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Synthesis and Properties of Benzo[*b*]-1,10-phenanthrolines and Their Ruthenium(II) Complexes

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ABSTRACT: *Friedländer reactions of 4-aminoacridine-3-carbaldehyde with 1,3-, 1,4-di-, and 1,3,5-triacetylbenzenes afforded a series of corresponding (benzo[b]-1,10-phenanthrolin-2-yl)benzenes as new N,N,C-polydentates. Reaction with 1,2-diacetylbenzene afforded 1,2-di(benzo[b]-1,10-phenanthrol-2-yl)-benzene with unexpected benzo[b]-1,10-phenanthroline and 3-oxoindeno[1,2-b]benzo[j]-1,10-phenanthroline in a ratio of 1:1.2:1. Metal complex formation of the ligands was examined to provide two isomeric Ru complexes, a pentaaza-coordinated (N5Cl) complex [Ru(tpy)(***3aH***)Cl](PF$_6$) and a hexacoordinated (N5C) complex [Ru(tpy)(**3a**)](PF$_6$) in a ratio of 1:4 with 71% overall yield, whereas* **3b-eH** *afforded complex mixtures upon reactions with Ru(tpy)Cl$_3$.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:650–656, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20358

INTRODUCTION

Studies on the benzo[*b*]-1,10-phenanthroline (bphen) molecule, first reported in 1962 [1], have been focused on the synthesis of biologically intriguing molecules with a bphen moiety in part [2]. Even this molecule can be a good aromatic ligand, only very limited numbers of studies on its complexation ability of the system with bphen in part have been pursued with small organic molecules [3]. A mixed ruthenium(II) complex $[Ru(bpy)_2L]^{2+}$, where L is 5,6-dihydrobenzo[*b*]-1,10-phenanthroline, is the only reported complex with a ligand related to bphen [4]. Such limit may stem from the fact that unsymmetrical bidentates lead to two geometric isomers of tris-complexes that can give rise to a pair of enantiomers, which thus may not allow easy separation and/or isolation of a single identity.

Recently, interest in *N*,*N*,*C*-terdentates is growing owing to the intriguing spectral [5] as well as light-emitting properties [6] of cyclometalated species and potentials for the activation of C—H bond [7]. One reason can be that bphen can act as an *N*,*N*,*C*-terdentate by introducing a substituent especially phenyl group at the C2 position. To the best of our knowledge, *N*,*N*,*C*-terdentates with an acridine nucleus have never been reported as yet.

Although a couple of synthetic methods for bphen and its derivatives have been reported (for a review concerning the synthesis of benzo[*b*]-1,10-phenanthroline, see Alvarez and Joule [8].), the Friedländer condensation [9] can be a method of choice. We recently introduced 4-aminoacridine-3-carbaldehyde (**1**) as a new Friedländer synthon for the preparation of 2-substituted bphens [10].

As a part of our interest in new *N*,*N*,*C*-polydentates ligands and their metal complex chemistry [5b,11], we herein describe the application of

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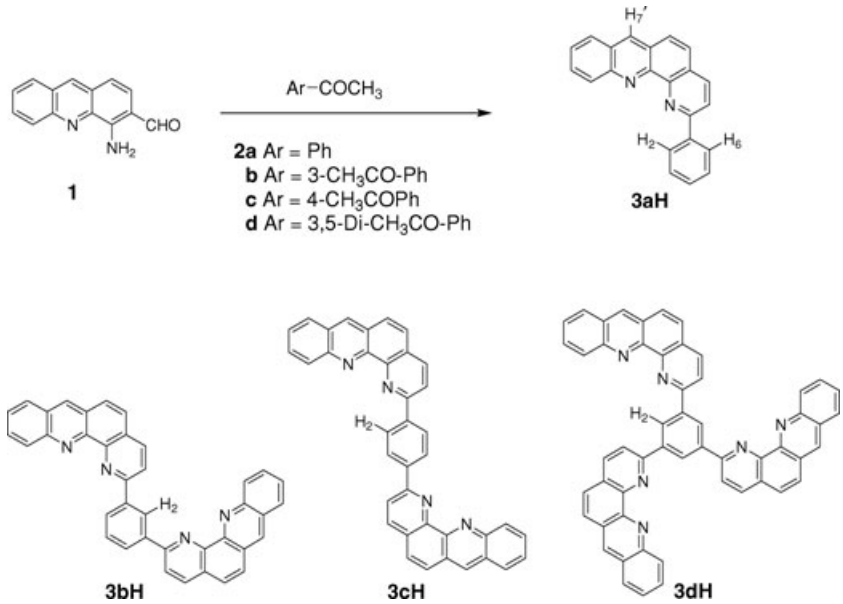
1 as a Friedländer synthon for the synthesis of new *N,N,C*-terdentates and their complexation abilities.

