Letter

Synthesis and photophysics of ruthenium(II) complexes with multiple pyrenylethynylene subunits

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We describe the synthesis and photophysical properties of new Ru(II) complexes bearing different numbers of pyrenylethynylene substituents in either the 5 or 5,5′ positions of 2,2′-bipyridine. Static and dynamic absorption and luminescence measurements reveal the nature of the lowest excited states in each molecule. The 5-substituted complexes display behavior dominated by triplet intraligand π,π^* excited states, generating long-lived room temperature phosphorescence in the red. While the photophysical properties in the 5,5′-substituted case are still largely influenced by triplet intraligand π,π^* excited states, the data suggest the possibility of an excited state manifold composed of "mixed" intraligand and charge transfer character.

The introduction of selected organic chromophores into diimine ligand structures has generated a wide variety of inorganic complexes with novel photophysical properties.[1–14] Particularly noteworthy are those complexes that display low-lying metal-to-ligand charge transfer (MLCT) excited states whose triplet levels are coincident with those of the covalently linked organic system(s). Such metal-organic chromophores have generated room temperature (RT) excited state lifetimes in excess of 100 μs, which radiatively decay through the MLCT manifold. In cases where the metal center is ruthenium(II), most of the documented behavior can be explained by excited state equilibrium or slow back-energy transfer processes between ^{3}MLCT and intraligand (^{3}IL) excited states.[1–6,8] An alternative approach to generating long lifetime RT emission is to select a diimine ligand system whose ^{3}IL states are substantially lower in energy relative to the ^{3}MLCT level. Here, singlet MLCT excitation can lead to rapid intersystem crossing and the observation of either pure ^{3}IL or mixed ^{3}IL/intraligand charge transfer (^{3}ILCT) phosphorescence at RT.[7,9–11,13,14] In a recent report our groups demonstrated that RT phosphorescence can also be generated in Pt(II) diimine bis(acetylide) chromophores, where the ^{3}IL excited states are remote from the diimine ligand structure.[11]

A fundamental issue in this area concerns the "transition" of photophysics in molecules where either MLCT or IL excited states dominate the behavior. For example, small structural modifications that alter the energy of the MLCT and/or the IL states can completely transform the observed photophysics towards either extreme. The Ziessel and Schanze groups have very recently illustrated this transitional behavior in structurally related oligo(thiophene-bipyridine)-containing Ru(II) complexes.[13,14] Compelling evidence was presented for one of their polynuclear complexes in which the photophysics could best be described as a composite of MLCT and IL behavior, somewhat in between that expected for each.[14] At the present time this effect may be explained by a thermal excited state equilibrium or by configuration mixing.

In the current work we present evidence of long-lived RT photoluminescence in three new Ru(II) complexes, **3a**, **4a**, and **5a** (Scheme 1), that contain different numbers of pyrenylethynylene substituents in either the 5 or 5,5′ positions of 2,2′-bipyridine (bipy). We have measured the static and dynamic UV-vis absorption and photoluminescence properties of these molecules along with model systems containing the appropriate –Br or –C≡C–tolyl substituents. The 5–C≡C–pyrenyl substituted complexes display behavior consistent with triplet intraligand π,π^* excited states, yielding long-lived room temperature phosphorescence in the red. In the 5,5′ –C≡C–pyrenyl substituted case, where the MLCT and IL excited states are in close energetic proximity, the resulting photophysical properties appear to be a composite of those of the two states. In the cases of complexes bearing the –C≡C–tolyl functionality, our photophysical data parallel that reported by Schanze and coworkers on the –C≡C–phenyl analogs.[12]

Due to the pronounced insolubility of pyrene substituted bipy ligands, a result of the weak dipole moment and the planarity of the molecules, the target complexes could not be synthesized according to classical procedures. We circumvented this problem through preparation of the pivotal starting materials bearing unsubstituted (**1**) and 5-bromo substituted (**2**) bipy ligands. This allows us to produce the Ru tris-bipy complexes **3**, **4**, and **5** with varying numbers of reactive bromo functions. Quite interesting to note is that these complexes react smoothly under Sonogashira–Hagihara cross-coupling conditions[15] with 1-ethynylpyrene to provide the desired pyrene substituted complexes in very good yield (Scheme 1).[16] This is a convenient and versatile protocol because of the mild conditions and the possibility to introduce various ethynyl grafted fragments such as 4-tolyl, which will serve as important model compounds in photophysical investigations.

