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1,5-Naphthyridine As a New Linker for the Construction of Bridging Ligands and Their Corresponding Ru(II) Complexes

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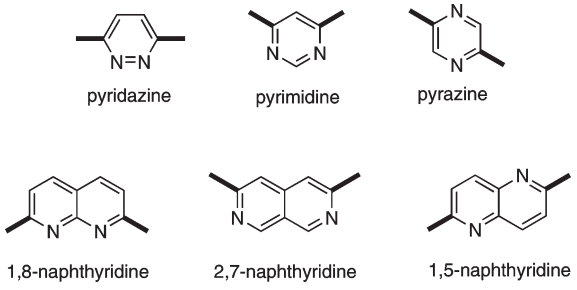
The 1,5-naphthyridine (1,5-nap) molecule has been elaborated into a series of new bidentate and tridentate ligands using Stille coupling or Friedländer condensation methodologies. Thus 2-(tri-*n*-butylstannyl)pyridine was coupled with 2-chloro, 4-chloro, or 2,6-dichloro 1,5-nap to prepare the analogous bidentate ligands. The condensation of 2-aminonicotinaldehyde or 8-amino-7-quinolinecarbaldehyde with a variety of acetyl derivatives of 1,5-nap produced ligands incorporating 1,8-naphthyrid-2-yl or 1,10-phenanthrolin-2-yl groups, respectively. These ligands were treated with either $[Ru(bpy\text{-}d_8)_2Cl_2]$ or $[Ru(tpy)Cl_3]$ to prepare the corresponding heteroleptic mono- and dinuclear Ru(II) complexes. The NMR spectra of these complexes were simplified by the use of bpy-d_8 as an auxiliary ligand, allowing straightforward product identification. The long wavelength absorption of both the ligands and the complexes are shifted to lower energy with increasing delocalization or the incorporation of a second metal. Protonation of a remote uncomplexed nitrogen leads to the red-shifting of the absorption band. The degree of communication between the metal centers in dinuclear complexes can be evaluated from the comproportionation constant measured by electrochemistry. When compared to the pyrazine linker, communication through the 1,5-nap linker appears to be somewhat less efficient.

Introduction

Polynuclear metal complexes represent an important branch of supramolecular chemistry in that they rely on coordinative bonds to hold molecular architectures in place.[1] The shape, size, and function of such polynuclear complexes depends to a large extent on the nature of the bridging ligands which connect the metal centers. Because of the convenient features of pyridine as a coordinating molecule, its higher oligomers have found considerable utility in the construction of bridging ligands and thereby in the construction of polynuclear supramolecular assemblies.[2] The simplest bidentate and tridentate polypyridines are 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2′;6,2″-terpyridine (tpy). These ligating units have been connected in many ways to provide a wide variety of bridging ligands. The degree of communication between the metal centers in such assemblies is often governed by electronic interactions that are transmitted through the bridging ligand backbone. To facilitate such interaction, it is of interest to have two metal centers share a common aza-aromatic ring in a supramolecular assembly. These shared aza-aromatic rings can be viewed as linkers and several examples are given in Scheme 1. When a 2-pyridyl ring is substituted at the indicated positions on the linker, a bis-bidentate bridging ligand results where the orientation of two bound metals, as well as their electronic interaction, is controlled by the linker.

Scheme 1. Linkers for the Construction of Bridging Ligands



Of particular interest are linkers such as pyrimidine and pyrazine because they orient coordinated metals more away from one another allowing for the construction of larger assemblies.[3]

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(1) (a) Lehn, J. M. *Supramolecular Chemistry*; Wiley-VCH: New York, 1995. (b) Lehn, J. -M. Science 1993, 260, 1762–1763.

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(3) (a) Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750–4758. (b) Phillips, I. G.; Steel, P. J. *Aust. J. Chem.* **1998**, *51*, 371–382. (c) Campagna, S.; Serroni, S.; Juris, A.; Venturi, M.; Balzani, V. *New. J. Chem.* **1996**, *20*, 773–780. (d) Marcaccio, M.; Paolucci, F.; Paradise, C.; Carano, M.; Roffia, S.; Fontanesi, C.; Yellowlees, L. J.; Serroni, S.; Campagna, S.; Balzani, V. *J. Electroanal. Chem.* **2002**, *532*, 99–112.

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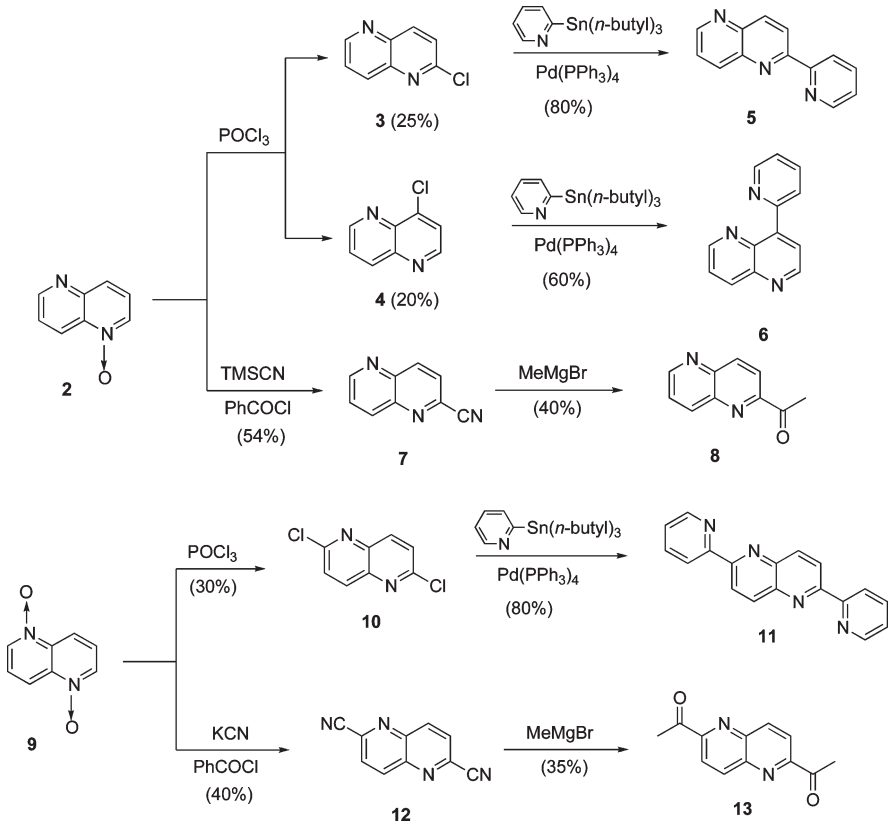
Linkers such as pyridazine and 1,8-naphthyridine are more limited in this regard. In this work we introduce a new linker group, 1,5-naphthyridine (1,5-nap), which, like pyrazine, orients two metals away from one another. Although the naphthyridine system is more delocalized than pyrazine, the two coordinating nitrogens are separated by three bonds in both systems. This work presents the synthesis of a variety of new bridging ligands using 1,5-nap as a linker as well as their corresponding Ru(II) complexes. The photophysical and electrochemical properties of the complexes will also be presented and compared with other similar systems.

Synthesis of the Ligands

The synthesis of the ligands begins with functionalization of the parent 1,5-nap (**1**) that can be prepared in gram quantities by the classical Skraup reaction of 3-aminopyridine.[4] Treatment of **1** with either *m*-chloroperbenzoic acid or hydrogen peroxide leads to the mono-N-oxide (**2**) or di-N-oxide (**9**) respectively.[5] The mono-N-oxide reacts with phosphorus oxychloride to provide a mixture of the 2-chloro- (**3**) and 4-chloro (**4**) 1,5-nap derivatives which could be separated by chromatography on silica gel.[6] Similar treatment of the di-N-oxide gave a modest yield of the 2,6-dichloro-1,5-nap **10**. Subsequent Stille coupling with 2-pyridyl tri-*n*-butylstannane affords the tridentate 2-pyridyl-1,5-naps **5** and **6** and the tetradentate di-2-pyridyl derivative **11** in good yields. Alternatively, the two N-oxides can be treated with either TMS cyanide or potassium cyanide to provide the 2-cyano (**7**) or 2,6-dicyano (**12**) derivatives[7] which, upon treatment with methyl magnesium bromide can be converted to the analogous acetyl derivatives **8** and **13** in modest yields.



The incorporation of an acetyl group allows one to exploit Friedländer methodology in the development of interesting new bridging ligands.[8] We investigated the direct acetylation of 1,5-nap using pyruvic acid in the presence of silver nitrate and ammonium persulfate.[9] Acetylation is specific for either the 2- or the 4-position of the naphthyridine ring with the former position being slightly preferred. Four products were obtained, including the 2-acetyl (12%) and 2,6-diacetyl (12%) derivatives prepared earlier. Additionally, we isolated a 10% yield of the 4,8-diacetyl species **14** and a 25% yield of the 2,8-diacetyl **15**. These materials could be separated in reasonable quantities by a combination of chromatography and recrystallization.

(4) (a) Rapoport, H.; Batcho, A. D. *J. Org. Chem.* **1967**, *28*, 1753–1759. (b) Albert, A. *J. Chem. Soc.* **1960**, 1790–1793. (c) Hamada, Y.; Takeuchi, I. *Chem. Pharm. Bull.* **1971**, *19*, 1857–1862.

(5) Hart, E. P. *J. Chem. Soc.* **1954**, 1879–1882.

(6) (a) Newkome, G. R.; Gabris, S. J.; Majestic, V. K.; Fronczek, F. R.; Chiari, G. *J. Org. Chem.* **1981**, *46*, 833–837. (b) Newkome, G. R.; Gabris, S. J. *Heterocyclic Chem.* **1974**, *15*, 685. (c) Fitchett, C. M.; Steel, P. J. *Polyhedron* **2007**, *26*, 400–405.

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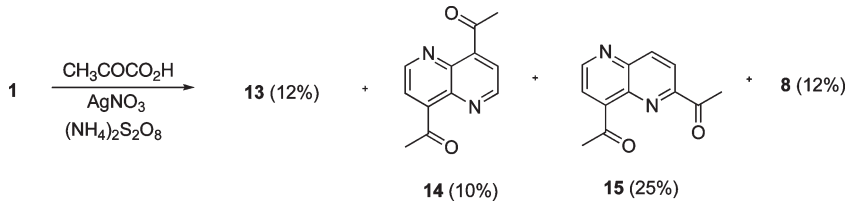
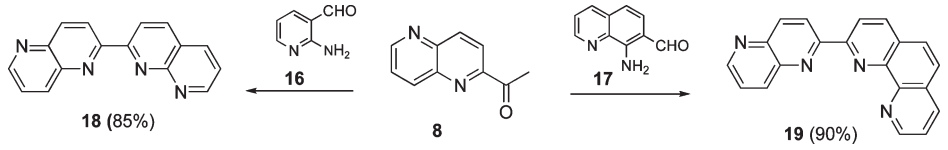
(8) (a) Zong, R.; Wang, D.; Hammitt, R.; Thummel, R. P. *J. Org. Chem.* **2006**, *71*, 167–175. (b) Wu, F.; Thummel, R. P. *Inorg. Chim. Acta.* **2002**, *327*, 26–30.

(9) (a) Caronna, T.; Fronza, G.; Menisci, F.; Porta, O. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 2035–2038. (b) Fontana, F.; Menisci, F.; Barbosa, M. C. N.; Vismara, E. *J. Org. Chem.* **1991**, *56*, 2866–2869.

