

# Ruthenium(II) and Osmium(II) Complexes Bearing Bipyridine and the N-Heterocyclic Carbene-Based C<sup>^</sup>N<sup>^</sup>C Pincer Ligand: An Experimental and Density Functional Theory Study

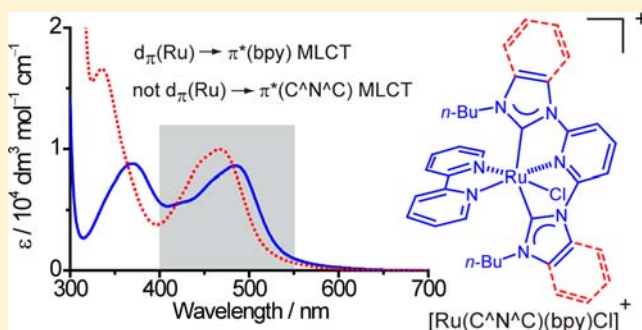
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## Supporting Information

**ABSTRACT:** Ruthenium(II) and osmium(II) complexes  $[M(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)L]^{n+}$  ( $L = Cl^{-}$ ,  $n = 1$ ;  $L = CH_3CN$ ,  $t$ -BuNC,  $n = 2$ ) containing a neutral tridentate N-heterocyclic carbene (NHC)-based pincer ligand, either 2,6-bis(1-butylimidazol-2-ylidene)pyridine ( $C^{\wedge}N^{\wedge}C^1$ ) or 2,6-bis(3-butylbenzimidazol-2-ylidene)pyridine ( $C^{\wedge}N^{\wedge}C^2$ ), and a neutral 2,2'-bipyridine-type aromatic diimine have been prepared. Investigations into the effects of varying  $M$  (Ru and Os),  $C^{\wedge}N^{\wedge}C$ ,  $N^{\wedge}N$ , and  $L$  on the structural, electrochemical, absorption, and emission characteristics associated with  $[M(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)L]^{n+}$  are presented. Interestingly, spectroscopic findings and time-dependent density functional theory (TD-DFT) calculations in this work support a  $d_{\pi}(Ru^{II}/Os^{II}) \rightarrow \pi^*(N^{\wedge}N)$  metal-to-ligand charge transfer (MLCT) assignment for the lowest-energy transition in  $[M(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)L]^{n+}$  and not a  $d_{\pi}(Ru^{II}/Os^{II}) \rightarrow \pi^*(C^{\wedge}N^{\wedge}C)$  MLCT assignment. This is in stark contrast to  $[Ru(tpy)(bpy)Cl]^{+}$  and  $[Os(tpy)(bpy)Cl]^{+}$  ( $tpy = 2,2':6',2''$ -terpyridine,  $bpy = 2,2'$ -bipyridine) for which the lowest-energy transitions are assigned as  $d_{\pi}(Ru/Os) \rightarrow \pi^*(tpy)$  MLCT transitions.  $[Ru^{II}(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)L]^{n+}$  is emissive with emission maxima of around 600–700 nm observed upon photoexcitation of their  $d_{\pi}(Ru^{II}) \rightarrow \pi^*(N^{\wedge}N)$  MLCT bands. The electronic structures for  $[Ru(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)Cl]^0$  have also been probed by spectroelectrochemistry, electron paramagnetic resonance (EPR) spectroscopy, and DFT calculations, which reveal that the lowest unoccupied molecular orbitals (LUMOs) for  $[Ru(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)Cl]^+$  are  $N^{\wedge}N$ -based.



## INTRODUCTION

Ruthenium(II) complexes containing polypyridyl ligands, and other  $d^6$  transition-metal counterparts, have long been a research focus in the design of functional molecular material.<sup>1–13</sup> This is because they exhibit rich photophysics and photochemistry originating from the triplet  $[d_{\pi}(M) \rightarrow \pi^*(\text{polypyridyl})]$  metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) excited state. In the last two decades, these polypyridyl complexes have found tremendous application in solar energy harvesting,<sup>11,14,15</sup> organic light-emitting devices (OLEDs),<sup>16,17</sup> photocatalysis,<sup>1,3,18</sup> and biolabeling reagents.<sup>19</sup> Meanwhile, the pursuit of polypyridyl complexes featuring desirable photophysical and photochemical properties remains unabated.

Regarding the design of polypyridyl Ru(II) luminophores, we initiated a program to develop new organometallic Ru(II) complexes with the general formula  $[Ru^{II}(N^{\wedge}N)(X_3)(L)]^{n+}$ , where  $N^{\wedge}N$  represents 2,2'-bipyridine-like aromatic diimines,  $(X_3)$  represents tridentate triazacyclononane/trithiacyclononane, and  $L$  represents monodentate organometallic ligands including acetylides, alkoxycarbene, allenylidene, cyanide,

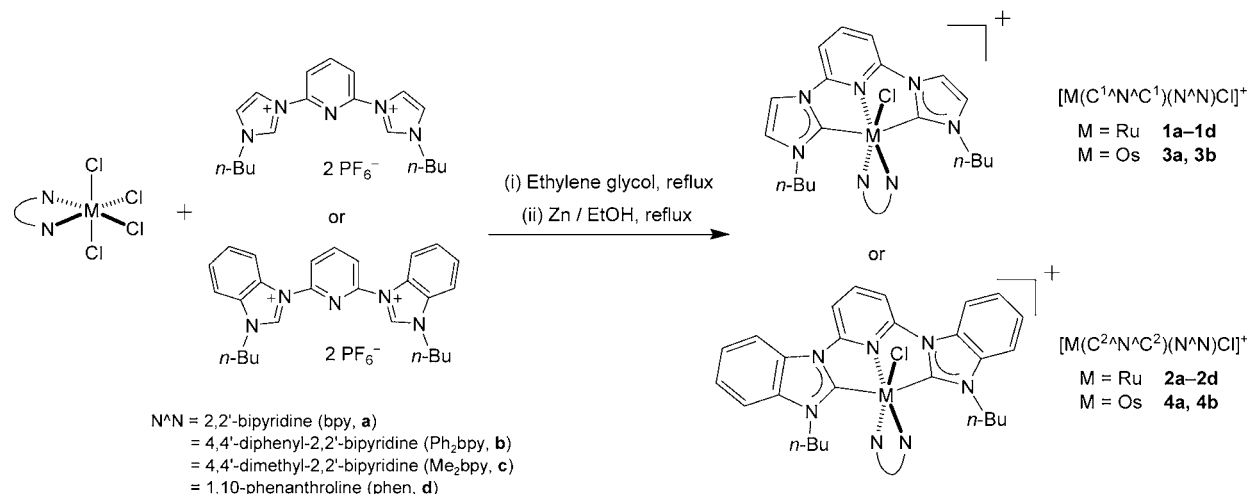
isocyanide, and indolizine.<sup>20</sup> Recently, we also performed detailed spectroscopic studies for Os(II)-diimine complexes  $[Os(C^{\wedge}C^{\wedge}C)(N^{\wedge}N)(CO)]^{+}$ , where  $C^{\wedge}C^{\wedge}C$  represents tridentate N-heterocyclic carbene (NHC)-based pincer ligand 1,3-bis(1-methylimidazol-2-ylidene)phenyl anion or the 1,3-bis(3-methylbenzimidazol-2-ylidene)phenyl anion, and we discovered that the  $C^{\wedge}C^{\wedge}C$  ligands can be used to modulate the photophysical properties of an  $[Os(N^{\wedge}N)]$  moiety via the formation of hybrid  $[Os + C^{\wedge}C^{\wedge}C]$  frontier orbitals.<sup>21</sup> Significantly, the  $[Os(C^{\wedge}C^{\wedge}C)(N^{\wedge}N)(CO)]^{+}$  complexes are emissive in the red spectral region with an extraordinarily longer emission lifetime (around 1–6  $\mu\text{s}$  at room temperature in fluid solution) than for their classical diimine congeners  $[Os(bpy)_3]^{2+}$  and  $[Os(phen)_3]^{2+}$ .

As an extension of our investigation to elucidate the effect of metal–carbon bonding interactions with respect to the photophysical properties of an  $[M(N^{\wedge}N)]$  moiety, we now

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Scheme 1



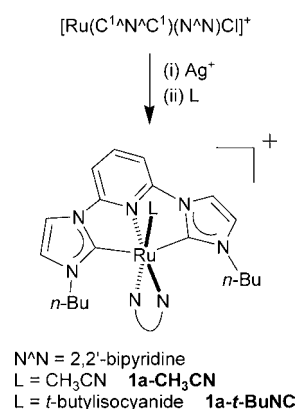
present the synthesis of, and spectroscopic and theoretical studies for  $[Ru^{II}(C^A N^A C)(N^A N)L]^{n+}$  ( $L = Cl^-$ ,  $n = 1$ ;  $L = CH_3CN$ ,  $t-BuNC$ ,  $n = 2$ ) and  $[Os^{II}(C^A N^A C)(N^A N)Cl]^+$ , where  $C^A N^A C$  represents neutral tridentate NHC-based pincer ligands 2,6-bis(1-butylimidazol-2-ylidene)pyridine ( $C^1^A^N^A^C^1$ ) and 2,6-bis(3-butylbenzimidazol-2-ylidene)pyridine ( $C^2^A^N^A^C^2$ ). Our results indicate that the lowest-energy electronic excited states for these  $C^A N^A C$ -ligated complexes are  $d_\pi(M) \rightarrow \pi^*(N^A N)$  rather than  $d_\pi(M) \rightarrow \pi^*(C^A N^A C)$  in nature, which is striking because the frameworks of  $C^1^A^N^A^C^1$  and  $C^2^A^N^A^C^2$  contain more electronegative N atoms and are more conjugated than  $N^A N$ . The electronic structures for  $[Ru(C^A N^A C)(N^A N)Cl]^0$  have also been probed by spectroelectrochemical, EPR, and DFT studies, which reveal that the LUMOs for  $[Ru(C^A N^A C)(N^A N)Cl]^+$  are  $N^A N$ -based.

## RESULT AND DISCUSSION

**Synthesis and Characterization.** Ruthenium complexes  $[Ru(C^A N^A C)(N^A N)Cl]^+$  (**1a–1d**, **2a–2d**) were synthesized by reacting  $[Ru(N^A N)Cl_4]$  with pyridine-bridged bisimidazolium or bisbenzimidazolium hexafluorophosphate (precursors for  $C^1^A^N^A^C^1$  and  $C^2^A^N^A^C^2$ , respectively) in refluxing ethylene glycol followed by reduction using Zn granules (Scheme 1). Osmium analogues **3a**, **3b**, **4a**, and **4b** were prepared in an analogous fashion using  $[Os(N^A N)Cl_4]$  in place of  $[Ru(N^A N)Cl_4]$ .<sup>22</sup> These Os congeners are used for spectroscopic comparison with their Ru counterparts; therefore, only the bpy- and Ph<sub>2</sub>bpy-ligated derivatives, **a** and **b**, were prepared. CH<sub>3</sub>CN- and isocyanide-ligated ruthenium complexes **1a-CH<sub>3</sub>CN** and **1a-*t*-BuNC** were synthesized according to Scheme 2. Both <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy signify that in solution at room temperature these complexes possess a plane of symmetry on the NMR time scale. For example, there are 16 sets of aromatic <sup>13</sup>C NMR signals for both **1a** and **3a**. The <sup>13</sup>C NMR signals at 188.8–207.6 and 181.6–191.8 ppm for **1**, **2** and **3**, **4** are typical of metalated N-heterocyclic carbenes in Ru(II) and Os(II) complexes, respectively.<sup>22,23</sup>

The molecular structures of **1b**, **1c**, **2a**, and **4a** were determined by X-ray crystallography. Their perspective views are depicted in Figure 1, and selected bond distances and angles are summarized in Table 1. In each case, the Ru or Os atom adopts a distorted octahedral geometry, with the  $C^A N^A C$  pincer coordinating meridionally in an almost planar configuration. It