The photophysical data measured for all compounds in this study are collected in Table 1. The spectroscopic properties of **3a** and **4a** in CH_3CN are qualitatively similar, demonstrating that the number of appended –C≡C–pyrenyl units has no marked influence on the photophysical properties of these systems. For brevity, comparisons will be made between **3a** and **5a** as both chromophores bear two –C≡C–pyrenyl substituents.

Fig. 1 presents the UV-vis absorption and emission spectra obtained for **3a** and **5a** in CH_3CN. The UV portions of the

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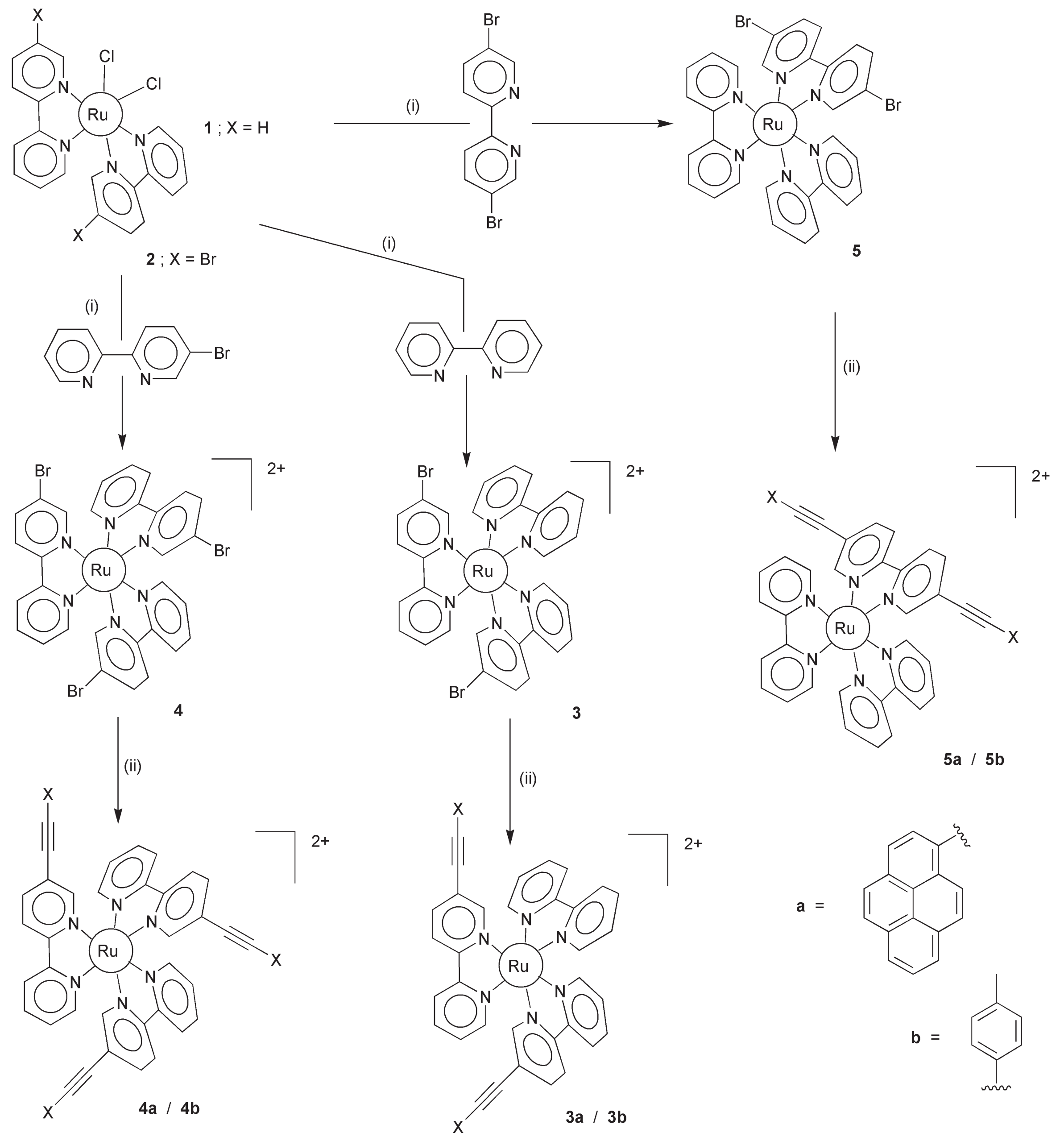

Scheme 1 Conditions: (i) EtOH–H_2O (6:1 v/v), 80 °C; (ii) $[Pd(PPh_3)_4]$ (6 mol %), CH_3CN–C_6H_6 (1:1), $i Pr_2NH$, 60 °C. All counterions are PF_6^- and the complexes were isolated as mixtures of diastereoisomers.

