### Polyhedron 173 (2019) 114109

Contents lists available at ScienceDirect

### Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Syntheses, crystal structures and MMCT properties of cyanide-bridged binuclear Ru–Fe complexes



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#### ARTICLE INFO

Article history: Received 21 June 2019 Accepted 11 August 2019 Available online 16 August 2019

Keywords: Mixed-valence Metal to metal charge transfer (MMCT) Class II Fe Ru

### ABSTRACT

In this report, two new binuclear mixed-valence (MV) compounds and their one-electron oxidation products, [MeCpLRu( $\mu$ -CN)Fe(dppe)Cp][PF<sub>6</sub>]<sub>n</sub> (L = dppe, (PPh<sub>3</sub>)<sub>2</sub>) (n = 1, 2), were synthesized and thoroughly characterized by single-crystal X-ray diffraction analysis. Complexes  $1^{2+}$  and  $2^{2+}$  are one-electron oxidation products of  $1^{1+}$  and  $2^+$ , respectively. The electronic absorption results indicate that there exists metal to metal charge transfer (MMCT) in the one-electron oxidation products, which is strongly supported by the theoretical calculations. Complexes  $1^{2+}$  and  $2^{2+}$  can be defined as Class II MV compounds. It is found that the MMCT band is obviously red-shifted on going from  $1^{2+}$  to  $2^{2+}$ , because the donating electron ability of (PPh<sub>3</sub>)<sub>2</sub> is stronger than that of dppe.

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### 1. Introduction

Electron transfer (ET) processes, a ubiquitous phenomenon in many fields [1,2] such as physics, chemistry and so on, can be investigated further through the mixed-valence (MV) multinuclear transition-metal compounds [3–5]. Since the Creutz and Taube ion was reported in the 1960s [6], a large number of MV binuclear compounds have been synthesized and characterized, their magnetic, optical, electrical properties have also been studied [7-11]. As a result, numerous potential applications are emerged in nonlinear optical devices, redox-active molecular switches [12-15]. catalytic and energetic conversion [16,17]. The MV systems often show inter-valence charge transfer (IVCT) absorption bands, whose energy, intensity and bandwidth at half-height are related to the fundamental factors that affect intramolecular electron communications in systems. Cyanide-bridged complexes are the most representative candidates among thousands of MV species, because the cvanide group, as a short-range linear-bridged ligand with unique coordination character, can drive the electronic and magnetic communication effectively among the connected metal centers [5,7,18]. Due to great efforts made by experimentalists and theoreticians, some related theories about mixed valence complexes have been put forward to learn the nature of ET well [19-25]. To explore factors which influence the electronic and magnetic coupling properties, our group has taken strategies including changing ligands on centric metal, varying the orientation of bridge-cyanide group or using different meals [26–28]. Recently, some work has been reported about binuclear cyanide-bridged complexes with different degrees of MMCT property which implies it is worthy to synthesize and investigate binuclear cyanide-bridged complexes.

Herein, we report the syntheses and characterization of two new binuclear MV heterometallic complexes and their oneelectron oxidation products,  $[MeCpL_2Ru(\mu-CN)Cp(dppe)Fe][PF_6]_n$  $(L_2 = dppe, (PPh_3)_2)$  (n = 1, 2). These complexes help us to investigate the influences of different ligands on electronic coupling between metallic atoms. The time-dependent density functional theory (TD-DFT) calculations are consistent well with our resuluts. On the basis of the Hush Equation [25], the analysis of electronic absorption band and the Robin and Day's classification [29], the targeted complexes could be attributed as Class II MV species.

