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# Different Degree of Electron Delocalization in Mixed-Valence Ru-Ru-Ru Compounds via Cyanido-/Isocyanido-Bridge Isomerism

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**Abstract:** The two stable pairs of trimetallic compounds trans-[Cp\*(dppe)Ru( $\mu$ -NC)Ru(dmap)<sub>4</sub>( $\mu$ -CN)Ru(dppe)Cp\*][PF<sub>6</sub>]<sub>n</sub> (**1**[PF<sub>6</sub>]<sub>n</sub>,  $n = 2, 3; Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadiene; dppe = 1,2bis- (diphenylphosphino)ethane) and trans-[Cp\*(dppe)Ru( $\mu$ -CN)Ru-(dmap)<sub>4</sub>( $\mu$ -NC)Ru(dppe)Cp\*][PF<sub>6</sub>]<sub>n</sub> (**2**[PF<sub>6</sub>]<sub>n</sub>, n = 2, 3) with cyanide/isocyanide isomerism have been synthesized and fully characterized. **1**<sup>3+</sup>[PF<sub>6</sub>]<sub>3</sub> and **2**<sup>3+</sup>[PF<sub>6</sub>]<sub>3</sub> are the one-electron oxidation products of **1**<sup>2+</sup>[PF<sub>6</sub>]<sub>2</sub> and **2**<sup>2+</sup>[PF<sub>6</sub>]<sub>2</sub>, respectively. The investigated results suggest that **1**[PF<sub>6</sub>]<sub>3</sub> is a class III mixed-valence compound. Whereas, **2**[PF<sub>6</sub>]<sub>3</sub> might be an unusually symmetrical class II-III mixed-valence compound composed of the two asymmetrical delocalized Ru<sup>III</sup>-NC-Ru<sup>II</sup> mixed-valence subunits.

Electron transfer is one of the most fundamental processes in chemistry, physics and biology.<sup>[1]</sup> Mixed-valence (MV) compounds are excellent model systems for understanding the electron transfer processes and have attracted a great deal of attentions over the past decades.<sup>[2]</sup> Furthermore, MV compounds have applications in various fields ranging from biology to electronic devices such as quantum cellular automata,<sup>[3]</sup> molecule switch<sup>[4]</sup> and phase-coherent logic.<sup>[5]</sup> To interpret electron transfer processes in MV compounds, some important theories have been developed.<sup>[2a, 2d, 6]</sup> According to Robin and Day, any MV compounds can be classified into one of three classes: Class I, the electronic interaction is null or very weak; Class II, the electronic interaction is moderate, but the charge is still localized; and Class III, the electronic interaction is very strong, the charge is delocalized.<sup>[2a]</sup> Both classes II and III compounds generally exhibit an absorption in the visible or nearinfrared region. Generally, the two classes can be distinguished based on the following two criterions: First, class II MV compounds exhibit a broad and weak absorption, but class III mixed-valence compounds show a narrow and intense absorption; Second, the energy of the absorption of class II mixed-valence compounds is solvent dependent, but that of class III mixed-valence compounds is solvent independent. In addition to the Robin and Day classification, Meyer et al. proposed a new category of the borderline class II-III systems which exhibit an intermediate behavior between class II and class III.<sup>[2d]</sup> The energy of the absorption of class II-III mixedvalence compounds is solvent independent, but the charge is localized.<sup>[2i]</sup> To date, it has been reported a huge amount of MV

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compounds, but most of which belong to Class II systems. For cyanido-bridged MV compounds,<sup>[2h, 7]</sup> there have been even few well-characterized examples of fully delocalized (class III) MV systems. In 2014, Baraldo and co-workers reported the first example of class III cyanido-bridged species which was confirmed by in situ NIR and IR spectroscopy and supported by DFT calculations.<sup>[8]</sup> Most recently, we have reported an example of delocalized cyanide-bridged MV compound induced by thermal electron transfer.<sup>[9]</sup> Unfortunately, however, their molecular structures were not obtained. Thus, isolation and fully characterization of Class III cyanido-bridged MV compounds are still challengeable.

