data are summarized in Table 3. The ligands show two irreversible reductions. It is expected that the first reduction would involve the addition of an electron to the C=O, and the second reduction would be associated with a phen ring. Oxidation of the metal complexes involves the removal of an electron from a ruthenium d orbital, and thus, for the tetradentate complexes, one observes a strong dependence on the axial ligand. The 4-CF_3-py ligand destabilizes the Ru(III) state and thus affords the highest potential at +1.59 V. The effect diminishes with 4-CH_3-py (+1.47 V) and is lowest with 4-NMe_2-py at a potential of +1.12 V. This effect closely mirrors what was observed for the MLCT electronic transition. Two reduction waves are observed for these three systems where electron donation is generally associated with a π^* orbital on the most-electronegative ligand. Metal complexation tends to increase electron affinity, and thus, we assign the first reduction to the C=O group of ligand **1**. The low reduction potential for the 4-CF_3-py system may involve the addition of an electron to the axial ligand. For the dinuclear complex, the oxidation is split into two closely overlapping waves centered at +1.58 V, indicating some communication between the metal centers. The three reduction waves correspond to the carbonyl group at −0.52 V and a phen and bpy at −1.12 and −1.57 V, respectively.

Table 3. Redox Potentials of Ruthenium Complexes[a]

compound	$E_{1/2,SCE}$,[b] V (ΔE, mV) oxidations	reductions
1		−1.22[c], −1.46[c]
8		−1.11 (393), −1.37 (365)
[Ru(**1**)(4-CF_3-py)$_2$](PF_6)$_2$	+1.59 (75)	−0.26 (101), −1.52[c]
[Ru(**1**)(4-CH_3-py)$_2$](PF_6)$_2$	+1.47 (87)	−0.36 (83), −1.00[c]
[Ru(**1**)(4-NMe_2-py)$_2$](PF_6)$_2$	+1.12 (98)	−0.36 (174), −1.00 (185)
[Ru(**8**)$_2$](PF_6)$_2$	+1.55 (83)	−0.45 (86), −0.62 (83), −1.21 (84), −1.39 (83)
[Ru(**8**)(tpy)](PF_6)$_2$	+1.44 (91)	−0.56[d](64), −1.14[d](73), −1.44[d](89)
[(bpy)$_2$Ru(**1**)Ru(bpy)$_2$](PF_6)$_4$	+1.58[e](188)	−0.52 (73); −1.12 (70); −1.57[c]

[a] All samples measured in 0.1 M NBu_4PF_6/CH_3CN; concentration of complexes c = 2 mM; T = 25 °C; scan rate υ = 100 mV s^{-1} (1 V s^{-1} for **1**, **8**), $\Delta E = E_{1/2,ap} - E_{1/2,cp}$. [b] Spectra were referenced internally against ferricenium/ferrocene; 460 mV were added to obtain potentials vs. SCE. [c] Irreversible, only E_{cp} given. [d] c = 0.2 mM. [e] Overlapping.

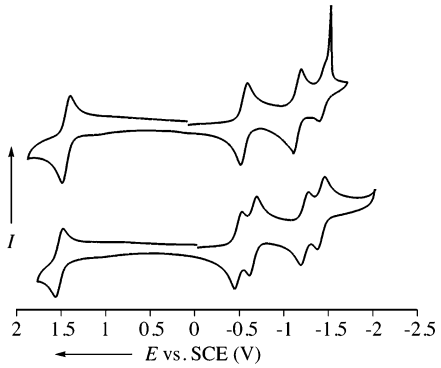

Figure 3. Cyclic voltammogram of [Ru(**8**)(tpy)](PF_6)$_2$ (top) and [Ru(**8**)$_2$]-(PF_6)$_2$ (bottom) measured in 0.1 M NBu_4PF_6/CH_3CN at 25 °C, scan rate = 100 mV s^{-1}. The spike in the third wave (top) is reduced at lower concentration or higher scan rates.

The homo- and heteroleptic complexes of ligand **8** are well behaved. Since **8** is more electronegative than tpy, the oxidation wave for $[Ru(\mathbf{8})_2](PF_6)_2$ is more positive than the oxidation for $[Ru(\mathbf{8})(tpy)](PF_6)_2$. The reduction waves are clearly associated with the ligands (Figure 3). For $[Ru(\mathbf{8})_2](PF_6)_2$, two closely spaced waves at −0.45 and −0.62 V correspond to the addition of an electron to the C═O group of each ligand while the two waves at −1.21 and −1.39 V correspond to the addition of an electron to the phen ring of each ligand. For $[Ru(\mathbf{8})(tpy)](PF_6)_2$, the waves at −0.56 and −1.14 V would similarly correspond to reduction of the carbonyl group and phen ring of **8** while the wave at −1.44 V involves reduction of the tpy ligand.