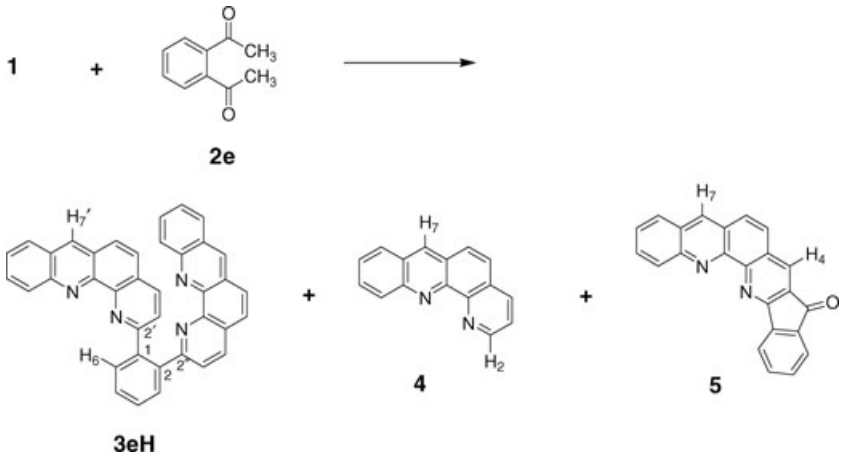
RESULTS AND DISCUSSION

Synthesis of the ligands was straightforward as shown below. Condensation of **1** with diacetylbenzenes (**2b,c,d**) under refluxing EtOH in the presence of catalytic KOH provided three isomeric di(benzo[*b*]-1,10-phenanthrolin-2-yl)benzenes (**3H**), which provide an interesting series of ligands wherein the orientation of the ligand will be regularly controlled. In addition, treatment of 1,3,5-triacetylbenzene (**2d**) with 3 equivalents of **1** afforded a propeller-shaped ligand, wherein three benzo[*b*]-1,10-phenanthroline moieties might interact in a cooperative fashion above or below the plane of the central benzene ring.



The ligands prepared could be readily characterized by their ^{1}H NMR spectra as well as electrospray ionization mass spectrometry. Even it is not always possible to completely resolve and assign all the proton resonances, certain features were characteristic and diagnostic. Typically, H7′ of the benzo[*b*]-1,10-phenanthroline moiety and H2 (and/or H6) in the phenyl ring of **3H** are the ones to allow easy assignment by comparing their chemical shifts and splitting patterns as well as numbers of protons. In **3aH**, these protons were resonanced at δ 8.76 as a one-proton singlet and δ 8.41 as a two-proton doublet ($J = 8.1$ Hz), respectively. Similarly, H7′ and H2 of **3cH** were resonanced at δ 9.17 as a two- proton singlet and at δ 8.76 as a four-proton singlet, respectively. By introducing an additional bphen moiety at C4, chemical shifts of these protons were downfield shifted by 0.41 and 0.35 ppm, respectively. In addition, an introduction of bphen moiety at C3 of the benzene ring led to more dramatic shift of H2 by 0.96 ppm to be resonanced at δ 9.38 as a one-proton triplet ($J = 1.3$ Hz) in **3bH**. In trisubstituted system **3dH**, H2 was found at δ 9.49 as a three-proton singlet because of the two adjacent N1s of bphen moiety that is comparable to δ 9.30 for 1,3,5-tri(1,10-phenanthrolin-2-yl)benzene [12]. Resonances of remaining protons were assigned by comparing ^{1}H NMR data of the parent bphen and were confirmed by double-quantum filtered COSY experiments and NOE effect for the selected protons.

