

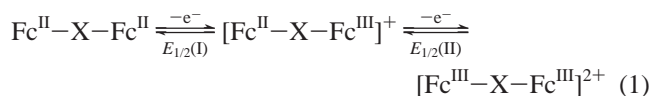
trans-Bis(alkynyl) Diruthenium(III) Tetra(amidinate): An Effective Facilitator of Electronic Delocalization

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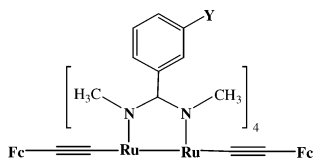
Linear conjugated molecules, along with carbon nanotubes and metallic nanowires, represent the majority of active materials used in molecular electronic devices.¹ Many laboratories including ours are investigating the possibility of realizing molecular electronic wires based on oligomeric metallaynes consisting of alternating metal compound and σ -bonded polyyne-diyl linker,² and our interest focuses on diruthenium-metallayne.³ High electron mobility along the $\text{Ru}_2-(\text{C}\equiv\text{C})_n-$ backbone is obviously a key prerequisite in realizing molecular electronic wires. Recently, we demonstrated the facile electronic delocalization across the polyyne-diyl bridge between two Ru_2 termini and explored the distance-dependence of electronic coupling therein.³ Clearly, the remaining question is whether the diruthenium unit, the other constituent of metallayne wires, will facilitate the electron transfer along the conjugated backbone. Similar questions have been raised in recent studies of other metallo-systems.⁴ A straightforward solution is to covalently attach two ferrocenyl (Fc) units at the opposite ends of the molecular fragment (X) and use both the free energy of comproportionation (ΔG_c) and spectroscopic characteristics of the mixed-valence ion to gauge the electron delocalization across X:⁴



$$\Delta G_c = E_{1/2(\text{II})} - E_{1/2(\text{I})} \quad (2)$$

The ferrocenylethynyl group ($\text{FcC}\equiv\text{C}$) in particular has been utilized in assessing charge mobility across mononuclear metal compounds,⁵ cluster compounds,⁶ and a diplatinum compound.⁷ We have designed compounds **1–3** (Scheme 1), where two $\text{FcC}\equiv\text{C}$ occupy the opposite axial positions of the $\text{Ru}_2(\text{Y-DMBA})_4$ unit (Y-DMBA are *m*-substituted dimethylbenzamidinate), and hoped to probe the electron mobility across the $\text{Ru}_2(\text{Y-DMBA})_4$.

Scheme 1. Compounds **1** (Y = H), **2** (Y = OCH₃), and **3** (Y = OC₄H₉)



Analogous to the alkynyl- $\text{Ru}_2(\text{DMBA})_4$ chemistry reported earlier,^{3b} reactions between $\text{Ru}_2(\text{Y-DMBA})_4\text{Cl}_2$ with $\text{LiC}\equiv\text{CFc}$ in THF afforded compounds **1–3** as red crystalline diamagnetic materials, which exhibit spectroscopic characteristics similar to those of other $\text{Ru}_2(\text{DMBA})_4(\text{C}_2\text{R})_2$ compounds and yield proper molecular

ion peaks in FAB-MS. In addition, X-ray single-crystal structure analysis of **1** (Figure 1) confirmed the expected axial σ -coordination of both ferrocenylacetylides to the Ru_2 core with an edge–edge distance of 11.6 Å between two Fc units.

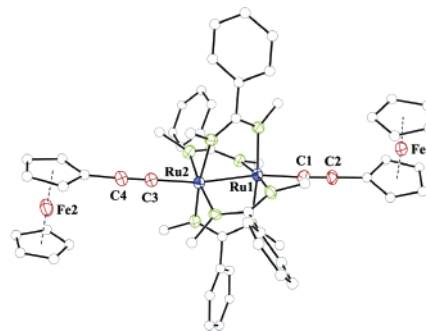


Figure 1. ORTEP view of molecule **1** at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Ru1–Ru2, 2.439(1); Ru1–C1, 1.981(8); Ru2–C3, 1.977(9).

