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# Asymmetric Mixed-Valence Complexes that Consist of Cyclometalated Ruthenium and Ferrocene: Synthesis, Characterization, and Electronic-Coupling Studies

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Abstract: Three bis-tridentate ferrocene-containing cyclometalated ruthenium complexes,  $[(Fcdpb)Ru(tpy)]^+$  $(1^+)$ ,  $[(Fctpy)Ru(dpb)]^+$   $(2^+)$ , and  $[(Fcdpb)Ru(Fctpy)]^+$   $(3^+)$ , have been prepared and characterized, where Fcdpb is the 2-deprotonated form of 1,3-di(2-pyridyl)-5-ferrocenylbenzene, tpy is 2,2':6',2"-terpyridine, dpb is the 2-deprotonated form of 1,3-di(2-pyridyl)benzene, and Fctpy is 4'-ferrocenyl-2,2':6',2"-terpyridine. Single crystals of compounds  $2^+$  and  $3^+$  have been studied by X-ray analysis. Complexes  $1^+$ and  $2^+$  displayed two anodic redox waves, whilst three well-separated redox couples were observed for compound  $3^+$ . A combined experimental and computational study suggested that the ferrocene unit on the Fcdpb moiety

**Keywords:** cyclometalation • ferrocene • mixed-valent compounds • redox-active compounds • ruthenium in compounds  $1^+$  and  $3^+$  was oxidized first. In contrast, the order of the oxidation of ruthenium and ferrocene in complex  $2^+$  was reversed. Metal-tometal-charge-transfer transitions (MM'CT) have been observed for the singly oxidized states  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$ in the near-infrared region. Hush analysis showed that the metal-metal electronic couplings in compounds  $1^{2+}$  and  $3^{2+}$  were much stronger than those in compound  $2^{2+}$ .

# Introduction

Since the pioneering work of Creutz and Taube,<sup>[1]</sup> mixed-valence (MV) systems have received tremendous interest over the last three decades.<sup>[2]</sup> They are of interest for many reasons. Studies of MV systems have provided useful information regarding the charge delocalization in species with multiple redox sites and the influence of some key factors on intramolecular electron-transfer processes between the individual components.<sup>[3]</sup> This information has allowed the identification of promising candidates for molecular wires and other components for molecular electronics.<sup>[4]</sup> MV components with strong electronic coupling between redox sites usually exhibit intense absorption in the near-infrared (NIR) region, which makes them excellent materials for NIR elec-

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trochromic devices after their deposition onto electrode surfaces.<sup>[5]</sup>

Most of the reported MV systems have concentrated on homobimetallic complexes that are bridged by an unsaturated organic bridge.<sup>[2,3]</sup> One of the most widely used redox species is ferrocene (Fc),<sup>[6]</sup> which is characterized by a welldefined ferrocene/ferrocenium (Fc0/+) redox pair. In addition, the synthesis and structural modification of ferrocene derivatives are straightforward. A large number of bridged bis-ferrocene derivatives are known and the electronic coupling between individual metal centers can be finely tuned.<sup>[6]</sup> Another interesting redox species for MV chemistry is cyclometalated ruthenium,<sup>[7]</sup> which features a chelate ring that contains a Ru-C bond. Owing to the presence of an anionic carbon ligand, cyclometalated ruthenium complexes often display much lower Ru<sup>II/III</sup> redox potentials than their noncyclometalated analogues. However, the potential of the Ru<sup>II/III</sup> couple can be varied by using different auxiliary ligands.<sup>[8]</sup> Recent studies have demonstrated that cyclometalated ruthenium complexes are useful for constructing homobimetallic MV systems<sup>[9]</sup> and dye-sensitized solar cells.<sup>[10]</sup> Interestingly, these MV systems often display strong metal-metal electronic coupling with the aid of an anionic bis-carbon bridging ligand.

Compared to homobimetallic complexes, heterobimetallic MV systems are equally important and have received much attention from both experimental and theoretical points of view.<sup>[11]</sup> Herein, we present the synthesis, characterization, and electronic-coupling studies of three heterometallic com-

plexes,  $[(Fcdpb)Ru(tpy)]^+$  (1<sup>+</sup>),  $[(Fctpy)Ru(dpb)]^+$  (2<sup>+</sup>), and  $[(Fcdpb)Ru(Fctpy)]^+$  (3<sup>+</sup>), which consist of both ferrocene and cyclometalated ruthenium redox species, where Fcdpb is the 2-deprotonated form of 1,3-di(2-pyridyl)-5-ferrocenylbenzene, tpy is 2,2':6',2"-terpyridine, dpb is the 2-deprotonated form of 1,3-di(2-pyridyl)benzene, and Fctpy is 4'-ferrocenyl-2,2':6',2"-terpyridine (Scheme 1). Considering that cyclometalated ruthenium complexes are readily accessible, that their Ru<sup>II/III</sup> potentials can be easily modulated, and that they have very interesting electronic and spectroscopic properties,<sup>[8-10]</sup> these systems would be of great interest. Moreover, because cyclometalated ruthenium itself is struc-



Scheme 1. Ferrocene-containing cyclometalated  $(1^+-3^+)$  and noncyclometalated ruthenium complexes  $(4^{2+} \text{ and } 5^{2+})$ .