To our surprise, the reaction of **1** with **2e**, however, afforded 1,2-di(benzo[*b*]-1,10-phenanthrolin-2-yl)benzene (**3eH**), benzo[*b*]-1,10-phenanthroline (**4**), and 3-oxoindeno[1,2-*b*]benzo[*h*]-1,10-phenanthroline (**5**) in 72% of overall yield with a ratio of 1:1.2:1. Similar pattern of the Friedländer reaction to afford **4** from the

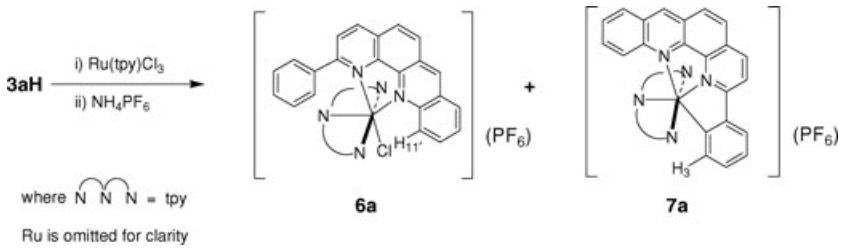


reaction of **1** with triacetylmethane was examined and reported previously [13].

It is worth to note that the ^{1}H NMR spectrum of **3eH** showed complex proton resonances, implying the presence of two diastereomers via twisting chiral axes C1—C2′— and C2—C2″— bond. Two adjacent bphen rings impose steric congestion around C1—C2′— and C2—C2″— bonds, enough to interrupt free rotation through these bonds (similar phenomena were additionally observed in the series of 1,2-diheteroarylbenzene, which will be due in the future). Attempts to separate two diastereomers have not yet been successful. Studies on the interconversion of conformational isomers are in progress.

Structures of **4** and **5** were confirmed by spectroscopic methods. ^{1}H NMR spectrum of **4** showed a doublet of doublet at δ 9.23 with characteristically small coupling constants $J_{2,3} = 4.5$ Hz, and $J_{2,4} = 1.5$ Hz for H2, and the rest of the resonances were assigned by double-quantum filtered COSY experiments and NOE effect for the selected protons. Isolation of the compound **5** is the most surprising. ^{1}H NMR showed 12 proton resonances in which two singlets at δ 9.43 and δ 8.67 covered for H4 and H7, six doublets for six protons, and four triplets for four protons. ^{13}C NMR showed 23 carbon resonances, one of which resonanced at δ 194.54 for C=O. The mechanism for the formation of **5** remains to be explored.

Attempts to prepare metal complexes with $[RuCl_3(H_2O)_3]$ were not successful, but instead afforded only complex mixtures that have not been yet separated or identified. The reaction of **3aH** with $[Ru(tpy)Cl_3]$ [14] (tpy = 2,2′;6′,2″-terpyridine) in refluxing aqous EtOH, followed by anion metathesis, however, afforded two metal complexes, a pentaaza-coordinated (N5Cl) complex [Ru(tpy)(**3aH**)Cl](PF$_6$) (**6a**) and a hexa-coordinated (N5C) complex [Ru(tpy)(**3a**)](PF$_6$) (**7a**) in a ratio of 1:4.



