Bidentate Ligands That Contain Pyrrole in Place of Pyridine

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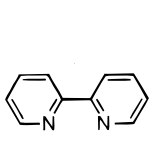
A series of ligands are prepared that are analogues of benzo-fused derivatives of 2,2′-bipyridine (bpy), in which pyrrole has been substituted for a pyridine ring. These ligands include 2-(2′-pyridyl)-indole, 2-(2′-pyrrolyl)-quinoline, and pyrrolo[3,2-*h*]quinoline. A novel reductive cyclization approach to the latter species is presented. All these ligands react with $[Ru(bpy\text{-}d_8)_2Cl_2]$, undergoing cyclometalation with concurrent deprotonation, to form complexes of the type $[Ru(L)(bpy\text{-}d_8)_2]^+$ where L binds as a monoanionic ligand. The complexes are readily characterized by their ^1H NMR spectra. Changes in the redox potentials and the electronic absorption spectra of both the ligands and the complexes are interpreted in terms of charge delocalization on the ligand.

Introduction

Two of the most important classes of ligands are the polypyridines and the porphyrins. In the former class of ligand, we may include 2,2′-bipyridine (bpy, **1**), 2,2′;6′,2″-terpyridine, 1,10-phenanthroline (phen), and a variety of other homologous and benzo-fused derivatives.[1−5] The latter class of ligands is embodied by porphyrin (**2**), phthalocyanine, and a variety of "tailor-made" analogues.[6−8] The bipyridines are considered to be ligands of the diimine-type, which is to say that in at least one of their resonance forms, they possess the N═C−C═N functionality which, when oriented in a cisoid fashion, is well disposed to coordinate and thus form a five-membered chelate ring with an appropriate metal. The porphyrin system, on the other hand, consists of four pyrrole rings joined at their 2,5-positions by methine units. Covalent resonance theory demands that adjacent pyrrole rings have their bonds organized such that one ring presents an N−H unit to the core of the molecule while the other presents an imine C═N function. In the metalloporphyrins, the porphyrin core has lost two protons and thus binds as a dinegative ligand. Although the pyrrole ring of porphyrins has been replaced by pyridine, the converse exchange, the replacement of a pyridine ring in bpy by a pyrrole to afford 2-(2′-pyridyl)pyrrole (**3**) has not been methodically examined.



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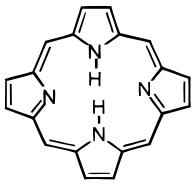

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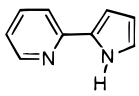

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The fundamental properties of pyridine and pyrrole very nicely compliment one another. Pyridine is π-deficient but exhibits Lewis basicity because of its available lone-pair electrons. As such, it is a good H-bond acceptor. Pyrrole or indole, on the other hand, is π-excessive and exhibits increased reactivity toward electrophiles. It is comparably nonbasic and a good H-bond donor. The juxtaposition of these two nuclei in a 1,4-relationship is particularly interesting in that the two centers can potentially be interacting. It is noteworthy that the indole nucleus, unlike its quinoline counterpart, fluoresces strongly in the UV.

In earlier work, we have examined several cavity-shaped molecules incorporating pyrrole and pyridine subunits arranged so as to complement one another in forming hydrogen bonds to appropriate guests.[9−11] In particular, we found that urea could form four well-organized hydrogen bonds with such hosts, using both lone pairs of electrons on oxygen to bind to the pyrrole N−H donors and two amide hydrogens that were accepted by the host pyridine lone pairs.

Another feature of the juxtaposed pyridine and pyrrole nuclei, found in 2-(2′-pyridyl)indole (**4aH**) and related systems, involves photoinduced double proton transfer that occurs in concert with an alcohol solvent molecule, leading to a bond-shifted tautomer in the excited state.[12,13] Ground-state analogues have also been prepared and studied by methylation of systems such as **4** and **5** followed by deprotonation.[14]

This paper will initiate the examination of a series of ligands related to 2-(2′-pyridyl)pyrrole (**3**). Being less readily prepared,[15−17] study of the parent **3** itself will not be undertaken

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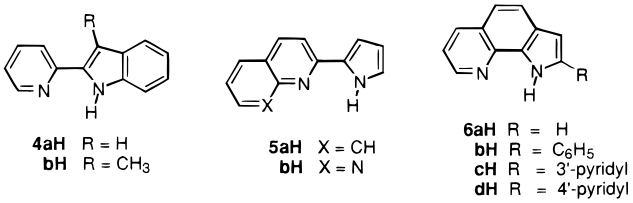
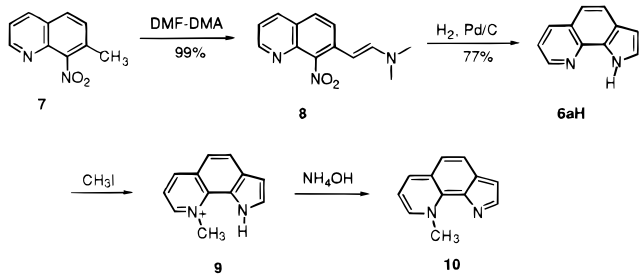
at this time; rather, we will investigate a series of benzo-fused derivatives **4**−**6**. The fusion of a benzo-ring at the 4,5-position on the pyrrole moiety of **3** provides the 2-(2′-pyridyl)indole (**4aH**). Benzo fusion at the 5,6-position of the pyridine ring of **3** provides the 2-(2′-pyrrolyl)quinoline (**5aH**). Benzo-fusion to the central bond of **3** provides pyrrolo[3,2-*h*]quinoline (**6aH**), which is an analogue of 1,10-phenanthroline.

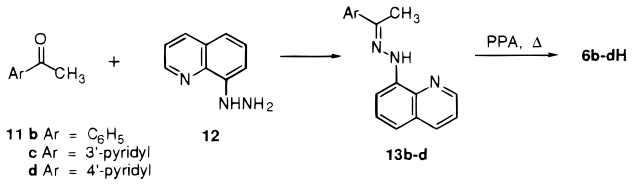


Synthesis and Properties of the Ligands

The synthesis of **4a**,**b** and **5a**,**b** has been presented in earlier work.[14] A three-step preparation of the parent pyrrolo[3,2-*h*]-quinoline (**6a**) starting from 8-hydrazinoquinoline has been reported.[18,19] We have developed a simple alternative approach starting from readily available 8-nitro-7-methylquinoline (**7**).[20−22] Treatment of **7** with dimethylformamide dimethylacetal (DMF-DMA) affords an almost quantitative yield of the *N*,*N*-dimethylaminoethene derivative **8** which undergoes reduction and ring closure to afford **6aH** in good yield.

