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Regioselective C−H Activation of Cyclometalated Bis-Tridentate Ruthenium Complexes

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Supporting Information

ABSTRACT: A series of bis-tridentate Ru(II) complexes consisting of trimethyl-4,4′,4″-tricarboxylate-2,2′:6′,2″-terpyridine (Me_3tctpy) and derivatized 6-phenyl-2,2′-bipyridine (pbpy) ligands are reported. Each complex is attached to a terminal triphenylamine (TPA) substituent at the central ring of pbpy through a thiophene bridge to benefit light absorption, while the anionic ring of pbpy is functionalized with substituents to modulate the metal-based redox potential. The cyclometalation step was found to favor the isomer where the electron-donating groups (EDGs; i.e., −OEt, −SEt) are situated *ortho* to the organometallic bond rather than the sterically favored *para* position, while the *para* isomer is formed in exclusivity when electron-withdrawing groups (e.g., $-CF_3$) are installed on the anionic ring. Moreover, the distribution of the isomeric products is affected by the identity of the chalcogen: *ortho*:*para* = 1:0 and 3:1 where EDG = −OEt and −SEt, respectively. Because our molecular scaffold rules out certain cyclometalation pathways (e.g., oxidative addition, agostic interactions, σ-bond metathesis), we are able to experimentally establish that the observed regioselectivity is in accordance with an electrophilic metalation where the relative stabilities of the products and carbanionic intermediates govern the ratio of the isomers formed.

INTRODUCTION

Ruthenium(II) coordination complexes bearing a single cyclometalating ligand [e.g., 6-phenyl-2,2′-bipyridine (pbpy); 2-phenylpyridine (ppy)] have received a lot of recent attention owing to their ability to generate high power conversion efficiencies in the dye-sensitized solar cell (DSSC).[1−13] Indeed, Grätzel et al.[2] and our program[11] have demonstrated that cell efficiencies in excess of 8% can be reached by Ru(II) complexes bearing bidentate and tridentate cyclometalating ligands, respectively. An important aspect of this class of dyestuffs is that the character of the highest occupied molecular orbital (HOMO) is often localized to the anionic ring of the cyclometalated ligand and the metal.[5] Chemical modification of this anionic ring therefore enables acute control of the metal-based oxidation potential, thus offering an additional handle for optimizing DSSC chromophores.[14]

When designing bis-tridentate Ru(II) complexes for light-harvesting applications, additional chromophoric units can compensate for the narrow absorption spectra and modest extinction coefficients characteristic of these compounds.[4,15] On this basis, we recently developed a bichromic manifold that couples a triphenylamine (TPA) group to the cyclometalated Ru core where the oxidation potential of each chromophore can be modified by the judicious placement of electron-donating groups (EDGs) and electron-withdrawing groups (EWGs).[12] Our studies involving the modification of the anionic ring of the pbpy chelate revealed a curious trend: EWGs (e.g., $-CF_3$) were positioned *para* to the organometallic bond of the cyclometalated product, whereas EDGs (e.g., −OMe) favored the *ortho* position.[12] While this phenomenon is not without precedent,[16,17] we set out to better understand the mechanistic details of this regioselectivity by modifying our bichromic scaffold with bulky chalcogen-containing substituents about the anionic ring (Chart 1; derivatives where $-R_1$ is substituted with methoxy groups and $-R_3$ with EWGs are also reported to aid in the characterization of the different isomers.) These alkoxy and thiolate substituents were selected to examine how electronic and steric interactions affect the frontier orbitals

Chart 1. Designation of Compounds[a]

Complex	Ligand	Substituent		
		-R_1	-R_2	-R_3
1	L1	-H	-H	-OEt
2	L2	-OMe	-H	-OEt
3	L3	-H	-H	-SEt
4	L4	-OMe	-H	-SEt
5	L6	-H	$-CF_3$	-H
6	L7	-OMe	$-CF_3$	-H
7	L8	-H	-H	-H

[a]Counterion = NO_3^- for **1** and **2** and HCO_3^- for **3** and **4**. Complexes **5**−**7** were previously reported and are included for reference purposes.[12]

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and the cyclometalation pathway, and also because chalcogens are common constituents in DSSC dyes[18] (it has been postulated that highly polarizable chalcogens can enhance the interaction with the electrolyte used in high-performance DSSCs[19,20]). This article unravels the underlying factors that dictate the *ortho*-assisted C−H activation step to aid in our ability to chemically control the frontier molecular orbitals of these complexes.

EXPERIMENTAL SECTION

Preparation of Compounds. All reagents were purchased from Aldrich and used without further purification except for $RuCl_3 \cdot 3H_2O$ (Pressure Chemical Company) and trimethyl-4,4′,4″-tricarboxylate-2,2′:6′,2″-terpyridine (**L5**; Helio Chemical Company, Switzerland). Purification by column chromatography was carried out using silica (Silicycle: Ultrapure Flash Silica). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Merck, Germany) and visualized under UV light. Routine ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual nondeuterated solvent. Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; m = multiplet. All proton assignments correspond to the generic molecular schemes that are provided (Figure 1). Organic precursors

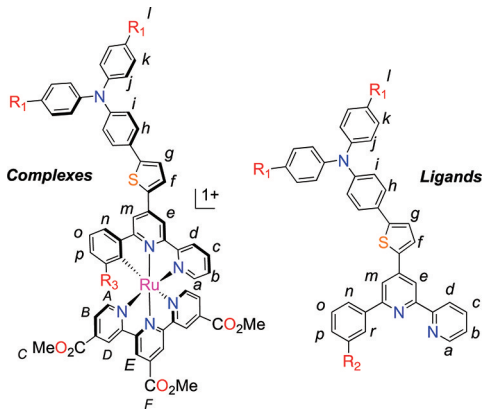

Figure 1. Generic labeling scheme for ^{1}H NMR signal assignments.

1-(3-mercaptophenyl)ethanone[21] (**P1**), (*E*)-3-(5-bromothiophen-2-yl)-1-precursors (pyridin-2-yl)prop-2-en-1-one[22] (**P3**), *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline[23] (**P8**), and 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline[24] (**P9**), *N*,*N*-diphenyl-4-(5-(6-(3-(trifluoromethyl)phenyl)-2,2′-bipyridin-4-yl)-thiophen-2-yl)aniline (**L6**),[12] 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(5-(6-(3-(trifluoromethyl)phenyl)-2,2′-bipyridin-4-yl)thiophen-2-yl)phenyl)aniline (**L7**),[12] *N*,*N*-diphenyl-4-(5-(6-phenyl-2,2′-bipyridin-4-yl)thiophen-2-yl)aniline (**L8**),[11] and complexes **5**,[11] **6**,[11] and **7**[11] were prepared as previously reported.

1-(3-Mercaptophenyl)ethanone (P1). The following is a modification of a previously reported procedure (no characterization data were presented).[21] To a solution of 3-acetylbenzenesulfonyl chloride (2.50 g, 11.4 mmol) in anhydrous toluene (30 mL) was slowly added Ph_3P (9.00 g, 34.3 mmol) under a N_2 atmosphere. Water (10 mL) was added to the mixture, which was then stirred for 10 min before an extraction step with 10% NaOH (2 × 25 mL). The alkaline aqueous extract was successively washed with toluene (2 × 20 mL), acidified with 1 M HCl (60 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The organic extract was dried with $MgSO_4$, and the solvent was removed *in vacuo* to yield 1.09 g (62.5%) of the product as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 1H, H_r), 7.66 (d, 1H, ^3J = 7.8 Hz, H_n), 7.39 (d, 1H, ^3J = 7.8 Hz, H_p), 7.27 (t, 1H, ^3J = 7.8, H_o), 3.55 (s, 1H, H_{SH}), 2.52 (s, 3H, H_m); ^{13}C NMR ($CDCl_3$) δ 197.5, 137.9, 133.6, 132.2, 129.4, 128.9, 125.7; HRMS (EI) m/z = 152.0291 [$(M)^+$] (calcd for $C_8H_8OS^+$ m/z = 152.0296).