The two ruthenium(II) complexes were separated carefully by chromatography on alumina. The assignment of each proton resonance has been made by double-quantum filtered COSY experiments and by comparing with the values of related complexes of 6-phenyl-2,2′-bipyridine [5c] and 2-phenyl-1,10-phenanthroline [15]. Total 24 proton resonances in 250 MHz ^{1}H NMR spectrum of **7a** reflected disappearance of H2 of the phenyl ring to support the structure of hexa-coordinated species, which was additionally supported by ^{13}C NMR spectrum. The ^{13}C NMR spectrum of **7a** showed a characteristic quaternary (confirmed by DEPT, $\theta = 135^\circ$) carbon

TABLE 1 UV Absorption Spectral Data of **3**, **6a**, and **7a**

Compound	λ_{max} *(log* ε*) (95% EtOH)*
3aH	254 (4.74) 315 (4.60) 356 (3.99)
3bH	253 (5.09) 320 (4.84) 360 (4.28)
3cH	260 (5.08) 331 (4.87) 364 (4.66)
3dH	253 (5.57) 320 (5.34) 360 (4.88)
6a	253 (5.03) 276 (4.66) 321 (4.90) 376 (4.11) 490–580 (4.22)
7a	253 (4.96) 276 (5.16) 321 (4.85) 373 (4.06) 490–580 (4.22)

resonance at δ 184.99, which well matched to values of cycloruthenated sp^2-carbons (Ru-C) as reported in the literature [16]. In addition, H3 of phenyl is not only held approximately over the plane of the central pyridine ring of orthogonal tpy but also positioned next to cycloruthenated C2 to give a resonance at δ 5.65, thus upfield-shifted by 1.9 ppm. Resonance of H11′ was also significantly upfield-shifted to δ 6.84 ($\Delta\delta$ 1.57) upon formation of the Ru complex owing to the shielding effect induced by the central pyridine ring of orthogonal tpy.

On the other hand, ^{1}H NMR spectrum of pentaaza-coordinated species **6a** showed 25 proton resonances. Two characteristics could be noted. H11′ of **6a** was down-field resonanced at δ 9.74 ($\Delta\delta$ 1.04), due to the deshielding effect of the lone pairs of electrons in Cl on the ruthenium core as previously reported [5,15]. In addition, H2 (with H6) of phenyl group was resonanced at δ 6.25, thus upfield-shifted by 2.43 ppm due to π-stacking effect with the central pyridine ring of orthogonal tpy reflecting the free rotatability of C1—C2′ bond in **3aH**. The resonances at δ 6.85 for H3 and H5 of phenyl were also explained in the same fashion.

The electronic absorption data for the ligands (**3**) and Ru(II) complexes (**6a** and **7a**) are summarized in Table 1. The ligands showed three major absorptions in the region of 253–260, 315–331, and 356–364 nm for the π to π^* electron transition. As the numbers of bphen increased from **3aH** to **3bH**, **3bH** and **3dH**, the intensities of both absorptions increased, which might reflect degree of delocalization of π system between the central benzene and the bphen.

Absorption patterns of the complexes **6a** and **7a** are quite similar and showed two major ligand-based absorptions and one metal-to-ligand charge transfer (MLCT). Stronger ligand-based absorption at 276 nm of **7a** may reflect that the planarity of the ligand moiety induced by Ru—C bond formation leads to increase in π-electron conjugation. The broad absorption plateaus in the range of 490–580 nm are attributed to the typical MLCT, that is characteristic of most Ru(II) polypyridine complexes [17]. The MLCT band for $[Ru(tpy)_2]^{2+}$ in acetonitrile appears at 474 nm. An approximate 16–106 nm shift to lower energy for the two complexes may be explained by destabilization of the metal t_{2g} orbital, which is caused by either the chloride or carbanion being a stronger π donor than the pyridine ligand [18]. These values are somewhat longer wavelength shifted from closely related complexes $[Ru(tpy)(\mathbf{L})]^+$ and $[Ru(tpy)(\mathbf{LH})Cl]^+$; where **LH** is 2-phenyl-1,10-phenanthroline [15]. Such phenomenon may reflect that the additionally fused benzene ring permits it to delocalize charge greater, and thus, the MLCT absorption envelope broadens in the direction to lower energy as has been reported previously [19].