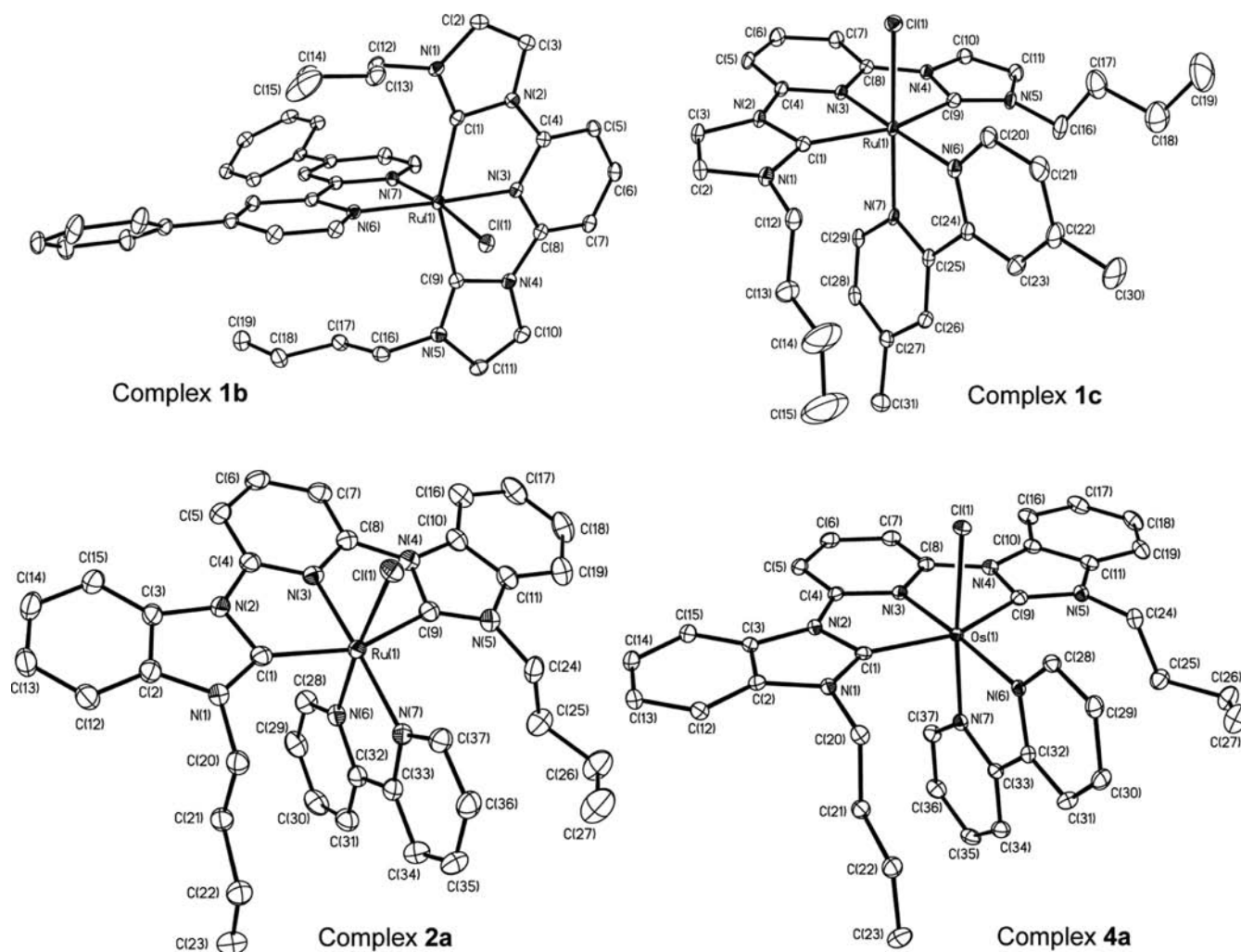
Scheme 2



is interesting that the structural parameters of the  $[M-(C^A N^A C)]$  moiety in this work are not sensitive to the changes in  $C^A N^A C$  (from  $C^1^A^N^A^C^1$  to  $C^2^A^N^A^C^2$ ) and M (from Ru to Os). For example, the bite angle for  $C^A N^A C$  in ruthenium complex **2a** is 156.3(1)°, and that for the corresponding osmium analogue (**4a**) is 155.4(1)°. Moreover, the Ru–C and Os–C bond distances are 2.033(2)–2.062(4) and 2.030(3)–2.040(2) Å, respectively. Overall, the similarity in the  $C^A N^A C$  bite angles and the M–C bond distances for M = Ru and Os indicate that the  $C^A N^A C$  pincers in this work are very rigid.

**UV–Visible Absorption and Theoretical Studies.** The UV–visible spectral data for the  $C^A N^A C$ -ligated complexes, together with those for  $[Ru(tpy)(bpy)Cl]^+$ ,  $[Os(tpy)(bpy)Cl]^+$ , and  $[Ru(C^1^A^N^A^C^1)_2]^{2+}$ , are summarized in Table S1. The  $[M(C^A N^A C)(N^A N)L]^{n+}$  complexes exhibit an intense high-energy absorption at  $\lambda \leq 320$  nm ( $\epsilon_{max} \geq 2 \times 10^4$  dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>) and moderately intense bands at  $\lambda \geq 320$  nm ( $\epsilon_{max} \approx 1 \times 10^4$  dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>), with tailing up to 600 and 800 nm for the Ru and Os derivatives, respectively. Because we are primarily interested in the lowest-energy transition of these complexes (depicted in Table 2), we will restrict our discussion to the impact of M,  $C^A N^A C$ , and  $N^A N$  upon this absorption.

Figure 2 depicts the absorption spectra of  $[M(C^A N^A C)(bpy)Cl]^+$  and  $[M(tpy)(bpy)Cl]^+$ . It is noted that the lowest-energy absorption bands for complexes bearing  $C^2^A^N^A^C^2$ , **2a** and **4a**, are blue-shifted by 749–803 cm<sup>−1</sup> with respect to their  $C^1^A^N^A^C^1$ -ligated counterparts, **1a** and **3a**, respectively. This



**Figure 1.** Perspective views of **1b**, **1c**, **2a**, and **4a** as represented by 30% probability ellipsoids; hydrogen atoms are omitted for clarity. Only one of the independent cations in **1b**(PF<sub>6</sub>) is depicted.

**Table 1.** Selected Bond Lengths (Å) and Bond Angles (deg) for **1b**, **1c**, **2a**, and **4a**

complex	<b>1b</b> <sup>a</sup>	<b>1c</b>	<b>2a</b>	<b>4a</b>
M–C	2.048(2)–2.061(2)	2.055(3), 2.062(4)	2.033(2), 2.048(2)	2.030(3), 2.040(2)
M–N <sub>C^N^C</sub>	1.998(2), 2.009(2)	2.015(3)	1.999(2)	2.007(2)
M–N <sub>N^N</sub>	2.031(2)–2.052(2)	2.040(3), 2.070(3)	2.041(2), 2.068(2)	2.043(2), 2.068(2)
M–Cl	2.427(1), 2.429(1)	2.437(1)	2.432(1)	2.436(1)
C–M– N <sub>C^N^C</sub>	77.5(1)–77.9(1)	77.3(1), 77.5(1)	78.1(1), 78.3(1)	77.6(1), 77.8(1)
∠C–M–C	155.0(1), 155.2(1)	154.7(1)	156.3(1)	155.4(1)
∠Py <sub>C^N^C</sub> / NHC	4.2–10.4	2.8, 6.8	0.7, 3.5	0.2, 2.9
∠NHC/ NHC <sup>c</sup>	10.4, 13.9	8.2	3.8	2.9

<sup>a</sup>The crystal contains two crystallographically independent cations in the asymmetric unit. <sup>b</sup>The angle between the mean plane of the pyridyl ring and the mean plane constructed by the imidazol-2-ylidene or benzimidazol-2-ylidene moiety (mean planes are calculated from all non-hydrogen atoms on the moiety). <sup>c</sup>The angle between the mean planes of the imidazol-2-ylidene or benzimidazol-2-ylidene moiety.

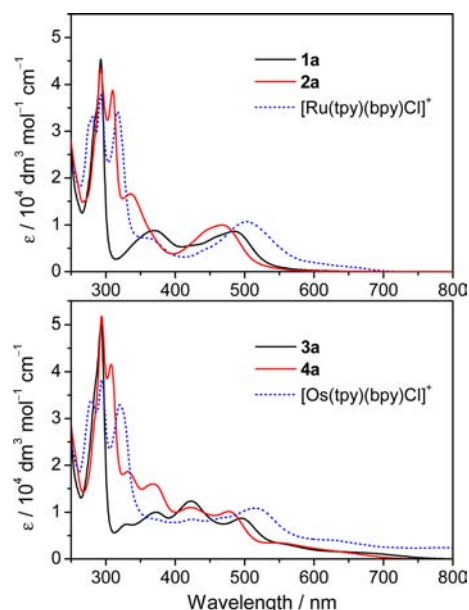
**Table 2.** Lowest-Energy Electronic Transition for the Complexes in CH<sub>3</sub>CN Solution at 298 K

complex	$\lambda_{\max}/\text{nm}$ ( $\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>
<b>1a</b>	485 (8600)
<b>1b</b>	503 (12 380)
<b>1c</b>	480 (8050)
<b>1d</b>	459 (12 690)
<b>2a</b>	467 (9940)
<b>2b</b>	485 (15 700)
<b>2c</b>	463 (10 270)
<b>2d</b>	456 (14 500)
<b>3a</b>	496 (8670), 558 (sh, 3180), 670 (sh, 1350)
<b>3b</b>	514 (sh, 12 130), 684 (sh, 2110)
<b>4a</b>	477 (10 160), 553 (sh, 3410)
<b>4b</b>	499 (sh, 13 760), 653 (sh, 2460)
<b>1a-CH<sub>3</sub>CN</b>	444 (7670)
<b>1a-<i>t</i>-BuNC</b>	423 (5450)
[Ru(tpy)(bpy)Cl] <sup>+</sup>	503 (10 690), 647 (sh, 1100)
[Os(tpy)(bpy)Cl] <sup>+</sup>	515 (10 840), 631 (sh, 3970), 807 (sh, 2320)
[Ru(C <sup>1</sup> N <sup>1</sup> C <sup>1</sup> ) <sub>2</sub> ] <sup>2+</sup>	385 (20 400), 434 (sh, 2510)

<sup>a</sup>See Supporting Information for detailed spectroscopic data.

finding suggests that the lowest-energy absorption bands for [M(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>)(N<sup>1</sup>N)Cl]<sup>+</sup> are unlikely to be derived from d<sub>π</sub>(M)

→ π\*(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>) MLCT transitions because C<sup>2</sup>N<sup>1</sup>C<sup>2</sup> is more conjugated than C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>. Instead, this finding is consistent



**Figure 2.** UV–visible absorption spectra of  $[M(C^{\wedge}N^{\wedge}C)(bpy)Cl]^+$  and  $[M(tpy)(bpy)Cl]^+$  in  $CH_3CN$  at 298 K.

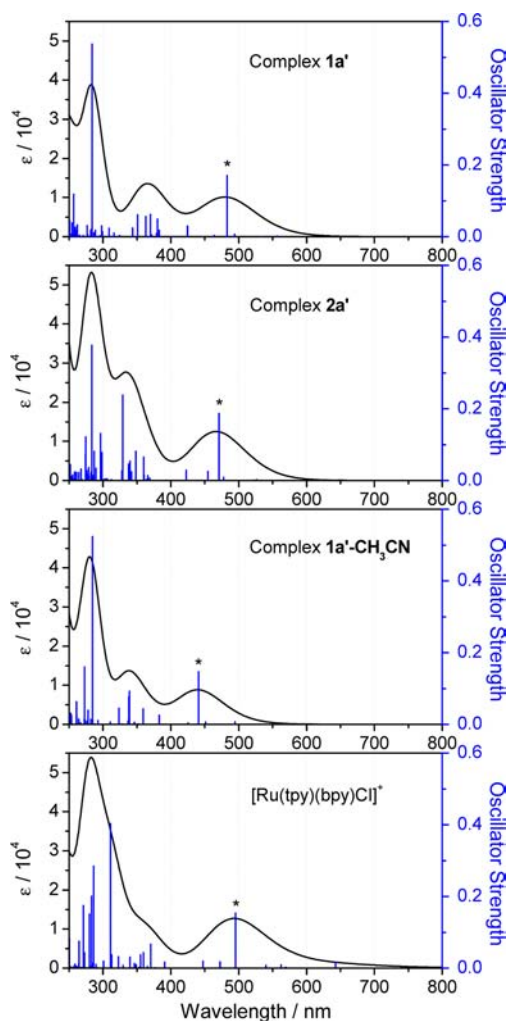
with a  $d_{\pi}(M) \rightarrow \pi^*(N^{\wedge}N)$  MLCT assignment because the donor strength of benzimidazol-2-ylidene (the NHC on  $C^{\wedge}N^{\wedge}C^2$ ) was determined to be weaker than that of imidazol-2-ylidene (the NHC on  $C^1\wedge N^{\wedge}C^1$ ) by Huynh et al.<sup>24</sup> Moreover, this  $d_{\pi}(M) \rightarrow \pi^*(N^{\wedge}N)$  MLCT assignment is further reinforced by the findings that (1) the absorption bands for  $[Os(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)Cl]^+$  are mildly red-shifted compared to their corresponding Ru analogues (Figure S1) and (2) the absorption energies for  $[M(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)Cl]^+$  are in the order of  $c$  ( $N^{\wedge}N = Me_2bpy$ ) >  $a$  ( $bpy$ ) >  $b$  ( $Ph_2bpy$ ) (Figure S2), which parallels the energies of the  $\pi^*$  level of  $N^{\wedge}N$ . This is in striking contrast to  $[Ru(tpy)(bpy)Cl]^+$  and  $[Os(tpy)(bpy)Cl]^+$  in which the lowest-energy transitions are always assigned as  $d_{\pi}(Ru^{II}/Os^{II}) \rightarrow \pi^*(tpy)$  MLCT transition. It is also worthwhile mentioning that the lowest-energy absorption bands for  $[M(C^{\wedge}N^{\wedge}C)(bpy)Cl]^+$  are higher in energy than those of  $[M(tpy)(bpy)Cl]^+$ , even though the framework of the  $C^{\wedge}N^{\wedge}C$  pincers contains more electronegative N atoms (five N atoms) than tpy (three N atoms only).

Apart from the lowest-energy absorption bands, there are two spectral features worth mentioning. First, each spectrum for  $[Os(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)Cl]^+$  displays noticeable tailing at  $\lambda \geq 500$  nm, which is less apparent in the case of  $[Ru(C^{\wedge}N^{\wedge}C)(N^{\wedge}N)Cl]^+$ . These tailings are typically assigned to spin-forbidden triplet charge-transfer transitions, which are promoted by the strong spin–orbit coupling induced by the Ru(II) and Os(II) centers.<sup>25</sup> Second, the spectra of Ru complexes at first glance look different from those of Os complexes in the 300–500 nm region. For example, Os complexes **3a** and **4a** exhibit four well-resolved absorption bands each in the 300–500 nm region, whereas Ru complexes **1a** and **2a** exhibit only two absorption bands each (Figure 2). However, theoretical calculations suggest that the nature of the transitions for both Ru and Os complexes are the same in this spectral region (Table S2); therefore, the aforementioned spectral difference is likely due to vibronic fine structure.

