ORGANOMETALLICS

Ruthenium-Amine Electronic Coupling Bridged through Phen-1,3diyl Versus Phen-1,4-diyl: Reverse of the Charge Transfer Direction

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Supporting Information

ABSTRACT: Three tris-bidentate cyclometalated ruthenium complexes with a di(*p*-anisyl)amino $[5(PF_6)]$, di(*p*-tolyl)-amino $[6(PF_6)]$, or di(*p*-chlorophenyl)amino $[7(PF_6)]$ substituent on the cyclometalating phenyl ring have been prepared, where the amine nitrogen is in the meta position to the cyclometalated site (bridged through the phen-1,3-diyl unit). The structure of $6(PF_6)$ has been confirmed by single-crystal X-ray diffraction analysis. Two consecutive redox waves



are evident at +0.48 and +0.87 V versus Ag/AgCl for $5(PF_6)$, +0.51 and +1.02 V for $6(PF_6)$, and +0.53 and +1.18 V for $7(PF_6)$, respectively. The first wave is assigned to the Ru(II/III) process, and the second wave is attributed to the N(0/+) process. After one-electron oxidation using SbCl₅, these complexes display distinct absorptions in the near-infrared region, which are assigned to the nitrogen-to-ruthenium intervalence charge-transfer (ICVT) transitions. The energies of the IVCT transitions vary linearly versus the potential splitting of the Ru(II/III) and N(0/+) process. The charge-transfer direction in these complexes is reversed with respect to a previously reported ruthenium–amine system where the amine nitrogen is in the para position to the cyclometalated site (bridged through the phen-1,4-diyl unit).

INTRODUCTION

The study of electron-transfer in mix–valence (MV) systems $[M^1-BL-M^2]^{n\pm}$ (BL = bridging ligand) has been the focus of many research activities.¹ The charge-bearing sites M¹ and M² can either be an organometallic² or a purely organic unit³ with well-defined redox processes. By analyzing the intervalence charge-transfer (IVCT) transition in the near-infrared (NIR) region, useful information, such as reorganization energy (λ), electronic coupling parameter (V_{ab}), and degree of charge delocalization, can be accessed.^{1–3} This information is of fundamental importance for the understanding of the electron transfer process occurring in natural systems and the design of molecular materials for electronics and optoelectronics.⁴

When $M^1 = M^2$, the two-state Marcus–Hush theory⁵ predicts the energy of the IVCT band $E_{op} = \lambda$. In the case of the redox asymmetric system $(M^1 \neq M^2)$, an additional term ΔG^0 , the energy difference between the ground state and charge-separated state, is needed, namely, $E_{op} = \lambda + \Delta G^0$. The variation of the electronic nature of donor and/or acceptor will change ΔG^0 , and consequently E_{op} . The examination of the influence of different substituents on the IVCT band and electron transfer parameters bears much interest in MV chemistry.⁶

One topic of current interest is the reverse of the charge transfer direction in systems with donor and acceptor of similar redox potentials. For instance, Nishihara and co-workers reported that the charge transfer direction in ferrocene– dithiolene hybrids can be reversed by attaching a platinum component to the dithiolene unit.⁷ In the studies of electron transfer between a [Ru(NNN)(NCN)]-type cyclometalated ruthenium and ferrocene, we previously found that the charge transfer direction was different when the ferrocene unit was attached on the NNN ligand versus NCN ligand.⁸ These materials have implications for the design of new charge transfer systems and molecular switches.⁴

Triarylamines show one-electron oxidation processes centered on nitrogen $(N^{0/+})$ and are extensively used in symmetric organic MV systems.9 Cyclometalated ruthenium complexes with an anionic carbon ligand possess Ru^{II/III} processes at relatively low potentials with respect to noncyclometalated ruthenium complexes.¹⁰ Their uses in symmetric bisruthenium systems have been well-documented.¹¹ We previously reported a hybrid of triarylamine and cyclometalated ruthenium, where the amine nitrogen is in the para position to the cyclometalated site (bridged through phenyl-1,4-diyl) (see Figure 1).¹² The odd electron is quite delocalized but more biased at the triarylamine site, according to electrochemical, spectroscopic, electronic paramagnetic resonance (EPR), and density functional theory (DFT) results. This complex shows narrow and intense Ru \rightarrow N⁺ IVCT transitions at 1050 nm in the MV state. In this contribution, we present the synthesis and electron transfer studies of complexes $5(PF_6)-7(PF_6)$ (Scheme 1), where the amine nitrogen is in the meta position to the

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Figure 1. Ruthenium-amine hybrid.



cyclometalated site (bridged through phenyl-1,3-diyl) and a reversed charge transfer from N to Ru is realized (after one-electron oxidation).