Reactions of $Ru(tpy)Cl_3$ with **3bH, 3cH, 3dH**, and **3eH** were also pursued, but to afford complex mixtures does not allow us to either isolate or identify any single Ru(II) complex as yet. Formation of such complex mixtures might be explained by formation of the diastereomeric isomers when two $[Ru(tpy)]^+$ moieties were introduced and/or by electronic as well as steric factors around the central phenyl ring.

In conclusion, the Friedländer reaction of 4-aminoacridine-3-carbaldehyde with acetylbenzenes afforded a series of corresponding benzo[*b*]-1,10-phenanthrolines in fairly good yields. Reaction of the aldehyde with 1,2-diacetylbenzene afforded 1,2-di(benzo[*b*]-1,10-phenanthrolin-2-yl)benzene and unexpected benzo[*b*]-1,10-phenanthroline and 3-oxoindeno[1,2-*b*]benzo[*h*]-1,10-phenanthroline in a ratio of 1:1.2:1. Reaction of **3aH** with $[Ru(tpy)Cl_3]$ afforded two isomeric metal complexes, a pentaaza-coordinated (N5Cl) complex $[Ru(tpy)(\mathbf{3aH})Cl](PF_6)$ and a hexa-coordinated (N5C) complex $[Ru(tpy)(\mathbf{3a})](PF_6)$ in a ratio of 1:4 with 71% of overall yields, whereas **3bH, 3cH, 3dH**, and **3eH** afforded complex mixtures. Studies on the photophysical and biological properties of ligands as well as their ability to form metal complexes with a variety of transition metals are in progress, which will be due in the near future.

EXPERIMENTAL

Melting points were determined using a Fischer–Jones melting points apparatus and are not corrected. IR spectra were obtained using a Perkin–Elmer 1330 spectrophotometer. NMR spectra were obtained using a Bruker-250 spectrometer 250 MHz or 400 MHz for ^{1}H NMR and 62.5 MHz or 100 MHz for ^{13}C NMR and are reported as parts per million (ppm) from the internal standard TMS. Compound **3aH** was prepared by employing previously reported

method [10]. Chemicals and solvents were commercial reagent grade and were used without further purification. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on a LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). Elemental analyses were done on a Hewlett–Packard model 185B elemental analyzer.

*1,3-Di(benzo[b]-1,10-phenanthrolin-2-yl)-benzene (**3bH**) (General Procedure)*

A mixture of **1** (108 mg, 0.48 mmol) and 1,3-diacetylbenzene (38.9 mg, 0.24 mmol) in 10 mL of absolute EtOH with saturated ethanolic KOH (1.3 mL) was refluxed for 8 h. The solvent was evaporated under reduced pressure, and resulting solid was chromatographed on silica gel eluting with CH_2Cl_2:CH_3OH (9:1) followed by increasing the ratio of CH_3OH up to 1:1. Latter fractions of CH_2Cl_2:CH_3OH (1:1) afforded 187 mg (72%) of yellow needles, mp 215°; UV λ_{max} (log ε) (95% EtOH): 253 (5.09), 320 (4.84), 360 (4.28) nm; IR: 3050, 1610, 1475, 1260, 1245, 1220, 1180, 981 cm^{-1}, ^1H NMR: δ 9.38 (t, $J = 1.8$ Hz, 1H, H2), 8.74 (s, 2H, H7′, and H7″), 8.66 (d, 2H, $J = 9.1$ Hz, H4′ and H4″), 8.62 (dd, 2H, $J = 8.0$, 1.7 Hz, H11′ and H11″), 8.41 (d, 2H, $J = 8.4$ Hz, H6′ and H6″), 8.31 (d, 2H, $J = 8.4$ Hz, H5′ and H5″), 8.04 (dd, 2H, $J = 7.6$, 1.2 Hz, H8′ and H8″), 7.86–7.80 (m, 5H), 7.71 (d, $J = 9.1$ Hz, H3′ and H3″), 7.63 (dt, 2H, $J = 7.6$, 1.2 Hz, H9′ and H9″); ^{13}C NMR: δ 156.90, 148.37, 147.16, 146.60, 139.87, 136.86, 136.49, 131.05, 130.00, 129.41, 129.17, 128.36, 127.60, 127.37, 127.12, 126.81 (two Cs), 126.76 (two Cs), 125.86. Elemental analysis for $C_{38}H_{22}$N4-H_2O: C, 82.60 (calc. 82.59); H, 4.38 (4.38); N, 10.12(10.14).