Table 1 Photophysical properties at room temperature and 77 K[a]

Compound	$\lambda_{abs\ max}$/ nm	ε_{max}/ M^{-1} cm^{-1}	$\lambda_{em\ max}$ (300 K)/ nm	τ_{em} (TRPL)[b] / µs	τ (TA)[c] / µs	Φ_{em}[d]	$\lambda_{em\ max}$[e] (77 K)/ nm	ΔE_S[f] / cm^{-1}	k_r[g] / 10^4 s^{-1}	k_{nr}[g] / 10^6 s^{-1}
3	450	12 100	616	0.84	0.77	0.0630	583	920	7.50	1.27
3a	420	54 100	671	56.5	46.2	0.0110	669	45	0.02	0.02
3b	460	7530	640	1.51	1.10	0.0920	608	823	6.09	0.73
4	450	11 900	611	0.50	0.51	0.0440	580	875	8.80	2.09
4a	420	70 400	672	65.1	59.4	0.0086	671	22	0.01	0.02
4b	468	9800	634	1.38	1.29	0.1220	606	729	8.84	0.83
5	448	11 040	636	1.26	1.10	0.0880	595	1084	6.98	0.87
5a	443	57 700	690	4.96	5.00	0.0130	682	170	0.26	0.21
5b	440	9800	675	0.72	0.69	0.0370	639	835	5.14	1.44

[a] Argon-saturated CH_3CN solutions unless otherwise noted. [b] Emission lifetimes represent an average of at least five measurements and have uncertainty of less than 10%. Here the data were obtained using 450 ± 2 nm excitation. Lifetimes were independent of monitoring wavelength throughout the emission envelope. [c] Transient absorption decay lifetime, measured with either 355 or 532 nm excitation. [d] Photoluminescence quantum yield was calculated using $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.062$) in CH_3CN as quantum counter, ±10%. [e] Emission spectra were taken at 77 K in 4:1 EtOH–MeOH with 450 nm excitation. [f] Thermally induced Stokes shift was calculated from the difference in $\lambda_{em\ max}$ at 300 K and 77 K. [g] $k_r = \Phi_{em}/\tau_{em}$; $k_{nr} = 1/[\tau_{em}(1 - \Phi_{em})]$. It is assumed that the emitting excited state is produced with unit efficiency.

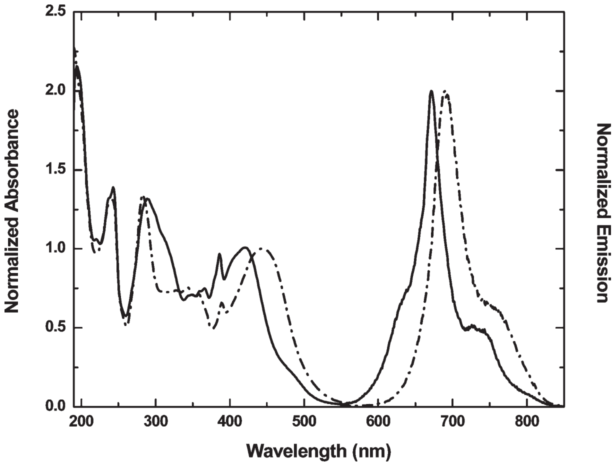

Fig. 1 Room temperature absorption and emission spectra of **3a** (solid line) and **5a** (dash-dotted line) in degassed CH_3CN solution. The emission spectra were measured with 450 ± 2 nm excitation.

absorption spectra are dominated by ligand-localized π,π* transitions whereas the visible portions of the spectra contain π,π* transitions occurring within the pyrenyl containing ligand(s) (near 420 nm in **3a** and **4a**), in addition to a combination of MLCT transitions, $d\pi(Ru) \rightarrow \pi^*(bipy)$ and $d\pi(Ru) \rightarrow \pi^*(bipy(C{\equiv}C\text{–}pyrene)_n)$.