RESULTS AND DISCUSSION

Syntheses and Single-Crystal Structure. Complexes $5(PF_6) - 7(PF_6)$ were prepared as outlined in Scheme 1. The Stille coupling between 1,4-dibromobenzene and 2-(tributylstannyl)pyridine gave 2-(4-bromophenyl)pyridine in 57% yield.¹³ Ligands 2-4 were synthesized from the palladiumcatalyzed C-N coupling¹⁴ between 2-(4-bromophenyl)pyridine and corresponding diphenylamine derivatives. The MeO, Me, and Cl substituents on the ligand were selected to vary the redox potential of the amine site. The reaction of 2-4with $[Ru(p-cymene)Cl_2]_2$ in the presence of KPF₆ and NaOH gave a ruthenium intermediate, which was complexed with 2,2'bipyridine (bpy) to afford $5(PF_6)-7(PF_6)$ in moderate yields. Similar procedures have been used for the synthesis of cyclometalated ruthenium complexes.¹⁵ The MALDI mass spectra of $5(PF_6) - 7(PF_6)$ show signals corresponding to the losses of the PF₆ anion (795.2, 763.3, and 803.0, respectively). The ¹³C NMR signal around at 195 ppm is assigned to the carbon atom connected to the ruthenium ion.

A single crystal of $6(PF_6)(CHCl_3)$ was obtained by diffusion of petroleum ether into a solution in $CHCl_3$.¹⁶ The thermal ellipsoid plot of the X-ray structure is displayed in Figure 2. The ruthenium ion has a $[(NN)_2(CN)]$ -type tris-bidentate coodination geometry. The Ru1–C1 bond has a length of 2.04 Å. The Ru1–N3 bond opposite to the Ru1–C1 bond has a length of 2.15 Å. Other Ru–N bonds are in the range of 2.05–2.10 Å. Similar geometrical distances have been reported for cyclometalated ruthenium complexes.¹⁷



Figure 2. Thermal ellipsoid plot of the single-crystal structure of $6(PF_6)(CHCl_3)$ with 30% probability. Hydrogen atoms, solvent, and anion are omitted for clarity. Atom color code: carbon, gray; nitrogen, blue; ruthenium, magenta. Selected bond length and angle: Ru1–C1, 2.04 Å; C2–N6, 1.43 Å; Ru1–N1, 2.05 Å; Ru1–N2, 2.05 Å; Ru1–N3, 2.15 Å; Ru1–N4, 2.07 Å; Ru1–N5, 2.10 Å; \angle C1–Ru1–N5 = 79.3°; \angle N5–Ru1–N3 = 95.4°.

Electrochemical Studies. Figure 3 (panels a and b) shows the cyclic voltammograms (CVs) and differential pulse



Figure 3. (a) DPVs and (b) CVs of $5(PF_6)$ (black curves), $6(PF_6)$ (red curves), and $7(PF_6)$ (blue curves) in CH₂Cl₂. (c) CVs of **2** (black curves), **3** (red curves), and **4** (blue curves) in CH₂Cl₂.

voltammograms (DPVs) of $5(PF_6)-7(PF_6)$ versus Ag/AgCl. All complexes display two well-defined redox processes. The first series waves are at +0.48, +0.51, and +0.53 V for $5(PF_6) 7(PF_6)$, respectively. The second series waves are at +0.87, +1.02, and +1.18 V, respectively. The potential differences between the anodic and cathodic peaks of all redox couples in Figure 3b are in the range of 70–95 mV. This difference is slightly bigger than that of a typical diffusion-controlled oneelectron Nernstian wave (59 mV). In consideration of the fact that complex [Ru(bpy)₂(ppy)](PF_6) [ppy is the 2-deprotonated form of (pyrid-2-yl)benzene] has a Ru^{II/III} potential of +0.70 V versus NHE (around +0.50 V vs Ag/AgCl)¹⁸ and compounds 2–4 have the N^{0/+} potential of +0.74, +0.90, and +1.10 V, respectively (Figure 3c), it would be safe to conclude that the Ru^{II/III} process occurs prior to the N^{0/+} process for $5(PF_6)-7(PF_6)$. This is in stark contrast with the previously reported complex $1(PF_6)_2$, where the Ru^{II/III} process occurs after the N^{0/+} process.¹² The potential difference ΔE between the Ru^{II/III} process and N^{0/+} process is 390, 510, and 650 mV for $5(PF_6)-7(PF_6)$, respectively. The comproportionation constant K_c for the equation Ru^{II}-N⁰ + Ru^{III}-N⁺ $\rightarrow 2(Ru^{III}-N^0)$ of these three complexes is calculated to be 4.1 $\times 10^6$, 4.4 $\times 10^8$, and 10.4 $\times 10^{10}$, respectively. These results are summarized in Table 1.