## Abstract in Chinese:

我们制备了三种含有二茂铁结构的环金属钌配合物 [(Fcdpb)Ru(tpy)]<sup>+</sup>(1<sup>+</sup>), [(Fctpy)Ru(dpb)]<sup>+</sup>(2<sup>+</sup>),和 [(Fcdpb)Ru(Fctpy)]<sup>+</sup>(3<sup>+</sup>)。其中,Fcdpb是1,3-二-2-吡 啶-5-二茂铁苯的2-位去质子化配体,tpy是2,2:6',2"-联 三吡啶,dpb是1,3-二-2-吡啶苯的2-位去质子化配体, Fctpy是4-二茂铁-2,2':6',2"-联三吡啶。化合物2<sup>+</sup>和3<sup>+</sup> 的结构由单晶衍射得到证实。化合物1<sup>+</sup>和2<sup>+</sup>显示两个 金属氧化还原峰,而化合物3<sup>+</sup>显示三个氧化还原峰。 实验和理论计算表明,在化合物1<sup>+</sup>和3<sup>+</sup>中,Fcdpb配体 上的二茂铁比金属钌先氧化,而配合物2<sup>+</sup>中的两个金 属氧化顺序刚好相反。单电子氧化配合物1<sup>2+</sup>,2<sup>2+</sup>,和3<sup>2+</sup> 在近红外区域显示金属到金属的电荷转移跃迁。Hush 分析表明配合物1<sup>2+</sup>和3<sup>2+</sup>具有较强的金属-金属电子相 互作用。 turally asymmetric, the connection mode between ruthenium and ferrocene can be varied. In complex 1<sup>+</sup>, the ferrocene motif and the ruthenium atom are bridged through a benzene-1,4-divl moiety, whereas, in complex  $2^+$ , they are bridged through a pyridine-4-yl moiety, and complex  $3^+$  has two appended ferrocene moieties. We have recently reported on asymmetric MV compounds that were composed of triarylamine and cyclometalated ruthenium species<sup>[12]</sup> and found that the connection mode between those two components played an important role in determining the nature of the electronic coupling between them. We considered that a similar situation would happen in systems that were composed of ferrocene and cyclometalated ruthenium. Thus, complexes  $1^+-3^+$ , with various connection modes, were designed and synthesized. The electronic properties of these complexes have been studied and compared with two ferrocene-containing noncyclometalated ruthenium complexes, (5<sup>2+</sup>: [(Fctpy)Ru(tpy)]<sup>2+</sup>  $(4^{2+})$ and  $[Ru(Fctpy)_2]^{2+}$ Scheme 1).<sup>[13]</sup>

We noticed that some heterobimetallic or multimetallic systems that consisted of ferrocene and ruthenium components have been reported previously. Indeed Taube, Henry, Lewis, and co-workers reported the first Ru-Fc heterobimetallic complex that was bridged by a cyano moiety in the early 1980s.<sup>[14]</sup> The ruthenium component, [Ru(NH<sub>3</sub>)<sub>5</sub>], was found to be oxidized first and a weak metal-to-metalcharge-transfer (MM'CT) band from Fc to Ru<sup>III</sup> was observed at around 1100 nm in MeCN ( $\varepsilon_{max} < 400 \,\mathrm{m^{-1} cm^{-1}}$ ). In the mid-1990s, Sato et al. synthesized a series of covalently connected heterobimetallic systems,<sup>[15]</sup> including some Ru-Fc complexes<sup>[15a]</sup> in which the Fc units were first oxidized and the resulting MM'CT bands were quite intense ( $\varepsilon_{max}$  $\approx$  2000–4000 m<sup>-1</sup> cm<sup>-1</sup>,  $\lambda_{max} \approx$  1550 nm). Later, Kwan and coworkers studied two heterobimetallic complexes, [Fc(4 $py)Ru(NH_3)_5](PF_6)_2$  and  $[Fc(3-py)Ru(NH_3)_5](PF_6)_2$ ,<sup>[16]</sup> in which Fc(4-py) and Fc(3-py) are 4-ferrocenylpyridine and 3ferrocenylpyridine, respectively. They found that, in these complexes, the ruthenium atom was oxidized first and the resulting MM'CT band from Fc to Ru<sup>III</sup> was solvent dependent, thus suggesting a moderate coupling between the two metals. Long and co-workers synthesized a series of ferrocene-containing bis(acetylide) ruthenium complexes and found that the oxidation of ferrocene occurred before that of the ruthenium center.<sup>[17]</sup> A MM'CT band from Ru<sup>II</sup> to Fc<sup>+</sup> was evident in the region between 1000 and 2000 nm. A heterobimetallic complex, [Ru(CH=CHFc)Cl(CO)(PiPr<sub>3</sub>)<sub>2</sub>], was recently investigated by Winter and co-workers, who concluded that the first oxidation was associated with both redox constituents but was more biased towards the ferrocene site.<sup>[18]</sup> Two distinct NIR absorption bands (1349 and 2164 nm) were observed for the singly oxidized form and both of them were assigned to iron-centered d-d type transitions instead of MM'CT transitions. In addition to these efforts, other ferrocene-hybridized ruthenium complexes have also been prepared and studied.<sup>[19]</sup> However, cyclometalated ruthenium complexes have not been employed in this context.

# **Results and Discussion**

## Synthesis

Complexes [1](PF<sub>6</sub>), [2](PF<sub>6</sub>), and [3](PF<sub>6</sub>) were synthesized as outlined in Scheme 2. A  $[Pd(PPh_3)_4]$ -catalyzed Suzuki coupling between 3,5-di(2-pyridyl)bromobenzene<sup>[12]</sup> (6) and



Scheme 2. Synthesis of compound  $1^+-3^+$ ; anions are  $PF_6^-$ .