Visible excitation leads to structured luminescence spectra in both molecules, with peaks at 671 (**3a**) and 690 (**5a**) nm. In both cases, the excitation spectra are completely superimposable with the absorption spectra between 300 and 550 nm, indicating that internal conversion and intersystem crossing leads to a single low-energy emissive state at RT. While these emissions are significantly quenched by oxygen, the intensity of each spectrum diminishes symmetrically, supporting the notion that only one emissive state is present in these molecules.[7,9] The photoluminescence quantum yields for **3a**, **4a**, and **5a** in deaerated CH_3CN measured relative to $[Ru(bipy)_3]^{2+}$ are 0.045, 0.013, and 0.033, respectively. The RT emission lifetimes of **3a**, **4a**, and **5a** measured with a broadband N_2-pumped dye laser (λ_{ex} = 450 nm) in deaerated CH_3CN are 56, 65, and 5 μs, respectively. While the lifetime of **5a** is significantly shorter than that of the structurally related **3a** and **4a**, all complexes are longer lived than what is expected for Ru(II) diimine MLCT complexes. In all three cases the values calculated for the k_r and k_{nr} based upon these data are significantly smaller (by 1 to 3 orders of magnitude) than what is observed for typical MLCT excited states (Table 1).[14,17]

The emission spectra of **3a** and **5a** measured at 77 K in 4:1 EtOH–MeOH have maxima similar to their RT counterparts, with thermally induced Stokes shifts (ΔE_S) of 45 and 170 cm^{-1}, respectively (Fig. 2 and Table 1). The small values of ΔE_S indicate that the excited states in these complexes are relatively nonpolar. For illustrative purposes, Fig. 2 presents the data obtained for **3a**. The 77 K spectra are narrower in shape, but display similar vibronic progression as their RT spectra. These results are consistent with the notion that the emissions from **3a** and **5a** are not likely to be charge transfer in character. In fact, the six model systems containing either –Br (**3**–**5**) or –C≡C–tolyl (**3b**, **4b**, **5b**) substituents in place of the –C≡C–pyrenyl units display characteristic MLCT emission behavior, exhibiting broad structureless emissions at RT with large values of ΔE_S and lifetimes ranging from 500 ns to 1.5 μs with characteristic values of k_r and k_{nr} (~10^4 s^{-1} and 10^6 s^{-1}, respectively; see Table 1).[17] The luminescence data are consistent with ^{3}IL (π,π*)-based emission in the pyrenyl containing Ru(II) complexes.

Nanosecond laser flash photolysis experiments also support the ^{3}IL emission assignment in **3a**, **4a**, and **5a**. Fig. 3 presents

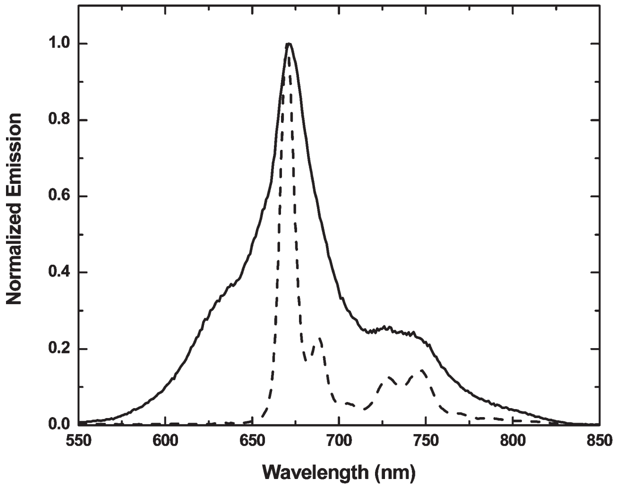

Fig. 2 Emission spectra of **3a** at room temperature (solid line) and 77 K (dashed line) in 4:1 EtOH–MeOH. The spectra were measured with 450 ± 2 nm excitation.

the excited state absorption spectrum of **3a** in CH_3CN measured 4 μs after a 532 nm laser pulse. The transient difference spectrum of the structurally related MLCT complex (**3b**) is also presented for comparative purposes. It is clear that the spectra exhibit features that are distinct, supporting the notion