Table	1.	Electrochemical	Data ^{<i>a</i>}
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compound	E_1 (V)	E_2 (V)	$\Delta E \ (mV)^b$	$K_{\rm c}^{\ c}$
$1(PF_6)_2$	0.27	0.68	410	8.9×10^{6}
2	0.74	-	_	_
3	0.90	-	_	_
4	1.10	-	_	_
$5(PF_6)$	0.48	0.87	390	4.1×10^{6}
$6(PF_6)$	0.51	1.02	510	4.4×10^{8}
$7(PF_6)$	0.53	1.18	650	10.4×10^{10}
$[Ru(bpy)_2(ppy)](PF_6)^d$	0.50	-	_	_

^{*a*}Potentials were reported vs Ag/AgCl. Potentials versus ferrocene^{0/+} can be estimated by subtracting 0.45 V. ^{*b*} $\Delta E = E_2 - E_1$. ^{*c*} $K_c = 10^{(\Delta E/59)}$. ^{*d*}See ref 18.

Because complexes $5(PF_6)-7(PF_6)$ have substituents with significantly different electronic nature on the amine component, the energetic asymmetry ΔG^0 must be different for three compounds, which results in the big difference of the above ΔE values.

Spectroscopic Studies. To probe the electron transfer process of $5(PF_6) - 7(PF_6)$, their absorption spectral changes were monitored upon single (one-electron) and double (the second one-electron) oxidation with SbCl₅ in CH₂Cl₂ (Figure 4).^{6,9,11} During these two-step processes, $5(PF_6)-7(PF_6)$ exhibited similar spectral changes. In the single oxidation step, the absorption bands in the visible region decreased significantly, and a broad transition in the NIR region appeared. The latter band is assigned to the $N \rightarrow Ru$ IVCT transition, and it disappeared in the double oxidation step. The intense peak around 800 nm in Figure 4 (panels b, d, and f) is due to the Nº+-localized transition, which has previously observed in oneelectron-oxidized form of triarylamines.9,19 This, in turn, supports that the second oxidation step of $5(PF_6)-7(PF_6)$ is associated with the N^{0/+} process. The appearance and disappearance of the IVCT band was also evidenced during spectroelectrochemical measurements (Figure S1 of the Supporting Information).

The substituents on the amine component has a dramatic impact on the energy (E_{op}) and band shape of the IVCT band of $S^{2+}-7^{2+}$ (Figure 5 and Table 2). For example, the IVCT band of 7^{2+} is around 400 nm blue shifted with respect to that of S^{2+} , and the former is much narrower relative to the latter. Such an effect clearly arises from the increased redox asymmetry of 7^{2+} versus S^{2+} , as reflected by their different ΔE values. A plot of E_{op} versus the redox splitting ΔE is approximately linear (Figure 5b). Such a correlation has previously been found in redox asymmetric MV systems,²⁰ indicating that the optical electron transfer has a common λ , and the IVCT band varies almost exclusively with ΔE .

The IVCT bands of $5^{2+}-7^{2+}$ are moderate and broad. They are assigned to the Robin-Day class II systems.^{2,3} The coupling parameter V_{ab} was estimated to be about 500 cm⁻¹ for three complexes, according to the Hush formula⁵ $V_{ab} = 0.0206 \times$ $(\varepsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2}/(r_{ab})$, where $\nu_{max} = E_{op}$ in cm⁻¹, $\Delta\nu_{1/2}$ is the bandwidth at half-height after Guassin-fitting, and r_{ab} is taken to be the Ru–N distance from the crystallographic data (5.52 Å).

It should be pointed out that no distinct emission has been observed for complexes $5(PF_6)-7(PF_6)$ in CH_2Cl_2 solution at room temperature. Previous studies showed that the emission of conventional polypyridyl ruthenium complexes with a Ru–C bond is very weak.¹⁸

DFT Studies. No distinct EPR signal has been observed for $5(PF_6)-7(PF_6)$ after one-electron oxidation using SbCl₅. This may be caused by the fast spin relaxation of the ruthenium ion. The geometry of the closed-shell complex 6^+ was optimized using the B3LYP, B3PW91, MPW1PW91, or PBE1PBE functionals (see details in the Experimental Section). However, all calculations led to the highest occupied molecular orbital (HOMO) dominated by the triarylamine unit (Figure S2 of the Supporting Information), which is separated from the HOMO-1 with over 0.5 eV. In addition, the DFT-predicted spin-density of the open-shell state 6^{2+} using the B3LYP functional is also mainly distributed among the triarylamine component (Figure S3 of the Supporting Information). These theoretical results suggest that the triarylamine component in 6^{2+} will be first oxidized. However, the above electrochemical and spectroscopic experimental findings strongly suggest that the ruthenium component in $5(PF_6) - 7(PF_6)$ is first oxidized. This means that the current DFT method is not suitable for predicting the electronic structures of these complexes. However, the discrepancy between theoretical and experimental results may be caused by the overestimation of delocalization by DFT methods.

