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# Wire-like diruthenium $\sigma$ -alkynyl compounds and charge mobility therein

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## Abstract

Described in this short review is the chemistry of wire-like diruthenium  $\sigma$ -alkynyl species, which are promising building blocks for organometallic molecular wires. Two series of carbon-rich compounds have been studied: (a) polyyn-diyls with diruthenium capping units, and (b) bi-ferrocenes with a diruthenium alkynyl bridge. Investigations of both the charge transfer process across the polyyn-diyls and the role of diruthenium cores in enhancing charge mobility are achieved through X-ray structure determination, spectroscopic, voltammetric and spectroelectrochemical measurements. **To cite this article:** B. Xi, T. Ren, C. R. Chimie 12 (2009). © 2008 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

**Keywords:** Diruthenium; Polyyn-diyl bridge; Molecular wire; Alkynyl organometallics

## 1. Introduction

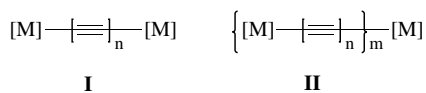
The study of transition-metal  $\sigma$ -alkynyl complexes can be traced back to 1960s [1,2]. Since the mid-1980s, this area has attracted much more intense interests as evidenced by increasing numbers of research papers from approximately 200 to over 20,000 [3]. Compared with the pure organic conjugated systems [4,5], introduction of metal units into the polymeric or oligomeric systems may result in a broad range of improved properties including electronic communication (molecular wires) [6,7], nonlinear optical effects [8], luminescence and photoconductivity [9,10].

In the research of utilizing metal  $\sigma$ -alkynyl complexes as building blocks for molecular electronic devices, two types of metal alkynyl wires were

proposed (Chart 1) [6,11]. Polyyn-diyls ( $C_{2n}$ ) capped by two metal termini (type **I** in Chart 1) are very attractive prototypes of “organometallic molecular wires”. Many of the pioneering efforts focused on the design of type **I** wires featuring facile charge transfer across the  $sp$  carbon chain (polyyn-diyls), with [M] as CpFe(P–P) [12], CpRe(P)NO [13–15], CpRu(P)<sub>2</sub> [16], and Mn(P–P)<sub>2</sub>I [17] where P and P–P denote mono- and bidentate phosphines, respectively. Mono-disperse oligomers (type **II** in Chart 1) could be better alternatives than dimers (**I**) on the aspects of controlling length and connecting to the outside world, from the practical applications point of view. However, some limitations preclude the possibility of many metal complexes as candidates for type **II** wires. To form oligomers, the metal units should be capable of forming bis-alkynyl complexes, and in addition, the selection of the metal center [M] is also critical to avoid insulating behavior [6,18]. Examples of

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Chart 1. Dimeric (**I**) and metallayne (**II**) wires.

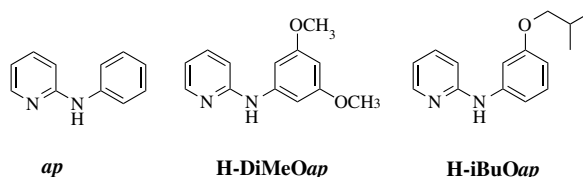
well-characterized type **II** oligomers are rare, and those based on  $\text{Ru}_2(\text{DPhF})_4$ -butadiynyl [19] and  $\text{Ru}(\text{P}-\text{P})_2$ - $\sigma$ -arylacetylide monomers [20,21] are noteworthy.

Our effort in developing organometallic molecular wires focuses on using diruthenium paddlewheel species as  $[\text{M}]$  [22–25], due to their attractive features including the controlled syntheses of the mono- and bis-alkynyl complexes, the stability toward ambient atmosphere and heat, the redox flexibility, and very small HOMO–LUMO gaps (1.2–1.5 eV) [26–34]. As excellent chromophores and electrophores, the diruthenium alkynyl complexes have been studied as promising building blocks for novel (opto)electronic materials [23].

## 2. $\text{Ru}_2$ polyyn-diyls

Our investigation of diruthenium alkynyl compounds of a paddlewheel motif demonstrated that  $\sigma$ -alkynyl compounds of  $[\text{Ru}_2\text{L}_4]$  have good charge mobility along the axial direction.  $\text{Ru}_2(\text{II,III})$  based wire-like compounds (type **I**) with  $n$  up to 10 have been prepared with various supporting ligands ( $L$ ). Compounds of long polyyn-diyl segments are desired for better understanding of the electron coupling within the type **I** molecules and the distance dependence of  $H_{\text{ad}}$  (adiabatic electronic coupling elements).

The  $N,N'$ -bidentate bridging ligands ( $L$ ) utilized in supporting the  $\text{Ru}_2$  core include 2-anilinopyridinate ( $ap$ ) and its anilino-substituted derivatives, 2-(3,5-dimethoxyanilino)pyridinate ( $\text{DiMeOap}$ ), and 2-(*i*-butoxyanilino)pyridinate ( $i\text{BuOap}$ ) (Chart 2). Using  $ap$  as the auxiliary ligand, type **I** compounds with  $n$  up to 6 were prepared and studied [35,36]. Both of the modified  $ap$  ligands afford significantly improved solubility in common organic solvents [37,38], and

Chart 2.  $N,N'$ -bidentate ligands supporting the  $\text{Ru}_2$  core.

facilitate the preparation of type **I** compounds with  $n$  up to 10, and the access to compounds of odd  $n$  as well.

### 2.1. Monomers and dimers

Wire-like molecules  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_2)$ ,  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_4)$  and  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_6)$  ( $L = \text{DiMeOap}$ , compounds **A1–A3**;  $L = ap$ , compounds **A1'–A3'**) were synthesized through anion metathesis between  $[\text{Ru}_2\text{L}_4]\text{-Cl}$  and  $\text{LiC}_{2n}\text{Li}$  [35,36]. However, this technique became impractical with longer polyyn-diyl ligands, due to the instability of  $\text{LiC}_{2n}\text{Li}$  with  $n \geq 4$ . Hence, the longer type **I** compounds ( $n \geq 4$ ) were prepared through the Glaser oxidative coupling [39] of their corresponding “half” molecules which are the monomer type in Chart 3.