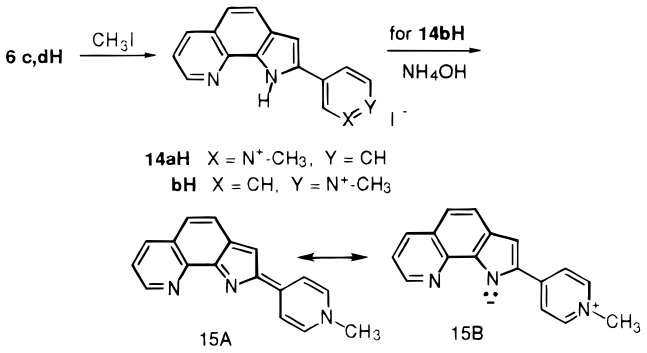


The 2-substituted derivatives **6b-dH** can be prepared via the 8-quinolinehydrazone of the appropriate acetyl aromatic, which then undergoes Fisher cyclization upon heating with polyphosphoric acid (PPA).[23]



One of the interesting features of molecules such as **4aH** and **6aH** is their potential to exist in a tautomeric form. Intramolecular hydrogen transfer from the acidic N−H to the basic pyridyl nitrogen would provide such a tautomer. The consequent loss of aromatic stabilization makes such a process somewhat unfavorable. By methylating the pyridyl nitrogen, however, we can cause deprotonation of the indole to become irreversible and thus stabilize the tautomer. Thus, **6aH** may be methylated with iodomethane and then treated with base to provide the bridged diaza[13]annulene **10**. This species possesses a 14π periphery, is quite stable, and is apparently diatropic by NMR.

From the point of view of ligand design, **10** is not useful because the lone pair electrons on the pyridyl nitrogen are now part of the delocalized π-system. This problem may be circumvented by inducing tautomerization into an appropriately appended pyridinium ring. Thus, methylation of the 4-pyridyl derivative **6dH** occurs exclusively at the less hindered 4-pyridyl group, providing the salt **14bH**, which then deprotonates to give the diazafulvalene derivative **15A**. This species now possesses the diimine functionality needed to act as a neutral chelating ligand. Methylation of the analogous 3-pyridyl derivative **6cH** provides **14aH** which, as expected, does not afford a tautomer upon deprotonation.



All the species **4**−**6**, as well as their corresponding salts and tautomers, could be readily characterized by high-field NMR. When necessary, 2D-COSY techniques were used to establish proton connectivities.

A useful way to analyze the electronic character of these species is by inspection of their absorption spectra (Table 1). The pyrroloquinolines **6aH** and **14aH** exhibit a long wavelength $\pi-\pi^*$ band at 315−326 nm. The 4-pyridyl system **14bH** is capable of more extended delocalization and thus absorbs at lower energy (390 nm). Conversion of **6aH** to its salt **9** induces a bathochromic shift of 51 nm, whereas the corresponding tautomer **10** appears red, absorbing at 448 nm.

The electronic spectra of the series **6aH**, **14a**,**bH**, and **15** reflect the degree of conjugative interaction. Due to the absence of effective delocalization in **14aH**, the absorption spectrum of this species resembles its precursor **6cH** with a bathochromic tail. The 4′-pyridyl analogue behaves quite differently (Figure 1). Compared with its precursor, the salt **14bH** exhibits a 66-

Table 1. Electronic Absorption Data[a] for Pyrrolo[3,2-*h*]quinolines, Salts, and Tautomers

compound	λ_{max} (nm)
6aH	324 (3.72), 262 (4.90), 211 (4.72)
6bH	315 (4.54), 287 (4.71), 205 (4.73)
6cH	318 (4.47), 286 (4.63), 209 (4.28)
6dH	324 (4.38), 290 (4.47), 256 (4.07)
9	375 (4.10), 277 (4.73), 246 (4.62)
10	448 (4.02), 298 (4.44), 254 (4.44)
14aH	326 (4.35), 296 (4.40), 247 (4.40), 209 (4.51)
14bH	390 (4.52), 306 (4.10), 248 (4.48)
15	460 (4.27), 393 (4.39), 307 (4.02), 279 (4.00), 248 (4.21)

[a] 10^{-5} M in CH_3CN, log ϵ in parentheses.

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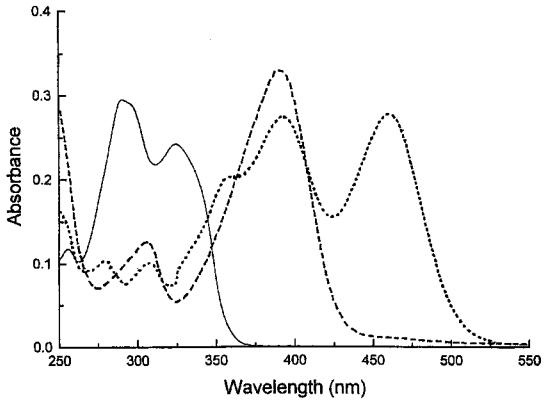
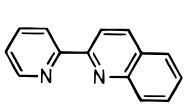


Figure 1. Electronic absorption spectra of **6dH** (——), **14bH** (- - -), and **15** (·····) in CH_3CN (10^{-5} M) at 25 °C.

nm bathochromic shift, indicating a strong conjugative interaction of the pyridinium ring with the parent pyrrolo[3,2-*h*]quinoline. Interestingly, the tautomer **15** shows strong bands at 460 and 393 nm, suggesting that both polar (**15B**) and nonpolar (**15A**) resonance forms make significant contributions to the hybrid.

Behavior as Ligands

As described earlier, the parent systems in this study, **4aH**, **5aH**, and **6aH**, are benzo-fused analogues of 2-(2′-pyridyl)-pyrrole. The pyridine analogues which may be used for comparison are 2-(2′-pyridyl)quinoline (**16**) and 1,10-phenanthroline (**17**). The pyrrole containing ligands will be compared with **16** and **17** with respect to both geometric and electronic influences on the properties of their complexes with Ru(II).



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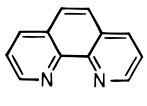

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To effectively coordinate in a bidentate fashion, the pyrrole containing ligands must deprotonate and, as such, then act as monoanionic ligands. This deprotonation and cyclometalation process has previously been examined for **4a** complexation with Pd(II).[24] During the reaction of the ligand with $[Ru(bpy)_2Cl_2]$, the deprotonation step occurs spontaneously, so that after the initial coordination with the pyridyl nitrogen, oxidative addition of Ru(II) to the N−H occurs. The complexes were generally formed in moderate yields (40−80%). For **5a**,**b**, where the fused benzo or pyrido ring is more encumbering than for **4a**,**b**, the yields were lower. For **6d**, the pendant 4-pyridyl ring is the most nucleophilic site. Its interference with the chelation process lowers the yield of desired material to only 5%.

Since the pyrrole containing ligands are unsymmetrical, the resulting $[Ru(bpy)_2L]^+$ complexes lack a symmetry axis, causing the 16 proton resonances for the two auxiliary bpys to be nonequivalent. To remove these signals, and thus greatly simplify the NMR spectrum, we prepared the complexes employing bpy-d_8 as the auxiliary ligand, so that only peaks from the ligand of interest appear in the ^{1}H NMR.[25,26]

Shifts in the proton resonances of the ligands occur as a result of complexation with Ru(II). These shifts reflect changes in charge density of the ligand as well as changes in shielding and deshielding effects due to the local environment in the complex. The most dramatic shift occurs for H7 of **4a**,**b**, which moves upfield 2.11−2.13 ppm upon complexation. This proton points toward the face of an auxiliary bpy-d_8, which accounts for some of the shielding.