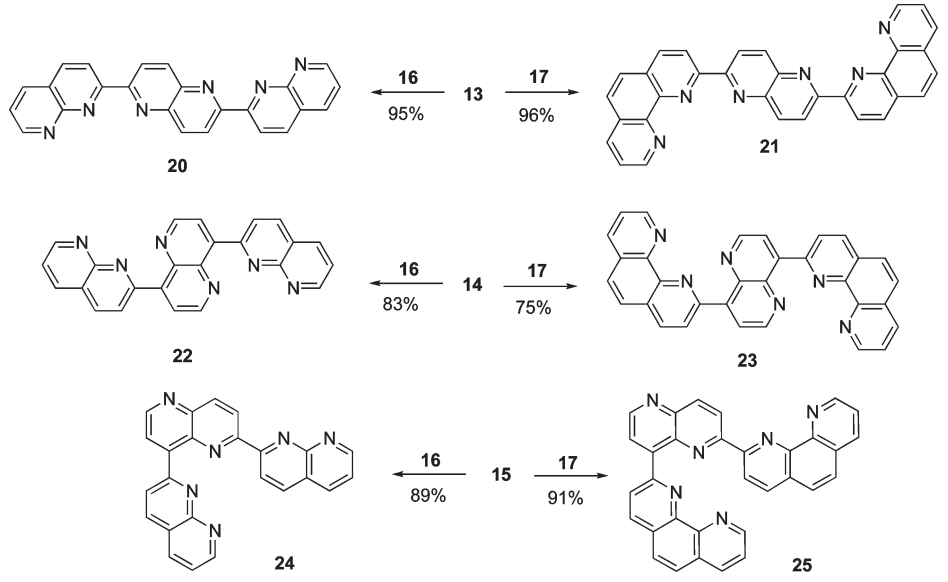


These various acetyl derivatives of 1,5-nap were then elaborated through the Friedländer condensation. Thus, the condensation of 2-acetyl-1,5-nap (**8**) with 2-aminonicotinaldehyde (**16**)[10] afforded an 85% yield of the unsymmetrical binaphthyridine **18**. The corresponding reaction of **8** with 8-amino-7-quinolinecarbaldehyde (**17**)[11] in turn provided the 2-phenanthrolinyl substituted derivative **19**.



The diacetyl 1,5-naps **13**−**15** could be elaborated in a similar fashion by the Friedländer condensation with 2 equiv of the *o*-aminoaldehydes **16** and **17**. The reactions proceeded in yields of 75 − 96% and, in the case of **13** and **14**, afforded symmetrical bis-bidentate or bis tridentate bridging ligands. In the case of the 2,8-diacetyl precursor **15**, the 2:1 Friedländer products were unsymmetrical.

The acetyl precursors as well as the Friedländer and Stille products could be readily characterized by ^{1}H NMR spectroscopy. Analysis of the spectra was facilitated by the fact that all these naphthyridine derivatives possessed several independent spin systems often consisting of either two or three protons.[12] The 3-proton patterns were associated with the less substituted pyridine ring of either a 1,5 or 1,8-naphthyrid-2-yl or a 1,10-phenanthrolin-2-yl substituent. The remaining signals were all two ortho-coupled protons which appeared as doublets. It is well established that the proton ortho to the pyridine nitrogen is deshielded and appears considerably downfield from the other protons. It also displays a relatively small three bond coupling ($J \sim 4.5$ Hz) with the neighboring proton. The higher symmetry of systems such as **11** and **20**−**23** made proton assignments



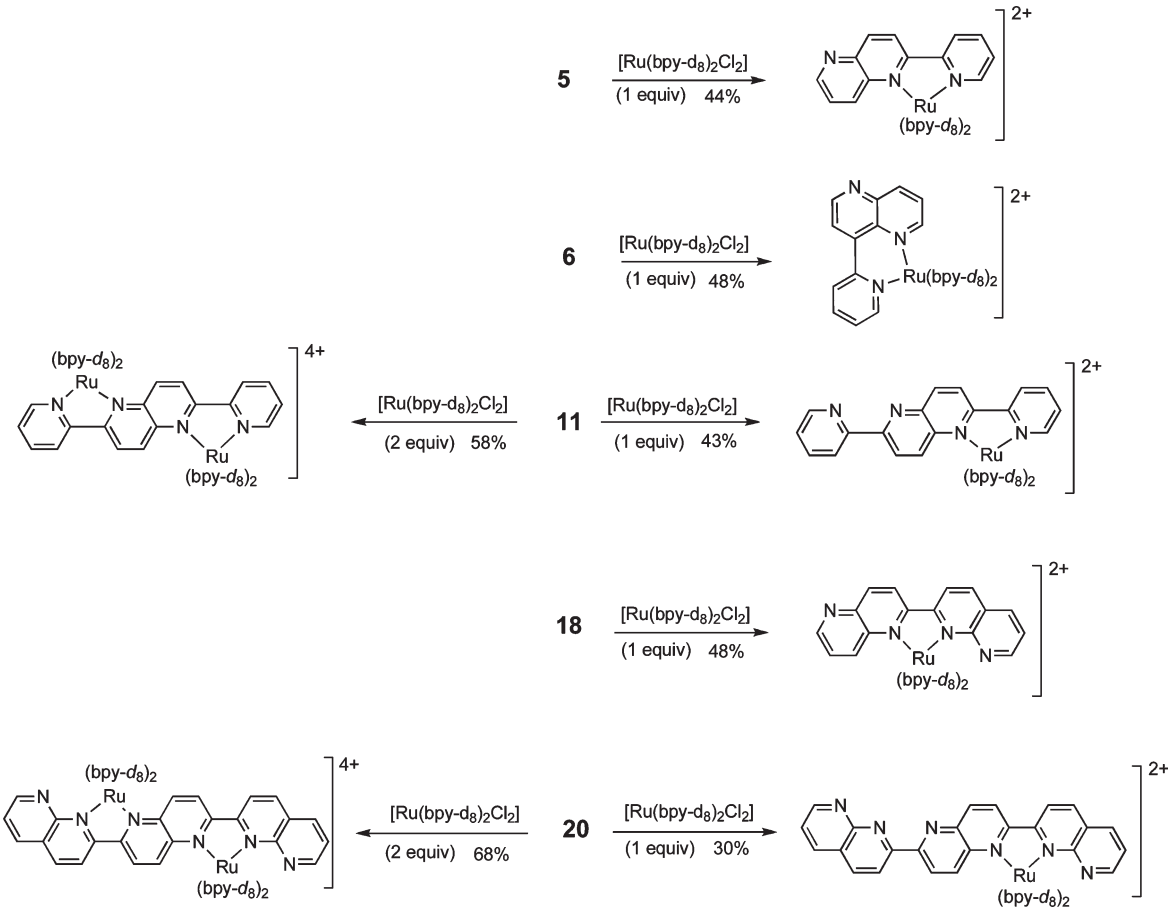
relatively straightforward. For the less symmetrical systems such as **24** and **25**, proton assignments on the two appended 1,8-naphthyridine and 1,10-phenanthroline rings were less clear. The C-13 NMR spectra and elemental analyses were all consistent with the assigned structures.

Ru(II) Complexes

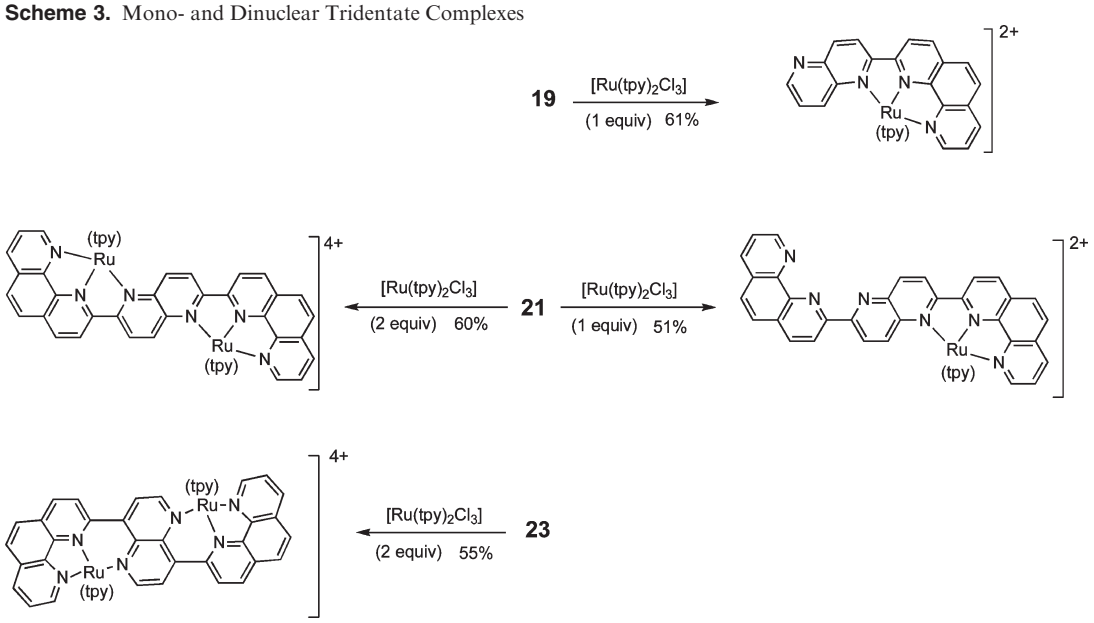
The pyrid-2-yl and 1,8-naphthyrid-2-yl derivatives of 1,5-nap were converted into their heteroleptic Ru(II) complexes by treatment with either 1 or 2 equiv of $[Ru(bpy\text{-}d_8)_2Cl_2]$, and the prepared complexes are shown in Scheme 2.

(10) Majewicz, T. G.; Caluwe, P. *J. Org. Chem.* **1974**, *39*, 720–721.
(11) Riesgo, E. G.; Jin, X.; Thummel, R. P. *J. Org. Chem.* **1996**, *61*, 3017–3022.
(12) Ezell, E. L.; Thummel, R. P.; Martin, G. E. *J. Heterocyclic Chem.* **1984**, *21*, 817–823.

Scheme 2. Mono- and Dinuclear Bidentate Complexes



Scheme 3. Mono- and Dinuclear Tridentate Complexes



By substituting the bpy-d_8 analogue for the more commonly used [Ru(bpy)$_2$Cl$_2$], the ^{1}H NMR spectra of the resulting complexes were greatly simplified and showed only resonances from the parent ligand, allowing the complexes to be unambiguously identified by NMR.[13] It should be remembered that each metal center can exist as a Δ or Λ stereoisomer. For the mononuclear complexes these stereoisomers are indistinguishable by NMR but for the dinuclear complexes they led to Δ,Δ/Λ,Λ and Δ,Λ diastereomers. The signals from these two diastereomers were most often closely overlapping, making multiplicities sometimes difficult to discern. This point is illustrated by the ^{1}H NMR of

(13) Chirayil, S.; Thummel, R. P. *Inorg. Chem.* **1989**, *28*, 813–814.