On the other hand, it is important to investigate the factors influencing intervalence charge transfer (IVCT) of cyanidobridged MV compounds, including the nature of the metals and their ligands, the shape and length of the chains and the orientation of the cyanido bridges.<sup>[2h]</sup> To date, much efforts have been devoted to the investigations on the former two influencing factors.<sup>[2h, 7]</sup> However, it is relatively less known but significant how IVCT is influenced by the orientation of the cvanido bridges.<sup>[10]</sup> Particularly, there have been even few reports about influences of M'-NC-M-CN-M'  $\rightarrow$  M'-CN-M-NC-M' isomerism on IVCT of cvanidometal-bridged MV compounds. Herein, we report the stable pairs of MV compounds [Cp\*(dppe)Ru<sup>III</sup>(µ-NC)- $Ru^{II}(dmap)_4(\mu-CN)Ru^{II}(dppe)Cp^*][PF_6]_3$  $(1[PF_6]_3)$ and [Cp\*(dppe)Ru<sup>II</sup>(μ-CN)Ru<sup>III</sup>(dmap)<sub>4</sub>(μ-NC)Ru<sup>II</sup>(dppe)Cp\*][PF<sub>6</sub>]<sub>3</sub> (2[PF<sub>6</sub>]<sub>3</sub>) with cyanide/isocyanide isomerism. The investigations show that the former belongs to class III species, and the latter might be a class II-III MV complex which is composed of two

asymmetrical delocalized Ru<sup>III</sup>-NC-Ru<sup>II</sup> MV units.



Figure 1. Cyclic voltammogram of  $1[PF_6]_2$  recorded in  $CH_2CI_2/0.1M$  [TBA]PF<sub>6</sub> at 100 mV s<sup>-1</sup> scan rate.

In this work, we first synthesized the two isomeric divalent compounds, trans-[Cp\*(dppe)Ru<sup>II</sup>( $\mu$ -NC)Ru<sup>II</sup>(dmap)<sub>4</sub>( $\mu$ -CN)Ru<sup>II</sup>(dppe)Cp\*][PF<sub>6</sub>]<sub>2</sub> (**1**[PF<sub>6</sub>]<sub>2</sub>) and trans-[Cp\*(dppe)Ru<sup>II</sup>( $\mu$ -CN)Ru<sup>II</sup>(dmap)<sub>4</sub>( $\mu$ -NC)Ru<sup>II</sup>(dppe)Cp\*][PF<sub>6</sub>]<sub>2</sub> (**2**[PF<sub>6</sub>]<sub>2</sub>), which differ only in the orientation of the bridging CN. That is, **1**[PF<sub>6</sub>]<sub>2</sub> and **2**[PF<sub>6</sub>]<sub>2</sub> exist in the Ru-NC-Ru-CN-Ru and Ru-CN-Ru-NC-Ru forms, respectively. **1**<sup>2+</sup> was synthesized by the reaction of



Figure 2. (a) Molecular structure (top) and computed spin density (central Ru, 0.236; terminal Ru, 0.319 and 0.347) (bottom, 0.0004 e/bohr<sup>3</sup>) of  $1^{3+}$ ; (b) Molecular structure (top) and computed spin density (central Ru, 0.597; terminal Ru, 0.161 and 0.163) (bottom, 0.0004 e/bohr<sup>3</sup>) of  $2^{3+}$  (the calculated ground-state energy difference between  $1^{3+}$  and  $2^{3+}$  is 0.68 eV). Hydrogen atoms, [PF<sub>6</sub>]<sup>-</sup> anions, and solvent molecules have been omitted for clarity. Light blue, Ru; pink, P; white, C; blue, N.

trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub> with Cp\*Ru(dppe)Cl in methanol, and the isomer 2<sup>2+</sup> was obtained by reacting Cp\*Ru(dppe)CN with Ru(dmap)<sub>6</sub>Cl<sub>2</sub> in ethanol. Electrochemical explorations of 1<sup>2+</sup> and  $2^{2+}$  in dichloromethane were performed, as shown in Figures 1 and S2. The electrochemical data are summarized in Table S1. Cyclic voltammogram (CV) of 12+ exhibits three chemically reversible one-electron oxidation waves (Figure 1). The first two waves (0 and 0.36 V vs. Cp<sub>2</sub>Fe<sup>3+/2+</sup>) are attributed to the oxidation processes of the terminal Ru centers, while the last one (0.53 V vs. Cp<sub>2</sub>Fe<sup>3+/2+</sup>) is due to the oxidation process of the central Ru center. The large potential separation of 0.36 V between the first two oxidations indicate the high stability of 1<sup>3+</sup> with the comproportionation constant ( $K_c$ ) of 1.72 x 10<sup>6</sup>. CV of 2<sup>2+</sup> also shows three chemically reversible redox waves (Figure S1). The first redox wave (-0.20 V vs. Cp<sub>2</sub>Fe<sup>3+/2+</sup>) is attributed to the oxidation process of the central Ru<sup>II</sup>, while the other two waves (0.66 and 0.78 V vs.  $Cp_2Fe^{3+/2+}$ ) are due to the oxidation processes of the two terminal Rull. The second separation of 0.12V in 22+ suggests the presence of electronic interaction between the two terminal Ru centers. It should be noted, however, that the small potential separation of 0.12 V does not suggest that 2<sup>3+</sup> must be a localized mixed valence species.<sup>[2i, 11]</sup> Based on the electrochemical measurement, the reaction of 12+ with 1 equiv. of  $Cp_2Fe(PF_6)$  gave rise to the stable MV trans-[Cp\*(dppe)Ru<sup>III</sup>(µ-NC)Ru<sup>II</sup>(dmap)<sub>4</sub>(µcompound CN)Ru<sup>II</sup>(dppe)Cp\*][PF<sub>6</sub>]<sub>3</sub> (1[PF<sub>6</sub>]<sub>3</sub>), and the reaction of  $2^{2+}$  with 1 equiv. of  $Cp_2Fe(PF_6)$  resulted in the stable isomeric MV trans-[Cp\*(dppe)Ru<sup>II</sup>(µ-CN)Ru<sup>III</sup>(dmap)<sub>4</sub>(µcompound NC)Ru<sup>II</sup>(dppe)Cp\*][PF<sub>6</sub>]<sub>3</sub> (2[PF<sub>6</sub>]<sub>3</sub>). In order to probe the electronic characteristics of compound 23+, the analogues trans- $[Cp(dppe)(\mu-CN)Ru(dmap)_4(\mu-NC)Ru(dppe)Cp][PF_6]_n$  (3[PF\_6]\_n,

n = 2, 3, Cp = 1,3-cyclopentadiene) as reference compounds were also prepared in the similar way to  $2[PF_6]_3$  excepting for CpRu(dppe)CN instead of Cp\*Ru(dppe)CN (Supporting Information). The electrochemical data for  $3[PF_6]_2$  are also included in Table S1. The redox behavior of  $3[PF_6]_2$  (Figure S3) is similar to that of  $2[PF_6]_2$  but with the poorer redox reversible waves for the two terminal Cp(dppe)Ru fragments. All compounds  $1[PF_6]_n$ ,  $2[PF_6]_n$  and  $3[PF_6]_n$  (n = 2, 3) were characterized by elemental analyses, single crystal X-ray diffraction analyses, and IR, UV-vis-NIR and EPR spectra.

