





Heterobimetallic Complexes

Phenyl-Bridged Ferrocene/Ruthenium Alkynyl Heterobimetallic Complexes: Syntheses, Characterization, and Electrochemical, Spectroscopic, and Computational Investigation

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Abstract: Two isomeric phenyl-bridged ferrocenyl and ruthenium alkynyl complexes **1** and **2** are synthesized and characterized through NMR, elemental analysis, and X-ray single-crystal diffraction. The electronic properties of the complexes are investigated via electrochemical studies, UV/Vis-NIR and IR spectroelectrochemistry, and theoretical calculations. Cyclic voltammetry and square-wave voltammetry technologies show two successive redox behaviors from Ru(II) and ferrocenyl centers in **1** and **2**, respectively. These behaviors are supported

Introduction

Conjugative binuclear and polynuclear organometallic complexes have received tremendous interest due to their potential applications as dye-sensitized solar cells,^[1] electrochromic materials,^[2] redox switchable NLOs,^[3] and luminescent materials.^[4] Interestingly, electron transfer properties are evaluated on the basis of mixed-valence systems generated by redox-active bimetallic complexes^[5] that are similar to the classical inorganic Creutz–Taube ion.^[6] This approach provides a well-defined method for studying charge delocalization and exploring novel optical transition properties.

Recently, a large number of conjugated ligand-linked mononuclear and binuclear metal complexes and their redox and mixed valence properties have been investigated, and considerable redox-active end-groups, such as ferrocene,^[7] M(dppe)Cp* or M(dppe)₂Cl (M = Ru, Fe, Os, Mo; dppe:1,2-bis[diphenylphosphino]ethane; Cp* = pentamethylcyclopentadiene),^[8] and RuCl(CO)(P ligand) (P ligand = [PiPr₃]₂ or [PMe₃]₃),^[9] cyclometalated Ru,^[10] and polynuclear terminals,^[11] and others,^[5a,12] are applied and feature effective stepwise redox processes. In addition, different carbon-rich bridge cores, including polyene,^[9e] polyacetylene,^[11c] and polycyclic aromatic hydrocarbons^[8f,13] have been introduced into mixed-valence systems to tune elecby the dominant spin–spin density distribution in RuCp*(dppe) terminals. The large potential difference ($\Delta E_{1/2}$) and comproportionation constants (K_c) observed in complex **1** suggest that **1**⁺ has better chemical stability than **2**⁺. Strong electronic communication from **1**⁺ are detected through the observed NIR absorption band in **1**⁺ and large $\Delta \nu$ (C=C) value of **1** \rightarrow **1**⁺. The broad NIR absorption in **1**⁺ is reproduced and assigned to ferrocenyl to the Ru(III) center charge transfer transition with major contributions from the β -HOSO $\rightarrow\beta$ -LUSO transition.

tronic communication between two redox-active centers. Increasing attention has been paid to asymmetrical heterobimetallic mixed-valence models $[M_1$ -bridge- $M_2]^{n+}$,^[14] which include two different mixed-valent isomers (valence tautomers), namely, $[M_1^{ox}$ -bridge- $M_2^{red}]^{n+}$ and $[M_1^{red}$ -bridge- $M_2^{ox}]^{n+}$. These isomers exhibit ground-state energy difference (ΔG^0), which contributes to the energy of optical transition \tilde{v}_{max} but not to total reorganization energy (λ).^[15] Therefore, considering this point, Hush's theory is equally applicable to the intervalence charge transfer analysis of such asymmetrical systems.^[16]

Ferrocene and Ru units with reversible redox couple nature and good chemical stability often serve as end-groups and are applied to construct heterobimetallic complexes.^[17] As early as 1994, the groups of Sato^[17b] and Long^[17a] successively reported ferrocenylacetylene-ruthenium complexes, wherein the Ru termini are $Ru(PP)(\eta-C_5H_5)$ (PP = 2PPh₃, dppe [1,2-bis{diphenylphosphino}ethane] or dppf (1,l'-bis[diphenylphosphino]ferrocene) and $Ru(dppm)_2Cl$ (dppm = 1,2-bis[diphenylphosphino]methane). Strong electronic coupling is discovered in this type of asymmetrical redox system through electrochemical and spectroscopic technologies. Subsequently, several Fe-Ru systems bridged by rich-carbon chains are constructed by Long^[17c] and Bruce^[17e] et al. These complexes have revealed lower oxidation potential than ferrocenylacetylide and exhibited electronic communication from Fc to Ru^{III} in Fe^{II}Ru^{III} mixedvalence systems. By contrast, the groups of Jia,^[17d] Winter,^[17f] Zhong,^[17g] Chen,^[17h] and Patra^[17i] demonstrated that high redox potentials occur at the Ru termini rather than at Fc. This phenomenon indicates that the redox potential of Ru terminals is regulated on a large scale by the different auxiliary ligands and the coordination forms of the Ru center. In addition, variable bridge cores can play a significant role in tuning electronic interactions between two heteronuclear end-caps.^[18] Recently,

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000042.