Experimental Section

NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 (^{1}H) and 75 MHz (^{13}C), respectively, and the spectra were referenced to the residual solvent peak. Coupling constants, *J*, are in Hertz. Infrared spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrophotometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer. Melting points are uncorrected, and CHN analyses were performed by QTI, Whitehouse, NJ.

The synthesis of **2** was a variation of a known method.[11] The 2-pyridyl-acetone,[7] 8-aminoquinoline-7-carbaldehyde,[3a] $[Ru(DMSO)_4Cl_2]$,[12] $[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[13] and $[Ru(tpy)Cl_3]$[14] were prepared according to known procedures. $[Pd(MeCN)_4](BF_4)_2$ was obtained from Strem Chemicals.

Cyclic voltammograms were recorded on a BAS-epsilon voltammograph, using 0.1 M solutions of NBu_4PF_6 (recrystallized from EtOH) in CH_3CN (distilled from CaH_2) as the electrolyte. The concentration of the analyte was typically 2 mM, and the scan rate was 100 mV s^{-1}. The working electrode was glassy carbon, and the auxiliary electrode was a Pt wire. SCE was used as the reference electrode and placed in a separate compartment containing KCl solution. This solution and the analyte were connected through a Pt wire. The voltagramms were referenced internally against ferrocene/ferricenium after each measurement[15] and related to SCE by adding 460 mV. This adjustment was obtained by comparing published[16] and measured values for $E_{1/2}(Ru^{II/III})$ for $[Ru(bpy)_3](PF_6)$.

2,3,4-Pentanetrione-3-oxime (2). To a solution of 2,5-pentanedione (5.00 g, 49.9 mmol) in H_2SO_4 (1 M, 100 mL), $NaNO_2$ (4.14 g, 60.0 mmol) was added over 5 min at room temperature. After 30 min, the mixture was extracted with CH_2Cl_2 (5 × 100 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated to afford **2** (5.48 g, 85%) as a white solid; mp = 69.5−72 °C (lit[11] mp = 75 °C); ^{1}H NMR ($CDCl_3$,): δ 10.27 (s, 1H, NOH), 2.42 (s, 3H, CH_3), 2.41 (s, 3H, CH_3).

1-(Pyrid-2′-yl)propane-1,2-dione-1-oxime (6). To a solution of 2-pyridyl-acetone (407 mg, 3.01 mmol) in H_2SO_4 (0.5 M, 10 mL) was added a solution of $NaNO_2$ (227 mg, 3.30 mmol) in water (1 mL). After 10 min, the mixture was neutralized by the addition of a solution of $NaHCO_3$. The white precipitate was isolated by filtration, washed with water, and dried in vacuo to provide **6** (320 mg, 65%) as a white powder; mp = 138−139 °C (lit[6] mp = 135−137 °C); ^{1}H NMR (acetone-d_6): δ 14.00 (s, 1H, NOH), 8.64 (ddd, 1H, *J* = 4.8, 1.5, 0.9, H6′), 7.94 (ddd, 1H, *J* = 8.1, 7.8, 2.1, H4′), 7.71 (dm, 1H, *J* = 8.4, H3′), 7.48 (ddd, 1H, *J* = 7.5, 5.1, 0.9, H5′), 2.45 (s, 3H, CH_3).