### 2. Experimental

### 2.1. Physical measurements

The elemental analyses (C, H and N) were conducted on Vario MICRO elemental analyzer. Infrared (IR) spectra characterization was carried out on a Vertex 70 FT-IR spectrophotometer with KBr pellets. Electronic absorption spectra in the UV-vis-NIR





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regions were collected with the PerkinElmer Lambda 950 UV–vis– NIR spectrophotometer. The electrochemical experiments were measured under argon by V3-Studio in the dichloromethane solutions which promoting electrolyte is 0.1 M (Bu<sub>4</sub>N)PF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup>. The electrolytic cell consists of glassy graphite, platinum and Ag/AgCl as working, counter and reference electrode, respectively. The single-crystal X-ray diffraction data for all these complexes were collected on a Saturn724 + CCD diffractometer equipped with graphite monochromatic Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation by using an  $\omega$ -scan model technique at 293 K. All crystallographic structures were solved by direct methods using SHELXL-2014/7 and refined with Olex 2 program package [30,31].

### 3. Materials and synthesis

### 3.1. Materials

All operations were conducted in an argon atmosphere through the standard Schlenk techniques useless extra stated. Cp(dppe)Fe (NCCH<sub>3</sub>)Br (dppe = bis(diphenylphosphino)ehane, Cp = cyclopentadienyl) was prepared by the previous literature [32]. Dichloromethane for CV was dried by distillation over calcium hydride under nitrogen atmosphere. Methanol was dried by distillation over magnesium. All other reactants were purchased commercially and used directly without further purification.

### 3.2. Synthesis

### 3.2.1. Preparation of MeCp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>Cl

Under argon atmosphere, the compound of methylcyclopentadiene dimer (Scheme 1) was heated to decomposition at 230 °C and then collected the product. The other procedures are similar to that for Cp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>Cl [33], excepting that the decomposition product replaces cyclopentadiene. The ethanol (30 ml) solution with PPh<sub>3</sub> (4.04 g, 15 mmol) was stirred for 15 min. Then, RuCl<sub>3</sub> (1.00 g, 4.82 mmol) and methylcyclpentadiene (5 ml) were added. The solution was refluxed for 4 h until a large amount of yellow precipitate generated. The yellow solid, MeCp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>Cl (MeCp = methylcyclopentadiene), was filtered, washed with methanol and hexanes. Yield: 1.85 g; 63%.

### 3.2.2. Preparation of MeCp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>CN

KCN (2.58 g, 39.62 mmol) was added to a solution of MeCp (PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>Cl (2.14 g, 3 mmol) in methanol(20 ml). The solution was refluxed until a large amount of golden-yellow solid generated. The precipitate was collected, washed with methanol, water and ethyl ether, giving the yellow product (1.73 g, 79%). IR (KBr, cm<sup>-1</sup>): 2061 (C=N).

### 3.2.3. Preparation of MeCp(dppe)Ru<sup>II</sup>CN

1.2 equiv of dppe (0.8 g, 2.0 mmol) was added to a solution of MeCp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>Cl (1.17 g, 1.60 mmol) in toluene (30 ml). The mixture was refluxed overnight. The resulting solution was purified by chromatograph. Evaporation of the obtained eluate gave the orange crystals of MeCp(dppe)Ru<sup>II</sup>Cl. The synthetic procedure of



MeCp(dppe)Ru<sup>II</sup>CN was similar to that for MeCp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>CN by using MeCp(dppe)Ru<sup>II</sup>Cl instead of MeCp(PPh<sub>3</sub>)<sub>2</sub>Ru<sup>II</sup>Cl. Yield: 0.54 mg; 56%. IR (KBr, cm<sup>-1</sup>): 2071 ( $C \equiv N$ ).

### 3.2.4. Preparation of $[MeCp(dppe)Ru^{II}(\mu-CN)Fe^{II}(dppe)Cp](PF_6)$ , **1** [**PF**<sub>6</sub>]

Under argon atmosphere, Cp(dppe)Fe(NCCH<sub>3</sub>)Br (0.22 g, 0.34 mmol) was added to a solution of MeCp(dppe)RuCN (0.20 g, 0.331 mol) in CH<sub>3</sub>OH (25 ml), resulting a claret solution. After stirring for 6 h at 50 °C, NH<sub>4</sub>PF<sub>6</sub> (0.08 g, 0.500 mol) was introduced to the solution and the reaction proceeds for extra one hour. Then the solution was filtered and the obtained solid was washed by diethyl ether. The product was crystallized from the diethyl ether and dichloromethane at room temperature as the claret crystals (0.31 g, 72%). Elemental analysis calcd (%) for **1**[**PF**<sub>6</sub>]: C, 59.31; H, 4.59; N, 1.06. Found: C, 57.95; H, 4.51; N, 1.06. IR (KBr, cm<sup>-1</sup>): 2081 (C $\equiv$ N).