Scheme 1. Synthetic path for phenyl-bridged asymmetrical dinuclear Fe-Ru complexes 1-2.

explorations on the mechanism of charge transfer in the form through-bond or through-space shape have widely focused on symmetrical organic^[19] or inorganic^[20] mixed-valence systems. To date, examples of ferrocenyl and Ru-ethynyl linked by two bridge isomers (1,4- and 1,3-phenyl) have not been reported. Thus, this paper reports the syntheses of two isomeric heterobimetallic complexes (ferrocenyl-1,4-benzene-C=C-RuCp*dppe) **1** and (ferrocenyl-1,3-benzene-C=C-RuCp*dppe) **2** (Cp* = η -C₅Me₅; dppe = 1,2-bis[diphenylphosphino]ethane) (Scheme 1). The bonding properties and electronic coupling of the two complexes are investigated through X-ray single-crystal diffraction, (spectro)electrochemistry, and density functional theory (DFT) calculations.

Results and Discussion

Syntheses, Characterization, and Crystallographic Analysis

The synthetic route toward heterobimetallic 1-2 is outlined in Scheme 1. First, intermediates 1a and 2a were prepared via the diazotization reactions of ferrocene and bromoaniline in accordance with a similar procedure in the literature.^[21] These intermediates acted as the starting materials for the syntheses of precursors 1b and 2b. Finally, the TMS-protected compounds 1b and 2b were deprotected using KF and reacted in situ with (RuCl[dppe]Cp*) under reflux conditions.[22] The target complexes 1-2 were obtained through filtration and characterized using conventional spectroscopic methods. The characteristic ¹H NMR and ¹³C NMR signals from the RuCp*(dppe) of the two isomeric complexes were similar to those of previously reported monoruthenium ethynyl complexes.^[23] The ¹H NMR spectra exhibited the characteristic CH₃ proton signal from η -C₅Me₅ in approximately 1.56 ppm and the two -CH₂- proton signals of dppe between 2.04-2.75 ppm. The three types of protons in ferrocenyl resonated at 4.02–4.26 ppm. The corresponding ¹³C NMR spectrum exhibited the intense carbon signals of η -C₅Me₅ at 10.0 and 92.5 ppm and those of CH_2 from dppe at 29.4 ppm. In addition, two C=C carbon peaks were located in approximately 86.5 ppm, and the low-field carbon shift of approximately 109.6 ppm was attributed to the coordination of the metal Ru atom with the C=C bond. The single peak at about 80 ppm of ³¹P NMR further characterized these structures.

The molecular structure of complex 1 (CCDC number: 1977229) was determined through X-ray crystallography to gain insight into its bonding properties and solid structure and compare with the DFT-optimized structures. A deep red-colored single crystal of 1 suitable for single-crystal X-ray diffraction was grown by layering hexanes on CH₂Cl₂ solution. The molecular structure of **1** and its packing viewing along the axis *a*, *b*, and c directions are displayed in Figure 1 and Figure 2. Table S1 presents the details of data collection and refinement. The selected bond lengths and angles of the crystal structure 1 and the DFT-optimized structures $\mathbf{1}^{n+}-\mathbf{2}^{n+}$ (n = 0, 1) obtained using the (U)B3LYP/6-31G* theory (Lanl2DZ for the Ru, Fe atom) function are provided in Table 1 and Table S2, respectively. As shown in Figure 1, the Ru(dppe)Cp* terminal group from the molecular structure of 1 exhibited pseudo-octahedral geometry. The lengths of the two Ru–P bonds were 2.270 and 2.2257 Å



Figure 1. Molecular structure of complex **1** showing the atom labeling scheme.





and those of the Ru ethynyl fragments, namely, Ru(1)-C(37), C(37)–C(38), and C(38)–C(39), were 1.999, 1.211, and 1.433 Å, respectively. The bond lengths of the geometry-optimized structure 1_{cal} were negligibly different from those of the crystal structure, and an elongation of the triple bond (C[37]-C[38]) and a shortening of the single bond (Ru[1]-C[37] and C[38]-C[39]) were observed. Given the oxidation of the full-optimized structure from the neutral state 1-2 to monocations 1+-2+, the bonds of Ru(1)-C(37) and C(38)-C(39) for 1 and Ru(1)-C(33) and C(34)-C(26) were gradually shortened, whereas those of C(37)-C(38) for **1** and the triple bond C(33)–C(34) for **2** were extended. These results suggested that the first-step oxidation can originate from the Ru center. In addition, three packing views along the axis a, b, and c directions all revealed a lamellar crystal packing model, the end groups (ferrocenyl and RuCp*(dppe)) of molecules overlapped with each other, and displayed headto-tail form (Figure 2).



Figure 2. Molecular packing viewing of complex 1 (a) along axis a, (b) along axis b, (c) along axis c.