Phenanthrolin-2-yl-pyrid-2-yl-methanone (8). A mixture of **6** (271 mg, 1.65 mmol), 8-aminoquinoline-7-carbaldehyde (**3**, 285 mg, 1.66 mmol), and pyrrolidine (0.3 mL) in 100% EtOH (10 mL) was heated to reflux under Ar for 24 h. The resulting solution was allowed to stand in the open air for 3 days, during which time a precipitate formed. The solvent was evaporated, and the residue was suspended in a mixture of CH_2Cl_2 and hexanes (2:1, 10 mL). The oxime **7** was isolated as a brown powder (338 mg, 68%) and used directly in the next step without further purification. A solution of **7** (325 mg, 1.08 mmol) and $K_2Cr_2O_7$ (318 mg, 1.08 mmol) in 1.8 M H_2SO_2 (45 mL) was left at 25 °C for 20 h and then neutralized with $NaHCO_3$, and CH_2Cl_2 was added. The heterogeneous mixture was filtered through Celite, and the solids were washed with CH_2Cl_2. The aqueous portion of the filtrate was extracted with CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$) and concentrated. Recrystallization from acetone provided **8** (164 mg, 53%) as a cream-colored solid: mp > 280 °C; ^{1}H NMR ($CDCl_3$): δ 9.16 (dd, 1H, *J* = 4.2, 2.1), 8.75 (ddd, 1H, *J* = 3.9, 1.8, 1.2), 8.48 (ddd, 1H, *J* = 7.5, 1.5, 0.6), 8.41 (d, 1H, *J* = 8.1), 8.29−8.25 (m, 2H), 7.91 (td, 1H, *J* = 7.8, 1.8), 7.89−7.83 (m, 2H), 7.63 (dd, 1H, *J* = 8.4, 4.2), 7.47 (ddd, 1H, *J* = 7.5, 4.8, 1.2); ^{13}C NMR ($CDCl_3$): δ 192.6, 154.7, 153.5, 150.5, 149.3, 146.2, 145.2, 136.7, 136.6, 136.1, 129.7, 129.0, 128.4, 126.6, 126.4, 126.2, 123.4, 123.2; IR: 1666, 1329, 949, 680 cm^{-1}. Anal. Calcd for $C_{18}H_{11}N_3O$: C, 75.87; H, 3.89; N, 14.73. Found: C, 74.92; H, 3.44; N, 14.56.

Di-(phenathrolin-2-yl)-methanone Oxime (4). The oxime **2** (235 mg, 1.82 mmol), 8-aminoquinoline-7-carbaldehyde (**3**, 629 mmol, 3.65 mmol), and piperidine (1.0 mL) were heated to reflux under Ar in EtOH (100%, 20 mL) for 72 h. After cooling, filtration, washing with EtOH, and drying in vacuo, a cream-colored powder (517 mg, 71%) was obtained: mp > 280 °C; ^{1}H NMR (DMSO-d_6): δ 13.38 (s, 1H, NOH), 9.01 (dd, 1H, *J* = 4.5, 1.5), 8.86 (dd, 1H, *J* = 4.5, 1.5), 8.69 (d, 1H, *J* = 8.1), 8.62 (d, 1H, *J* = 8.7), 8.52 (dd, 1H, *J* = 8.1, 1.5), 8.44 (dd, 1H, *J* = 8.1, 1.5), 8.34 (d, 1H, *J* = 8.1), 8.14−7.98 (m, 5H), 7.76 (dd, 1H, *J* = 7.5, 4.2), 7.66 (dd, 1H, *J* = 8.4, 4.5); no ^{13}C NMR was obtained due to low solubility; IR: 1618, 1507, 1388, 1108, 980, 856, 691 cm^{-1}.

Di-(phenathrolin-2-yl)-methanone (1). A solution of **4** (1.533 g, 3.82 mmol) and $K_2Cr_2O_7$ (843 mg, 2.87 mmol) in H_2SO_4 (2 M, 90 mL) was kept at 25 °C for 6 h. The mixture was neutralized with $NaCO_3$ solution, and $CHCl_3$ (0.25 L) was added. The heterogeneous mixture was filtered through Celite, and the solids were washed with $CHCl_3$. The aqueous phase was extracted with $CHCl_3$, and the combined organic phases were dried ($MgSO_4$), concentrated, and further dried in vacuo to afford **1** (564 mg, 38%) as a light yellow solid: mp ($CHCl_3$) > 280 °C; ^{1}H NMR ($CDCl_3$): δ 9.16 (dd, 2H, *J* = 4.2, 1.5), 8.88 (d, 2H, *J* = 8.4), 8.51 (d, 2H, *J* = 8.1), 8.27 (d, 2H, *J* = 7.8), 7.90 (s, br., 4H), 7.64 (dd, 2H, *J* = 7.8, 4.5); ^{13}C NMR ($CDCl_3$): δ 191.6, 153.7, 150.5, 146.3, 145.5, 136.7, 136.1, 130.0, 128.9, 128.7, 126.2, 124.9, 123.3; IR: 1674, 1556, 1487, 1393, 1319, 1276, 1103, 976, 863, 842 cm^{-1}. Anal. Calcd for $C_{25}H_{14}N_4O$: C, 77.71; H, 3.65; N, 14.50. Found: C, 77.28; H, 3.34; N, 14.29.