The structural analyses revealed that the two pairs of isomers  $1^{2+}/2^{2+}$  and  $1^{3+}/2^{3+}$  crystallize in the space group Pc and C2/c, respectively. Whereas, both compounds 3<sup>2+</sup> and 3<sup>3+</sup> crystallize in the space group  $P2_1/c$ . The crystal structures of  $1^{n+}$ ,  $2^{n+}$  (n = 2, 3) are similar differing only in bond lengths and in orientation of the bridging CN. Thus, only molecular structures of 1<sup>3+</sup> and 2<sup>3+</sup> are shown in Figure 2, and the other structures are shown in Figures S4-S7 in Supporting Information. Crystallographic details and selected bond lengths and angles are summarized in Tables S2-S6 in Supporting Information. In  $1^{3+}$ , the presence of a more counter anion of  $PF_6^-$  per compound confirms that it is the one-electron oxidized form of 12+. According to the CV results, one of the terminal Ru<sup>2+</sup> of 1<sup>2+</sup> should be first oxidized into Ru<sup>3+</sup>, that is from Ru<sup>II</sup>-Ru<sup>II</sup> (1<sup>2+</sup>) to Ru<sup>II</sup>-Ru<sup>III</sup>-Ru<sup>III</sup> (1<sup>3+</sup>). However, the cation structure of 1<sup>3+</sup> is centrosymmetric, the central Ru locates in the center of the inversion and the two terminal Ru are strictly equivalent, suggesting 1<sup>3+</sup> may be fully delocalized. Furthermore, the bond lengths of Ru-P (av. 2.300(1) Å), Ru-C<sub>CN</sub> (av. 2.076(4) Å) and Ru-N<sub>CN</sub> (av. 2.077(4) Å) in 1<sup>3+</sup> are virtually indistinguishable from those in 12+ (av. 2.299(3), 2.060(12) and 2.068(9) Å) within

experimental error. The similar phenomenon was also observed in the Ru-N distance of [Ru<sup>III</sup>(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> vs [Ru<sup>II</sup>(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> and was explained by the high electron self-exchange rate between Ru<sup>II</sup> and Ru<sup>III</sup>.<sup>[12]</sup> Herein, the indistinguishable bond lengths may further suggest the presence of the electron delocalization along Ru-NC-Ru-CN-Ru in 13+, strongly supported by the IR, UV/Vis/NIR and EPR spectra (see below). In contrast to 12+, based on the CV results, the central Ru2+ of 22+ should be first oxidized into Ru3+, resulting in 23+ with a symmetrical Ru11-Ru<sup>III</sup>-Ru<sup>II</sup> arrangement. Thus, the crystal structure of 2<sup>3+</sup> may be easily centrosymmetric in crystallization. Indeed, the singlecrystal X-ray diffraction analyses showed that the cation structure of 2<sup>3+</sup> is centrosymmetric and the oxidized Ru<sup>III</sup> locates in the center of the inversion. Several changes in individual bond lengths can be discerned upon oxidation, although 23+ and 22+ present common features. Particularly, the Ru-C<sub>CN</sub> and Ru-N<sub>CN</sub> bond lengths in  $2^{3+}$  are shorter about 0.04 and 0.03 Å than  $2^{2+}$ , respectively, whereas the C=N bond lengths are longer about 0.02 Å in the former. This may result from the electronic delocalization between the terminal ruthenium and the central ruthenium<sup>[13]</sup> or throughout Ru-CN-Ru-NC-Ru.



Figure 3. UV/Vis/NIR spectra of (a)  $1^{2+}$  (black) and  $1^{3+}$  (red); (b)  $2^{2+}$  (pink) and  $2^{3+}$  (blue) in CH\_2Cl\_2.