ferroceneboronic acid afforded 1,3-di(2-pyridyl)-5-ferrocenylbenzene (7, FcdpbH) in 32% yield. The use of K<sub>3</sub>PO<sub>4</sub> as the base and dry 1,4-dioxane as the solvent was found to be important for the success of this reaction. These conditions have previously been used for Suzuki coupling reactions between ferroceneboronic acid and organic triflates.<sup>[20]</sup> No product was isolated when using  $K_2CO_3$  as the base in a mixture of tetrahydrofuran (THF) and water. First, ligand 7 was allowed to react with p-cymeneruthenium(II)-dichloride dimer in the presence of KPF6 and NaOH in MeCN to yield a cyclometalated ruthenium intermediate,  $[8](PF_6)$ , which was then treated with tpy and Fctpy<sup>[13]</sup> to give compounds  $[1](PF_6)$  and  $[3](PF_6)$  in 52% and 46% yield, respectively. Similar methods have been reported for the synthesis of tris-bidentate<sup>[10c]</sup> or bis-tridentate<sup>[21]</sup> cyclometalated ruthenium complexes. In a similar way, 1,3-di(2-pyridyl)benzene (9, dpbH) was transformed into cyclometalated ruthenium intermediate  $[10](PF_6)$ , followed by treatment with Fctpy to give complex  $[2](PF_6)$  in 45% yield. The details of the synthesis and characterization data are given in the Experimental Section.

## **Single-Crystal Structures**

Single crystals of compounds [2](PF<sub>6</sub>) and [3](PF<sub>6</sub>) that were suitable for X-ray analysis<sup>[22]</sup> were obtained by the slow diffusion of petroleum ether into a solution of the individual complex in CHCl<sub>3</sub>. ORTEPs of these two complexes are shown in Figure 1. The coordination geometry of the ruthenium atoms is distorted octahedral and they are surrounded by two tridentate ligands. One ligand is a NCN-type cyclometalating ligand and the other is a NNN-type noncyclometalating ligand. The Ru–C bond (Ru1–C1) in compounds [2](PF<sub>6</sub>) and [3](PF<sub>6</sub>) is 1.97 Å long in both cases. The Ru–



Figure 1. ORTEPs of a)  $[2](PF_6)$  and b)  $[3](PF_6)$ ; thermal ellipsoids are set at 50% probability. Solvent molecules and anions are omitted for clarity.

N bond that is opposite to the Ru–C bond (Ru1–N1) is 2.03 and 2.02 Å in compounds [2](PF<sub>6</sub>) and [3](PF<sub>6</sub>), respectively. Other Ru–N bond lengths are in the range 2.07–2.10 Å. Similar structures of cyclometalated ruthenium complexes have been reported previously.<sup>[8]</sup> In complex [2](PF<sub>6</sub>), the torsion angle between the cyclopentadiene (Cp) ligand with the NNN ligand is 9.2°. In complex [3](PF<sub>6</sub>), the torsion angles between the Cp ligand and the NCN and NNN ligands are 13.3 and 3.8°, respectively.

## **Electrochemical Studies**

The electronic properties of compounds  $1^+$ ,  $2^+$ , and  $3^+$  were studied by electrochemical analysis and compared with compounds  $4^{2+}$  and  $5^{2+}$  (Figure 2 and Table 1). Cyclic voltammograms (CVs) of compounds  $1^+$  and  $2^+$  with wider potential windows are provided in the Supporting Information, Figure S1–S3. Complex  $1^+$  shows two widely separated anodic couples at +0.41 and +0.74 V versus Ag/AgCl. The first wave is ascribed to the Fc<sup>0/+</sup> process and the second wave is assigned to the Ru<sup>II/III</sup> process. This assignment is consistent with the fact that the Fc<sup>0/+</sup> process of the pristine ligand (7) ( $E_{1/2}$ (Fc<sup>0/+</sup>)=0.53 V; see the Supporting Information, Figure S4) is slightly easier than that of a model cyclometalated



Figure 2. CVs (a–c) and DPVs (d–f) of compounds  $[1](PF_6)$  (a,d),  $[2](PF_6)$  (b,e), and  $[3](PF_6)$  (c,f) in CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 100 mVs<sup>-1</sup>.

Table 1. Electrochemical data.<sup>[a]</sup>

Compound	$E_{1/2}$ (an Fc <sup>0/+</sup>	odic) [V] Ru <sup>II/III</sup>	$E_{1/2}$ (cathodic) [V]
$[(Fcdpb)Ru(tpy)](PF_6) (1^+)$	+0.41	+0.74	-1.54
$[(Fctpy)Ru(dpb)](PF_6)$ (2 <sup>+</sup> )	+0.69	+0.58	-1.52
$[(Fcdpb)Ru(Fctpy)](PF_6) (3^+)$	+0.40, +0.75	+0.60	-1.55
$[(Fctpy)Ru(tpy)](PF_6)_2^{[b]}(4^{2+})$	+0.59	+1.42	-1.21, -1.52
$[Ru(Fctpy)_2](PF_6)_2^{[b]}(5^{2+})$	+0.58	+1.39	-1.22, -1.52
[(dpb)Ru(tpy)](PF <sub>6</sub> ) <sup>[c]</sup>	-	+0.56	-1.51
FcdpbH (7)	+0.53	-	-
Fctpy	+0.65	-	-

[a] The potential is reported as the  $E_{1/2}$  value versus Ag/AgCl. Potentials versus Fc<sup>0/+</sup> can be derived by subtracting 0.45 V. [b] See reference [13]. [c] See references [8a] and [8e].

ruthenium complex,  $[(dpb)Ru(tpy)]^+$  ( $E_{1/2}(Ru^{II/III}) = 0.56 V$ ).<sup>[8a,e]</sup> The Fc<sup>0/+</sup> process in complex **1**<sup>+</sup> becomes much easier, owing to a combined inductive and electron delocalization effect that is caused by the ruthenium component. On the other hand, the Ru<sup>II/III</sup> process in compound **1**<sup>+</sup> becomes more difficult than that in  $[(dpb)Ru(tpy)]^+$ , owing to the presence of an electron-withdrawing ferrocenium unit. This assignment is also corroborated by computational results (see below).