1-(3-(Ethylthio)phenyl)ethanone (P2). To a solution of **P1** (645 mg, 4.24 mmol) in EtOH (50 mL) was added potassium carbonate (594 mg, 4.24 mmol) and excess ethyl bromide (2 mL). The mixture was heated slightly below reflux overnight. The solvent was removed *in vacuo*, and the residue was purified by column chromatography [SiO_2: CH_2Cl_2; R_f = 0.53] to yield 0.77 g of the product as a pale yellow oil in quantitative yield. ^{1}H NMR ($CDCl_3$): δ 7.82 (s, 1H, H_r), 7.66 (d, 1H, ^3J = 7.7 Hz, H_n), 7.42 (d, 1H, ^3J = 7.8 Hz, H_p), 7.30 (t, 1H, ^3J = 7.7 Hz, H_o), 2.92 (q, 2H, ^3J = 7.4 Hz, $-SCH_2CH_3$), 2.52 (s, 3H, H_m), 1.26 (t, 3H, ^3J = 7.4 Hz, $-SCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 197.7, 138.0, 137.7, 133.0, 129.0, 128.0, 125.7, 27.4, 26.7, 14.3. HRMS (EI): m/z 180.0615 [$(M)^+$] (calcd for $C_{10}H_{12}OS^+$ m/z = 180.0609).

1-(2-(3-Ethoxyphenyl)-2-oxoethyl)pyridinium Iodide (P4). To a flask containing 1-(3-ethoxyphenyl)ethanone (3.44 g, 21.0 mmol) in pyridine (20 mL) was added iodine (6.38 g, 25.1 mmol). The reaction mixture was then stirred at 100 °C for 2.5 h. After cooling the reaction mixture to room temperature, the brown precipitate was isolated by vacuum filtration, washed with Et_2O, and air-dried. The solid was recrystallized from hot EtOH to yield 4.83 g (62.4%) of the product as a tan solid. ^{1}H NMR (MeOH): δ 8.93 (d, 2H, ^3J = 6.7 Hz, H_s), 8.73 (t, 1H, ^3J = 7.9 Hz, H_u), 8.22 (t, 2H, ^3J = 6.8 Hz, H_t), 7.70 (d, 1H, ^3J = 7.7 Hz, H_n), 7.59 (s, 1H, H_r), 7.53 (t, 1H, ^3J = 8.0 Hz, H_o), 7.31 (d, 1H, ^3J = 8.1 Hz, H_p), 6.43 (s, 2H, H_m), 4.14 (q, 2H, ^3J = 7.0 Hz, $-OCH_2CH_3$), 1.43 (t, 3H, ^3J = 7.0 Hz, $-OCH_2CH_3$). ^{13}C NMR (MeOH): δ 191.2, 161.1, 147.9, 147.8, 136.3, 131.6, 129.3, 129.2, 122.7, 121.9, 114.7, 65.2, 15.2. HRMS (ESI): m/z 242.1175 [$(M)^+$] (calcd for $C_{15}H_{16}NO_2^+$ m/z = 242.1176).

1-(2-(3-(Ethylthio)phenyl)-2-oxoethyl)pyridinium Iodide (P5). To a solution of **P2** (2.12 g, 11.7 mmol) in pyridine (15 mL) was added iodine (3.59 g, 14.1 mmol). The mixture was heated to 100 °C under N_2 for 2.5 h. After the reaction mixture was cooled to room temperature, a brown-tan precipitate was collected by vacuum filtration, washed with Et_2O, and air-dried. The resulting golden brown solid was triturated with EtOH to yield 3.70 g (81.8%) of the product as an off-white solid. ^{1}H NMR ($CDCl_3$): δ 8.99 (d, 2H, ^3J = 6.4 Hz, H_s), 8.75 (t, 1H, ^3J = 7.9 Hz, H_u), 8.29 (t, 2H, ^3J = 6.9 Hz, H_t), 7.91 (s, 1H, H_r), 7.85 (d, 1H, ^3J = 7.3 Hz, H_n), 7.73 (d, 1H, ^3J = 7.8 Hz, H_p), 7.61 (t, 1H, ^3J = 7.7 Hz, H_o), 6.50 (s, 2H, H_m), 3.10 (q, 2H, ^3J = 7.4 Hz, $-SCH_2CH_3$), 1.27 (t, 3H, ^3J = 7.3 Hz, $-SCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 190.4, 146.4, 146.2, 138.0, 134.2, 133.4, 129.8, 127.9, 126.9, 125.2, 66.3, 26.0, 14.0. HRMS (ESI): m/z 258.0941 [$(M)^+$] (calcd for $C_{15}H_{16}NOS^+$ m/z 258.0947).

4-(5-Bromothiophen-2-yl)-6-(3-ethoxyphenyl)-2,2′-bipyridine (P6). **P4** (2.79 g, 7.10 mmol), **P3** (2.09 g, 7.10 mmol), ammonium acetate (14.2 g, 184 mmol), and formamide (25 mL) were stirred at 120 °C under N_2 for 18 h. After the solution was cooled to room temperature, the precipitate was isolated by vacuum filtration and further purified by column chromatography [SiO_2: CH_2Cl_2/EtOAc, 9:1; R_f = 0.76]. Recrystallization from hot absolute EtOH yielded 2.06 g (62.9%) of the product as a light brown powder. ^{1}H NMR ($CDCl_3$): δ 8.69 (d, 1H, ^3J = 4.7 Hz, H_a), 8.61 (d, 1H, ^3J = 8.0 Hz, H_d), 8.50 (d, 1H, ^4J = 1.5 Hz, H_e), 7.84 (dt, 1H, ^3J = 7.7, ^4J = 1.8 Hz, H_c), 7.78 (d, 1H, ^4J = 1.6 Hz, H_m), 7.72 (t, 1H, ^4J = 1.9 Hz, H_q), 7.68 (d, 1H, ^3J = 7.9 Hz, H_n), 7.42 (d, 1H, ^3J = 4.0 Hz, H_f), 7.40 (t, 1H, ^3J = 7.9 Hz, H_o), 7.33 (dt, 1H, ^3J = 4.8, ^4J = 1.0 Hz, H_b), 7.10 (d, 1H, ^3J = 3.9 Hz, H_g), 6.98 (dd, 1H, ^3J = 8.1, ^4J = 2.4 Hz, H_p), 4.14 (q, 2H, ^3J = 7.0 Hz, $-OCH_2CH_3$), 1.47 (t, 3H, ^3J = 7.0 Hz, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 159.7, 157.5, 156.7, 156.1, 149.3, 143.4, 142.5, 140.7, 137.1, 131.4, 130.0, 126.0, 124.2, 121.7, 119.5, 116.5, 115.5, 115.4, 114.3, 113.7, 63.8, 15.1. HRMS (EI): m/z 438.0236 [$(M)^+$] (calcd for $C_{22}H_{17}N_2OS^{81}Br^+$ m/z 438.0225).

4-(5-Bromothiophen-2-yl)-6-(3-(ethylthio)phenyl)-2,2′-bipyridine (P7). A mixture of **P3** (2.50 g, 8.50 mmol), **P5** (3.27 g, 8.50 mmol), and ammonium acetate (17.11 g, 221 mmol) in formamide (25 mL) was stirred and heated at 120 °C under N_2 overnight. After cooling the reaction mixture to room temperature the solid was filtered to produce a waxy solid. The solid was dissolved in CH_2Cl_2 (150 mL), and the resulting solution was washed with water (2 × 50 mL) then brine

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(2 × 50 mL), dried with $MgSO_4$, and dried *in vacuo* to yield a tan powder. Purification by column chromatography using a CH_2Cl_2/EtOAc gradient [SiO_2: CH_2Cl_2/EtOAc, 9:1; R_f = 0.93] and recrystallization in EtOH yielded 2.19 g (56.8%) of the product as an off-white solid. ^{1}H NMR ($CDCl_3$): δ 8.66 (d, 1H, ^3J = 4.1 Hz, H_a), 8.55 (d, 1H, ^3J = 8.0 Hz, H_d), 8.45 (d, 1H, ^4J = 1.2 Hz, H_e), 8.09 (s, 1H, H_r), 7.87 (m, 1H, H_n), 7.81 (dt, 1H, ^3J = 7.6, ^4J = 1.5 Hz, H_c), 7.69 (d, 1H, ^4J = 1.2 Hz, H_m), 7.40–7.36 (m, 2H, H_p, H_o), 7.33 (d, 1H, ^3J = 3.9 Hz, H_f), 7.29 (t, 1H, ^3J = 5.9 Hz, H_b), 7.05 (d, 1H, ^3J = 3.8 Hz, H_g), 3.02 (q, 2H, ^3J = 7.3 Hz, $-SCH_2CH_3$), 1.36 (t, 3H, ^3J = 7.3 Hz, $-SCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 156.8, 156.6, 155.8, 149.1, 143.2, 142.3, 139.7, 137.4, 137.0, 131.3, 129.7, 129.3, 127.8, 125.9, 124.6, 124.1, 121.5, 116.2, 115.4, 114.3, 27.9, 14.5. HRMS (EI): *m/z* 454.0005 [$(M)^+$] (calcd for $C_{22}H_{17}BrN_2S_2$ *m/z* 453.9996).