As the reference compound of  $2^{3+}$ , the molecular structure of  $3^{3+}$  is very similar to that of  $2^{3+}$ , both compounds contain the same central Ru<sup>III</sup>. Upon replacement of Cp<sup>\*</sup> by Cp from  $2^{3+}$  to  $3^{3+}$ , their most remarkable difference is the Ru<sub>1</sub><sup>III</sup>-N<sub>CN</sub> and Ru<sub>2</sub><sup>II</sup>-C<sub>CN</sub>/Ru<sub>3</sub><sup>II</sup>-C<sub>CN</sub> bond lengths. It was found that Ru<sub>1</sub><sup>III</sup>-N<sub>CN</sub> bond length is 0.04 Å longer in  $2^{3+}$  (av. 2.046(6) Å) than in  $3^{3+}$  (av. 2.000(6) Å) , and the Ru<sub>2</sub><sup>II</sup>-C<sub>CN</sub>/Ru<sub>3</sub><sup>II</sup>-C<sub>CN</sub> bond length is longer by 0.01 Å in the former [av. 1.984(5) Å in  $2^{3+}$  and av. 1.970(8) Å in  $3^{2+}$ ], pointing to the presence of the electron delocalization in compound  $2^{3+}$ , so that the oxidation state of the ruthenium atom

in both sites approaches the averaged value. That is, the oxidation state of the central  $Ru^{III}$  decreases and that of the terminal  $Ru^{II}$  increases in compound  $2^{3+}$ .

Comparison of the electronic spectra of the compounds further reveals their intrinsic electronic characteristics. As shown in Figure 3, the UV/Vis/NIR spectra of 12+ is similar to 22+ and both of them contain only one absorption band at about 28570 cm<sup>-1</sup> and do not exhibit any absorption band in Vis/NIR region. Upon oxidation, the spectrum of 1<sup>3+</sup> displays three new bands in Vis-NIR region, and the band at about 28570 cm<sup>-1</sup> in 1<sup>2+</sup> disappears. The two bands of 1<sup>3+</sup> at 14869 cm<sup>-1</sup> and 12556 cm<sup>-1</sup> are attributed to the LMCT of the central Ru<sup>III.[8,14]</sup> The similar bands can also be observed in 2<sup>3+</sup> (17168 cm<sup>-1</sup>, 14427 cm<sup>-1</sup>) but are blue-shifted, which result from the oxidation of the central Ru<sup>II</sup> into Ru<sup>III</sup>. The IVCT band of  $1^{3+}$  appears around  $\lambda_{max} = 5045$ cm<sup>-1</sup> (Table S7) and is narrow and asymmetrical. This intense and narrow absorption with a cutoff, which are Gaussian on the high energy side and skewed on the low energy side, resembles that of other class III systems.<sup>[2d, 2i, 8]</sup> These results indicate that the odd electron of  $1^{3+}$  may be delocalized and the central ruthenium shows some natures like Ru<sup>III</sup>. Moreover, the IVCT energy is solvent independent (Figure S9). This is also the expected behavior for a class III MV compound,<sup>[8, 15]</sup> suggesting the IVCT band arises from the electron resonate in the system rather than IVCT. The IVCT band of  $2^{3+}$  appears around  $\lambda_{max} =$ 8870 cm<sup>-1</sup> (Table S7), which is the ET processes between the terminal Ru<sup>II</sup> and the central Ru<sup>III</sup>. This band is also cutoff and solvent independent (Figure S10), indicating that  $2^{3+}$  may be a class II-III or class III MV compound. The reference compound 3<sup>3+</sup> shows similar LMCT and IVCT absorption, but the MLCT band of terminal Ru still remain (Figure S11). However, the MLCT band of 2 has disappear when the 22+ was oxidized into 2<sup>3+</sup>. Those results indicate that the electron of Ru<sup>II</sup> of 3<sup>3+</sup> is more localized, which is supported by the result of the DFT calculations (Table S8).

