# Electronic Coupling between Two Cyclometalated Ruthenium Centers Bridged by 1,3,6,8-Tetrakis(1-butyl-1H-1,2,3-triazol-4-yl)pyrene

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Ⓢ *Supporting Information*

ABSTRACT: A new bridging ligand 1,3,6,8-tetrakis(1-butyl-1H-1,2,3-triazol-4-yl)pyrene (ttapyr) was designed and synthesized by "click" chemistry. This ligand was used to construct a linear dimetallic biscyclometalated Ru(II) complex [(tpy)Ru-(ttapyr)Ru(tpy)]$^{2+}$ and a monometallic complex [(tpy)Ru-(ttapyr)]$^{+}$, where tpy is 2,2′:6′,2″-terpyridine. The electronic properties of these complexes were studied and compared by electrochemical and spectroscopic methods with the aid of DFT calculations. One-electron oxidation of [(tpy)Ru(ttapyr)Ru-(tpy)]$^{2+}$ with cerium ammonium nitrate produced a mixed-valent complex [(tpy)Ru(ttapyr)Ru(tpy)]$^{3+}$. The intramolecular electronic coupling between individual metal centers was quantified by the intervalence charge transfer transition analysis. Mixed-valent complex [(tpy)Ru(ttapyr)Ru(tpy)]$^{3+}$ exhibits a metal-centered rhombic EPR signal at 77 K with an average g factor of 2.203.
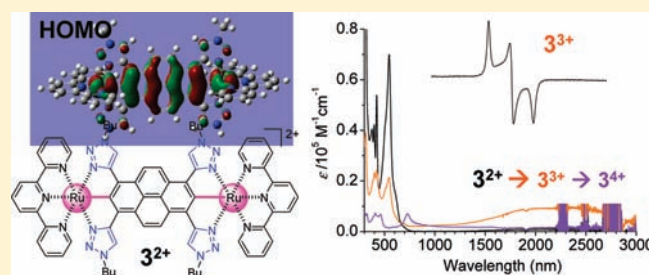
■ INTRODUCTION

Mixed-valence (MV) compounds, particularly dimetallic MV complexes, have received a great deal of interest in the past four decades.[1] One prototype complex is the Cruetz—Taube ion, namely, {[Ru(NH$_3$)$_5$](pyrazine)[Ru(NH$_3$)$_5$]$^{5+}$}.[2] This complex exhibits strong metal—metal electronic coupling between two ruthenium centers and belongs to a Robin—Day[3] class III or class II/III borderline MV system. Following that tremendous numbers of dimetallic MV complexes have been synthesized and investigated.[1] These studies find that the electronic communication between individual metal centers greatly depends on the distance between redox centers, the ability of the bridging ligand to delocalize the electronic charge, and the coordination environments of metal components.[1] Recently, we have been interested in the syntheses and studies of multimetallic cyclometalated ruthenium complexes[4] bridged by various polyazine ligands, such as 2,3-di(2-pyridyl)-5,6-diphenylpyrazine (dpdpz)[5] and 1,3,6,8-tetra(2-pyridyl)pyrene (tppyr).[6] The special characteristics of cyclometalated ruthenium complexes introduced by Ru—C σ bonds present in these complexes make them useful in constructing molecular wires[7] and as solar cell sensitizers.[8] Interestingly, dimetallic cyclometalated MV systems often display stronger metal—metal electronic communications than noncyclometalated analogues.[7]