The mono-adduct with  $k=2$  was prepared from a reaction between  $[\text{Ru}_2\text{L}_4]\text{-Cl}$  and  $\text{LiC}_4\text{SiMe}_3$ . After the removal of terminal protection group  $\text{-SiMe}_3$  ( $\text{K}_2\text{CO}_3$ ,  $\text{THF/MeOH}$ ), a two-carbon  $sp$  chain extension reaction was achieved by the Glaser oxidative coupling [39] of  $[\text{Ru}_2\text{L}_4]\text{-C}_4\text{H}$  and excess  $\text{HC}\equiv\text{CSiMe}_3$  (*Hay* conditions:  $\text{O}_2$ , cat.  $\text{CuCl}$ ,  $\text{TMEDA}$  and acetone) to give  $[\text{Ru}_2\text{L}_4]\text{-C}_6\text{SiMe}_3$  (monomer with  $k=3$ ). However, extending this sequence to longer monomers ( $k=4$  and 5) was unsuccessful with the problem of increasing tendency for homo-coupling of  $[\text{Ru}_2\text{L}_4]\text{-C}_{2k}\text{H}$  during the reaction. The *Cadiot–Chodkiewicz* (*Cadiot* for short) coupling method [39] was successfully employed by Gladysz and coworkers to extend  $\text{Re}-(\text{C}\equiv\text{C})_n$ -chains [40], which involved the formation of a copper alkynyl complex intermediate. As shown in Scheme 1, the extension of  $\text{Ru}_2-(\text{C}\equiv\text{C})_k$ -monomers ( $k > 2$ ) under *Cadiot* conditions was achieved with significantly

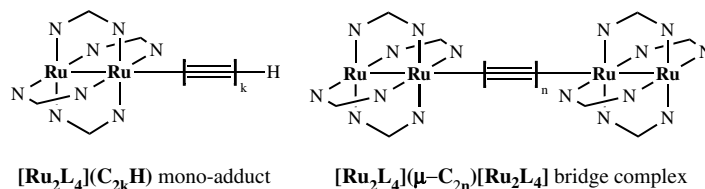
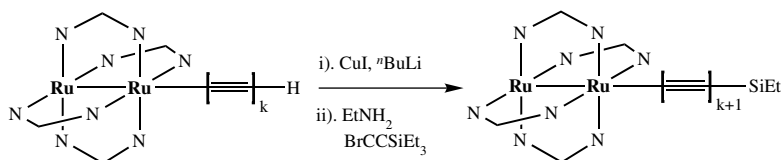


Chart 3. Diruthenium mono-alkynyl building block and wire-like bridge compound.



Scheme 1. Extension of carbon chain for monomers through Cadiot coupling.

increased yields compared to those under *Hay* conditions.

The longer dimers, namely the  $[\text{Ru}_2\text{L}_4](\mu\text{-C}_{2n})[\text{Ru}_2\text{L}_4]$  ( $n \geq 4$ ) type compounds (Chart 3), were synthesized through either oxidative homo-coupling of corresponding monomers (for dimers with even-numbered  $n$  ( $\text{C}_8$ ,  $\text{C}_{12}$ ,  $\text{C}_{16}$  and  $\text{C}_{20}$ )) or cross coupling of two different monomers (for type **I** dimers with odd  $n$  ( $\text{C}_{10}$ ,  $\text{C}_{14}$  and  $\text{C}_{18}$ )) (Scheme 2), under *Hay* conditions in moderate to good yields. During the preparation of the latter type compounds, symmetric dimers ( $\text{Ru}_2\text{-}\mu\text{-C}_{2n}\text{-Ru}_2$  and  $\text{Ru}_2'\text{-}\mu\text{-C}_{2n}\text{-Ru}_2'$ ) were generated as the byproducts and tedious chromatography, typically preparative TLC, was necessitated for separation.

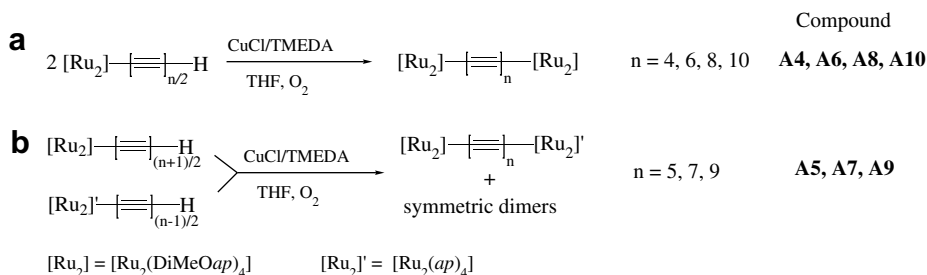
Type **I** dimers are generally difficult to crystallize and only molecules containing  $\text{C}_4$  (short),  $\text{C}_6$  (short), and  $\text{C}_8$  (medium) bridges have been structurally characterized in our diruthenium system (Fig. 1) [23,35,36].

Clearly, the coordination environment of the  $[\text{Ru}_2\text{L}_4]$  cores in dimers is identical to that of monomer type compounds (i.e.  $[\text{Ru}_2\text{L}_4]\text{-C}_2\text{Y}$ ). The  $N,N'$ -bidentate bridging ligands in both monomers and dimers adopt the (4,0) arrangement, namely that all anilino N-centers coordinate to the Ru center (4 site) and all pyridine N-centers coordinate to the other Ru center (0 site). Compared to its corresponding monomer, there is no significant change of Ru–Ru distance in the dimer ( $\sim 2.33 \text{ \AA}$ ), while Ru– $\text{C}_\alpha$  bond became shorter ( $\sim 2.02 \text{ \AA}$ ) due to the strengthened Ru– $\text{C}_\alpha$  interaction on the formation of polyyne-diyls systems.

## 2.2. Characterizations

### 2.2.1. Redox properties

In the type **I** compounds, exploration of the electron mobility across the polyyne-diyl chains is related to the investigation of the electronic coupling between two redox-active  $[\text{Ru}_2\text{L}_4]$  moieties, which was assessed on the basis of the comparison of their voltammetric behavior (CV/DPV) with that of the “half” molecule (monomer). For instance, the cyclic voltammogram of monomer  $[\text{Ru}_2]\text{-C}_4\text{TMS}$  ( $[\text{Ru}_2] = [\text{Ru}_2(\text{DiMeOap})_4]$ ) exhibits two reversible one-electron processes at ca. 0.5 V (oxidation) and ca.  $-0.7 \text{ V}$  (reduction) [38]. On the other hand, the dimer molecule,  $[\text{Ru}_2]_2(\mu\text{-C}_6)$  (**A3**) clearly exhibits more complex redox features including multiple reversible one-electron couples within the same potential window (Fig. 2): two stepwise oxidations ( $2+/1+$ ) and ( $+1/0$ ) at potentials close to 0.5 V and two stepwise reductions ( $0/-1$ ) and ( $-1/-2$ ) at potentials close to  $-0.7 \text{ V}$ . Both oxidation couples and the first (least cathodic) two reduction couples are  $\text{Ru}_2$  based. The pairwise appearance of one-electron couples instead of a two-electron wave is an indicative of significant electronic coupling between two  $[\text{Ru}_2]$  units. Moreover, the potential splitting within each pair ( $\Delta E_{1/2}$ ) is proportional to the coupling strength and can serve as a *qualitative* indicator, as well known in the mixed-valence chemistry [41–43]. In addition, the potential differences within the oxidations ( $\Delta E_{1/2}(+1)$ ) and reductions ( $\Delta E_{1/2}(-1)$ ) allow the estimation of comproportionation constants for the corresponding mixed-valence cation ( $K_{\text{com}}(+1)$ ) and anion ( $K_{\text{com}}(-1)$ ), respectively [41–44],



Scheme 2. Homo/cross-coupling of mono-adduct to yield dimers.