Complex  $2^+$  displays two anodic waves at +0.58 and +0.69 V versus Ag/AgCl. Considering that the  $E_{1/2}(\text{Ru}^{II/III})$ value of  $[(\text{dpb})\text{Ru}(\text{tpy})]^+$  is less positive than the  $E_{1/2}(\text{Fc}^{0/+})$ value for ligand Fctpy (0.65 V; see the Supporting Information, Figure S5), the oxidation of the ruthenium component, mixed with some amount of ligand oxidation, is believed to take place prior to that of the ferrocene unit. Three wellseparated redox pairs at +0.40, +0.60, and +0.75 V are evident for complex  $3^+$  in the same region. By comparing Figure 2 a-c, it is safe to assign the first wave to the oxidation of the ferrocene unit on the NCN ligand (Fc1; Figure 1b). However, the assignment of the other two waves is more difficult. We believe that the order of the Ru<sup>II/III</sup> and Fc2<sup>0/+</sup> (the ferrocene unit that is substituted on the NNN ligand) processes in complex 3<sup>+</sup> should be the same as those in complex  $2^+$ . Thus, the second and third waves in complex  $3^+$  are assigned to the Ru<sup>II/III</sup> and Fc2<sup>0/+</sup> processes, respectively. If this order was reversed, the  $E_{1/2}(Ru^{II/III})$  value for complex  $3^+$  should be much more positive than that in complex  $1^+$ , owing to the presence of two electron-withdrawing ferrocenium units. However, the third wave of complex 3<sup>+</sup> is located at essentially the same potential as the  $Ru^{{\scriptscriptstyle \rm II/III}}$  process of complex 1<sup>+</sup>. On the other hand, when the Ru<sup>II/III</sup> process occurs before the Fc2<sup>0/+</sup> process, the  $E_{1/2}(Ru^{II/III})$  value for complex  $3^+$  should be less positive than that in complex  $1^+$ because the presence of an additional electron-donating Fc moiety would make the oxidation of ruthenium more feasible. This fact supports the assignment of the second anodic wave of complex 3<sup>+</sup> to the Ru<sup>II/III</sup> process. More conclusive evidence for the assignment of the redox behavior of complex 3<sup>+</sup> comes from the spectroelectrochemistry experiments (see below), which shows that the spectroscopic changes for the single and double oxidations of complexes  $1^+$  and  $3^+$  are basically the same. This result means that the first two oxidation waves of these two complexes are of the same character.

Oxidation of the ferrocene units in compounds  $4^{2+}$  and  $5^{2+}$  ( $E_{1/2}(Fc^{0/+}) = 0.59$  and 0.58 V versus Ag/AgCl, respective- $(1)^{[13]}$  is more difficult than that of the  $Fc^{0/+}$  moiety in complex  $1^+$  (+0.41 V) and the Fc1<sup>0/+</sup> group in complex  $3^+$ (+0.40 V). This result reflects the electron-donating nature of the cyclometalated  $Ru^{II}$  component. However, the  $E_{1/2}$ -(Fc<sup>0/+</sup>) values for complexes  $4^{2+}$  and  $5^{2+}$  are less positive than the  $Fc^{0/+}$  value of complex  $2^+$  (+0.69 V) and the  $Fc2^{0/+}$ value of complex  $3^+$  (+0.75 V), thus indicating that the oxidized cyclometalated Ru<sup>III</sup> component is more electronwithdrawing than the [Ru<sup>II</sup>(tpy)<sub>2</sub>] unit. At more positive potentials, complexes 1<sup>+</sup>, 2<sup>+</sup>, and 3<sup>+</sup> all exhibit some irreversible oxidation peaks (see the Supporting Information, Figure S1-S3), possibly caused by ferrocene decomposition. Similar irreversible waves have been found in noncyclometalated complexes  $4^{2+}$  and  $5^{2+}$ .<sup>[13]</sup> In the cathodic scan, they all show a ligand-based reduction couple, which is associated with the reduction of an individual NNN ligand.

#### **Density Functional Theory (DFT) Calculations**

DFT calculations of complexes  $1^+$ ,  $2^+$ , and  $3^+$  were performed at the B3LYP/LANL2DZ/6-31G\*/vacuo level to assist in the understanding of their electronic structures (for details, see the Experimental Section). The starting coordinates were taken from the X-ray data of the cationic fragment of compounds [2](PF<sub>6</sub>) and [3](PF<sub>6</sub>). The Supporting Information, Figures S6–S8 show isodensity plots of selected frontier orbitals along with energy diagrams. The LUMOs and closely spaced LUMO+1 orbitals of all of the complexes are associated with the individual NNN ligand. Their LUMO+2 orbitals, which are much higher lying, are all dominated by the NCN ligand. These results are in agreement with above electrochemical assignment that the first catho-

dic waves are associated with the reduction of the NNN ligand.

The orbital compositions of the frontier-occupied orbitals differ from each other: The closely spaced HOMO and HOMO-1 in complex  $1^+$  are mainly associated with the ferrocene segment and the HOMO level has some contributions from the cyclometalated phenyl ring and ruthenium atom (see the Supporting Information, Figure S6). The HOMO-2 orbital has contributions from across the whole Fc-phenyl-Ru array. The low-lying HOMO-3 orbital is dominated by the ruthenium component. These orbital arrangements may suggest that the ferrocene unit in complex  $1^+$  may firstly be oxidized during the anodic scan.

The HOMO of complex  $2^+$  is dominated by the cyclometalated phenyl ring and the ruthenium atom (see the Supporting Information, Figure S7); this result is commonly observed in many monometallic cyclometalated ruthenium complexes.<sup>[8]</sup> The low-lying HOMO-1, HOMO-2, HOMO-3, and HOMO-4 levels have contributions from both the ferrocene segment and the ruthenium components. The HOMO, HOMO-1, and HOMO-2 in complex  $3^+$  (see the Supporting Information, Figure S8) resemble those in complex  $1^+$ . The HOMO-3 and HOMO-4 in complex  $3^+$ are mainly associated with the ruthenium component, whereas the HOMO-5 and HOMO-6 are dominated by the ferrocene unit on the NNN ligand side.