### 3.2.5. Preparation of $[MeCp(dppe)Ru^{II}(\mu-CN)Fe^{III}(dppe)Cp](PF_6)_2$ , **1** [PF<sub>6</sub>]<sub>2</sub>

To a 20 ml dichloromethane solution of **1** (0.31 g, 0.235 mol) was added 1 equiv of  $(Cp)_2FePF_6$  (0.08 g, 0.242 mol). At room temperature, the mixture solution was stirred for 2 h. The solution was filtered and the solvent was condensed to 3 ml under reduced pressure. A large amount of diethyl ether was added and the product was formed as a precipitate. The product was obtained in diethyl ether and dichloromethane at room temperature as the dark red crystals (0.30 g, 88.2%). Elemental analysis calcd (%) for **1**[**PF**<sub>6</sub>]<sub>2</sub>: C, 54.52; H, 4.16; N, 0.96. Found: C, 54.43; H, 4.20; N, 0.83. IR (KBr, cm<sup>-1</sup>): 2015 (C $\equiv$ N).

### 3.2.6. Preparation of $[MeCp(PPh_3)_2Ru^{ll}(\mu-CN)Fe^{ll}(dppe)Cp](PF_6)$ , **2** [**PF**<sub>6</sub>]

Under argon atmosphere, Cp(dppe)Fe(NCCH<sub>3</sub>)Br (0.17 g, 0.265 mol) was added to a solution of MeCp(PPh<sub>3</sub>)<sub>2</sub>RuCN (0.20 g, 0.273 mol) in CH<sub>3</sub>OH (25 ml). After stirring for 6 h at 50 °C, NH<sub>4</sub>PF<sub>6</sub> (0.06 g, 0.368 mol) was introduced to the solution and the reaction proceeds for another one hour. The solvent was removed under reduced pressure totally, and the obtained solid was dissolved in a small amount of dichloromethane, and layered by diethyl ether at room temperature. The orange crystals (0.28 g, 77.8%) were obtained. Elemental analysis calcd (%) for **2[PF<sub>6</sub>]**: C, 63.71; H, 4.77; N, 1.00. Found: C, 64.64; H, 4.70; N, 0.97. IR (KBr, cm<sup>-1</sup>): 2069 (C $\equiv$ N).

## 3.2.7. Preparation of $[MeCp(PPh_3)_2Ru^{II}(\mu-CN)Fe^{III}(dppe)Cp](PF_6)_2$ , **2** $[PF_6]_2$

To a 20 ml dichloromethane solution of **3** (0.35 g, 0.251 mol) was added 1 equiv of  $(Cp)_2FePF_6$  (0.1 g, 0.302 mol). At room temperature, the mixture solution was stirred for 2 h. After that, the solution was concentrated to 3 ml under reduced pressure and then 70 ml diethyl ether was added, giving a precipitate. The product was obtained in diethyl ether and dichloromethane at room temperature as the dark green crystals (0.33 g, 84.6%). Elemental analysis calcd (%) for **2[PF<sub>6</sub>]**<sub>2</sub>: C, 51.70; H, 3.72; N, 0.78. Found: C, 51.81; H, 3.74; N, 0.73. IR (KBr, cm<sup>-1</sup>): 1986 (C $\equiv$ N).