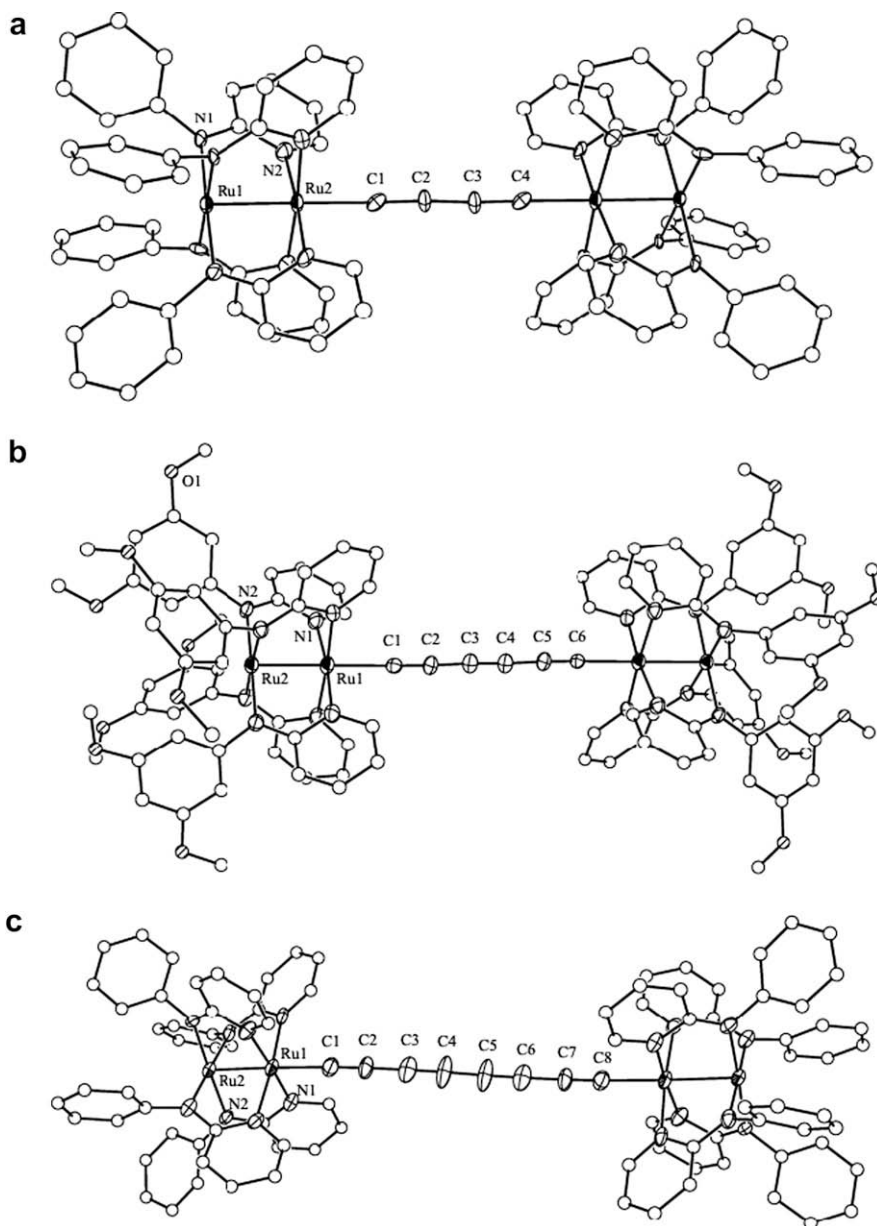


Fig. 1. Structural plots of (a)  $[\text{Ru}_2(\text{ap})_4]_2(\mu\text{-C}_4)$ , (b)  $[\text{Ru}_2(\text{DiMeOap})_4]_2(\mu\text{-C}_6)$ , (c)  $[\text{Ru}_2(\text{ap})_4]_2(\mu\text{-C}_8)$ .

which are summarized in Table 1. Finally,  $[\text{Ru}_2\text{L}_4]$  monomers with L as both *ap* and DiMeOap exhibit almost identical redox potentials (differences within 30 mV), which indicates minimal effect of ligand L on the electronic structures of  $\text{Ru}_2$  core [38,45].

The voltammetric plots (differential pulse voltammetry) in Fig. 3 and electrode potential data in Table 1 reveal similar redox behaviors within  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_{2n})$  type compounds and some noteworthy trends. First, for each dimer, the difference between  $E_{1/2}(0/-1)$  and  $E_{1/2}$

$(-1/-2)$  ( $\Delta E_{1/2}(-1)$ ) is much larger than the difference between  $E_{1/2}(+2/+1)$  and  $E_{1/2}(+1/0)$  ( $\Delta E_{1/2}(+1)$ ), which suggests that the  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_{2n})$  type compounds are much better electron carrier than hole carrier, partly due to the electron-deficient nature of both the diruthenium core and polyyne-diyl bridge [36]. Second, as the polyyne-diyl chain elongates, both  $\Delta E_{1/2}(+1)$  and  $\Delta E_{1/2}(-1)$  gradually decrease (from resolved one-electron couples to merged pseudo two-electron waves) indicating the decrease of electronic coupling

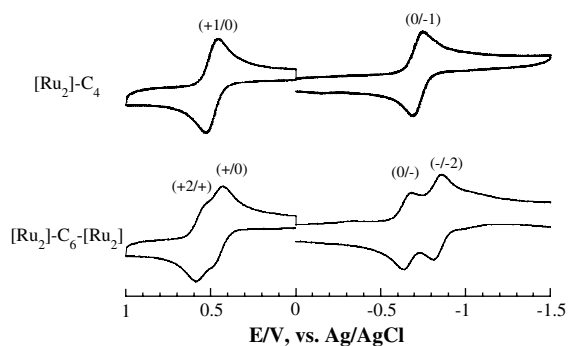


Fig. 2. Cyclic voltammograms of  $[\text{Ru}_2]\text{-C}_4\text{TMS}$  (monomer) and **A3** (dimer) recorded in 0.20 M THF solution of  $\text{Bu}_4\text{NPF}_6$  at a scan rate of 0.10 V/s.

between two  $\text{Ru}_2$  centers. This trend is consistent with the consensus that the degree of coupling between a pair of donor–acceptor centers decays exponentially as the distance increases [41,43,46]. Third, potentials for all redox couples display a significant anodic shift as the polyene chain elongates, which is attributed to the electron-deficient nature of the added acetylene units. Additionally, the second pair of one-electron reductions at more negative potentials was tentatively assigned as polyyne-diyl based [36].