#### **Spectroscopic Studies**

The absorption spectra of compounds [1](PF<sub>6</sub>), [2](PF<sub>6</sub>), and [3](PF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> were compared with those of model compounds [(dpb)Ru(tpy)]<sup>+</sup> and [4](PF<sub>6</sub>)<sub>2</sub> (Figure 3). Complex 1<sup>+</sup> shows a very similar absorption pattern to that of [(dpb)Ru(tpy)]<sup>+</sup> in the visible-light region, albeit with a slightly red-shifted absorption maximum (510 versus 498 nm). These bands are ascribed to the Ru-based metalto-ligand-charge-transfer (MLCT) transitions. In addition to the Ru-based MLCT transitions at around 510 nm, complexes 2<sup>+</sup> and 3<sup>+</sup> display some shoulder bands on their lower-energy side. Similar transitions are also evident in the absorption spectrum of complex 4<sup>2+</sup>. According to previous resonance-Raman measurements,<sup>[13c]</sup> these bands are as-



Figure 3. Absorption spectra of  $[(Fcdpb)Ru(tpy)]^+$  (1<sup>+</sup>),  $[(Fctpy)Ru(dpb)]^+$  (2<sup>+</sup>),  $[(Fcdpb)Ru(Fctpy)]^+$  (3<sup>+</sup>),  $[(dpb)Ru(tpy)]^+$ , and  $[(Fctpy)Ru(tpy)]^{2+}$  (4<sup>2+</sup>) in CH<sub>2</sub>Cl<sub>2</sub>.

cribed to Fe-based MLCT transitions. This assignment is supported by TDDFT analysis of complexes  $1^+$  and  $2^+$  (see the Supporting Information, Table S1 and Figure S9). The predicted S6 and S7 excitations of complex  $2^+$  at 532 and 531 nm are responsible for the experimentally observed shoulder bands between 560 and 600 nm. These two excitations are associated with charge transfer from the HOMO-1, HOMO-2, and HOMO-3 orbitals of complex  $2^+$ ; these orbitals have both ruthenium and iron character (see the Supporting Information, Figure S7). However, this feature is not present in complex  $1^+$ .

## **Oxidative Titration and NIR-Transition Analysis**

To study the electronic coupling effect, complexes  $1^+$ ,  $2^+$ , and  $3^+$  were oxidized by either chemical or electrochemical methods and changes in their corresponding absorption spectra were recorded. Figure 4 shows the changes in the absorption spectra of complex  $1^+$  upon the gradual addition of a solution of SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub>, which has previously been used for the generation of organic MV systems.<sup>[23]</sup> When up to one equivalent of oxidant was added, the MLCT transitions in the visible-light region decreased a little with the concomitant emergence of two distinct absorption bands in the NIR region (Figure 4a). When more SbCl<sub>5</sub> was added, the MLCT transitions continued to decrease and the two new NIR bands were found to decrease as well (Figure 4b). When a solution of complex  $1^+$  in MeCN was titrated against cerium ammonium nitrate (CAN) in a similar way,<sup>[24]</sup> very similar spectroscopic changes were recorded (see the Supporting Information, Figure S9). The NIR bands



Figure 4. Changes in the absorption spectra of  $[1](PF_6)$  in  $CH_2Cl_2$  upon a) single- and b) double oxidation by gradually adding  $SbCl_5$ . Inset in (a): Gaussian-fitting of the NIR bands (in wavenumbers) of the singly oxidized form.

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of the singly oxidized state  $(1^{2+})$  show almost the same absorption patterns and energies in  $CH_2Cl_2$  or in MeCN (Figure 5), which suggests that the electron is largely delocalized across the dimetallic unit.



Figure 5. Comparison of the NIR spectra of compounds  $1^{2+}$  and  $3^{2+}$ ; \* denotes artifacts that are due to an imperfect compensation of the background.

Complex  $3^+$  exhibited similar spectroscopic changes upon single and double oxidation with the gradual addition of a solution of SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub> (see the Supporting Information, Figure S11). The NIR bands of the singly oxidized state  $(3^{2+})$  are slightly red-shifted and more intense than those of complex  $1^{2+}$  (Figure 5). The appearance and disappearance of the NIR bands of complexes  $1^+$  and  $3^+$  upon stepwise oxidation could also be realized by electrolysis by using a transparent indium-tin-oxide (ITO) glass electrode (see the Supporting Information, Figure S12 and S13). For instance, when the applied potential was gradually increased from +0.32 to +0.52 V and from +0.55 to +0.70 V versus Ag/AgCl during the spectroelectrochemical measurements of complex  $3^+$  (corresponding to the first and second oxidation event), similar NIR bands were found to increase and decrease again (see the Supporting Information, Figure S13). Upon further increasing the potential, the absorption bands in the visible-light region decreased a little. This result supports the previous electrochemical assignment of complex  $3^+$ , in which three anodic waves at +0.40, +0.60, and +0.75 V are due to the Fc1<sup>0/+</sup>, Ru<sup>II/III</sup>, and Fc2<sup>0/+</sup> processes, respectively.

Figure 6 shows the changes in the absorption spectra of complex  $2^+$  in CH<sub>2</sub>Cl<sub>2</sub> upon oxidative titration with SbCl<sub>5</sub>. In the single-oxidation process, the MLCT transitions in the visible-light region decreased and the appearance of a shallow and broad absorption in the NIR region was evident. In the double-oxidation process, both the MLCT and NIR bands decreased in intensity. Enlarged NIR spectroscopic changes are shown in the inset of Figure 6b. This new absorption band at around 1000 nm is assigned to ferrocenium-associated ligand-to-metal-charge-transfer transitions.