*1,4-Di(benzo[b]-1,10-phenanthrolin-2-yl)-benzene (**3cH**)*

Yellow needles (78%), mp >250°; UV: λ_{max} (log ε) (95% EtOH): 260 (5.08), 331 (4.87), 364 (4.66); IR: 3050, 1608, 1475, 1255, 1245, 1225, 1180, 980 cm^{-1}, ^1H NMR: δ 9.17 (s, 2H, H7′ and H7″), 8.77 (s, 4H, H2, H3, H5, H6), 8.64 (d, 2H, $J = 8.6$ Hz, H6′ and H6″), 8.60 (d, 2H, $J = 8.6$ Hz, H5′ and H5″), 8.51 (d, 2H, $J = 8.3$ Hz, H11′ and H11), 8.30 (d, $J = 8.6$ Hz, H8′ and H8″), 8.11 (d, $J = 8.7$ Hz, H4′ and H4″), 8.01 (d, 2H, $J = 8.7$ Hz, H3′ and H3″), 8.00 (t, 2H, $J = 8.3$ Hz, H10′ and H10″), 7.78 (t, 2H, $J = 8.3$ Hz, H9′ and H9″). ^{13}C NMR: δ 155.23, 146.73, 146.01, 145.33, 139.80, 137.78, 131.57, 129.11, 128.91, 128.73, 128.21 (two Cs), 127.42, 127.34, 127.27, 127.17, 126.42, 121.67. Elemental analysis for $C_{38}H_{22}N_4$-H_2O: C, 82.49 (calc. 82.59); H, 4.41 (4.38); N, 10.13 (10.14).

*1,3,5-Tri(benzo[b]-1,10-phenanthrolin-2-yl)-benzene (**3dH**)*

Pale yellow needles (72%), mp >250°; UV: λ_{max} (log ε) (95% EtOH): 253 (5.57), 320 (5.34), 360 (4.88); IR: 3060, 1613, 1480, 1255, 1250, 1220, 1190, 980 cm^{-1}; ^1H NMR: δ 9.49 (s, 3H, H2, H4, and H6), 8.84 (s, 3H, H7′), 8.82 (d, 3H, $J = 8.5$ Hz, H6′), 8.74 (d, 3H, $J = 8.5$ Hz, H5′), 8.46 (d, 3H, $J = 7.4$ Hz, H11′), 8.38 (d, 3H, $J = 10.3$ Hz, H8′), 8.12 (d, 3H, $J = 8.9$ Hz, H4′), 8.02 (d, 3H, $J = 8.9$ Hz, H3′), 7.79 (dt, 3H, $J = 7.4$, 0.8 Hz, H10′), 7.74 (td, 3H, $J = 7.4$, 0.8 Hz, H9′); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 156.04, 147.68, 146.86, 146.21, 140.70, 137.69, 136.23, 130.99, 130.13, 129.82, 128.69, 128.38, 128.02, 127.31, 127.15 (two Cs), 126.96, 126.15. Elemental analysis for $C_{54}H_{30}N_6$-$0.75H_2O$: C, 83.74 (calc. 83.54); H, 4.04 (4.09); N, 10.76(10.82).

*Reaction of **1** with **2e***

Reaction mixture was chromatographed on alumina eluting with CH_2Cl_2 and followed by CH_2Cl_2:CH_3OH (18:1) to afford three isolable compounds. The fractions of CH_2Cl_2 afforded **4** and **5**, and the latter fractions of CH_2Cl_2:CH_3OH (18:1) afforded **3eH**.