Electrochemical Studies

The electrochemical behaviors were investigated via cyclic voltammetry and square-wave voltammetry methods by using nBu_4NPF_6 (0.1 M) as the supporting electrolyte in dry CH_2Cl_2 solution to understand further the redox properties of complexes 1a-2a and 1-2. As shown in Figure 3 and Table 2, the mononuclear ferrocenyl complexes 1a and 2a exhibited welldefined redox processes with half-wave potential $(E_{1/2})$ values of 0.522 and 0.530 V, respectively. Subsequently, two continuous single-electron redox behaviors were found in heterobimetallic complexes 1-2, and the two separated reversible redox peaks of complex 1 (0.212 and 0.574 V) and 2 (0.283 and 0.564 V) corresponded to the Ru(II) and ferrocene end groups, respectively. Ethynylbenzene-RuCp*dppe has been investigated by many groups.^[8h,8i] The electrochemical data exhibited $E_{1/2}$ values between 0-0.23 V, depending on measurement condition and reference. In addition, we have reported the α -benzothio-

Table 1. Selected bond lengths [Å] and angles [deg] from the crystal structure of **1** and the full DFT-optimized structures $\mathbf{1}^{n+}(n = 0, 1)$.

	1 _{exp}	1 _{cal}	1+
Ru(1)-C(37)	1.999	2.022	1.951
Ru(1)-P(1, 2)	2.270, 2.257	2.340, 2.336	2.378, 2.395
C(37)-C(38)	1.211	1.235	1.247
C(38)-C(39)	1.433	1.426	1.409
C(39)-C(40)	1.384	1.416	1.419
C(40)-C(41)	1.380	1.390	1.385
C(41)-C(42)	1.387	1.408	1.412
C(42)-C(43)	1.394	1.407	1.413
C(43)-C(44)	1.382	1.391	1.389
C(44)-C(39)	1.406	1.414	1.420
C(42)-C(49)	1.476	1.475	1.467
C(49)-C(48)	1.423	1.438	1.440
C(49)-Fe(1)	2.052	2.103	2.094
P(1)-Ru(1)-P(2)	83.21	83.62	82.30
Ru(1)-C(37)-C(38)	176.10	176.00	174.76
C(37)-C(38)-C(39)	174.18	179.59	178.36

phene-ethynyl ruthenium complex,^[8]] in the same experimental condition, and the $E_{1/2}$ value is 0.011 V. Based on the above data, we can conclude that ethynylbenzene-RuCp*dppe has lower half-wave potential than ferrocenyl site, and the two redox processes are consequently assigned. This assignment to redox reaction order was in contrast with the reported heterobimetallic [(tppz)(PPh₃)₂RuC=C-C₆H₄-C=CFc](ClO₄) complex due to the higher redox potential from the Ru center than that from ferrocenyl,^[17h] which was contributed to different auxiliary ligands from ruthenium center. In addition, additional C=C bond insertion between phenyl and ferrocenyl caused the distance



Figure 3. CVs (a) and SWVs (b) of intermediates **1a–2a** and heterobimetallic complexes **1–2** in CH_2CI_2 solution (scan rate: 0.1 V s⁻¹, f = 10 Hz).

Table 2. Electrochemical data for intermediates $1a\mathchar`-2a$ and heterobinuclear iron-Ru complexes 1 and $2^{\rm [a]}$

Complexes	$F_{1/2}(1)[V]$	$F_{1/2}(2)$ [V]	Δ <i>F</i> [mV] ^[b]	<i>K</i> _e [c]
	=1/2(1/10)	=1/2(=/[[•]		
1a	-	0.522	-	-
2a	-	0.530	-	-
1	0.212	0.574	362	1.32×10^{6}
2	0.283	0.564	281	5.62×10^4

[a] Potential data in volts vs. Fc⁺/Fc are from single scan cyclic voltammograms recorded at 298 K in 0.1 μ dichloromethane solution of (Bu₄N)(PF₆). [b] $\Delta E = E_{1/2}(2) - E_{1/2}(1)$ denotes the potential difference between two redox processes. [c] The comproportionation constants, K_{cr} were calculated by the formula $K_c = \exp(\Delta E/25.69)$ at 298 K.





between two redox centers to increase and featured that reported $[(tppz)(PPh_3)_2RuC=C-C_6H_4-C=CFc](CIO_4)$ complex exhibit smaller $\Delta E_{1/2}$ (320 mV)^[17h] than that of complex **1** (362 mV). However, for $[(tppz)(PPh_3)_2RuC \equiv CFc](CIO_4)$ complex with shorter redox centers distance, which revealed larger $\Delta E_{1/2}$ (780 mV).^[17h] Above comparative results indicated that distance dependence of $\Delta E_{1/2}$ value. Compared with those of **1a** and **2a**, the redox potentials of ferrocenyl units (Fc/Fc⁺) of 1 and 2 were positive because of the electron delocalization effect from the oxidation of the low-potential Ru center from Ru(II) to Ru(III). In addition, the redox potential of Ru center in complex 1 shifted to a lower potential than that in complex 2, accounting for the large difference in the $\Delta E_{1/2}$ and the comproportionation constant (K_c) in complex **1**. $\Delta E_{1/2}$ and K_c are crucial parameters for evaluating thermodynamic stability. Thus, these results implied that the mixed-valence complex 1⁺ had higher chemical stability than 2^+ . In addition, the ΔE splitting depends on several factors,^[24] among which the electrostatic repulsion, the solvent and the supporting electrolyte, so ΔE value should not be taken as a parameter for quantitative measurement of the electronic coupling. Therefore, the electronic coupling degree will be explored further by the following spectroelectrochemical studies and spin density distribution.