To rationalize the nature of the electronic transitions, time-dependent density functional theory (TD-DFT) calculations were performed for 1,3-bis(1-methylimidazol-2-ylidene)-

pyridine ( $MeC^1\wedge N^{\wedge}C^{1Me}$ )- and 1,3-bis(3-methylbenzimidazol-2-ylidene)pyridine ( $MeC^2\wedge N^{\wedge}C^{2Me}$ )-ligated model complexes  $[Ru(MeC^1\wedge N^{\wedge}C^{1Me})(bpy)Cl]^+$  (**1a'**),  $[Ru(MeC^2\wedge N^{\wedge}C^{2Me})(bpy)Cl]^+$  (**2a'**),  $[Os(MeC^1\wedge N^{\wedge}C^{1Me})(bpy)Cl]^+$  (**3a'**),  $[Os(MeC^2\wedge N^{\wedge}C^{2Me})(bpy)Cl]^+$  (**4a'**), and  $[Ru(MeC^1\wedge N^{\wedge}C^{1Me})(bpy)(CH_3CN)]^{2+}$  (**1a'-CH<sub>3</sub>CN**), in which their metal cores are the same as those in **1a**, **2a**, **3a**, **4a**, and **1a-CH<sub>3</sub>CN**, but the butyl chains on the  $C^{\wedge}N^{\wedge}C$  are replaced by methyl groups to reduce the computational cost. tpy-ligated complexes  $[Ru(tpy)(bpy)Cl]^+$  and  $[Os(tpy)(bpy)Cl]^+$  were also calculated for comparison. Symmetry ( $C_s$  point group) was imposed in each calculation to provide a simple model for interpreting the nature of the molecular orbitals and the origin of the electronic transitions, and this is justified because all of the complexes possess a plane of symmetry in solution on the NMR time scale. The M06 functional<sup>26</sup> developed by Truhlar and Zhao was employed because it is a functional parametrized for transition metals and has been demonstrated to give greater accuracy than other hybrid functionals in transition metal and organometallic chemistry. The conductor polarizable continuum model (CPCM)<sup>27</sup> was also applied to account for solvent effects in electronic transitions. Calculated excitation energies, oscillator strengths, and simulated absorption spectra (constructed by the convolution of the calculated transitions with Gaussian functions) for selected complexes are depicted in Figure 3. The simulated spectra not only feature profiles that resemble the corresponding experimental spectra, but the trends for the calculated lowest-energy transition ( $\lambda_{max}$  in the order **1a'-CH<sub>3</sub>CN** < **2a'** < **1a'** <  $[Ru(tpy)(bpy)Cl]^+$  and **4a'** < **3a'** <  $[Os(tpy)(bpy)Cl]^+$ ) also parallel those observed experimentally. For ease of discussion, only the calculated vertical transitions with  $\lambda > 400$  nm are summarized in Table 3 (see Table S2 for  $\lambda = 300$ – $400$  nm), and only those with oscillator strength ( $f$ ) > 0.1 within this spectral region would be regarded as the lowest-energy electronic transitions calculated. Table 4 summarizes the compositions of the molecular orbitals (MOs) involved in the lowest-energy electronic transitions of these complexes.

For  $MeC^1\wedge N^{\wedge}C^{1Me}$ -ligated model complexes **1a'**, **3a'**, and **1a'-CH<sub>3</sub>CN**, the calculated lowest-energy dipole allowed transitions mainly originate from HOMO–1  $\rightarrow$  LUMO transitions, whereas those for  $MeC^2\wedge N^{\wedge}C^{2Me}$ -ligated complexes **2a'** and **4a'** are dominated by the HOMO–2  $\rightarrow$  LUMO transitions. However, the nature of the transition is similar in all these complexes in terms of molecular orbital composition: in **1a'**, **3a'**, and **1a'-CH<sub>3</sub>CN**, the HOMO–1 has a greater  $d(M)$  contribution (16.3–18.9%) than that in LUMO (3.2–4.5%), whereas the LUMO has a greater  $N^{\wedge}N$  contribution (36.5–50.7%) than that in HOMO–1 (3.6–5.4%); in **2a'** and **4a'**, HOMO–2 also has a greater  $d(M)$  contribution (18.4–22.4%) than that in the LUMO (2.9–3.4%), and the LUMO has a greater  $N^{\wedge}N$  contribution (26.4–26.5%) than that in HOMO–2 (4.6–6.1%). Thus, the lowest-energy transitions for these  $C^{\wedge}N^{\wedge}C$ -ligated complexes contain  $d(Ru/Os) \rightarrow N^{\wedge}N$  MLCT character, consistent with the spectroscopic assignment deduced experimentally. Moreover, the contribution of  $C^{\wedge}N^{\wedge}C$  to HOMO–1 for **1a'**, **3a'**, and **1a'-CH<sub>3</sub>CN**, HOMO–2 for **2a'** and **4a'**, and LUMO for all of these complexes is significant (44.8–78.9%), thereby indicating that the  $C^{\wedge}N^{\wedge}C$  ligands contribute significantly to both the  $d(Ru/Os)$  and  $\pi^*(N^{\wedge}N)$  levels. It should be pointed out that although the  $d(Ru/Os)$  and  $\pi^*(N^{\wedge}N)$  levels contain considerable  $C^{\wedge}N^{\wedge}C$  contributions, the nature of the



**Figure 3.** Calculated absorption spectra for model complexes **1a'**, **2a'**, **1a'-CH<sub>3</sub>CN**, and **[Ru(tpy)(bpy)Cl]<sup>+</sup>** from TD-DFT (M06 functional)/CPCM calculations. Excitation energies and oscillator strengths are shown by the blue vertical lines; spectra (in black) are convoluted with a Gaussian function having a full width at half-maximum of 0.25 eV. Electronic difference density plots for the marked vertical transitions (\*) are depicted in Figure 4.

concerned transition should be regarded as a net  $d_{\pi}(\text{Ru/Os}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$  charge transfer. The electronic difference density plots for **1a'**, **2a'**, and **1a'-CH<sub>3</sub>CN** in their lowest-energy excited state (Figure 4, generated by taking the difference in the excited-state electron density and ground-state electron density) clearly show that electronic charge is depleted from the  $d_{\pi}(\text{Ru})$  center and accumulated at the  $\pi^*(\text{N}^{\wedge}\text{N})$  moiety. However, the nature of the lowest-energy dipole allowed transitions for **[Ru(tpy)(bpy)Cl]<sup>+</sup>** and **[Os(tpy)(bpy)Cl]<sup>+</sup>** was calculated to be a mixture of vertical transitions involving molecular orbitals around the HOMO–LUMO gap, and these transitions are best described as mainly  $d(\text{Ru/Os}) \rightarrow \pi^*(\text{tpy})$  MLCT in nature with minor  $d(\text{Ru/Os}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$  MLCT character. The electronic difference density plots for **[Ru(tpy)(bpy)Cl]<sup>+</sup>** in its lowest-energy excited-state also illustrate that the electronic charge is depleted from the  $d_{\pi}(\text{Ru})$  center and accumulated at the tpy and bpy ligands (Figure 4).

**Electrochemistry and Spectroelectrochemistry.** Electrochemical data for all complexes are summarized in Table 5. The first oxidation waves for **[Ru(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>)(N<sup>1</sup>N)Cl]<sup>+</sup>** are

about 250 mV more positive than their corresponding Os analogues, signifying the contribution of the metal center to the HOMO, and are assigned as M(II/III) couples. The M(II/III) oxidation couples for **[M(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>)(N<sup>1</sup>N)Cl]<sup>+</sup>** are about 150 mV more cathodic than **[M(C<sup>2</sup>N<sup>1</sup>C<sup>2</sup>)(N<sup>1</sup>N)Cl]<sup>+</sup>**, consistent with the relative donor strength of imidazol-2-ylidene and benzimidazol-2-ylidene discussed in the previous section. The irreversibility of the first reduction processes in some of the **[M(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>)(N<sup>1</sup>N)Cl]<sup>+</sup>** complexes hampers the comparison of the reduction waves.

Thin-layer UV–visible spectroelectrochemistry was employed to acquire the absorption spectra for **1a<sup>-</sup>**, **1a<sup>+</sup>** (Figure 5), **2a<sup>-</sup>**, and **2a<sup>+</sup>** (Figure S5). The isosbestic spectral changes suggest that the electrochemical reductions and oxidations of **1a** and **2a** are clean conversions.<sup>28</sup> Reductions of **1a** and **2a** result in an enhancement of the absorption at ~350 nm and new absorptions at ~500 and ~550 nm. These features are unlikely to originate from anionic C<sup>1</sup>N<sup>1</sup>C<sup>1</sup> radicals (C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>•<sup>-</sup>, cf. spectroscopic changes during the first electrochemical reduction of **[Ru(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>** depicted in Figure S6) but are characteristic absorptions for anionic bpy radicals (bpy•<sup>-</sup>),<sup>29</sup> indicating that the LUMOs of the **[M(C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>)(N<sup>1</sup>N)Cl]<sup>+</sup>** complexes are largely N<sup>1</sup>N-centered. The oxidation of **1a** and **2a** diminishes the  $d_{\pi}(\text{Ru}^{\text{II}}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$  MLCT band, an expected consequence of removing an electron from the  $d_{\pi}(\text{Ru}^{\text{II}})$  orbital.

#### Electron Paramagnetic Resonance Spectroscopy.

Complexes **1a<sup>-</sup>** and **2a<sup>-</sup>** (electrochemically generated one-electron reduced forms of **1a** and **2a**) were characterized by X-band EPR spectroscopy. For spectroscopic comparison, the EPR spectrum of **[Ru([14]aneS4)(bpy)]<sup>+</sup>** (one-electron reduced form of **[Ru([14]aneS4)(bpy)]<sup>2+</sup>**, [14]aneS4 = 1,4,8,11-tetrathiacyclotetradecane) was also acquired. These complexes display essentially identical EPR spectra at 30 K in frozen CH<sub>3</sub>CN solution (Figures 6 and S9), with narrow line widths and a narrow distribution of *g* values that does not differ significantly from that of the free electron (Table 6), features typical of organic-centered unpaired spin. Simulation of the spectra required the inclusion of <sup>101</sup>Ru and <sup>99</sup>Ru superhyperfine coupling ( $I = 5/2$ ), with  $A_{xx} = 0$ ,  $A_{yy} = 10 \times 10^{-4}$ , and  $A_{zz} = 2 \times 10^{-4} \text{ cm}^{-1}$  being used in the case of **1a<sup>-</sup>** and **2a<sup>-</sup>**. Notably, a minor organic radical impurity species was observed in the samples of **1a<sup>-</sup>** and **2a<sup>-</sup>** but was not simulated because of its very low concentration.

The persistence of **1a<sup>-</sup>** in fluid solution (Figure 7,  $g_{\text{iso}} = 1.998$ ) reinforces the notion that the unpaired spin in this system is ligand-centered. In addition to <sup>101</sup>Ru and <sup>99</sup>Ru superhyperfine coupling ( $A_{\text{iso}}\{\text{<sup>101</sup>Ru, <sup>99</sup>Ru}\} = 3.5 \times 10^{-4} \text{ cm}^{-1}$ ), which was also present at 30 K, clearly resolved <sup>14</sup>N superhyperfine coupling to two equivalent N atoms was observed ( $A_{\text{iso}}\{\text{<sup>14</sup>N}\} = 3.9 \times 10^{-4} \text{ cm}^{-1}$ ). Though this does not irrefutably revoke the possibility of a C<sup>1</sup>N<sup>1</sup>C<sup>1</sup>-centered radical, the characteristic bpy•<sup>-</sup> absorption observed for **1a<sup>-</sup>** and **2a<sup>-</sup>**, together with the calculated spin density for model complex **1a<sup>-</sup>** (Figure 8), strongly suggests that the EPR signal originates from a bpy•<sup>-</sup> radical anion. Unfortunately, we were unable to obtain a room-temperature spectrum of **2a<sup>-</sup>** and **[Ru([14]aneS4)(bpy)]<sup>+</sup>**, presumably because of the greater instability of these species. However, the identical nature of the frozen solution EPR spectra of **1a<sup>-</sup>**, **2a<sup>-</sup>**, and **[Ru([14]aneS4)(bpy)]<sup>+</sup>** implies that they have a similar origin (i.e., each of them contains a bpy•<sup>-</sup> radical anion).

