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Long-distance electronic interaction in a molecular wire consisting of a ferrocenyl–ethynyl unit bridging two [(η^5-C_5H_5)(dppe)M] metal centers

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ABSTRACT

Several multinuclear ferrocenyl–ethynyl complexes of formula [(η^5-C_5H_5)(dppe)M^{II}–C≡C–$(fc)_n$–C≡C–M^{II}(dppe)(η^5-C_5H_5)] (fc = ferrocenyl; dppe = $Ph_2PCH_2CH_2PPh_2$; **1**: $M^{II} = Ru^{2+}$, $n = 1$; **2**: $M^{II} = Ru^{2+}$, $n = 2$; **3**: $M^{II} = Ru^{2+}$, $n = 3$; **4**: $M^{II} = Fe^{2+}$, $n = 2$; **5**: $M^{II} = Fe^{2+}$, $n = 3$) were studied. Structural determinations of **2** and **4** confirm the ferrocenyl group directly linked to the ethynyl linkage which is linked to the pseudo-octahedral [(η^5-C_5H_5)(dppe)M] metal center. Complexes of **1**–**5** undergo sequential reversible oxidation events from 0.0 V to 1.0 V referred to the Ag/AgCl electrode in anhydrous CH_2Cl_2 solution and the low-potential waves have been assigned to the end-capped metallic centers. The *solid-state* and *solution-state* electronic configurations in the resulting oxidation products of $[\mathbf{1}]^+$ and $[\mathbf{2}]^{2+}$ were characterized by IR, X-band EPR spectroscopy, and UV–Vis at room temperature and 77 K. In $[\mathbf{1}]^+$ and $[\mathbf{2}]^{2+}$, broad intervalence transition band near 1600 nm is assigned to the intervalence transition involving photo-induced electron transfer between the Ru^{3+} and Fe^{2+} metal centers, indicating the existence of strong metal-to-metal interaction. Application of Hush's theoretical analysis of intervalence transition band to determine the nature and magnitude of the electronic coupling between the metal sites in complexes $[\mathbf{1}]^+$ and $[\mathbf{2}]^{2+}$ is also reported. Computational calculations reveal that the ferrocenyl–ethynyl-based orbitals do mix significantly with the (η^5-C_5H_5)(dppe)Ru metallic orbitals. It clearly appears from this work that the ferrocenyl–ethynyl spacers strongly contribute in propagating electron delocalization.

1. Introduction

The insight provided by the rich chemistry of bridged mixed-valence binuclear complexes has promoted a great deal of both experimental and theoretical studies. Considerable work has been focused on the use of mixed-valence complexes to probe electronic coupling between well-separated metal sites [1–3]. Recently, the study of homo- and hetero-metallic binuclear transition metal complexes in which the end-capped metal centers are connected by π-conjugated organic linear spacers has been an intriguing area of research, since such system may provide the possibility to study the electronic coupling between the redox-active end-capped metal centers, or propose as models for molecular wires. In this context, end-capping of unsaturated organic spacers with various redox-active groups, such as ferrocene, ruthenium(II) polypyridine [4–9], [RuL_2Cl] ($L_2 = 2PPh_3$, $Ph_2PCH_2CH_2PPh_2$ (dppe)) [10,11], and [M(η^5-C_5H_5)L_2] (M = Fe(II), Ru(II), and Os(II)) metal centers [12–21], have been most studied where they are intended to promote the long-range electronic coupling. The nature of the end-capped metal center and π-conjugated organic spacer plays significantly important role in determining the magnitude of electronic coupling. The magnitude of electrochemical data $\Delta E_{1/2}$ has been taken as an indication of the magnitude of electronic coupling between two redox metal centers, where $\Delta E_{1/2}$ is the difference in redox potentials associated with the first and second oxidation of the metal centers. The electrochemical response of binuclear transition metal complexes bridged with polyynes and related ligands derived from polyynes (μ-C≡C–X–C≡C, X = C≡CC≡C, 1,4-C_6H_4, 2,5-thiophene, and 2,5-pyridine) has been comprehensively studied. The compounds [(η^5-C_5Me_5)Re(NO)(PPh_3)]$_2$(μ-C≡C)$_n$ ($n = 2$, 3 and 4) [21–24] display reversible electrochemical response, the cyclic voltammogram (CV) of these compounds being characterized by two one-electron redox waves. Furthermore, the decreasing of the $\Delta E_{1/2}$ value from 0.53 V in $n = 2$, 0.38 V in $n = 3$ to 0.28 V in $n = 4$ indicates that the magnitude of Re^{2+}–Re^{2+} interaction is decreased significantly on the number of C≡C moiety. Furthermore, complexes with an odd numbered carbon linear or cyclic bridge has been recently found to promote very efficient electronic communication between two [RuCl(dppe)$_2$]$^+$ metal centers [25].