CONCLUSION

In summary, the charge transfer direction in the cyclometalated ruthenium-amine MV system was reversed by changing the para position of two redox sites to the meta position. The IVCT energy and shape can be tuned by substituents on the amine component. This information is of interest and importance for the design and synthesis of new asymmetric MV systems.

EXPERIMENTAL SECTION

Synthesis. NMR spectra were recorded in the designated solvent on Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvent. Mass data were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is α -cyano-4-hydroxycinnamic acid. Microanalysis was carried out using Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

2-(4-Bromophenyl)pyridine. This compound was prepared according to a known procedure.¹³ To a solution of 1,4-dibromobenzene (2.0 mmol, 472 mg) and 2-(tributylstannyl)pyridine (2.0 mmol, 736 mg) in 15 mL of dry toluene were added Pd(PPh₃)₂Cl₂ (0.080 mmol, 56.2 mg) and LiCl (16.0 mmol, 678 mg). The mixture was bubbled with nitrogen for 15 min and heated at 110 °C for 10 h. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: CH₂Cl₂/petroleum ether, 2/1) to afford 269 mg of 2-(4-bromophenyl)pyridine as a white solid in 57% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.25 (overlapped with solvent residual, 1H), 7.61 (d,



Figure 4. Electronic absorption spectral changes of (a and b) $S(PF_6)$, (c and d) $G(PF_6)$, and (e and f) $7(PF_6)$ in CH_2Cl_2 upon (a, c, and e) single and (b, d, and f) double oxidation with $SbCl_5$. Symbol *: artifacts.

J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.66–7.70 (m, overlapped, 2H), 8.68 (d, J = 4.8 Hz, 1H).

2-[4-(Di-p-anisylamino)phenyl]pyridine (2). To a solution of 2-(4-bromophenyl)pyridine (1.0 mmol, 234 mg) and 4,4'-dimethoxydiphenylamine (1.5 mmol, 344 mg) in 15 mL of dry toluene were added Pd2(dba)3 (0.050 mmol, 45.8 mg), 1,1'-bis-(diphenylphosphino)ferrocene (dppf, 0.050 mmol, 27.7 mg) and NaO'Bu (1.2 mmol, 115.3 mg). The mixture was bubbled with nitrogen for 10 min and then heated at 110 °C for 30 h. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 8/1) to afford 119 mg of 2 as a yellow solid in 46% yield. ¹H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 6H), 6.85 (d, J = 8.8 Hz, 4H), 6.99 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 4H), 7.15 (t, J = 6.0 Hz, 1H), 7.62-7.76 (m, overlapped, 2H), 7.81 (d, J = 8.8 Hz, 2H), 8.63 (d, J = 4.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 55.50, 114.75, 119.58, 120.10, 121.13, 126.86, 127.55, 131.10, 136.59, 140.62, 149.49, 149.59, 156.10, 157.22. EI-HRMS (m/z) calcd for $C_{25}H_{22}N_2O_2$: 382.1681; found: 382.1687.

2-(4-(Di-*p***-tolylamino)phenyl)pyridine (3).** To a solution of 2-(4-bromophenyl)pyridine (1.0 mmol, 234 mg) and di-*p*-tolylamine (1.5 mmol, 296 mg) in 15 mL of dry toluene were added $Pd_2(dba)_3$ (0.050 mmol, 45.8 mg), dppf (0.050 mmol, 27.7 mg), and NaO^tBu (1.2 mmol, 115.3 mg). The mixture was bubbled with nitrogen for 10 min and then heated at 110 °C for 30 h. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: petroleum ether/CH₂Cl₂/ethyl acetate, 15/15/2) to afford 182 mg of **3** as a yellow solid in 52% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.33 (s, 6H), 7.05–7.12 (m, overlapped, 10H), 7.15–7.20 (m, 1H), 7.63 (m, overlapped, 2H), 7.83 (d, J = 8.8 Hz, 2H), 8.64 (d, J = 4.4 Hz, 1H). ¹³C NMR (400 MHz, CDCl₃): δ 20.87, 119.74, 121.28, 121.99, 124.99, 127.58, 129.96, 132.16, 132.93, 136.59, 145.01, 149.08, 149.56, 157.20. EI-HRMS (m/z) calcd for C₂₅H₂₂N₂: 350.1783; found: 350.1788.