On the other hand, the copper(I)-catalyzed azide—alkyne 1,3-dipolar cycloaddition (CuAAC), one of the so-called click reactions, has drawn much attention because this reaction is effective, selective, and devoid of byproducts.[9] We are particularly interested in the application of this reaction to coordination chemistry.[10] 1,4-Disubstituted 1,2,3-triazoles produced in this reaction share similar structural and electronic features with polyazine ligands and thus show good ability to coordinate to transition metals. Some 1,2,3-triazole-containing ligands, such as 2,6-bis(1,2,3-triazol-4-yl)pyridines,[11] 2-(1H-1,2,3-triazol-4-yl)-pyridine,[12] and phenyl-1H-1,2,3-triazoles,[13] have been demonstrated to chelate Ru, Ir, and Re to form stable coordination complexes. We recently report the use of the CuAAC reaction for the synthesis of tridentate cyclometalating ligands 1,3-di(1,2,3-triazol-4-yl)benzene (dtab) and preparation of cyclometalated ruthenium complexes with these ligands.[14] It was found that the electronic properties of these complexes could be fine tuned by changing the substituents on the ligand. Some favorable features of these complexes, such as the simple and efficient approach to "click" ligand and more positions are available for structural variations and modifications, encourage us to design and synthesize new cyclometalating bridging ligands with 1,2,3-triazole components and construct MV complexes from these ligands. To the best of our knowledge, few MV systems with a 1,2,3-triazole-containing bridging ligand have been documented.

■ RESULTS AND DISCUSSION

We report in this paper a new ditopic ligand, 1,3,6,8-tetrakis-(1-butyl-1H-1,2,3-triazol-4-yl)pyrene (ttapyr, **1**, Scheme 1), for bridging two cyclometalated ruthenium centers and the electronic coupling between them. This ligand consists of a central

Scheme 1. Synthesis of Compounds 1−3[a]
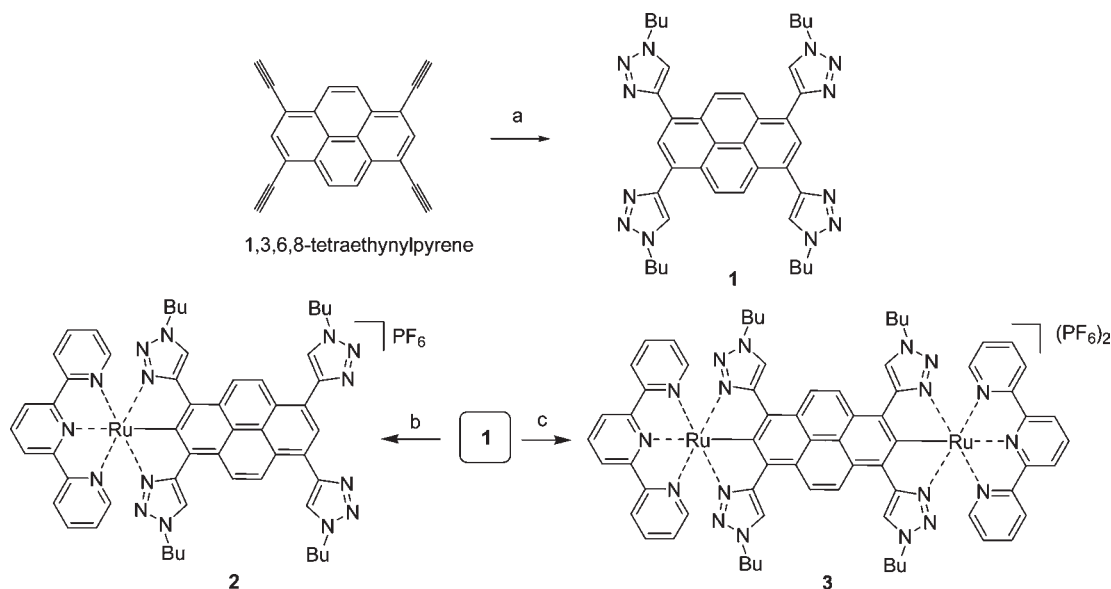
[a] Conditions: (a) $^nBuN_3$, $CuSO_4\cdot5H_2O$, sodium ascorbate, THF/H_2O 2:1, 70 °C, 12 h, 92%; (b) 1 equiv of Ru(tpy)Cl$_3$, AgOTf, ^tBuOH, DMF, KPF$_6$, 23%; (c) 2 equiv of Ru(tpy)Cl$_3$, AgOTf, ^tBuOH, DMF, KPF$_6$, 45%.
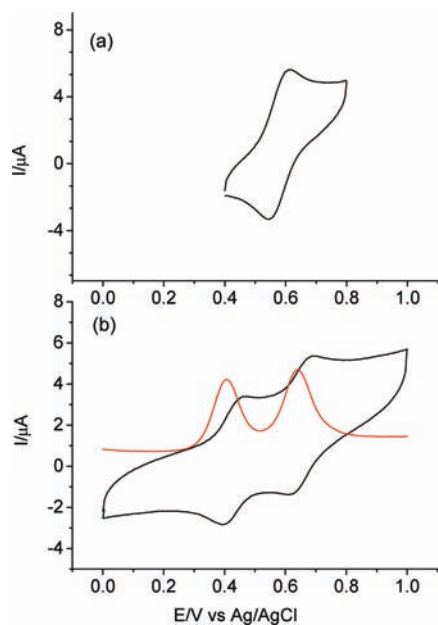