Table 3. Calculated Vertical Transition Energies ( $\lambda > 400$  nm) for the Model Complexes from TD-DFT/CPCM Calculations<sup>a</sup>

complex	experimental $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	TD-DFT/CPCM calculations	
		excitation energy/nm (oscillator strength)	composition of the excited-state wave functions <sup>b</sup>
1a'	485 (8600)	483 (0.1703)	0.66 $\Psi_{\text{H} \rightarrow \text{L}}$ + 0.19 $\Psi_{\text{H} \rightarrow \text{L}}$ + 0.13 $\Psi_{\text{H} \rightarrow \text{L}+1}$
		424 (0.0292)	0.62 $\Psi_{\text{H} \rightarrow \text{L}+1}$ - 0.27 $\Psi_{\text{H} \rightarrow \text{L}+3}$
2a'	467 (9940)	471 (0.1871)	0.67 $\Psi_{\text{H} \rightarrow \text{L}}$ + 0.15 $\Psi_{\text{H} \rightarrow \text{L}+1}$ + 0.13 $\Psi_{\text{H} \rightarrow \text{L}}$
		454 (0.0251)	0.64 $\Psi_{\text{H} \rightarrow \text{L}+1}$ + 0.27 $\Psi_{\text{H} \rightarrow \text{L}+1}$
		423 (0.0287)	0.65 $\Psi_{\text{H} \rightarrow \text{L}+1}$ - 0.12 $\Psi_{\text{H} \rightarrow \text{L}+1}$ - 0.12 $\Psi_{\text{H} \rightarrow \text{L}+3}$
1a'-CH <sub>3</sub> CN	444 (7670)	441 (0.1471)	0.69 $\Psi_{\text{H} \rightarrow \text{L}}$ - 0.10 $\Psi_{\text{H} \rightarrow \text{L}+1}$
		[Ru(tpy)(bpy)Cl] <sup>+</sup>	503 (10 690)
3a'	496 (8670)	495 (0.0478)	0.60 $\Psi_{\text{H} \rightarrow \text{L}+2}$ + 0.35 $\Psi_{\text{H} \rightarrow \text{L}+1}$
		499 (0.1891)	0.67 $\Psi_{\text{H} \rightarrow \text{L}}$ + 0.14 $\Psi_{\text{H} \rightarrow \text{L}}$ - 0.11 $\Psi_{\text{H} \rightarrow \text{L}+1}$ + 0.10 $\Psi_{\text{H} \rightarrow \text{L}+4}$
4a'	477 (10 160)	438 (0.0353)	0.62 $\Psi_{\text{H} \rightarrow \text{L}+1}$ + 0.23 $\Psi_{\text{H} \rightarrow \text{L}+3}$ + 0.16 $\Psi_{\text{H} \rightarrow \text{L}+4}$ + 0.12 $\Psi_{\text{H} \rightarrow \text{L}+2}$
		488 (0.2105)	0.68 $\Psi_{\text{H} \rightarrow \text{L}}$ + 0.13 $\Psi_{\text{H} \rightarrow \text{L}+1}$
		469 (0.0329)	0.67 $\Psi_{\text{H} \rightarrow \text{L}+1}$ - 0.18 $\Psi_{\text{H} \rightarrow \text{L}+1}$
[Os(tpy)(bpy)Cl] <sup>+</sup>	515 (10 840)	436 (0.0386)	0.65 $\Psi_{\text{H} \rightarrow \text{L}+1}$ + 0.14 $\Psi_{\text{H} \rightarrow \text{L}+5}$ - 0.11 $\Psi_{\text{H} \rightarrow \text{L}+2}$
		517 (0.0575)	0.65 $\Psi_{\text{H} \rightarrow \text{L}+2}$ + 0.24 $\Psi_{\text{H} \rightarrow \text{L}+1}$
		514 (0.2068)	0.40 $\Psi_{\text{H} \rightarrow \text{L}}$ + 0.33 $\Psi_{\text{H} \rightarrow \text{L}+1}$ - 0.30 $\Psi_{\text{H} \rightarrow \text{L}+2}$ - 0.26 $\Psi_{\text{H} \rightarrow \text{L}+2}$ - 0.24 $\Psi_{\text{H} \rightarrow \text{L}+1}$

<sup>a</sup>Excitations with oscillator strength  $< 2 \times 10^{-2}$  are omitted. <sup>b</sup>The sum of the squares of the CI expansion coefficients is normalized to be 0.5.

**Emission Spectroscopy.** Ruthenium complexes **1** and **2** are emissive with emission maxima at around 600–700 nm upon photoexcitation at their lowest-energy absorption bands, and no emission signals were detected for osmium complexes **3** and **4** within the UV–visible region. The [Ru(C<sup>^</sup>N<sup>^</sup>C)(N<sup>^</sup>N)-L]<sup>+</sup> complexes in this work exhibit quantum yields ( $\Phi$ ) and emission lifetimes ( $\tau$ ) of up to  $10^{-3}$  and  $10^3$  ns, respectively. Figure 9 depicts the excitation and emission spectra for **2a** in CH<sub>3</sub>CN at 298 K. The photophysical parameters (Table 7) are sensitive to the changes in C<sup>^</sup>N<sup>^</sup>C, N<sup>^</sup>N, and L. More specifically, the trends for the emission maxima parallel those for the lowest-energy absorption bands: (1) the emission energies for [Ru(C<sup>2</sup><sup>^</sup>N<sup>^</sup>C<sup>2</sup>)(N<sup>^</sup>N)Cl]<sup>+</sup> are higher than the corresponding [Ru(C<sup>1</sup><sup>^</sup>N<sup>^</sup>C<sup>1</sup>)(N<sup>^</sup>N)Cl]<sup>+</sup> analogues; (2) the emission wavelengths for [Ru(C<sup>^</sup>N<sup>^</sup>C)(N<sup>^</sup>N)Cl]<sup>+</sup> are in the order **b** > **a** > **c**; and (3) the emission energies for [Ru(C<sup>1</sup><sup>^</sup>N<sup>^</sup>C<sup>1</sup>)(N<sup>^</sup>N)L]<sup>+</sup> are in the order **1a-f-BuNC** > **1a-CH<sub>3</sub>CN**. These findings, together with the resemblance of the excitation profiles to the absorption spectra, signify that the emissions originate from the energy dissipation of the  $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$  MLCT transitions.

## CONCLUSIONS

Utilizing NHC-derived ligands to manipulate the photophysical properties of transition-metal complexes has become a topic of intense research recently. In this work, Ru(II) and Os(II) complexes bearing C<sup>^</sup>N<sup>^</sup>C pincer and bipyridine-type ligands have been prepared. This joint experimental and theoretical investigation reveals that the lowest-energy electronic transition associated with the complexes originates from a  $d_{\pi}(\text{Ru}^{\text{II}}/\text{Os}^{\text{II}}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$  MLCT transition rather than a  $d_{\pi}(\text{Ru}^{\text{II}}/\text{Os}^{\text{II}}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})$  MLCT transition, although the C<sup>^</sup>N<sup>^</sup>C ligands contribute significantly to the frontier orbitals. This is in stark contrast to [Ru(tpy)(bpy)Cl]<sup>+</sup> and [Os(tpy)(bpy)Cl]<sup>+</sup>, for which the lowest-energy transitions are always assigned as  $d_{\pi}(\text{Ru}^{\text{II}}/\text{Os}^{\text{II}}) \rightarrow \pi^*(\text{tpy})$  MLCT transitions. Even though the emission properties for the Ru–NHC complexes in this work are not as good as for the functionalized terpyridine–Ru complexes reported by Hammarström and co-workers ( $\Phi$  up to

$7 \times 10^{-2}$ ,  $\tau$  up to 5.5  $\mu\text{s}$ ),<sup>30</sup> the [M(C<sup>^</sup>N<sup>^</sup>C)(N<sup>^</sup>N)L]<sup>+</sup> system may allow for the generation of highly reactive M–L bonded species (singly or multiply bonded), and work is in progress in this direction.

## EXPERIMENTAL SECTION

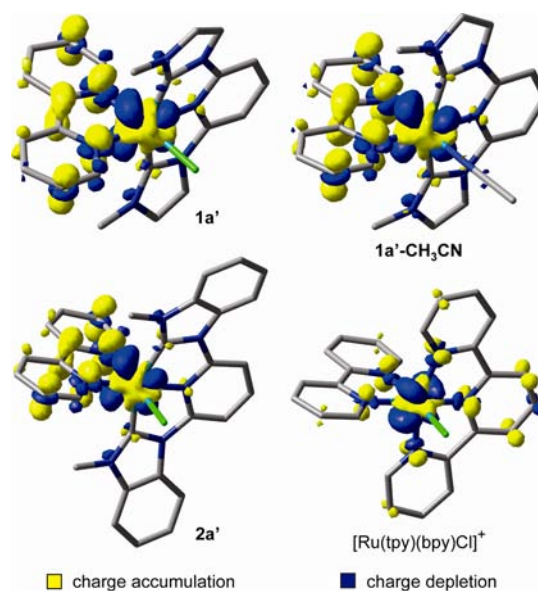
**General Procedure.** All reactions were performed under an argon atmosphere using standard Schlenk techniques, unless otherwise stated. All reagents and solvents were used as received. The C<sup>^</sup>N<sup>^</sup>C ligand precursors (i.e., pyridine-bridged bisimidazolium or bisbenzimidazolium hexafluorophosphate,<sup>31</sup> [Ru(N<sup>^</sup>N)Cl]<sub>2</sub>,<sup>32</sup> [M(tpy)(bpy)Cl]<sup>+</sup> (M = Ru and Os),<sup>33</sup> [Ru(C<sup>1</sup><sup>^</sup>N<sup>^</sup>C<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>,<sup>23b</sup> and [Ru([14]-aneS4)(bpy)](PF<sub>6</sub>)<sub>2</sub><sup>34</sup>) were prepared according to literature methods. [Os(N<sup>^</sup>N)Cl]<sub>2</sub> was synthesized by a modified procedure of Buckingham et al.<sup>22,35</sup> <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, DEPT-135, <sup>1</sup>H–<sup>1</sup>H COSY, and <sup>1</sup>H–<sup>13</sup>C HSQC NMR spectra were recorded on a Bruker 400 DRX FT-NMR spectrometer. Peak positions were calibrated using solvent residue peaks as an internal standard. Electrospray mass spectrometry was performed on a PE-SCIEX API 3000 triple quadrupole mass spectrometer. Infrared spectra were recorded as KBr plates on an Avatar 360 FTIR spectrometer. UV–visible spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analyses were carried out on an Elementar Vario Micro Cube carbon–hydrogen–nitrogen elemental microanalyzer. Cyclic voltammetry was performed with a CH Instruments model 600C series electrochemical analyzer/workstation. All of the electrochemical measurements were performed in CH<sub>3</sub>CN solution with [Bu<sub>4</sub>N]PF<sub>6</sub> (0.1 M) as a supporting electrolyte at room temperature. The glassy-carbon working electrode was polished with 0.05  $\mu\text{m}$  alumina on a microcloth, sonicated for 5 min in deionized water, and rinsed with CH<sub>3</sub>CN before use. An Ag/AgNO<sub>3</sub> (0.1 M in CH<sub>3</sub>CN) electrode was used as a reference electrode with a platinum wire as the counter electrode. All solutions were degassed with nitrogen before experiments. The  $E_{1/2}$  value of the ferrocenium/ferrocene couple (Cp<sub>2</sub>Fe<sup>+/0</sup>) measured in the same solution was used as an internal reference. Steady-state emission spectra were obtained on a Jobin Yvon Fluorolog-3-TCSPC spectrophotometer. Sample and standard solutions were degassed with at least three freeze–pump–thaw cycles. The emission quantum yields were measured by the method of Demas and Crosby<sup>36</sup> with [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in degassed CH<sub>3</sub>CN as the standard ( $\Phi_{\text{r}} = 0.062$ ) and calculated with  $\Phi_{\text{s}} = \Phi_{\text{r}}(B_{\text{r}}/B_{\text{s}})(n_{\text{s}}/n_{\text{r}})^2(D_{\text{s}}/D_{\text{r}})$ , where subscripts *s* and *r* refer to sample and reference standard solutions, respectively, *n*

**Table 4.** Selected Molecular Orbital Compositions (%) for the Model Complexes from the TD-DFT/CPCM Calculations

complex	MO	% composition				
		M(s, p)	M(d)	N^N	C^N^C/ tpy	L
1a'	HOMO-2	2.55	10.93	52.61	31.35	2.56
	HOMO-1	1.47	18.06	4.58	75.87	0.02
	HOMO	9.05	31.07	3.22	50.20	6.45
	LUMO	1.20	3.57	38.52	56.64	0.07
2a'	LUMO+1	11.18	0.76	52.43	28.05	7.58
	HOMO-2	0.75	18.37	4.64	76.15	0.09
	HOMO-1	3.45	11.18	56.66	25.72	2.99
	HOMO	4.92	19.98	2.02	68.70	4.38
1a'-CH <sub>3</sub> CN	LUMO	1.09	2.86	26.51	69.49	0.04
	LUMO+1	8.26	0.39	41.81	44.38	5.16
	HOMO-2	11.51	29.30	35.90	18.36	4.93
	HOMO-1	0.84	16.32	3.60	78.88	0.36
[Ru(tpy)(bpy)Cl] <sup>+</sup>	HOMO	0.85	27.13	2.62	67.52	1.88
	LUMO	1.25	3.18	50.69	44.78	0.10
	LUMO+1	2.49	1.09	64.91	25.96	5.55
	HOMO-2	0.65	38.06	6.24	54.92	0.13
[Ru(tpy)(bpy)Cl] <sup>+</sup>	HOMO-1	3.39	15.78	63.21	13.87	3.75
	HOMO	4.61	52.92	4.98	26.62	10.87
	LUMO	6.45	1.82	61.47	28.91	1.35
	LUMO+1	0.51	2.3	37.80	59.27	0.13
3a'	LUMO+2	0.06	3.22	18.28	78.29	0.15
	HOMO-2	4.88	8.24	62.54	22.77	1.57
	HOMO-1	2.72	18.93	5.37	72.96	0.02
	HOMO	4.75	30.90	3.00	56.16	5.19
4a'	LUMO	1.15	4.51	36.47	57.77	0.09
	LUMO+1	9.17	1.03	63.76	21.06	4.97
	HOMO-2	2.44	22.35	6.06	68.62	0.52
	HOMO-1	13.58	9.43	46.25	28.23	2.51
[Os(tpy)(bpy)Cl] <sup>+</sup>	HOMO	3.12	19.43	2.06	72.37	3.01
	LUMO	0.68	3.36	26.42	69.48	0.05
	LUMO+1	6.33	0.67	53.63	35.61	3.76
	HOMO-2	2.21	36.25	6.52	54.90	0.11
[Os(tpy)(bpy)Cl] <sup>+</sup>	HOMO-1	2.60	21.09	57.68	14.62	4.01
	HOMO	2.55	52.22	4.94	31.99	8.29
	LUMO	4.68	3.87	54.71	35.26	1.48
	LUMO+1	0.35	3.46	37.06	58.98	0.14
[Os(tpy)(bpy)Cl] <sup>+</sup>	LUMO+2	0.13	4.89	16.13	78.62	0.22

is the refractive index of the solvents,  $D$  is the integrated intensity, and  $\Phi$  is the luminescence quantum yield. Quantity  $B$  is calculated from  $B = 1 - 10^{-AL}$ , where  $A$  is the absorbance at the excitation wavelength and  $L$  is the optical path length.