*4-(5-(6-(3-Ethoxyphenyl)-2,2′-bipyridin-4-yl)thiophen-2-yl)-N,N-diphenylaniline (**L1H**).* **P6** (498 mg, 1.14 mmol) and *N*,*N*-diphenyl-4-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**P8**) (470 mg, 1.27 mmol) were solubilized in a THF/H_2O (9:1, 125 mL) solution and sparged with N_2 for 10 min. To this solution were then added K_2CO_3 (875 mg, 6.33 mmol) and $Pd(PPh_3)_4$ (102 mg, 0.09 mmol), and the reaction mixture was set to reflux for 14 h under N_2. The reaction mixture was cooled to room temperature and then poured into water. The product was extracted with Et_2O and washed with brine. Organic fractions were combined and dried with $MgSO_4$, filtered, and concentrated by removing the solvent *in vacuo*. The product was purified by column chromatography [SiO_2: CH_2Cl_2/EtOAc, 19:1; R_f = 0.49] to yield 468 mg (68.3%) of the product as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.72 (dd, 1H, ^3J = 4.7, ^4J = 0.8 Hz, H_a), 8.64 (d, 1H, ^3J = 8.0 Hz, H_d), 8.60 (d, 1H, ^4J = 1.6 Hz, H_e), 7.89 (d, 1H, ^4J = 1.6 Hz, H_m), 7.84 (td, 1H, ^3J = 7.6, ^4J = 1.8 Hz, H_c), 7.76 (t, 1H, ^4J = 1.4 Hz, H_r), 7.73 (d, 1H, ^3J = 7.8 Hz, H_n), 7.63 (d, 1H, ^3J = 3.9 Hz, H_f), 7.51 (d, 2H, ^3J = 8.7 Hz, H_h), 7.42 (t, 1H, ^3J = 7.9 Hz, H_o), 7.32 (ddd, 1H, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.8 Hz, H_b), 7.30–7.25 (m, 5H, H_k, H_g), 7.13 (d, 4H, ^3J = 8.3 Hz, H_j), 7.10–7.03 (m, 4H, H_i, H_l), 6.99 (dd, 1H, ^3J = 7.5, ^4J = 1.8 Hz, H_p), 4.16 (q, 2H, ^3J = 7.0 Hz, $-OCH_2CH_3$), 1.48 (t, 3H, ^3J = 7.0 Hz, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 159.6, 157.2, 156.4, 156.3 149.2, 148.0, 147.5, 146.1, 143.3, 141.0, 139.9. 137.0, 129.9, 129.6, 127.9, 126.8, 126.7, 124.9, 124.1, 123.5, 123.5, 123.4, 121.7, 119.6, 116.5, 115.4, 115.2, 113.7, 63.8, 15.1. HRMS (EI): *m/z* 601.2162 [$(M)^+$] (calcd for $C_{40}H_{31}N_3OS^+$ *m/z* 601.2188).

*4-(5-(6-(3-Ethoxyphenyl)-2,2′-bipyridin-4-yl)thiophen-2-yl)-N,N-bis(4-methoyphenyl)aniline (**L2H**).* 4-Methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P9**) (510 mg, 1.18 mmol) and **P6** (465 mg, 1.06 mmol) were solubilized in a 9:1 THF/H_2O (125 mL) solution and degassed for 10 min by sparging with N_2. K_2CO_3 (820 mg, 5.91 mmol) and $Pd(PPh_3)_4$ (100 mg, 0.09 mmol) were then added, and the reaction mixture was refluxed under N_2 overnight. The reaction was then cooled to room temperature and poured into H_2O, and the product extracted with Et_2O. After the Et_2O layer was washed with brine, the organic fractions were collected and dried with $MgSO_4$. The solvent was removed *in vacuo* after filtration to yield an oil, which was solubilized in CH_2Cl_2 and preabsorbed on silica. The sample was purified by column chromatography [SiO_2: CH_2Cl_2/EtOAc, 9:1; R_f = 0.66] to yield 480 mg (68.2%) of the product as a bright yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.71 (d, 1H, ^3J = 4.6 Hz, H_a), 8.63 (d, 1H, ^3J = 7.9 Hz, H_d), 8.58 (d, 1H, ^4J = 1.5 Hz, H_e), 7.89 (d, 1H, ^4J = 1.5, H_m), 7.83 (td, 1H, ^3J = 7.7, ^4J = 1.7 Hz, H_c), 7.75 (s, 1H, H_r), 7.72 (d, 1H, ^3J = 7.8 Hz, H_n), 7.62 (d, 1H, ^3J = 3.8 Hz, H_f), 7.45 (d, 2H, ^3J = 8.8 Hz, H_h), 7.41 (t, 1H, ^3J = 7.9 Hz, H_o), 7.32 (dd, 1H, ^3J = 4.9, ^4J = 1.0 Hz, H_b), 7.21 (d, 1H, ^3J = 3.8 Hz, H_g), 7.08 (d, 4H, ^3J = 8.3 Hz, H_j), 6.98 (dd, 1H, ^3J = 8.1, ^4J = 1.9 Hz, H_p), 6.92 (d, 2H, ^3J = 8.7 Hz, H_i), 6.83 (d, 4H, ^3J = 8.3 Hz, H_k), 4.16 (q, 2H, ^3J = 7.2 Hz, $-OCH_2CH_3$), 3.79 (s, 6H, $-OCH_3$), 1.47 (t, 3H, ^3J = 7.2 Hz, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 159.6, 157.3, 156.4, 156.3, 156.2, 149.2, 148.9, 146.6, 143.4, 141.0, 140.7, 139.4, 137.1, 129.9, 127.0, 126.7, 125.9, 124.0, 122.9, 121.7, 120.4, 119.6, 116.5, 115.4, 115.2, 115.0, 113.7, 63.8, 55.7, 15.1. HRMS (EI): *m/z* 661.2383 [$(M)^+$] (calcd for $C_{42}H_{35}N_3O_3S^+$ *m/z* 661.2399).

*4-(5-(6-(3-(Ethylthio)phenyl)-2,2′-bipyridin-4-yl)thiophen-2-yl)-N,N-diphenylaniline (**L3H**).* After a solution of **P7** (549 mg, 1.21 mmol) and **P8** (500 mg, 1.35 mmol) in THF/water (9:1; 125 mL) was sparged with N_2 for 10 min, K_2CO_3 (933 mg, 6.73 mmol) and $Pd(PPh_3)_4$ (109 mg, 0.09 mmol) were added, and the reaction was left to reflux for 14 h under N_2. The reaction mixture was then cooled and poured into H_2O. The product was extracted with Et_2O (3 × 75 mL) and washed with brine (3 × 100 mL). The organic layer was dried with $MgSO_4$ prior to the removal of the solvent *in vacuo*. The residual brown oil was purified by column chromatography [SiO_2: CH_2Cl_2/EtOAc (9:1); R_f = 0.94] to yield 702 mg (93.8%) of the product as a bright yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.72 (d, 1H, ^3J = 4.8 Hz, H_a), 8.63 (d, 1H, ^3J = 8.0 Hz, H_d), 8.61 (d, 1H, ^4J = 1.5 Hz, H_e), 8.17 (s, 1H, H_n), 7.96 (dt, 1H, ^3J = 6.6, ^4J = 2.2 Hz, H_r), 7.89 (d, 1H, ^4J = 1.5 Hz, H_m), 7.85 (dt, 1H, ^3J = 7.7, ^4J = 1.8 Hz, H_c), 7.64 (d, 1H, ^3J = 3.8 Hz, H_f), 7.52 (d, 2H, ^3J = 8.7 Hz, H_h), 7.49–7.41 (m, 2H, H_p, H_q), 7.33 (ddd, 1H, ^3J = 7.5, ^3J = 4.8, ^4J = 1.1 Hz, H_b), 7.28 (t, 4H, ^3J = 7.9 Hz, H_k), 7.26 (d, 1H, ^3J = 4.3 Hz, H_g), 7.14 (d, 4H, ^3J = 7.5 Hz, H_j), 7.09 (d, 2H, ^3J = 8.6 Hz, H_i), 7.06 (t, 2H, ^3J = 7.4 Hz, H_l), 3.05 (q, 2H, ^3J = 7.3 Hz, $-SCH_2CH_3$), 1.38 (t, 3H, ^3J = 7.3 Hz, $-SCH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 156.9, 156.5, 156.2, 149.2, 148.0, 147.5, 146.2, 143.4, 140.2, 139.8, 137.4, 137.1, 129.8, 129.6, 129.4, 128.0, 127.8, 126.9, 126.8, 125.0, 124.9, 124.8, 124.1, 123.5, 123.4, 121.7, 116.4, 115.5, 28.1, 14.6. HRMS (EI): *m/z* 617.1951 [$(M)^+$] (calcd for $C_{40}H_{31}N_3S_2^+$ *m/z* 617.1959).