On the basis of this spectroscopic analysis and that of previously reported heterobimetallic Ru–Fc systems,<sup>[14–18]</sup> the major NIR bands of complexes  $1^{2+}$  and  $3^{2+}$  (around 1800 nm) are assigned to Ru<sup>II</sup> $\rightarrow$ Fe<sup>III</sup> MM'CT transitions and



Figure 6. Changes in the absorption spectra of  $[2](PF_6)$  in  $CH_2Cl_2$  upon a) single- and b) double oxidation by gradually adding  $SbCl_5$ . Inset in (a): Gaussian-fitting of the NIR bands (in wavenumbers) of the singly oxidized form. Inset in (b): Enlarged spectra in the NIR region.

the lower-energy NIR bands at around 2500 nm are assigned to Fe-centered d-d-type transitions. As far as complex  $2^{2+}$  is concerned, the observed weak NIR band at 1910 nm is assigned to the  $Fe^{II} \rightarrow Ru^{III} MM'CT$  transition. The NIR bands of complexes  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$  were fitted to two Gaussian functions (insets in Figure 4a and 6a; also see the Supporting Information, Figure S11) and the parameters for the MM'CT bands are given in Table 2. According to Hush theory,<sup>[11n,o,25]</sup> the predicted half-width for the intervalence charge-transfer bands of asymmetric MV systems,  $\Delta v_{1/2(\text{theo})}$ , equals  $[2310(\nu_{max}-\nu_0)]^{1/2}$ , where  $\nu_0$  is the internal energy difference between the two oxidation-state isomers. Although the exact  $v_0$  value cannot be directly derived from electrochemical data, it can be estimated to an upper limit by the difference between the redox potentials of the two centers in the molecules.<sup>[11]</sup> From the CV data (Figure 2), the potential differences in complexes  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$  are 0.33, 0.11, and 0.20 V, respectively. These values correspond to  $v_0 =$ 2660, 890, and 1610 cm<sup>-1</sup>, respectively. Thus, the theoretical lower limits of  $\Delta v_{1/2(\text{theo})}$  for complexes  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$  are

Table 2. Parameters for the NIR transitions in the singly oxidized states  $1^{2+}\text{--}3^{2+}\text{-}^{[a]}$ 

	<b>1</b> <sup>2+</sup>	<b>2</b> <sup>2+</sup>	<b>3</b> <sup>2+</sup>
$\lambda_{\max}$ [nm]	1780	1910	1825
$\nu_{\rm max}  [{\rm cm}^{-1}]$	5620	5230	5480
$\varepsilon_{\rm max} \left[ {\rm M}^{-1} {\rm cm}^{-1} \right]$	2860	370	4160
$\Delta v_{1/2(\text{obsv})} [\text{cm}^{-1}]$	2830	2490	2740
$\Delta v_{1/2(\text{theo})} [\text{cm}^{-1}]$	2790	3160	2990
$r_{ab}  [\text{\AA}]^{[b]}$	7.96	7.80	8.00
$H_{\rm MM'}  [\rm cm^{-1}]^{[c]}$	550	180	640

[a] These data were obtained from chemical oxidation in CH<sub>2</sub>Cl<sub>2</sub>.
[b] DFT-optimized Ru–Fe distance. [c] Calculated according to the Hush formula.

2790, 3160, 2990 cm<sup>-1</sup>, respectively. For complexes  $1^{2+}$  and  $3^{2+}$ , the observed half-widths  $(\Delta \nu_{1/2(\text{obsd})})$  are very close to the  $\Delta \nu_{1/2(\text{theo})}$  values. For complex  $2^{2+}$ , the observed half-width is narrower than the  $\Delta \nu_{1/2(\text{theo})}$  value. However, its MM'CT band is rather weak ( $\varepsilon_{\text{max}} = 370 \,\text{m}^{-1} \,\text{cm}^{-1}$ ). Because the NIR bands of complexes  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$  are somewhat weak and broad, all three complexes are assigned to Robin–Day class II systems.<sup>[26]</sup> According to the Hush formula,  $H = 0.0206 \times (\varepsilon_{\text{max}} \nu_{\text{max}} \Delta \nu_{1/2})^{1/2} / (r_{ab})$ ,<sup>[11n,p,25]</sup> where  $r_{ab}$  is taken to be the Ru–Fe distance, the electronic-coupling parameters  $(H_{\text{MM}})$  in CH<sub>2</sub>Cl<sub>2</sub> are estimated to be 550, 180, and 640 cm<sup>-1</sup> for complexes  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$ , respectively. This result suggests that the metal–metal electronic couplings in complexes  $1^{2+}$  and  $3^{2+}$  are much stronger than those in complex  $2^{2+}$ .

## **DFT** Computations of the Singly Oxidized States

DFT calculations were performed on the singly oxidized states  $1^{2+}$ ,  $2^{2+}$ , and  $3^{2+}$ . The Mulliken spin-density plots  $(\alpha - \beta)$  of these complexes (Figure 7) show that the ferrocene



Figure 7. Spin-density plots.

unit on the NCN ligand side is predominantly responsible for the spins of complexes  $1^{2+}$  and  $3^{2+}$ . However, the spin population of complex  $2^{2+}$  is dominated by the ruthenium component. These results are in agreement with the above electrochemical assignment and spectroscopic analysis. That is, the ferrocene unit on the NCN ligand side of complexes  $1^+$  and  $3^+$  and the ruthenium site of complex  $2^+$  are responsible for their first one-electron-oxidation processes. TDDFT calculations have been performed for complexes  $1^{2+}$  and  $2^{2+}$  at the same level of theory (see the Supporting Information, Table S2 and Figure S14). However, the S1 excitation of  $1^{2+}$  was predicted at a negative energy. In the low-energy region of complex  $2^{2+}$ , the oscillator strengths of all of the predicted excitations are either zero or negligible; this result means that these methods are not suitable for the TDDFT calculations of complexes  $1^{2+}$  and  $2^{2+}$ . We will look for other suitable methods in the future.