*Benzo[b]-1,10-phenanthroline (**4**).* Pale yellow needles [29%, $R_f = 0.25$ (CH_2Cl_2)], mp 114°; (lit. [1], mp 113°, lit. [13] 113–114°).

*3-Oxoindeno[1,2-b]benzo[h]-1,10-phenanthroline (**5**).* Pale yellow needles [23%, $R_f = 0.10$ (CH_2Cl_2)], mp >300°; ^1H NMR: δ 9.43 (s, 1H, H4), 8.74 (d, 1H, $J = 9.2$ Hz, H5/H6), 8. 67 (s, 1H, H7), 8.60 (d, 1H, $J = 8.4$ Hz, H11), 8.03 (d, 1H, $J = 7.8$ Hz, H8), 7.93 (d, 1H, $J = 9.2$ Hz, H6/H5), 7.85 (ddd, 1H, $J = 8.4$, 7.8, 1.3 Hz, H10), 7.75 (d, 1H, $J = 7.5$ Hz, H6′), 7.72 (d, 1H, $J = 7.5$ Hz, H3′), 7.64 (td, 1H, $J = 7.8$, 1.2 Hz, H9), 7.55 (td, 1H, $J = 7.5$, 0.8 Hz, H4′), 7.36 (t, 1H, $J = 7.5$ Hz, H5′). ^{13}C NMR: δ 194.54, 149.05, 148.66, 146.56, 142.50, 141.95, 138.44, 135.35, 133.95, 133.64, 130.86, 130.80, 130.60, 130.14, 127.80, 127.69, 127.18, 126.73, 125.66, 125.18, 121.48, 121.18. ESI mass (M+1): 333.4. Elemental analysis for $C_{23}H_{12}N_{2O}$-H_2O: C, 78.88 (calc. 78.84); H, 4.00 (4.03); N, 7.99 (8.00).

*1,2-Di(benzo[b]-1,10-phenanthrolin-2-yl)benzene (**3eH**).* Pale yellow needles (24%, $R_f = 0.10$ (CH_2Cl_2:CH_3OH (18:1)). mp >300°; IR: 3050, 1615, 1470, 1255, 1245, 1220, 1190, 980 cm^{-1}; ^1H NMR:

δ 9.03 (dm, 2H, $J = 8.7$, 1.9 Hz, H3 and H6), 8.67 (s, 2H, H7′ and H7″), 8.26 (d, 2H, $J = 8.8$ Hz, H11′ and H11″), 7.98 (overlapped d, 4H, $J = 8.8$ Hz), 7.87–7.64 (m, 6H), 7.55–7.45 (m, 4H), 7.32 (t, 2H, $J = 7.5$ Hz). Elemental analysis for $C_{38}H_{22}N_4$: C, 85.28 (calc. 85.37); H, 4.18 (4.15); N, 10.54 (10.48).