Figure 1. Cyclic voltammograms of **2** (a) and **3** (b) in acetonitrile containing 0.1 M $^nBu_4NClO_4$ as the supporting electrolyte at a scan rate of 100 mV/s. The red line in b is the differential pulse voltammetry (DPV) of **3**, with a step potential of 5 mV and amplitude of 50 mV. The working electrode is glassy carbon, the counter electrode is a platinum wire, and the reference electrode is Ag/AgCl in saturated aqueous NaCl solution.

pyrene backbone and four 1,2,3-triazole groups on the corners. The coplanar arrangement of four triazoles and the central pyrene backbone, when forming a dinuclear cyclometalated Ru complex, should enhance electron delocalization over metal centers. In addition, the butyl group in the triazole unit can be easily changed to other substituents by click reaction, which will

allow us to adjust the electronic properties of these complexes. As shown in Scheme 1, ligand **1** was synthesized via CuAAC reaction between 1,3,6,8-tetraethynylpyrene and n-butyl azide in 92% yield. Subsequent reaction of 1 or 2 equiv of Ru(tpy)Cl$_3$ (tpy = 2,2′:6′,2″-terpyridine) with **1** in the presence of silver triflate, followed by anion exchange with KPF$_6$, provided cyclometalated mono- or diruthenium complexes, **2** or **3**, respectively.

