The Preparation and Study of Bis(2-quinolyl) and Bis(2-[1,8]naphthyridyl) Derivatives of Pyrimidine and Pyrazine as Bridging Ligands for Ru^{II}

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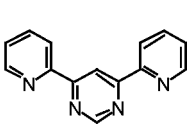
The 2:1 Friedländer condensation of 2-aminobenzaldehyde or 2-aminonicotinaldehyde with either 4,6-diacetylpyrimidine or 2,5-diacetylpyrazine leads to a family of four new bis(bidentate) bridging ligands. Subsequent complexation of these ligands with $[RuCl_2(bpy)_2]$ (bpy = 2,2′-bipyridine) leads to the corresponding mononuclear and dinuclear mixed-ligand Ru^{II} complexes. Analysis of the ^1H NMR spectra of these systems affords some insight into their conformational properties. Electronic spectra of the complexes evidence two long-wavelength absorption bands which correspond to typical metal-to-ligand charge transfer states. The energies of these states may be explained by electronegativities of the pendant rings on the bridging ligand as well as the substitution pattern on the central ring. For the dinuclear complexes the lowest energy absorption shows components associated with coordination to the pendant and the central rings. The appearance of two metal-based oxidations gives good evidence for strong intermetalic interaction and Koopman's theorem is obeyed for all systems.

Introduction

One recurrent theme in the burgeoning field of supramolecular chemistry is the construction of organized assemblies through the judicious juxtaposition of appropriate ligands and metals. These systems take advantage of complementarity effects in the ligands as well as the principle of maximum occupation of sites to allow for the formation of a wide variety of multimetallic networks having interesting and often useful shapes. The bridging ligands used for this construction often have two equivalent bidentate chelating sites which allow the formation of linear assemblies as well as multidirectional dendritic structures.[1] Two such building blocks which have found considerable utility are 4,6-bis(2′-pyridyl)pyrimidine (**1**)[2] and 2,5-bis(2′-pyridyl)pyrazine (**2**).[3] Tris(complexation) of either ligand around a single Ru^{II} center leaves three equivalent bidentate sites available for further elaboration. If these sites are occupied by $[Ru(L)_2]^{2+}$ fragments where L = **1** or **2**, further branching is possible and polynuclear dendritic structures result. One reason for the strong interest in such systems is their potential to act as antennae where metal-based chromophores on the periphery could gather light energy and funnel it to a central, often different, metallic core.



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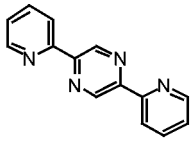

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There are several problems associated with these multimetallic dendritic systems. Firstly, the asymmetric chelating sites of the bridging ligands lead to metal-based stereocenters, Δ or Λ, so that the number of stereoisomers increases with the number of metal atoms in the system. The problems associated with separating and evaluating individual stereoisomers have been largely ignored since the photochemical properties of these very similar stereoisomers does not appear to differ substantially.[4] Nevertheless, impressive progress has been made in the construction of stereochemically discrete systems.[5] The other issue of concern is the directionality of energy or electron transfer. Photoexcitation of such dendritic systems often involves a metal-to-ligand charge transfer (MLCT) state in which the photoexcited electron is promoted from the metal atom to the most electronegative ligand.[6] Although **1** and **2** are more electronegative than 2,2′-bipyridine (bpy), their π*-states are not that much lower than that of bpy and it occurred to us that more electronegative analogues of these ligands might enhance the directionality of energy transfer.

In earlier work we have used the Friedländer condensation of 8-aminoquinoline-7-carbaldehyde with diacetyl derivatives of pyrimidine and pyrazine to afford bis([1,10]-phenanthrolinyl)diazines and we have examined the be-

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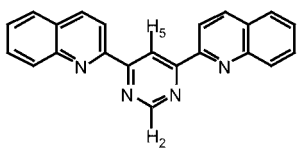
havior of these ligands as bis(tridentate) chelators.[7] In this work we will utilize a similar Friedländer approach to prepare the 2-quinolyl and 2-[1,8]naphthyridyl derivatives of these same diazines (**3**−**6**) and examine the properties of their mono- and dinuclear Ru^{II} complexes.



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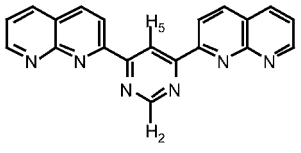

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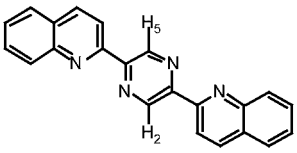

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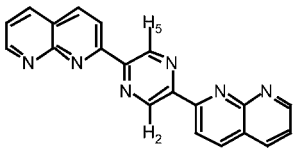

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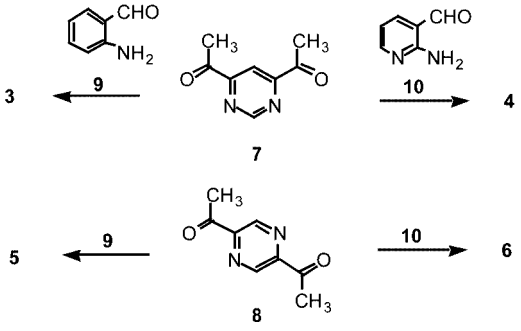
Results and Discussion

The ligands were synthesized by a Friedländer reaction[8] between 2 equiv. of 2-aminobenzaldehyde (**9**) or 2-aminonicotinaldehyde (**10**) and either 4,6-diacetylpyrimidine (**7**)[9] or 2,5-diacetylpyrazine (**8**).[10] The reactions proceed smoothly in refluxing ethanol to provide the ligands **3**−**6** in yields of 40−98%. The ligands were characterized by their ^1H NMR spectra which were readily assigned due to high symmetry. The quinoline and naphthyridine rings give characteristic and similar patterns with little variation between the pyrimidine and pyrazine systems. The central pyrimidine ring shows two singlets with 2-H appearing at δ = 9.48−9.51 ppm. The singlet of 5-H (being closer to the substituent rings) shows more variation appearing at δ = 9.78 ppm for the quinoline and at δ = 10.09 ppm for the naphthyridine derivatives. The central pyrazine ring shows only one singlet at δ = 9.95 ppm for **5** and at δ = 10.51 ppm for the more deshielded **6**.



