A New Direction in Carbon-Rich Organometallic Wires: Diruthenium Compounds Bridged by *E*-Hex-3-ene-1,5-diyn-diyl

Yanhui Shi,† Gordon T. Yee,‡ Guangbin Wang,‡ and Tong Ren*,†

Department of Chemistry, University of Miami, Coral Gables, Florida 33146, and Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061
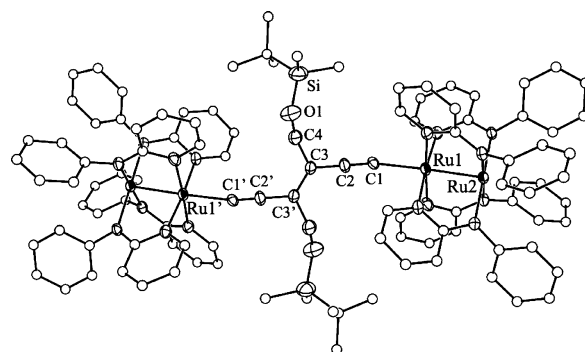
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The synthesis and characterization of wire-like carbon-rich organometallic species has been topical in recent years.[1] The majority of the work has been focused on metal units linked by a σ-oligoyndiyl bridge (C_{2m}), where facile electronic delocalization between two metal centers across the C_{2m} bridge, namely wire-like character, has been inferred from voltammetric studies.[2] Compounds with bridges such as oligoen-diyl (($(CH)_{2m}$),[3] cumulenes[4] and ene−ynes[5] are rarer, but exhibit wire-like behavior as well. Our contributions to the area include the synthesis of $[Ru_2(ap)_4]_2$-(μ-C_{2m}) (*ap* is 2-anilinopyridinate) and elucidation of high electron mobility between two Ru_2 units across the C_{2m} bridge, and subsequent demonstration of the efficacy of the Ru_2 unit in mediating electron transfer.[6] We have been intrigued by the prospect of new types of organometallic wires based on other carbon-rich scaffolds, such as *E*-hex-3-ene-1,5-diyne (DEE) and tetraethyne−ethene (TEE),[7] which may result in significantly enhanced electron-transfer rates. In this communication, we report the first examples of transition metal compounds of 3,4-bis(*tert*-butyldimethylsily-loxymethylene)-*E*-hex-3-ene-1,5-diyne (DEE*),[8] $Ru_2(ap)_4(DEE*)$ (**1**), $[Ru_2(ap)_4]_2(\mu$-C,C'-DEE*) (**2a**), and $[Ru_2(MeO$-$ap)_4]_2(\mu$-C,C'-DEE*) (**2b**), and the wire-like character of **2a/2b** based on their voltammetric and magnetic properties (Scheme 1.).

Scheme 1. $Ru_2(XAp)_4$−DEE* Compounds **1** and **2**

1: X = Y = H

2a: X = H, Y = $Ru_2(Xap)_4$

2b: X = OCH_3, Y = $Ru_2(Xap)_4$
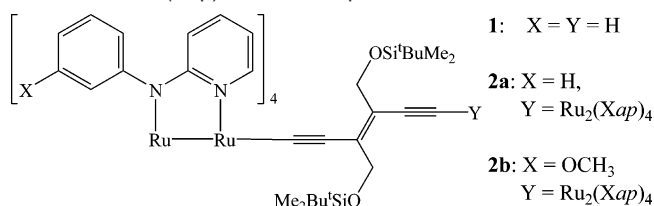
Compound **1** was prepared by treating $Ru_2(ap)_4Cl^{9b}$ with 1.1 equiv of LiDEE* and isolated as a green microcrystalline solid that exhibits physical properties almost identical to those of $Ru_2(ap)_4$-(C_2R).[9] Compounds **2a** and **2b** were obtained by reacting $Ru_2(Xap)_4$-Cl with 0.55 equiv of Li_2DEE* in good yields (>80%). The bridging nature of DEE* ligand in **2** was established from a single-crystal structural analysis of **2a**, as shown in Figure 1. While the Ru−Ru distance in **2a** is comparable to that of $Ru_2(ap)_4(C_2R)$ (ca. 2.32 Å), the Ru−C distance is significantly lengthened from that of $Ru_2(ap)_4(C_2R)$ (2.08 Å).[9] Also noteworthy is the significant deviation from linearity in the Ru−C1−C2 angle in **2a**. These features are likely the consequence of steric crowding caused by the Si^tBuMe_2 groups. Clearly, the bond lengths and angles within the C1−C2−C3−C3′−C2′−C1′ fragment in **2a** conform to the hex-3-ene-1,5-diyn-diyl formalism and agree with that reported for the organic parent molecules.[10] Consequently, the degree of π-conjuga-

† University of Miami.
‡ Virginia Polytechnic Institute and State University.