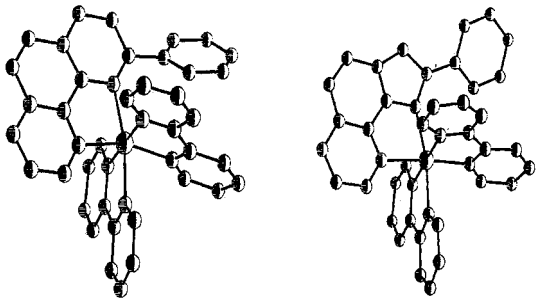

Figure 2. Molecular mechanics simulation of $[Ru(\mathbf{L})(bpy)_2]^{2+}$ (left) and $[Ru(\mathbf{6b})(bpy)_2]^+$ (right) where **L** = 2-phenyl-1,10-phenanthroline.

For comparison, we can consider $[Ru(\mathbf{5a})(bpy\text{-}d_8)_2]^+$ or $[Ru(\mathbf{16})(bpy\text{-}d_8)_2]^{2+}$. For both of these complexes, H8 should point even more toward the orthogonal bpy-d_8, and complexation induced upfield shifts of +0.82 and +0.48 ppm are observed, respectively, suggesting that the major part of the shift for ligand **4** is due to the increased negative charge on the indole nucleus. In fact, all the proton resonances for the pyrrole containing ligands experience a similar upfield shift due to this increase of negative charge on the coordinated ligand.[27,28] The sole exceptions are H3 and H3′, which are held in a more deshielded environment due to the planar cisoid conformation required for chelation.

From a geometric viewpoint, the pyrrole containing ligands are more "open," which is to say that the nitrogens are further separated, than their pyridine counterparts. Thus, we expect a larger N−Ru−N angle and, when coordinated to Ru(II), the benzo ring of **4a** will be further from the metal center than the benzo ring of **16**.

This situation is perhaps best illustrated for the 2-phenyl derivative **6b** as compared with the analogous 2-phenyl-1,10-phenanthroline. Figure 2 depicts a molecular mechanics simulation for the mixed ligand Ru(II) complexes of both ligands.[29] In the phenanthroline case, the 2-phenyl substituent is nearly orthogonal to the parent ring and thus parallel to the pyridine ring of an auxiliary bpy. The steric crowding in this system is somewhat compensated by a favorable phenylpyridyl π-stacking interaction. From the NMR spectrum of this complex, we find that rotation about the 2,2′-bond is restricted at room temperature. Similar systems have been analyzed by variable temperature NMR to detect conformational mobility of a pendant aromatic substituent.[30−32] For the mixed ligand complex of 2-phenylphen (Figure 2), raising the temperature to +65 °C effects coalescence of the *ortho* and *meta* phenyl protons and reveals a rotational energy barrier of 16.3 kcal/mol.

For the pyrrole analogue $[Ru(\mathbf{6b})(bpy\text{-}d_8)_2]^+$, the phenyl ring points further away from the site of complexation, and free

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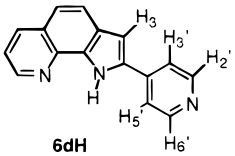
Table 2. ^{1}H NMR Data for Systems Related to 2-(4′-Pyridyl)-pyrrolo[3,2-*h*]quinoline[a]



6dH

ligand/complex	H_2'/H_6'	H_3'/H_5'	H_3
6dH[b]	8.59	7.58	7.18
[Ru(**6d**)(bpy-d_8)$_2$]$^{+c}$	7.98	6.82	6.74
14bH[d]	8.87	8.65	7.87
15[d]	8.38	8.23	7.40
[Ru(**15**)(bpy-d_8)$_2$]$^{+c}$	7.80	7.35	7.15

[a] Reported in ppm downfield from Me_4Si. [b] $CDCl_3$. [c] CD_3CN. [d] DMSO-d_6.

rotation about the 2,2′-bond is possible at room temperature. The unfortunate coincidence of the phenyl ring signals for this complex does not allow an estimate of the rotational barrier by lowering the temperature.

Ligand **15** is interesting in that it can function as a neutral chelating diimine species. The complex [Ru(**15**)(bpy-d_8)$_2$]$^{2+}$ may be prepared either directly from **15** or from **14bH**, which deprotonates to **15** upon complexation. The proton resonances of the pendant pyridinium ring, as well as the pyrrole H3, are good indicators of electronic changes that occur upon quaternization or complexation, and these data are summarized in Table 2. As expected, quaternization of the pendant pyridine creates a deshielding effect and causes a downfield shift of all five protons. This shift is less pronounced for H2′/H6′, which were already deshielded in **6dH** due to the proximal nitrogen. When **6dH** is complexed with Ru(II), the ligand becomes anionic, and this increased negative charge causes an upfield shift of 0.44−0.76 ppm. Some of this shielding effect in the pyridine moiety may also be due to π-stacking with an orthogonal bpy-d_8. When the quaternized species **14bH** is deprotonated, deshielding is diminished, and upfield shifts of 0.42−0.49 ppm are evidenced. Complexation of **15** again leads to increased shielding, and the shifts are consistent with what was observed for **6d**, with H3′/H5′ showing the strongest effect (0.88 ppm) and H3 showing the weakest (0.25 ppm). It is noteworthy that for **15** and its complex, the major resonance contributor appears to be **15B**, because free rotation about the 4,2′-bond is demonstrated by the equivalency of H2′ and H6′ as well as H3′ and H5′.

An important property of Ru(II) polypyridine complexes is the nature of the excited state as reflected in the electronic absorption and emission spectra. The longest wavelength band characterizes the lowest energy excited state, which is generally associated with the promotion of an electron from a metal based d-orbital to the π*-orbital of the most electronegative ligand, the so-called metal-to-ligand charge transfer (MLCT) state.[33] In this excited state, the metal becomes photooxidized (Ru^{II} to Ru^{III}) so that good electron donating ligands will stabilize the state and lower its energy. At the same time, such good donor ligands will be poor MLCT acceptors.

Table 3 lists the electronic absorption and emission data for the complexes under consideration. For all complexes of **4**, **5**, and **6**, we observe a long-wavelength band in the range of 490−508 nm. Considering the pronounced structural variations among these eight ligands, the narrowness of the absorption range suggests that the pyrrole containing ligands are not involved in the MLCT transition, which rather involves the bpy-d_8 ligands that are common to all the complexes. Stabilization of the photooxidized excited state by the anionic ligands would account for the bathochromic shift over the expected value of about 450 nm, as evidenced by the model complexes [Ru(**16**)(bpy-d_8)$_2$]$^{2+}$ and [Ru(**17**)(bpy-d_8)$_2$]$^{2+}$.

The second longest wavelength band appears to be reasonably consistent with MLCT to the pyrrole containing ligand, which would be a poorer acceptor due to its anionic character. Ligands **4a**,**b** and **5a** should have similar electronegativities, and for their complexes, this band comes at 358−385 nm. Ligand **5b** is more electronegative, and the band is shifted to 472 nm. For the complexes of **6a**−**d** and **14a**, the 2-substituents, being nearly orthogonal, have relatively little electronic influence on the coordinated pyrroloquinoline ring, and this band is observed in the range of 445−467 nm. The increased energy of the 2-substituted derivatives as compared to **6a** (467 nm) may be more due to steric disruption of the ligand field.