Ru^{II} complexes were prepared by treating the ligands **3**−**6** with either 1 or 2 equiv. of $[Ru(bpy)_2Cl_2]$ in refluxing aqueous ethanol. The complexes were precipitated as their hexafluorophosphate salts and purified by chromatography on alumina (CH_3CN/toluene) or silica gel (CH_3CN/H_2O/satd. KNO_3, 5:4:1). Due to stereochemical complexities, only the ^1H singlets on the central diazine ring of the complexes could be confidently assigned.

The mononuclear complexes of **3** and **4** display two singlets, δ = 8.45 (2-H) and 9.81 (5-H) for **3** and δ = 8.63 (2-H) and 9.86 (5-H) for **4**. The coordination of $[Ru(bpy)_2]^{2+}$ disrupts the symmetry of **5** and **6** so that their mononuclear complexes also exhibit two singlets, δ = 8.86 (2-H) and 9.86 (5-H) for **5** and δ = 9.09 (2-H) and 9.93 (5-H) for **6.**

The dinuclear complexes of **3**−**6** possess two chiral octahedral centers and therefore exist as both *rac* (ΔΔ and ΛΛ) and *meso* (ΔΛ) diastereomers (Figure 1). The existence of two diastereomers, each having 22−24 unique protons, gives rise to rather complex ^1H NMR spectra. However, the protons on the central rings appear as singlets making them easier to identify and assign. For the dinuclear complex of **3**, two singlets are observed at δ = 7.53 and 9.54 ppm, which can be assigned, respectively, to 2-H and 5-H of the major diastereomer. The singlet assigned to 2-H is shifted upfield with respect to the mononuclear complex because this proton is now shielded by two pyridine rings. We assign the singlet at δ = 9.63 to 5-H of the minor diastereomer and thus integration of the two 5-H signals gives a diastereomeric ratio of 7:3. The dinuclear complex of **4** also shows two singlets at δ = 7.91 and 9.67 ppm which are assigned to 2-H and 5-H, respectively, of the major diastereomer. The two singlets at δ = 7.84 and 9.72 ppm are assigned to the minor diastereomer and a diastereomeric ratio of 4:1 was determined. For the dinuclear complexes involving pyrazine ligands **5** and **6**, 2-H and 5-H are equivalent so that only one singlet is observed for these protons, appearing at δ = 8.47 and 8.53 ppm for the major and minor diastereomers of $[(bpy)_2Ru(\mathbf{5})Ru(bpy)_2]^{4+}$ and at δ = 8.66 and 8.73 ppm for the major and minor diastereomers of $[(bpy)_2Ru(\mathbf{6})Ru(bpy)_2]^{4+}$. Due to the complexity of the spectra, clear diastereomeric ratios could not be determined.

The electronic absorption and luminescence spectra of the ligands **3**−**6** and their Ru^{II} complexes were determined in acetonitrile solution and the data are collected in Table 1. The ligands show low energy absorption bands in the range of 316−355 nm and several interesting correlations can be made involving the energies of these absorptions and structure. First, the ligands involving naphthyridine, **4** and **6**, absorb at longer wavelengths (324 and 355 nm) than their quinoline counterparts (316 and 340 nm) which agrees with increased electronegativity due to two additional nitrogen atoms. However, for the two isomeric quinoline systems, the one involving a central pyrazine ring (**5**) absorbs at 24 nm longer wavelength than the one involving a central pyrimidine ring (**3**). For the two isomeric naphthyridine systems the difference is 31 nm. This difference can be explained by considering the planar conformations available to the ligands. From a chelation point of view it is convenient to view them in their *syn*,*syn* conformation. However, this conformation involves unfavorable N−N lone pair interactions as well as some H−H congestion which can be relieved in the *anti*,*anti* conformation. For **3** and **4** the *anti*,*anti* form provides a less extended structure while for the pyrazine