$[Ru(8)_2](PF_6)_2$. In a 100 mL flask, a mixture containing $RuCl_3\cdot 3H_2O$ (27.2 mg, 110 μmol) and **8** (69.3 mg, 242 μmol) in ethylene

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glycol/water (9:1, 8 mL) was briefly sonicated and then heated to reflux in a modified microwave oven[17] for 2 × 4 min. The cooled reaction mixture was added to aqueous NH_4PF_6 (1%, 40 mL). The precipitated complex was isolated by filtration through Celite. It was redissolved in CH_3CN and purified by chromatography (silica, acetone/1 M $NaNO_3$, 85:15). Acetone was evaporated from the product fractions, and the residual solution was added to aqueous NH_4PF_6. The pure complex (83 mg, 78%) was isolated by filtration, washed with water and ether, and dried in vacuo: ^{1}H NMR (CD_3CN): δ 9.20 (d, 2H, J = 8.7), 9.12 (d, 2H, J = 8.4), 8.44 (ddd, 2H, J = 7.8, 1.5, 0.6), 8.40 (d, 2H, J = 8.7), 8.39 (dd, 2H, J = 7.2, 1.2), 8.26 (d, 2H, J = 8.7), 7.86 (ddd, 2H, J = 8.4, 7.5, 1.5), 7.75 (dd, 2H, J = 5.4, 1.2), 7.66 (ddd, 2H, J = 6.0, 1.5, 0.6), 7.43 (dd, 2H, J = 8.1, 5.1), 7.09 (ddd, 2H, J = 5.7, 5.4, 1.5); IR: 1662, 832 cm^{-1}. Anal. Calcd for $C_{36}H_{22}F_{12}N_6O_2P_2Ru$: C, 44.97; H, 2.31; N, 8.74. Found: C, 44.89; H, 1.99; N, 8.65.

[Ru(8)(tpy)](PF$_6$)$_2$. A mixture containing [Ru(tpy)Cl_3] (66.9 mg, 151.8 μmol) and **8** (43.3 mg, 152 μmol) in ethylene glycol (10 mL) was briefly sonicated and then heated to reflux in a modified microwave oven[17] for 2 × 4 min. The cooled reaction mixture was added to aqueous NH_4PF_6 (1%, 40 mL). The precipitated complex was isolated by filtration through Celite and purified by chromatography (silica, acetone/1 M $NaNO_3$, 80:15). Acetone was evaporated from the product fractions, and the residual solution was added to aqueous NH_4PF_6 to afford a brown precipitate. Two consecutive recrystallizations from hot acetone/water gave brown crystals (57.6 mg, 42%): ^{1}H NMR (CD_3CN): δ 9.19 (d, 1H, J = 8.4), 9.02 (d, 1H, J = 8.7), 8.76 (d, 2H, J = 7.8), 8.57 (ddd, 1H, J = 8.1, 1.5, 0.6), 8.54−8.41 (m, 5H), 8.29 (d, 1H, J = 9.0), 7.96−7.85 (m, 3H), 7.67 (ddd, 1H, J = 6.0, 1.5, 0.6), 7.54−7.48 (m, 4H), 7.29 (td, 1H, J = 5.7, 2.1), 7.08 (ddd, 2H, J = 6.0, 5.4, 1.5), IR: 1652, 835 cm^{-1}. Anal. Calcd for $C_{22}H_{22}F_{12}N_6OP_2Ru$: C, 43.58; H, 2.44; N, 9.24. Found: C, 43.47; H, 2.04; N, 9.25.

[Pd(1)](BF$_4$)$_2$. Ligand **1** (20.7 mg, 53.6 μmol) was added to a solution of [Pd(CH_3CN)$_4$](BF$_4$)$_2$ (23.8 mg, 53.6 μmol) in CH_3CN (2 mL). The ligand dissolved quickly, and a yellowish precipitate formed. After 20 h, the solid was isolated by filtration, washed with CH_3CN, and dried in vacuo to afford [Pd(**1**)](BF$_4$)$_2$ (29.2 mg, 82%): ^{1}H NMR (DMSO-d_6): δ 9.64 (d, 2H, J = 5.1), 9.44 (d, 2H, J = 9.0), 9.28 (d, 2H, J = 8.1), 9.11 (d, 2H, J = 9), 9.63, 8.57 (AB, 4H, J = 9.0), 8.45 (dd, 2H, J = 8.4, 5.7); IR: 1691, 1055, 1039 cm^{-1}; ESI-MS (CH_3CN): 578 (13%, [M − BF_4]$^+$), 246 (100%, [M − 2(BF$_4$)]$^{2+}$). Anal. Calcd for $C_{25}H_{14}B_2F_8N_4OPd$: C, 45.06; H, 2.12; N, 8.41. Found: C, 44.99; H, 1.77; N, 8.39.