### 4. Results

#### 4.1. X-ray structure determination

The crystallographic structures of complexes  $1^+$ ,  $2^+$  and their one-electron oxidation products  $1^{2^+}$ ,  $2^{2^+}$  were determined at room temperature by single crystal X-ray analysis. The space groups are  $P\bar{1}$  for  $1^+$  and  $2^{2^+}$ ,  $P2_1/n$  for  $1^{2^+}$ , and *Cc* for  $2^+$ , respectively. It should



3

be noted, however, the determined centrosymmetric structure of 1<sup>+</sup> originates from the superimposition of the opposite arrangement of two asymmetric 1<sup>+</sup>, which results in the positional disorders of Ru(1)/Fe(1), C(1)/N(1) along Ru(1)-C(1) $\equiv$ N(1)-Fe(1) and the methyl group on Cp. Some selected bond lengths and angles are listed in the Table 1 except for 1<sup>+</sup>. Tables S1 and S2 shows the crystal data and structure refinement for complexes. The structures of complexes 2[PF<sub>6</sub>]<sub>2</sub> and 2[PF<sub>6</sub>]<sub>2</sub> are shown in Fig. 1. The structures of  $1[PF_6]$  and  $1[PF_6]_2$  are similar to those of (a) 2 [**PF**<sub>6</sub>]<sub>2</sub> and (b) **2**[**PF**<sub>6</sub>]<sub>2</sub>, thus only the structure of complex **2**[**PF**<sub>6</sub>]<sub>2</sub> and  $2[PF_6]_2$  are described herein. For complex 2, the Ru atom was coordinated to a MeCp fragment, two P atoms of PPh<sub>3</sub> fragment and one C atom of the cyanide group while the Fe atom was connected to a Cp moiety, two P atom of dppe and one N atom of the cyanide group. Ru(1)-C(1)=N(1)-Fe(1) of all the complexes are close to linearity with the angle of  $Ru(1)-C(1) \equiv N(1)$  and  $C(1) \equiv N(1)$ N(1)-Fe(1) over 165°. Comparison with some similar compounds [34], the Ru–C≡N–Fe chain of these complexes is less linear, presenting a significant torsion around the cyanide bridge. It is a result of the large ligand coordinated to metallic atoms. Some primary bond lengths vary as oxidation proceeds, such as Ru-P, Fe-P and so on. Upon oxidation, the Ru–P bond lengths decrease by 0.02 Å from  $2^+$  (av. 2.3286(11) Å) to  $2^{2+}$  (av. 2.3479(17) Å). Meanwhile, the Fe–P bond lengths of  $2^{2+}$  (av. 2.269(2) Å) are longer than the corresponding Fe-P bond lengths of 2<sup>+</sup> (av, 2.2038(12) Å) because of the less back-binding from the Fe atom to the phosphorus ligands. Once oxidation occurs, the bond lengths of Ru(1)-C(1)and Fe(1)-N(1) in complex 2 get shorter, decreasing from 2.023 (5) Å to 1.970(5) Å and from 1.973(4) Å to 1.895(5) Å, respectively. These variation trends are similar to those found in our previous work [28,34,35], which can be confirmed that the oxidation state of Fe in 2<sup>+</sup> and 2<sup>2+</sup> is +2 and +3, respectively. Moreover, it suggests that some electron delocalization exists in 2<sup>2+</sup> along Ru<sup>II</sup>-CN-Fe<sup>III</sup>, which is strongly supported by the DFT calculations results (see below). In  $1^+$ , bond lengths of Ru(Fe)-P and Ru(Fe)-C(N) are a result of the average of Ru-P and Fe-P, Ru-C and Fe-N bond

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Selected bond lengths (Å) and angles (°) for compounds 1 and compounds.

	1[PF <sub>6</sub> ] <sub>2</sub>	2[PF <sub>6</sub> ]	2[PF <sub>6</sub> ] <sub>2</sub>
Ru(1)-C(1)	1.966 (7)	2.023 (5)	1.969 (6)
Fe(1)-N(1)	1.923 (6)	1.973 (4)	1.893 (5)
Ru(1)–P (av.)	2.291 (2)	2.3286 (11)	2.3478 (17)
Fe(1)-P (av.)	2.282 (2)	2.2038 (12)	2.269 (2)
C(1)-N(1)	1.163 (8)	1.148 (5)	1.167 (7)
Ru(1)-C(1)=N(1)	173.9 (6)	169.3 (4)	171.1 (5)
$Fe(1)-N(1)\equiv C(1)$	166.7 (6)	165.6 (4)	168.0 (4)
Fe(1)-P (av.) C(1)-N(1) Ru(1)-C(1) $\equiv$ N(1) Fe(1)-N(1) $\equiv$ C(1)	2.282 (2) 1.163 (8) 173.9 (6) 166.7 (6)	2.2038 (12) 1.148 (5) 169.3 (4) 165.6 (4)	2.269 (2) 1.167 (7) 171.1 (5) 168.0 (4)