The electron localization/delocalization can influence the intramolecular vibrational motions. Therefore, electron movements can be monitored by IR spectra. The IR spectra of  $\mathbf{1^{2+}}$  and its isomer  $\mathbf{2^{2+}}$  display a cyanide stretching vibration absorption at 2050 cm<sup>-1</sup> (Figure 4a) and 2058 cm<sup>-1</sup> (Figure 4b), respectively. It has been reported that for the localized trinuclear asymmetric cyanido-bridged systems (RuIII-NC-RuII-CN-RuII or Fe<sup>III</sup>-NC-Ru<sup>II</sup>-CN-Fe<sup>II</sup>), two cyanide stretching vibrations are observed.<sup>[7e, 7f, 16]</sup> Upon oxidation, however, the spectra of the MV species 1<sup>3+</sup> exhibits only a broad absorption at 1970 cm<sup>-1</sup> (Figure 4a), the characteristic of class III MV systems<sup>[2c, 8, 15b, 17]</sup>, indicating the two CN are equivalent on the timescale of IR spectroscopy. The IR spectrum of 23+ exhibits also one cyanide stretching vibration absorption at 2000 cm<sup>-1</sup> (Figure 4b). This single sharp v(CN) band might be explained by the symmetric structure of 2<sup>3+</sup> [Ru<sup>II</sup>-CN-Ru<sup>III</sup>-NC-Ru<sup>II</sup>], because similar results have been observed in the localized symmetric cyanido-bridged system (RuIII-NC-RuII-CN-RuIII and FeIII-NC-RuII-CN-FeIII). [7e, 7f] Hence, the MV compound 2<sup>3+</sup> might be at the borderline of class II and class III, namely class II-III species defined by Meyer.<sup>[2d]</sup>

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Figure 4. IR spectra of  $1^{2\ast}$  (red) and  $1^{3\ast}$  (black) (a),  $2^{2\ast}$  (green) and  $2^{3\ast}$  (blue) (b) in CH\_2Cl\_2.

In order to further verify our classification, EPR spectra were run for the two mixed-valence compounds 13+ and 23+ in solid at various temperatures ranging from 150 K to 291 K. For the comparison purpose, The solid EPR spectrum of 3<sup>3+</sup> was measured at 291 K. The EPR spectra of 13+ at different temperatures contain only isotropic signal with no hyperfine coupling (Figure 5a). The g values at each temperature are almost a constant of about 2.003 (Figure S13a) which is smaller than Cp\*Ru(dppe) mononuclear metal (g ~ 2.1)<sup>[18]</sup>, typical of free electron (g = 2.0023). Compound  $1^{3+}$  with such an isotropic feature is in stark contrast to previously reported MV trinuclear cyanide-bridged compounds, which exhibit anisotropic features.<sup>[7e]</sup> The characters of free electron and temperatureindependent behavior of the EPR spectra between 150 and 291 K further confirm the fully delocalized class III nature of 1<sup>3+</sup>.<sup>[19, 20]</sup> In contrast, the EPR spectra of  $2^{3+}$  exhibit anisotropic feature at low temperatures (Figure 4b, for more details, see Figure S13b). suggesting the unpaired electron on 2<sup>3+</sup> may be localized or the rate of electron transfer is slower than the EPR timescal. With the temperature increasing, the anisotropic feature fades away. When the temperature goes to 291 K, the anisotropic feature disappears and only the isotropic signal can be observed. Moreover, the g value (2.005) at 291 K is close to that of free electron (q = 2.0023). This indicates that intramolecular electrontransfer rate of  $2^{3+}$  is faster than the EPR timescale at 291 K. In this case, the unpaired electron on  $2^{3+}$  is delocalized, the DFT calculations support this nature of  $2^{3+}$  (Figure 2 and Table S8). Thereore, the unpaired electron on 2<sup>3+</sup> may be localized at low temperature and delocalized at high temperature, which is