The electronic properties of **2** and **3** were first studied by electrochemical methods. Their cyclic voltammograms (CV) are shown in Figure 1 and Figures S1 and S2 in the Supporting Information. To aid in the understanding of their electronic structures, density functional theory (DFT) calculation of similar monometallic and dimetallic complexes bridged by 1,3,6,8-tetrakis(1-methyl-1H-1,2,3-triazol-4-yl)pyrene (Me-ttapyr) was undertaken, and some frontier orbitals are shown in Figure 2. The anodic scan of **2** displays one reversible and one irreversible oxidation wave at +0.58 and +1.26 V vs Ag/AgCl, respectively. This kind of electrochemical behavior is typical for cyclometalated ruthenium complexes.[4−8,14] Previous reports assign the first redox wave to the Ru$^{II/III}$ redox process and the second one to the further oxidation of the metal center or oxidative decomposition of the cyclometalating ligand.[4−8] However, DFT calculation of [(tpy)Ru(Me-ttapyr)]$^+$ suggests that the highest occupied molecular orbital (HOMO) is dominated by the ttapyr part, with a node in the middle of the central axis (Figure 2). The metal center only has a minor contribution. It should be noted that molecular orbital topologies provide useful information about the role of the individual structural component in electrochemical events. However, redox processes should not be simply described as population or depopulation of certain frontier orbital, especially considering that DFT calculation tends to overestimate the electron delocalization. We prefer to assign the redox wave at +0.58 V of complex **2** to a predominant metal-based oxidation process on the basis of its well-defined reversibility. However, some ligand character must be involved in this process (similar assignment also applies to the electrochemical
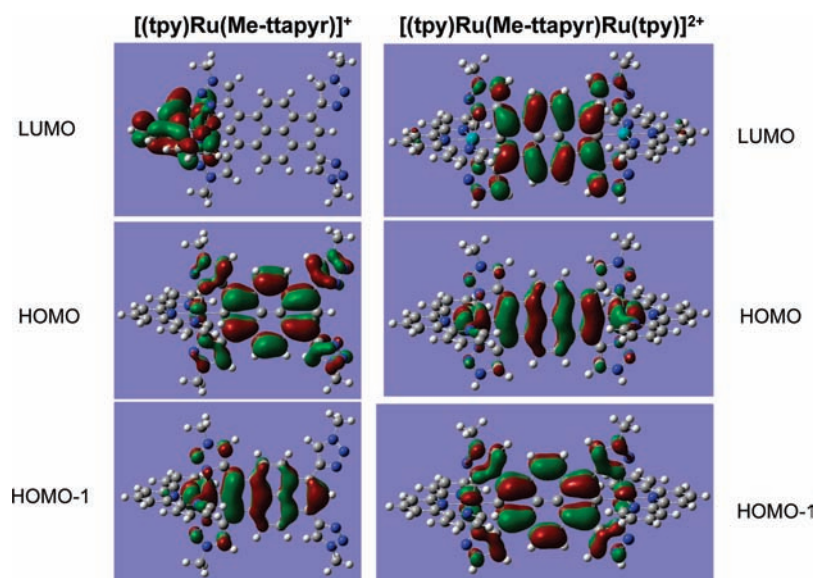
Figure 2. Isodensity plots of a few calculated HOMO and LUMO orbitals for complexes with Me-ttapyr. All orbitals have been computed at an isovalue of 0.02.
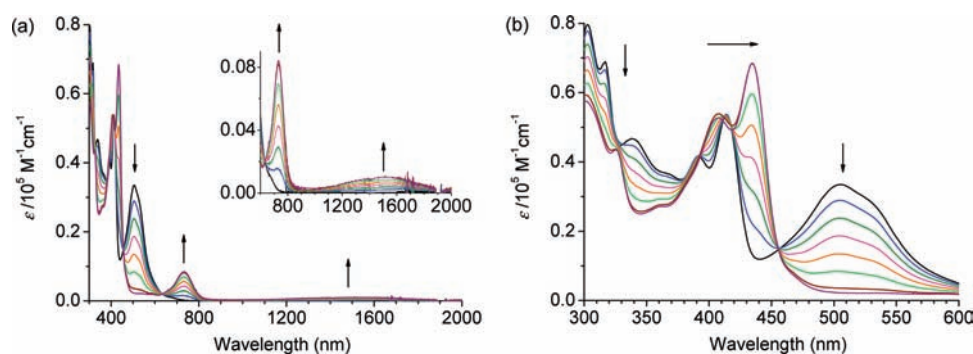

Figure 3. UV−vis−NIR electronic absorption spectral changes of **2** in acetonitrile after gradual addition of cerium ammonium nitrate. The plot in b and the inset in a are partially enlarged drawings.

behavior of complex **3**).[4−8] The cathodic scan of **2** shows two reduction waves at −1.54 and −1.74 V, which could be ascribed to reduction of the ancillary tpy and the cyclometalating ligand, respectively (Figure S1, Supporting Information).[14]

On the other hand, two reversible oxidation waves at +0.428 and +0.653 V vs Ag/AgCl in the CV profile of **3** are evident (Figure 1b), with a potential difference (ΔE) of 225 mV between two half-wave potentials. Differential pulse voltammetry (DPV) of **3** (red line in Figure 1b) also confirms the splitting between two redox waves (ΔE = 230 mV). DFT calculation of $[(tpy)Ru(Me\text{-}ttapyr)Ru(tpy)]^{2+}$ indicates that the central Ru−ttapyr−Ru motif, as a whole unit, contributes to the HOMO level. This suggests the above oxidation events are associated with both the metal and the cyclometalating ligand. However, as is clear from the EPR studies, which is presented in a later section of this paper, the unpaired radical generated by one-electron oxidation of **3** is metal centered. Thus, we would prefer the use of Ru^{II}−Ru^{III} formation to represent the MV species generated by either the electrochemical or the chemical method. The comproportionation constant K_c for the equilibrium Ru^{II}−Ru^{II} + Ru^{III}−Ru^{III} ↔ 2 Ru^{II}−Ru^{III} is 6510 for complex **3** in the case of ΔE = 225 mV.[15] This indicates the high thermodynamic

stability of the in-situ electrochemically generated MV complex Ru^{II}−Ru^{III}. The ΔE or K_c value of **3** is comparable to that of a similar cyclometalated diruthenium complex bridged by tppyr under identical electrochemical measurement conditions.[6] It should be noted that electrochemical data are largely dependent on the measurement conditions, such as the solvent and supporting electrolyte used.[16] However, the ΔE value between two redox waves may serve as a parameter for qualitatively estimating the relative electronic coupling between two metal centers in a family of closely related complexes if measured under the same conditions. In this sense, the electronic coupling between two cyclometalated Ru centers through ttapyr would be comparable to those bridged by tppyr, assuming metal-based redox processes.