lengths due to the positional disorder. However, similar bond length changes of complexes  $1^*$  and  $1^{2*}$  to those changes of  $2^*$ and  $2^{2*}$  should be expected. Furthermore, there are some differences between molecular structures in complexes  $1^{2*}$  and  $2^{2*}$ . The Ru–P bond lengths in complex  $1^{2*}$  (2.291(2) Å) are obviously shorter than those in complex  $2^{2*}$  (2.3478(17) Å). By contrast, the Fe–P bond lengths in complex  $1^{2*}$  (2.282(2) Å) are longer than those in complex  $2^{2*}$  (2.269(2) Å), suggesting that the more electron delocalization along Ru<sup>II</sup>–CN–Fe<sup>III</sup> in  $2^{2*}$  than in  $1^{2*}$ . These facts may suggest that in MV complexes, the more electron-rich ligand in the electron-donating fragment is supported some electron delocalization between metal centers in different oxidation states.

### 4.2. Electrochemistry

The cyclic voltammetry (CV) for both complexes, **1** and **2**, was acquired in dichloromethane in order to identify its redox sites. The results are displayed in Fig. 2 and Table 2. As a reference to the Cp<sub>2</sub>Fe<sup>+/0</sup>, cyclic voltammograms present two-pair stable electrochemically reversible redox waves. The signals of complexes 1  $[\mathbf{PF}_6]_n$  (*n* = 1, 2) are located at -0.25 V and 0.86 V, while the wave couples of complex  $2[PF_6]_n$  (n = 1, 2) are observed at -0.12 V and 0.82 V. Based on the electrochemically cyclic voltammograms,  $(Cp)_2FePF_6$  was chosen as oxidant for the preparation of oxidized products. According to the previous paper [34,36,37], the lower potentials are attributed to Fe<sup>II</sup>/Fe<sup>III</sup> moiety while the higher potentials belong to Ru<sup>II</sup>/Ru<sup>III</sup> center. Looking insight into the CV, the potential of Ru of complex **1** is a bit bigger than that of complex **2**. The reason is that the  $(PPh_3)_2$  moiety has a greater ability to donate electron than the dppe moiety. What is worth mentioning is that the  $\triangle E$  between Ru and Fe of complex **1** is larger than that of complex 2, which implies the interaction between metals is enhanced in mixed valence binuclear compound as the increasing donating electron ligand.

### 4.3. IR spectroscopy

The IR spectra were conducted to explore the stretching frequency of CN in all the redox states of complexes to compare the structural changes. All the cyanide stretches with sharp peaks locate between 2100 and 1980 cm<sup>-1</sup> as shown in the Fig. 3. Compared to the precursors, the signal of v(CN) of the products moves to a higher frequency because of the kinematic effect, which impedes the vibration of CN group due to the attachment of the Fe metal [36–39]. The signal of **1**<sup>+</sup> display a band at 2081 cm<sup>-1</sup> while **2**<sup>+</sup> is at 2067 cm<sup>-1</sup>. With respect to the similar complexes,



Fig. 1. Molecular structures of (a) 2[PF<sub>6</sub>] and (b) 2[PF<sub>6</sub>]<sub>2</sub> (hydrogen atoms have been removed for clarity).



Fig. 2. Cyclic voltammograms of 1[PF<sub>6</sub>]<sub>n</sub> (left) and 2[PF<sub>6</sub>]<sub>n</sub> (right) (n = 1,2) in a 0.10 M dichloromethane solution of Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup> vs Cp<sub>2</sub>Fe<sup>+/0</sup>.