**[M(C^N^C)(N^N)Cl](PF<sub>6</sub>), 1-4(PF<sub>6</sub>).** A mixture of [M(N^N)Cl<sub>4</sub>] (M = Ru or Os, 0.75 mmol) and pyridine-bridged bisimidazolium or bisbenzimidazolium hexafluorophosphate (0.83 mmol) was refluxed in ethylene glycol (5 mL) under argon for 1.5 h. Upon cooling to room temperature, the mixture was added to an aqueous NH<sub>4</sub>PF<sub>6</sub> solution (5 mL), and the precipitate was filtered and washed with water (2 × 5 mL). The precipitate was then refluxed with zinc granules (1.0 mmol) in EtOH (50 mL) under argon for 1 h. Upon cooling to room temperature, the solvent was removed to afford a solid (brownish red for M = Ru; dark brown for M = Os). The crude product was purified by column chromatography (basic alumina, gradual elution with CH<sub>3</sub>CN/toluene (from 1:8 to 1:2 v/v) as the eluent) as an orange band for M = Ru and a brown band for M = Os, respectively. After the removal of the solvent, the solid was recrystallized by the slow

**Figure 4.** Electronic difference density plots for 1a', 2a', 1a'-CH<sub>3</sub>CN, and [Ru(tpy)(bpy)Cl]<sup>+</sup> of the lowest-energy excited states (corresponding to the vertical transitions marked with \* in Figure 3; isodensity value = 0.003 au).**Table 5.** Electrochemical Data<sup>a</sup>

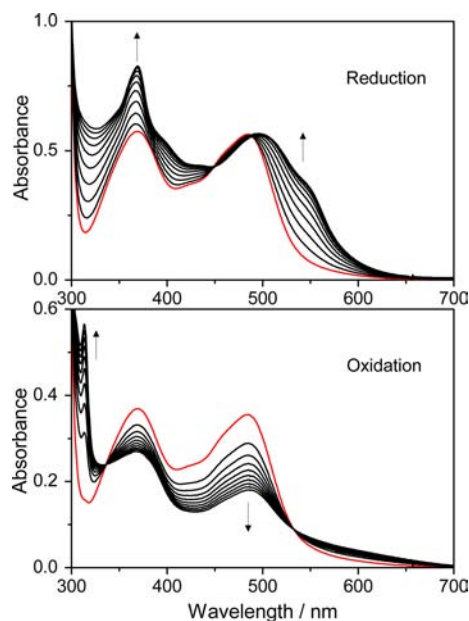
complex	$E_{1/2}/V$ vs Cp <sub>2</sub> Fe <sup>+0/b</sup>	
	[M(II)L]/M(II)L <sup>*-</sup>	[M(III)]/M(II)
1a	-2.06 <sup>c</sup>	+0.25
1b	-1.94	+0.24
1c	-2.02	+0.20
1d	-2.05 <sup>d</sup>	+0.24
2a	-1.98 <sup>c</sup>	+0.41
2b	-1.87	+0.39
2c	-1.96	+0.35
2d	-1.91	+0.39
3a	-1.99	+0.01
3b	-1.92	-0.01
4a	-1.91	+0.16
4b	-1.85	+0.14
1a-CH <sub>3</sub> CN	-1.89	+0.74
1a- <i>t</i> -BuNC	-1.84	+0.93
[Ru(tpy)(bpy)Cl] <sup>+</sup>	-1.87 <sup>d</sup>	+0.40
[Os(tpy)(bpy)Cl] <sup>+</sup>	-1.88 <sup>d</sup>	+0.06
[Ru(C <sup>1</sup> ^N^C <sup>1</sup> ) <sub>2</sub> ] <sup>2+</sup>	-2.37 <sup>d</sup>	+0.76

<sup>a</sup>Supporting electrolyte: 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>3</sub>CN. <sup>b</sup> $E_{1/2} = (E_{pc} + E_{pa})/2$  at 298 K for reversible couples. <sup>c</sup>Quasi-reversible; the recorded potential is the cathodic peak potential at a scan rate of 100 mV s<sup>-1</sup>. <sup>d</sup>Irreversible; the recorded potential is the cathodic peak potential at scan rate of 100 mV s<sup>-1</sup>.

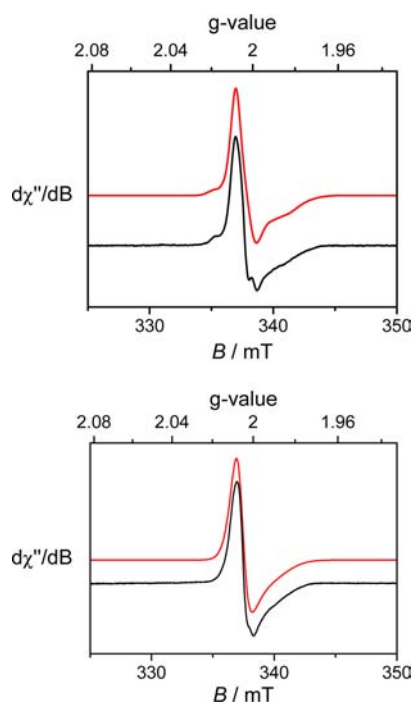
diffusion of Et<sub>2</sub>O into CH<sub>3</sub>CN or CH<sub>3</sub>NO<sub>2</sub> solution to give red crystals for M = Ru and dark-brown crystals for M = Os, respectively.

**[Ru(C<sup>1</sup>^N^C<sup>1</sup>)(bpy)(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>2</sub>, 1a-CH<sub>3</sub>CN(PF<sub>6</sub>)<sub>2</sub>.** A mixture of 1a(PF<sub>6</sub>) (0.10 mmol) and AgPF<sub>6</sub> (0.10 mmol) in CH<sub>3</sub>CN (25 mL) was refluxed under argon for 3 h. Upon cooling to room temperature, the resultant mixture was filtered and the filtrate was evaporated in vacuo. The resulting orange residue was recrystallized by the slow diffusion of Et<sub>2</sub>O into CH<sub>3</sub>CN solution to give orange crystals.

**[Ru(C<sup>1</sup>^N^C<sup>1</sup>)(bpy)(*t*-BuNC)](PF<sub>6</sub>)<sub>2</sub>, 1a-*t*-BuNC(PF<sub>6</sub>)<sub>2</sub>.** 1a(PF<sub>6</sub>) (0.08 mmol) was refluxed with AgNO<sub>3</sub> (0.08 mmol) in an acetone/H<sub>2</sub>O mixture (3:1 v/v, 20 mL) under argon for 3 h. The resultant solution was filtered into an aqueous NH<sub>4</sub>PF<sub>6</sub> solution (5 mL), and



**Figure 5.** UV–visible absorption spectroscopy changes during the first electrochemical reduction (top, at  $-2.25$  V vs  $\text{Cp}_2\text{Fe}^{+/0}$ ) and oxidation (bottom, at  $+0.40$  V vs  $\text{Cp}_2\text{Fe}^{+/0}$ ) of **1a** in  $\text{CH}_3\text{CN}$  solution containing  $0.1$  M  $[\text{Bu}_4\text{N}]\text{PF}_6$  at  $298$  K (spectra recorded at  $10$  s intervals; initial traces shown in red).



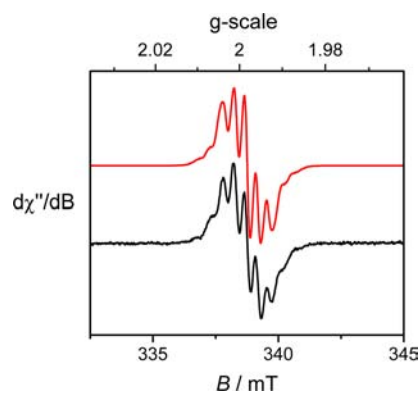
**Figure 6.** Perpendicular-mode X-band EPR spectra (black lines) and spectral simulations (red lines) of **1a<sup>-</sup>** (top) and  $[\text{Ru}([\text{14}]\text{aneS4})(\text{bpy})]^+$  (bottom) recorded in  $\text{CH}_3\text{CN}$  solution containing  $0.2$  M  $[\text{Bu}_4\text{N}]\text{PF}_6$  at  $30$  K. Conditions: frequency,  $9.47$  GHz; power,  $0.05$  mW for **1a<sup>-</sup>** and  $0.01$  mW for  $[\text{Ru}([\text{14}]\text{aneS4})(\text{bpy})]^+$ ; and modulation,  $0.2$  mT. Simulations were performed using a combination of the parameters listed in Table 6 and those detailed in the text.

the solvent was removed in vacuo to give a red solid. This red solid was then reflux with *tert*-butylisocyanide (*t*-BuNC) ( $0.44$  mmol) in methanol ( $15$  mL) under argon for  $18$  h. Upon cooling to room temperature, an aqueous  $\text{NH}_4\text{PF}_6$  solution ( $5$  mL) was added to the

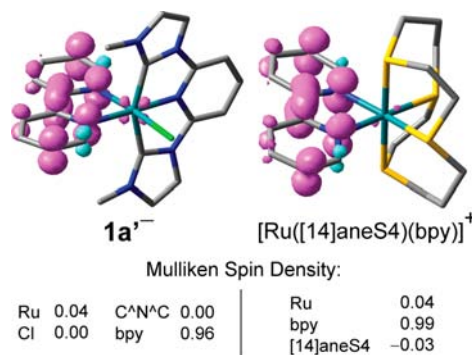
**Table 6.** Anisotropic  $g$  Values for **1a<sup>-</sup>**, **2a<sup>-</sup>**, and  $[\text{Ru}([\text{14}]\text{aneS4})(\text{bpy})]^+$  Obtained by the Simulation of Frozen Solution ( $30$  K) Spectra

complex	$g_{xx}$	$g_{yy}$	$g_{zz}$	$\langle g \rangle^a$	$\Delta g^b$
<b>1a<sup>-</sup></b>	2.008	2.001	1.987	1.999	0.021
<b>2a<sup>-</sup></b>	2.008	2.001	1.987	1.998	0.021
$[\text{Ru}([\text{14}]\text{aneS4})(\text{bpy})]^+$	2.006	2.006	1.991	2.001	0.015

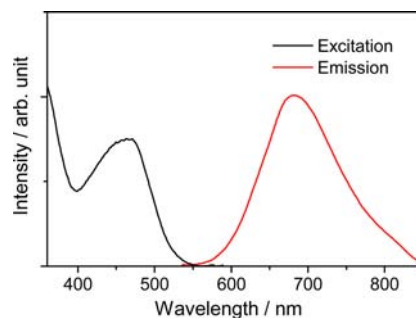
<sup>a</sup> $\langle g \rangle = 1/3(g_{xx} + g_{yy} + g_{zz})$ . <sup>b</sup>Anisotropy,  $\Delta g = g_{xx} - g_{zz}$ .



**Figure 7.** Perpendicular-mode X-band EPR spectrum (black line) and spectral simulation (red line) of **1a<sup>-</sup>** recorded in  $\text{CH}_3\text{CN}$  solution containing  $0.2$  M  $[\text{Bu}_4\text{N}]\text{PF}_6$  at room temperature. Conditions: frequency,  $9.47$  GHz; power,  $1.00$  mW; and modulation,  $0.2$  mT. Simulations were performed using the parameters detailed in the text.



**Figure 8.** Mulliken spin-density distribution in **1a<sup>-</sup>** and  $[\text{Ru}([\text{14}]\text{aneS4})(\text{bpy})]^+$  (surface isovalue =  $0.005$  au) from DFT/CPCM calculations. Positive and negative spin densities are shown in pink and cyan, respectively.



**Figure 9.** Excitation and emission spectra for complex **2a** in  $\text{CH}_3\text{CN}$  solution at  $298$  K.

resultant solution, and the resultant yellow precipitates were filtered and then washed with  $\text{H}_2\text{O}$  ( $2 \times 5$  mL) and  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL). The



**Table 7. Emission Data for the Complexes in Solution at 298 K<sup>a,b</sup>**

complex	$\lambda_{em}/nm$	quantum yield ( $\Phi$ )	lifetime ( $\tau$ )/ns
Solvent = CH <sub>3</sub> CN			
1a	c	c	c
1b	c	c	c
1c	709	c	10
1d	714	$1.36 \times 10^{-4}$	38
2a	694	$1.66 \times 10^{-4}$	39
2b	704	$2.23 \times 10^{-4}$	41
2c	680	$2.39 \times 10^{-4}$	26
2d	681	$4.85 \times 10^{-4}$	88
1a-CH <sub>3</sub> CN	626	$2.98 \times 10^{-3}$	324
1a- <i>t</i> -BuNC	598	$2.31 \times 10^{-4}$	45
Solvent = CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>			
1b	721	$2.18 \times 10^{-4}$	21
2b	699	$4.81 \times 10^{-4}$	53
1a- <i>t</i> -BuNC	595	$1.41 \times 10^{-4}$	17

<sup>a</sup>Concentration:  $3 \times 10^{-5}$  M. <sup>b</sup> $\lambda_{ex} = 450$  nm. <sup>c</sup>The emission signal is too weak to be processed. <sup>d</sup>Only complexes with good solubility in CH<sub>2</sub>Cl<sub>2</sub> were measured.

crude products were recrystallized by the slow diffusion of Et<sub>2</sub>O into CH<sub>3</sub>CN solution to give yellow crystals.