The complex of **15** involves a formally neutral but quite dipolar ligand. Of the two long-wavelength absorption bands, one can assign the band at 386 nm to MLCT involving **15**, whereas the band at 457 nm appears more like a normal bpy-centered transition without the stabilizing effect of an anionic ligand.

The complexes were nonemissive at room temperature but did emit at 77 K. These emission bands fall into three groups. The highest energy bands belong to the complexes of **4a**,**b**, whereas the lowest energy bands are associated with complexes of **5a**,**b**. The complexes of **6a**−**d** fall between the highest and lowest energy bands with a fairly monotonic increase in energy along the series.

The electrochemical properties of the complexes are summarized in Table 4 and are consistent with the photochemical model. The oxidation potentials for the Ru(II) complexes of ligands **4**−**6** range from 0.58 to 0.94 V, indicating that oxidation is considerably facilitated as compared with the model complexes of **16** and **17**, which appear at 1.26 and 1.23 V, respectively. If one considers that the anionic ligand assists in stabilizing the Ru(III) state, this potential should be a direct measure of that stabilizing or donor ability. The indole systems **4** are the best donors, showing the lowest potentials. The effect of the 2-substituent for ligands **6b**−**d** appears to be minimal, with the oxidation potential for all four pyrrolo[3,2-*h*]quinoline complexes falling in the narrow range of 0.74−0.80 V.

The reduction process for Ru(II) polypyridine complexes is normally ligand-based and involves the addition of an electron to the most electronegative ligand. The complexes of **4**−**6** all involve formally anionic ligands, and thus reduction would be expected to occur on the auxiliary bpy-d_8 species. The first and second reductions for [Ru(bpy)$_3$]$^{2+}$ occur at −1.33 and −1.52 V, respectively,[35] and correlate well with the corresponding value ranges of −1.19 to −1.44 and −1.42 to −1.72 V observed for the complexes of **4**−**6**.

The complexes of **14a** and **15** both exhibit an irreversible wave at −1.02 and −1.37 V, respectively. This reduction is attributed to the pendant pyridinium ring. The more facile reduction of **14a** is consistent with a higher concentration of positive charge resulting from less conjugative interaction of the pyridinium ring with the parent pyrrolo[3,2-*h*]quinoline

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Table 3. Electronic Absorption and Emission Data[a] for $Ru^{II}(\mathbf{L})(bpy\text{-}d_8)_2$ Complexes

ligand L	absorption (298 K) λ_{max} (nm)	emission (77 K) λ_{max} (nm)
4a	493 (3.98), 358 (4.36), 335 (4.36), 291 (4.71)	654
4b	493 (3.92), 361 (4.23), 332 (4.25), 291 (4.60)	660
5a	508 (4.07), 385 (4.31), 331 (4.37), 291 (4.82)	732
5b	507 (4.25), 472 (4.28), 406 (4.44), 338 (4.44), 292 (4.92)	721
6a	503 (3.92), 467 (3.86), 350 (3.98), 289 (4.69)	707
6b	495 (4.04), 458 (4.03), 291 (4.88)	686
6c	496 (3.81), 449 (3.79), 291 (4.69)	676
6d	490 (3.96), 458 (3.94), 323 (4.37), 291 (4.74)	666
14a	481 (3.89), 445 (3.89), 339 (4.10), 290 (4.62)	670
15	457 (4.14), 386 (4.46), 290 (4.74)	649
16	484 (3.96), 444 (4.04), 286 (4.75)	660
17	448 (4.31), 285 (4.91)	575[b]

[a] 10^{-5} M in CH_3CN, log ϵ in parentheses. [b] Reported for the corresponding protio complex, ref 34.

Table 4. Half-Wave Redox Potentials for $Ru^{II}(\mathbf{L})(bpy\text{-}d_8)_2$ Complexes[a,b]

ligand L	$E_{1/2}$(ox)		$E_{1/2}$(red)	
4a	0.58[c,d]		−1.22 (90)	−1.48 (100)
4b	0.64[c,d]		−1.26 (150)	−1.52 (130)
5a	0.94[c,d]		−1.19 (120)	−1.42 (140)
5b	0.73[c,d]		−1.44 (120)	−1.72 (110)
6a	0.80[c]		−1.37 (90)	−1.62 (120)
6b	0.78[c]		−1.32 (120)	−1.60 (150)
6c	0.74[c]		−1.43 (110)	−1.68 (130)
6d	0.79[c]		−1.37 (70)	−1.63 (100)
14a	1.08[c]	−1.02[c]	−1.17 (70)	−1.47 (100)
15	0.83[c,d]	−1.37[c]	−1.54 (70)	−1.84 (130)
16	1.26 (90)		−1.19 (30)	−1.57 (100)
17[e]	1.19 (150)		−1.51 (125)	−1.67 (200)

[a] Potentials are in volts vs. SSCE, difference between anodic and cathodic peaks (mV) is given in parentheses. [b] Solutions are in 0.1 M TBAP; the solvent was CH_3CN; $T = 25 \pm 1$ °C. [c] Irreversible. [d] Becomes quasi-reversible at higher sweep rates. [e] For protio-bpy complex.

nucleus. The free ligand **14a** shows a similar irreversible reduction at −1.36 V. The subsequent reduction waves observed for **14a** appear consistent with reduction of the auxiliary ligand, whereas in the case of **15** this assignment is less clear.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a General Electric QE−300 spectrometer at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million downfield from Me_4Si. The proton numbering scheme for **6a**−**dH** is given in Table 2. Electronic spectra were obtained on a Perkin-Elmer 330 spectrophotometer. Emission spectra were measured on a Perkin-Elmer LS-5 spectrophotometer. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. Mass spectra were obtained on a Hewlett-Packard 5989B mass spectrometer (59987A Electrospray) using the Atmospheric Pressure Ionization (API) method at a temperature of 160 °C for the complexes and Atmospheric Pressure Chemical Ionization (APCI) at 300 °C for the ligands; M denotes the positive ion. Cyclic voltammograms were recorded using a BAS CV-27 voltammograph and a Houston Instruments model 100 X-Y recorder according to a procedure which has been described previously.[36] All solvents were freshly distilled reagent grade, and all melting points are uncorrected.

The preparations of ligands **4a**,**b** and **5a**,**b** have been described.[14] Literature procedures were followed for the preparation of 8-hydrazinoquinoline,[10] 7-(*β*-trans-*N*,*N*-dimethylaminoethenyl)-8-nitroquinoline,[37] and $[Ru(bpy\text{-}d_8)_2Cl_2]$.[25]

Pyrrolo[3,2-*h*]quinoline (6aH). A mixture of 7-(*β*-*trans*-*N*,*N*-dimethylaminoethenyl)-8-nitroquinoline (1.70 g, 7.0 mmol) and 5% Pd/C (0.40 g) in EtOAc (150 mL) was hydrogenated (40 atm) for 2 h. The reaction mixture was filtered through Celite, and the filtrate was evaporated to provide a viscous oil, which was purified by chromatography on alumina (25 g), eluting with EtOAc/CH_2Cl_2 (1:1), to give **6aH** as a brown solid (0.91 g, 77%), which was recrystallized from hexanes: mp 97−98 °C (lit.[7a] mp 99.5−100.5 °C); ^{1}H NMR ($CDCl_3$) δ 11.47 (bs, 1H, NH), 8.87 (dd, 1H, J = 4.5 Hz, 1.5 Hz, H_8), 8.31 (dd, 1H, J = 8.4 Hz, 1.5 Hz, H_6), 7.84 (d, 1H, J = 8.7 Hz, H_5 or H_4), 7.48 (d, 1H, J = 8.4 Hz, H_4 or H_5), 7.44 (q, 1H, H_7), 7.42 (t, 1H, J = 2.4 Hz, H_3), 6.75 (t, 1H, J = 2.4 Hz, H_2).