**Table 2** Electrochemical Data (vs  $Cp_2Fe^{+/0}$ ) for complexes **1**[**PF**<sub>6</sub>]<sub>*n*</sub> and **2**[**PF**<sub>6</sub>]<sub>*n*</sub> (*n* = 1, 2) in 0.10 M dicholoromethane solution of Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup>.

		$E_{1/2}(E_{\rm a}-E_{\rm c})/{\rm V}~{\rm (V)}$		
Complexes	L	Fe <sup>2+/3+</sup>	Ru <sup>2+/3+</sup>	$\triangle E/V$
1 2	dppe (PPh <sub>2</sub> ) <sub>2</sub>	-0.25 -0.12	0.86 0.82	1.11 0.94

**Table 3** The IP spectra bands y(CN) of complexity

The IR spectra bands, v(CN), of complexes  $1[PF_6]_n$  and  $2[PF_6]_n$  (n = 1, 2) and their raw materials (in KBr, cm<sup>-1</sup>).

Complexes	v(CN)	riangle v
MeCp(dppe)Ru-CN	2071	
1[PF <sub>6</sub> ]	2081	10
1[PF <sub>6</sub> ] <sub>2</sub>	2015	-56
MeCp(PPh <sub>3</sub> ) <sub>2</sub> Ru-CN	2061	
2[PF <sub>6</sub> ]	2067	6
2[PF <sub>6</sub> ] <sub>2</sub>	1986	-75

[Cp(dppe)RuCNFe(dppe)Cp][PF<sub>6</sub>] [40] and [Cp(PPh<sub>3</sub>)<sub>2</sub>RuCNFe (dppe)Cp][PF<sub>6</sub>] [39], the v(CN) of **1**<sup>+</sup> and **2**<sup>+</sup> reveals a red-shift. This indicates that with the stronger electron-donor ligand, the increasing feedback effect from Ru<sup>II</sup> into the anti-bond of CN group makes bond order of CN decrease. It leads to the v(CN) shifted to the lower vibrational frequency. Due to the same reason, the v(CN) of the oxidized form are shifted into the lower frequency region and show more intense, as shown in Fig. 3 and Table 3. The similar phenomena have been found in many similar mixed valence complexes. This intensification can be attributed to the vibronic coupling with MMCT [41–44]. Besides, the v(CN) stretching frequencies of series complexes **1** are larger than that of series complexes **2**. This is because the donor characteristic property of the (PPh<sub>3</sub>)<sub>2</sub> moiety is stronger than the dppe moiety, which is in accordance with the CV results.

#### 4.4. UV-VIS-NIR spectroscopy

In order to investigate the changes of electronic properties of various oxidation states of the complexes, the UV/Vis/NIR spectra

of the complexes were measured in the  $CH_2Cl_2$  solution, as shown in Fig. 4. The absorption maxima data for all complexes are listed in Table 4. From the Fig. 4, the complexes of 1<sup>+</sup> and 2<sup>+</sup> don't present any absorption band in the NIR region. But their oxidized complexes give rise to the new intense absorption bands at a  $\lambda_{max}$  of 626.0 nm for 1<sup>2+</sup> and 718.4 nm for 2<sup>2+</sup>. The two intensive bands of these complexes in the visible to near–infrared region are attributed to the broad MMCT bands from the Ru<sup>II</sup> center to Fe<sup>III</sup> center [39,45,46]. The red-shift of about 92 nm of 2<sup>2+</sup> relative to 1<sup>2+</sup> shows that the former has a lower MMCT energy. Based on the MMCT band shape and the theoretical calculation (see below), the mixed valence complexes of 1<sup>2+</sup> and 2<sup>2+</sup> can be defined as the typical Class II mixed-valence compounds according to the Robin and Day's categorization [29].

#### 4.5. TDDFT/DFT calculations

The TDDFT//DFT was operated through B3LYP/lanl2dz [47] in order to understand the nature of electronic distribution and



Fig. 3. Stretches frequencies of CN group for complexes 1 and 2.



Fig. 4. The UV-VIS-NIR absorption spectra of complexes 1 (left) and 2 (right).