2-[4-(Di-*p***-chlorophenylamino)phenyl]pyridine (4).** To a solution of 2-(4-bromophenyl)pyridine (1.0 mmol, 234 mg) and bis(4-chlorophenyl)amine (1.5 mmol, 357 mg) in 15 mL of dry toluene were added Pd₂(dba)₃ (0.050 mmol, 45.8 mg), dppf (0.050 mmol, 27.7 mg), and NaO^tBu (1.2 mmol, 115.3 mg). The mixture was bubbled with nitrogen for 10 min and then heated at 110 °C for 30 h. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: petroleum ether/CH₂Cl₂, 1/2) to afford 171 mg of **4** as a yellow solid in 44% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.04 (d, *J* = 8.4 Hz, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.18–7.30 (m, overlapped, 5H), 7.67–7.76 (m, overlapped, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 8.66 (d, *J* = 4.8 Hz, 1H). ¹³C NMR (400 MHz, CDCl₃): δ 119.96, 121.75, 123.65, 125.58, 128.04, 128.44, 129.56, 134.16, 136.72, 145.77, 147.85, 149.69, 156.75. EI-HRMS (*m*/*z*) calcd for C₂₃H₁₆Cl₂N₂: 390.0691; found: 390.0695.

Synthesis of Complex 5(PF₆). To a suspension of $[Ru(p-cymene)Cl_2]_2$ (0.060 mmol, 36.7 mg), KPF₆ (0.20 mmol, 37.2 mg), and crushed NaOH (0.10 mmol, 4.0 mg) in 10 mL of dry CH₃CN was added ligand 2 (0.10 mmol, 38.2 mg). The resulting mixture was stirred at 55 °C for 15 h under a nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was subjected to flash column chromatography on neutral Al₂O₃ (CH₂Cl₂/CH₃CN, 20/1).



Figure 5. (a) Observed and Gaussian-simulated IVCT transitions of 5^{2+} (black curves), 6^{2+} (red curves), and 7^{2+} (blue curves) as a function of wavenumbers. Symbol *: artifacts. (b) Linear fit of E_{op} vs ΔE . $R^2 = 0.93997$.

The yellow band was collected, and the solvent was removed to give an intermediate as a yellow solid. To this intermediate were added 2,2'-bipyridine (bpy, 0.25 mmol, 39.1 mg) and 10 mL of distilled DMF. The resulting mixture was stirred at 130 °C for 5 h under nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (ethyl acetate/acetone/H2O, 15/15/1) to give 47 mg of $5(PF_6)$ as a deep red solid in 51% yield. ¹H NMR (400 MHz, CD_3CN): δ 3.79 (s, 6H), 5.62 (d, J = 2.4 Hz, 1H), 6.30 (dd, J = 8.8, 2.4 Hz, 1H), 6.70-6.85 (m, overlapped, 9H), 6.90 (t, J = 6.4 Hz, 1H), 7.20-7.30 (m, 2H), 7.35-7.45 (m, 2H), 7.45-7.55 (m, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 8.0 Hz, 2H), 7.89 (d, J = 5.2 Hz, 2H), 7.95 (t, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H),8.18 (d, J = 5.6 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H). ¹³C NMR (100 MHz, CD₃CN): δ 56.11, 112.45, 115.48, 121.47, 123.83, 124.20, 124.40, 124.83, 125.51, 126.85, 127.08, 127.83, 128.32, 134.02, 134.39, 136.72, 136.29, 137.11, 137.85, 141.09, 149.66, 150.06, 150.48, 150.81, 150.48, 150.81, 151.06, 154.87, 156.05, 157.16, 157.64, 158.60, 167.93, 195.00. MALDI-MS (m/z): 795.2 for $[M - PF_6]^+$. Anal. Calcd for $C_{45}H_{37}F_6N_6O_2PRu$: C, 57.51; H, 3.97; N, 8.94; found: C, 57.46; H, 4.19; N, 8.68.

Synthesis of Complex 6(PF₆). To a suspension of $[Ru(p-cymene)Cl_2]_2$ (0.060 mmol, 36.7 mg), KPF₆ (0.20 mmol, 37.2 mg), and crushed NaOH (0.10 mmol, 4.0 mg) in 10 mL of dry CH₃CN was added ligand 3 (0.10 mmol, 35.1 mg). The resulting mixture was stirred at 55 °C for 15 h under a nitrogen atmosphere. The solvent was then removed under reduced pressure. The residue was subjected to flash column chromatography on neutral Al₂O₃ (CH₂Cl₂/CH₃CN, 10/1). The yellow band was collected, and the solvent was removed to