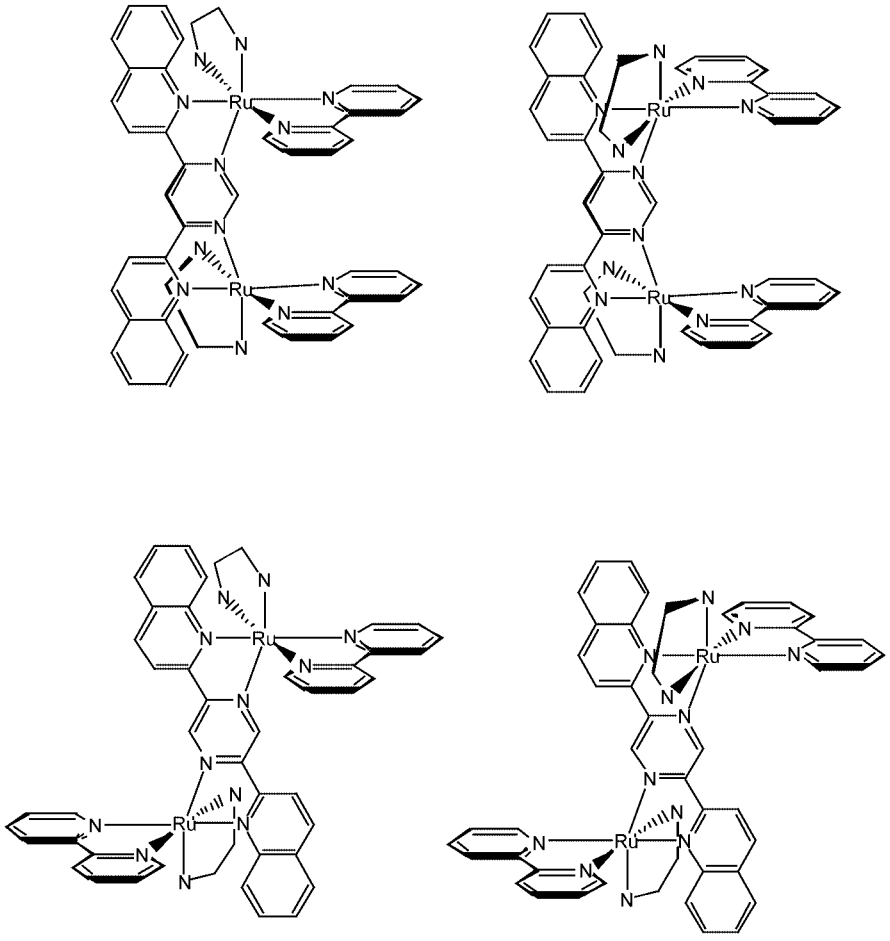
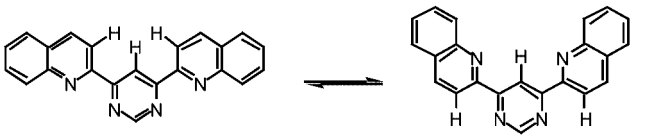
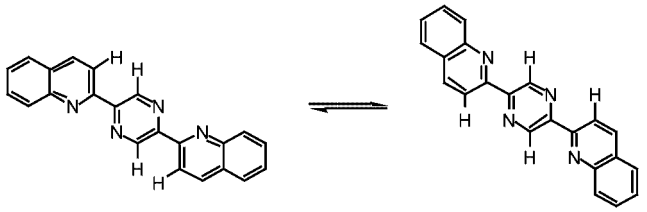


Figure 1. Stereochemical representation of the diastereomeric forms of $[(bpy)_2Ru(\mathbf{3})Ru(bpy)_2]^{4+}$ (top) and $[(bpy)_2Ru(\mathbf{5})Ru(bpy)_2]^{4+}$ (bottom)

systems **5** and **6** both conformations have a similar longitudinal arrangement, explaining the lower energy absorption. It is intriguing to speculate that a bulky C-2 substituent on either **3** or **4** would inhibit the normal bidentate coordination and one might expect to see some cyclometalation through the potential tridentate *anti*,*anti* conformation.



3 (syn, syn) **3** (anti, anti)



5 (syn, syn) **5** (anti, anti)

Table 1. Photophysical data for free ligands

Ligand	Absorption[a] λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])	Emission[a] λ_{em} [nm] (rel. int.)
3	316 (24934), 250 (58052), 206 (53344)	406 (m)
4	324 (26776), 231 (43578)	430 (m)
5	340 (28140), 262 (26964), 207 (41490)	435 (s)
6	355 (27946), 253 (18544)	440 (m)

[a] 5×10^{-5} M in CH_3CN at 25 °C; s = strong, m = medium.

The absorption properties of the mononuclear complexes $[Ru(\mathbf{3}-\mathbf{6})(bpy)_2]^{2+}$ are well behaved and consistent with structure. Each complex shows two long-wavelength absorption bands which are associated with a metal-to-ligand charge transfer (MLCT) wherein a photoexcited electron is promoted from a metal d-orbital to the π*-orbital of a ligand (Figures 2 and 3). The longer wavelength band in the region of 510−559 nm correlates with MLCT to the more electronegative bridging ligand while the shorter wavelength band, in the much narrower range of 427−431 nm, correlates with MLCT to the auxiliary bpy ligand. The more

electronegative naphthyridine ligands have lower energy π*-states and thus absorb at lower energy with a difference from the corresponding quinoline ligands of 32 nm when the central ring is pyrimidine and 33 nm when the central ring is pyrazine.

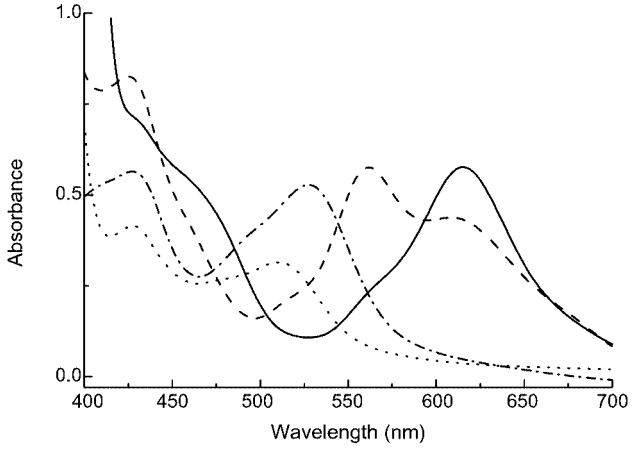


Figure 2. Long-wavelength portion of the electronic absorption spectra of the quinoline-containing systems $[Ru(\mathbf{3})(bpy)_2]^{2+}$ (dash-dot), $[Ru(\mathbf{5})(bpy)_2]^{2+}$ (dot), $[(bpy)_2Ru(\mathbf{3})Ru(bpy)_2]^{4+}$ (dash), and $[(bpy)_2Ru(\mathbf{5})Ru(bpy)_2]^{4+}$ (solid)