UV/Vis-NIR Spectroelectrochemical Studies

UV/Vis-NIR spectroscopy was monitored by potential-controlled electrochemical oxidation within the OTTLE cell in CH₂Cl₂/10⁻¹ м NBu₄PF₆ at 298 K to explore the electronic transition of complexes 1-2 and their various oxidation states. The gradual spectral changes accompanying the one- and two-electron oxidation of complex 1 are displayed in Figure 4. The UV/ Vis-NIR spectra of 2^{n+} (n = 0, 1, 2) generated through electrolytic experiments are shown in Figure S1. The detailed electronic absorption spectroscopic data are listed in Table 3. As shown in Figure 4 and Figure S1, an evident intense band at 330 nm for complex 1 and two weak peaks at 228 and 317 nm for complex **2** exhibited the $\pi \rightarrow \pi^*$ transition character.^[17i,18] The gradual disappearance of the strong $\pi \rightarrow \pi^*$ absorption upon gradual one-electron oxidation to singly oxidized states for complex 1 was accompanied by the emergence of three new absorption bands at 428, 743, and 1396 nm. The broad NIR

band indicated that the intervalence charge transfer transition occurred in 1⁺ from Fc to the Ru(III) center. This phenomenon was proven by the following TDDFT calculations. Upon continuous oxidation to the dication 1^{2+} , two obvious peaks at 743 and 1396 nm weakened and almost disappeared, and a weak band was found at 1055 nm. By contrast, as the meta-phenyl-bridged rutheniumethynyl ferrocenyl complex 2 was oxidized to 2+ through electrolysis, the NIR absorption became barely detectable, and only the $\pi \rightarrow \pi^*$ absorption collapse was observed. Moreover, weak peaks appeared at 410 and 711 nm. Finally, the absorption of the monocation 2⁺ almost remained unchanged after the potentials were continuously increased. These results revealed that the isomeric mixed-valence systems had different spectral features and indicated that the mixed-valence system 1⁺ may exhibit better charge delocalization and interaction between Ru-Fc end groups than 2⁺.

Table 3. Electron absorption spectroscopic data of 1^{n+} and 2^{n+} (n = 0, 1, 2).

Complex	UV/Vis/NIR absorption λ_{max} [nm] (ε_{max} (dm ³ mol ⁻¹ cm ⁻¹))
1	330 (13440)
1+	428 (5599), 743 (3251), 1396 (2042)
1 ²⁺	382 (5557), 477 (3678), 749 (1497), 1055 (1510)
2	228 (19108), 317 (13195)
2 ⁺	273 (24325), 410 (2196), 711 (487)
2 ²⁺	709 (352)

In order to quantify the magnitude of the electronic coupling and determine the class in which the MV complex 1⁺ belongs, we analyzed the NIR IVCT absorption (Figure S2) of 1⁺ by virtue of Husy's theory.^[25] According to NIR absorption with almost symmetrical peak shape in 1⁺ and the following TDDFT prediction, we concluded that the NIR absorption can mainly be assigned to inter-valence charge transfer(IVCT) transition. Therefore, we obtained related parameters by analyzing this band ($\nu_{max} = 7110 \text{ cm}^{-1}$, $\Delta \nu_{1/2} = 4051 \text{ cm}^{-1}$, and $\varepsilon_{max} =$ 2005 $\ensuremath{\,{\rm M}^{-1}}\xspace$ cm^^1), and according to the Hush formula, $^{[26]}$ electronic coupling parameter $H_{ab} = 2.06 \times 10^{-2} (\varepsilon_{max} \nu_{max} \Delta \nu_{1/2})^{1/2} /$ (r_{ab}) , where r_{ab} is the linear distance between metal ruthenium and iron atoms in the crystal structure (10.481 Å), and the calculated $H_{\rm ab}$ was 472 cm⁻¹, which was much lower than $v_{\rm max}/2$ (3555 cm⁻¹). Above results indicated that MV complex 1⁺ may be classified as a class II MV system.



Figure 4. UV/Vis-NIR spectral changes recorded during the oxidation $1 \rightarrow 1^+$ (a) and $1^+ \rightarrow 1^{2+}$ (b) in CH₂Cl₂/0.1 \bowtie nBu₄NPF₆ at 298 K within an OTTLE cell.