[Ru(1)(4-CH$_3$-py)$_2$](PF$_6$)$_2$. A solution of [Ru(DMSO)$_4$Cl$_2$] (94.7 mg, 195 μmol) and **1** (75.5 mg, 195 μmol) in dry $CHCl_3$ (800 mL) was heated to reflux under Ar for 48 h. The reaction mixture was concentrated, and the resulting black solid was dried in vacuo and added to a solution of $AgBF_4$ (84 mg, 430 μmol) in degassed MeOH (30 mL). The mixture was heated to reflux under Ar for 20 h. AgCl was removed by filtration under Ar, and 4-methylpyridine (0.40 mL) was added to the filtrate. The mixture was heated to reflux under Ar for 40 h. The solvent was evaporated, and CH_2Cl_2 (8 mL) was added to the residue to precipitate material which was isolated by filtration. Addition of EtOAc (4 mL) to the filtrate yielded more product. The combined precipitate was purified by chromatography (silica, acetone/1 M $NaNO_3$, 100:15). The product fractions were concentrated, and the solid residue was extracted with CH_3CN (80 mL) with the assistance of ultrasound. Filtration gave a dark green solution. The volume was reduced to 2 mL, and water (2 mL) was added. The complex was precipitated with aqueous NH_4PF_6 (1%, 40 mL) and isolated by filtration through Celite. It was washed with water, air-dried, and redissolved in CH_3CN. Filtration and evaporation of the solvent yielded a dark green solid (31.6 mg, 17%): ^{1}H NMR (acetone-d_6): δ 10.69 (dd, 2H, J = 5.1, 1.2), 9.20 (d, 2H, J = 8.7), 9.04 (dd, 2H, J = 7.8, 1.2), 9.02 (d, 2H, J = 8.4), 8.53−8.49 (m, 4H), 8.43 (d, 2H, J = 8.7), 7.93, 6.71 (AA′BB′, 8H), 1.97 (s, 6H); IR: 1654, 1599, 1504, 1389, 1334, 834 cm^{-1}. Anal. Calcd for $C_{37}H_{28}F_{12}N_6OP_2Ru$-0.5 CH_3CN: C, 46.37; H, 3.02; N, 9.25. Found: C, 46.30; H, 2.59; N, 9.25.

[Ru(1)(4-Me$_2$N-py)$_2$](PF$_6$)$_2$. [Ru(DMSO)$_4$Cl$_2$] (100.0 mg, 207 μmol), **1** (79.5 mg, 206 μmol), $AgBF_4$ (88 mg, 45 μmol), and 4-(*N*,*N*-dimethylamino)pyridine (480 mg, 4.0 mmol) were treated as described for the 4-CH_3-py system. The tetrafluoroborate salt crystallized from the methanolic reaction mixture and was isolated by filtration and further purified by chromatography (silica, CH_3CN/1 M $NaNO_3$, 85:15). Precipitation with NH_4PF_6 afforded a brown solid (33.7 mg, 16%): ^{1}H NMR (acetone-d_6): δ 10.66 (dd, 2H, J = 5.1, 1.5), 9.15 (d, 2H, J = 8.1), 9.05 (dd, 2H, J = 8.4, 1.2), 8.97 (d, 2H, J = 9), 8.55−8.44 (m, 6H), 2.67 (s, 12H); IR: 1625, 1229, 841, 821 cm^{-1}. Anal. Calcd for $C_{39}H_{34}F_{12}N_8OP_2Ru\cdot H_2O$: C, 45.05; H, 3.49; N, 10.78. Found: C, 44.94; H, 3.57; N, 10.72.