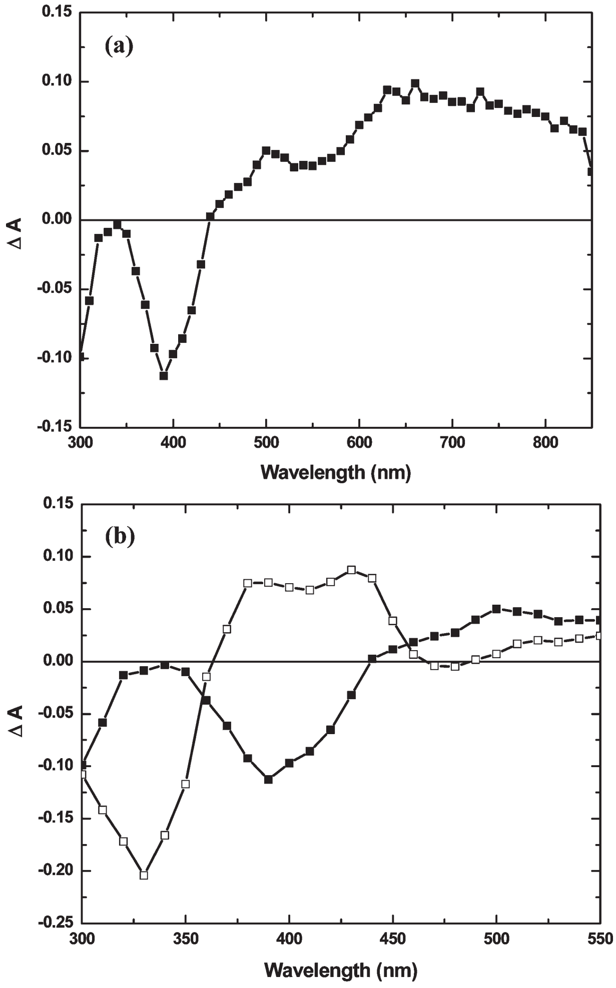

Fig. 3 (a) Excited state absorption difference spectrum of **3a** in deaerated CH_3CN measured 4 μs after a 532 nm laser pulse. (b) Transient absorption difference spectra of **3b** (open squares) in deaerated CH_3CN measured 270 ns after a 532 nm laser pulse. The spectrum in part (a) between 300 to 550 nm is superimposed for comparative purposes (filled squares).

that the excited states in the two molecules have different characters. In both cases, the kinetic response of the absorption transients mirrors that observed in their respective luminescence decay. Therefore, we assign the difference spectrum in **3a** to the proposed ^{3}IL excited states (ground state bleaching of the bipy-pyrenyl ligand near 420 nm and absorption transients above 450 nm). We note that transients similar to those observed in our model compounds (**3b**, **4b**, and **5b**) have already been documented for $[Ru(bipy)_2(5,5'$ –C≡C–phenyl-2,2′-bipy)]$^{2+}$.[12] The unfamiliar appearance of these transients [such as that exhibited in Fig. 3(b)] results from extremely large values for $\Delta\varepsilon$ (large radical anion signal) throughout the visible, which are so dominant that they completely obscure the MLCT ground state bleaching signals in the visible.[12,14] Since the complexes in this study were prepared from Ru(II) coordinated bromo-containing diimine ligands, we cannot explore the photophysical processes in the free ligands that bear the pyrenylethynylene fragments at the present time. We note that the same spectroscopic transients were observed at all delay times in our nanosecond experiment, indicating that the lowest excited state is produced promptly within the 7 ns laser pulse in all cases.

A new synthetic protocol for the preparation of Ru(II) bipyridine complexes bearing multiple appended ethynylpyrenyl or 4-ethynyltolyl fragments has been presented. In cases where two or three pyrenyl modules are present in the diimine ligand structures, extended RT excited state lifetimes in deaerated solution were observed. In all cases it appears that the lowest excited states are ^{3}IL in character. While the data presented for **3a** and **4a** are consistent with relatively "pure" ^{3}IL-based phosphorescence emerging from the pyrenyl containing diimine ligand(s), **5a** appears to exhibit photophysics with a "mixed" ^{3}MLCT and ^{3}IL character. By simply comparing the data collected in Table 1, **5a** clearly exhibits behavior that is different but somewhat intermediate to that of **3a** and **4a** (both definitively ^{3}IL character) and the Ru(II) model complexes that possess MLCT character. At present, we are uncertain if the apparent "mixed" behavior in **5a** results from properties inherent to the 5,5′-substituted pyrenyl ligand or if it arises from excited state equilibrium or from configuration mixing.[14] Future studies are planned to investigate the photophysical properties of the uncoordinated diimine ligand structures in order to probe these concepts. Although **3a** and **4a** also possess energetically proximate ^{3}MLCT and ^{3}IL states, we cannot ascertain the role of the ^{3}MLCT states on the photophysics of these structures. By comparison to the best structural models available (**3b**, **4b**), it is clear that the photophysics are dominated by the ^{3}IL states in both compounds. The absorption and emission properties exhibited by the free 5-substituted ligand will greatly assist in making more definitive assignments. Looking beyond the compounds described in the present work, additional diimine ligand structures that facilitate the tuning of ^{3}MLCT and ^{3}IL energies are essential to a comprehensive understanding of the photophysical properties in complex metal-organic structures. The current work illustrates that with appropriately substituted ligands, Ru(II) MLCT complexes can generate long-lived phosphorescence at RT. Such molecules are of fundamental interest yet are also poised for application in optoelectronic and luminescence-based technologies.