### 2.2.2. Spectroelectrochemistry

As established in the mixed-valence chemistry, the splitting in potentials of oxidation/reduction pairs ( $\Delta E_{1/2}$ ) and the resultant comproportionation constant  $K_{\text{com}}$  usually serve as *qualitative* indicators of the nature of mixed-valency. These parameters generated from the electrochemical measurements significantly depend on the nature of solvents and electrolytes [47], and hence may be inappropriate as *quantitative* measures. A more suitable approach is to examine spectroscopic characteristics of the mixed-valence species, namely the intervalence transitions between

donor and acceptor  $\text{Ru}_2$  moieties as mediated by the polyyne-diyl bridge, through spectroelectrochemical studies [41,43,44,48]. Fig. 4 shows electronic absorption spectra derived from spectroelectrochemical studies of  $[\text{Ru}_2(\text{ap})_4]_2(\mu\text{-C}_4)$  **A2'** and its reference compound  $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{TMS})$  [36]. Upon either one-electron reduction or one-electron oxidation, intervalence charge transfer (IVCT) bands appeared and half-widths (bandwidths at half-peak height) were estimated from spectral deconvolution assuming Gaussian profiles (data are summarized in Table 2). The band at ca.  $8450\text{ cm}^{-1}$  is clearly attributed to the CT between two  $\text{Ru}_2$  moieties of  $\{[\text{Ru}_2(\text{ap})_4]_2(\mu\text{-C}_4)\}^{-1}$ . The lower energy band ( $5670\text{ cm}^{-1}$ ) is likely due to the mixing of LMCT and IVCT states in such

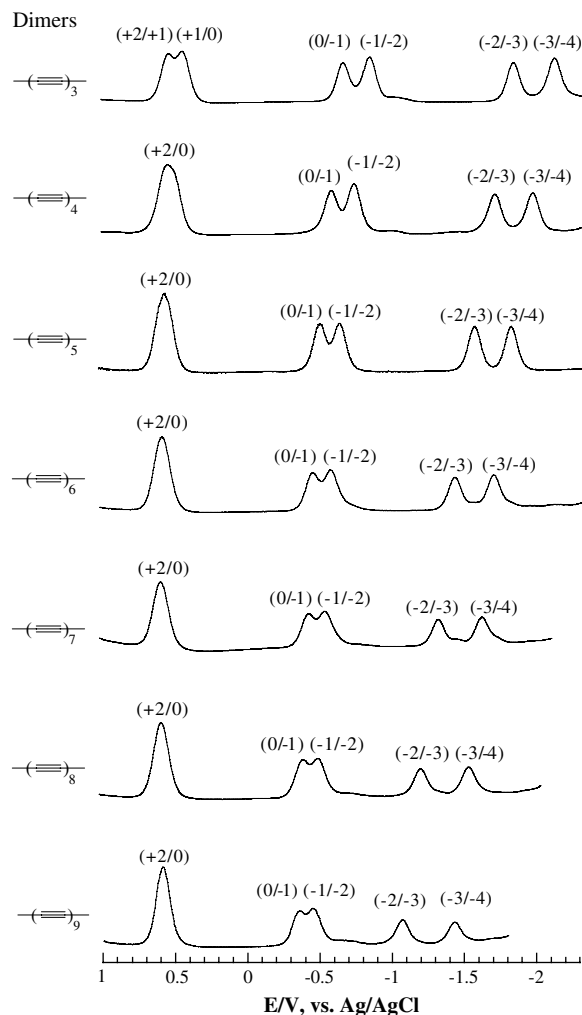


Fig. 3. Differential pulse voltammograms of dimers **A3–A9** recorded in 0.20 M THF solution of  $\text{Bu}_4\text{NPF}_6$  at a scan rate of 0.10 V/s.

Table 1  
Electrode potentials (V) for dimers **A3–A9** from DPV measurement<sup>a</sup>

Compounds	+2/+1	+1/0	0/-1	-1/-2	-2/-3	-3/-4	$K_{\text{com}}(-1)^b$
<b>A3</b>	0.54	0.44	-0.65	-0.83	-1.81	-2.80	1300
<b>A4</b>	0.54 (2e <sup>-</sup> )		-0.57	-0.72	-1.68	-1.94	370
<b>A5</b>	0.56 (2e <sup>-</sup> )		-0.52	-0.64	-1.55	-1.80	130
<b>A6</b>	0.57 (2e <sup>-</sup> )		-0.45	-0.57	-1.42	-1.69	110
<b>A7</b>	0.58 (2e <sup>-</sup> )		-0.43	-0.54	-1.31	-1.60	70
<b>A8</b>	0.58 (2e <sup>-</sup> )		-0.39	-0.49	-1.19	-1.51	60
<b>A9</b>	0.59 (2e <sup>-</sup> )		-0.36	-0.45	-1.07	-1.43	40

<sup>a</sup> Unpublished results.

<sup>b</sup>  $K_{\text{com}}(-1) = \exp(\Delta E_{1/2}/0.0257)$  at 25 °C.