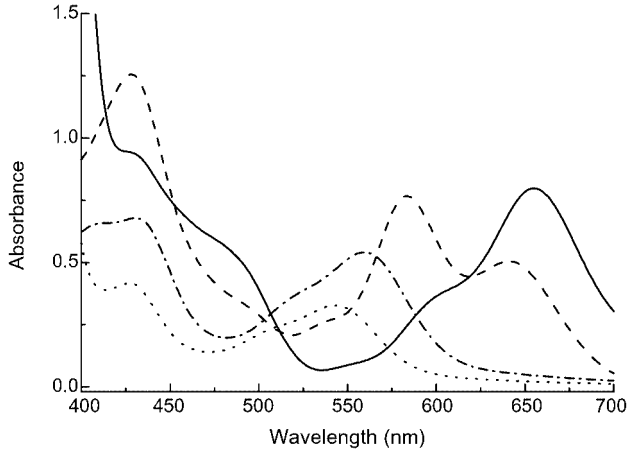


Figure 3. Long-wavelength portion of the electronic absorption spectra of the 1,8-naphthyridine-containing systems $[Ru(\mathbf{4})(bpy)_2]^{2+}$ (dash-dot), $[Ru(\mathbf{6})(bpy)_2]^{2+}$ (dot), $[(bpy)_2Ru(\mathbf{4})Ru(bpy)_2]^{4+}$ (dash), and $[(bpy)_2Ru(\mathbf{6})Ru(bpy)_2]^{4+}$ (solid)

It is especially interesting that the MLCT bands for the pyrimidine and pyrazine systems are reversed in energy when compared to the free ligands, with the pyrimidine complexes showing lower energy absorptions. The conformational effects cited for the free ligands are less important for the complexes. Rather the pendant, uncomplexed quinoline or naphthyridine may be considered as a substituent on the diazine portion of the bidentate chelator. For the pyrimidine systems this substituent is located in the 4-position where it will have a stronger resonance interaction with the coordinated metal atom. For the pyrazine systems, the substituent is in the 3-position and the delocalizing effect is weaker.

The absorption properties of the dinuclear complexes $[(bpy)_2Ru(\mathbf{3}-\mathbf{6})Ru(bpy)_2]^{4+}$ are somewhat unusual. Once again, there are long- and short-wavelength components to the MLCT absorption bands. All four systems show bands at 425−428 nm which correspond to charge transfer to the less electronegative bpy ligands. However, the long-wavelength component consists of two bands. For the naphthyridine systems these bands appear at longer wavelengths than for the quinoline systems. Charge transfer to the bridging ligands may involve either the pendant quinoline or naphthyridine moiety as the receptor or the central diazine ring as the receptor with the latter species being lower in energy. Thus, we observe that the long-wavelength contribution is more intense for the pyrazine systems where the *para* disposition of the metal centers on the pyrazine ring provides better communication and consequent delocalization than for the *meta*-substituted pyrimidine rings where charge transfer to the pendant groups is preferred.

The luminescence properties of the complexes were measured at room temperature in acetonitrile solution. As expected, the mononuclear complexes showed modest emission while the dinuclear complexes were less intense and completely quenched in the cases of $[(bpy)_2Ru(\mathbf{4}, \mathbf{6})Ru(bpy)_2]^{4+}$.

The half-wave redox potentials of the complexes were measured in acetonitrile and the data are collected in Table 2. For systems of this type, oxidations are typically associated with the removal of an electron from a metal d-orbital while reduction involves the addition of an electron to the π*-orbital of a coordinated ligand. In this regard the mononuclear complexes are well behaved. Metal-based $Ru^{II,III}$ oxidation occurs at +1.34−1.46 V. Pyrimidine is more basic than pyrazine and thus better able to stabilize a positive charge, which explains the lower oxidation potential of the complexes of **3** and **4**. Three reduction waves are observed for the mononuclear complexes, which can be associated with the addition of an electron to the π*-orbital of each of the three ligands around the metal atom. The first reduction for each system involves the ligands **3**−**6** and is more positive for the more electronegative ligands containing the naphthyridine ring. Plotting the lowest energy absorptions against the energy gap between the frontier redox couples gives a good linear relationship with a slope of 0.75 and a correlation coefficient of 0.9952 demonstrating good agreement with Koopman's theorem.

The dinuclear complexes show strong interaction between the two complexed metal centers as evidenced by two well-separated oxidation waves. Analogous with the mononuclear complexes, the naphthyridine-containing systems oxidize more readily, at less positive potentials, than the quinoline-containing systems. The separation between the two oxidations is greater for the pyrazines (+0.23 V) than for the pyrimidines (+0.14 to +0.15 V). Comproportionation constants may be calculated for all four complexes and fall in the range of 230−7730, in good agreement with previously reported systems involving **1** and **2**.[11]

Table 2. Photophysical and electrochemical data for mono- and dinuclear Ru^{II} complexes