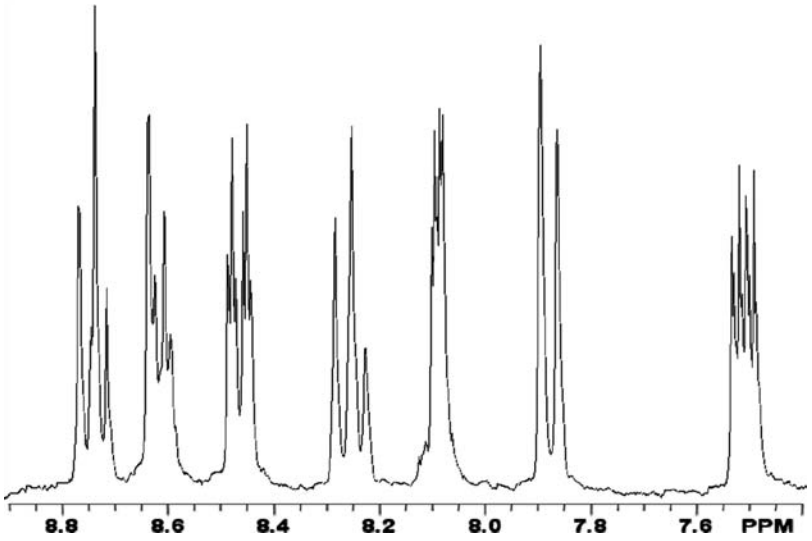


Figure 1. Aromatic region of the 300 MHz ^{1}H NMR spectrum of $[(bpy\text{-}d_8)_2Ru(\mathbf{20})Ru(bpy\text{-}d_8)_2](PF_6)_4$ in CD_3CN at 25 °C.

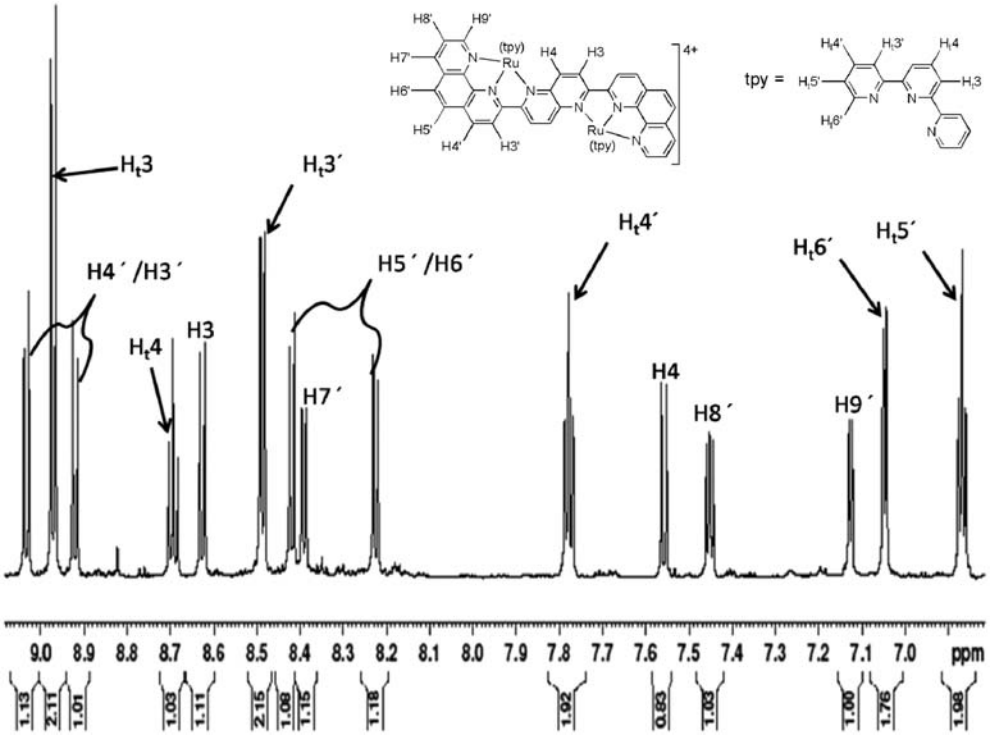


Figure 2. Aromatic region of the 800 MHz ^{1}H NMR spectrum of $[(tpy)Ru(\mathbf{21})Ru(tpy)](PF_6)_2$ in CD_3CN at 25 °C; H_t = tpy proton.

Table 1. Photophysical Data for Ligands **4**, **6**, **11**, and **18**−**25**[a]

ligand	absorption λ_{max} (nm) (ε, $M^{-1}cm^{-1}$)	emission λ_{max} (nm)
4	283 (16,292), 293 (13,459), 322 (14,657),	432
6	289 (14,364)	452
11	296 (21,200), 309 (22,340), 337 (23,435), 341 (22,300)	435
18	240 (78,040), 275 (24,000), 285 (23,100), 323 (36,560), 335 (39,360)	440
19	229 (55,740), 241 (shoulder), 287 (39,820), 332 (26,430)	433
20	231 (39,000), 243 (30,420), 356 (27,580), 372 (24,650)	459
21	355 (15,888), 373 (15,290)	458
22	215 (9,040), 272 (2,870), 328 (3,690)	460
23	230 (62,240), 265 (35,790), 331 (16,240), 347 (13,470)	463
24	243 (75,336), 334 (44,199)	453
25	230 (78,714), 268 (37,737), 337 (29,353), 352 (25,830)	453

[a] Electronic absorption and emission spectra were recorded in CH_3CN (5×10^{-5} M) at $T = 25 \pm 1°$ C. The emission spectra were obtained by excitation at longest wavelength λ_{max} of the free ligand.

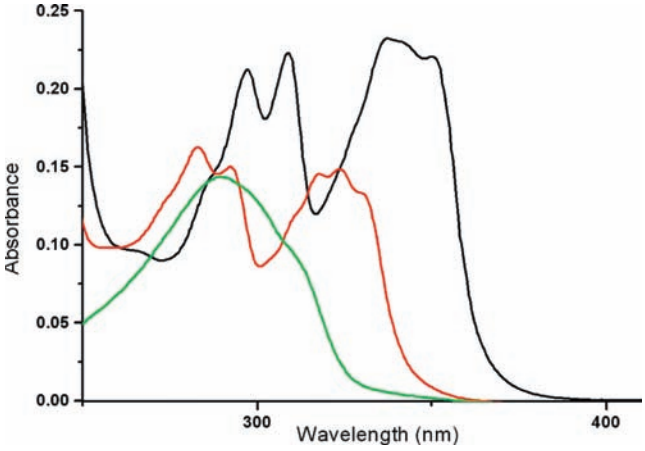


Figure 3. Electronic absorption spectra of **5** (red), **6** (green), and **11** (black) in CH_3CN (10^{-5} M).

$[(bpy\text{-}d_8)_2Ru(\mathbf{20})Ru(bpy\text{-}d_8)_2](PF_6)_4$ (Figure 1) which shows seven well resolved equal area peaks each of which is associated with two nearly equivalent diastereomeric protons.

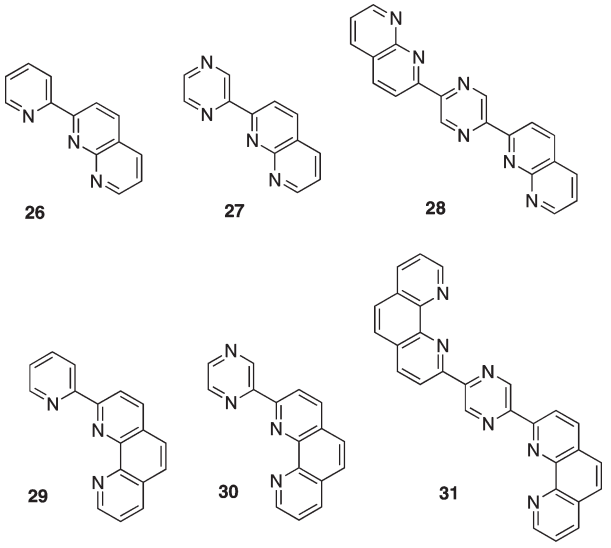
The phenanthroline-substituted 1,5-naps **19**, **21**, and **23** formed mono- and/or dinuclear bis-tridentate complexes with Ru(II). Treatment with 1 equiv of $[Ru(tpy)Cl_3]$ led to the mononuclear complexes of **19** and **21**, and 2 equiv of the same reagent provided dinuclear complexes of **21** and **23** (Scheme 3).

Ru(tpy) complexes possess higher symmetries than those derived from $Ru(bpy)_2$, and hence their NMR spectra are often less complicated, allowing them to be interpreted without the need for a perdeuterated auxiliary ligand. Thus, the symmetrical dinuclear complexes of **21** and **23** show 15 signals integrating for 9 protons apiece for the bridging ligand and 6 signals for the two tpys. The tpy ligands integrate for 4H per signal except the H4 triplet which integrates for 2H. Often all these signals could be resolved and using 2D-connectivities they could be assigned as shown for $[(tpy)\text{-}Ru\text{-}(\mathbf{21})Ru(tpy)](PF_6)_2$ in Figure 2.

Properties of Ligands and Complexes

The electronic absorption and emission spectra of the 1,5-naphthyridyl ligands were measured at room temperature in CH_3CN, and the data are collected in Table 1. Most of the systems show a prominent band below 300 nm which corresponds to their $\pi-\pi^*$ absorption as well as a longer wavelength band at 322−373 nm which is attributed to n-π^* absorption. The effect of pyrid-2-yl substitution on the parent 1,5-naphthyridine is illustrated in Figure 3. The lowest energy absorption is shown by the 2,6-disubstituted system **11** where the two pyrid-2-yl rings exert both an electronegativity and a delocalization effect. This effect is less pronounced for the monosubstituted derivative **5** which is blue-shifted by about 20 nm. For the 4-substituted 1,5-naphthyridine **6**, a more pronounced blue-shift is observed with a single broadband centered at 289 nm. This system enjoys less delocalization than the isomeric **5**. The energy minimized geometries of both **5** and **6** were analyzed, and it was found that while the dihedral angle between the pyridine and naphthyridine rings in **5** is only about 1°, the same dihedral angle for **6** is about 35°. When excited in their longest wavelength absorption band, all the ligands show modest emission.

The electronic spectra of the heteroleptic $[Ru(bpy\text{-}d_8)_2L]^{2+}$ complexes of these same three ligands, **5**, **6**, and **11**, were recorded in acetonitrile, and the data are collected together with that for other bidentate Ru(II) complexes in Table 2. For the sake of comparison we have also included data for complexes involving several other related systems **26**−**31** which we reported earlier.[14−16] The question arises of a possible isotope effect complicating the interchangeable use of bpy and bpy-d_8 as the auxiliary ligand. To examine this question we prepared $[Ru(bpy)_2(\mathbf{6})]^{2+}$ and compared its photophysical and electrochemical properties with the analogous bpy-d_8 complex and found no difference in these properties.



For $[Ru(bpy\text{-}d_8)_2L]^{2+}$ where L = **5**, **6**, and **11**, the lowest energy absorption is attributed to a metal-to-ligand charge transfer (MLCT) which is associated with the photoexcitation of a metal d-orbital electron to a ligand π^*-orbital. Since there are two different ligands associated with the Ru(II) center, two components are observed for this MLCT absorption band (Figure 4). The high energy component found at 432−444 nm is assigned to MLCT to the bpy ligand while the band at 491−504 nm for the mononuclear complexes corresponds to MLCT into the 1,5-nap ligand. For the dinuclear complex of the bridging ligand **11**, a 67 nm red shift of this long wavelength band is observed.

To evaluate the electronic impact of the 1,5-naphthyridyl linker versus pyrazine, we compared the heteroleptic complexes of **18**, **26**, and **27**, and these are illustrated in Figure 5. The difference in the absorption energies of the pyridyl and pyrazinyl systems, **26** and **27**, is small. However the 1,5-naphthyridinyl system **18** shows a 43 nm red shift of the long wavelength band, implying that the 1,5-nap moiety is a substantially better acceptor than 2-pyridyl or pyrazinyl because of increased delocalization in the 10 π azaaromatic ring.