To further probe the electronic delocalization of **2** and **3**, the UV−vis−NIR absorption spectral changes of **2** and **3** upon gradual addition of cerium ammonium nitrate (CAN) are monitored (Figures 3 and 4). Monoruthenium complex **2** displays multiple intraligand (IL) π−π^* transitions at 274, 304, 316, 339, 391, and 414 nm. The former four peaks are ascribed to tpy-based IL transitions, and the latter two peaks are attributed to ttapyr-based π−π^* transitions. The peak in the visible region (centered at 504 nm) is assigned to an admixture of ligand-to-ligand charge
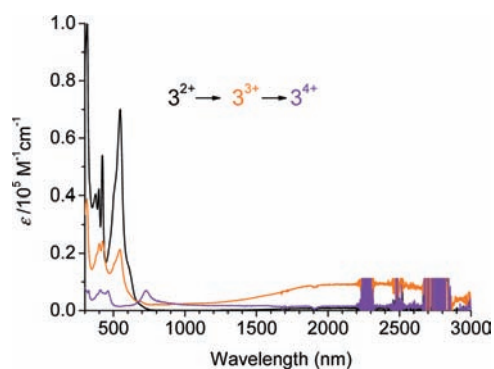
Figure 4. UV—vis—NIR electronic absorption spectral changes of **3** in acetonitrile after one or two-electron oxidation by cerium ammonium nitrate. See Figure S3 in the Supporting Information for gradual changes.
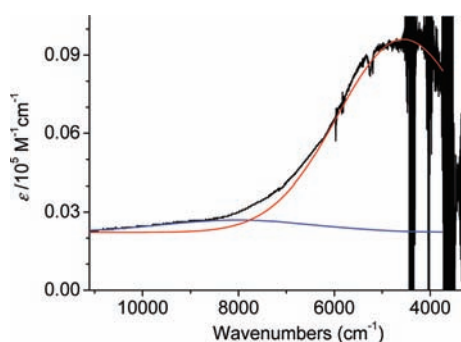

Figure 5. Absorption spectra of the IVCT transition of MV complex of **3** generated by addition of 1 equiv of CAN. See text for details.

Figure 6. EPR signal of bisruthenium complex **3** at 77 K after one-electron oxidation by adding 1 equiv of cerium ammonium nitrate in acetonitrile. The spectrometer frequency ν is 9.52×10^9 Hz.

transfer (LLCT, ttapyr → tpy) and metal-to-ligand charge transfer (MLCT, Ru → tpy) transitions. Upon gradual addition of CAN, tpy-associated IL transitions decrease slightly and ttapyr-associated $\pi-\pi^*$ transitions shift bathochromically. Concomitantly, the visible band at 504 nm was found to decrease significantly and continually, and the emergence of two new bands at 733 and 1500 nm is evident. These new bands are tentatively attributable to the ligand-to-metal charge transfer (LMCT) from both tpy and ttapyr ligands. However, further evidence is in demand to support this assertion. The observation of clear isosbestic points at 455 and 620 nm suggests a clean conversion of the oxidation process.