Complex	Absorption[a] λ_{max} [nm] (ε [$M^{-1}cm^{-1}$])	Emission[b] λ_{em} [nm] (rel. int)	$E_{1/2}$ [V][a] OX	RED
$[Ru(\mathbf{3})(bpy)_2]^{2+}$	527 (10556), 427 (11286)	762 (m)	+1.38	−0.76, −1.29, −1.60
$[Ru(\mathbf{4})(bpy)_2]^{2+}$	559 (10816), 431 (13580)	817 (w)	+1.34	−0.62, −1.12, −1.57
$[Ru(\mathbf{5})(bpy)_2]^{2+}$	510 (6292), 427 (8294)	745 (m)	+1.46	−0.76, −1.26, −1.57
$[Ru(\mathbf{6})(bpy)_2]^{2+}$	543 (6546), 427 (8340)	807 (w)	+1.40	−0.63, −1.06, −1.59
$[(bpy)_2Ru(\mathbf{3})Ru(bpy)_2]^{4+}$	613 (8704), 562 (11512), 461 (8188), 425 (16514)	838 (w)	+1.49, +1.64	−0.34, −0.83, −1.49, −1.73
$[(bpy)_2Ru(\mathbf{4})Ru(bpy)_2]^{4+}$	640 (10062), 584 (15332), 489 (6900), 428 (25120)	no emission	+1.37, +1.51	−0.30, −0.76, −1.49
$[(bpy)_2Ru(\mathbf{5})Ru(bpy)_2]^{4+}$	615 (14016), 573 (5702), 457 (11098), 428 (14276)	829 (w)	+1.45, +1.68	−0.36, −0.79, −1.43, −1.74
$[(bpy)_2Ru(\mathbf{6})Ru(bpy)_2]^{4+}$	615 (14016), 573 (5702), 457 (11098), 428 (14276)	no emission	+1.34, +1.57	−0.31, −0.67, −1.49

[a] Solutions were 0.1 M TBAP in CH_3CN; the sweep rate was 200 mV/s. [b] 5×10^{-5} M in CH_3CN at 25 °C; m = medium, w = weak.

The dinuclear complexes exhibit 3−4 reduction waves with the first reductions falling in the range of −0.30 to −0.36 V and the second reductions in the range of −0.67 to −0.83 V. Both of these reductions are associated with the bridging ligand while the third reduction at −1.43 to −1.49 V is associated with one of the bpy ligands. The bridging ligand reductions are consistent with structure in that the naphthyridine-containing ligands reduce more readily than the quinoline containing ones.

Summary

Four bis(bidenate) bridging ligands have been prepared containing a central pyrimidine or pyrazine ring symmetrically substituted with either two 2-quinolyl or two 2-[1,8]naphthyridyl moieties. Mixed-ligand complexes of these ligands have been prepared by incorporating either one or two $[Ru(bpy)_2]^{2+}$ centers into the available bidentate sites. The resulting complexes possess one stereocenter at each metal atom resulting in an inseparable mixture of diastereomers for the dinuclear systems as evidenced by characteristic ^1H NMR singlets for protons on the central diazine ring. MLCT absorptions are observed for charge transfer to the bridging ligand in the range of 510−559 nm for the mononuclear complexes. For the dinuclear complexes this band splits into two components, at 562−612 and 613−655 nm, which are tentatively associated with the central and pendant rings on the bridging ligand. Charge transfer to the auxiliary bpy remains fairly constant for all complexes in the range of 425−431 nm. Clear splitting of the metal-based oxidation potential indicates interaction between two bound metal atoms with the pyrazine system showing the stronger coupling. Reduction potentials correlate well with electronegativities of the bridging ligand.

Experimental Section

General: Nuclear magnetic resonance spectra were recorded at 300 MHz for ^1H and at 75 MHz for $^{13}C\{^1H\}$ referenced to TMS in $CDCl_3$ and to the solvent peak in all other solvents (CD_3CN). Electronic spectra were obtained with a Perkin−Elmer Lambda 3B spectrophotometer. Emission spectra were obtained with a Perkin−Elmer LS-50 luminescence spectrometer. Cyclic voltammetry (CV) was carried out in a conventional three-electrode cell with a BAS-27 voltammeter and a Houston Instruments model 100 X-Y recorder according to a previously described procedure.[12] Mass spectra were obtained with an Applied Biosystems Voyager System 4160 MALDI-TOF spectrometer. Melting points were measured with a Hoover capillary melting point apparatus and are not corrected. Elemental analyses were performed by Quantitative Technologies Inc., P. O. Box 470, Whitehouse, NJ 08888, USA. 2,5-Diacetylpyrazine,[10] 4,6-diacetylpyrimidine,[9] 2-aminobenzaldehyde,[13] 2-aminonicotinaldehyde,[14] and $[Ru(bpy)_2Cl_2]$[15] were prepared according to published procedures.

4,6-Bis(2′-quinolinyl)pyrimidine (3): 50% ethanolic KOH (2 mL) was added to a stirred solution of 4,6-diacetylpyrimidine (50 mg, 0.30 mmol) and 2-aminobenzaldehyde (73 mg, 0.60 mmol) in EtOH (10 mL). The solution was allowed to reflux overnight. After cooling to room temperature, the precipitate was filtered and rinsed with EtOH. The product was purified by chromatography (silica gel, hexanes/EtOAc, 1:1) to give **3** (91 mg, 91%) as a white solid; m.p. 230−233 °C. ^1H NMR ($CDCl_3$): δ = 9.80 (s, 1 H), 9.49 (s, 1 H), 8.66 (d, J = 8.7 Hz, 2 H), 8.37 (d, J = 8.7 Hz, 2 H), 8.36 (d, J = 8.4 Hz, 2 H), 7.92 (d, J = 8.1 Hz, 2 H), 7.82 (t, J = 7.2 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 164.1, 158.6, 154.1, 148.1, 137.1, 130.3, 129.9, 128.9, 127.64, 127.61, 118.9, 115.0. MS: m/z = 334 [M^+]. $C_{22}H_{14}N_4 \cdot 0.5H_2O$ (343): calcd. C 76.97, H 4.37, N 16.32; found C 76.58, H 3.71, N 16.16.