IR Spectroelectrochemical Studies

The characteristic C=C stretching frequency^[27] of complexes 1 and 2 provided powerful spectroscopic probes for investigating the charge delocalization properties of their respective mixedvalence states 1⁺ and 2⁺. Therefore, IR spectroelectrochemical experiments were conducted on complexes 1 and 2, and different valence states, namely, $\mathbf{1}^{n+}$ and $\mathbf{2}^{n+}$ (n = 0, 1, 2), were generated in the electrolytic experiments in CH_2CI_2/NBu_4PF_6 (0.1 M) at 298 K for IR spectroscopy. The corresponding IR spectra in the v(C=C) region are displayed in Figure 5 and Figure S3, and the v(C=C) vibrational frequencies (cm⁻¹) are listed in Table 4. The v(C=C) bands of neutral complexes 1 and 2 appeared at 2066 and 2065 cm⁻¹, respectively. Upon the first oxidation to 1^+ and 2^+ , the v(C=C) absorptions from neutral molecules were replaced by two medium intense low-energy absorptions (1+: 1973 and 1927 cm⁻¹; 2⁺: 1972 and 1933 cm⁻¹) and revealed essential properties based on the redox reaction of rutheniumethynyl units. The calculated maximum v(C=C) shift $(\Delta v[C=C])$ from neutral molecules to monocations was 139 cm⁻¹ for $1 \rightarrow 1^+$, which was slightly larger than that calculated for $2\rightarrow 2^+$ (132 cm⁻¹). The comparison of the $\Delta \nu$ (C=C) data similarly revealed that the singly oxidized state 1+ (1,4-phenyl-bridged rutheniumethynyl-ferrocenyl) had stronger charge delocalization properties than 2⁺ because the 1,4-benzene bridge in 1⁺ can provide effective electron transfer path.^[28] Slight shifts in ν (C=C) were found after full oxidization to dications 1^{2+} and 2^{2+} , and only two weak absorptions at 1970 and 1928 cm⁻¹ and a broad peak at 1928 cm^{-1} for 2^{2+} that can originate from the minor contributions of the second-step oxidation of the iron center were found for 1^{2+} .



Figure 5. IR spectral absorptions of the Ru(C=C) stretching vibration for 1^{n+} (n = 0, 1, 2) generated by electrolysis experiments in CH₂Cl₂/NBu₄PF₆ (0.1 m) at 298 K (neutral state: black line; monocation: red line; dication: blue line).

DFT and TDDFT Calculations

Complexes [1]ⁿ⁺ and [2]ⁿ⁺ (n = 0, 1, 2) were optimized using DFT calculations on the basis of (U)B3LYP/6-31G* theory (Lanl2DZ for the Ru and Fe atom) to further understand the electronic properties of heterobimetallic Ru–Fe structures. The solvent effects were considered on the basis of the conductor polarizable continuum model (CPCM) in CH₂Cl₂ (see details in the Experimental Section). The representative frontier molecular



Table 4. Infrared v(C=C) vibrational frequencies (cm⁻¹) of the rutheniumethynyl-ferrocene complexes **1–2** in their various oxidation states.

Complex	Freq.	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2
1	ν(C≡C)	2066(m)	1973(w), 1927(s)	1970(w), 1928(w)
2		2065(m)	1972(w), 1933(m)	1938(w)

orbital energies of neutral compounds [1] and [2] are shown in Figure 6. The selected frontier molecular orbitals from $[1]^+-[2]^+$ and $[1]^{2+}-[2]^{2+}$ are displayed in Figures S4–S5. The spin density distribution with the Mulliken segmental analysis of $[1]^+$ and $[2]^+$ is depicted in Figure 7. The molecular orbitals LUMO+1, LUMO, HOMO, and HOMO-1 of neutral [1] and [2] featured similar energy values but different orbital compositions. The HO-MOs from [1] were delocalized over the entire Ru–Fc system with large contributions from the Ru–ethynyl terminal, in which the contribution from ferrocenyl to HOMOs was almost nonexistent for [2]. A large difference can be observed in the LUMO+1 orbital.



Figure 6. Selected frontier molecular orbital energies and profiles for compounds [1]-[2]. Contour values: ± 0.02 (e/bohr³)^{1/2}.



Figure 7. Spin-density distributions in [1]⁺ and [2]⁺ with the corresponding compositions (ferrocenyl/phenyl/C=C/RuCp*dppe). Contour values: ± 0.02 (e/ bohr³)^{1/2}.

The DFT-calculated spin densities of $[1]^+$ and $[2]^+$ showed similar Mulliken composition difference with the HOMOs of [1]and [2]. The spin density distribution from $[1]^+$ was delocalized over the rutheniumethynyl–phenyl–Fc skeleton with predominant contributions from the RuCp*(dppe) moiety (56 %) and a minor contribution from the Fc metal center (5 %). For $[2]^+$, a







Figure 8. Isosurface plots of molecular orbitals involved in the major electronic excitations for [1] and [1]⁺. Contour values: ±0.02 (e/bohr³)^{1/2}.

Table 5. Major electronic excitations for neutral molecules [1]-[2] and singly oxidized species [1]+-[2]+ determined by TD-DFT methods.