**Complex 1a(PF<sub>6</sub>) (M = Ru, C<sup>1</sup>ANAC<sup>1</sup>, N<sup>AN</sup> = bpy).** Yield 0.38 g, 67.1%. Anal. Calcd for C<sub>29</sub>H<sub>33</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 45.77; H, 4.37; N, 12.88. Found: C, 43.56; H, 4.31; N, 11.93. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  0.61–0.78 (m, 10H, Bu), 0.89–1.00 (m, 2H, Bu), 1.26–1.37 (m, 2H, Bu), 3.20–3.34 (m, 4H, Bu), 6.88–6.92 (m, 1H, H<sub>c</sub>), 7.10 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.32–7.34 (m, 1H, H<sub>d</sub>), 7.64–7.72 (m, 4H, H<sub>b</sub> + H<sub>j</sub> + H<sub>f</sub>), 7.93 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 8.01–8.07 (m, 2H, H<sub>e</sub> + H<sub>i</sub>), 8.23 (d,  $J = 8.4$  Hz, 1H, H<sub>e</sub>), 8.44 (d,  $J = 8.4$  Hz, 1H, H<sub>b</sub>), 10.25–10.27 (m, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN):  $\delta$  13.77, 20.24, 34.68, 50.64 (Bu), 106.47 (C<sub>j</sub>), 118.08 (C<sub>k</sub>/C<sub>l</sub>), 123.54 (C<sub>k</sub>/C<sub>l</sub>), 123.66 (C<sub>e</sub>), 123.95 (C<sub>b</sub>), 126.20 (C<sub>c</sub>), 126.60 (C<sub>b</sub>/C<sub>f</sub>), 135.03 (C<sub>b</sub>/C<sub>f</sub>), 135.25 (C<sub>g</sub>), 139.04 (C<sub>i</sub>), 153.03 (C<sub>a</sub>), 153.05 (C<sub>d</sub>), 155.99, 156.82, 158.22 (quaternary carbons), 196.09 (Ru–C<sub>NHC</sub>). ESI-MS:  $m/z$  616.4 [M<sup>+</sup>].

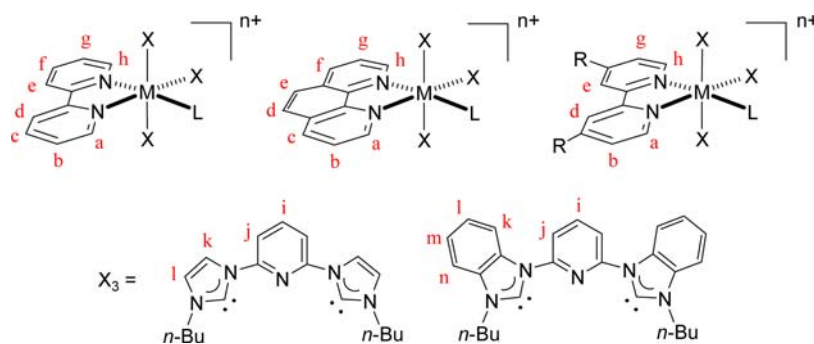
**Complex 1b(PF<sub>6</sub>) (M = Ru, C<sup>1</sup>ANAC<sup>1</sup>, N<sup>AN</sup> = Ph<sub>2</sub>bpy).** Yield 0.30 g, 44.3%. Anal. Calcd for C<sub>41</sub>H<sub>41</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 53.92; H, 4.53; N, 10.74. Found: C, 52.65; H, 4.57; N, 9.50. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  0.60–0.82 (m, 10H, Bu), 0.95–1.13 (m, 2H, Bu), 1.33–1.43 (m, 2H, Bu), 3.29–3.43 (m, 4H, Bu), 7.13 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.19 (dd,  $J = 6.0, 2.0$  Hz, 1H, H<sub>g</sub>), 7.38 (d,  $J = 6.2$  Hz, 1H, H<sub>b</sub>), 7.47–7.53 (m, 3H on Ph), 7.57–7.60 (m, 1H on Ph), 7.63–7.67 (m, 2H on Ph), 7.72 (d,  $J = 8.4$  Hz, 2H, H<sub>i</sub>), 7.75–7.77 (m, 2H on Ph), 7.96 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 8.00–8.08 (m, 4H, H<sub>b</sub> + H<sub>j</sub> + 2H on Ph), 8.67 (d,  $J = 2.0$  Hz, 1H, H<sub>e</sub>), 8.87 (d,  $J = 2.0$  Hz, 1H, H<sub>d</sub>), 10.29 (d,  $J = 6.2$  Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN):  $\delta$  13.79, 20.32, 34.76, 50.75 (Bu), 106.55 (C<sub>j</sub>), 118.11 (C<sub>k</sub>/C<sub>l</sub>), 121.38

(C<sub>e</sub>), 121.70 (C<sub>d</sub>), 123.77 (C<sub>g</sub> + C<sub>k</sub>/C<sub>l</sub>), 124.23 (C<sub>b</sub>), 128.07, 128.14, 130.19, 130.43 (eight carbons on Ph, resolved with the <sup>1</sup>H–<sup>13</sup>C HSQC NMR experiment), 130.79, 130.83 (two carbons on Ph), 137.07, 137.69 (quaternary carbons), 139.11 (C<sub>i</sub>), 147.06, 147.12 (quaternary carbons), 153.09 (C<sub>a</sub>), 153.11 (C<sub>h</sub>), 155.55, 157.35, 158.74 (quaternary carbons), 196.05 (Ru–C<sub>NHC</sub>). ESI-MS:  $m/z$  768.5 [M<sup>+</sup>].

**Complex 1c(PF<sub>6</sub>) (M = Ru, C<sup>1</sup>ANAC<sup>1</sup>, N<sup>AN</sup> = Me<sub>2</sub>bpy).** Yield 0.34 g, 57.7%. Anal. Calcd for C<sub>31</sub>H<sub>37</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 47.18; H, 4.73; N, 12.42. Found: C, 46.32; H, 4.31; N, 11.73. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  0.62–0.83 (m, 10H, Bu), 0.89–0.99 (m, 2H, Bu), 1.27–1.38 (m, 2H, Bu), 2.32 (s, 3H, Me on Me<sub>2</sub>bpy), 2.61 (s, 3H, Me on Me<sub>2</sub>bpy); 3.23–3.36 (m, 4H, Bu); 6.28–6.75 (m, 1H, H<sub>g</sub>), 7.08–7.10 (m, 3H, H<sub>h</sub> + H<sub>k</sub>/H<sub>l</sub>), 7.53–7.55 (m, 1H, H<sub>b</sub>), 7.66 (d,  $J = 8.4$  Hz, 2H, H<sub>i</sub>), 7.92 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.99 (t,  $J = 8.2$  Hz, 1H, H<sub>j</sub>), 8.10 (s, 1H, H<sub>e</sub>), 8.30 (s, 1H, H<sub>d</sub>), 10.03 (d,  $J = 6.0$  Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN):  $\delta$  13.74, 20.29, 34.74, 50.61 (Bu), 20.80, 21.10 (Me on Me<sub>2</sub>bpy), 106.28 (C<sub>j</sub>), 117.99 (C<sub>k</sub>/C<sub>l</sub>), 123.59 (C<sub>k</sub>/C<sub>l</sub>), 124.21 (C<sub>e</sub>), 124.45 (C<sub>d</sub>), 127.13 (C<sub>e</sub>), 127.58 (C<sub>b</sub>), 138.53 (C<sub>i</sub>), 147.37, 147.46 (quaternary carbons), 152.10 (C<sub>h</sub>), 152.24 (C<sub>a</sub>), 155.80, 156.44, 157.75 (quaternary carbons), 196.63 (Ru–C<sub>NHC</sub>). ESI-MS:  $m/z$  644.4 [M<sup>+</sup>].

**Complex 1d(PF<sub>6</sub>) (M = Ru, C<sup>1</sup>ANAC<sup>1</sup>, N<sup>AN</sup> = phen).** Yield 0.36 g, 61.1%. Anal. Calcd for C<sub>31</sub>H<sub>33</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 47.42; H, 4.24; N, 12.49. Found: C, 46.34; H, 3.91; N, 11.78. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  0.23–0.44 (m, 12H, Bu), 0.99–1.08 (m, 2H, Bu), 3.02–3.09 (m, 4H, Bu), 7.03 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.27 (dd,  $J = 8.0, 5.6$  Hz, 1H, H<sub>g</sub>), 7.70 (dd,  $J = 5.2, 1.2$  Hz, 1H, H<sub>f</sub>), 7.73 (d,  $J = 8.0$  Hz, 2H, H<sub>i</sub>), 7.94 (d,  $J = 2.0$  Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 8.04–8.10 (m, 3H, H<sub>b</sub> + H<sub>d</sub>/H<sub>e</sub> + H<sub>j</sub>), 8.19 (d,  $J = 8.8$  Hz, 1H, H<sub>d</sub>/H<sub>e</sub>), 8.22 (dd,  $J = 8.0, 0.8$  Hz, 1H, H<sub>b</sub>), 8.61 (dd,  $J = 8.0, 1.2$  Hz, 1H, H<sub>c</sub>), 10.46 (dd,  $J = 5.2, 1.2$  Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN):  $\delta$  13.55, 19.93, 34.52, 50.53 (Bu), 106.50 (C<sub>j</sub>), 118.10 (C<sub>k</sub>/C<sub>l</sub>), 123.59 (C<sub>k</sub>/C<sub>l</sub>), 125.21 (C<sub>g</sub>), 125.86 (C<sub>b</sub>), 128.19 (C<sub>d</sub>/C<sub>e</sub>), 128.49 (C<sub>d</sub>/C<sub>e</sub>), 130.97, 131.58 (quaternary carbons), 133.95 (C<sub>h</sub>), 134.08 (C<sub>c</sub>), 139.07 (C<sub>i</sub>), 148.37, 148.93 (quaternary carbons), 153.36 (C<sub>a</sub>), 153.45 (C<sub>f</sub>), 155.85 (quaternary carbon), 196.22 (Ru–C<sub>NHC</sub>). ESI-MS:  $m/z$  640.3 [M<sup>+</sup>].

**Complex 2a(PF<sub>6</sub>) (M = Ru, C<sup>2</sup>ANAC<sup>2</sup>, N<sup>AN</sup> = bpy).** Yield 0.34 g, 53.1%. Anal. Calcd for C<sub>37</sub>H<sub>37</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 51.60; H, 4.33; N, 11.38. Found: C, 50.79; H, 4.19; N, 11.53. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  0.71–1.03 (m, 12H, Bu), 1.44–1.55 (m, 2H, Bu), 3.40–3.50 (m, 2H, Bu), 3.64–3.71 (m, 2H, Bu), 6.86–6.89 (m, 1H, H<sub>f</sub>), 7.39 (d,  $J = 5.6$  Hz, 1H, H<sub>e</sub>), 7.43–7.52 (m, 6H, H<sub>k</sub>/H<sub>l</sub>/H<sub>m</sub>/H<sub>n</sub>), 7.66–7.70 (m, 1H, H<sub>g</sub>), 7.80–7.84 (m, 1H, H<sub>b</sub>), 8.14–8.19 (m, 1H, H<sub>c</sub>), 8.22–8.25 (m, 5H, H<sub>i</sub> + H<sub>j</sub> + H<sub>k</sub>/H<sub>l</sub>/H<sub>m</sub>/H<sub>n</sub>), 8.29 (d,  $J = 8.0$  Hz, 1H, H<sub>b</sub>), 8.54 (d,  $J = 8.4$  Hz, 1H, H<sub>d</sub>), 10.31 (d,  $J = 5.6$  Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN):  $\delta$  13.91, 20.58, 33.62, 48.11 (Bu), 107.85 (C<sub>j</sub>), 111.98 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 112.78 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 123.76 (C<sub>h</sub>), 124.34 (C<sub>d</sub>), 125.10 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 125.51 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 126.50 (C<sub>i</sub>), 127.19 (C<sub>b</sub>), 132.73 (quaternary carbon), 135.96 (C<sub>g</sub>), 136.16 (C<sub>c</sub>), 136.35 (quaternary carbon), 139.54 (C<sub>i</sub>), 153.22 (C<sub>a</sub>),

**Scheme 3. Labeling Scheme for H and C Atoms in 1–4**

153.42 (C<sub>e</sub>), 156.03, 156.97, 157.76 (quaternary carbons), 207.08 (Ru–C<sub>NHC</sub>). ESI-MS: *m/z* 716.4 [M<sup>+</sup>].