4,6-Bis(2′-[1′,8′]naphthyridyl)pyrimidine (4): 50% ethanolic KOH (2 mL) was added to a stirred solution of 4,6-diacetylpyrimidine (100 mg, 0.61 mmol) and 2-aminonicotinaldehyde (164 mg, 1.34 mmol) in EtOH (10 mL). The solution was allowed to reflux overnight. After cooling to room temperature, the solvent was evaporated and the resulting solids were dissolved in $CHCl_3$ (50 mL). The organic phase was washed with water (50 mL), and brine (50 mL), dried ($MgSO_4$) and concentrated. The solid residue was purified by washing with cold EtOH until the washings ran clear to give **4** (84 mg, 41%) as a gray solid; m.p. > 280 °C. ^1H NMR ($CDCl_3$): δ = 10.07 (s, 1 H), 9.51 (s, 1 H), 9.24 (dd, J = 4.2, 1.8 Hz, 2 H), 8.78 (d, J = 8.4 Hz, 2 H), 8.42 (d, J = 8.7 Hz, 2 H), 8.22 (dd, J = 8.1, 1.8 Hz, 2 H), 7.57 (dd, J = 8.1, 4.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 163.8, 158.4, 157.1, 155.4, 154.2, 138.5, 137.2,

123.7, 123.0, 120.1, 116.5. MS: m/z = 336 [M^+]. $C_{20}H_{12}N_6 \cdot 0.5H_2O$ (345): calcd. C 69.57, H 3.77, N 24.34; found C 69.59, H 3.26, N 24.39.

2,5-Bis(2′-quinolinyl)pyrazine (5): 50% ethanolic KOH (2 mL) was added to a stirred solution of 2,5-diacetylpyrazine (100 mg, 0.61 mmol) and 2-aminobenzaldehyde (155 mg, 1.27 mmol) in EtOH (20 mL). The solution was allowed to reflux overnight. After cooling to room temperature, the precipitate was filtered and rinsed with EtOH. The solid product was recrystallized from EtOH to give **5** (81 mg, 40%) as a light brown solid; m.p. 262−264 °C. ^{1}H NMR ($CDCl_3$): δ = 10.03 (s, 2 H), 8.64 (d, J = 8.7 Hz, 2 H), 8.2−8.5 (m, 4 H), 7.91 (d, J = 8.1 Hz, 2 H), 7.82 (t, J = 8.1 Hz, 2 H), 7.63 (t, J = 7.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 152.9, 149.3, 146.3, 142.0, 136.6, 129.3, 128.5, 127.5, 126.7, 126.6, 118.3. MS: m/z = 334 [M^+]. $C_{22}H_{14}N_4 \cdot 0.25CHCl_3$ (364): calcd. C 73.39, H 3.92, N 15.39; found C 73.25, H 3.33, N 15.33.

2,5-Bis(2′-[1′,8′]naphthyridyl)pyrazine (6): Solid KOH (200 mg) was added to a stirred solution of 2,5-diacetylpyrazine (400 mg, 2.44 mmol) and 2-aminonicotinaldehyde (625 mg, 5.12 mmol) in EtOH (10 mL). The solution was allowed to reflux for 5 h after which it was cooled to room temperature and the solids were collected by vacuum filtration. The solid product was purified by washing with cold EtOH until the washings ran clear to give **6** (820 mg, 98%) as a gray solid; m.p. > 280 °C. ^{1}H NMR ($CDCl_3$): δ = 10.15 (s, 2 H), 9.22 (dd, J = 3.9, 1.8 Hz, 2 H), 8.83 (d, J = 8.4 Hz, 2 H), 8.41 (d, J = 8.7 Hz, 2 H), 8.30 (dd, J = 8.1, 2.1 Hz, 2 H), 7.57 (dd, J = 8.1, 4.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 157.5, 155.8, 154.2, 150.4, 143.2, 138.2, 137.1, 123.3, 122.6, 120.5. MS: m/z = 336 [M^+]. $C_{20}H_{12}N_6 \cdot 0.25H_2O$ (341): calcd. C 70.48, H 3.67, N 24.67; found C, 70.24, H 3.36, N 24.27.

[Ru(3)(bpy)$_2$](PF$_6$)$_2$: A stirred suspension of **3** (20 mg, 0.06 mmol) and [Ru(bpy)$_2$Cl$_2$] (62 mg, 0.12 mmol) in EtOH/H_2O (3:1, 12 mL) was heated at reflux overnight after which the solution was cooled to room temperature, and filtered. NH_4PF_6 (20 mg) was added and the solution was concentrated. The product was purified by chromatography (silica gel, CH_3CN/H_2O/sat. KNO_3, 5:4:1) and the counterion was exchanged with satd. NH_4PF_6 to give [Ru(**3**)(bpy)$_2$](PF$_6$)$_2$ (38 mg, 66%) as a red solid. ^{1}H NMR (CD_3CN): δ = 9.81 (s, 1 H), 8.95 (d, J = 8.7 Hz, 1 H), 8.72 (d, J = 8.7 Hz, 1 H), 8.63 (d, J = 8.7 Hz, 2 H), 8.58 (d, J = 6.9 Hz, 2 H), 8.46 (s, 1 H), 8.39 (d, J = 8.1 Hz, 1 H), 8.32 (m, 2 H), 8.0−8.2 (m, 6 H), 7.9−8.0 (m, 3 H), 7.77 (t, J = 6.9 Hz, 2 H), 7.69 (t, J = 7.5 Hz, 2 H), 7.50 (m, 2 H), 7.2−7.4 (m, 4 H). MS: m/z = 893 [$M^+ - PF_6$], 748 [$M^+ - 2\ PF_6$].[16]