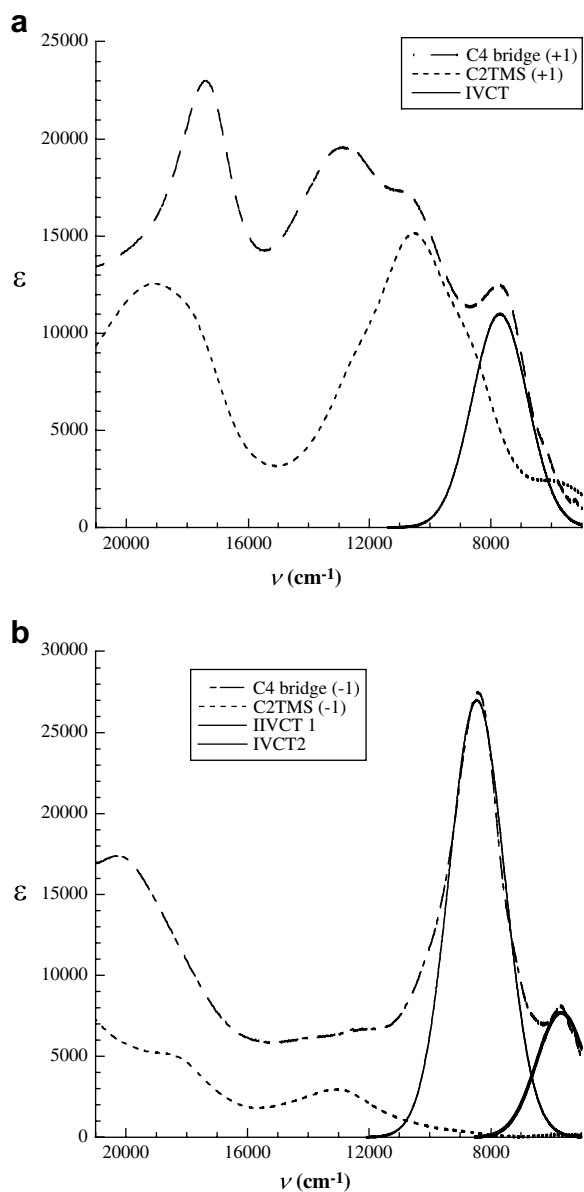


Fig. 4. Spectroelectrochemistry results of **A2'** and its "half" molecule  $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{TMS})$ : (a) spectra with one deconvoluted IVCT band upon one-electron oxidation (b) spectra with two deconvoluted IVCT bands upon one-electron reduction.

a strongly delocalized system, and a definitive answer awaits a high level computational study. Based on the comparison of the estimated half-widths with those predicted from the Hush model, which describes weakly coupled mixed-valence species (Robin-Day class II) [49,50], the mixed-valence cation and anion of compound **A2'** are strongly coupled species due to the narrowness of the observed IVCT bands [36,44]. They may be regarded as the class III species close to the

Table 2

Spectroelectrochemistry results<sup>a</sup> of mixed-valence ions of  $[\text{Ru}_2(\text{ap})_4]_2(\mu\text{-C}_4)$ .

Mixed-valence species	$E_{\text{IVCT}}$	$\epsilon$	$\Delta\nu_{1/2}$	$\Delta\nu_{1/2}(\text{Hush})^b$	$\Gamma^c$
$(\text{A2}')^{1-}$	8450	27000	1820	4420	0.59
	5670	7700	1630	3620	0.55
$(\text{A2}')^{1+}$	7700	11000	1820	4220	0.57

<sup>a</sup>  $E_{\text{IVCT}}$ ,  $\Delta\nu_{1/2}$  and  $\Delta\nu_{1/2}(\text{Hush})$  in  $\text{cm}^{-1}$  and extinction coefficient ( $\epsilon$ ) in  $\text{M}^{-1} \text{cm}^{-1}$ .

<sup>b</sup>  $\Delta\nu_{1/2}(\text{Hush}) = (2310\nu_{\text{max}})^{1/2}$ .

<sup>c</sup>  $\Gamma = 1 - \Delta\nu_{1/2}/\Delta\nu_{1/2}(\text{Hush})$ .

borderline of class II–III using the  $\Gamma$  parameter analysis [51].

The IVCT bands are also useful in estimating the adiabatic electronic coupling element  $H_{\text{ad}}$  for the series of  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_{2n})$  through  $H_{\text{ad}} = (\Delta G_{\text{r}} E_{\text{IVCT}})^{1/2}$ , where  $\Delta G_{\text{r}}$  is the free energy of resonance exchange and  $E_{\text{IVCT}}$  is related to the energy of IVCT band [52]. Furthermore, the electronic coupling attenuation constant  $\gamma$ , an efficient measure of the medium's ability to mediate electronic coupling, can be extracted using the equation  $H_{\text{ad}} = H_0 \exp(-\gamma R)$ , where  $H_{\text{ad}}$  and  $H_0$  are donor and acceptor wave function resonance exchanges at distance  $R$  and van der Waals contact distance, respectively, and  $R$  is the separation between the donor and acceptor from van der Waals contacts [41,43,44]. The success of extending the polyyne-diyl bridge to  $\text{C}_{20}$  provides the possibility of probing the electronic coupling over a long distance. For the reduced mixed-valence ions of the  $[\text{Ru}_2\text{L}_4]_2(\mu\text{-C}_{2n})$  compounds, two estimated  $\gamma$  were derived from a  $\ln(H_{\text{ad}})$  versus  $d_{\text{Ru}_2\text{-Ru}_2}$  plot<sup>1</sup> (Fig. 5):  $\gamma_1 = 0.100 \text{ \AA}^{-1}$  for  $n = 1\text{--}3$  and  $\gamma_2 = 0.015 \text{ \AA}^{-1}$  for  $n = 4\text{--}10$ , which are comparable to that found for oligoene-bridged pentaamineruthenium(II,III) donor–acceptor pairs ( $\gamma = 0.070 \text{ \AA}^{-1}$ ) [53] and  $\text{Fc}\text{--}\text{Fc}^+$  donor–acceptor pairs ( $\gamma = 0.087 \text{ \AA}^{-1}$ ) [54]. The appearance of dual attenuation parameters (bimodal) within a homologous series of molecules is relative rare [55], but has been frequently documented in electron transfer mediated by peptide chains [56]. The bimodal behavior in the latter case has been interpreted as superexchange (tunneling) at shorter distances and hopping at longer distances, although the precise mechanisms await more detailed studies.

<sup>1</sup> The energies of IVCT for most of the members in this series are currently unavailable and that of **A2'** was used instead.