Complex	Wavelength [nm]	Osc. str (f)	Major contributions	Main assignment
[1]	383	0.0936	HOMO-LUMO+1 (52 %)	π-π*
	364	0.0319	HOMO-LUMO+4 (44 %)	ILCT
[1]+	1298	0.0854	$β$ -HOSO \rightarrow $β$ -LUSO (78 %)	MM'CT
	926	0.0705	α -HOSO-1 \rightarrow α -LUSO+9 (47 %)	MLCT
	778	0.0766	α -HOSO-1 $\rightarrow \alpha$ -LUSO+9 (32 %)	MLCT
	727	0.1971	$β$ -HOSO-4 \rightarrow $β$ -LUSO (52 %)	MLCT/ILCT
[2]	364	0.0211	HOMO-1-LUMO+1 (40 %)	ILCT
	359	0.0834	HOMO-LUMO+3 (40 %)	π-π*
[2] ⁺	1018	0.0160	β -HOSO \rightarrow β -LUSO (95 %)	MM′CT
	711	0.1431	β-HOSO-3 \rightarrow β-LUSO (62 %)	MLCT/ILCT

large spin density residue was present on the RuCp*(dppe) center (62 %) and received almost no contribution from the Fc unit. These results indicated that the first one-electron oxidation processes (complex **1**: $E_{1/2}(1) = 0.212$ V; complex **2**: $E_{1/2}(1) =$ 0.283 V) were associated with Ru-dominated initial oxidation steps and further confirmed the greater electronic communication between the Ru–iron center in [**1**]⁺ than in [**2**]⁺, which was previously suggested by the electrochemical and spectroelectrochemical results. In addition, 38 %–39 % of the contribution to the spin density arising from the bridge linker (benzene ethynyl) revealed that bridge ligands partially participated in redox processes.

TDDFT calculations for neutral [1]-[2] and singly oxidized states [1]⁺ and [2]⁺ were performed on the above DFT-optimized structure on the basis of CPCM in CH₂Cl₂ to understand their spectral absorptions. Selected frontier orbitals that were involved in major transitions for $[1]^{n+}$ and $[2]^{n+}$ (n = 0, 1) are shown in Figure 8 and Figure S6, and the corresponding parameters are listed in Table 5. First, for neutral [1] and [2], the absorptions in the UV region can be assigned mainly to π - π * transitions and intraligand (IL)-CT by TDDFT predictions (Table 4 and Figure 8 and Figure S6). For [1]⁺, the NIR absorption at 1396 nm from UV-Vis-NIR spectroscopy was well reproduced by the TDDFT calculations. As shown in Table 4, the calculated NIR electronic transitions were found at 1298 nm, which was close to the experimental results, and dominated by the contribution from $\beta\text{-HOSO}{\rightarrow}\beta\text{-LUSO}$ (78 %) with 0.0854 of Osc. str (f) that embodied the evident ferrocenyl \rightarrow Ru unit charge transfer (MM'CT) character. TDDFT revealed that [2]+ displayed MM'CT, but its intensity was weaker with 0.0160 of Osc. str (f) than that

of [1]⁺, such that that the NIR transition signal cannot be detected in the spectroelectrochemical experiments. In addition, 700–800 nm absorption bands were considered as MLCT/ILCT, which had major contributions from the α -HOSO-1 $\rightarrow \alpha$ -LUSO+9 and the β -HOSO-4 $\rightarrow \beta$ -LUSO transitions for [1]⁺ and the β -HOSO-3 $\rightarrow \beta$ -LUSO for [2]⁺.

Conclusion

In this report, we described the syntheses and structural characterization of the isomeric phenyl-bridged rutheniumethynyl ferrocenyl heterobimetallic complexes 1 and 2 and illustrated their electronic and spectral properties in different redox states. Electrochemical studies indicated that the two complexes exhibited two well-separated redox processes based on Ru(II)/Ru(III) and Fc/Fc⁺ couples. The first redox behavior from the Ru(II)/Ru(III) couple was confirmed by the spin density distribution calculations of [1]⁺ and [2]⁺. The large $\Delta E_{1/2}$ and K_c values indicated that the chemical stability of 1⁺ was better than that of 2⁺. The broad NIR absorption observed in 1⁺ was assigned to Fc to Ru (MM'CT) by TDDFT calculations. 2⁺ almost lacked absorption in the NIR region. The comparison of $\Delta \nu$ (C=C) generated by $1 \rightarrow 1^+$ and $2 \rightarrow 2^+$ revealed that considerable charge delocalization can occur in 1⁺. Thus, the theoretical and experimental results indicated that the 1,4-phenyl-bridged rutheniumethynyl and ferrocenyl complex 1 featured better electronic communication between the heterobinuclear centers than the metaisomer 2. This work will provide a novel path for the design of complicated mixed-valence systems with RuCp*(dppe) and ferrocenyl as end groups though bridge unit modification.



Experimental Section

General Materials: All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were predried, distilled, and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. The reagents 4-bromoaniline, 3-bromoaniline, ferrocene, trimethylsilylacetylene, KF, Pd(PPh₃)₄ and NaNO₂ were commercially available. RuCp*(dppe)Cl^[29] and Intermediates **1a**, **2a**, **1b** and **2b** were prepared by similar reported literature.^[21,22]

General Synthesis of Intermediates 1a and 2a

1a: Under ice bath (5 °C), to a H₂O (10 mL) and concentrated HCI (10 mL) solution of 4-bromoaniline (2.22 g, 0.13 mol), portionwise addition of H₂O (10 mL) solution of NaNO₂ (0.89 g, 0.13 mol), after the reaction mixture was stirred 1 h, urea (0.3 g, 0.005 mol) was added to the system to remove the rest HNO₂, and generated a yellow diazotized salt solution which was kept under 0 °C, to which added gradually (about 1-2 h) a diethyl ether solution (50 mL) of containing ferrocene (1.20 g, 6.45 mmol), $C_{16}H_{33}(CH_3)_3NBr$ (0.12 g, 0.33 mmol). The reaction mixture was stirred at room temperature for 0.5 h. After completion of the reaction, the diethyl ether was removed, and the crude product was purified by steam distillation to remove the rest ferrocene and recrystallized by petroleum ether. Yield 1.0 g (45 %) of orange red solid. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.04 (5H, s, Fc-H), 4.33 (2H, t, J(HH) = 5.0 Hz, Fc-H), 4.61 (2H, t, J(HH) = 5.0 Hz, Fc-H), 7.34 (2H, d, J(HH) = 10.0 Hz), 7.40 (2H, d, J(HH) = 10.0 Hz).