[(bpy)$_2$Ru(3)Ru(bpy)$_2$](PF$_6$)$_4$: A stirred suspension of **3** (34 mg, 0.033 mmol) and [Ru(bpy)$_2$Cl$_2$] (66 mg, 0.066 mmol) in EtOH/H_2O (3:1, 12 mL) was heated at reflux overnight after which the solution was cooled to room temperature, filtered, NH_4PF_6 (20 mg) was added and the solution was concentrated. The product was purified by chromatography (silica gel, CH_3CN/H_2O/satd. KNO_3, 5:4:1) and the counterion was exchanged with satd. NH_4PF_6 to give [(bpy)$_2$Ru(**3**)Ru(bpy)$_2$](PF$_6$)$_4$ (16 mg, 28%) as a green solid. The dinuclear complex exists as a mixture of diastereomers which were not further separated: ^{1}H NMR (CD_3CN): δ = 9.63 (s, 1 H), 9.54 (s, 1 H), 9.00 (2 overlapping d, J = 8.7 Hz), 9.73 (2 overlapping d, J = 9.0 Hz), 8.55 (d, J = 8.1 Hz), 8.41 (t, J = 7.5 Hz), 8.26 (t, J = 7.8 Hz), 7.8−8.3 (m), 7.6−7.8 (m), 7.1−7.6 (m), 7.00 (t, J = 7.2 Hz). MS: m/z = 1594 [$M^+ - PF_6$], 1452 [$M^+ - 2\ PF_6$], 1306 [$M^+ - 3\ PF_6$].[16]

[Ru(4)(bpy)$_2$](PF$_6$)$_2$: A stirred suspension of **4** (17 mg, 0.051 mmol) and [Ru(bpy)$_2$Cl$_2$] (27 mg, 0.051 mmol) in EtOH/H_2O (3:1, 12 mL) was heated at reflux overnight after which the solution was cooled to room temperature, and filtered. NH_4PF_6 (17 mg) was added and the solution was concentrated. The product was purified by chromatography (alumina, CH_3CN/toluene, 1:1) followed by recrystallization (CH_3CN/toluene, 1:1) to give [Ru(**4**)Ru(bpy)$_2$](PF$_6$)$_2$ (30 mg, 47%) as red crystals. ^{1}H NMR (CD_3CN): δ = 9.86 (d, J = 0.9 Hz, 1 H), 9.24 (dd, J = 4.2, 1.8 Hz, 1 H), 9.06 (d, J = 8.7 Hz, 1 H), 8.74 (d, J = 8.7 Hz, 1 H), 8.68 (d, J = 8.4 Hz, 1 H), 8.60−8.65 (m, 2 H), 8.55 (dd, J = 8.1, 4.8 Hz, 1 H), 8.49 (d, J = 8.1 Hz, 1 H), 8.37 (t, J = 6.9 Hz, 2 H), 8.16 (dd, J = 4.2, 1.8 Hz, 1 H), 8.12 (dd, J = 7.8, 1.8 Hz, 1 H), 8.0−8.1 (m, 2 H), 7.95 (td, J = 7.8, 1.5 Hz, 1 H), 7.80 (t, J = 4.8 Hz, 2 H), 7.67−7.77 (m, 3 H), 7.59 (dd, J = 8.4, 4.2 Hz, 1 H), 7.2−7.5 (m, 4 H). MS: m/z = 895 [$M^+ - PF_6$], 750 [$M^+ - 2\ PF_6$]. $C_{40}H_{28}F_{12}N_{10}P_2Ru \cdot 0.3PhCH_3 \cdot 1.0H_2O$ (1085): calcd. C 46.58, H 2.98, N 12.91; found C, 46.87, H 2.67, N 12.90.

[(bpy)$_2$Ru(4)Ru(bpy)$_2$](PF$_6$)$_4$: A stirred solution of **4** (30 mg, 0.089 mmol) and [Ru(bpy)Cl$_2$] (100 mg, 0.191 mmol) in EtOH/H_2O (3:1, 12 mL) was refluxed under argon overnight. The dark green solution was cooled, NH_4PF_6 (50 mg) was added and the solvent was evaporated to give a black solid. The material was purified by chromatography (silica gel, CH_3CN/H_2O/satd. KNO_3, 5:4:1) and the counterion was exchanged with saturated NH_4PF_6 to give [(bpy)$_2$Ru(**4**)Ru(bpy)$_2$](PF$_6$)$_4$ (90 mg, 58%) as a green solid: ^{1}H NMR (CD_3CN): δ = 9.66 (s), 9.13 (d, J = 8.7 Hz), 8.80 (d, J = 8.7 Hz), 8.2−8.6 (m), 7.9−8.2 (m), 7.0−7.7 (m). MS: m/z = 1596 [$M^+ - PF_6$], 1451 [$M^+ - 2\ PF_6$], 1306 [$M^+ - 3\ PF_6$], 1161 [$M^+ - 4\ PF_6$]. $C_{60}H_{44}F_{24}N_{14}P_4Ru_2 \cdot 0.5H_2O$ (1752): calcd. C 41.12, H 2.57, N 11.19; found C 40.79, H 2.52, N 10.96.