Figure 1. Molecular structure of **2a**. Selected bond lengths (Å) and angles (deg): Ru1−Ru2, 2.3281(8); Ru1−C1, 2.137(6); C1−C2, 1.175(8); C2−C3, 1.441(8); C3−C3′, 1.339(12); Ru2−Ru1−C1, 178.1(2); Ru1−C1−C2, 169.0(6); C1−C2−C3, 177.4(7); C2−C3−C4, 115.9(6); C2−C3−C3′, 121.5(7). An inversion center is situated between C3 and C3′.
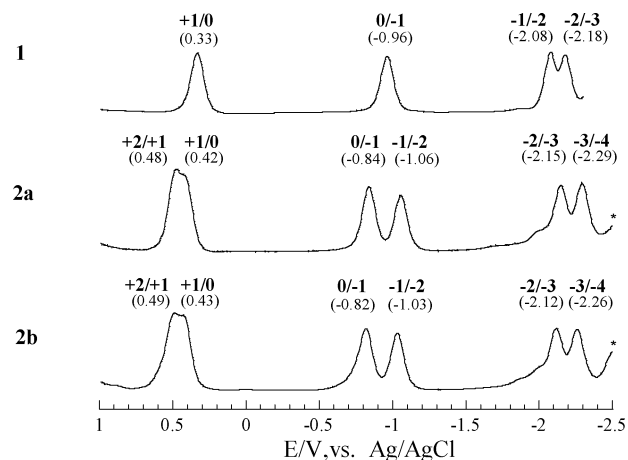
Figure 2. DPVs of compounds **1** and **2** recorded in THF with the assignment (E_p/V) of all redox couples marked; * denotes the solvent background.

tion along the Ru_2−DEE*−Ru_2 linkage cannot be unequivocally determined from the structural data.

Voltammetric measurements are a more direct and effective means of ascertaining the degree of conjugation in wire-like metallaynes.[2,6] Differential pulse voltammograms (DPV) recorded for **1** and **2a/2b** are shown in Figure 2. Within the potential window of +1 to −1.5 V, **1** exhibits two one-electron couples, an oxidation and a reduction, and both are Ru_2-based.[9b] In comparison, both **2a** and **2b** exhibit a pair of overlapping but resolved oxidation couples, and a pair of cleanly separated reduction couples. The pairwise appearances are indicative of the conjugation between two Ru_2 termini across the bridging DEE*.[6] The separation between two oxidation couples, ca. 0.06 V, indicates that the monocation (**2**)$^+$ is a class II mixed-valent species in the Robin−Day classification.[11]

The much larger separation between two reduction couples (0.22 V) clearly reveals the monoanion (**2**)⁻ to be a class III mixed-valent species. Hence, the conjugated Ru₂(X*ap*)₄−DEE*−Ru₂-(X*ap*)₄ molecule is a poor *hole-wire* but an excellent *electron-wire*, a feature previously noted for [Ru₂(*ap*)₄]₂(μ-C₂ₘ).[6] Pairwise reductions in the very cathodic region were observed for both **1** and **2a/2b**, and the exact nature of these couples is being investigated.