Considering the increased delocalizing ability of naphthyridyl versus pyridyl, it became of interest to look at 2,6-di(1′,8′-naphthyrid-2′-yl)-1,5-nap (**20**) as a bridging ligand. Figure 6 compares the mono- and dinuclear heteroleptic complexes of this ligand with the analogous pyrazine-linked systems. All four complexes show a high energy component at 427−435 nm for MLCT into the bpy ligand. The strong 435 nm

(14) Brown, D. S. Ph.D. Dissertation, University of Houston, Houston, Texas, 2003.
(15) Brown, D.; Muranjan, S.; Thummel, R. P. *Eur. J. Inorg. Chem.* **2003**, 3547–3553.
(16) Brown, D.; Zong, R.; Thummel, R. P. *Eur. J. Inorg. Chem.* **2004**, 3269–3272.

Table 2. Photophysical and Electrochemical Data for the Ru(II) Complexes of bpy-Type Ligands

complex	absorp λ_{max} (nm) (ε, $M^{-1}cm^{-1}$)[a]	λ_{em} (nm)	Φ[b]	$E_{1/2}$ (ox)[c]	$E_{1/2}$ (red)[c]	K_c
$[Ru(\mathbf{5})(bpy\text{-}d_8)_2]^{2+}$	437 (8839), 491 (7420)	800	0.0018	+1.36	−0.95, −1.44, −1.66	
$[Ru(\mathbf{6})(bpy\text{-}d_8)_2]^{2+}$	444 (10,165), 504 (6234), 557 (2826)	740	0.00036	+1.31	−1.00, −1.40, −1.55 −1.82	
$[Ru(\mathbf{11})(bpy\text{-}d_8)_2]^{2+}$	437 (10,922), 499 (9028)	720	0.0028	+1.38	−0.93, −1.45, −1.64	
$[Ru(\mathbf{18})(bpy\text{-}d_8)_2]^{2+}$	431 (40,150), 560 (40,000)	820	0.00048	+1.33	−0.74, −1.24, −1.48	
$[Ru(\mathbf{20})(bpy\text{-}d_8)_2]^{2+}$	432 (14,150), 570 (11,350)	620	0.0024	+1.35	−0.66, −1.09	
$[Ru(\mathbf{26})(bpy)_2]^{2+}$	442 (43,420), 506 (40,120)	745 (m)[d]		+1.26	−0.96, −1.49, −1.73[d]	
$[Ru(\mathbf{27})(bpy)_2]^{2+}$	426 (40,260), 517 (40,050)	772 (m)[d]		+1.38	−0.79, −1.36, −1.67[d]	
$[Ru(\mathbf{28})(bpy\text{-}d_8)_2]^{2+}$	427 (32,400), 543 (24,760)	807 (w)[e]		+1.40	−0.63, −1.06, −1.59[e]	
$[((bpy\text{-}d_8)_2Ru)_2(\mathbf{11})]^{4+}$	432 (10,876), 525 (6045), 566 (8082)	810	0.0011	+1.44, +1.45	−0.56, −1.09, −1.52	1.4
$[((bpy\text{-}d_8)_2Ru)_2(\mathbf{20})]^{4+}$	435 (120,400), 580 (6300), 644 (8400)	no emission		+1.28, +1.44	−0.28, −0.65, −1.42	506
$[((bpy)_2Ru)_2(\mathbf{28})]^{4+}$	434 (55,080), 471 (40,500), 592 (6500), 655 (15,500)	no emission[e]		+1.34, +1.57	−0.31, −0.67, −1.49	7730[e]

[a] CH_3CN (5×10^{-5} M). [b] Referenced to $[Ru(bpy)_3](PF_6)_2$ in CH_3CN at 25 °C. [c] Potentials are in volts vs SCE; solutions are in 0.1 M TBAP; the solvent was CH_3CN; $T = 25 \pm 1$ °C; K_c = comproportionation constant. [d] Reference 14. [e] Reference 15.

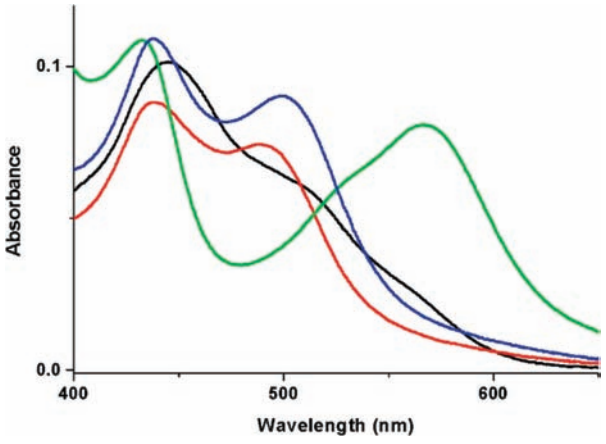


Figure 4. Electronic absorption spectra of $[Ru(bpy\text{-}d_8)_2L](PF_6)_2$ where L = **5** (red), **6** (black), **11** (blue); and $[(bpy\text{-}d_8)_2Ru(\mathbf{11})Ru(bpy\text{-}d_8)_2](PF_6)_4$ (green) in CH_3CN (5×10^{-5} M).

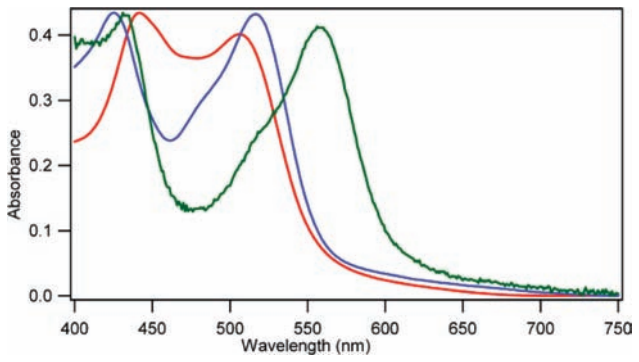


Figure 5. Electronic absorption spectra of $[Ru(bpy\text{-}d_8)_2L](PF_6)_2$ where L = **18** (green), **26** (red), **27** (blue) in CH_3CN (5×10^{-5} M).

absorbance of the dinuclear 1,5-nap-bridged system is somewhat unusual. In the long wavelength region a pronounced red-shift is observed for the dinuclear complexes as compared with their mononuclear counterparts. The magnitude of this red shift is less for the 1,5-nap-linked system (74 nm) than for the pyrazine-linked one (112 nm). The greater red shift for the pyrazine system indicates that the two metal centers communicate better through this monocyclic linker.

Table 3 summarizes the electronic absorption data for the mono- and dinuclear Ru(II) complexes of the tridentate and bis-tridentate ligands. In comparing $[Ru(\mathbf{19})(tpy)]^{2+}$ and $[Ru(\mathbf{21})(tpy)]^{2+}$, in which the latter is simply a phen substituted derivative of the former, one sees a small red shift of

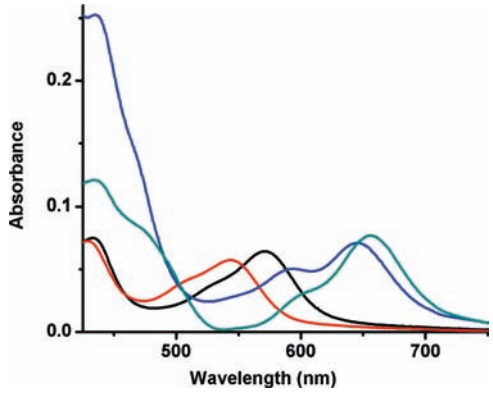


Figure 6. Electronic absorption spectra of $[(bpy)_2Ru(\mathbf{20})](PF_6)_2$ (black), $[(bpy)_2Ru(\mathbf{28})](PF_6)_2$ (red), $[(bpy)_2Ru(\mathbf{20})Ru(bpy)_2](PF_6)_4$ (green), and $[(bpy)_2Ru(\mathbf{28})Ru(bpy)_2](PF_6)_4$ (blue), in CH_3CN (5×10^{-5} M).

3 nm in the two longer wavelength bands upon going from **19** to **21**. When a second Ru(II) is coordinated to **21**, the red shift is much more pronounced, and the long wavelength band shifts from 531 to 606 nm. For the bidentate complexes of **5** and **6** we saw a strong red shift as the size of the chelate ring was increased from five atoms to six.[17] The chelate ring size effect is even more pronounced in comparing the dinuclear complex of **21** (606 nm) with that of **23** (693 nm). In considering the long wavelength absorption of the dinuclear complex of **31** (636 nm), it appears that the chelate ring size effect is more influential than the ability of the linker (pyrazine vs 1,5-nap) to improve metal−metal communication.

The room temperature emission spectra of the complexes were measured in CH_3CN, and the emission maxima and quantum yields are reported in Tables 2 and 3. All the complexes were weak emitters with the highest quantum yield being only 0.3%. Such behavior is not unusual for systems involving tpy-like tridentate complexation or for dinuclear systems where intramolecular quenching is to be expected. The weak emission of the tris-bidentate complexes of **5**, **11**, **18**, and **20** may be due, in part, to the presence of uncoordinated nitrogens which can participate in intramolecular excited state quenching. In earler work, we have shown that tris-bidentate Ru(II) complexes involving a

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Table 3. Photophysical and Electrochemical Data of Ru(II) Complexes of tpy-Type Ligands

complexes	absorp λ_{max} (nm) (ε, $M^{-1}cm^{-1}$)[a]	λ_{em} (nm)	Φ[b]	$E_{1/2}$ (ox)[c]	$E_{1/2}$ (red)[c]	K_c
[Ru(**19**)(tpy)]$^{2+}$	305 (45,890), 359 (49,380), 455 (9480), 528 (9240)	750	0.0007	+1.37	−0.82, −1.32, −1.66	
[Ru(**21**)(tpy)]$^{2+}$	304 (39,600), 382 (37,790), 458 (6950), 531 (6540)	765	0.00042	+1.40	−0.75, −1.15, −1.52	
[Ru(**29**)(tpy)]$^{2+}$	231 (46,528), 295 (55,038), 469 (12,056), 488 (11,792)	no emission		+1.33	−1.06, −1.45, −1.78[d]	
[Ru(**30**)(tpy)]$^{2+}$	329 (31,628), 343 (25,548), 448 (8710), 506 (8320)	720	0.00032	+1.42	−0.88, −1.39, −1.69[d]	
[Ru(**31**)(tpy-d_{11})]$^{2+}$	329 (26,060), 351 (16,390), 426 (8520), 531 (4890)	744[e]	0.0030[e]	+1.40	−0.74, −1.18, −1.55[e]	
[((tpy)Ru)$_2$(**21**)]$^{4+}$	303 (49,470), 387 (59,720), 457 (4840), 606 (5060)	840	0.00014	+1.42, +1.50	−0.38, −0.84, −1.41	24
[((tpy)Ru)$_2$(**23**)]$^{4+}$	301 (31,600), 369 (13,310), 454 (10,900), 693 (3300)	825	0.00032	+1.43, +1.58	−0.20, −0.60, −1.23	343
[((tpy-d_{11})Ru)$_2$(**31**)]$^{4+}$	447 (14,520), 586 (6010), 636 (15,300)	839[e]	0.00011[e]	+1.36, +1.56	−0.35, −0.76, −1.37	2404[e]

[a] CH_3CN (5×10^{-5} M). [b] Referenced to [Ru(bpy)$_3$](PF$_6$)$_2$ in CH_3CN at 25 °C. [c] Potentials are in volts vs SCE; solutions are in 0.1 M TBAP; the solvent was CH_3CN; $T = 25 \pm 1$ °C; K_c = comproportionation constant. [d] Reference 14. [e] Reference 16.