[Ru(5)(bpy)$_2$](PF$_6$)$_2$: A stirred suspension of **5** (30 mg, 0.08 mmol) and [Ru(bpy)$_2$Cl$_2$] (94 mg, 0.18 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux overnight after which the solution was cooled to room temperature, filtered, NH_4PF_6 (60 mg) was added and the solution was concentrated. Chromatography (silica gel, CH_2Cl_2/CH_3CN, 3:2) gave [Ru(**5**)(bpy)$_2$](PF$_6$)$_2$ (35 mg, 37%) as a red solid. ^{1}H NMR (CD_3CN): δ = 9.86 (s, 1 H), 8.86 (s, 1 H), 8.4−8.8 (m), 8.34 (m), 7.9−8.2 (m), 7.6−7.9 (m), 7.54 (AB pattern, J = 6.9 Hz), 7.48 (d, J = 8.4 Hz), 7.2−7.4 (m). MS: m/z = 893 [$M^+ - PF_6$], 748 [$M^+ - 2\ PF_6$]. $C_{42}H_{30}F_{12}N_8P_2Ru \cdot CHCl_3$ (1156): calcd. C 44.71, H 2.68, N 9.70; found C 44.86, H 2.16, N 9.64.

[(bpy)$_2$Ru(5)Ru(bpy)$_2$](PF$_6$)$_4$: A stirred solution of **5** (30 mg, 0.08 mmol) and [Ru(bpy)Cl$_2$] (94 mg, 0.18 mmol) in EtOH/H_2O (3:1, 20 mL) was refluxed under Ar overnight. The dark green solution was cooled, NH_4PF_6 (60 mg) was added and the solvent was evaporated to give a black solid. The material was purified by chromatography (silica gel, CH_2Cl_2/CH_3CN, 65:35) and the counterion was exchanged with satd. NH_4PF_6 to give [(bpy)$_2$Ru(**5**)Ru(bpy)$_2$](PF$_6$)$_4$ (35 mg, 22%) as a green solid. The dinuclear complex exists as a mixture of diastereomers which were not further separated. ^{1}H NMR (CD_3CN): δ = 8.73 (t, J = 7.8 Hz), 8.66 (t, J = 9.0 Hz), 8.52 (s) 8.4−8.5 (m) 8.2−8.4 (m), 8.11 (t, J = 7.8 Hz), 7.8−8.1 (m), 7.6−7.7 (m), 7.4−7.6 (m) 7.2−7.4 (m), 7.06 (t, J = 7.5 Hz). MS: m/z = 1594 [$M^+ - PF_6$], 1304 [$M^+ - 3\ PF_6$]. $C_{60}H_{44}F_{24}N_{14}P_4Ru_2 \cdot 0.1KPF_6$ (1754): calcd. C 39.28, H 2.47, N 8.26; found C 38.70, H 2.39, N 8.73.

[Ru(6)(bpy)$_2$](PF$_6$)$_2$: A stirred suspension of **6** (50 mg, 0.15 mmol) and [Ru(bpy)$_2$Cl$_2$] (79 mg, 0.15 mmol) in EtOH/H_2O (3:1, 12 mL) was heated at reflux overnight after which the solution was cooled to room temperature, filtered, NH_4PF_6 (49 mg) was added and the solution was concentrated. Chromatography (alumina, CH_3CN/toluene, 1:1) gave [Ru(**6**)(bpy)$_2$](PF$_6$)$_2$ (86 mg, 55%) as a red solid. ^{1}H NMR (CD_3CN): δ = 9.93 (s, 1 H), 9.0−9.2 (m, 2 H), 8.83 (d,

J = 8.7 Hz, 1 H), 8.6−8.8 (2 overlapping doublets, 2 H), 8.57(d, J = 8.4 Hz, 1 H), 8.46 (dd, J = 8.1, 1.8 Hz, 1 H), 8.41 (dd, J = 8.1, 1.8 Hz, 1 H), 8.13 (dd, J = 4.2, 2.1 Hz, 1 H), 7.63 (dd, J = 8.1, 4.2 Hz, 1 H), 7.57 (dd, J = 8.1, 4.2 Hz, 1 H). MS: m/z = 895 [$M^+ - PF_6$], 750 [$M^+ - 2\ PF_6$]. $C_{40}H_{28}F_{12}N_{10}P_2Ru$ (1039): calcd. C 46.20, H 2.69, N 13.47; found C 46.58, H 2.61, N 13.06.

[(bpy)$_2$Ru(6)Ru(bpy)$_2$](PF$_6$)$_4$: A stirred solution of **6** (30 mg, 0.09 mmol) and [Ru(bpy)Cl_2] (100 mg, 0.19 mmol) in EtOH/H_2O (3:1, 12 mL) was refluxed under Ar overnight. The dark green solution was cooled, NH_4PF_6 (58 mg) was added and the solvent was evaporated to give a black solid. The material was purified by chromatography (silica gel, CH_3CN/H_2O/sat. KNO_3, 5:4:1) and the counterion was exchanged with satd. NH_4PF_6 to give [(bpy)$_2$Ru(**6**)-Ru(bpy)$_2$](PF$_6$)$_4$ (100 mg, 65%) as a green solid: ^{1}H NMR (CD_3CN): δ = 8.75 (s), 8.6−8.7 (m), 8.53 (t, J = 8.1 Hz), 8.3−8.5 (m), 7.8- 8.3 (m), 7.65−7.8 (m), 7.55−7.65 (m), 7.3−7.5 (m), 7.18 (m), 7.52 (m) ppm. $C_{60}H_{44}F_{24}N_{14}P_4Ru_2$ (1743): calcd. C 41.33, H 2.53, N 11.25; found C 41.46, H 2.74, N 11.51.

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