*4-(5-(6-(3-(Ethylthio)phenyl)-2,2′-bipyridin-4-yl)thiophen-2-yl)-N,N-bis(4-methoxyphenyl)aniline (**L4H**).* **P7** (475 mg, 1.05 mmol) and **P9** (502 mg, 1.16 mmol) were solubilized in a THF/water solution (125 mL, 9:1 v/v) and sparged with N_2 for 10 min. Following the addition of K_2CO_3 (801 mg, 5.80 mmol) and $Pd(PPh_3)_4$ (102 mg, 0.09 mmol), the reaction mixture was left to reflux overnight under an inert atmosphere. After the reaction mixture was cooled to room temperature it was poured into H_2O. The product was extracted with Et_2O (2 × 100 mL) and washed with brine (2 × 100 mL). The organic fraction was dried with $MgSO_4$ prior to the removal of the solvent *in vacuo*. The resulting oil was purified by column chromatography [SiO_2: CH_2Cl_2/EtOAc (9:1); R_f = 0.91] to yield 335 mg (47.4%) of the product as a bright yellow solid. ^{1}H NMR ($CDCl_3$): δ 8.70 (d, 1H, ^3J = 4.3 Hz, H_a), 8.62 (d, 1H, ^3J = 8.0 Hz, H_d), 8.59 (s, 1H, H_e), 8.16 (s, 1H, H_r), 7.94 (m, 1H, H_n), 7.86 (s, 1H, H_m), 7.82 (dt, 1H, ^3J = 7.8 Hz, ^4J = 1.6 Hz, H_c), 7.59 (d, 1H, ^3J = 3.8 Hz, H_f), 7.46–7.38 (m, 4H, H_h, H_p, H_o), 7.31 (t, 1H, ^3J = 6.7 Hz, H_b), 7.20 (d, 1H, ^3J = 3.8 Hz, H_g), 7.08 (d, 4H, ^3J = 8.9 Hz, H_j), 6.92 (d, 2H, ^3J = 8.0 Hz, H_i), 6.85 (d, 4H, ^3J = 8.9 Hz, H_k), 3.79 (s, 6H, $-OCH_3$), 3.04 (q, 2H, ^3J = 7.3 Hz, $-SCH_2CH_3$), 1.38 (t, 3H, ^3J = 7.3 Hz, $-SCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 156.4, 156.2, 156.1, 156.0, 149.0, 148.7, 146.4, 143.1, 140.4, 139.9, 138.9, 137.3, 136.8, 129.4, 129.2, 127.6, 126.8, 126.7, 126.4, 125.6, 124.6, 123.9, 122.7, 121.4, 120.1, 116.0, 115.2, 114.8, 55.5, 27.8, 14.5. HRMS (EI): *m/z* 677.2187 [$(M)^+$] (calcd for $C_{42}H_{35}N_3O_2S_2^+$ *m/z* 677.2171).

*[Ru(**P7**)(**L5**)]NO_3 (**P10**).* To a suspension of **P7** (553 mg, 1.22 mmol) in MeOH/H_2O/THF (5:1:1, 210 mL) were added Ru(**L5**)Cl_3 (750 mg, 1.22 mmol) and *N*-ethylmorpholine (0.5 mL). After the reaction mixture was left to reflux overnight under an N_2 atmosphere, $AgNO_3$ (622 mg, 3.66 mmol) was added followed by an additional 2 h reflux. The hot solution was filtered, and then the solvent was removed *in vacuo*. Purification of the solid by column chromatography [SiO_2: CH_2Cl_2/MeOH (9:1); R_f = 0.48] yielded 635 mg (50.9%) of the product as a black powder. Low yields were attributed to the difficulty of separating the *ortho* and *para* isomeric products; e.g., *ortho*/*para* 3:1 as determined by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 9.10 (s, 2H, H_E), 8.94 (d, 1H, ^3J = 7.2 Hz, H_d), 8.92 (s, 1H, H_e), 8.86 (s, 2H, H_D), 8.22 (s, 1H, H_m), 8.05 (d, 1H, ^3J = 3.9 Hz, H_f), 7.84 (td, 1H, ^3J = 7.8, ^4J = 1.2 Hz, H_c), 7.70 (d, 1H, ^3J = 7.9 Hz, H_n), 7.68 (d, 2H, ^3J = 5.9 Hz, H_A), 7.65 (dd, 2H, ^3J = 5.9, ^4J = 1.4 Hz, H_B), 7.25 (d, 1H, ^3J = 3.5 Hz, H_g), 6.99 (t, 1H, ^3J = 6.4 Hz, H_b), 6.88 (t, 1H, ^3J = 7.8 Hz, H_o), 6.56 (d, 1H, ^3J = 5.3 Hz, H_a), 6.37 (d, 1H, ^3J = 7.7 Hz, H_p), 4.20 (s, 3H, H_F), 3.94 (s, 6H, H_C), 2.14 (q, 2H, ^3J = 7.3 Hz, $-SCH_2CH_3$), 0.68 (t, 3H, ^3J = 7.3 Hz, $-SCH_2CH_3$); HRMS (ESI): *m/z* 954.0112 [$(M)^+$] (calcd for $C_{43}H_{33}BrN_5O_6RuS_2^+$ *m/z* 954.0126). Anal. Calcd for $C_{43}H_{33}BrN_6O_9RuS_2{\cdot}2H_2O$: C, 48.77; H, 3.52; N, 7.94. Found: C, 48.87; H, 3.34; N, 7.75.

[Ru(L1)(L5)]NO$_3$ (1). To a quantity of **L1H** (242 mg, 0.40 mmol) suspended in MeOH/H$_2$O/THF (5:1:1, 210 mL) were added Ru(**L5**)Cl$_3$ (248 mg, 0.40 mmol) and *N*-ethylmorpholine (0.5 mL). The solution was left to reflux for 14 h and was then cooled to room temperature. To this solution was added AgNO$_3$ (204 mg, 1.20 mmol) prior to an additional 2 h reflux. The solution was filtered while warm prior to the removal of the solvent *in vacuo*. The residue was purified by column chromatography [SiO$_2$: CH$_2$Cl$_2$/MeOH (9:1); R_f = 0.50], yielding 328 mg (78.8%) of the product as a black crystalline solid. ^{1}H NMR (CDCl$_3$): δ 9.10 (s, 2H, H_E), 8.94 (d, 1H, ^3J = 8.3 Hz, H_d), 8.91 (d, 1H, ^4J = 1.2 Hz, H_e), 8.87 (d, 2H, ^4J = 1.1 Hz, H_D), 8.31 (d, 1H, ^4J = 1.2 Hz, H_m), 8.19 (d, 1H, ^3J = 3.9 Hz, H_f), 7.90 (dt, 1H, ^3J = 7.8, ^4J = 1.4 Hz, H_c), 7.68 (d, 2H, ^3J = 5.9 Hz, H_A), 7.63 (dd, 2H, ^3J = 5.9, ^4J = 1.6 Hz, H_B), 7.60−7.56 (m, 3H, H_h, H_n), 7.43 (d, 1H, ^4J = 3.9 Hz, H_g), 7.29 (t, 4H, ^3J = 8.3 Hz, H_k), 7.18−6.98 (m, 9H, H_j, H_i, H_l, H_b), 6.83 (t, 1H, ^3J = 7.8 Hz, H_o), 6.74 (d, 1H, ^3J = 5.4 Hz, H_a), 5.98 (d, 1H, ^3J = 7.9 Hz, H_p), 4.20 (s, 3H, H_F), 3.95 (s, 6H, H_C), 3.06 (q, 2H, ^3J = 6.9 Hz, −O*CH*$_2$CH$_3$), 0.49 (t, 3H, ^3J = 6.9 Hz, −OCH$_2$*CH*$_3$). HRMS (ESI): *m*/*z* 1103.2278 [(M)$^+$] (calcd for C$_{61}$H$_{47}$N$_6$O$_7$RuS$^+$ *m*/*z* 1103.2297). Anal. Calcd for C$_{61}$H$_{47}$N$_7$O$_{10}$RuS·2H$_2$O: C, 60.69; H, 4.26; N, 8.12. Found: C, 60.38; H, 4.09; N, 7.90.