The absorption spectral changes of the dimetallic complex **3** in response to addition of CAN (Figure 4 and Figure S3 in the Supporting Information) are quite different from those of **2**. Complex **3** also displays a number of tpy-associated IL transitions below 350 nm and three ttapyr-based $\pi-\pi^*$ transitions in the region between 350 and 450 nm (see Figure S4, Supporting Information, for enlarged plots). The MLCT/LLCT transitions centered at 547 nm are located in a lower energy region as compared to those of **2**. Upon gradual addition of 1 equiv of CAN, both ttapyr-associated IL transitions and MLCT/LLCT transitions decrease significantly and a new broad band in the NIR region grows gradually. Upon further addition of CAN to 2 equiv, ttapyr-associated IL transitions and MLCT transitions continue to decrease. However, the new NIR band also decreases gradually until it disappears completely. On the basis of these facts, the new NIR band is assigned to the intervalence charge
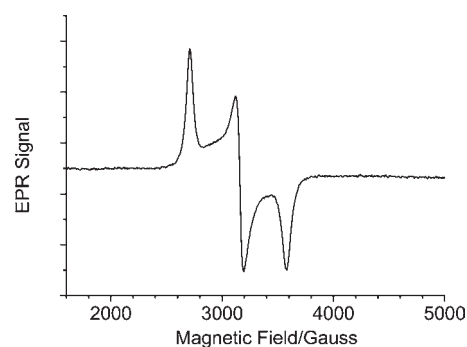
transfer (IVCT) transition of the in-situ-generated MV complex. However, it should be stressed again that this MV complex is not truly mixed valent with a $Ru^{II}-Ru^{III}$ composition, as discussed in the electrochemical studies. The significant and continual diminution of both ttapyr-associated IL transitions and MLCT/LLCT transitions upon addition of 2 equiv of CAN suggests that the oxidation processes occur at both metal centers and the bridging ttapyr ligand.

The dramatically different absorption spectral response of **2** and **3** after oxidation can be understood by taking account of the significant difference of their electronic structures (Figure 2). The HOMO level of **2** is dominated by the ttapyr part with a nodal structure in the central axis, while the central Ru—ttapyr unit, as a whole, contributes to HOMO−1. Complex **3** is just the opposite. Similar nodal structure is present in its HOMO−1 level but not in the HOMO. Occupied orbitals without a nodal structure, such as the HOMO of **3** and HOMO−1 of **2**, may be largely responsible for the ttapyr-associated $\pi-\pi^*$ transitions. Thus, one-electron oxidation of **3** caused a significant decrease of the ttapyr-associated $\pi-\pi^*$ transitions. However, those of **2** largely persisted.

The IVCT transition of MV complex of **3** is shown in Figure 5. The black line is a plot from the experimental data generated by adding 1 equiv of CAN. Red and blue lines are Gaussian-fitted plots of the black line after deleting irregular noises. The red line is assigned to the IVCT transition, and the blue line at 1250 nm is attributed to a LMCT transition. Noteworthy is that a similar LMCT transition, albeit with a lower energy (1500 nm), has been observed in the case of the monoruthenium complex **2** (Figure 3). The IVCT band is centered at 2180 nm ($\nu_{max} = 4580$ cm^{-1}, $\varepsilon_{max} = 9100$ M^{-1} cm^{-1}), with the full width at half-height ($\Delta\nu_{1/2}$) of 3200 cm^{-1}. According to Hush's expression,[17] the theoretical $\Delta\nu_{1/2}$ value equals $(2310\nu_{max})^{1/2} = (2310 \times 4580)^{1/2} = 3252$ cm^{-1}. It is clear that the experimental value of $\Delta\nu_{1/2}$ is very close to the theoretical value. The Γ parameter, introduced by Creutz, Sutin, and co-workers,[18] of MV compound of **3** is 0.02, as determined by $\Gamma = 1 - \Delta\nu_{1/2exp}/\Delta\nu_{1/2theo}$. This suggests that the mixed-valence compound of **3** is a Robin and Day class II system. The electronic coupling parameter H_{ab} is calculated to be 670 cm^{-1}, according to the Hush formula[19] $H_{ab} = 2.06 \times 10^{-2}(\varepsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2}/r_{ab}$, where r_{ab} is taken to be the calculated Ru—Ru distance (11.16 Å).