Magnetic measurements are another effective tool for probing the degree of electronic interactions between the metal units as mediated by the organic bridge.[12] Isolated Ru₂(II,III) species typically exhibit an $S = \frac{3}{2}$ ground state, and their magnetic properties are adequately described by a zero-field-splitting (ZFS) model that converges to a χT value of ca. 1.2 emu-K/mol as $T \rightarrow$ 0 K.[13] As shown by the data in Figure 3 for **2b**, χT of both **2a** and **2b** fall from a value appropriate for two uncoupled Ru₂⁵⁺ units at room temperature (ca. 3.8 emu-K/mol) to almost zero in a smooth fashion as the temperature is decreased, which cannot be accounted for by the ZFS model. Clearly, antiferromagnetic coupling between two Ru₂ termini is responsible for the nonmagnetic ground state indicated by $\chi T \approx 0$. A satisfactory fit was achieved with a model that assumes isotropic coupling as described by the Heisenberg Hamiltonian, $H = -2JS_1 \cdot S_2$, that ignores ZFS to yield the expression shown in the insert of Figure 3 ($x = J/kT$). Nonlinear least-squares fit yielded $g = 2.10(2)$ and $J/k = -15(1)$ K for **2a**, and $g = 2.09(1)$ and $J/k = -15(1)$ K for **2b**, and both the measured data and fit for **2b** are shown in Figure 3. The agreement between the model and the data, especially in the low T regime, is not perfect probably because of the neglect of ZFS of low-lying excited states.[14] Interestingly, previous study of the chainlike compounds {[Ru₂-(OAc)₄(μ-L)]⁺/⁰}∞ revealed only weak couplings ($zJ/cm^{-1} = -2.3$ for L = pyrazine and −0.33 for L = N(CN)₂⁻) between adjacent Ru₂ units that are five or six bonds apart.[15] In comparison, two Ru₂ units in **2a/2b** experience much stronger coupling despite a spacing of seven bonds, a testament to the efficacy of DEE* ligand as a coupling unit. Among limited examples of magnetic interaction mediated by carbon-rich bridges, strong couplings among Cp*Feᴵᴵᴵ-(dppe) centers bridged with di/tri(ethynyl)benzene (J/k ranging from 14 to 94) are noteworthy.[16]

$$\chi T = \frac{2Ng^2\mu_B^2}{k}\left\{\frac{\exp 2x + 5\exp 6x + 14\exp 12x}{1 + 3\exp 2x + 5\exp 6x + 7\exp 12x}\right\}$$
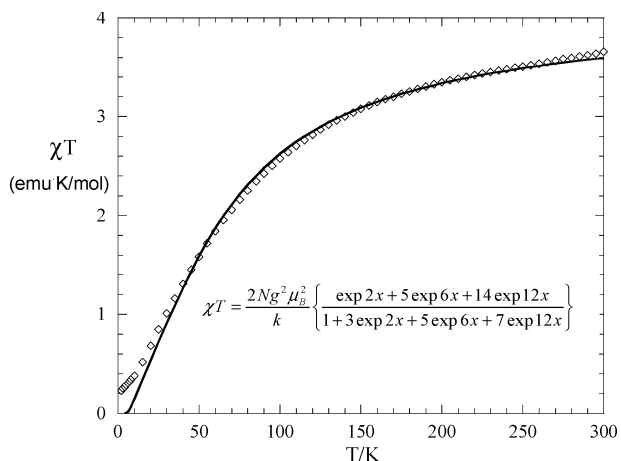
Figure 3. Measured magnetic susceptibilities (χT, as diamonds) and its fit according to the Heisenberg model (solid line) of compound **2b**.

We have demonstrated the feasibility of synthesizing transition metal compounds of the DEE* ligand and its capacity to mediate both electron transfer and spin coupling. While there is no literature precedent for transition metal complexes containiqng DEE, several Pt compounds of TEE, a close relative of DEE, have been studied, and it was noted that no electronic interaction across the TEE bridge could be detected in the oligomers of *trans*-Pt(TEE)₂P₂ (P is monodentate phosphine).[17] Electronic couplings through a carbon-rich bridge are commonly mediated by the LUMO of the bridge.[6] Preliminary MO analysis (Supporting Information) reveals that the LUMOs of both TEE and DEE are indeed π* orbitals, and the contribution from the Cα center (terminal carbon that bonds to the metal center) is notably smaller in TEE than that in DEE. This subtle difference in orbital population may account for the contrast between the behaviors of **2a/2b** and Pt-TEE systems. The magnetism of 1-D, 2-D, and 3-D assemblies of diruthenium compounds has received intense attention during the last two decades,[18] and compounds **1** and **2** represent promising new synthons for such assemblies.

Supporting Information Available: Synthesis and characterization of **1** and **2**, and MO analysis of DEE and TEE models; X-ray crystallographic details (in CIF format) of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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