[Ru(L2)(L5)]NO$_3$ (2). To a suspension of **L2H** (246 mg, 0.40 mmol) in MeOH/H$_2$O/THF (5:1:1, 210 mL) were added Ru(**L5**)Cl$_3$ (265 mg, 0.40 mmol) and *N*-ethylmorpholine (0.5 mL). After the reaction mixture was left to reflux for 14 h, it was cooled to room temperature, and AgNO$_3$ (0.204 g, 1.20 mmol) was added before the reaction was left to reflux for an additional 2 h. The solution was gravity filtered while warm prior to removal of the solvent *in vacuo* to yield a dark red solid. This solid was preabsorbed on silica and purified by column chromatography [SiO$_2$: CH$_2$Cl$_2$/MeOH, 9:1; R_f = 0.89] to yield 367 mg (75.4%) of the product as a fine black powder. ^{1}H NMR (CDCl$_3$): δ 9.10 (s, 2H, H_E), 8.87 (s, 2H, H_D), 8.85 (d, 1H, ^3J = 7.1 Hz, H_d), 8.83 (s, 1H, H_e), 8.30 (s, 1H, H_m), 8.13 (d, 1H, ^3J = 3.9 Hz, H_f), 7.87 (t, 1H, ^3J = 7.9 Hz, H_c), 7.66 (d, 2H, ^3J = 5.9 Hz, H_A), 7.61 (dd, 2H, ^3J = 5.9, ^4J = 1.3 Hz, H_B), 7.57 (d, 1H, ^3J = 7.8 Hz, H_n), 7.47 (d, 2H, ^3J = 8.7 Hz, H_h), 7.31 (d, 1H, ^3J = 3.8 Hz, H_g), 7.08 (d, 4H, ^3J = 8.9 Hz, H_j), 7.01 (t, 1H, ^3J = 6.5 Hz, H_b), 6.92 (d, 2H, ^3J = 8.7 Hz, H_i), 6.84 (d, 4H, ^3J = 8.9 Hz, H_k), 6.81 (t, 1H, ^3J = 7.7 Hz, H_o), 6.75 (d, 1H, ^3J = 5.4 Hz, H_a), 5.97 (d, 1H, ^3J = 8.0 Hz, H_p), 4.18 (s, 3H, H_F), 3.93 (s, 6H, H_C), 3.79 (s, 6H, −*OCH*$_3$), 3.05 (q, 2H, ^3J = 6.9 Hz, −O*CH*$_2$CH$_3$), 0.48 (t, 3H, ^3J = 6.9 Hz, −OCH$_2$*CH*$_3$). HRMS (ESI): *m*/*z* 1163.2495 [(M)$^+$] (calcd for C$_{63}$H$_{51}$N$_6$O$_9$RuS$^+$: *m*/*z* = 1163.2509). Anal. Calcd for C$_{63}$H$_{51}$N$_7$O$_{12}$RuS·2H$_2$O: C, 59.71; H, 4.37; N, 7.74. Found: C, 59.36; H, 4.37; N, 7.52.

[Ru(L3)(L5)]HCO$_3$ (3). A combination of **P10** (250 mg, 0.25 mmol) and **P8** (115 mg, 0.31 mmol) in 25 mL of anhydrous DMF was sparged with N$_2$ for 20 min. K$_2$CO$_3$ (345 mg, 2.50 mmol) and Pd(PPh$_3$)$_4$ (40 mg, 0.03 mmol) were then added to the reaction mixture, which was left to stir at 70 °C overnight. The filtered solution was then concentrated by rotary evaporation, followed by the addition of H$_2$O and CH$_2$Cl$_2$. The organic fraction was isolated and dried with MgSO$_4$ prior to the removal of solvent *in vacuo*. The solid was preabsorbed onto silica and purified by column chromatography [SiO$_2$: CH$_2$Cl$_2$/MeOH (9:1); R_f = 0.50] to yield 0.25 g (85.0%) of the product as a dark solid. A gradient elution (6:4) was employed to remove the second and third fractions, which correspond to saponified products. ^{1}H NMR (CDCl$_3$): δ 9.14 (d, 1H, ^3J = 8.3 Hz, H_d), 9.10 (s, 2H, H_E), 9.05 (d, 1H, ^4J = 1.2 Hz, H_e), 8.86 (d, 2H, ^4J = 1.1 Hz, H_D), 8.37 (d, 1H, ^3J = 3.9 Hz, H_f), 8.34 (d, 1H, ^4J = 1.2 Hz, H_m), 7.92 (t, 1H, ^3J = 7.8 Hz, H_c), 7.75 (d, 1H, ^3J = 7.3 Hz, H_n), 7.70 (d, 2H, ^3J = 5.9 Hz, H_A), 7.65 (dd, 2H, ^3J = 5.9, ^4J = 1.6 Hz, H_B), 7.59 (d, 2H, ^3J = 8.8 Hz, H_h), 7.46 (d, 1H, ^4J = 3.9 Hz, H_g), 7.29 (t, 4H, ^3J = 8.3 Hz, H_k), 7.18−7.03 (m, 9H, H_j, H_i, H_l, H_b), 6.90 (t, 1H, ^3J = 7.8 Hz, H_o), 6.54 (d, 1H, ^3J = 5.4 Hz, H_a), 6.37 (d, 1H, ^3J = 7.9 Hz, H_p), 4.21 (s, 3H, H_F), 3.96 (s, 6H, H_C), 2.14 (q, 2H, ^3J = 6.9 Hz, −S*CH*$_2$CH$_3$), 0.69 (t, 3H, ^3J = 6.9 Hz, −SCH$_2$*CH*$_3$). HRMS (ESI): *m*/*z* 1119.2060 [(M)$^+$] (calcd for C$_{61}$H$_{47}$N$_6$O$_6$RuS$_2^+$ *m*/*z* = 1119.2069). Anal. Calcd for C$_{62}$H$_{48}$N$_6$O$_9$RuS$_2$·3H$_2$O: C, 60.04; H, 4.39; N, 6.78. Found: C, 59.93; H, 4.54; N, 7.05.