The initial attempt to assess electronic coupling strengths between two Fc units in **1–3** was based on voltammetric techniques, in analogy to previous work on similar systems.^{5–7} The DPV of compound **1** (differential pulse voltammogram, Figure 2) consists of one one-electron reduction at -1.22 V (**A**) attributed to the Ru_2 core, and three one-electron oxidations (**B–D**) between 0.4 and 1.0 V. One of three oxidations is Ru_2 -based because all $\text{Ru}_2(\text{DMBA})_4(\text{C}_2\text{R})_2$ compounds undergo one-electron oxidation in this region,^{3b} and the other two are associated with ferrocenyl units. Nearly identical DPVs were also recorded for compounds **2** and **3** (Supporting Information). However, the definitive assignments of three oxidation couples, which is Ru_2 -based and which are Fc-based, is not apparent but can be achieved through spectroelectrochemistry.

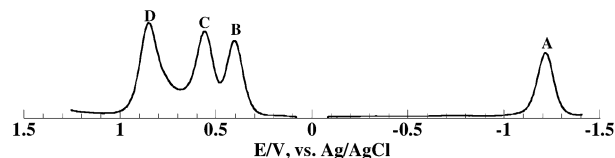


Figure 2. DPV of **1** recorded in 0.2 M Bu_4NPF_6 solution (THF).

The spectroelectrochemistry of **1** did not yield usable results due to the precipitation of both 1^{2+} and 1^{3+} generated in situ. Precipitation was not a problem with the more soluble derivatives **2** and **3**, and spectroelectrochemical studies of their oxidation products (see Supporting Information) gave clean isosbestic points and were reversible ($>95\%$ recovery). The spectra of **3** and its cationic derivatives are shown in Figure 3.

In Figure 3, a comparison of the spectra of **3** and 3^{3+} shows a subtle shift in the visible absorption and the appearance of a very broad low energy band (band I) in the spectrum of 3^{3+} that extends

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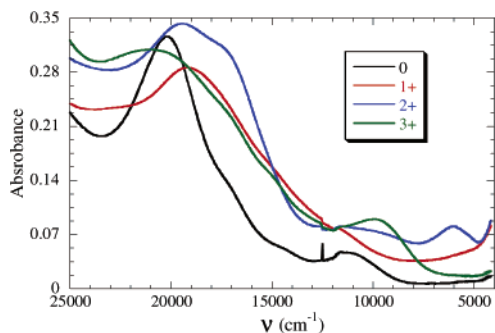


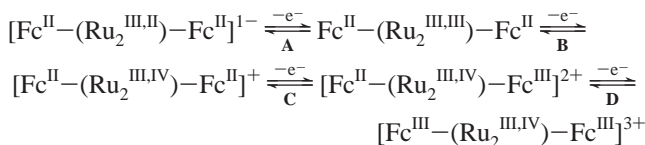
Figure 3. Spectroelectrochemistry of **3** in 0.10 M Bu₄NPF₆ THF solution.

Table 1. Voltammetric and Spectroscopic Data of Fc–X–Fc Compounds

X	<i>d</i> ^a	Δ <i>G</i> _c ^b	<i>v</i> _{IVCT} (Δ <i>v</i> _{1/2}) ^c	ref
–C ₂ –	1.45	0.35	5560 (3200)	8
–C ₄ –	4.0	0.23	6410 (>5000)	8
–C ₂ Ru(dppm) ₂ C ₂ –	6.63	0.10	8470 (>5000)	8
–C ₂ Ru(dppm) ₂ C ₂ –	9.36	0.22	4770 (3300)	5c,d
–C ₂ Cu ₃ (dppm) ₃ C ₂ –	8.39	0.11	8000 (3800)	6c
–C ₂ Pt ₂ (dppm) ₂ C ₂ –	12.00	0.25	11 300 (2800)	7
2	11.60	0.31	6000 (800)	this work
3	11.60	0.30	6040 (600)	this work