give an intermediate as a yellow solid. To this intermediate were added 2,2'-bipyridine (0.25 mmol, 39.1 mg) and 10 mL dry DMF. The resulting mixture was stirred at 130 °C for 5 h under nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/acetone/H₂O, 8/8/3) to give 41 mg of $6(PF_6)$ as a deep red solid in 45% yield. ¹H NMR (400 MHz, CD₃CN): δ 2.31 (s, 6H), 5.70 (d, J = 2.4 Hz, 1H), 6.39 (dd, J = 8.4, 2.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 4H), 6.80 (t, J = 6.0 Hz, 1H), 6.91 (t, J = 6.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 4H), 7.24 (t, J = 6.4 Hz, 1H), 7.29 (t, J = 6.0 Hz, 1H),7.39 (t, J = 6.4 Hz, 1H), 7.40–7.52 (m, overlapped, 3H), 7.58 (t, J =6.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.79–7.85 (m, overlapped, 3H), 7.88 (d, J = 5.6 Hz, 1H), 7.91 (d, J = 5.6 Hz, 1H), 7.98 (t, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 5.2 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CD₃CN): δ 20.46, 118.49, 119.06, 121.50, 122.38, 123.26, 123.37, 123.69, 123.90, 125.93, 126.45, 126.45, 126.78, 127.50, 130.32, 133.58, 133.60, 134.15, 135.37, 135.91, 136.14, 136.75, 136.84, 145.29, 148.33, 149.95, 150.16, 150.47, 150.83, 154.68, 155.71, 157.16, 157.37, 158.29, 167.23, 193.50. MALDI-MS (m/z): 763.3 for $[M - PF_{6}]^{+}$. Anal. Calcd for C45H37F6N6PRu: C, 59.53; H, 4.11; N, 9.26; found: C, 59.18; H, 4.19; N, 9.11.

Synthesis of Complex $7(PF_6)$. To a suspension of [Ru(pcymene)Cl₂]₂ (0.060 mmol, 36.7 mg), KPF₆ (0.20 mmol, 37.2 mg), and crushed NaOH (0.10 mmol, 4.0 mg) in 10 mL dry $\rm CH_3CN$ was added ligand 4 (0.10 mmol, 39.0 mg). The resulting mixture was stirred at 55 °C for 15 h under a nitrogen atmosphere. The solvent was then removed under reduced pressure. The residue was subjected to flash column chromatography on neutral Al₂O₃ (CH₂Cl₂/CH₃CN, 10/1). The yellow band was collected, and the solvent was removed to give an intermediate as a yellow solid. To this intermediate were added 2,2'-bipyridine (0.25 mmol, 39.1 mg) and 10 mL dry DMF. The resulting mixture was stirred at 130 °C for 5 h under a nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/acetone/H₂O, 15/15/1) to give 45 mg of 7(PF₆) as a deep red solid in 48% yield. ¹H NMR (400 MHz, CD₃CN): δ 5.70 (d, J = 2.4 Hz, 1H), 6.53 (dd, J = 8.4, 2.4 Hz, 1H), 6.80–6.90 (m, overlapped, 5H), 6.96 (t, J = 6.4 Hz, 1H), 7.20 (d, J = 8.8 Hz, 4H), 7.25-7.30 (m, 2H), 7.40 (t, J = 6.4 Hz, 1H), 7.49 (t, J = 4.8 Hz, 2H), 7.56–7.62 (m, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.80–7.90 (m, 4H), 7.91 (d, J = 5.2 Hz, 1H), 7.97 (t, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H),8.16 (d, J = 6.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 8.4 Hz, 1H). ¹³C NMR (100 MHz, CD₃CN): δ 115.28, 118.79, 122.00, 123.31, 123.37, 123.73, 123.95, 125.17, 126.53, 126.61, 126.71, 126.81, 127.49, 128.25, 128.52, 129.75, 133.70, 134.25, 135.49, 136.14, 136.84, 140.58, 146.42, 147.46, 149.77, 150.28, 150.65, 150.74, 154.60, 155.62, 157.16, 157.21, 158.18, 167.19, 195.34. MALDI-MS (m/z): 803.0 for $[M - PF_6]^+$. Anal. Calcd for C43H31Cl2F6N6PRu: C, 54.44; H, 3.29; N, 8.86; found: C, 54.62; H, 3.54; N, 8.40.

Spectroscopic Measurement. UV–vis/NIR spectra were recorded using a PE Lambda 750 UV–vis/NIR spectrophotometer. Oxidative spectroelectrochemistry was performed in a thin-layer cell (optical length 0.2 cm), in which an ITO glass electrode was set in the indicated solvent containing the compound to be studied (the concentration is around 1×10^{-4} M) and 0.1 M Bu₄NClO₄ as the supporting electrolyte. A platinum wire and Ag/AgCl in saturated aqueous NaCl solution was used as a counter electrode and a reference

Table	2.	Parameters	of	the	NIR	Transitions'
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	$E_{\rm op}~({\rm cm}^{-1})$	$E_{\rm op}~({\rm eV})$	$\Delta u_{1/2} \ (\mathrm{cm}^{-1})$	$\varepsilon_{max} (M^{-1} cm^{-1})$	$V_{\rm ab}^{\ \ b} \ ({\rm cm}^{-1})$
1^{2+c}	9520	1.20	3640	20000	2760
5 ²⁺	4390	0.54	2880	1500	510
6 ²⁺	4680	0.58	2300	1700	500
7^{2+}	5420	0.67	1940	1840	520

 ${}^{a}S^{2+} - 7^{2+}$ were obtained from chemical oxidation with SbCl₅ in CH₂Cl₂. b Calculated from the Hush formula. ^cSee ref 12.

electrode, respectively. The cell was put into the spectrophotometer to monitor spectral changes during electrolysis.