9-Methylpyrrolo[3,2-*h*]quinolinium iodide (9). A mixture of pyrrolo[3,2-*h*]quinoline (0.46 g, 2.7 mmol) and CH_3I (1.42 g, 10.0 mmol) in CH_3CN (20 mL) was refluxed for 24 h to provide **9** as a yellow solid (0.59 g, 70%), which was washed with a small amount of cold acetone and was further purified by recrystallization from H_2O: mp 187−189 °C; ^{1}H NMR (DMSO-d_6) δ 12.53 (s, 1H, NH), 9.23 (d, 1H, J = 6.0 Hz, H_8), 9.20 (d, 1H, J = 8.1 Hz, H_6), 8.22 (d, 1H, J = 8.7 Hz, H_4 or H_5), 8.01−7.97 (m, overlapping, 2H, H_3 and H_7), 7.93 (d, 1H, J = 8.7 Hz, H_5 or H_4), 7.06 (t, 1H, J = 1.8 Hz, H_2), 4.90 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ 146.2, 145.4, 133.0, 131.0, 130.0, 127.1, 124.9, 121.2, 120.7, 118.7, 105.1, 48.5. Anal. Calcd for $C_{12}H_{11}N_2I$: C, 46.45; H, 3.55; N, 9.03. Found: C, 46.06; H, 3.37; N, 8.79; MS *m*/*z* 183 (M^+).

1-Methyl-3,3′-ethenyl-2-(2′-pyrrolenylidene)-1,2-dihydropyridine (10). A solution of 9-methylpyrrolo[3,2-*h*]quinolinium iodide (150 mg, 0.5 mmol) in water (20 mL) was stirred with NH_4OH (20 mL) for 10 min and then extracted with CH_2Cl_2 (2 × 60 mL). The CH_2Cl_2 layers were washed with NH_4OH (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated to provide **10** as a brown yellow solid (62 mg, 70%): mp 156−158 °C; ^{1}H NMR (DMSO-d_6) δ 8.70 (d, 1H, J = 5.4 Hz, H_8), 8.68 (d, 1H, J = 7.5 Hz, H_6), 7.93 (d, 1H, J = 8.4 Hz, H_4 or H_5), 7.85 (d, 1H, J = 1.2 Hz, H_3), 7.44 (dd, 1H, H_7), 7.31 (d, 1H, J = 8.4 Hz, H_5 or H_4), 6.71 (d, 1H, J = 1.5 Hz, H_2), 5.04 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ 142.9, 142.1, 141.3, 134.8, 132.8, 132.6, 126.4, 124.8, 114.6, 113.4, 103.7, 48.8; MS *m*/*z* 183 (M + 1).

8-Quinolinylhydrazone of acetophenone (13b). A mixture of acetophenone (0.51 g, 4.30 mmol) and 8-hydrazinoquinoline (0.65 g, 4.30 mmol) in absolute EtOH (10 mL) was refluxed for 2 h to provide **13b** (1.0 g, 89%): mp 135−136 °C; ^{1}H NMR ($CDCl_3$) δ 9.56 (broad s, 1 H, NH), 8.77 (dd, 1 H, J = 4.2, 1.4 Hz, $H_{2'}$), 8.12 (d, 1 H, J = 8.0 Hz, $H_{4'}$), 7.9 (dd, 1 H, J = 7.4, 1.4 Hz, H_2), 7.75 (d, 1 H, J = 7.6 Hz, $H_{5'}$), 7.52 (t, 1 H, J = 7.8 Hz, $H_{6'}$), 7.44−7.33 (m, 3 H), 7.26 (t, J = 7.8 Hz, $H_{7'}$), 2.40 (s, $-CH_3$); IR (KBr) 3295 (NH), 3020, 2960, 1665, 1530, 1460, 1420, 1335, 1105, 800 cm^{-1}.

2-Phenylpyrrolo[3,2-*h*]quinoline (6bH). The hydrazone **13b** (0.56 g, 2.14 mmol) was mixed with PPA (12 g) and heated at 120 °C for 4 h to give 0.42 g of crude product. This material was purified by column chromatography (20 g of SiO_2, 1:4 EtOAc/CH_2Cl_2) to provide **6bH** (0.38 g, 73%): mp 156−157 °C; ^{1}H NMR ($CDCl_3$) δ 10.42 (broad s, 1 H, NH), 8.79 (dd, 1 H, J = 4.4, 1.3 Hz, H_8), 8.25 (d, 1 H, J = 8.1 Hz, H_6), 7.81−7.77 (m, 3 H), 7.48−7.43 (m, 3 H), 7.37 (dd, 1 H, J = 8.1, 4.4 Hz, H_7), 7.35−7.26 (m, 1 H), 7.01 (d, 1 H, J = 2.3 Hz, H_3); ^{13}C NMR ($CDCl_3$) δ 147.2, 138.3, 137.3, 132.0, 130.8, 129.1, 128.5, 127.8, 125.3, 125.2, 122.0, 120.0, 119.1, 101.4, 96.1; IR (KBr) 3420 (NH), 3040, 2985, 1580, 1520, 1460, 1360, 1300, 830 cm^{-1}.

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8-Quinolylhydrazone of 3-acetylpyridine (13c). Following the procedure described for **13b**, a mixture of 3-acetylpyridine (0.60 g, 5 mmol) and 8-hydrazinoquinoline (0.80 g, 5 mmol) in absolute EtOH (20 mL) was heated at reflux for 2 h to provide **13c** as a yellow solid (1.14 g, 87%): mp 135−137 °C; ^{1}H NMR ($CDCl_3$) δ 9.66 (s, 1H, NH), 9.07 (d, 1H, J = 2.1 Hz, $H_{2'}$), 8.75 (dd, 1H, J = 3.9 Hz, 1.2 Hz, $H_{6'}$ or H_2), 8.54 (dd, 1H, J = 5.1 Hz, 1.2 Hz, H_2 or $H_{6'}$), 8.19 (dd, 1H, J = 8.1 Hz, 1.5 Hz, H_4 or $H_{4'}$), 8.11 (dd, 1H, J = 8.1 Hz, 0.9 Hz, $H_{4'}$ or H_4), 7.72 (d, 1H, J = 7.5 Hz, H_5), 7.51 (t, 1H, J = 8.1 Hz, H_6), 7.40 (dd, 1H, $H_{5'}$ or H_3), 7.32 (dd, 1H, H_3 or $H_{5'}$), 7.27 (d, 1H, J = 8.1 Hz, H_7), 2.42 (s, 3H, CH_3).