Very recently, we have described the electrochemical and photophysical properties for a series of complexes containing

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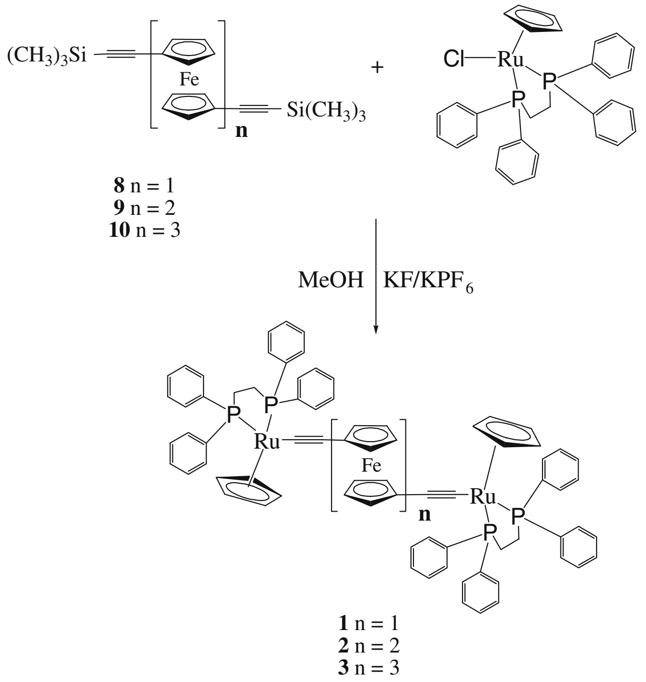
bis-(2,2′:6′,2″-terpyridyl)polyferrocene redox-active spacers end-capped with photoactive and redox-active Ru^{2+}-terpyridine terminals ($[(tpy)Ru^{II}\text{-}(tpy\text{-}(fc)_n\text{-}tpy)\text{-}Ru^{II}(tpy)]^{4+}$ (tpy = terpyridine, fc = ferrocenyl, n = 1–3) and $[(tpy)Ru^{II}\text{-}(tpy\text{-}C{\equiv}C\text{–}(fc)_n\text{–}C{\equiv}C\text{-}tpy)\text{-}Ru^{II}(tpy)]^{4+}$ (n = 2–3)) to study the electronic interaction between the end-capped Ru^{2+} metal centers [26–28]. In our previous papers, the CV electrochemical measurements for these binuclear Ru^{2+} complexes were dominated by the Ru^{2+}/Ru^{3+} redox couple ($E_{1/2}$ from 1.35 to 1.38 V), Fe^{2+}/Fe^{3+} redox couples ($E_{1/2}$ from 0.4 to 1.0 V) and $tpy/tpy^{-}/tpy^{2-}$ redox couples ($E_{1/2}$ from −1.3 to −1.5 V). Note worthily, a single irreversible wave was found for the Ru^{2+}/Ru^{3+} redox couple. We suggested that the electronic coupling between the two Ru^{2+} centers is relatively weak. In attempting to modulate the electronic coupling between the two terminal Ru^{2+} centers by manipulation of the energetic of the end-capped metal centers and the connecting spacer, we now describe the electrochemical and photophysical properties of **1**–**7** (Schemes 1 and 2). The preparation and X-ray crystallographic structure analysis of **1** were previously reported by Bruce [19]. Quasi-reversible and irreversible waves were observed in the cyclic voltammetry (CV) measurements of complexes **1**. Our design principle for wire-like molecules **1**–**5** is that the redox-active ferrocenyl–ethynyl spacer can enhance the capability of transfer information along the stepwise molecular axis through stronger σ-bonding of M^{2+}–C≡C in comparison with tpy-ferrocenyl-tpy spacer. Furthermore, it has been found that the 18-electron ferrocene complex can be easily oxidized to form a stable 17-electron ferrocenium complex. As shown in Scheme 3, rapid intramolecular electron transfer between the two ruthenium centers in mixed-valence diruthenium complex could occur through the ferrocenyl spacer. Thus, the ferrocenyl spacer that can provide an effective hetero-nuclear electron delocalization along main chain can serve as model system for molecular wire.