[Ru(L4)(L5)]HCO$_3$ (4). A mixture of **P9** (130 mg, 0.30 mmol) and **P10** (262 mg, 0.26 mmol) in anhydrous DMF (25 mL) was sparged with N$_2$ for 20 min. Following the addition of K$_2$CO$_3$ (355 mg, 2.56 mmol) and Pd(PPh$_3$)$_4$ (36 mg, 0.03 mmol), the reaction mixture was left overnight under N$_2$ at 70 °C. The reaction mixture was then dried *in vacuo*, preabsorbed onto silica, and purified by column chromatography [SiO$_2$: CH$_2$Cl$_2$/MeOH, (9:1); R_f = 0.39] to yield 120 mg (37.6%) of the product as a fine black powder. A gradient elution (6:4) was employed to remove the second and third fractions corresponding to the mono- and disaponified products, respectively. ^{1}H NMR (CDCl$_3$): δ 9.31 (d, 1H, ^3J = 8.1 Hz, H_d), 9.12 (s, 1H, H_e), 9.08 (s, 2H, H_E), 8.85 (s, 2H, H_D), 8.52 (d, 1H, ^3J = 3.7 Hz, H_f), 8.32 (s, 1H, H_m), 7.94 (t, 1H, ^3J = 7.8 Hz, H_c), 7.74 (d, 1H, ^3J = 7.8 Hz, H_n), 7.68 (d, 2H, ^3J = 5.9 Hz, H_A), 7.63 (d, 2H, ^3J = 5.9 Hz, H_B), 7.48 (d, 1H, ^3J = 8.5 Hz, H_h), 7.36 (d, 1H, ^3J = 3.9 Hz, H_g), 7.09 (d, 4H, ^3J = 8.9 Hz, H_k), 7.07 (t, 1H, ^3J = 7.8 Hz, H_b), 6.93 (d, 2H, ^3J = 8.4 Hz, H_i), 6.87 (t, 1H, ^3J = 7.7 Hz, H_o), 6.84 (d, 4H, ^3J = 8.9 Hz, H_j), 6.53 (d, 1H, ^3J = 5.3 Hz, H_a), 6.35 (d, 1H, ^3J = 7.7 Hz, H_p), 4.19 (s, 3H, H_F), 3.94 (s, 6H, H_C), 3.79 (s, 6H, −*OCH*$_3$), 2.13 (q, 2H, ^3J = 7.3 Hz, −S*CH*$_2$CH$_3$), 0.68 (t, 3H, ^3J = 7.3 Hz, −SCH$_2$*CH*$_3$). HRMS (ESI): *m*/*z* 1179.2277 [(M)$^+$] (calcd for C$_{63}$H$_{51}$N$_6$O$_8$RuS$_2^+$ *m*/*z* = 1179.2280). Anal. Calcd for C$_{64}$H$_{52}$N$_6$O$_{11}$RuS$_2$·5H$_2$O: C, 57.52; H, 4.68; N, 6.29. Found: C, 57.88; H, 4.31; N, 6.17.

Physical Methods. Elemental analysis, electrospray ionization mass spectrometry (ESI-MS), and electron impact (EI) mass spectrometry data were collected at the Chemistry Instrumentation Facility of the University of Calgary. Electrochemical measurements were performed under anaerobic conditions with a Princeton Applied Research VersaStat 3 potentiostat using a dry MeCN solvent, a glassy carbon working electrode, a platinum counter electrode, a silver pseudoreference electrode, and a 0.1 M NBu$_4$BF$_4$ supporting electrolyte. Electronic spectroscopic data were collected on MeCN solutions using a Cary 5000 UV−vis spectrophotometer (Varian). Steady-state emission spectra were obtained at room temperature using an Edinburgh Instruments FLS920 spectrometer equipped with a Xe900 450-W steady-state xenon arc lamp, a TMS300-X excitation monochromator, a TMS300-M emission monochromator, and a Hamamatsu R2658P PMT detector and corrected for detector response. Lifetime measurements were obtained at room temperature using an Edinburgh Instruments FLS920 spectrometer equipped with a Fianium SC400 super continuum white light source and a Hamamatsu R3809U-50 multichannel plate detector, and data were analyzed with Edinburgh Instruments F900 software. Curve fitting of the data was performed using a nonlinear least-squares procedure in the F900 software.

Computational Methods. The Gaussian 03 computational package[25] was used to perform ground-state and transition-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee−Yang−Parr nonlocal correlation functional B3LYP[26−28] and the LANL2DZ basis set[29,30] with an effective core potential for Ru, and a 6-31G* basis set was used for S, C, N, O, and H atoms.[31] Time-dependent density functional theory calculations were also performed using this methodology, and the first 60 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. We modeled the solvent with the polarizable continuum model using MeCN as the solvent.[32]

RESULTS

Synthesis and Structural Characterization. We previously developed a modular synthetic approach to isolate the TPA-functionalized tridentate ligands relevant to this study (Scheme 1).[11,12] Each of these ligands can be accessed using well-established synthetic methods and produced on reasonably large scales. The Kröhnke reagents **P4** and **P5** are prepared from the respective substituted acetylphenones, commercially available 3′-ethoxyacetophenone, and **P2**. Kröhnke condensations with enone **P3** yielded the bromothiophene-substituted

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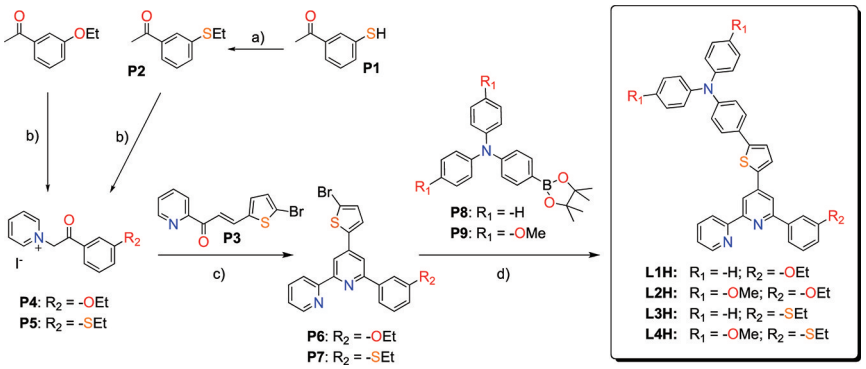
Scheme 1. Syntheses of Ligands L1H−L4H.[a]

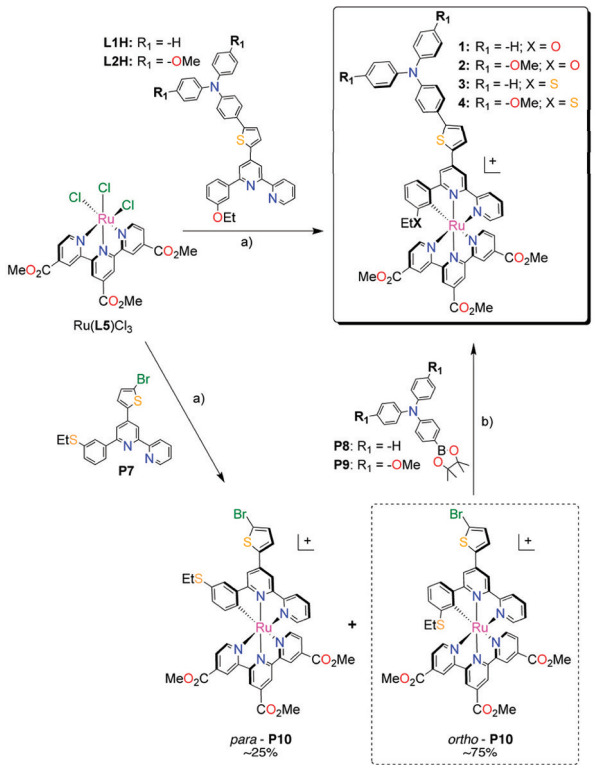


[a]Reaction conditions: (a) $BrCH_2CH_3$, K_2CO_3, EtOH, 78 °C, 14 h; (b) I_2, pyridine, 100 °C, 2.5 h; (c) ammonium acetate, formamide, 120 °C, 14 h; (d) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O (9:1 v/v); 65 °C, 14 h.

pro-ligands **P6** and **P7**, which were poised for further reactions with Suzuki reagents **P8** and **P9** to furnish ligands **L1H−L4H** in high yields.

Cyclometalated Ru(II) complexes **1** and **2** could be isolated in high yields (e.g., >75%) through the reaction of the Ru(**L5**)Cl_3 synthon with **L1H** and **L2H**, respectively (Scheme 2).

Scheme 2. Assembly of Complexes 1−4[a]



[a]Reaction conditions: (a) Step 1: MeOH/H_2O/THF (5:1:1 v/v/v), *N*-ethylmorpholine, 65 °C, N_2, 14 h; step 2: $AgNO_3$, 65 °C, N_2, 2 h; (b) *ortho* product (dashed enclosure) was reacted using K_2CO_3, $Pd(PPh_3)_4$, DMF, 70 °C, N_2, 14 h.