Electrochemical Measurement. All CV measurements were taken using a CHI 620D potentiostat with a one-compartment electrochemical cell under an atmosphere of nitrogen. All measurements were carried out in denoted solvents containing 0.1 M "Bu₄NClO₄ as the supporting electrolyte at a scan rate of 100 mV/s. The working electrode was a glassy carbon with a diameter of 3 mm. The electrode was polished prior to use with 0.05 μ m alumina and rinsed thoroughly with water and acetone. A large area platinum wire coil was used as the counter electrode. All potentials are referenced to Ag/AgCl electrode in saturated aqueous NaCl without regard for the liquid junction potential. Potentials versus ferrocene^{0/+} can be deduced by subtracting 0.45 V.

X-ray Crystallography. The X-ray diffraction data were collected using a Rigaku Saturn 724 diffractometer on a rotating anode (Mo K radiation, 0.71073 Å) at 173 K. The structure was solved by the direct method using SHELXS-97²¹ and refined with Olex2.²² The structure graphic shown in Figure 2 was generated using Olex2.

Computational Methods. DFT and TDDFT calculations are carried out using the B3LYP,²³ B3PW91,²⁴ MPW1PW91,²⁵ or PBE1PBE²⁶ exchange correlation functional and implemented in *Gaussian* 03.²⁷ The electronic structures of complexes were determined using a general basis set with the Los Alamos effective core potential LanL2DZ basis set for ruthenium and 6-31G* for other atoms.²⁸ Solvent effects (CH₂Cl₂) are included in all calculations with the conductor-like polarizable continuum model (CPCM).²⁹ All orbitals have been computed at an isovalue of 0.02 e/bohr.³

ASSOCIATED CONTENT

S Supporting Information

Crystallographic data of $6(PF_6)(CHCl_3)$ in CIF format, absorption spectral changes of $5(PF_6)-7(PF_6)$ during electrolysis, DFT calculations results, and NMR and mass spectra of new compounds. 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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REFERENCES

(1) (a) Creutz, C.; Taube, H. J. Am. Chem. Soc. 1969, 91, 3988.

- (b) D'Alessandro, D. M.; Keene, F. R. Chem. Rev. 2006, 106, 2270.
- (c) Kaim, W.; Lahiri, G. K. Angew. Chem., Int. Ed. 2007, 46, 1778.
- (d) Chisholm, M. H.; Lear, B. J. Chem. Soc. Rev. 2011, 40, 5254.
- (2) (a) Aguirre-Etcheverry, P.; O'Hare, D. Chem. Rev. 2010, 110, 4839. (b) Low, P. J. Coord. Chem. Rev. 2013, 257, 1507.
- (3) (a) Hankache, J.; Wenger, O. S. Chem. Rev. 2011, 111, 5138.
 (b) Heckmann, S.; Lambert, C. Angew. Chem., Int. Ed. 2012, 51, 326.
 (c) Nelsen, S. E. Chem.—Eur. J. 2000, 6, 581.
- (4) (a) Paul, F.; Lapinte, C. Coord. Chem. Rev. 1998, 178, 431.
 (b) Low, P. J. Dalton Trans. 2005, 2821. (c) Akita, M.; Koike, T. Dalton Trans. 2008, 3523.

(5) (a) Hush, N. S. Coord. Chem. Rev. **1985**, 64, 135. (b) Hush, N. S. Prog. Inorg. Chem. **1967**, 8, 391.

(6) (a) Ratera, I.; Sporer, C.; Ruiz-Molina, D.; Ventosa, N.; Baggerman, J.; Brouwer, A. M.; Rovira, C.; Veciana, J. J. Am. Chem. Soc. 2007, 129, 6117. (b) Glover, S. D.; Kubiak, C. P. J. Am. Chem. Soc. 2011, 133, 8721.

(7) Kusamoto, T.; Takada, K.; Sakamoto, R.; Kume, S.; Nishihara, H. Inorg. Chem. **2012**, *51*, 12102.

(8) (a) Wu, S.-H.; Shen, J.-J.; Yao, J.; Zhong, Y.-W. *Chem. Asian J.* **2013**, *8*, 138. (b) Wu, S.-H.; Shao, J.-Y.; Kang, H.-W.; Yao, J.; Zhong, Y.-W. *Chem. Asian J.* 10.1002/asia.201300739.