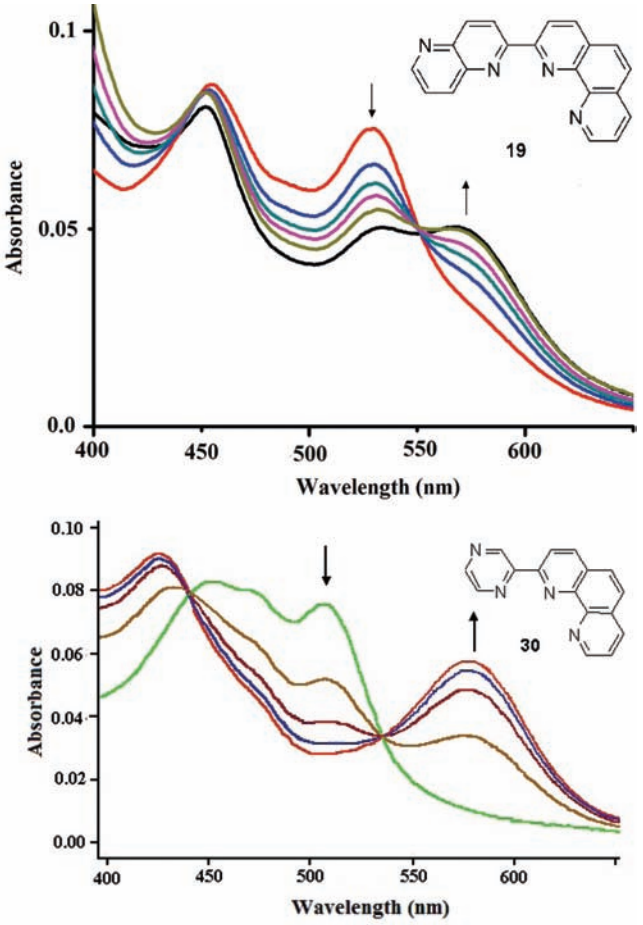

Figure 7. Titration of [Ru(**19**)(tpy)]$^{2+}$ with CF_3COOH (100%) (top) and [Ru(**30**)(tpy)]$^{2+}$ with CF_3SO_3H (2.21 M) (bottom); in CH_3CN (5×10^{-5} M); added volume = 0, 10, 20, 30, 40, 50 μL.

six-membered chelate ring such as [Ru(bpy-d_8)$_2$(**6**)]$^{2+}$ have significantly reduced excited state lifetimes.[17b]

Another effective method for probing the effectiveness of pyrazine versus 1,5-naphthyridine as a linker is to examine the effect of protonation at the uncoordinated nitrogen of the linker. To this end we examined the titration of [Ru(**19**)(tpy)]$^{2+}$ and [Ru(**30**)(tpy)]$^{2+}$ with acid and Figure 7 illustrates the result of that study. The low energy absorption band at 528 nm of [Ru(**19**)(tpy)]$^{2+}$ is associated with MLCT to the 1,5-nap half of ligand **19**. Protonation at the remote N5 position makes this moiety a better electron acceptor, and thus lowers the energy of the absorption giving rise to a new band at 575 nm. The red shift is 47 nm, and the absorption changes through the addition of 50 μL of CF_3COOH are modest. By contrast, the similar changes in the pyrazine analogue [Ru(**30**)(tpy)]$^{2+}$ are more marked with complete disappearance of the band at 506 nm and the rapid appearance of a new red-shifted band at 570 nm. The magnitude of this shift (64 nm) is also greater than for the 1,5-nap complex.

The half-wave redox potentials for the complexes are summarized in Tables 2 and 3, and several important trends may be noted. Oxidation involves the removal of an electron from a metal-based d orbital, and for the 1,5-binap complexes the potential for this process falls in the relatively narrow range of +1.31 to +1.40 V. Reduction, on the other hand, involves the addition of an electron to a ligand π^*-orbital and thus is more sensitive to electronegativity changes in the ligand. Ligand **20** with three naphthyridine rings is the best acceptor and hence shows the most positive reduction potential for both its mononuclear (−0.66 V) and dinuclear (−0.28 V) complexes. Ligands **5**, **6**, **26**, and **29** each contain only three nitrogens and therefore are the least electronegative. Being poorer acceptors, the first reduction potentials of their mononuclear complexes are the least positive, falling in the range of −0.95 to −1.06 V. Complexes with ligands having four nitrogens show somewhat more positive potentials. As expected, the dinuclear complex of **23** which shows the smallest difference between its first oxidation and reduction also shows the lowest energy electronic absorption band.

Although the two metal centers occupy identical coordination environments in all the dinuclear complexes, in each case we observe two oxidation waves, indicating the existence of metal−metal communication. This interaction can be evaluated as a comproportionation constant (K_c) derived from the difference in the observed oxidation potentials.[18] These values have been calculated and are included in the tables. The two simplest bridging ligands, **11** and **21**, show the smallest K_c values. The difference between the two oxidation waves for the dinuclear complex of **11** is almost imperceptible. For **20** and **23** the communication is somewhat better but still substantially less than for the two pyrazine-linked dinuclear complexes which show K_c values of 2404 and 7730.

In this study we have developed a straightforward and general approach to the synthesis of a variety of ligands which involve the 1,5-naphthyridine nucleus as a coordinating entity. Many of these ligands use 1,5-nap as a linker between two equivalent sites giving rise to both bis-bidentate and bis-trisdentate ligands. Ru(II) complexes have been prepared from these ligands, and their photophysical and electrochemical properties have been examined and correlated with structure. The efficiency of the 1,5-nap linker has

(18) (a) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146–1148.

been compared to the previously studied pyrazine linker, and the latter is found to promote better communication between two bound metals.

Future studies might examine the complexation properties of the mononuclear complexes of the bridging ligands **11**, **20**, and **21**. Heterobimetallic complexes of these systems might evidence interesting energy transfer properties, as well as possible sensing potential. The homoleptic complex $[Ru(\mathbf{21})_2]^{2+}$ has two vacant tridentate sites and thus presents an even more intriguing situation for multimetal complexation. Finally, we plan to examine the synthon 3-amino-2-pyridinecarbaldehyde as a convenient entry to a variety of other related 1, 5-naphthyridine ligands.

Experimental Section

NMR spectra were obtained at 300 or 800 MHz for ^{1}H and 75 MHz for ^{13}C NMR. Chemical shifts were reported in parts per million relative to the residual proton or carbon of the corresponding solvent. Luminescence measurements were carried out with a Perkin-Elmer LS-50B luminescence spectrometer. UV−vis spectra were recorded on a Lambda 3B spectrometer. All spectra were corrected for the background spectrum of the solvent. Cyclic voltammetric (CV) measurements were carried out using a BAS Epsilon Electroanalytical System. The CV experiments were performed in acetonitrile solution using a one compartment cell equipped with glassy carbon working electrode, a saturated calomel reference electrode (SCE), a Pt wire as the auxiliary electrode, and NBu_4PF_6 (0.1 M) as an electrolyte. Melting points were measured on Thomas-Hoover capillary melting point apparatus and are not corrected. A household microwave oven (900 W, 60 Hz), modified according to a previously published description,[19] was used in the formation of the complexes. Elemental analyses were carried out by QTI, P.O. Box 470, Whitehouse, NJ 08888−0470. Elemental analysis cannot be performed on bpy-d_8 containing complexes. The [*cis*-Ru(bpy-d_8)$_2$Cl$_2$],[20] 2-aminonicotinaldehyde (**16**),[10] and 8-amino-7-quinolinecarbaldehyde (**17**)[11] were prepared according to reported procedures. All other chemicals are commercially available, and all solvents are reagent grade.

1,5-Naphthyridine Mono-N-oxide (2). A mixture of **1** (0.30 g, 2.3 mmol) and *m*-chloroperbenzoic acid (0.746 g, 4.6 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 4 h. The solution was diluted with CH_2Cl_2 (100 mL) and washed with Na_2CO_3 (3 × 25 mL). The solution was concentrated to give **2** as a white solid (0.390 g, 95%), mp 143−147 °C (lit.[5] mp 150−155 °C): ^{1}H NMR ($CDCl_3$) δ 9.02 (d, J = 5.4 Hz, 2H), 8.53 (d, J = 6.3 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.66 (dd, 1H), 7.50 (dd, J = 8.7, 6.3 Hz, 1H).

1,5-Naphthyridine Di-N-oxide (9). A mixture of **1** (1.0 g, 7.69 mmol), acetic acid (25 mL), and hydrogen peroxide (28%, 12 mL) was heated at 60 °C for 2 h. The solution was concentrated to 2−3 mL, made basic with KOH, and extracted with $CHCl_3$ (6 × 20 mL). The extracts were dried over anhydrous K_2CO_3 and concentrated to provide **9** as a white solid (0.60 g, 50%), mp 290−295 °C (lit.[5] mp 299−301 °C): ^{1}H- NMR ($CDCl_3$) δ 8.59 (d, J = 6.0 Hz, 2H), 8.53 (d, J = 9.3 Hz, 2H), 7.55 (dd, J = 8.7 Hz, 2H).

2-Chloro-1,5-naphthyridine (3) and 4-Chloro-1,5-naphthyridine (4). The mono-N-oxide **2** (1.0 g, 6.9 mmol) was added to cold, freshly distilled $POCl_3$ (35 mL), and the mixture was refluxed for 20 min. After cooling, the solution was carefully poured onto ice, and neutralized with NH_4OH. The resultant solid was filtered and dried in vacuum. Chromatography on silica gel, eluting with EtOAc/hexane (1:3) provided **3** and **4** as white solids.

Compound **3**: (0.26 g, 25%): mp. 105−107 °C (lit.[5,6c] mp 109−111 °C): ^{1}H NMR ($CDCl_3$) δ 8.99 (dd, J = 4.5 Hz, 1H), 8.37−8.31 (2 overlapping d, 2H), 7.68 (dd, 1H), 7.63 (d, 1H).

Compound **4**: (0.23 g, 20%): mp 95−98 °C: ^{1}H NMR ($CDCl_3$) δ 9.04 (d, J = 2.7 Hz, 1H), 8.81 (d, J = 4.8 Hz, 1H), 8.39 (d, J = 8.1 Hz, 1H), 7.73−7.67 (overlapping d and dd, 2H); ^{13}C NMR ($CDCl_3$) δ 151.7, 150.8, 145.1, 144.2, 141.0, 138.1, 125.4, 124.6.

2-Cyano-1,5-naphthyridine (7). A solution of **2** (0.50 g, 3.43 mmol) and trimethylsilylcyanide (1.71 g, 17.25 mmol) in CH_2Cl_2 (100 mL) was stirred while benzoyl chloride (1.20 g, 8.55 mmol) was added dropwise over 15 min. The solution was stirred for another 30 min and then washed with water (2 × 20 mL), $NaHCO_3$ (3 × 10 mL), and brine (2 × 10 mL). The organic phase was dried ($MgSO_4$) and concentrated to afford **7** as a white solid (0.29 g, 54%), mp 196−198 °C: ^{1}H NMR (DMSO-d_6) δ 9.10 (dd, J = 4.2 Hz, 1H), 8.54 (d, J = 9.6 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.76 (dd, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 154.2, 144.5, 143.7, 139.3, 137.9, 134.5, 126.9, 126.2, 117.2; IR 2232 cm^{-1}.