Experimental

Preparation of ruthenium complexes

To a stirred and argon-degassed acetonitrile–benzene solution (50/50, v/v) of the ruthenium(II) precursor, were progressively added $[Pd^\circ(PPh_3)_4]$, diisopropylamine and the acetylenic derivative. The mixture was heated under argon at 60 °C for *ca.* 16 h until complete consumption of the starting material (TLC check). After the solution had cooled to room temperature, potassium hexafluorophosphate in water was added and the solution was evaporated to dryness. The crude precipitate was washed twice with water, once with diethyl ether, then purified by chromatography on alumina. The fractions containing the pure complex were evaporated to dryness and recrystallized by slow evaporation of CH_2Cl_2 from a mixture of CH_2Cl_2–hexane. The photophysical measurements were performed according to ref. 4. The complete set of data will appear in a subsequent full account.

All complexes were unambiguously characterized by NMR, MS and IR spectroscopies, as well as elemental analysis and all data were consistent with the proposed structures. Selected data are as follows. **3a**: 86%, ESI-MS 1163.2 $[M-PF_6]^+$, 509.3 $[M-2PF_6]^{2+}$; FT-IR $\nu_{C\equiv C}$ 2192 cm^{-1}; anal. calcd for $C_{66}H_{40}F_{12}N_6P_2Ru$: C, 60.60; H, 3.08; N, 6.42; found: C, 60.40; H, 2.81; N, 6.17. **3b**: 95%, FAB$^+$-MS 943.3 $[M-PF_6]^+$, 798.2 $[M-2PF_6+H]^{2+}$; FT-IR $\nu_{C\equiv C}$ 2219/2183 cm^{-1}; anal. calcd for $C_{48}H_{36}F_{12}N_6P_2Ru{\cdot}CH_3CN$: C, 53.20; H, 3.48; N, 8.69; found: C, 53.09; H, 3.19; N, 8.54. **4a**: 68%, ESI-MS 1387.4 $[M-PF_6]^+$, 621.2 $[M-2PF_6]^{2+}$; FT-IR $\nu_{C\equiv C}$ 2192 cm^{-1}; anal. calcd for $C_{84}H_{48}F_{12}N_6P_2Ru$: C, 65.84; H, 3.16; N, 5.48; found: C, 65.68 H, 2.93; N, 5.23. **4b**: 94%, FAB-MS 1057.2 $[M-PF_6]^+$, FT-IR $\nu_{C\equiv C}$ 2218/2193 cm^{-1}; anal. calcd for $C_{57}H_{41}F_{12}N_6P_2Ru{\cdot}CH_3CN$: C, 57.06; H, 3.57; N, 7.80; found: C, 56.87; H, 3.47; N, 7.64. **5a**: 69%, FAB-MS 1163.4 $[M-PF_6]^+$, 509.2 $[M-2PF_6]^{2+}$; FT-IR $\nu_{C\equiv C}$ 2192 cm^{-1}; anal. calcd for $C_{66}H_{40}F_{12}N_6P_2Ru$: C, 60.60; H, 3.08; N, 6.42; Ffound: C, 60.42; H, 2.87; N, 6.13. **5b**: 94%, FAB-MS 943.2 $[M-PF_6]^+$; FT-IR $\nu_{C\equiv C}$ 2219/2182 cm^{-1}; anal. calcd for $C_{48}H_{36}F_{12}N_6P_2Ru{\cdot}CH_3CN$: C, 53.20; H, 3.48; N, 8.69; found: C, 52.95; H, 3.27; N, 8.49.

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