2-(3′-Pyridyl)-pyrrolo[3,2-*h*]quinoline (6cH). Following the procedure described for **6bH**, the hydrazone **13c** (1.02 g, 3.9 mmol) was treated with PPA (10 g) at 120−130 °C for 2 h to provide **6cH** as an off-white solid (0.82 g, 86%): mp 181−183 °C; ^{1}H NMR ($CDCl_3$) δ 11.10 (s, 1H, NH), 9.06 (s, 1H, $H_{2'}$), 8.74 (d, 1H, J = 4.2 Hz, H_8), 8.54 (d, 1H, J = 4.2 Hz, $H_{6'}$), 8.26 (d, 1H, J = 8.1 Hz, H_6), 7.98 (d, 1H, J = 7.2 Hz, $H_{4'}$), 7.81 (d, 1H, J = 8.4 Hz, H_4 or H_5), 7.48 (d, 1H, J = 8.7 Hz, H_5 or H_4), 7.36 (dd, 1H, H_7), 7.29 (dd, 1H, $H_{5'}$), 7.06 (s, 1H, H_3). Anal. Calcd for $C_{16}H_{11}N_3 \cdot 0.5H_2O$: C, 75.59; H, 4.72; N, 16.54. Found: C, 75.89; H, 4.76; N, 16.48; MS *m*/*z* 245 (M^+).

2-[3′-(1-Methylpyridyl)]-pyrrolo[3,2-*h*]quinolinium iodide (14aH). The 2-(3′-pyridyl)-pyrrolo[3,2-*h*]quinoline (0.30 g, 1.2 mmol) was dissolved in CH_3CN (20 mL) with heating. Excess CH_3I (1.5 g, 10.6 mmol) was added, and the mixture was heated at reflux for 30 min. After cooling, **14aH** was obtained as a yellow solid (0.33 g, 70%): mp 220−223 °C; ^{1}H NMR (DMSO-d_6) δ 13.10 (s, 1H, NH), 9.70 (s, 1H, $H_{2'}$), 9.14 (d, 1H, J = 8.4 Hz, $H_{4'}$), 8.92 (d, 1H, J = 4.2 Hz, H_8), 8.83 (d, 1H, J = 6.0 Hz, $H_{6'}$), 8.42 (d, 1H, J = 8.4 Hz, H_6), 8.17 (dd, 1H, $H_{5'}$), 7.84 (d, 1H, J = 8.7 Hz, H_4 or H_5), 7.57 (d, 1H, J = 8.7 Hz, H_5 or H_4), 7.57−7.54 (m, overlapping, 2H, H_3 and H_7), 4.39 (s, 3H, CH_3). Anal. Calcd for $C_{17}H_{14}N_3I$: C, 52.71; H, 3.62; N, 10.85. Found: C, 52.33; H, 3.62; N, 10.60; MS *m*/*z* 259 (M-1$^+$).

8-Quinolylhydrazone of 4-acetylpyridine (13d). Following the procedure described for **13b**, a mixture of 8-hydrazinoquinoline (0.80 g, 5 mmol), 4-acetylpyridine (0.60 g, 0.5 mmol), and HOAc (2 drops) in EtOH (25 mL) was heated at reflux for 4 h to provide **13d** as a yellow solid (1.22 g, 93%): mp 151−152 °C; ^{1}H NMR ($CDCl_3$) δ 9.81 (s, 1H, NH), 8.78 (dd, 1H, J = 3.6 Hz, 0.9 Hz, H_2), 8.61 (d, 2H, J = 6.0 Hz, $H_{2'}$ and $H_{6'}$), 8.14 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.77 (m, overlapping, 3H, $H_{3'}$, $H_{5'}$ and H_4 or H_5), 7.54 (t, 1H, J = 7.8 Hz, H_6), 7.43 (t, 1H, H_3), 7.33 (d, 1H, J = 8.1 Hz, H_7), 2.41 (s, 3H, CH_3).

2-(4′-Pyridyl)-pyrrolo[3,2-*h*]quinoline (6dH). Following the procedure described for **6bH**, the hydrazone **13d** (0.66 g, 2.5 mmol) was treated with PPA (10 g) at 120 °C for 2 h to afford **6dH** as a brown-gray solid (0.55 g, 90%): mp 218−219 °C; ^{1}H NMR ($CDCl_3$) δ 11.19 (s, 1H, NH), 8.75 (dd, 1H, J = 4.2 Hz, 1.2 Hz, H_8), 8.59 (d, 2H, J = 5.7 Hz, $H_{2'}$ and $H_{6'}$), 8.26 (dd, 1H, J = 8.1 Hz, 1.2 Hz, H_6), 7.80 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.58 (d, 2H, J = 6.0 Hz, $H_{3'}$ and $H_{5'}$), 7.48 (d, 1H, J = 8.7 Hz, H_4 or H_5), 7.39 (dd, 1H, H_7), 7.18 (s, 1H, H_3); ^{13}C NMR ($CDCl_3$) δ 150.4, 148.1, 139.2, 137.9, 136.8, 134.6, 132.4, 127.8, 125.8, 121.8, 120.4, 119.9, 119.1, 103.8; MS *m*/*z* 245 (M^+).

2-[4′-(1′-Methylpyridyl)]-pyrrolo[3,2-*h*]quinolinium iodide (14bH). A mixture of 2-(4′-pyridyl)-pyrrolo[3,2-*h*]quinoline (0.20 g, 0.8 mmol) and CH_3I (1.00 g, 7.0 mmol) in CH_3CN was stirred for 10 min at 45 °C. The salt **14bH** was obtained as a yellow solid (0.20 g, 65%): mp > 300 °C; ^{1}H NMR (DMSO-d_6) δ 13.36 (s, 1H, NH), 8.94 (d, 1H, J = 3.3 Hz, H_8), 8.87 (d, 2H, J = 6.6 Hz, $H_{2'}$ and $H_{6'}$), 8.65 (d, 2H, J = 6.9 Hz, $H_{3'}$ and $H_{5'}$), 8.43 (d, 1H, J = 7.5 Hz, H_6), 7.87 (s, 1H, H_3), 7.83 (d, 1H, J = 8.7 Hz, H_4 or H_5), 7.61 (dd, 1H, H_7), 7.59 (d, 1H, J = 9.0 Hz, H_5 or H_4), 4.23 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ 148.7, 145.6, 145.0, 138.0, 136.6, 135.3, 131.5, 127.1, 126.4, 121.7, 121.3, 121.2, 121.1, 109.9, 46.7. Anal. Calcd for $C_{17}H_{14}N_3I \cdot H_2O$: C, 50.37; H, 3.95; N, 10.37. Found: C, 50.01; H, 3.70; N, 10.05; MS *m*/*z* 259 (M-1$^+$).