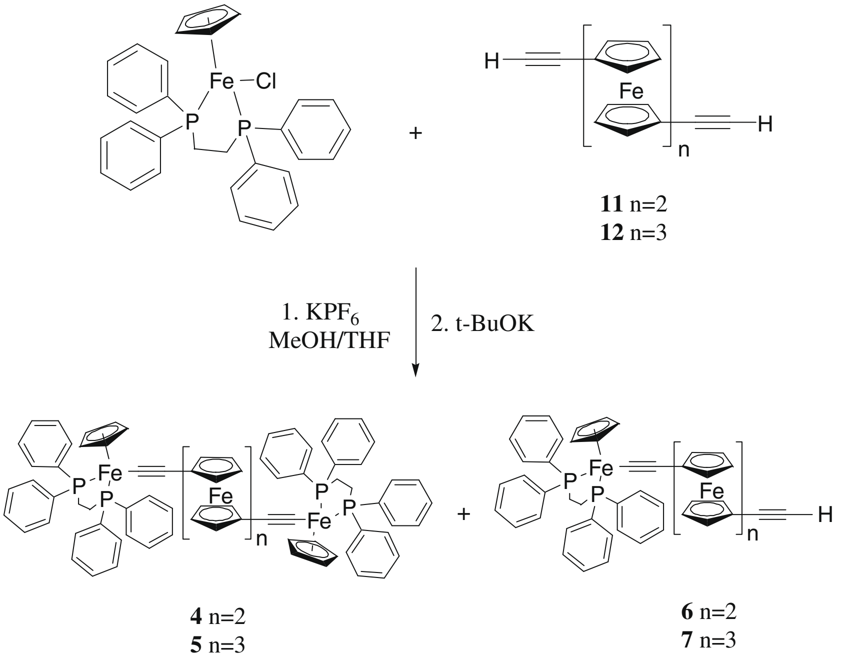


Scheme 1. Synthesis of the discussed Ru^{2+} complexes with ferrocenyl–ethynyl spacers.

2. Results and discussion

2.1. Synthesis and characterization

Binuclear complexes of **1**–**7** were prepared by reacting ferrocenylethynyl spacers (**8**–**12**) with stoichiometric amount of $(\eta^5\text{-}C_5H_5)(dppe)MCl$. Complexes were purified by column chromatography and recrystallization. All complexes were fully characterized by 1D and 2D NMR techniques, IR, MS and elemental analysis. Structures of complexes **1**–**5** were characterized by ^{31}P NMR showing a singlet for the four equivalent phosphorus nuclei at ~87 ppm in the $[Ru(\eta^5\text{-}C_5H_5)L_2]$ end-capped complexes (**1**–**3)** and at ~107 ppm in the $[Fe(\eta^5\text{-}C_5H_5)L_2]$ end-capped complexes (**4**–**5**). The ethynyl carbons in **1**–**3** were identified by ^{13}C NMR showing a singlet at ~107 ppm for the carbon bonded to the ferrocenyl



Scheme 2. Synthesis of the discussed Fe^{2+} complexes with ferrocenyl–ethynyl spacers.