Complex 2^{2+} after oxidation with CAN is EPR silent at room temperature and 77 K. However, one-electron-oxidized complex 3^{3+} exhibits a rhombic EPR signal at 77 K typical for a low-spin

Ru^{III} species (Figure 6). The electron g factor g_1, g_2, and g_3 is 2.512, 2.155, and 1.900, respectively. The isotropic g factor of $\langle g \rangle = 2.203$, derived according to $\langle g \rangle = [(g_1{}^2 + g_2{}^2 + g_3{}^2)/3]^{1/2}$. The total g anisotropy $\Delta g = g_1 - g_3 = 0.612$. We notice that a true metal-centered spin of a cetecholatoruthenium(III) complex has a $\langle g \rangle$ value of 2.476 with $\Delta g = 0.833$.[20] The pronounced rhombicity of the EPR signal and relatively low $\langle g \rangle$ and Δg values of complex 3^{3+} point to a metal-centered spin albeit with considerable ligand participation, which is in agreement with the experimental findings observed in the electrochemical and spectroscopic studies.

To conclude, a dimetallic biscyclometalated Ru complex 3^{2+} bridged by "click" ligand ttapyr was synthesized. Compared to the previously reported MV system bridged by tppyr,[6] comparable but relatively lower, electronic coupling was found to be present between mixed-valent redox centers of one-electron-oxidized complex 3^{3+}, as suggested by electrochemical and spectroscopic analyses. DFT calculations and EPR studies indicate that one-electron oxidation of 3^{2+} is mainly associated with the metal center, albeit with substantial participation from the anionic ligand part. This feature may make ttapyr an appealing bridging ligand for building highly conductive one-dimensional molecular wires and encourage chemists to design and synthesize new 1,2,3-triazole-containing bridging ligand using "click" strategy.

■ EXPERIMENTAL SECTION

Spectrascopic Measurement. All optical ultraviolet−visible (UV−vis) absorption spectra were obtained using a TU-1810DSPC spectrometer of Beijing Purkinje General Instrument Co. Ltd. at room temperature in denoted solvents with a conventional 1.0 cm quartz cell. UV−vis−NIR spectra were recorded using a Shimadzu UV-3600 UV−vis−NIR spectrophotometer.

Electrochemical Measurement. All cyclic voltammetry (CV) scans were taken using a CHI620D potentiostat. All measurements were carried out in 0.1 M Bu_4NClO_4/acetonitrile at a scan rate of 100 mV/s with a Ag/AgCl reference electrode. The working electrode is a glassy carbon electrode, and a platinum coil is used as the counter electrode.

Computational Methods. DFT calculations are carried out using the B3LYP exchange correlation functional[21] and implemented in the Gaussian 03 program package.[22] 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 in vacuum.[23]

Synthesis. NMR spectra were recorded in the designated solvent on a Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvent for ^{1}H NMR (δ 7.26 ppm for CDCl₃ and 1.92 ppm for CD₃CN) and ^{13}C NMR (δ 77.00 ppm for CDCl₃). MS data were obtained with a Bruker Daltonics Inc. ApexII FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is α-cyano-4-hydroxycinnamic acid (CCA). Microanalysis was carried out using Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, CAS. 1,3,6,8-Tetraethynylpyrene,[24] n-butyl azide,[25] and (tpy)RuCl₃[26] were prepared according to known procedures.

Synthesis of ttapyr (1). 1,3,6,8-Tetraethynylpyrene (12.4 mg, 0.042 mmol), ^{n}BuN₃ (21 mg, 0.21 mmol), CuSO₄·5H₂O (3 mg, 0.015 mmol), and sodium ascorbate (4 mg, 0.02 mmol) were added to a solution of THF (5 mL) and H₂O (2 mL) under N₂ atmosphere. The mixture was heated to 70 °C with vigorous stirring for 12 h. Then the solution was extracted with CH₂Cl₂, and the combined organic phase was dried with anhydrous MgSO₄. After the solvent was removed, the residue was purified by column chromatography on silica gel using CH₂Cl₂/EtOAc 5:1 as the eluent. The product **1** was obtained as a yellowish solid (26.7 mg, 92% yield). ^{1}H NMR (400 MHz, CDCl₃): δ 8.78 (s, 4 H), 8.58 (s, 2 H), 8.04 (s, 4H), 4.55 (t, J = 7.2 Hz, 8 H), 2.05 (m, 8 H), 1.51 (m, 8 H), 1.04 (t, J = 7.3 Hz, 12 H). ^{13}C NMR (100 MHz, CDCl₃): δ 146.60, 128.12, 127.84, 125.29, 125.24, 125.12, 123.33, 50.22, 32.31, 19.80, 13.52. EI-MS: m/z calcd for $C_{40}H_{46}N_{12}$ 694.4, found 694.0. EI-HRMS: calcd 694.3968 for $C_{40}H_{46}N_{12}$, found 694.3974.