2-[4′-(1′-Methylpyridinylidene)]-2H-pyrrolo[3,2-*h*]quinoline (15). A mixture of 2-[4′-(1′-methylpyridyl)]-pyrrolo[3,2-*h*]quinolinium iodide (150 mg, 0.4 mmol) and sodium acetate (2.0 g) in water (40 mL) was heated until it dissolved completely. After cooling to room temperature, ammonium hydroxide (20 mL) was added, and the solution was stirred for 10 min. The solution was then extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed with ammonium hydroxide and dried over anhydrous Na_2CO_3. The solvent was evaporated to provide **15** as a brown-red solid (62 mg, 61%): mp 224−227 °C; ^{1}H NMR (DMSO-d_6) δ 8.65 (d, 1H, J = 4.2 Hz, H_8), 8.38 (d, 2H, J = 6.0 Hz, $H_{2'}$ and $H_{6'}$), 8.23 (d, 2H, J = 6.0 Hz, $H_{3'}$ and $H_{5'}$), 8.05 (d, 1H, J = 8.1 Hz, H_6), 7.55 (d, 1H, J = 8.4 Hz, H_4 or H_5) 7.40 (s, 1H, H_3), 7.26 (m, 1H, H_7), 7.03 (d, 1H, J = 8.1 Hz, H_4 or H_5), 4.03 (s, 3H, CH_3). Anal. Calcd for $C_{17}H_{13}N_3 \cdot CH_2Cl_2$: C, 62.79; H, 4.36; N, 12.20. Found: C, 63.27; H, 4.76; N, 12.39.

[Ru(4a)(bpy-d_8)$_2$](PF$_6$). A mixture of [Ru(bpy-d_8)$_2$Cl$_2$] (54 mg, 0.1 mmol) and 2-(2′-pyridyl)-indole (**4aH**, 19 mg, 0.1 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 30 h under Ar. After the hot reaction mixture was filtered, a solution of NH_4PF_6 (50 mg, 0.3 mmol) in EtOH/H_2O (3:1, 5 mL) was added to the filtrate. The solvent was evaporated to produce a brown solid. The residue was purified by chromatography on alumina (15 g). After unreacted **4aH** was eluted with CH_2Cl_2/hexanes (2:1), a following fraction, eluted with CH_2Cl_2, was evaporated to produce the complex as a brown red solid (45 mg, 49%): ^{1}H NMR (CD_3CN) δ 8.00 (d, 1H, J = 7.8 Hz, $H_{3'}$), 7.69 (t, 1H, J = 7.8 Hz, $H_{4'}$), 7.45 (d, 1H, J = 8.1 Hz, H_4), 7.33 (d, 1H, J = 5.4 Hz, $H_{6'}$), 7.18 (s 1H, H_3), 6.88 (t, 1H, J = 6.6 Hz, $H_{5'}$), 6.67 (t, 1H, J = 7.5 Hz, H_5), 6.45 (t, 1H, J = 7.5 Hz, H_6), 5.36 (d, 1H, J = 8.4 Hz, H_7); MS *m*/*z* 626 (M + 4$^+$).

[Ru(4b)(bpy-d_8)$_2$](PF$_6$). Following the procedure described for [Ru(**4a**)(bpy-d_8)$_2$](PF$_6$), a mixture of 3-methyl-2-(2′-pyridyl)-indole (**4bH**, 32 mg, 0.15 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (80 mg, 0.15 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 15 h to afford the complex as a brown red solid (51 mg, 43%): ^{1}H NMR (CD_3CN) δ 8.06 (d, 1H, J = 7.8 Hz, $H_{3'}$), 7.72 (t, 1H, J = 7.5 Hz, $H_{4'}$), 7.44 (d, 1H, J = 8.1 Hz, H_4), 7.40 (d, 1H, J = 5.4 Hz, $H_{6'}$), 6.86 (t, 1H, J = 6.9 Hz, $H_{5'}$), 6.63 (t, 1H, J = 7.5 Hz, H_5), 6.44 (t, 1H, J = 7.5 Hz, H_6), 5.32 (d, 1H, J = 8.4 Hz, H_7), 2.70 (s, 3H, CH_3); MS *m*/*z* 640 (M + 4$^+$).

[Ru(5a)(bpy-d_8)](PF$_6$). Following the procedure described for [Ru(**4a**)(bpy-d_8)$_2$](PF$_6$), a mixture of 2-(2′-pyrrolyl)-quinoline (**5aH**, 39 mg, 0.2 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (107 mg, 0.2 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to afford the complex as a brown red solid (29 mg, 19%): ^{1}H NMR (CD_3CN) δ 7.96 (d, 1H, J = 8.7 Hz, H_4), 7.79 (d, 1H, J = 8.7 Hz, H_3), 7.65 (d, 1H, J = 7.8 Hz, H_5), 7.19 (t, 1H, J = 7.2 Hz, H_6), 7.11−7.09 (m, overlapping, 2H, H_8 and $H_{3'}$), 7.01 (t, 1H, J = 7.5 Hz, H_7), 6.21 (m, 1H, $H_{4'}$), 5.89 (s, 1H, $H_{5'}$); MS *m*/*z* 626 (M + 4$^+$).

[Ru(5b)(bpy-d_8)$_2$](PF$_6$). Following the procedure described for [Ru(**4a**)(bpy-d_8)$_2$](PF$_6$), a mixture of 2-(2′-pyrrolyl)-[1,8]-naphthyridine (**5bH**, 59 mg, 0.3 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (161 mg, 0.3 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to afford the complex as a brown red solid (20 mg, 13%): ^{1}H NMR (CD_3CN) δ 7.96 (dd, 1H, J = 8.7 Hz, 1.8 Hz, H_5), 7.91 (d, 1H, J = 8.7 Hz, H_4), 7.80 (dd, 1H, J = 4.5 Hz, 1.8 Hz, H_7), 7.77 (d, 1H, J = 8.7 Hz, H_3), 7.13 (dd, 1H, J = 3.9 Hz, 0.9 Hz, $H_{3'}$), 7.08 (q, 1H, H_6), 6.23 (q, 1H, $H_{4'}$), 6.02 (q, 1H, $H_{5'}$).

[Ru(16)(bpy-d_8)$_2$](PF$_6$)$_2$. Following the procedure described for [Ru(**4a**)(bpy-d_8)$_2$](PF$_6$), a mixture of 2-(2′-pyridyl)-quinoline (**16**, 21 mg, 0.1 mmol) and [Ru(bpy-d_8)$_2$Cl$_2$] (54 mg, 0.1 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to afford the complex[38,39] as a brown red solid (20 mg, 22%): ^{1}H NMR (CD_3CN) δ 8.70 (d, 1H, J = 8.1 Hz, $H_{3'}$), 8.54 (AB quartet, 2H, H_3 and H_4), 8.13 (t, 1H, J = 7.8 Hz, $H_{4'}$), 8.00 (d, 1H, J = 8.1 Hz, H_5), 7.62 (d, 1H, J = 5.7 Hz, $H_{6'}$), 7.59 (t, 1H, J = 7.8 Hz, H_6), 7.43 (d, 1H, J = 7.5 Hz, H_8), 7.40 (t, 1H, J = 7.2 Hz, $H_{5'}$), 7.26 (t, 1H, J = 7.8 Hz, H_7); MS *m*/*z* 317 (M − 1$^+$).