2a: The procedure of **2a** was similar to that for **1a**. 3-bromoanilne (2.22 g, 0.13 mol), NaNO₂ (0.89 g, 0.13 mol), ferrocene (1.2 g, 6.45 mmol), $C_{16}H_{33}(CH_3)_3NBr$ (0.12 g, 0.33 mmol), urea (0.3 g, 5 mmol), concentrated HCI (10 mL). Yield: 1.5 g (68 %) of an orange red solid. ¹H NMR (500 MHz, CDCI₃): δ (ppm) 4.06 (5H, s, Fc-H), 4.33 (2H, t, J(HH) = 5.0 Hz, Fc-H), 4.62 (2H, t, J(HH) = 5.0 Hz, Fc-H), 7.15 (1H, t, J(HH) = 10.0 Hz), 7.31 (1H, d, J(HH) = 10.0 Hz), 7.39 (1H, t, J(HH) = 10.0 Hz), 7.59 (1H, t, J(HH) = 5.0 Hz).

General Synthesis of Intermediates 1b and 2b

1b: Trimethylsilylacetylene (0.70 mL, 5.00 mmol) was added to a stirred solution of **1a** (341 mg, 1.00 mmol), Cul (19 mg, 0.10 mmol), and [Pd(PPh₃)₄] (116 mg, 0.10 mmol) in Et₃N (10 mL) and THF (20 mL) under an argon atmosphere, the mixture was heated to reflux for 24 h. The solution was then cooled down and filtered through a bed of Celite. The filtrate was evaporated under reduced pressure and purified by silica gel column chromatography (hexane) to give **1a** of a red brown solid. Yield: 180 mg, 50 %. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.27$ (s, 9H, SiMe₃), 4.02 (s, 5H, Fc-H), 4.35 (2H, t, J(HH) = 5.0 Hz, Fc-H), 7.31–7.36 (br, 2H, Ph-H), 7.40 (s, 2H, Ph-H).

2b: The procedure of **2b** was similar to that for **1b. 2a** (341 mg, 1.00 mmol), Cul (19 mg, 0.10 mmol), Pd(PPh₃)₄ (116 mg, 0.10 mmol), triethylamine (10 mL) and THF (20 mL), (trimethylsilyl)acetylene (0.70 mL, 5.00 mmol). Yield: 200 mg (56 %) of a red brown solid. ¹H NMR (500 MHz, CDCl₃): δ = 0.26 (s, 9H, SiMe₃), 4.04 (5H, s, Fc-H), 4.30 (2H, t, *J*(HH) = 5.0 Hz, Fc-H), 4.63 (2H, t, *J*(HH) = 5.0 Hz, Fc-H), 7.14 (1H, d, *J*(HH) = 5.0 Hz), 7.29 (1H, d, *J*(HH) = 5.0 Hz), 7.41 (1H, s), 7.60 (1H, d, *J*(HH) = 5.0 Hz).

General Synthesis of Heterobimetallic Rutheniumethynyl Ferrocenyl Complexes.^[8f]

Preparation for 1: A solution of $Cp^*(dppe)RuCl$ (227 mg, 0.34 mmol), **1b** (100 mg, 0.28 mmol), and KF (129 mg, 2.21 mmol) in 20 mL of CH₃OH and 4 mL of THF was heated to reflux under



nitrogen atmosphere for 24 h. The crude product was collected by filtration, washed with methanol and hexane. The solid was dissolved in dichloromethane and precipitated from slow diffusion with hexane. The solid was filtered and dried to give 1 as a red brown powder (140 mg, 52 %). ¹H NMR (500 MHz, CDCl₃): δ = 1.56 (s, 15H, CH₃), 2.06 (br, 2H), 2.70 (br, 2H), 4.03 (s, 5H, Fc), 4.23 (t, J(HH) = 5.0 Hz, 2H, Fc), 4.53 (t, J(HH) = 5.0 Hz, 2H, Fc), 6.73 (d, J(HH) = 10.0 Hz, 2H), 7.16 (d, J(HH) = 10.0 Hz, 2H), 7.20- 7.37 (m, 16H, dppe-Ph), 7.78-7.81 (m, 4H, dppe-Ph). ¹³C NMR (125 MHz, CDCl₃): $\delta = -10.04$ (CH₃), 29.42 (CH₂), 66.03 (Fc), 68.28 (Fc), 69.40 (Fc), 86.78 (Fc-C=C), 92.49 (C5H5), 109.84 (Ru-C=C), 125.45, 127.12, 127.16, 127.19, 127.33, 127.37, 127.40, 128.79, 129.11, 130.04, 132.71, 133.13, 133.18, 133.22, 133.71, 133.75, 133.79, 136.75, 137.13, 138.73, 138.99. 31 P NMR (200 MHz, CDCl₃): δ = 80.84. FTIR (KBr, υ , cm⁻¹): 2067 (C=C). Elemental analysis calcd. (%) for C₅₇H₆₁FeP₂Ru: C 70.95, H 6.37; found C 70.89, H 6.40.