(9) (a) Lambert, C.; Nöll, G. J. Am. Chem. Soc. 1999, 121, 8434.
(b) Lambert, C.; Nöll, G.; Schelter, J. Nat. Mater. 2002, 1, 69.
(c) Jones, S. C.; Coropceanu, V.; Barlow, S.; Kinnibrugh, T.; Timofeeva, T.; Brédas, J.-L.; Marder, S. R. J. Am. Chem. Soc. 2004, 126, 11782. (d) Chang, C.-C.; Yueh, H.; Chen, C.-T. Org. Lett. 2011, 13, 2702.

(10) Djukic, J.-P.; Sortais, J.-B.; Barloy, L.; Pfeffer, M. Eur. J. Inorg. Chem. 2009, 817.

(11) (a) Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmers, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 3717. (b) Fraysse, S.; Coudret, C.; Launay, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 5880. (c) Wadman, S. H.; Havenith, R. W. A.; Hartl, F.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2009**, *48*, 5685.

(12) Yao, C.-J.; Zheng, R.-H.; Shi, Q.; Zhong, Y.-W.; Yao, J. Chem. Commun. 2012, 48, 5680.

(13) Zhou, G.; He, Y.; Dang, J.; Zhao, X.; Yao, B.; Xie, Z.; Wang, L.; Wong. *Chem. Asian J.* **2010**, *5*, 2405.

(14) Yang, J.-S.; Lin, Y.-H.; Yang, C.-S. Org. Lett. 2002, 4, 777.

(15) Bomben, P. G.; Koivisto, B.; Berlinguette, C. P. Inorg. Chem. 2010, 49, 4960.

(16) Crystallographic data for **6**(PF₆)(CHCl₃): C₄₆H₃₈Cl₃F₆N₆PRu, M = 1027.21, triclinic, space group PĪ, a = 13.765(4), b = 14.046(4), c = 14.086(4) Å, $\alpha = 84.100(10)^{\circ}$, $\beta = 77.970(10)^{\circ}$, $\gamma = 82.130(9)^{\circ}$, U = 2630.8(12) Å³, T = 173 K, Z = 2, radiation type Mo K α , radiation wavelength 0.71073 Å, final R indices R1 = 0.0931, wR2 = 0.2301, R indices (all data) R1 = 0.1245, wR2 = 0.2522.

(17) Zhang, Y.-M.; Shao, J.-Y.; Yao, C.-J.; Zhong, Y.-W. Dalton Trans. **2012**, *41*, 9280.

(18) Bomben, P. G.; Robson, K. C. D.; Sedach, P. A.; Berlinguette, C. P. *Inorg. Chem.* **2009**, *48*, 9631.

(19) Sreenath, K.; Thomas, T. G.; Gopidas, K. R. Org. Lett. 2011, 13, 1134.

- (20) (a) Chang, J. P.; Fung, E. Y.; Curtis, J. C. Inorg. Chem. **1986**, 25, 4233. (b) Chen, Y. J.; Kao, C.-H.; Lin, S, J.; Tai, C.-C.; Kwan, K. S. Inorg. Chem. **2000**, 39, 189. (c) Lambert, C.; Noll, G. J. Chem. Soc., Perkin Trans. 2 **2002**, 2039.
- (21) Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112.

(22) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Crystallogr. 2009, 42, 339.

- (23) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785.
- (24) Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
- (25) Adamo, C.; Barone, V. J. Chem. Phys. 1998, 108, 664.
- (26) Adamo, C.; Barone, V. J. Chem. Phys. 1999, 110, 6158.
- (27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.;
- Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.;
 Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.;
 Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.;
 Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.;
 Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao,
 O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J.
 B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev,
 O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.;
 Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;
 Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.;
 Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman,
 J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.;
 Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.;
 Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.;
 Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen,

W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision E.01; Gaussian Inc.: Pittsburgh PA, 2007.

(28) (a) Dunning, T. H.; Hay, P. J. In Modern Theoretical Chemistry;
Schaefer, H. F., Ed.; Plenum: New York, 1976; Vol. 3, p 1. (b) Hay, P.
J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270. (c) Wadt, W. R.; Hay, P.
J. J. Chem. Phys. 1985, 82, 284. (d) Hay, P. J.; Wadt, W. R. J. Chem.
Phys. 1985, 82, 299.

(29) (a) Klamt, A.; Schüürmann, G. J. Chem. Soc., Perkin Trans. 2
1993, 799. (b) Andzelm, J.; Kölmel, C.; Klamt, A. J. Chem. Phys. 1995, 103, 9312. (c) Barone, V.; Cossi, M. J. Phys. Chem. A 1998, 102, 1995. (d) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J. Comput. Chem. 2003, 24, 669.