### **Table 4** The electronic absorption data for the complexes $1[PF_6]_n$ and $2[PF_6]_n$ (n = 1, 2) in dichloromethane.

Complexes	λ/nm	$\epsilon/M^{-1} cm^{-1}$
1[PF <sub>6</sub> ] <sub>2</sub>	626.0	3096
2[PF <sub>6</sub> ] <sub>2</sub>	718.4	2871

### Table 5

Mulliken spin densities of mixed-valence species.

	Ru	Fe
1 <sup>2+</sup>	0.037917	1.199535
2 <sup>2+</sup>	0.046251	1.191370

transition further. As shown in Table 5, the spin densities of the mixed-valence species are essentially located on Fe<sup>III</sup>, supporting the attribution of complexes 1<sup>2+</sup> and 2<sup>2+</sup> as Class II MV compounds. For the mixed valence complex 1<sup>2+</sup>, the calculated absorption band present a band at 632.95 nm in the NIR region which is close to the experimental bands at 626 nm. Similarly, the calculated absorption band locates at 672.15 nm for the mixed valence complex 2<sup>2+</sup>, whose experimental band is at 718 nm. Both the calculated electronic transition bands in the NIR region are in good agreement with the experimentally observed transitions. Their electronic configurations are shown in Figs. 5 and 6. The figures display clearly that absorption bands of all the complexes can be attributed to MMCT from the Ru<sup>II</sup> unit to the Fe<sup>III</sup> unit upon one electron oxidized. The major contribution for the MMCT absorption band of



HOMO 250B

LUMO 251B

Fig. 5. Molecular orbital diagrams of HOMO (250B), HOMO (249B), HOMO (250B) and LUMO (251B) for 1<sup>2+</sup> in dichloromethane. The green and red areas represent gain and losses of density.



Fig. 6. Molecular orbital diagrams of HOMO (283B) and LUMO (284B) of 2<sup>2+</sup> in dichloromethane. The green and red areas represent gain and losses of density.

complex  $1^{2*}$  comes from molecular orbital 250B  $\rightarrow$  251B and 249B  $\rightarrow$  251B transitions. For complex  $2^{2*}$ , the contribution to the MMCT absorption band mainly comes from molecular orbital 283B  $\rightarrow$  284B transition.

### 5. Conclusion

In summary, we have synthesized and characterized two new binuclear compounds [MeCpL<sub>2</sub>Ru(µ-CN)Fe(dppe)Cp][PF<sub>6</sub>] (L<sub>2</sub> = dppe, (PPh<sub>3</sub>)<sub>2</sub>). Fortunately, their one-electron oxidation products [MeCpL<sub>2</sub>Ru(µ-CN)Fe(dppe)Cp][PF<sub>6</sub>]<sub>2</sub> have been successfully isolated and characterized including by single-crystal X-ray diffraction structural analyses. The crystal structure analyses and the IR characterization suggest that there exist electron delocalization on metals along Ru<sup>II</sup>-CN-Fe<sup>III</sup> in both **1**<sup>2+</sup> and **2**<sup>2+</sup>. The electronic absorption spectra reveal the presence of MMCT in **1**<sup>2+</sup> and **2**<sup>2+</sup>. What's more, it is found that **2**<sup>2+</sup> has a lower MMCT energy than complex **1**<sup>2+</sup>, indicating the ability to donate electrons of the (PPh<sub>3</sub>)<sub>2</sub> is larger than that of the dppe. This work suggests that the MMCT properties between metals can be fine-tuned by the small difference of the ligand around the metal center.

### Acknowledgements

We thank the National Science Foundation of China (21773243) and the Strategic Priority Research Program of Chinese Academy of Sciences (XDB20010200) for financial support.

### Appendix A. Supplementary data

CCDC 1914722 and 1914725 contains the supplementary crystallographic data for compounds  $1[PF_6]_n$  and  $2[PF_6]_n$  (n = 1, 2).. These data can be obtained free of charge via http://www. ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi. org/10.1016/j.poly.2019.114109.

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