Preparation for 2: The procedure of 2 was similar to that for 1. Cp*(dppe)RuCl (227 mg, 0.34 mmol), 2b (100 mg, 0.28 mmol), KF (129 mg, 2.21 mmol), CH₃OH (20 mL), THF (4 mL). Yield: 167 mg (62 %) of a yellow solid. ¹H NMR (500 MHz, CDCl₃): δ = 1.57 (s, 15H, CH₃), 2.06-2.09 (m, 2H), 2.68-2.73 (m, 2H), 4.03 (s, 5H, Fc), 4.25 (t, J(HH) = 5.0 Hz, 2H, Fc), 4.52 (t, J(HH) = 5.0 Hz, 2H, Fc), 6.68 (d, J(HH) = 5.0 Hz, 1H), 6.89 (s, 1H), 6.97 (t, J(HH) = 5.0 Hz, 1H), 7.03 (d, J(HH) = 5.0 Hz, 1H), 7.21-7.40 (m, 16H, dppe-Ph), 7.80-7.84 (m, 4H, dppe-Ph). ¹³C NMR (125 MHz, CDCl₃): δ = -10.04 (CH₃), 29.42 (CH₂), 66.56 (Fc), 68.34 (Fc), 69.48 (Fc), 86.53 (Fc-C=C), 92.49 (C₅H₅), 109.63 (Ru-C=C), 120.84, 127.13, 127.17, 127.21, 127.35, 127.38, 127.42, 127.90, 128.44, 128.83, 131.02, 133.13, 133.17, 133.22, 133.77, 133.81, 133.85, 136.76, 137.14, 137.80, 138.76, 139.03. $^{\rm 31}{\rm P}$ NMR (200 MHz, CDCl₃): δ = 81.00. FTIR (KBr, v, cm⁻¹): 2064 (C=C). Elemental analysis calcd. (%) for C₅₇H₆₁FeP₂Ru: C 70.95, H 6.37; found C 70.98, H 6.36.

Physical Measurements: ¹H, ¹³C, and ³¹P NMR spectra were collected on a Varian Mercury Plus 500 spectrometer (500 MHz). ¹H and ¹³C NMR chemical shifts are relative to TMS, and ³¹P NMR chemical shifts to 85 % H₃PO₄. Elemental analyses (C, H, N) were performed with a Vario EIIII Chnso instrument. Solid IR spectra was recorded on a Nicolet Avatar spectrometer from Nujol mulls that were suspended between KBr discs. Electrochemical measurements were conducted with a CHI 660C potentiostat. A single-compartment electrochemical cell contained a pre-polished platinum disk working electrode (d = 0.5 mm), a platinum wire counter electrode, and a silver wire pseudo-reference electrode. Spectroelectrochemical experiments at room temperature were performed with an airtight optically transparent thin-layer electrochemical (OTTLE) cell (optical path length of ca. 200 µm) equipped with a Pt minigrid working electrode and CaF₂ windows.^[30] The cell was positioned in the sample compartment of a Bruker Tensor FT-IR spectrometer (1 cm⁻¹ spectral resolution, 8 scans) or a Shimadzu UV-3600 UV/Vis-NIR spectrophotometer. The controlled-potential electrolyses were carried out with a CHI 660C potentiostat. Dry CH₂Cl₂ degassed by bubbling with argon for 10 min was used to prepare solutions of 10^{-3} M complexes and 10^{-1} M Bu₄NPF₆ (dry, recrystallized) added as the supporting electrolyte.

Computational Details: Density functional theory (DFT) calculations were performed using the Gaussian09 software^[31] at the B3LYP/6-31G* levels of theory. The basis set employed was 6-31G* (Lanl2DZ for Ru, Fe atom). Geometry optimization was performed without any symmetry constraints. Electronic transitions were calculated by the time-dependent DFT (TD-DFT) method. The solvation effects in dichloromethane are included for a part of the calculations with the conductor-like polarizable continuum model (CPCM).^[32] ChemPubSoc Europe

CCDC 1977229 (for 1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (21602049), the Natural Science Foundation of Hunan Province, China (Nos. 2017JJ3004), the Opening Subjects of Hunan Province Key Laboratory of Functional Metal-Organic Compounds (No. MO19K04), the Aid Programs for Technology Innovative Team and Key Discipline in Education Department of Hunan Province, and the Support Plan for Talents in Hengyang Normal University.

Keywords: Iron · Ruthenium · Ferrocenes · Electrochemistry · Mixed-valent compounds

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Received: January 15, 2020