Note that the *ortho*-cyclometalated isomers were obtained in exclusivity in both cases. Following this same synthetic protocol for **3** and **4** (from **L3H** and **L4H**, respectively) yielded a mixture of *ortho*- and *para*-substituted products (i.e., *ortho/para* 3:1 for **3** as determined by ^{1}H NMR spectroscopy) that could not be separated by column chromatography. We therefore had to rely on an alternative method to access the thioether derivatives. The combination of Ru(**L5**)Cl_3 with pro-ligand **P7** (which is devoid of a TPA group) also yields an *ortho/para* 3:1 product distribution for **P10**; however, the absence of the apolar TPA moiety enables the *ortho* product to be isolated from the reaction mixture by column chromatography[33] (Scheme 2). The *ortho* isomer of **P10** could then be functionalized with either **P8** or **P9** to afford **3** and **4**, respectively, using standard Suzuki conditions in DMF.

The ^{1}H NMR spectra reflect the mode of chalcogen substitution of the N^N^C chelate. The spectra for **2** and **4**, for example, indicate that the −OEt group donates more electron density into the anionic ring system than the −SEt group; that is, resonances corresponding to H_n, H_o, H_p, H_d, and H_e are upfield for **2** relative to **4** (Figure 2). The lower degree

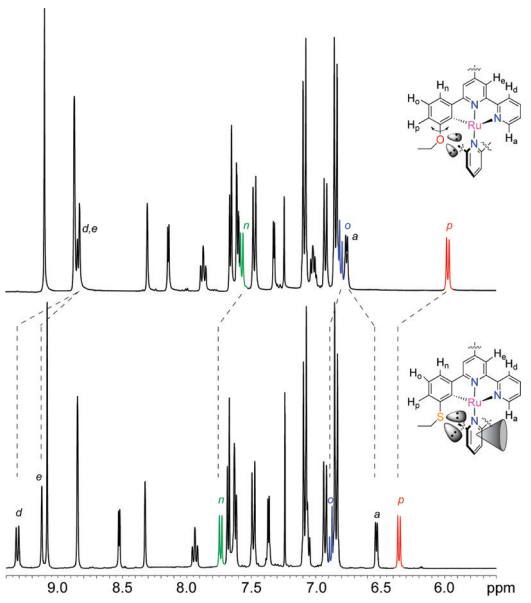


Figure 2. ^{1}H NMR spectra for $CDCl_3$ solutions of **2** (top) and **4** (bottom) at ambient temperature. Signals are assigned according to the labeling scheme provided in Figure 1.

of shielding of these protons is rationalized by the relative donation of the lone pairs of the respective chalcogens into the aromatic system affecting the electron density at the metal center. Molecular modeling shows that there is significant steric

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Table 1. Summary of Spectroscopic and Electrochemical Properties for Cyclometalated Complexes and Ligands Recorded in MeCN

	UV−vis absorbance data (nm)[a]	emission data		$E_{1/2}^{ox}$ (V vs NHE)[d]	
compound	λ_{max} ($\varepsilon \times 10^3$ $M^{-1}\cdot cm^{-1}$)	λ_{em} (nm)[b]	τ (ns); ϕ[c]	Ru(III)/Ru(II)	TPA/$TPA^{\bullet+}$
L1H	390 (38.1)	534 (390)	3.18 (0.97); 0.89		1.12
1	690^{sh} (4.3), 531 (31.2), 431 (49.9)	[e]	[e]	0.97	1.16
L2H	401 (36.3)	614 (400)	0.63 (1.02); 0.11		0.92
2	688^{sh} (3.8), 532 (30.4), 437 (43.9)	[e]	[e]	0.96	0.96[f]
L3H	391 (36.1)	526 (391)	2.94 (1.05); 0.80		1.12
3	686^{sh} (3.5), 574^{sh} (19.3), 530 (26.4), 430 (44.7)	[e]	[e]	1.03	1.18
L4H	402 (34.2)	611 (402)	3.26 (0.97); 0.17		0.92
4	686^{sh} (3.3), 574^{sh} (19.9), 530 (28.0), 435 (41.7)	[e]	[e]	1.04	0.92
P10	686^{sh} (3.4), 574^{sh} (14.3), 530 (16.6), 430 (24.6)	[e]	[e]	1.04	
5	686^{sh} (3.1), 574^{sh} (22.6), 516 (36.8), 425 (48.7)	[e]	[e]	1.15	1.15[f]
L5H	392 (39.8)	545 (391)	3.3 (0.94); 0.81		1.13
6	686^{sh} (2.7), 574^{sh} (20.6), 518 (34.5), 430 (38.6)	[e]	[e]	1.14	0.93
L6H	404 (33.0)	632 (403)	0.5 (0.97); 0.34		0.92
7	680^{sh} (3.5), 583^{sh}, 525 (26.3), 430 (39.8), 329 (42.7)	549 (429)	3.2 (1.02); 0.27	1.04	1.16
L7H	391 (36.0)	552 (389)	3.5 (0.99); 0.66	- [e]	1.14

[a]Recorded at ambient temperature. [b]λ_{ex} indicated in parenthesis in units of nm. Data recorded in deaerated solutions. [c]χ^2 indicated in parenthesis; absolute quantum yield measured with an integrating sphere. [d]Data collected using 0.1 M NBu_4BF_4 MeCN solutions at 100 mV/s and referenced to a $[Fc]/[Fc]^+$ internal standard followed by conversion to NHE; $[Fc]/[Fc^+]$ = +640 mV vs NHE in MeCN. [e]Not observed. [f]Peaks could not be resolved by differential pulse voltammetry (DPV) experiments recorded in MeCN. [sh]Shoulder

gearing in *ortho*-substituted products that inhibits rotation about the bond between the sp^3-hydridized chalcogen and the C_{phenyl}. We also contend that the relatively smaller sp^3 orbitals of the O atoms afford a greater degree of freedom for rotation than those of the S atoms (although the ethyl groups prohibit full rotation in both cases); thus, the larger and more diffuse sp^3 orbitals of the S atom of **4** restrict bond rotation, diminishing electron donation into the π-system of the anionic ring. Note that the diffuse nature of the sulfur orbitals increases the shielding of H_a because it resides in the cone of shielding of the central ring of the adjacent tridendate ligand (qualitatively described in the insets of Figure 2).

Electrochemical Behavior. The electrochemical properties of the free ligands and the corresponding metal complexes were examined in MeCN by cyclic voltammetry (Table 1). Each of the TPA-substituted ligands exhibits a single reversible one-electron oxidation ($E_{1/2,ox}$ = +0.92−1.14 V) that can be attenuated by substitution of the TPA (e.g., −OMe groups lower the oxidation potential by ∼200 mV).[11] The position of this oxidation wave shifts to modestly higher potentials upon coordination to the cationic Ru metal center; however, the TPA and metal-based oxidation potentials of the metal complexes can be independently modulated.

Consistent with our analysis of the NMR spectra that inferred −SEt is acting as a weaker donor than −OEt, the Ru(II)-based oxidation potential of **4** is anodically shifted by ∼80 mV relative to **2**. This observation has important implications in the context of sensitizing n-type semiconductors, where the HOMO should be localized to the TPA rather than the metal to induce favorable charge separation.[11,34,35] The weaker donor character of the −SEt group, for example, results in a higher metal-based oxidation potential to increase the potential for hole transfer to the TPA unit (i.e., the fragment of the molecule which the HOMO is localized to) following a light-induced metal-to-ligand charge-transfer (MLCT) event. Notwithstanding, the difference in energy between the HOMO and HOMO−1 is not sufficiently high when R_1 = H (i.e., **1** and **3**), thus indicating that the TPA unit needs to be furnished with EDGs (e.g., −OMe).

Optical Properties. UV−vis and fluorescence data of the ligands and title complexes are listed in Table 1. Emission was not observed for the cyclometalated complexes, a feature that is commonly observed for complexes of this type owing to the distorted octahedral metal environment and the energy gap law.[15,36,37] We invoke the latter argument to rationalize the lower quantum yields for the −OMe-substituted TPA ligands **L2H** and **L4H** relative to **L1H** and **L3H**.