supported by the change of the selected bond lengths of 23+ (Table S5) at 100K and 293K. Based on the variable temperature EPR behaviours and the strcutural data at different temperature, 2<sup>3+</sup> might be classified as a localized-to-delocalized (Class II-III) compound. The EPR of the more localized MV compound  $3^{3+}$  (Figure S14), however, displays anisotropic signals even at room temperature, suggesting the unpaired electron density is mainly located in the central Ru<sup>III</sup>, which is consistent with the result of DFT (Table S8). In conclusion, 1<sup>3+</sup> is a class III MV compound, and  $\mathbf{2^{3+}}$  might be regarded as a class II-III compound composed of the two asymmetrical delocalized Ru<sup>II</sup>-CN-Ru<sup>III</sup> subunits. That is, the central ruthenium center in 1<sup>3+</sup> is to mediate electron communication between the two terminal ruthenium centers, whereas the central ruthenium center in 2<sup>3+</sup> plays the role of the electron acceptor. Therefore, the electron transfer process of  $1^{3+}$  over the three metal centers could be described as three resonant states (Ru<sup>III</sup>-NC-Ru<sup>II</sup>-CN- $Ru^{II} \leftrightarrow Ru^{II}$ -NC-Ru<sup>III</sup>-CN-Ru<sup>II</sup>  $\leftrightarrow Ru^{II}$ -NC-Ru<sup>II</sup>-CN-Ru<sup>III</sup>); For the MV compound  $2^{3+}$ , the electron transfer process could be described as Ru<sup>II</sup>-CN-Ru<sup>III</sup>-NC-Ru<sup>II</sup> ↔ Ru<sup>III</sup>-CN-Ru<sup>II</sup>-NC-Ru<sup>II</sup> or Ru<sup>II</sup>-CN-Ru<sup>II</sup>-NC-Ru<sup>III</sup>.



Figure 5. Temperature-dependent EPR spectra of 1<sup>3+</sup> (a) and 2<sup>3+</sup> (b).

In summary, we have synthesized and structurally characterized two isomeric stable trinuclear MV compounds 1<sup>3+</sup> and 2<sup>3+</sup> with different orientation of the CN bridge. Therein, the strong evidences reveal that 1<sup>3+</sup> is the fully delocalized (class III) cyanidometal-bridged MV compound, which is the first example of the crystallographic characterized class III cyanido-bridged MV systems. Upon isomerization of Ru-NC-Ru-CN-Ru  $\rightarrow$  Ru-CN-Ru-NC-Ru, 23+ might behave class II-III cyanide-bridged MV species which is composed of the two asymmetric delocalized Ru<sup>II</sup>-CN-Ru<sup>III</sup> subunits. It should point out, however, that one could not completely exclude the other possibility for the assignment of 2<sup>3+.[21]</sup> From 1<sup>3+</sup> to 2<sup>3+</sup>, it seems that the electron delocalization throughout Ru-Ru-Ru is devided evenly into two electron delocalization parts from the central ruthenium center. This may have implication in designing molecular conducting devices.

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Keywords: cyanido-/isocyanido bridge • electron transfer • mixed-valennce compounds • Class II-III • Class III

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- [21] It might be possible that the single v(CN) band of 2<sup>3+</sup> results from rapid electron exchange between metals, given the fact that the IVCT absorption band is solvent-independent, thus 2<sup>3+</sup> might also be assigned into an unusual class III MV species with temperaturedependent EPR and X-ray structural data.

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Class II-III to Class III:  $2^{3+}$ behaves class II-III cyanidebridged MV species which is composed of the two asymmetric delocalized Ru<sup>II</sup>-CN-Ru<sup>III</sup> subunits. Upon isomerization of Ru-CN-Ru-NC-Ru  $\rightarrow$  Ru-NC-Ru-CN-Ru, the strong evidences reveal that  $1^{3+}$  is the fully delocalized (class III) cyanidometal-bridged MV compound.



Class III mixed-valence complex

Y. Y. Yang, X. Q. Zhu, S. M. Hu, S. D. Su, L. T. Zhang, X. T. Wu and T. L. Sheng\*

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Different Degree of Electron Delocalization in Mixed-Valence Ru-Ru-Ru Compounds via Cyanido-/Isocyanido-Bridge Isomerism

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