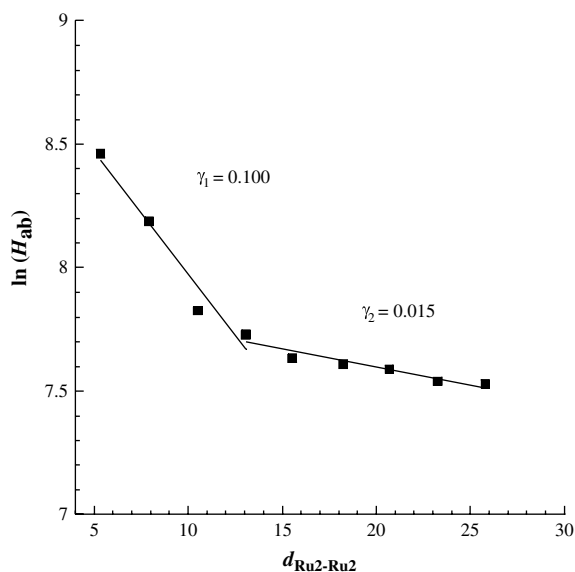
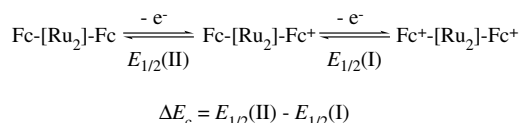


Fig. 5. Distance-dependence plot of  $\ln(H_{\text{ab}})$  ( $H_{\text{ad}}$  in  $\text{cm}^{-1}$ ) versus  $d_{\text{Ru}_2\text{-Ru}_2}$  (in Å).

### 3. Ru<sub>2</sub> bis-alkynyls capped by Fc termini

To realize the molecular wire as proposed in Chart 1, not only the charge transfer process on linear conjugated polyyn-diyl chains should be investigated, but also the role of the Ru<sub>2</sub> core in mediating electron mobility needs to be addressed [57,58]. This is realized by covalently attaching a pair of ferrocenyl units at the opposite ends of the Ru<sub>2</sub> fragment  $[\text{Fc}(\text{C}\equiv\text{C})_n\text{-Ru}_2\text{-(C}\equiv\text{C})_m\text{Fc}]$  and using both the comproportionation constant  $K_{\text{com}} = \exp(\Delta E_c/0.0257)$  (at room temperature, and  $\Delta E_c$  is defined by the equation below) [59] and spectroscopic characteristics of the mixed-valence ions to study the electron delocalization across the Ru<sub>2</sub> core [49].



In this diruthenium bis-alkynyl series, the *N,N'*-bidentate bridging ligands (L) utilized in supporting the Ru<sub>2</sub> core are *N,N'*-dimethylbenzamidinate (DMBA) and its phenyl-substituted derivative, *N,N'*-dimethyl-3-methoxy-benzamidinate (MeODMBA) (Chart 4). The modified DMBA ligand also has the advantage of significantly improved solubility of bis-compounds in common organic solvents [60].

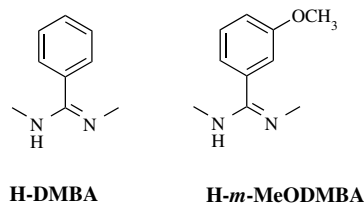


Chart 4. *N,N'*-dimethylbenzamidinate and its modified ligand.

#### 3.1. Alkynylation protocols

A series of diruthenium bis-alkynyl compounds which contain two Fc termini *trans*-(FcC<sub>2n</sub>)[Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>2m</sub>Fc) (Chart 5) were successfully synthesized through either anion metathesis [57,58] route or the weak-base protocol (Scheme 3) [23,60–63].

Weak-base protocol is superior to anion metathesis for the preparation of compounds containing functional groups (i.e. –NO<sub>2</sub>, –CN) sensitive to organolithium agents [61]. In addition, anaerobic or anhydrous conditions are not required, which facilitates the reaction monitoring and optimization (choice of base and stoichiometry of reactions) [23,63].

Symmetric compounds [Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>2n</sub>Fc)<sub>2</sub> were prepared in excellent yields, while unsymmetric compounds (FcC<sub>2n</sub>)[Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>2m</sub>Fc) were produced at lower yields after chromatographic separation from the symmetric compounds [57,58]. It is notable that compounds [Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>6</sub>Fc)<sub>2</sub> and [Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>8</sub>Fc)<sub>2</sub> cannot be synthesized through reactions between Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>Cl<sub>2</sub> and Li(C≡C)<sub>n</sub>Fc (*n* = 3 and 4), due to the instability and difficult isolation of H(C≡C)<sub>n</sub>Fc (*n* ≥ 3) [64].

Crystallization of the series of bis-alkynyl compounds was successful on less soluble Ru<sub>2</sub>(DMBA)<sub>4</sub>-based complexes [58]. Fig. 6 shows structural plots of compounds **B1**–**B3** determined via single-crystal X-ray diffraction and reveals similar structures under successive extensions by one acetylene unit [57,58]. Other features are: (1) two ferrocenyl groups occupy the opposite axial positions, and the longest edge–edge distance between

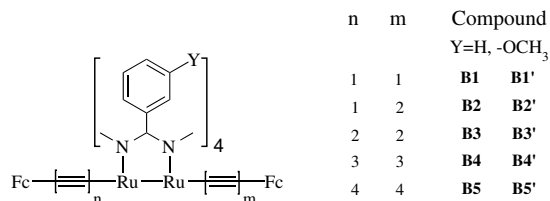
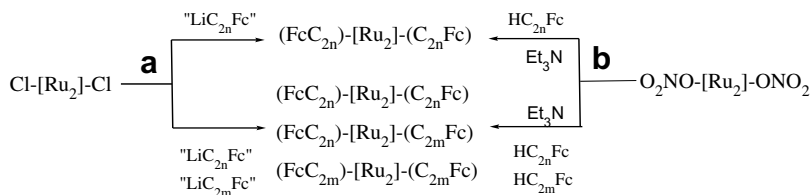


Chart 5. *trans*-(FcC<sub>2n</sub>)[Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>2m</sub>Fc) series.



Scheme 3. Synthetic routes (a) anion metathesis (b) weak-base protocol to the Fc-capped symmetric and unsymmetric compounds ([Ru<sub>2</sub>] = "Ru<sub>2</sub>(DMBA)" or "Ru<sub>2</sub>(MeODMBA)").

two Fc centers ( $C_w \dots C_w'$ ) is calculated as 21.6 Å for the symmetric compound **B4**; (2) the relative orientations between two Fc units are either almost *trans* to each other in **B1** (162°) or close to orthogonal in **B2** (104°) [58]; (3) In compounds **B1** and **B2**, Ru–N bond lengths vary and Ru'–Ru–C angles deviate from linearity. Such distortions from an idealized  $D_{4h}$  geometry have been documented in many bis-alkynyl compounds of a Ru<sub>2</sub>(III,III) core and were addressed by a second-order Jahn–Teller effect [31,32,60,61].