# Conclusions

In conclusion, three bis-tridentate complexes that consist of ferrocene and cyclometalated ruthenium have been successfully prepared and characterized. A combined experimental and computational study has shown that the electronic coupling between the iron and ruthenium centers is strongly dependent on the connection mode between two redox-active sites. When ferrocene is connected onto the cyclometalating (NCN) ligand, a charge transfer from the ruthenium to the iron center occurs in the singly oxidized state. On the other hand, when the ferrocene unit is connected onto the noncyclometalating (NNN) ligand, the charge transfer is reversed and the electronic coupling is much weaker. These studies will be of interest and importance for the design and synthesis of new redox-asymmetric MV systems. Compared to other reported heterobimetallic Ru-Fe complexes,<sup>[14-19]</sup> one advantage of this system is that the electronic nature of the cyclometalated ruthenium center can be easily varied by attaching different terminal ligands,[8c,d,f,9k] which would, in turn, influence the intermetallic electronic coupling. Such studies are currently underway in our laboratory.

## **Experimental Section**

#### Synthesis

General

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm relative to residual protons of the deuterated solvent (<sup>1</sup>H NMR:  $\delta$ =7.26 ppm for CDCl<sub>3</sub> and  $\delta$ =1.92 ppm for CD<sub>3</sub>CN). MS was performed on Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometers. The matrix for MALDI-TOF measurements was  $\alpha$ -cyano-4-hydroxycinnamic acid. Elemental analysis was carried out on a Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, the Chinese Academy of Sciences. Ferroceneboronic acid was purchased from Aladdin Reagent (China).

#### Synthesis of 1,3-Di(2-pyridyl)-5-ferrocenylbenzene (7)

A mixture of 3,5-di(2-pyridyl)bromobenzene<sup>[12]</sup> (155 mg, 0.50 mmol), ferroceneboronic acid (138 mg, 0.60 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (15.0 mg, 0.013 mmol), and K<sub>3</sub>PO<sub>4</sub> (212 mg, 1.0 mmol) in freshly distilled 1,4-dioxane (20 mL) was heated at reflux for 24 h under a nitrogen atmosphere. After the reaction was complete, the mixture was cooled to RT and the solvent was removed under reduced pressure. The residue was subjected to flash column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 7:1) to yield compound **7** as an orange solid in 32% yield (65 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.08 (s, 5H), 4.41 (t, *J* = 1.2 Hz, 2H), 4.90 (t, *J* = 1.2 Hz, 2H), 7.34–7.37 (m, 2H), 7.89 (t, *J* = 6.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 8.24 (s, 2H), 8.59 (s, 1H), 8.73 ppm (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 66.9, 69.1, 69.7, 85.1, 120.8, 122.3, 123.4, 125.3, 136.7, 140.0, 140.6, 149.7, 157.4 ppm; MS (EI): *m*/*z* calcd for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>Fe: 416.0976; found: 416.0981.

#### Synthesis of Intermediate [8](PF<sub>6</sub>)

ligand 7 (41.6 mg, 0.10 mmol) was added to a suspension of  $[[RuCl_2(p-cymene)]_2]$  (37.0 mg, 0.060 mmol), KPF<sub>6</sub> (36.8 mg, 0.20 mmol), and crushed NaOH (4.0 mg, 0.10 mmol) in dry MeCN (10 mL). The resulting mixture was stirred at 50 °C for 20 h under a nitrogen atmosphere and the solvent was then removed under reduced pressure. The residue was subjected to flash column chromatography on neutral Al<sub>2</sub>O<sub>3</sub> (MeCN). The yellow band was collected and the solvent was removed to give [**8**]-

 $(PF_6)$  as an orange solid (50 mg). The yield was calculated to be 59% by assuming a chemical structure of [(Fcdpb)Ru(*p*-cymene)(CH<sub>3</sub>CN)](PF<sub>6</sub>). MS (MALDI): m/z: 651.2 [(Fcdpb)Ru(*p*-cymene)]<sup>+</sup>, 517.2 [(Fcdpb)Ru]<sup>+</sup>. This sample was used directly in the next transformation without further purification or characterization.

#### Synthesis of Complex [1](PF<sub>6</sub>)

Ligand 2,2':6',2"-terpyridine (10.0 mg, 0.040 mmol) was added to a solution of [8](PF<sub>6</sub>) (20.0 mg, 0.025 mmol) in DMF (10 mL). The resulting mixture was heated at reflux for 5 h under a nitrogen atmosphere before being cooled to RT. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeCN, 1:1) to give [1](PF<sub>6</sub>) as a purple solid in 52 % yield (12 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$ =4.25 (s, 5H), 4.50 (m, 2H), 5.09 (m, 2H), 6.64 (t, J=7.2 Hz, 2H), 6.97–7.01 (m, 4H), 7.16 (s, 2H), 7.61–7.71 (m, 4H), 8.24 (d, J=8 Hz, 3H), 8.41 (d, J=5.6 Hz, 4H), 8.74 ppm (d, J=8.4 Hz, 2H); MS (MALDI): *m*/*z*: 750.2 [*M*–PF<sub>6</sub>]<sup>+</sup>; elemental analysis calcd (%) for C<sub>41</sub>H<sub>30</sub>F<sub>6</sub>N<sub>5</sub>FePRu·2H<sub>2</sub>O: C 52.92, H 3.68, N 7.53; found: C 52.64, H 3.45, N 7.61.