**Complex 2b(PF<sub>6</sub>) (M = Ru, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>2</sup>∧N<sup>∧</sup>C<sup>2</sup>, N<sup>∧</sup>N = Ph<sub>2</sub>bpy).** Yield 0.33 g, 43.5%. Anal. Calcd for C<sub>49</sub>H<sub>45</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 58.07; H, 4.48; N, 9.67. Found: C, 56.96; H, 3.90; N, 9.21. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.68–0.96 (m, 10H, Bu), 1.00–1.11 (m, 2H, Bu), 1.50–1.62 (m, 2H, Bu), 3.55–3.77 (m, 4H, Bu), 7.16 (dd, *J* = 6.2, 1.8 Hz, 1H, H<sub>g</sub>), 7.42 (m, 1H, H<sub>h</sub>), 7.45–7.52 (m, 9H, H<sub>k</sub>/H<sub>n</sub> + H<sub>i</sub>/H<sub>m</sub> + 5H on Ph), 7.60–7.73 (m, 5H, H<sub>i</sub>/H<sub>m</sub> + 3H on Ph), 8.06–8.08 (m, 2H on Ph), 8.12 (dd, *J* = 6.0, 1.8 Hz, 1H, H<sub>b</sub>), 8.22–8.25 (m, 5H, H<sub>i</sub> + H<sub>j</sub> + H<sub>k</sub>/H<sub>n</sub>), 8.72 (d, *J* = 2.0 Hz, 1H, H<sub>c</sub>), 8.96 (d, *J* = 2 Hz, 1H, H<sub>d</sub>), 10.35 (d, *J* = 6.2 Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.93, 20.66, 33.68, 48.23 (Bu), 107.91 (C<sub>i</sub>), 111.99 (C<sub>k</sub>/C<sub>n</sub>), 112.78 (C<sub>k</sub>/C<sub>n</sub>), 121.58 (C<sub>e</sub>), 122.07 (C<sub>d</sub>), 124.02 (C<sub>g</sub>), 124.76 (C<sub>f</sub>), 125.11 (C<sub>m</sub>/C<sub>l</sub>), 125.52 (two carbons on Ph, resolved with the <sup>1</sup>H–<sup>13</sup>C HSQC NMR experiment), 128.10 (C<sub>m</sub>/C<sub>l</sub>), 128.25 (two carbons on Ph, resolved with the <sup>1</sup>H–<sup>13</sup>C HSQC NMR experiment), 130.17, 130.50 (four carbons on Ph, resolved with the <sup>1</sup>H–<sup>13</sup>C HSQC NMR experiment), 130.91, 131.06 (two carbons on Ph), 132.72, 136.39, 136.85, 137.53 (quaternary carbons), 139.59 (C<sub>i</sub>), 147.96, 148.01 (quaternary carbons), 153.25 (C<sub>a</sub>), 153.45 (C<sub>h</sub>), 155.98, 157.51, 158.26 (quaternary carbons), 207.03 (Ru–C<sub>NHC</sub>). ESI-MS: *m/z* 868.5 [M<sup>+</sup>].

**Complex 2c(PF<sub>6</sub>) (M = Ru, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>2</sup>∧N<sup>∧</sup>C<sup>2</sup>, N<sup>∧</sup>N = Me<sub>2</sub>bpy).** Yield 0.36 g, 54.4%. Anal. Calcd for C<sub>39</sub>H<sub>41</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 52.67; H, 4.65; N, 11.03. Found: C, 51.78; H, 4.31; N, 10.50. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.72–1.01 (m, 12H, Bu), 1.48–1.56 (m, 2H, Bu), 2.29 (s, 3H, Me on Me<sub>2</sub>bpy), 2.68 (s, 3H, Me on Me<sub>2</sub>bpy); 3.49–3.74 (m, 4H, Bu); 6.70 (dd, *J* = 6.0, 1.2 Hz, 1H, H<sub>g</sub>), 7.12 (d, *J* = 6.0 Hz, 1H, H<sub>h</sub>), 7.42–7.51 (m, 6H, H<sub>i</sub> + 4H of H<sub>k</sub>/H<sub>l</sub>/H<sub>m</sub>/H<sub>n</sub>), 7.67 (dd, *J* = 6.0, 1.2 Hz, 1H, H<sub>b</sub>), 8.09–8.21 (m, 6H, H<sub>d</sub>/H<sub>e</sub> + H<sub>i</sub> + 4H of H<sub>k</sub>/H<sub>l</sub>/H<sub>m</sub>/H<sub>n</sub>), 8.40 (s, 1H, H<sub>d</sub>/H<sub>e</sub>), 10.10 (d, *J* = 6.0 Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.88, 20.62, 33.64, 48.08 (Bu), 20.82, 21.19 (Me on Me<sub>2</sub>bpy), 107.70 (C<sub>i</sub>), 111.90 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 112.72 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 124.45 (C<sub>e</sub>), 124.84 (C<sub>d</sub>), 124.99 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 125.44 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 127.38 (C<sub>g</sub>), 128.13 (C<sub>b</sub>), 132.75, 136.38 (quaternary carbons), 139.09 (C<sub>i</sub>), 148.37, 148.47 (quaternary carbons), 152.41 (C<sub>a</sub>), 152.46 (C<sub>h</sub>), 156.19, 156.61, 157.32 (quaternary carbons), 207.59 (Ru–C<sub>NHC</sub>). ESI-MS: *m/z* 744.3 [M<sup>+</sup>].

**Complex 2d(PF<sub>6</sub>) (M = Ru, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>2</sup>∧N<sup>∧</sup>C<sup>2</sup>, N<sup>∧</sup>N = phen).** Yield 0.38 g, 57.3%. Anal. Calcd for C<sub>39</sub>H<sub>37</sub>N<sub>7</sub>ClRuPF<sub>6</sub>: C, 52.91; H, 4.21; N, 11.08. Found: C, 51.81; H, 3.89; N, 11.02. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.29–0.61 (m, 12H, Bu), 1.20–1.30 (m, 2H, Bu), 3.26–3.47 (m, 4H, Bu), 7.23–7.26 (m, 1H, H<sub>g</sub>), 7.40–7.44 (m, 4H, H<sub>k</sub>/H<sub>n</sub> + H<sub>m</sub>/H<sub>l</sub>), 7.47–7.51 (m, 2H, H<sub>m</sub>/H<sub>l</sub>), 7.74 (dd, *J* = 5.4, 1.2 Hz, 1H, H<sub>i</sub>), 8.08 (d, *J* = 8.8 Hz, 1H, H<sub>d</sub>/H<sub>e</sub>), 8.18–8.21 (m, 1H, H<sub>b</sub>), 8.24–8.28 (m, 7H, H<sub>d</sub>/H<sub>e</sub> + H<sub>i</sub> + H<sub>j</sub> + H<sub>k</sub>/H<sub>l</sub>), 8.73 (dd, *J* = 8.0, 1.2 Hz, 1H, H<sub>c</sub>), 10.52 (dd, *J* = 5.4, 1.2 Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.74, 20.29, 33.46, 48.00 (Bu), 107.84 (C<sub>i</sub>), 111.91 (C<sub>k</sub>/C<sub>n</sub>), 112.77 (C<sub>k</sub>/C<sub>n</sub>), 125.05 (C<sub>m</sub>/C<sub>l</sub>), 125.43 (C<sub>g</sub>), 125.44 (C<sub>m</sub>/C<sub>l</sub>), 126.33 (C<sub>b</sub>), 128.41 (C<sub>d</sub>/C<sub>e</sub>), 128.56 (C<sub>d</sub>/C<sub>e</sub>), 131.14, 131.80, 132.75 (quaternary carbons), 134.84 (C<sub>h</sub>), 134.97 (C<sub>f</sub>), 136.29 (quaternary carbon), 139.53 (C<sub>i</sub>), 148.36, 148.51 (quaternary carbons), 153.51 (C<sub>a</sub>), 153.94 (C<sub>f</sub>), 156.25 (quaternary carbon), 207.24 (Ru–C<sub>NHC</sub>). ESI-MS: *m/z* 740.3 [M<sup>+</sup>].

**Complex 3a(PF<sub>6</sub>) (M = Os, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>1</sup>∧N<sup>∧</sup>C<sup>1</sup>, N<sup>∧</sup>N = bpy).** Yield 0.28 g, 53.6%. Anal. Calcd for C<sub>29</sub>H<sub>33</sub>N<sub>7</sub>ClOsPF<sub>6</sub>: C, 40.96; H, 3.91; N, 11.53. Found: C, 40.08; H, 3.51; N, 10.88. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.61–0.90 (m, 12H, Bu), 1.20–1.30 (m, 2H, Bu), 3.12–3.26 (m, 4H, Bu), 6.69–6.73 (m, 1H, H<sub>g</sub>), 7.06 (d, *J* = 2.0 Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.44 (m, 1H, H<sub>d</sub>), 7.48–7.60 (m, 3H, H<sub>b</sub> + H<sub>f</sub> + H<sub>j</sub>), 7.71 (d, *J* = 8.0 Hz, 2H, H<sub>i</sub>), 7.76–7.81 (m, 1H, H<sub>g</sub>), 7.84 (d, 2.0 Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 8.20 (m, 1H, H<sub>c</sub>), 8.43 (m, 1H, H<sub>h</sub>), 10.44 (m, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.78, 20.26, 35.19, 50.17 (Bu), 104.05 (C<sub>i</sub>), 118.37 (C<sub>k</sub>/C<sub>l</sub>), 122.93 (C<sub>k</sub>/C<sub>l</sub>), 123.85 (C<sub>e</sub>), 124.54 (C<sub>f</sub>), 126.90 (C<sub>c</sub>), 127.48 (C<sub>b</sub>/C<sub>g</sub>), 133.59 (C<sub>g</sub>), 133.87 (C<sub>b</sub>/C<sub>g</sub>), 138.45 (C<sub>i</sub>), 151.05 (C<sub>a</sub>), 153.28 (C<sub>d</sub>), 157.20, 158.20, 161.43 (quaternary carbons), 181.70 (Os–C<sub>NHC</sub>). ESI-MS: *m/z* 705.4 [M<sup>+</sup>].

**Complex 3b(PF<sub>6</sub>) (M = Os, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>1</sup>∧N<sup>∧</sup>C<sup>1</sup>, N<sup>∧</sup>N = Ph<sub>2</sub>bpy).** Yield 0.26 g, 42.6%. Anal. Calcd for C<sub>41</sub>H<sub>41</sub>N<sub>7</sub>ClOsPF<sub>6</sub>: C,

49.12; H, 4.12; N, 9.78. Found: C, 48.47; H, 4.51; N, 9.18. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.60–0.81 (m, 10H, Bu), 0.87–0.97 (m, 2H, Bu), 1.25–1.36 (m, 2H, Bu), 3.22–3.36 (m, 4H, Bu), 7.02 (dd, *J* = 6.2, 2.0 Hz, 1H, H<sub>g</sub>), 7.09 (d, *J* = 2.0 Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.43–7.58 (m, 6H, H<sub>h</sub> + 5H on Ph), 7.62–7.66 (m, 2H, H<sub>i</sub> + 1H on Ph), 7.72–7.77 (m, 4H, H<sub>j</sub> + 2H on Ph), 7.85 (d, *J* = 2.0 Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.90 (dd, *J* = 6.2, 2.0 Hz, 1H, H<sub>b</sub>), 8.01–8.03 (m, 2H, Ph), 8.64 (d, *J* = 2.0 Hz, 1H, H<sub>c</sub>), 8.87 (d, *J* = 2.0 Hz, 1H, H<sub>d</sub>), 10.45 (d, *J* = 6.2 Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 14.07, 21.82, 33.76, 50.30 (Bu), 104.19 (C<sub>i</sub>), 118.42 (C<sub>k</sub>/C<sub>l</sub>), 121.55 (C<sub>e</sub>), 122.13 (C<sub>d</sub>), 123.08 (C<sub>k</sub>/C<sub>l</sub>), 124.53 (C<sub>g</sub>), 125.14 (C<sub>b</sub>), 126.20, 128.07, 128.08, 128.13, 129.16, 129.86, 130.15, 130.36, 130.71, 130.72 (ten carbons on Ph), 136.98, 137.46 (quaternary carbons), 138.61 (C<sub>i</sub>), 145.35, 145.82 (quaternary carbons), 151.11 (C<sub>a</sub>), 153.46 (C<sub>h</sub>), 157.14, 158.72, 161.96 (quaternary carbons), 181.64 (Os–C<sub>NHC</sub>). ESI-MS: *m/z* 858.4 [M<sup>+</sup>].

**Complex 4a(PF<sub>6</sub>) (M = Os, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>2</sup>∧N<sup>∧</sup>C<sup>2</sup>, N<sup>∧</sup>N = bpy).** Yield 0.30 g, 51.0%. Anal. Calcd for C<sub>37</sub>H<sub>37</sub>N<sub>7</sub>ClOsPF<sub>6</sub>: C, 46.76; H, 3.92; N, 10.32. Found: C, 45.91; H, 3.63; N, 10.34. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.68–0.93 (m, 12H, Bu), 1.39–1.48 (m, 2H, Bu), 3.31–3.60 (m, 4H, Bu), 6.70–6.74 (m, 1H, H<sub>g</sub>), 7.43–7.50 (m, 7H, H<sub>e</sub> + 6H of H<sub>k</sub>/H<sub>l</sub>/H<sub>m</sub>/H<sub>n</sub>), 7.55–7.59 (m, 1H, H<sub>g</sub>), 7.71–7.75 (m, 1H, H<sub>b</sub>), 7.80 (t, *J* = 8.2 Hz, 1H, H<sub>i</sub>), 7.93–7.97 (m, 1H, H<sub>c</sub>), 8.24–8.30 (m, 5H, H<sub>h</sub> + H<sub>j</sub> + H<sub>k</sub>/H<sub>l</sub>/H<sub>m</sub>/H<sub>n</sub>), 8.55 (m, 1H, H<sub>d</sub>), 10.52 (m, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.91, 20.59, 34.09, 47.61 (Bu), 105.49 (C<sub>i</sub>), 111.98 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 112.30 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 124.03 (C<sub>h</sub>), 124.99 (C<sub>d</sub>), 125.01 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 125.43 (C<sub>k</sub>/C<sub>l</sub>/C<sub>m</sub>/C<sub>n</sub>), 127.16 (C<sub>f</sub>), 128.00 (C<sub>b</sub>), 133.33 (quaternary carbon), 134.68 (C<sub>e</sub>), 135.27 (C<sub>g</sub>), 136.29 (quaternary carbon), 138.86 (C<sub>i</sub>), 151.50 (C<sub>a</sub>), 153.87 (C<sub>e</sub>), 157.49, 158.36, 160.71 (quaternary carbons), 191.75 (Os–C<sub>NHC</sub>). ESI-MS: *m/z* 805.4 [M<sup>+</sup>].