Metal Complex Formation of **3aH** *with Ru(tpy)Cl*$_3$

A mixture of Ru(tpy)Cl_3 (44 mg, 0.1 mmol), **3aH** (31 mg, 0.1 mmol), and Et_3N (three drops) in EtOH:H_2O (3:1, 12 mL) was refluxed for 12 h. After cooling to room temperature, reaction mixture was filtered to remove insoluble materials. To the filtrate, NH_4PF_6 (11.6 mg. 0.1 mmol) in water (5 mL) was added and the solvent was evaporated to dryness. The resulting residue was chromatographed on Al_2O_3 (30 g) eluting with CH_3CN:toluene (1:1). The early fractions ($R_f = 0.50$ (toluene: CH_3CN = 1:1)) gave N5C complex, [Ru(tpy)(**3a**)](PF_6) (**7a**), as purple needles (45 mg, 57%); mp >310°; ^{1}H NMR (CD_3CN) δ 8.98 (s, 1H, H7), 8.74 (d, 2H, $J = 8.0$ Hz, H3 and H5 of tpy), 8.53 (AB quartet, 2H, H5 and H6), 8.38 (d, 2H, $J = 8.1$ Hz, H3′ and H3″ of tpy), 8.20 (t, 1H, $J = 8.0$ Hz, H4 of tpy), 8.16–8.12 (m, 2H, H3 and H4), 8.06 (d, 1H, $J = 8.0$ Hz, H8), 7.93 (dd, 1H, $J = 7.5$, 1.2 Hz, H6 of phenyl), 7.64 (td, 2H, $J = 8.1$, 1.4 Hz, H4′ and H4″ of tpy), 7.48 (ddd, 1H, $J = 8.0$, 7.8, 1.2 Hz, H9), 7.33 (ddd, 1H, $J = 8.0$, 7.8, 1.5 Hz, H10), 7.26 (ddd, 2H, $J = 5.0$, 1.2, 0.5 Hz, H6′ and H6″ of tpy), 6.88–6.80 (m, 3H, H5′ and H5″ of tpy, H11), 6.77 (td, 1H, $J = 7.5$, 1.3 Hz, H5 of phenyl), 6.59 (td, 1H, $J = 7.5$, 1.3 Hz, H4 of phenyl), 5.65 (d, 1H, $J = 7.5$ Hz, H3 of phenyl). ^{13}C NMR (CD_3CN, 62.5 MHz): δ 184.99, 163.62, 158.03 (two C′s), 154.40 (two C′s), 152.04 (CH), 149.14, 148.05, 148.00, 137.07 (CH), 135.76 (CH), 135.00 (CH), 133.81 (CH), 132.73 (CH), 130.47 (CH), 130.22, 130.06 (CH), 130.03 (CH), 129.86, 129.37, 128.51 (CH), 127.48 (CH), 127.20 (CH), 126.89 (CH), 126.07 (CH), 125.95 (CH), 123.87 (CH), 123.67 (CH), 122.51 (CH), 119.01 (CH). ESI mass for $[RuC_{37}H_{24}N_5]^+$: 640.4. Elemental analysis for $[RuC_{37}H_{24}N_5](PF_6)$: C, 56.68 (calc. 56.64); H, 3.06 (3.08); N, 8.92 (8.93). The latter fractions ($R_f = 0.38$ (toluene:CH_3CN = 1:1)) gave N5Cl complex, [Ru(tpy)(**3aH**)Cl](PF_6) (**6a**), as brown red needles (12 mg, 14%); mp >310°; ^{1}H NMR (CD_3CN): δ 9.74 (dd, 1H, $J = 8.1$, 2.5 Hz, H11), 9.42 (s, 1H, H7), 8.51 (d, 1H, $J = 7.5$ Hz, H4), 8.34 (d, 1H, $J = 9.0$ Hz, H5/H6), 8.13 (d, 2H, $J = 8.0$ Hz, H3 and H5 of tpy), 8.12 (d, 1H, 7.5 Hz, H8), 7.98–7.89 (m, 4H, H6/H5, H10, H3′ and H3″ of tpy), 7.84 (td, 2H, $J = 7.8$, 1.4 Hz, H4′ and H4″ of tpy), 7.71 (t, 1H, $J = 8.1$ Hz, H4 of tpy), 7.48 (d, 2H, $J = 5.4$ Hz, H6′ and H6″ of tpy), 7.25 (t, 1H, $J = 7.8$ Hz, H4 of phenyl), 7.21 (d, 1H, $J = 8.0$ Hz, H9), 7.12 (ddd, 2H, $J = 7.8$, 5.4, 1.3 Hz, H5′ and H5″ of tpy), 6.85 (d, 2H, $J = 7.8$ Hz, H3 and H5 of phenyl), 6.24 (dd, 2H, $J = 7.8$, 0.9 Hz, H2 and H6 of phenyl). ESI mass for $[RuC_{37}H_{25}N_5Cl]^+$: 676.1. Elemental analysis for $[RuC_{37}H_{25}N_5Cl](PF_6)$: C, 54.23 (calc. 54.12); H, 3.06 (3.07); N, 8.54 (8.53).

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