Synthesis of Complexes 2 and 3. To 5 mL of acetone were added (tpy)RuCl₃ (19 mg, 0.043 mmol) and AgOTf (39 mg, 0.152 mmol), and the solution was then heated to reflux for 2 h. After that the solution was filtered through a pad of Celite to remove AgCl precipitate. The filtrate was concentrated, and the residue was dissolved in 6 mL of DMF. The solution was then transferred by syringe to a pressure vessel charged with 30 mg of **1** (0.043 mmol) in 6 mL of ^{t}BuOH. The mixture was bubbled with N₂ for 10 min before the vessel was capped and heated to reflux for 16 h. After cooling, the reaction mixture was filtered and the solvent was removed under vacuum. To the residue was added 3 mL of methanol, followed by addition of an excess of KPF₆. The resulting precipitate was collected by filtration and washing with water and ether. This crude product was purified by column chromatography on silica gel (eluent CH₂Cl₂/MeCN 10:1 to 3:1) to give 12 mg of **2** as a brown solid. The yield is 23%. It should be noted that another 10 mg (20% yield) of dimetallic complex **3** was also obtained in this reaction. Characterization data for complex **2** are as follows. ^{1}H NMR (400 MHz, CD₃CN): δ 9.11 (d, J = 9.4 Hz, 2 H), 8.69 (m, 6 H), 8.45 (s, 1 H), 8.39 (d, J = 9.7 Hz, 4 H), 8.24 (t, J = 9.6 Hz, 1 H), 7.69 (t, J = 9.6 Hz, 2 H), 7.19 (d, J = 5.4 Hz, 2 H), 6.87 (t, J = 6.3 Hz, 2 H), 4.59 (t, J = 7.1 Hz, 4 H), 4.17 (t, J = 7.1 Hz, 4 H), 1.96 (m, 4 H), 1.67 (m, 4 H), 1.49 (m, 4 H), 1.04 (t, J = 7.4 Hz, 6 H), 0.98 (m, 4 H), 0.69 (t, J = 7.4 Hz, 6 H). MALDI-TOF-MS: m/z 1028 $[M - PF_6]^+$. Anal. Calcd for $C_{55}H_{56}F_6N_{15}PRu \cdot 2H_2O$: C, 54.63; H, 5.00; N, 17.38. Found: C, 54.91; H, 4.81; N, 17.23.

Alternatively, complex **3** was synthesized using the same procedure for the preparation of **2** from (tpy)RuCl₃ (50 mg, 0.113 mmol), AgOTf (104 mg, 0.405 mmol), and ligand **1** (40 mg, 0.058 mmol). The yield is 45% (43 mg of complex **3** was obtained). ^{1}H NMR (400 MHz, CD₃CN): δ 8.78 (s, 4 H), 8.69 (d, J = 8.2 Hz, 8 H), 8.41(d, J = 8.0 Hz, 4 H), 8.25 (t, J = 8.3 Hz, 2 H), 7.72 (t, J = 7.9 Hz, 4 H), 7.29 (d, J = 5.3 Hz, 4 H), 6.95 (s, 4 H), 4.21 (t, J = 7.1 Hz, 8 H), 1.69 (m, 8 H), 1.01 (m, 8 H), 0.70 (t, J = 7.3 Hz, 12 H). MALDI-TOF-MS: m/z 1506 $[M - PF_6]^+$. Anal. Calcd For $C_{70}H_{66}F_{12}N_{18}P_2Ru_2$: C, 50.91; H, 4.03; N, 15.27. Found: C, 50.56; H, 3.87; N, 15.27.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. CV profiles and absorption spectra of **2** and **3** and NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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