### 3.2. Characterizations

#### 3.2.1. Redox properties

Both the cyclic and differential pulse voltammograms of more soluble Ru<sub>2</sub>(*m*-MeODMBA)<sub>4</sub>-based compounds recorded in THF are shown in Fig. 7. For instance, compound **B1'** exhibits three sequential one-electron oxidations (between +0.4 V and +1.0 V) and one one-electron reduction at  $\sim -1.2$  V in the potential window of  $-1.5$ – $+1.5$  V (vs. Ag/AgCl). Spectroelectrochemical studies (details discussed below) identified the reduction and first oxidation as Ru<sub>2</sub> based, while the second and third oxidations as Fc based. While the butadiynyl spaced di-ferrocene (Fc(C $\equiv$ C)<sub>4</sub>Fc) to a pseudo two-electron oxidation [65], compound **B1'** displays a remarkably large potential splitting of 310 mV, indicating a strong coupling between two ferrocenyl units ( $K_{\text{com}} \approx 173\,000$ ). As the Fc...Fc distance increases, similar redox behaviors to those illustrated in the [Ru<sub>2</sub>]( $\mu$ -C<sub>2n</sub>)-[Ru<sub>2</sub>] are observed: (1) all redox couples are positively shifted, which is attributed to the strong electron-withdrawing nature of the added acetylene units; (2) Ru<sub>2</sub> oxidation couples drastically shift and overlap with the first Fc oxidation couples as *n* is increased to generate a two-electron wave.

#### 3.2.2. Spectroelectrochemistry

Since the reduction couple is Ru<sub>2</sub> based, spectroelectrochemical measurements focused on oxidations

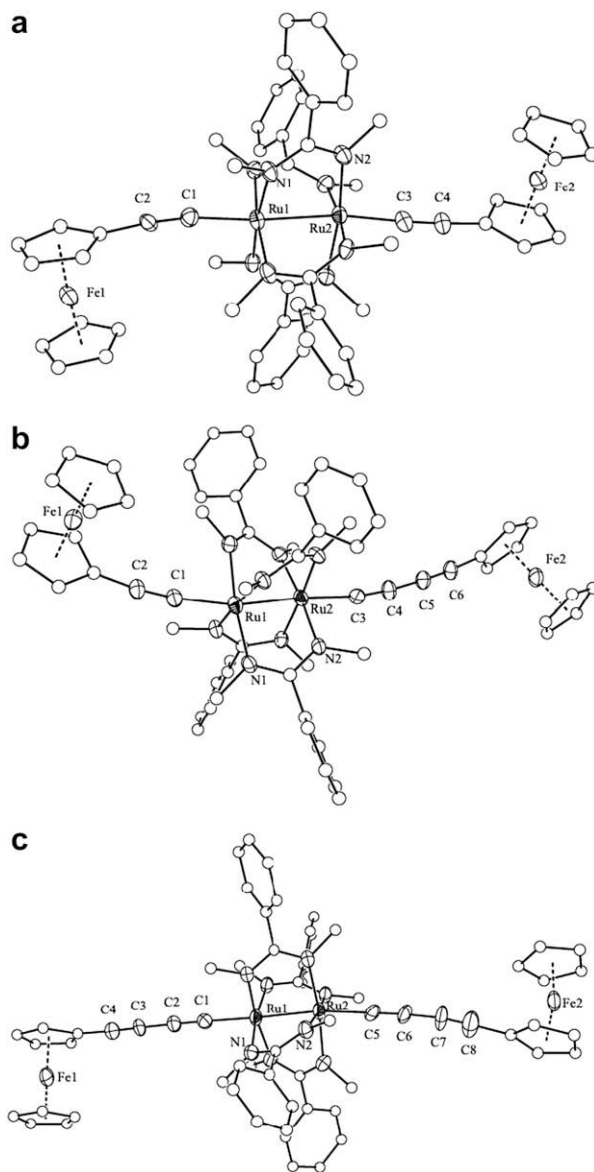


Fig. 6. Structural plots of (a) [Ru<sub>2</sub>(DMBA)<sub>4</sub>](C<sub>2</sub>Fc)<sub>2</sub> (**B1**), (b) [Ru<sub>2</sub>(DMBA)<sub>4</sub>](C<sub>2</sub>Fc)(C<sub>4</sub>Fc) (**B2**), (c) [Ru<sub>2</sub>(DMBA)<sub>4</sub>](C<sub>4</sub>Fc)<sub>2</sub> (**B3**).



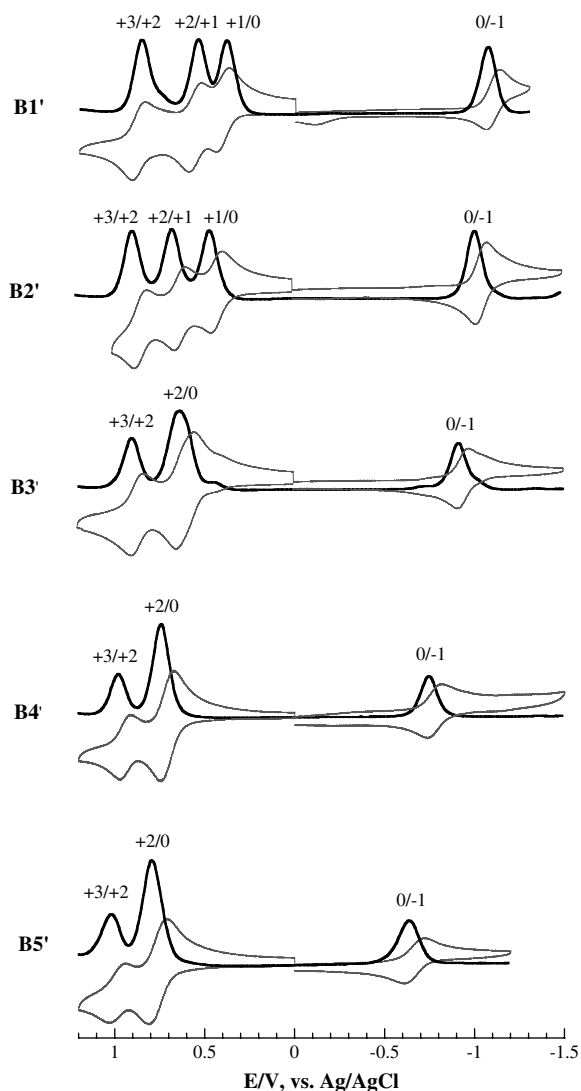


Fig. 7. Electrochemical results of *trans*-(FcC<sub>2n</sub>)[Ru<sub>2</sub>(MeODMBA)<sub>4</sub>] (C<sub>2m</sub>Fc) series (compounds **B1'**–**B5'**) recorded in 0.20 M THF solution of Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 0.10 V/s with a glassy carbon working electrode.