The UV−vis data for each of the complexes are similar except the bands centered at ca. 530 nm for the thiolate derivatives **3** and **4**, which exhibit slightly lower intensities relative to the alkoxy derivatives. TD-DFT calculations were performed on the geometry-optimized structures to aid in the assignment of the bands (e.g., Figure S1). In the case of **4**, for example, the lowest energy band at ca. 700 nm is predicted to correspond to the promotion of an electron from the HOMO−1 orbital (localized primarily at the Ru and anionic phenyl ring) to a LUMO distributed over the π^*-system of the Me_3tctpy ligand. (We do not, however, rule out direct population of a ^{3}MLCT state facilitated by the heavy Ru metal.[15]) The prominent band centered at ca. 570 nm arises from transitions between the HOMO that is predominantly TPA in character and the LUMO+1, and a higher energy transition from a metal-based HOMO−2 level to the LUMO+1. A major contribution to the high-energy band at ca. 430 nm is provided by a transition between the HOMO and LUMO+3, which is predominantly distributed over the π-system of the bipyridyl fragment of the N^N^C chelate. Note that all of these transitions are appropriate for sensitizing n-type semiconductors in that they involve the movement of electron density toward Me_3tctpy following light absorption.

DISCUSSION

Our program has a longstanding interest in developing cyclometalated Ru(II) chromophores for DSSC applications.[3,14,38,39]

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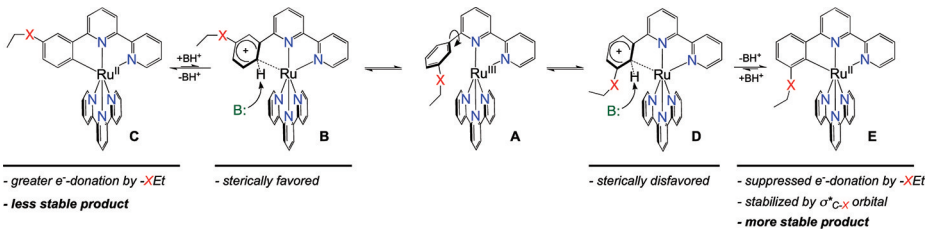
Scheme 3. Factors That Govern the C−H Activation Step for 1−4[a]



It is therefore critical that we have a clear understanding of the requisite C−H activation process during the formation of the target dyes, particularly in cases where different isomers can be generated. An examination of the title complexes and their byproducts offers some important clues into how steric interactions and electronic parameters affect the cyclometalation pathway (as it pertains to octahedral Ru(II) centers within a polypyridyl ligand environment).

The various mechanisms for C−H activation relevant to cyclometalation have been detailed in numerous reviews.[40−43] In general, there are three established mechanisms for cyclometalation: oxidative addition, electrophilic metalation, and σ-bond metathesis (summarized in Figure S3). There is also a less elaborated agostic pathway that possesses features characteristic of both oxidative addition and electrophilic metalation. Each of these pathways is classified according to the orientation of the C−H bond as it approaches the metal, how the C−H bond is cleaved, and the relative thermodynamic stabilities of the organometallic products.

One particular study that offers some insight into the favored *ortho* product distribution of **1**−**4** compares the C−H activation process for a series of haloarenes and anisole. In this study by Milstein et al.,[44] it was established that the *ortho*-metalated Ir pincer products were produced via an oxidative addition pathway that involved the stabilization of the transition state and the thermodynamic product by the coordination of the halide/oxygen to an empty metal orbital. This same analysis does not apply to our systems, however, as the metal will inherently be bound to five pyridine rings prior to C−H activation, and thus a second coordination site is not available for oxidative addition. (The same argument excludes σ-bond metathesis.) Moreover, an oxidative addition pathway demands an ∠MHC angle of 130° in the transition state for an idealized arrangement of the C−H bond and the metal d orbitals (i.e., this angle provides favorable overlap between the d_{Ru} and σ_{C-H} orbitals while accommodating back-donation from the d_{π} orbital to the σ^*_{C-H} to destabilize the C−H bond).[42] This bond angle in the transition state of our systems is predicted to be far from this idealized value [i.e., ∠MHC = 100.1° (−OEt) and 103.9° (−SEt); Figure S2]. An agostic pathway can also be eliminated because the Lewis bases present under our reaction conditions (e.g., MeOH, H_2O) are stronger donors than the C−H fragment of the phenyl ring and would therefore preclude a dominant interaction from occurring. Furthermore, agostic interactions typically require a geometric confinement of the molecule; yet in our case the pbpy ligand is able to undergo free rotation prior to cyclometalation because the O and S atoms at R_2 are unable to interact (due to geometric constraints) with the metal to mediate the agostic interaction.

Elimination of these other pathways led us to infer that the formation of **1**−**4** proceeds via an electrophilic metalation reaction (Figure S3). The high-valent Ru(III) precursor and electron-withdrawing methyl-ester groups afford an electrophilic metal center primed for electrophilic metalation, which are often observed for electron-poor late transition metals.[40] We also note that there exists a close contact between the Ru and C_{phenyl} atoms that would enable an electrophilic mechanism (Figure S2), while the large metal−chalcogen distances rule out a directing effect induced by a Lewis base coordination. Electrophilic metalations involving substituted aromatic molecules typically show little selectivity between different C−H bonds, and the observed selectivity is usually a consequence of steric factors. This trend, however, is not observed in the cases of **1**−**4**. A nonlinear extrapolation of the electrochemical data for the title compounds (and related complexes[4,11,12,45]) indicates that −OMe groups *para* and *ortho* to the organometallic bond lower the metal-based oxidation potential by ∼130 and ∼70 mV, respectively. Consequently, the *ortho* isomer is thermodynamically favored and prevails over the higher steric congestion provided by the ethyl groups. There also exists evidence in the literature that the preference for C−H activation of aromatic rings *ortho* to fluorine substituents arises because the carbanion is stabilized by the adjacent σ^*_{C-F} orbital.[16,17] We surmise that this same effect is operative for the σ^*_{C-O} orbital to favor the *ortho* isomer. This line of reasoning also translates to the thiolate derivatives; however, the poorer orbital overlap leads to a lower thermodynamic preference for substitution at the *ortho* position. Note that the difference in the metal-based oxidation potentials of the *para* and *ortho* isomers where X = SEt is nominal, which lends credence to the σ^*_{C-S} orbital playing a role in stabilizing the relatively sterically encumbered *ortho* product.

The relative isomeric ratios that are observed can therefore be attributed to a combination of the chalcogen stabilizing the carbanion of the activated phenyl ring through inductive effects and the relative thermodynamic stabilities of the products due to π-donation into the phenyl ring. Scheme 3 summarizes the proposed chalcogen-assisted *ortho*-metalation step commencing from the intermediate complex with five $Ru-N_{pyridine}$ bonds and a vacant coordination site due to dissociation of the Cl^- ligand (i.e., **A**). It is the bidendate coordination mode of the pbpy ligand, which enables free rotation of the benzene ring bearing the chalcogen substituent, that is responsible for the observation of the different isomers. Intermediate **A** can then undergo an electrophilic metalation step *para* to the substituent to form intermediate **B** prior to the formation of the *para* product **C**.

In cases where the phenyl ring is substituted by π-donating substituents, **E** is thermodynamically favored over **C**, thus shifting the equilibria in favor of the *ortho* isomer. However, steric congestion arising from the ethyl groups can inhibit appropriate orbital overlap with the aromatic π-system, leading to a diminution of the effective electron-donating character of the substituents. When X = −SEt, this steric gearing, in tandem

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with the poor orbital overlap between the thiolate and the aromatic π-system, suppresses electron donation into the aryl ring to render **C** and **E** nearly degenerate. When X = −OEt, this steric gearing stabilizes **E** relative to **C** (because of the more prominent differences in lone pair donation from the O atom into the phenyl ring) to govern the exclusive formation of the *ortho* isomer. This effect is compounded by stabilization of the carbanion by the σ^*_{C-O} orbital.

Summary. We have presented a series of bis-tridentate Ru(II) complexes bearing a cyclometalating ligand functionalized with EDGs and EWGs. This study lays out experimental evidence that sheds light on why the activation of the C−H bond *ortho* to the EDGs is favored, even in cases where there is significant steric congestion. We show that there is subtle interplay between steric interactions and the relative stabilities of both the products and the preceding intermediates that govern the formation of each of the isomers. These results offer important experimental insight into the C−H activation process.

■ ASSOCIATED CONTENT

Supporting Information

TD-DFT data and transition-state modeling are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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