2,6-Dichloro-1,5-naphthyridine (10). Following the procedure described **3** and **4**, the di-N-oxide **9** (1.0 g, 5.0 mmol) was treated with $POCl_3$ (35 mL) to provide a solid. Chromatography on silica gel, eluting with EtOAc/hexane (1:3) afforded **10** as a white solid (0.30 g, 40%), mp. 240−245 °C (lit.[5,6a,6b] mp 254−257 °C): ^{1}H NMR ($CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H).

2,6-Dicyano-1,5-naphthyridine (12). A solution of **9** (0.15 g, 0.93 mmol) and KCN (0.38 g, 5.78 mmol) in water (10 mL), was stirred while benzoyl chloride (0.52 g, 3.7 mmol) was added dropwise over 15 min. The solution was stirred for another 30 min to give a ppt which was filtered and washed with water (2 × 20 mL) and Et_2O (2 × 10 mL) to afford **12** as a white solid (0.07 g, 45%), mp 282−284 °C: ^{1}H NMR (DMSO-d_6) δ 8.86 (d, J = 8.5 Hz, 2H), 8.44 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 144.4, 139.8, 136.5, 129.0, 117.0; IR 2240 cm^{-1}.

2-Acetyl-1,5-naphthyridine (8). To a stirred solution of 2-cyano-1,5-naphthyridine (**7**, 0.08 g, 0.52 mmol) in dry THF (15 mL) was added dropwise MeMgBr (3.0 mol in hexane, 0.24 mL, 0.71 mmol). The solution was stirred for 2 h at 40 °C, after which the reaction was quenched with saturated NH_4Cl (5 mL). The solution was stirred for another 30 min and then neutralized with Na_2CO_3. The THF was evaporated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with brine (25 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **8** as a white solid (0.035 g, 40%), mp 124−125 °C: ^{1}H- NMR ($CDCl_3$) δ 9.07 (dd, J = 4.2, 1.5 Hz, 1H), 8.44 (2 overlapping d, 2H), 8.30 (d, J = 8.1 Hz, 1H), 7.68 (dd, J = 8.4, 4.2 Hz, 1H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 199.7, 153.6, 153.0, 144.9, 142.8, 138.36, 138.30, 124.9, 121.5, 25.6. Anal. Calcd for $C_{10}H_8N_2O$: C, 69.77; H, 4.65; N, 16.28. Found: C, 69.45; H, 4.69; N, 16.00.

2,6-Diacetyl-1,5-naphthyridine (13). Following the procedure described for **8**, a stirred solution of 2,6-dicyano-1,5-naphthyridine (**12**, 0.03 g, 0.16 mmol) in dry THF (15 mL) was treated dropwise with MeMgBr (3.0 mol in hexane, 0.20 mL, 0.64 mmol). The solution was stirred for 4 h at 40 °C and then quenched to give a ppt. The crude product was purified by chromatography on silica gel eluting with EtOAc/hexane (2:1) to give **13** as a white solid (0.015 g, 42%), mp 226−227 °C: ^{1}H- NMR ($CDCl_3$) δ 8.62 (d, J = 9.01 Hz, 2H), 8.43 (d, J = 9.01 Hz, 2H), 2.93 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 199.5, 154.9, 143.7, 139.1, 121.9, 25.5. Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.67; N, 13.08. Found: C, 67.02; H, 4.53; N, 12.77.

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Acetyl Derivatives of 1,5-naphthyridine (8 and 13−15). To a mixture of **1** (1.00 g, 7.70 mmol), $AgNO_3$ (0.44 g, 0.15 mmol), H_2SO_4 (1.0 mL), and pyruvic acid (0.68 g, 3.078 mmol) in water (60 mL) and CH_2Cl_2 (140 mL) was added $(NH_4)_2S_2O_8$ (5.08 g, 2.5 mmol) in small portions while stirring at room temperature for 4 h. The solution was made basic with NaOH. The CH_2Cl_2 fraction was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (4:1) to provide **13** and **14** as a white solids and a mixture of **8** and **15** that could not be separated by chromatography. Recrystallization of this mixture from cyclohexane, gave **15** as a white solid while the mother liquor contained **8** as a major component (>90%).

Compound **8**: (0.150 g, 12%), mp 124−125 °C. ^{1}H and ^{13}C NMR were identical to the sample prepared from 2-cyano-1, 5-naphthyridine.

Compound **13**: (0.200 g, 12%), mp 226−227 °C. ^{1}H and ^{13}C NMR were identical to the sample prepared from 2,6-dicyano-1,5-naphthyridine.

Compound **14**: (0.250 g, 10%), mp 157−158 °C. ^{1}H NMR ($CDCl_3$) δ 9.13 (d, J = 4.2 Hz, 2H), 7.76 (d, J = 4.2 Hz, 2H), 2.95 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 202.2, 151.5, 146.7, 140.8, 122.1, 32.8. Anal. Calcd for $C_{12}H_{10}N_2O_2 \cdot 0.1H_2O$: C, 66.72; H, 4.73; N, 12.97. Found: C, 66.53; H, 4.64; N, 12.50.

Compound **15**: (0.320 g, 25%), mp 145−147 °C. ^{1}H NMR ($CDCl_3$) δ 9.12 (d, J = 4.2 Hz, 1H), 8.52 (d, J = 8.71 Hz, 1H), 8.34 (d, J = 8.71 Hz, 1H), 7.78 (d, J = 4.2 Hz, 1H), 2.98 (s, 3H), 2.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 201.1, 198.9, 153.4, 153.2, 146.2, 145.1, 139.2, 138.9, 122.8, 121.7, 32.7, 25.9. Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.29; H, 4.67; N, 13.08. Found: C, 67.16; H, 4.70; N, 13.07.

2-(Pyrid-2′-yl)-1,5-naphthyridine (5). A mixture of 2-(tri-*n*-butylstannyl)pyridine (85−95%, 0.368 g, 1.00 mmol), **3** (0.150 g, 0.914 mmol), and tetrakis(triphenylphosphine)palladium(0) (5% mol, 0.104 mg, 0.09 mmol) in dry toluene (20 mL) was refluxed under Ar for 2 d. After cooling to room temperature, water (1 mL) was added, and the mixture was concentrated under reduced pressure. Chromatography on silica gel, eluting with hexane, followed by EtOAc/hexane (1:3) gave **5** as a white solid (0.150 g, 80%), mp 119−123 °C. ^{1}H NMR ($CDCl_3$) δ 8.97 (d, J = 3.9, Hz, 1H), 8.80 (d, J = 8.7 Hz, 1H), 8.75 (d, J = 6.6 Hz, 1H), 8.63 (d, J = 7.8 Hz, 1H), 8.50 (d, J = 8.7 Hz, 1H), 8.46 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 7.8 Hz, 1H), 7.66 (dd, J = 8.4, 4.2 Hz, 1H), 7.48 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 157.0, 155.7, 151.3, 149.5, 144.3, 143.5, 138.1, 137.7, 137.1, 124.6, 124.5, 122.7, 122.1; Anal. Calcd for $C_{18}H_{12}N_4$. 0.1. H_2O: C, 74.64; H, 4.30; N, 20.09. Found: C, 74.39; H, 4.17; N, 19.72.

4-(Pyrid-2′-yl)-1,5-naphthyridine (6). Following the procedure described for **5**, a mixture of 2-(tri-*n*-butylstannyl)pyridine (85−95%, 0.368 g, 1.00 mmol), **4** (0.150 g, 0.914 mmol), and tetrakis(triphenylphosphine)palladium(0) (5% mol, 0.104 mg, 0.09 mmol) in dry toluene (20 mL) provided a solid. Chromatography on silica gel, eluting with hexane, followed by EtOAc/hexane (1:3) gave **6** as a white solid (0.120 g, 60%), mp 75−78 °C. ^{1}H NMR ($CDCl_3$) δ 9.10 (d, J = 4.5 Hz, 1H), 9.04 (dd, J = 4.8, 2.1 Hz, 1H), 8.82 (d, J = 5.1 Hz, 1H), 8.49 (dd, J = 8.1, 2.1 Hz, 1H), 8.31 (d, J = 9.3 Hz, 1H), 8.10 (d, J = 4.5 Hz, 1H), 7.87 (dt, J = 7.8, 2.7 Hz, 1H), 7.64 (dd, J = 8.4, 4.2 Hz, 1H), 7.37 (dd, J = 7.8, 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 154.4, 151.5, 151.0, 150.1, 146.0, 144.6, 141.7, 138.1, 136.0, 127.6, 124.8, 124.3, 123.6; Anal. Calcd for $C_{18}H_{12}N_4 \cdot 0.1H_2O$: C, 74.89; H, 4.16; N, 19.37. Found: C, 74.97; H, 4.49; N, 19.48.

2,6-Di(pyrid-2′-yl)-1,5-naphthyridine (11). Following the procedure described for **5**, a mixture of 2-(tri-*n*-butylstannyl)pyridine (85−95%, 0.277 g, 0.753 mmol), **10** (0.050 g, 0.251 mmol), and tetrakis(triphenylphosphine)palladium(0) (5% mol, 0.029 mg, 0.025 mmol) in dry toluene (15 mL) provided a solid. Chromatography on silica gel, eluting with hexane, followed by CH_2Cl_2/hexane (1:1) gave a white solid, which was recrystallized from EtOH to provide **11** as a white crystals (50 mg, 80%), mp 245−247 °C. ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 8.72 (2 overlapping d, 4H), 8.57 (2 overlapping d, 4H), 7.88 (dt, J = 7.8 Hz, 2H), 7.38 (dd, J = 6.9, 5.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 156.0, 154.8, 148.5, 142.7, 137.3, 136.2, 123.6, 121.8, 121.1; Anal. Calcd for $C_{18}H_{12}N_4 \cdot 0.5$EtOH: C, 74.26; H, 4.56; N, 18.24. Found: C, 74.27; H, 4.13; N, 17.97.

2-(1′,8′-Naphthyrid-2′-yl)-1,5-naphthyridine (18). To a stirred solution of 2-acetyl-1,5-naphthyridine (**8**, 150 mg, 0.87 mmol) and 2-aminonicotinaldehyde (127 mg, 1.04 mmol) in EtOH (10 mL) was added solid KOH (100 mg). The solution was allowed to reflux overnight. After cooling to room temperature, the solution was filtered to give **18** as a white solid (190 mg, 85%), mp 240−243 °C. ^{1}H NMR ($CDCl_3$) δ 9.17 (d, J = 8.4 Hz, 1H), 9.13 (dd, J = 4.2, 2.1 Hz, 1H), 8.88 (2 overlapping d, 2H), 8.55 (d, J = 9.0 Hz, 1H), 8.53 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 9.01 Hz, 1H), 8.31 (dd, J = 8.4, 1.8 Hz, 1H), 7.71 (dd, J = 8.7, 3.9 Hz, 1H), 7.57 (dd, J = 8.1, 4.5 Hz, 1H) ; ^{13}C NMR ($CDCl_3$ + CD_3OD) δ 158.4, 155.9, 154.8, 153.4, 151.2, 143.6, 143.1, 138.2, 138.1, 137.7, 137.5, 124.7, 123.5, 123.3, 122.7, 120.6; Anal. Calcd for $C_{16}H_{10}N_4$-$1H_2O$: C, 69.50; H, 4.30; N, 20.28. Found: C, 69.16; H, 3.94; N, 20.26.