^a *d* is the edge–edge distance between two Fc in Å. ^b Defined in eq 2 in V. ^c Both in cm^{–1}.

from the NIR into IR region. The absorption maximum of band I occurs in the IR region and is out of the spectral range of our study. The spectrum of **3**²⁺ shows the presence of a new band (band II) centered at *v*_{max} = 6040 cm^{–1} in addition to band I. Both bands I and II disappear upon further oxidation as is seen in the spectrum of **3**³⁺. The appearance and disappearance of bands I and II upon the oxidation of **3** strongly suggest that these bands are intervalence charge–transfer transitions (IVCT). Very similar spectra and identical *v*_{max} values of band II were also obtained for compound **2** (Supporting Information). The bands II observed for both **2** and **3** have approximately the same energies as IVCT bands observed for biferrrocene⁸ (Table 1), and their rise and fall upon oxidations is unequivocal evidence that oxidation couples **C** and **D** are Fc–based.⁹ Hence, all observed redox couples of **1–3** are assigned as follows:



Accordingly, band I is assigned to Fc^{II} to Ru₂^{III,IV} charge transfer, and band II is assigned to Fc^{II} to Fc^{III} charge transfer. Furthermore, Δ*G*_c is ca. 0.30 V for **1–3**, which is comparable to that determined for biferrrocene⁸ and much larger than those for all aforementioned metallayne examples.^{5–7} This is truly remarkable considering the fact that the distance between two Fc units in **1–3** is 10 Å longer than that in biferrrocene and therefore reflects the ability of the Ru₂ moiety to mediate resonance exchange.

There are many factors that contribute to a Δ*G*_c value,¹⁰ and it is nontrivial to factor out the resonance exchange contribution.¹¹ However, the two-state Hush model¹¹ permits determination of resonance exchange from IVCT band properties, and so we undertook the deconvolution of band II, the Fc^{II} → Fc^{III} transition, from the spectrum of **3**²⁺ in Figure 3. Assuming a single Gaussian

band and constant background from band I, band II had *v*_{max} = 6040 cm^{–1}, Δ*v*_{1/2} = 600 cm^{–1}, and ε = 700 M^{–1} cm^{–1} (for **2**²⁺, band II had *v*_{max} = 6000 cm^{–1}, Δ*v*_{1/2} = 800 cm^{–1}, and ε = 1000 M^{–1} cm^{–1}). The width of band II is much narrower than the value predicted for a weakly coupled system ((2310*v*_{max})^{1/2} = 3730) and should be contrasted with the IVCT bandwidths of other mixed-valence Fc–X–Fc ions in Table 1. The disagreement between the calculated (Hush) and experimental bandwidth of band II for **2**²⁺ and **3**²⁺ is so great that it suggests that both complexes are delocalized systems, but further studies must be undertaken for this statement to be supported. The Hush model does not give good estimates of resonance exchange *H*_{ad} for strongly delocalized systems, and this is largely because the transition dipole moment length is not accurately measured by the separation between redox centers. For the delocalized case, *H*_{ad} = *v*_{max}/2, which would place resonance exchange coupling between the ferrocene moieties of **2**²⁺ and **3**²⁺ at ca. 3000 cm^{–1}.

Significant electronic couplings between two dinuclear paddlewheel species via a bridging ligand have been established through the structural and voltammetric studies in recent years.^{3,12} This Communication provides the first unambiguous example where the paddlewheel species themselves mediate facile electron transfer over a 10 Å distance, and hence a convincing argument for the potential role of paddlewheel species in molecular electronic devices.

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Supporting Information Available: Synthesis, characterization (PDF), and X-ray crystallographic details (CIF) of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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