only [57,58]. Spectroelectrochemical study of symmetric compound **B1'** provided absorption spectra of its oxidation products (**B1'**)<sup>+</sup>, (**B1'**)<sup>2+</sup> and (**B1'**)<sup>3+</sup>, which show clean isosbestic points with good reversibility (>95% recovery) (Fig. 8). The first oxidation to (**B1'**)<sup>+</sup> resulted in appearance of a very broad low energy band (band I) in the spectrum extending from the near-IR to IR region, with the maximum absorption out of the spectral range of study. The spectrum of dication (**B1'**)<sup>2+</sup> displays a new higher energy band (band II) around 6000 cm<sup>-1</sup> in addition to band I. Upon third oxidation to (**B1'**)<sup>3+</sup>, both bands disappeared. Bands I

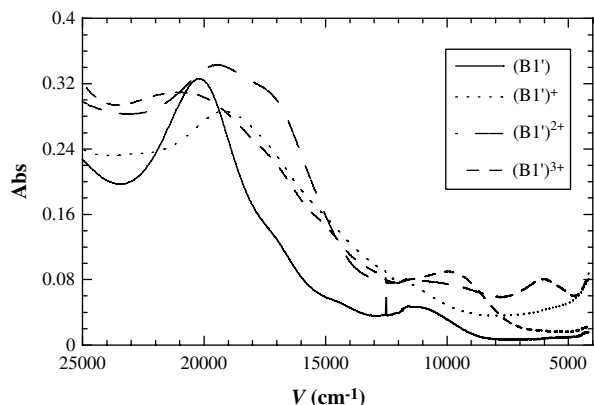


Fig. 8. Spectroelectrochemistry results of **B1'** upon sequential one-electron oxidation.

and II are assigned to IVCT bands; which vanished in (**B1'**)<sup>3+</sup> since both Fe are in the 3+ state. Compared to the IVCT bands observed for biferrrocene [65], band II has approximately the same energy and hence is assigned as Fc–[Ru<sub>2</sub>]<sup>+</sup>–Fc<sup>+</sup> based (Fc to Fc<sup>+</sup> transition). The other two oxidized forms are Fc–[Ru<sub>2</sub>]<sup>+</sup>–Fc ((**B1'**)<sup>+</sup>, mixed-valent, Fc to Ru<sub>2</sub><sup>7+</sup> transition) and Fc<sup>+</sup>–[Ru<sub>2</sub>]<sup>+</sup>–Fc<sup>+</sup> ((**B1'**)<sup>3+</sup>, no transitions), respectively. Unsymmetrical compound **B2'** and symmetric compound **B3'** exhibit similar spectroelectrochemical behaviors and data related to their mixed-valent species are listed in Table 3. Bandwidths of Fc to Fc<sup>+</sup> IVCT are generally narrower than those predicted by Hush model, even across a distance of 16.6 Å [23,49,57,58]. Obviously, the characteristics of the IVCT band are consistent with the magnitude of the comproportionation constants, indicating a valence delocalized state. The extent of delocalization is sufficient to classify (**B1'**)<sup>2+</sup>, (**B2'**)<sup>2+</sup> and (**B3'**)<sup>2+</sup> as Robin-Day class III, class II–III and II–III species, respectively [50,51]. In contrast, other Fc–X–Fc<sup>+</sup> systems (with X = none, acetylene, butadiyne or metal-containing units) exhibit very weak electronic communication despite short Fc–Fc<sup>+</sup> distances [65–67]. Thus, all these results evidence the proficiency of [Ru<sub>2</sub>] core in mediating superexchange electronic coupling (especially hole transfer) over a long distance. The mechanism of [Ru<sub>2</sub>] acting as an efficient charge transfer bridge is under investigation.

#### 4. Conclusions and outlook

Reviewed herein is our exploration in the chemistry of wire-like diruthenium  $\sigma$ -alkynyl species (Chart 1), including their syntheses, structural characterization, bulk solution voltammetry and

Table 3  
Electrochemical and spectroelectrochemical results of Fc–X–Fc<sup>+</sup> type species.

Fc–X–Fc <sup>+</sup>	C <sub>ω</sub> ...C <sub>ω'</sub> <sup>a</sup>	K <sub>com</sub>	E <sub>IVCT</sub> <sup>a</sup>	Δν <sub>1/2</sub>	Δν <sub>1/2</sub> (Hush) <sup>b</sup>	Γ	ref
None	1.45	821 000	5000	3700	3400	–	[57]
–C <sub>2</sub> –	4.0	7700	6410	5000	3850	–	[56]
–C <sub>4</sub> –	6.8	50	8470	5000	4420	–	[56]
–C <sub>2</sub> Ru(dppm) <sub>2</sub> C <sub>2</sub> –	9.36	5200	4770	3300	3320	–	[58]
<b>B1'</b>	11.58	173 000	6000	800	3720	0.78	[50,51]
<b>B2'</b>	13.84	3500	6230	1520	3790	0.60	[51]
<b>B3'</b>	16.60	–	6680	1780	3930	0.55	[51]

<sup>a</sup> C<sub>ω</sub>...C<sub>ω'</sub> (in Å) is the edge–edge distance between two Fc centers, E<sub>IVCT</sub>, Δν<sub>1/2</sub> and Δν<sub>1/2</sub>(Hush) in cm<sup>-1</sup>.

<sup>b</sup> Δν<sub>1/2</sub>(Hush) = (2310ν<sub>max</sub>)<sup>1/2</sup>.

spectroelectrochemistry. Facile *electron* transfer across the polyyn-diyl chains was demonstrated and very small electronic coupling attenuation constants were determined, which favor the realization of the proposed molecule wires [68,69]. Also illustrated is the exceptional ability of diruthenium unit in enhancing charge mobility (especially *hole* mobility) on the basis of the studies of the *trans*-(FcC<sub>2n</sub>)[Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>](C<sub>2m</sub>Fc) series. Nevertheless, several pertinent issues remain unresolved: (1) charge transfer mechanisms resulting in two different attenuation constants in one system [Ru<sub>2</sub>](μ-C<sub>2n</sub>)–[Ru<sub>2</sub>] and (2) mechanism of [Ru<sub>2</sub>] acting as an efficient charge transfer bridge between two ferrocenes. Also, the access to type **I** compounds with *n* beyond 10 is a challenging task, although one may find comfort in the recent breakthrough of Gladysz in preparing diplatinum compounds of *n* up to 14 [70,71]. Other related future efforts include seeking the in-depth knowledge of the ground-state electronic structures and the spectroscopic characteristics of these carbon-rich systems, controlling the direction of charge transfer (rectification) through donor/acceptor functionalization [63], and studying the distance dependence of the spin–spin interaction between two [Ru<sub>2</sub>] units [23,58].

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