**Complex 4b(PF<sub>6</sub>) (M = Os, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>2</sup>∧N<sup>∧</sup>C<sup>2</sup>, N<sup>∧</sup>N = Ph<sub>2</sub>bpy).** Yield 0.23 g, 34.9%. Anal. Calcd for C<sub>49</sub>H<sub>45</sub>N<sub>7</sub>ClOsPF<sub>6</sub>: C, 53.38; H, 4.11; N, 8.89. Found: C, 51.48; H, 4.21; N, 8.04. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.69–1.01 (m, 12H, Bu), 1.45–1.54 (m, 2H, Bu), 3.38–3.71 (m, 4H, Bu), 7.02 (dd, *J* = 6.4, 2.0 Hz, 1H, H<sub>g</sub>), 7.42–7.50 (m, 9H, H<sub>k</sub>/H<sub>l</sub> + H<sub>i</sub> + H<sub>m</sub> + 3H on Ph), 7.54 (d, *J* = 6.4 Hz, 1H, H<sub>h</sub>), 7.58–7.61 (m, 1H, Ph), 7.67–7.74 (m, 4H, Ph), 7.85 (t, *J* = 8.2 Hz, 1H, H<sub>i</sub>), 8.04 (dd, *J* = 6.4, 2.0 Hz, 1H, H<sub>b</sub>), 8.06–8.08 (m, 2H, Ph), 8.27–8.31 (m, 4H, H<sub>j</sub> + H<sub>k</sub>/H<sub>l</sub>), 8.72 (d, *J* = 2.0 Hz, 1H, H<sub>c</sub>), 8.97 (d, *J* = 2.0 Hz, 1H, H<sub>d</sub>), 10.55 (d, *J* = 6.4 Hz, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.94, 20.66, 34.15, 47.73 (Bu), 105.62 (C<sub>i</sub>), 112.01 (C<sub>k</sub>/C<sub>n</sub>), 112.32 (C<sub>k</sub>/C<sub>n</sub>), 121.73 (C<sub>e</sub>), 122.57 (C<sub>d</sub>), 124.72 (C<sub>g</sub>), 125.06 (C<sub>f</sub>/C<sub>m</sub>), 125.47 (C<sub>f</sub>/C<sub>m</sub>), 125.57 (C<sub>b</sub>), 128.15, 128.23, 130.15, 130.46 (8 carbons on Ph, resolved with the <sup>1</sup>H–<sup>13</sup>C HSQC NMR experiment), 130.91, 130.96 (two carbons on Ph), 133.33, 136.36, 136.73, 137.33 (quaternary carbons), 139.02 (C<sub>i</sub>), 146.41, 147.19 (quaternary carbons), 151.55 (C<sub>a</sub>), 154.03 (C<sub>h</sub>), 157.47, 158.87, 161.21 (quaternary carbons), 191.75 (Os–C<sub>NHC</sub>). ESI-MS: *m/z* 958.5 [M<sup>+</sup>].

**Complex 1a-CH<sub>3</sub>CN(PF<sub>6</sub>)<sub>2</sub> (M = Ru, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>1</sup>∧N<sup>∧</sup>C<sup>1</sup>, N<sup>∧</sup>N = bpy, L = CH<sub>3</sub>CN).** Yield 0.078 g, 86.6%. Anal. Calcd for C<sub>31</sub>H<sub>36</sub>N<sub>8</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 40.84; H, 3.98; N, 12.29. Found: C, 40.30; H, 3.53; N, 12.01. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.63–0.87 (m, 10H, Bu), 0.95–1.06 (m, 2H, Bu), 1.25–1.36 (m, 2H, Bu), 2.06 (s, 3H, CH<sub>3</sub>CN), 3.19–3.42 (m, 4H, Bu), 7.03–7.06 (m, 1H, H<sub>g</sub>), 7.18 (d, *J* = 2.0 Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 7.21 (m, 1H, H<sub>c</sub>), 7.73–7.82 (m, 4H, H<sub>b</sub> + H<sub>g</sub> + H<sub>j</sub>), 7.99 (d, *J* = 2.0 Hz, 2H, H<sub>k</sub>/H<sub>l</sub>), 8.13–8.17 (m, 1H, H<sub>c</sub>), 8.22 (t, *J* = 8.2 Hz, 1H, H<sub>i</sub>), 8.31 (d, *J* = 8.0 Hz, 1H, H<sub>b</sub>), 8.50 (d, *J* = 8.0 Hz, 1H, H<sub>d</sub>), 9.55 (m, 1H, H<sub>a</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 4.52 (CH<sub>3</sub>CN), 13.74, 20.16, 34.31, 50.91 (Bu), 107.83 (C<sub>i</sub>), 119.02 (C<sub>f</sub>/C<sub>l</sub>), 124.03 (C<sub>h</sub>), 124.21 (C<sub>k</sub>/C<sub>l</sub>), 124.77 (C<sub>d</sub>), 127.02 (C<sub>f</sub>), 127.54 (C<sub>b</sub>), 136.98 (C<sub>e</sub>), 137.09 (C<sub>g</sub>), 141.85 (C<sub>i</sub>), 151.96 (C<sub>e</sub>), 152.73 (C<sub>a</sub>), 155.26, 156.31, 156.81 (quaternary carbons), 191.12 (Ru–C<sub>NHC</sub>). ESI-MS: *m/z* 767.5 [M–PF<sub>6</sub>]<sup>+</sup>.

**Complex 1a-t-BuNC(PF<sub>6</sub>)<sub>2</sub> (M = Ru, C<sup>∧</sup>N<sup>∧</sup>C = C<sup>1</sup>∧N<sup>∧</sup>C<sup>1</sup>, N<sup>∧</sup>N = bpy, L = t-BuNC).** Yield 0.063 g, 82.4%. Anal. Calcd for C<sub>34</sub>H<sub>42</sub>N<sub>8</sub>RuP<sub>2</sub>F<sub>12</sub>: C, 42.82; H, 4.44; N, 11.75. Found: C, 42.40; H, 3.88; N, 11.41. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 0.68–0.88 (m, 10H, Bu), 1.01–1.18 (m, 2H, Bu), 1.25 (s, 9H, t-BuNC), 1.31–1.42 (m, 2H, Bu), 3.11–3.40 (m, 4H, Bu), 7.19–7.23 (m, 4H, H<sub>e</sub> + H<sub>f</sub> + H<sub>k</sub>/

H<sub>i</sub>), 7.73–7.77 (m, 3H, H<sub>b</sub> + H<sub>i</sub>), 7.91–7.97 (m, 3H, H<sub>g</sub> + H<sub>k</sub>/H<sub>l</sub>), 8.13–8.18 (m, 1H, H<sub>c</sub>), 8.28 (t, *J* = 8.2 Hz, 1H, H<sub>i</sub>), 8.40 (d, *J* = 8.4 Hz, 1H, H<sub>h</sub>), 8.51 (d, *J* = 8.2 Hz, 1H, H<sub>d</sub>), 9.44 (m, 1H, H<sub>e</sub>). <sup>13</sup>C NMR (100.6 MHz, CD<sub>3</sub>CN): δ 13.75, 20.18, 34.15, 50.99 (*n*-Bu), 30.60 ((CH<sub>3</sub>)<sub>3</sub>C–NC), 59.22 ((CH<sub>3</sub>)<sub>3</sub>C–NC), 108.39 (C<sub>j</sub>), 119.08 (C<sub>k</sub>/C<sub>l</sub>), 124.29 (C<sub>h</sub>), 124.51 (C<sub>k</sub>/C<sub>l</sub>), 125.29 (C<sub>d</sub>), 127.46 (C<sub>f</sub>), 128.17 (C<sub>b</sub>), 137.75 (C<sub>c</sub>), 138.72 (C<sub>g</sub>), 142.76 (C<sub>i</sub>), 150.04 (C<sub>e</sub>), 154.15 (quaternary carbon), 154.47 (C<sub>a</sub>), 154.99, 156.28 (quaternary carbons), 188.83 (Ru–C<sub>NHC</sub>). ESI-MS: *m/z* 809.4 [M–PF<sub>6</sub>]<sup>+</sup>.

**X-ray Crystallography.** X-ray diffraction data for **1b**(PF<sub>6</sub>), **1c**(PF<sub>6</sub>), **2a**(PF<sub>6</sub>)·CH<sub>3</sub>NO<sub>2</sub>, and **4a**(PF<sub>6</sub>)·CH<sub>3</sub>CN were collected on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer with Cu Kα radiation (λ = 1.54178 Å) at 133 K. The data were processed using CrysAlis.<sup>37</sup> The structures were solved by Patterson or Fourier methods and refined by full-matrix least-squares based on *F*<sup>2</sup> with programs SHELXS-97 and SHELXL-97<sup>38</sup> within WinGX.<sup>39</sup> All non-hydrogen atoms were refined anisotropically in the final stage of least-squares refinement. The positions of H atoms were calculated on the basis of riding mode with thermal parameters equal to 1.2 times that of the associated C atoms. Disorder of solvent molecule CH<sub>3</sub>CN in **4a**(PF<sub>6</sub>)·CH<sub>3</sub>CN was observed, and the split model was applied.

**Computational Methodology.** DFT calculations were performed on model complexes **1a'**, **2a'**, **3a'**, **4a'**, **1a'**–CH<sub>3</sub>CN, **1a'**<sup>−</sup>, tpy-ligated complexes [Ru(tpy)(bpy)Cl]<sup>+</sup> and [Os(tpy)(bpy)Cl]<sup>+</sup>, and [Ru([14]-andS4)(bpy)]<sup>+</sup>. Their electronic ground states were optimized with *Cs* symmetry imposed (except for **1a'**<sup>−</sup> and [Ru([14]andS4)(bpy)]<sup>+</sup>, which have no symmetry imposed) using the hybrid functional M06 by Truhlar and Zhao.<sup>26</sup> The M06 functional was employed because it is a functional parametrized for transition metals and had been demonstrated to a give higher accuracy than other hybrid functionals in transition metal and organometallic chemistry.<sup>26</sup> The ECP28MDF and ECP60MDF pseudopotentials were employed for the Ru and Os atoms respectively with the correlation-consistent cc-pVTZ-PP basis set of Peterson et al.<sup>40</sup> The 6-311+G\* basis set was employed for C, H, N, and Cl atoms.<sup>41</sup> Tight SCF convergence (10<sup>−8</sup> au) was used for all calculations. Frequency calculations were performed on all of the optimized structures. Because no imaginary vibrational frequencies were encountered, their optimized stationary points were confirmed to be local minima. The first 120 vertical electronic transitions for these complexes in CH<sub>3</sub>CN were computed at their respective gas-phase-optimized ground-state geometries using the time-dependent-DFT (TD-DFT) method with the same density functional and basis sets in the geometry optimizations. The conductor polarizable continuum model (CPCM)<sup>27</sup> was used to account for solvent effects upon the electronic transition. All of the calculations were performed using the Gaussian 09 program package (revision B.01).<sup>42</sup>

**EPR Measurements.** EPR samples were prepared by bulk electrolysis at −20 °C of 2 mM CH<sub>3</sub>CN solutions of **1a**, **2a**, and [Ru([14]aneS4)(bpy)]<sup>2+</sup> containing the 0.2 M [Bu<sub>4</sub>N]PF<sub>6</sub> electrolyte. Their CW X-band EPR spectra were recorded on a Bruker E500 ELEXSYS spectrometer with a standard Bruker cavity (ER4102ST) and an Oxford Instruments helium flow cryostat (ESR 910). Microwave frequencies were measured using a Hewlett-Packard frequency counter (HP5352B), and the field control was calibrated with a Bruker NMR field probe (ER035M). As a consequence of signal attenuation in fluid solution due to high solvent polarity, it was necessary to measure these spectra in a Q-band EPR tube inserted into an X-band tube. All spectral manipulation and simulations were performed using the Bruker XSOPHE Suite. Frozen solution spectra were simulated using Lorentzian line shapes and a spin Hamiltonian of the form  $\hat{H} = \mu_B g \mathbf{B} \cdot \mathbf{S} + \sum \mathbf{S} \mathbf{A} \mathbf{I}$ , where *g* and *A* are 3 × 3 electron Zeeman and magnetic hyperfine interaction matrices, respectively, and all other symbols have their usual meanings. Fluid solution spectra were simulated using a spin Hamiltonian of the form  $\hat{H} = g \mu_B \mathbf{B} \cdot \mathbf{S} + \sum \mathbf{S} \mathbf{a} \mathbf{S} \mathbf{I}$ , where the summation term is weighted over all naturally occurring isotopes of N and Ru and the other terms have their standard meanings. Satisfactory fits were achieved using a Gaussian line shape and the isotropic liquids model,  $\sigma_v = a + bM_I^2 + cM_I^3 + dM_I^3$ , which accounts for molecular tumbling.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional UV–visible absorption spectra, cyclic voltammograms, spectroelectrochemical traces, and EPR spectra. Optimized geometries and calculated vertical transition energies for model complexes. Crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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