2-(1′,10′-Phenanthrolin-2′-yl)-1,5-naphthyridine (19). Following the procedure described for **18**, the reaction of 2-acetyl-1, 5-naphthyridine (**8**, 75 mg, 0.436 mmol) with 8-aminoquinoline-7-carbaldehyde (82 mg, 0.479 mmol) provided a solid. Chromatography on silica gel, eluting with hexane, followed by CH_2Cl_2/MeOH (95:5) provided **19** as a white solid (0.11 g, 82%), mp 150−151 °C. ^{1}H NMR ($CDCl_3$) δ 9.60 (d, J = 9.0 Hz, 1H), 9.39 (d, J = 4.2 Hz, 1H), 9.13 (d, J = 8.1 Hz, 1H), 9.05 (dd, J = 4.5, 1.8 Hz, 1H), 8.66 (d, J = 8.7 Hz, 1H), 8.56 (d, J = 8.7 Hz, 1H), 8.50 (d, J = 8.41 Hz, 1H), 8.42 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.7, Hz, 1H), 7.92 (AB quartet, 2H), 7.76 (dd, J = 8.4, 4.5 Hz, 1H), 7.71 (dd, J = 8.1, 4.5 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ 156.5, 155.8, 151.4, 149.5, 144.4, 143.3, 138.8, 138.2, 137.8, 137.7, 137.5, 137.1, 129.5, 129.4, 127.2, 126.8, 124.4, 124.3, 123.2, 121.9; Anal. Calcd for $C_{20}H_{12}N_4$-$0.5CH_3OH$: C, 75.92; H, 4.32; N, 17.28. Found: C, 75.86; H, 3.87; N, 16.99.

2,6-Bis(1′,8′-naphthyrid-2′-yl)-1,5-naphthyridine (20). Following the procedure described for **18**, the reaction of 2,6-diacetyl-1,5-naphthyridine (**13**, 50 mg, 0.23 mmol) with 2-aminonicotinaldehyde (63 mg, 0.514 mmol) provided **20** as a white solid (0.09 g, 95%), mp >300 °C: ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 9.06 (d, J = 8.12 Hz, 2H), 8.96 (dd, J = 4.2, 1.5 Hz, 2H), 8.83 (d, J = 8.7 Hz, 2H), 8.55 (d, J = 8.7 Hz, 2H), 8.33 (d, J = 9.0 Hz, 2H), 8.24 (dd, J = 8.42, 2.1 Hz, 2H), 7.46 (dd, J = 8.3, 4.5 Hz, 2H); ^{13}C NMR could not be obtained because of poor solubility. Anal. Calcd for $C_{24}H_{14}N_6.H_2O$: C, 71.28; H, 3.96; N, 20.79. Found: C, 70.82; H, 3.69; N, 20.12.

2,6-Bis(1′,10′-Phenanthrolin-2′-yl)-1,5-naphthyridine (21). Following the procedure described for **18**, the reaction of 2, 6-diacetyl-1,5-naphthyridine (**13**, 50 mg, 0.234 mmol) with 8-aminoquinoline-7-carbaldehyde (88 mg, 0.514 mmol) provided **21** as a white solid (0.11 g, 96%), mp > 300 °C. ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 9.57 (d, J = 8.7 Hz, 2H), 9.16 (dd, J = 4.5, 1.5 Hz, 2H), 9.09 (d, J = 8.1 Hz, 2H), 8.73 (d, J = 9.0 Hz, 2H), 8.47 (d, J = 8.4 Hz, 2H), 8.33 (dd, J = 8.5, 1.8 Hz, 2H,), 7.88 (AB quartet, 4H), 7.71 (dd, J = 7.6, 4.5 Hz, 2H); ^{13}C NMR could not be obtained because of poor solubility; Anal. Calcd for $C_{32}H_{18}N_6 \cdot 2H_2O$: C, 70.52; H, 3.70; N, 15.18. Found: C, 70.93; H, 4.16; N, 15.23.

4,8-Bis(1′,8′-naphthyrid-2′-yl)-1,5-naphthyridine (22). Following the procedure described for **18**, the reaction of 4,8-diacetyl-1,5-naphthyridine (**14**, 50 mg, 0.234 mmol) with 2-aminonicotinaldehyde (63 mg, 0.51 mmol) provided **22** as a brown solid (0.08 g, 83%), mp >300 °C: ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 8.75 (d, J = 4.5 Hz, 2H), 8.70 (d, J = 4.5 Hz, 2H), 8.06 (s,

4H), 8.03 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 4.5 Hz, 2H), 7.22 (dd, J = 7.4, 4.5 Hz, 2H); ^{13}C NMR could not be obtained because of poor solubility; Anal. Calcd for $C_{24}H_{14}N_6 \cdot 1H_2O$: C, 71.28; H, 3.96; N, 20.79. Found: C, 71.75; H, 3.76; N, 20.46.

4,8-Bis(1′,10′-phenanthrolin-2′-yl)-1,5-naphthyridine (23). Following the procedure described for **18**, the reaction of 4, 8-diacetyl-1,5-naphthyridine (**14**, 50 mg, 0.234 mmol) with 8-aminoquinoline-7-carbaldehyde (88 mg, 0.514 mmol) provided **23** as a yellow solid (0.09 g, 75%), mp > 300 °C. ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 9.21 (d, J = 4.5 Hz, 2H), 9.17 (d, J = 8.4 Hz, 2H), 8.61 (d, J = 8.1 Hz, 2H), 8.55 (d, J = 4.5 Hz, 2H), 8.45 (d, J = 8.4 Hz, 2H), 8.32 (dd, J = 7.5, 2.1 Hz, 2H), 7.92 (AB quartet, 4H), 7.68 (dd, J = 8.0, 4.5 Hz, 2H); ^{13}C NMR could not be obtained because of poor solubility; Calcd for $C_{32}H_{18}N_6$-$2H_2O$: C, 70.52; H, 3.70; N, 15.18. Found: C, 70.93; H, 4.16; N, 15.23.

2,8-Bis(1′,8′-naphthyrid-2′-yl)-1,5-naphthyridine (24). Following the procedure described for **18**, the reaction of 2,8-diacetyl-1,5-naphthyridine (**15**, 50 mg, 0.234 mmol) with 2-aminonicotinaldehyde (63 mg, 0.514 mmol) provided **24** as a white solid (0.08 g, 89%), mp 250−253 °C: ^{1}H NMR ($CDCl_3$) δ 9.35 (d, J = 8.7 Hz, 1H), 9.27−9.22 (m, 3H), 8.72 (dd, 3H), 8.50 (d, J = 4.2 Hz, 1H), 8.46 (d, J = 9.01 Hz, 1H), 8.40 (dd, J = 8.1, 2.1 Hz, 1H), 8.32 (d, J = 7.8 Hz, 1H), 8.27 (dd, J = 8.1, 2.7 Hz, 1H), 7.64 (dd, J = 8.7, 4.2 Hz, 1H), 7.57 (dd, J = 7.8, 3.9 Hz, 1H). ^{13}C NMR ($CDCl_3$ + CD_3OD) δ 158.1, 157.9, 155.5, 155.2, 154.7, 153.36, 153.30, 151.4, 145.4, 144.0, 140.2, 138.0, 137.7, 137.4, 137.3, 136.1, 126.0, 125.3, 123.1, 122.9, 122.6, 122.5, 122.4, 121.2, 120.2; Calcd for $C_{24}H_{14}N_6 \cdot 1/3CHCl_3$: C, 68.55; H, 3.14; N, 19.73. Found: C, 68.55; H, 3.14; N, 19.83.

2,8-Bis(1′,10′-phenanthrolin-2′-yl)-1,5-naphthyridine (25). Following the procedure described for **18**, the reaction of 2, 6-diacetyl-1,5-naphthyridine (**15**, 50 mg, 0.234 mmol) with 8-aminoquinoline-7-carbaldehyde (88 mg, 0.514 mmol) provided **25** as a white solid (0.11 g, 91%), mp 233−237 °C. ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 9.49 (d, J = 9.0 Hz, 1H), 9.02 (m, 2H), 8.96 (d, J = 4.8 Hz, 1H), 8.64 (d, J = 7.8 Hz, 2H), 8.52 (d, J = 9.0 Hz, 1H), 8.43 (d, J = 4.8 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.31 (dd, J = 7.50, 1.5 Hz, 1H), 8.26 (dd, J = 8.1, 1.8 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.86 (AB quartet, 2H), 7.73 (s, 2H), 7.62 (dd, J = 7.5, 4.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 156.6, 156.3, 155.6, 155.4, 151.8, 150.9, 150.5, 146.4, 146.29, 146.25, 145.6, 144.7, 140.9, 138.5, 136.3, 136.1, 135.0, 129.0, 128.9, 128.3, 127.3, 127.2, 126.5, 126.4, 125.9, 123.5, 123.4, 123.11, 123.08, 121.5. Calcd for $C_{32}H_{18}N_6$-$0.5CHCl_3$: C, 77.98; H, 3.82; N, 18.18. Found: C, 77.48; H, 3.49; N, 18.12.

Ruthenium Complexes

[Ru(5)(bpy-d_8)$_2$](PF$_6$)$_2$. A mixture of **5** (20 mg, 0.09 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (48 mg, 0.09 mmol) in EtOH/H_2O (3:1, 10 mL) was heated at reflux overnight after which the solution was filtered and cooled to room temperature. NH_4PF_6 (50 mg) was added, and the solution was concentrated to give red precipitate which was filtered and air-dried. The product was purified by chromatography on alumina eluting with 10:1 CH_3Cl:MeOH to give [Ru(**5**)(bpy-d_8)$_2$](PF$_6$)$_2$ as a red solid (0.04 g, 44%). ^{1}H NMR (CD_3CN) δ 9.02 (2 overlapping d, 2H), 8.86 (d, J = 8.1 Hz, 1H), 8.79 (d, J = 9.3 Hz, 1H), 8.36 (d, J = 9.0 Hz, 1H), 8.21 (t, J = 7.5 Hz, 1H), 7.77 (m, 2H), 7.54 (t, J = 7.8 Hz, 1H).

[Ru(6)(bpy-d_8)$_2$](PF$_6$)$_2$. Following the procedure described for [Ru(**5**)(bpy-d_8)$_2$](PF$_6$)$_2$, a mixture of **6** (30 mg, 0.14 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (70 mg, 0.14 mmol) gave [Ru(**6**)(bpy)$_2$](PF$_6$)$_2$ as a red solid. The product was purified by column chromatography on alumina eluting with 10:1 CH_3Cl/MeOH (0.04 g, 48%). ^{1}H NMR (CD_3CN) δ 9.13 (d, J = 4.2 Hz, 1H), 8.42 (dd, J = 8.1, 1.5 Hz, 1H), 8.37 (dd, J = 7.8, 1.5 Hz, 1H), 8.30 (d, J = 4.5 Hz, 1H), 8.16 (m, 1H), 8.04 (t, J = 8.1 Hz, 1H), 7.54 (d, J = 5.7 Hz, 1H), 7.40 (dd, J = 7.8 Hz, 1H), 7.20 (dt, J = 8.1 Hz,1H).