[Ru(1)(4-CF$_3$-py)$_2$](PF$_6$)$_2$. [Ru(DMSO)$_4$Cl$_2$] (100.0 mg, 207 μmol), **1** (79.5 mg, 206 μmol), $AgBF_4$ (88 mg, 45 μmol), and 4-trifluoromethylpyridine (600 mg, 4.0 mmol) were treated as described for the 4-CH_3-py system. The tetrafluoroborate salt crystallized from the methanolic reaction mixture and was isolated by filtration and further purified by chromatography (silica, CH_3CN/1 M $NaNO_3$, 85:15). Precipitation with NH_4PF_6 afforded a dark green solid (31.7 mg, 14%): ^{1}H NMR (acetone-d_6): δ 10.67 (dd, 2H, J = 5.1, 1.2), 9.24 (d, 2H, J = 8.1), 9.08 (d, 2H, J = 8.4), 9.06 (dd, 2H, J = 8.4, 1.2), 8.54−8.42 (m, 10 H), 7.15 (d, 4H, J = 6.3); IR: 1660, 1601, 1420, 1332, 1091, 833 cm^{-1}; ESI-MS (CH_3CN): 877 (79%, [M − PF_6]$^+$), 366 (100%, [M − (PF$_6$)$_2$]$^{2+}$).

[(bpy)$_2$Ru(1)Ru(bpy)$_2$](PF$_6$)$_4$. A mixture of [Ru(bpy)$_2$Cl$_2$] (46.2 mg, 88.8 μmol), **1** (15.6 mg, 40.4 μmol), and ethylene glycol (8 mL) was heated to reflux in a modified microwave oven[17] for 4 min. The mixture was added to aqueous NH_4PF_6 (1%, 40 mL), and the precipitated complex was isolated by filtration. It was purified by chromatography (silica, CH_3CN/1M $NaNO_3$, 7:3). After concentration of the product fractions, the complex was precipitated with NH_4PF_6 to afford [(bpy)$_2$Ru(**1**)Ru(bpy)$_2$](PF$_6$)$_4$ (35.6 mg, 49%) as a brown powder: MALDI-MS: 1649 (M − PF_6)$^+$, 1503 (M − 2PF_6 + e$^-$)$^+$; IR: 1605, 834 cm^{-1}. Anal. Calcd for $C_{65}H_{46}F_{24}N_{12}OP_4Ru$: C, 43.54; H, 2.59; N, 9.37. Found: C, 43.62; H, 2.43; N, 9.01.

Crystal structure of [Ru(1)(4-Me-py)$_2$](PF$_6$)$_2$. The complex [Ru(**1**)(4-Me-py)$_2$](PF$_6$)$_2\cdot$(CH_3)$_2$CO (fw = 1021.74 g mol^{-1}) was crystallized from acetone and toluene to yield dark green needles. A crystal (0.50 × 0.06 × 0.03 mm^3) was measured on a Siemens SMART platform diffractometer equipped with a 1 K CCD area detector at 223 K, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Triclinic, $P\bar{1}$, a = 9.3774(10) Å, b = 10.4788(11) Å, c = 20.8407(22) Å, α = 82.873(2)°, β = 86.533(2)°, γ = 85.432(2)°, V = 2023.0(4) Å^3, Z = 2, ρ_{calc} = 1677 kg m^{-3}, μ = 0.568 mm^{-1}, $T_{min/max}$ = 0.6383/0.9401. θ = 1.96−23.53°. The data were integrated using the Siemens 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. Of the 9408 reflections which were collected, 5966 were unique. Of these, 3453 reflections were considered

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observed ($F^2 \geq 4\sigma(F^2)$) and used to refine 504 parameters. The structure was solved and refined (SHELXL-97)[18] against F^2. Hydrogen atoms were placed in ideal positions with riding motion. R1 = 0.0576, wR2 = 0.1357. The two PF_6 anions and the acetone solvent were found to be massively disordered, with three major orientations located at each site. This was treated by refinement of ideal rigid bodies, with occupancy factors determined by analysis of isotropic thermal parameters. The combination of extremely small sample size and severe disorder resulted in a disappointingly small number of observed data. Because of this, attempts to refine all but one of the disordered groups anisotropically failed, and it was finally necessary to refine them isotropically.

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Acknowledgment. R.P.T. thanks the Robert A. Welch Foundation (E-621) and the National Science Foundation (CHE-0352617) for financial support of this work. T.B. thanks the Swiss National Science Foundation for a post-doctoral fellowship. We also thank Dr. Dong Wang for assistance with emission studies and Dr. James Korp for assistance with the X-ray determinations using MRSEC/TCSUH Shared Experimental Facilities supported by the NSF under Award No. DMR-9632667.

Supporting Information Available: X-ray crystallographic files for [Ru(**1**)(4-CH_3-py)$_2$](PF_2)$_2$·(CH_3)$_2$CO (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC050996K