[Ru(6a)(bpy-d_8)$_2$](PF$_6$). A mixture of pyrrolo[3,2-*h*]quinoline (**6aH**, 51 mg, 0.3 mmol), [Ru(bpy-d_8)$_2$Cl$_2$] (161 mg, 0.3 mmol), and Et_3N (2 drops) in EtOH/H_2O (4:1, 25 mL) was heated at reflux for 20 h under Ar. After cooling, a solution of NH_4PF_6 (326 mg, 2 mmol) in H_2O (5 mL) was added. H_2O (50 mL) was added, and a precipitate formed. The brown solid was collected by filtration and purified by chromatography on alumina (25 mg). The first fraction eluted with CH_2Cl_2 provided unreacted ligand. The second fraction eluted with CH_2Cl_2/

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CH_3CN (4:1) provided the complex as a violet solid (175 mg, 79%): ^{1}H NMR (CD_3CN) δ 8.15 (d, 1H, J = 7.8 Hz, H_6), 7.78 (d, 1H, J = 8.4 Hz, H_4 or H_5), 7.40 (d, 1H, J = 5.1 Hz, H_8), 7.25 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.08 (dd, 1H, H_7), 6.72 (d, 1H, J = 1.8 Hz, H_3), 6.52 (d, 1H, J = 1.8 Hz, H_2); MS m/z 596 (M^+).

[Ru(6b)(bpy-d_8)$_2$](PF$_6$). Following the procedure described for [Ru(**6a**)(bpy-d_8)$_2$](PF$_6$), a mixture of 2-phenylpyrrolo[3,2-*h*]quinoline (**6bH**, 49 mg, 0.2 mmol), [Ru(bpy-d_8)$_2$Cl$_2$] (107 mg, 0.2 mmol), and Et_3N (2 drops) in EtOH/H_2O (3:1, 25 mL) was heated at reflux under Ar for 36 h to provide the complex as a violet solid (104 mg, 64%): ^{1}H NMR (CD_3CN) δ 8.16 (d, 1H, J = 8.1 Hz, H_6), 7.80 (d, 1H, J = 8.7 Hz, H_4 or H_5), 7.32−7.29 (m, overlapping, 2H, H_5 or H_4 and H_8), 7.04 (dd, 1H, H_7), 6.85 (m, 5H, Ar), 6.58 (s, 1H, H_3); MS m/z 675 ($M + 3^+$).

[Ru(6c)(bpy-d_8)$_2$](PF$_6$). Following the procedure described for [Ru(**6a**)(bpy-d_8)$_2$](PF$_6$), a mixture of [Ru(bpy-d_8)$_2$Cl$_2$] (161 mg, 0.3 mmol) and 2-(3′-pyridyl)-pyrrolo[3,2-*h*]quinoline (**6cH**, 74 mg, 0.3 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to provide the complex as a violet solid (103 mg, 42%): ^{1}H NMR (CD_3CN) δ 8.20 (d, 1H, J = 8.1 Hz, H_6), 8.15 (d, 1H, J = 1.8 Hz, $H_{2'}$), 8.07 (dd, 1H, J = 4.2 Hz, 0.9 Hz, $H_{6'}$), 7.82 (d, 1H, J = 8.4 Hz, H_4 or H_5), 7.35 (d, 1H, J = 3.9 Hz, H_8), 7.33 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.13−7.06 (m, overlapping, 2H, J = 8.1 Hz, $H_{4'}$ and H_7), 6.74 (dd, 1H, $H_{5'}$), 6.63 (s, 1H, H_3); MS m/z 675 ($M + 2^+$).

[Ru(6d)(bpy-d_8)$_2$](PF$_6$). Following the procedure described for [Ru(**6a**)(bpy-d_8)$_2$](PF$_6$), a mixture of [Ru(bpy-d_8)$_2$Cl$_2$] (107 mg, 0.2 mmol) and 2-(4′-pyridyl)-pyrrolo[3,2-*h*]quinoline (**6dH**, 49 mg, 0.2 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to provide the complex as a violet solid (8 mg, 5%): ^{1}H NMR (CD_3CN) δ 8.20 (dd, 1H, J = 8.1 Hz, 0.9 Hz, H_6), 7.98 (d, 2H, J = 5.7 Hz, $H_{2'}$ and $H_{6'}$), 7.82 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.35 (d, 1H, J = 4.8 Hz, H_8), 7.34 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.10 (dd, 1H, H_7), 6.82 (d, 2H, J = 5.7 Hz, $H_{3'}$ and $H_{5'}$), 6.74 (s, 1H, H_3); MS m/z 675 ($M + 2^+$).

[Ru(14a)(bpy-d_8)$_2$](PF$_6$). Following the procedure described for [Ru(**6a**)(bpy-d_8)$_2$](PF$_6$), a mixture of [Ru(bpy-d_8)$_2$Cl$_2$] (107 mg, 0.2 mmol) and 2-[3′-(1-methylpyridyl)]-pyrrolo[3,2-*h*]quinolinium iodide (**14aH**, 77 mg, 0.2 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to provide the complex as a violet solid (175 mg, 49%): ^{1}H NMR (CD_3CN) δ 8.46 (s, 1H, $H_{2'}$), 8.25 (d, 1H, J = 8.1 Hz, H_6), 8.08 (d, 1H, J = 6.0 Hz, $H_{6'}$), 7.86 (d, 1H, J = 8.7 Hz, H_4 or H_5), 7.54 (d, 1H, J = 8.4 Hz, $H_{4'}$), 7.42−7.39 (m, overlapping, 2H, H_8 and H_4 or H_5), 7.19−7.15 (m, overlapping, 2H, $H_{5'}$ and H_7), 6.83 (s, 1H, H_3), 4.15 (s, 3H, CH_3); MS m/z 343 ($M - 1^+$).

[Ru(15)(bpy-d_8)$_2$](PF$_6$)$_2$. Method A: Following the procedure described for [Ru(**6a**)(bpy-d_8)$_2$](PF$_6$), a mixture of [Ru(bpy-d_8)$_2$Cl$_2$] (107 mg, 0.2 mmol) and 2-[4′-(1′-methylpyridyl)]-pyrrolo[3,2-*h*]quinolinium iodide (**14bH**, 77 mg, 0.2 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to provide the complex as a violet solid (150 mg, 77%): ^{1}H NMR (CD_3CN) δ 8.26 (d, 1H, J = 8.1 Hz, H_6), 7.82 (d, 1H, J = 8.4 Hz, H_5 or H_4), 7.80 (d, 2H, J = 6.6 Hz, $H_{2'}$ and $H_{6'}$), 7.40 (d, 1H, J = 8.7 Hz, H_5 or H_4), 7.41 (d, 1H, J = 4.8 Hz, H_8), 7.35 (d, 2H, J = 6.6 Hz, $H_{3'}$ and $H_{5'}$), 7.22 (dd, 1H, H_7), 7.15 (s, 1H, H_3), 3.94 (s, 3H, CH_3); MS m/z 343 ($M - 1^+$).

Method B: Following the procedure described for [Ru(**6a**)(bpy-d_8)$_2$](PF$_6$), a mixture of [Ru(bpy-d_8)$_2$Cl$_2$] (80 mg, 0.15 mmol) and 2-[4′-(1′-methylpyridinylidene)]-2H-pyrro[3,2-*h*]quinoline (**15**, 39 mg, 0.15 mmol) in EtOH/H_2O (3:1, 20 mL) was heated at reflux for 24 h to provide a violet solid (110 mg, 75%) having an ^{1}H NMR and MS identical with the material described under Method A.

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