[Ru(11)(bpy-d_8)$_2$](PF$_6$)$_2$. Following the procedure described for [Ru(**5**)(bpy-d_8)$_2$](PF$_6$)$_2$, a mixture of **11** (20mg, 0.077 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (45 mg, 0.09 mmol) gave [Ru(**11**)(bpy-d_8)$_2$](PF$_6$)$_2$ as a red solid. The product was purified by chromatography on alumina eluting with 99:1 acetone/KPF_6 (saturated aqueous solution) (0.03 g, 43%). ^{1}H NMR (CD_3CN) δ 8.88 (t, J = 9.0 Hz, 2H), 8.70 (d, J = 9.3 Hz, 1H), 8.67 (d, J = 4.2 Hz, 1H), 8.57 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 9.0 Hz, 1H), 8.17 (t, J = 7.8, 1.5 Hz, 1H), 7.96 (dt, J = 8.1, 1.2 Hz, 1H), 7.76 (d, J = 9.6 Hz, 1H), 7.72 (d, J = 4.8 Hz, 1H), 7.47 (m, 2H).

[(bpy-d_8)$_2$Ru(11)Ru(bpy-d_8)](PF$_6$)$_4$. A mixture of **11** (20 mg, 0.07 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (106 mg, 0.210 mmol) in ethylene glycol (15 mL) is heated in microwave oven for 4 × 10 min to give a dark red solution which was filtered and diluted with water (20 mL). NH_4PF_6 (0.10 g, 0.64 mmol) was added to the solution, and a red precipitate formed which was filtered and air-dried. Column chromatography on alumina eluting with 90:9:1 acetone/hexane/KPF_6 (saturated aqueous solution) gave [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)](PF$_6$)$_4$ as a green solid (0.07 g, 58%). ^{1}H NMR (CD_3CN) δ 8.54 (2 overlapping d, 2H), 8.21 (two d, J = 9.3, 9.0 Hz, 2H), 8.10 (m, 2H), 7.88 (2 overlapping d, 2H), 7.65 (d, J = 5.7 Hz, 2H), 7.41 (m, 2H).

[Ru(18)(bpy-d_8)$_2$](PF$_6$)$_2$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)](PF$_6$)$_4$, a mixture of ligand **18** (20 mg, 0.08 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (45 mg, 0.09 mmol) in ethylene glycol (10 mL) gave a dark red solid. Chromatography on alumina eluting with 99:1 acetone/KPF_6 (saturated aqueous solution) gave [Ru(**18**)(bpy-d_8)$_2$](PF$_6$)$_2$ as a red solid (0.035 g, 48%). ^{1}H NMR (CD_3CN) δ 8.96 (dd, J = 4.5, 1.2 Hz, 1H), 8.88 (d, J = 8.4 Hz, 1H), 8.82 (d, J = 9.0 Hz, 1H), 8.75 (d, J = 9.3 Hz, 1H), 8.64 (d, J = 9.0 Hz, 1H), 8.46 (dd, J = 8.4, 1.5 Hz, 1H), 8.10 (dd, J = 3.9, 1.2 Hz, 1H), 7.74 (d, J = 9.3 Hz, 1H), 7.51 (dd, J = 7.8, 4.8 Hz, 1H), 7.25 (dd, J = 8.7, 4.2 Hz, 1H).

[Ru(19)(tpy)](PF$_6$)$_2$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)](PF$_6$)$_4$, a mixture of ligand **19** (30.0 mg, 0.097 mmol) and [Ru(tpy)Cl_3] (47.0 mg, 0.106 mmol) in ethylene glycol (10 mL) gave a dark red solid. Chromatography on alumina eluting with 99:1 MeCN/KPF_6 (saturated aqueous solution) gave [Ru(**19**)(tpy)](PF$_6$)$_2$ as a red solid (0.06 g, 61%). ^{1}H NMR (CD_3CN) δ 9.27 (d, J = 7.5 Hz, 1H), 9.04 (d, J = 9.0 Hz, 1H), 8.98 (d, J = 8.7 Hz, 1H), 8.90 (d, J = 8.7 Hz, 2H), 8.86 (m, 1H), 8.70 (d, J = 9.0 Hz, 1H), 8.59 (t, J = 8.1 Hz, 1H), 8.49−8.39 (m, 4H), 8.24 (d, J = 8.7 Hz, 1H), 7.81 (dt, 2H), 7.45 (dd, J = 7.8 Hz, 1H), 7.31 (m, 2H), 7.21−7.14 (m, 3H), 6.96 (m, 2H). Anal. Calcd for $C_{35}H_{23}N_7F_{12}P_2Ru$-$0.5H_2O$: C, 44.64; H, 2.50; N, 10.40. Found: C, 44.68; H, 2.12; N, 9.95.

[Ru(20)(bpy-d_8)$_2$](PF$_6$)$_2$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)](PF$_6$)$_4$, a mixture of ligand **20** (50.0 mg, 0.129 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$]

(63.0 mg, 0.129 mmol) in ethylene glycol (20 mL) gave a dark red solution, which was filtered and diluted with water (20 mL). NH_4PF_6 (0.105 g, 0.644 mmol) was added, and the solution was concentrated to give a red precipitate which was filtered and air-dried. Chromatography on alumina eluting with 99:1 acetone/KPF_6 (saturated aqueous solution) gave [Ru(**20**)(bpy-d_8)$_2$]$(PF_6)_2$ as a red solid (0.04 g, 30%). ^{1}H NMR (CD_3CN) δ 9.12 (dd, J = 4.3, 1.5 Hz, 1H), 8.92 (d, J = 9.4 Hz, 1H), 8.84 (d, J = 4.8 Hz, 1H), 8.81 (d, J = 4.8 Hz, 1H), 8.75 (d, J = 8.4 Hz, 2H), 8.55 (2 overlapping d, 2H), 8.45 (m, 2H), 8.10 (dd, J = 4.5, 2.4 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.63 (dd, J = 8.7, 3.9 Hz, 1H), 7.52 (dd, J = 8.4, 4.2 Hz, 1H).

[(bpy-d_8)$_2$Ru(20)Ru(bpy-d_8)](PF$_6$)$_4$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)]$(PF_6)_4$, a mixture of ligand **20** (50 mg, 0.13 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (135 mg, 0.280 mmol) in ethylene glycol (15 mL) gave a dark green solid. Column chromatography on alumina eluting with 90:9:1 acetone/hexane/KPF_6 (saturated aqueous solution) gave [(bpy-d_8)$_2$Ru(**20**)Ru(bpy-d_8)]$(PF_6)_4$ as a green solid (0.13 g, 68%): ^{1}H NMR (acetone-d_6) δ 8.70 (2 overlapping d, 2H), 8.58 (2 overlapping d, 2H), 8.45 (d, J = 8.4 Hz, 2H), 8.22 (2 overlapping d, 2H), 8.06 (broad s, 2H), 7.87 (d, J = 9.6 Hz, 2H), 7.50 (m, 2H).

[Ru(21)(tpy)](PF$_6$)$_2$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)]$(PF_6)_4$, a mixture of ligand **21** (50.0 mg, 0.102 mmol) and [Ru(tpy)Cl_3] (45.0 mg, 0.102 mmol) in ethylene glycol (15 mL) gave a dark red solid. Column chromatography on alumina eluting with 99:1 MeCN/KPF_6 (saturated aqueous solution) gave [Ru(**21**)(tpy)]$(PF_6)_2$ as a red solid (0.06 g, 51%). ^{1}H NMR (CD_3CN) δ 9.16 (d, J = 8.7 Hz, 1H), 9.05 (dd, J = 4.5 Hz, 1H), 9.01 (2 overlapping d, 3H), 8.88 (dd, J = 8.4 Hz, 2H), 8.79 (d, J = 8.1 Hz, 1H), 8.76 (d, J = 9.0 Hz, 1H), 8.68 (t, J = 7.5 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 7.8 Hz, 2H), 8.42 (m, 3H), 8.22 (d, J = 8.7 Hz, 1H), 8.00 (s, 2H), 7.83 (t, J = 8.1 Hz, 2H), 7.74 (dd, J = 8.7, 4.5 Hz, 1H), 7.47 (dd, J = 8.1, 4.3 Hz, 1H), 7.41 (d, J = 9.3 Hz, 1H), 7.30 (d, J = 5.4 Hz, 2H), 7.20 (d, J = 5.1 Hz, 1H), 7.01 (m, 1H). Anal. Calcd for $C_{47}H_{29}N_9F_{12}P_2Ru_1\cdot 1/2H_2O$: C, 50.82; H, 2.63; N, 11.35. Found: C, 50.43; H, 2.24; N, 11.14.

[(tpy)Ru(21)Ru(tpy)](PF$_6$)$_4$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)]$(PF_6)_4$, a mixture of ligand **21** (30 mg, 0.06 mmol) and [Ru(tpy)Cl_3] (59 mg, 0.13 mmol) in ethylene glycol (15 mL) gave a dark green solid. Chromatography on alumina eluting with 99:1 acetone/KPF_6 (saturated aqueous solution) gave [(tpy)Ru(**21**)Ru(tpy)]$(PF_6)_4$ as a green solid (0.08 g, 60%): ^{1}H NMR (CD_3CN) δ 9.03 (d, J = 9.6 Hz, 1H), 8.96 (d, J = 8.0 Hz, 2H), 8.92 (d, J = 8.8 Hz, 1H), 8.69 (t, J = 8.0 Hz, 1H), 8.63 (d, J = 9.6 Hz, 2H), 8.48 (d, J = 8.0 Hz, 2H), 8.40 (d, J = 8.8 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 9.6 Hz, 1H), 7.77 (t, J = 7.2 Hz, 2H), 7.55 (d, J = 9.6 Hz, 1H), 7.45 (overlapping d, 1H), 7.12 (d, J = 6.4 Hz, 1H), 7.04 (d, J = 5.6 Hz, 2H), 6.86 (t, J = 7.2 Hz, 2H). Anal. Calcd for $C_{62}H_{40}N_{12}F_{24}P_4Ru_2\cdot KPF_6$: C, 38.79; H, 2.08; N, 8.75. Found: C, 38.40; H, 2.04; N, 8.29.

[(tpy)Ru(23)Ru(tpy)](PF$_6$)$_4$. Following the procedure described for [(bpy-d_8)$_2$Ru(**11**)Ru(bpy-d_8)]$(PF_6)_4$, a mixture of **23** (15 mg, 0.03 mmol) and [Ru(tpy)Cl_3] (35.0 mg, 0.075 mmol) in ethylene glycol (15 mL) gave a dark green solid. Chromatography on alumina eluting with 99:1 MeCN/KPF_6 (saturated aqueous solution) gave [(tpy)Ru(**23**)Ru(tpy)]$(PF_6)_4$ as a green solid (0.03 g, 55%). ^{1}H NMR (acetone-d_6) δ 8.95 (d, J = 9.0 Hz, 2H), 8.77 (2 overlapping d, 6H), 8.53 (t, J = 8.1 Hz, 4H), 8.44 (d, J = 7.5 Hz, 4H), 8.37 (dd, J = 8.7, 6.6 Hz, 4H), 8.22 (m, 4H), 7.83 (dt, J = 7.5 Hz, 4H), 7.52−7.45 (m, 4H), 7.11 (d, J = 5.1 Hz, 4H), 6.84 (dd, J = 7.2 Hz, 4H). Anal. Calcd for $C_{62}H_{40}N_{12}F_{24}P_4Ru_2\cdot 0.25KPF_6/0.5MeCN$: C, 42.91; H, 2.32; N, 9.69. Found: C, 41.40; H, 2.35; N, 10.12.

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Supporting Information Available: ^{1}H NMR Spectra for Ru(II) complexes of **5**, **6**, **11**, **18**−**21**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.