#### Synthesis of Complex $[3](PF_6)$

To a solution of [8](PF<sub>6</sub>) (16.0 mg, 0.020 mmol) in DMF (10 mL) was added ligand 4'-ferrocenyl-2,2':6',2"-terpyridine<sup>[13]</sup> (16.0 mg, 0.040 mmol). The resulting mixture was heated at reflux for 5 h under a nitrogen atmosphere before cooling to RT. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeCN, 1:4) to give [**3**](PF<sub>6</sub>) as a purple solid in 46% yield (10 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  = 4.23 (s, 5H), 4.30 (s, 5H), 4.46 (m, 2H), 4.70 (t, *J* = 1.2 Hz, 2H), 5.06 (m, 2H), 5.32 (t, *J* = 1.2 Hz, 2H), 6.69 (t, *J* = 6 Hz, 2H), 6.96 (t, *J* = 9.2 Hz, 2H), 7.13 (d, *J* = 5.6 Hz, 4H), 7.64 (t, *J* = 6.4 Hz, 2H), 7.71 (t, *J* = 8.4 Hz, 2H), 8.26 (d, *J* = 8 Hz, 2H), 8.45 (s, 2H), 8.55 (d, *J* = 8 Hz, 2H), 8.78 ppm (s, 2H); MS (MALDI): *m/z*: 934.3 [*M*-PF<sub>6</sub>]<sup>+</sup>; elemental analysis calcd (%) for C<sub>51</sub>H<sub>38</sub>F<sub>6</sub>N<sub>5</sub>Fe<sub>2</sub>PRu·2H<sub>2</sub>O: C 54.95, H 3.80, N 6.28; found: C 54.65, H 3.41, N 6.62.

#### Synthesis of Intermediate $[10](PF_6)$

According to the same procedure for the synthesis of [8](PF<sub>6</sub>), intermediate [10](PF<sub>6</sub>) was prepared from 1,3-di(2-pyridyl)benzene (34.8 mg, 0.15 mmol), [{RuCl<sub>2</sub>(*p*-cymene)}<sub>2</sub>] (55.0 mg, 0.090 mmol), KPF<sub>6</sub> (55.8 mg, 0.15 mmol), and crushed NaOH (6.0 mg, 0.15 mmol) in 47% yield, assuming a chemical structure of [(Fcdpb)Ru(*p*-cymene)(CH<sub>3</sub>CN)](PF<sub>6</sub>). MS (MALDI): m/z: 464.1 [(dpb)Ru(*p*-cymene)]<sup>+</sup>. This sample was used directly in the next transformation without further purification and characterization.

#### Synthesis of Complex $[2](PF_6)$

A solution of ligand 4'-ferrocenyl-2,2':6',2"-terpyridine<sup>[13]</sup> (16.0 mg, 0.040 mmol) and [**10**](PF<sub>6</sub>) (12.0 mg, 0.020 mmol) in DMF (10 mL) was heated at reflux for 5 h under a nitrogen atmosphere. After cooling to RT, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeCN, 1:1) to give [**2**](PF<sub>6</sub>) as a purple solid in 45% yield (8 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  = 4.31 (s, 5H), 4.71 (m, 2H), 5.32 (m, 2H), 6.65 (t, J = 6.4 Hz, 2H), 6.98 (t, J = 6 Hz, 2H), 7.70 (t, J = 8 Hz, 2H), 8.10 (d, J = 8 Hz, 2H), 8.33 (s, 2H), 8.53(d, J = 8 Hz, 2H), 8.79 ppm (s, 2H); MS (MALDI): m/z: 750.2 [M-PF<sub>6</sub>]<sup>+</sup>; elemental analysis calcd (%) for C<sub>41</sub>H<sub>30</sub>F<sub>6</sub>N<sub>3</sub>FePRu-H<sub>2</sub>O: C 53.96, H 3.53, N 7.67; found: C 53.90, H 3.59, N 7.65.

#### Electrochemical Measurements

All cyclic voltammetric (CV) measurements were recorded on a CHI620D potentiostat with a one-compartment electrochemical cell under a nitrogen atmosphere. All measurements were performed in 0.1 M Bu<sub>4</sub>NCIO<sub>4</sub> in the indicated solvents at a scan rate of 100 mV s<sup>-1</sup>. The working electrode was a glassy carbon electrode with a diameter of 0.3 mm. The electrode was polished prior to use on 0.05 µm alumina and rinsed thoroughly with water and acetone. A large-area platinum-wire coil was used as the counter electrode. All potentials were referenced to a Ag/AgCl electrode in a saturated aqueous solution of NaCl without regard for the liquid-junction potential.

#### Spectroscopic Measurements

All optical UV/Vis absorption spectra were obtained on a TU-1810DSPC spectrometer (Beijing Purkinje General Instrument Co. Ltd.) at RT in the stated solvents with a conventional 1.0 cm quartz cell. UV/Vis/NIR spectra were recorded on 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 that contained the compound to be studied (about  $1 \times 10^{-4}$ M) and 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. Platinum wire and Ag/AgCl in a saturated aqueous solution of NaCl were used as the counter electrode and the reference electrode, respectively. The cell was placed into the spectrophotometer to monitor spectroscopic changes during electrolysis.

## Computational Methods

DFT calculations were performed by using the B3LYP exchange correlation functional<sup>[27]</sup> and implemented in the Gaussian 03 program package.<sup>[28]</sup> The electronic structures of the complexes were determined by using a general basis set with the Los Alamos effective core potential LanL2DZ basis set for ruthenium and 6-31G\* for the other atoms in vacuo.<sup>[29]</sup>

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