Organometallic Wires

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Linear Trimer of Diruthenium Linked by Butadiyn-Diyl Units: A Unique Electronic Wire**

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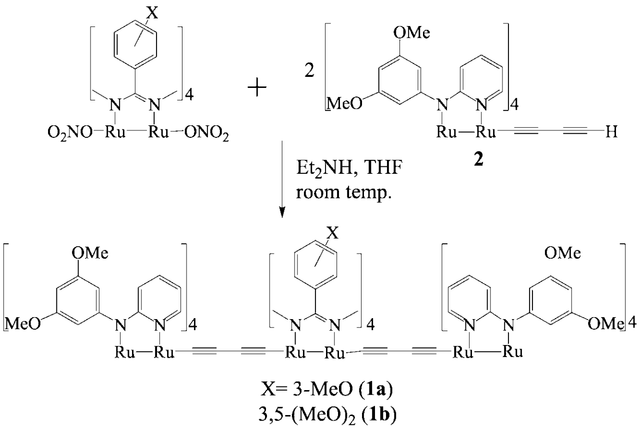
The proposal of molecular wires based on metal oligoynyl compounds has been around for some time.[1–3] Two types of structural motifs are featured prominently in these endeavors: dimers ([M]-$(C{\equiv}C)_n$-[M]) and oligomers ($\{[M]\text{-}(C{\equiv}C)_n\}_m$-[M]) bridged by a μ-C,C′-oligoyn-diyl unit. The earliest examples of dimers and oligomers were based on Pd^{2+} and Pt^{2+} species,[4] which are insulators with band gaps generally larger than 3 eV.[5] The significant electronic delocalization that is desired for molecular wires has been demonstrated in many dimeric compounds with metal centers, such as Fe, Re, and Ru.[6] Recent efforts in measuring the current–voltage characteristics of metal alkynyl compounds in nanojunctions yielded encouraging results as well.[7] Nevertheless, realizing similar delocalization in the $\{[M]\text{-}(C{\equiv}C)_n\}_m$-[M] type oligomers remains synthetically challenging.[8] The electronic delocalization in the [M]-$(C{\equiv}C)_n$-[M] type dimers is mediated by the polyyndiyl chains,[6] while the electronic delocalization across the [M] units has rarely been addressed. Hence, synthetic access to oligomers will provide the opportunity to assess electronic delocalization across both the carbon-rich backbone and metal centers. Studies of *trans*-[Fc$(C{\equiv}C)_n$-$Ru_2(DMBA)_4$-$(C{\equiv}C)_n$Fc] (DMBA is *N*,*N*′-dimethylbenzamidinate, Fc is ferrocenyl) type compounds revealed that the central $Ru_2(DMBA)_4$ unit mediates strong electronic couplings between two Fc termini over distances up to 2.7 nm.[9] Encouraged by these results, we began to explore the utility of $Ru_2(DMBA)_4$ species in forming oligomeric compounds. Reported herein are the synthesis and characterization of linear trimers **1a**/**b** (Scheme 1) that exhibit a multitude of unusual physical properties as a result of the strong intermetallic delocalization, and a theoretical rationale on the basis of density functional theory (DFT) calculations.



Scheme 1. Preparation of compounds **1**.

The preparation of trimeric compounds **1a**/**b** was accomplished from the reaction between $[Ru_2(DiMeOap)_4(C_4H)]$ (**2**)[10] and $[Ru_2(X\text{-}DMBA)_4(NO_3)_2]$[11] in a 2:1 ratio in the presence of Et_2NH.[12] Compounds **1a** and **1b** were purified by recrystallization from THF/hexanes in yields of 77 % and 58 %, respectively. Although the high-spin nature of **1a**/**b** prevents clean characterization by NMR spectroscopy, they were analyzed satisfactorily with mass spectrometry and elemental analysis. The trimeric nature of **1** was further confirmed through an X-ray diffraction study of **1a**[13] (Figure 1). The structural analysis of **1a** reveals that the coordination spheres of both the $\{Ru_2(DiMeOap)_4\}$ termini and central $\{Ru_2(m\text{-}MeO\text{-}DMBA)_4\}$ unit bear close resemblance to those of $[Ru_2(DiMeOap)_4(C_4SiMe_3)]$[10] and $[Ru_2(DMBA)_4(C_{2n}R')_2]$,[11] respectively. The C–C bond lengths in

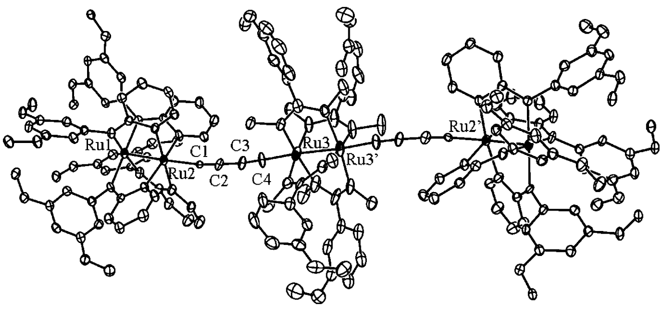


Figure 1. ORTEP plot of **1a** (thermal ellipsoids set 30% probability). The asymmetric unit of **1a** consists of one half of the trimer, which is related to the other half through an inversion center. Selected bond lengths [Å]: Ru1–Ru2 2.326(1), Ru3–Ru3′ 2.440(2), Ru2–C1 2.09(1), Ru3–C4 1.99(1), C1–C2 1.19(2), C2–C3 1.39(2), C3–C4 1.20(2).

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the butadiyn-diyl fragment follow the expected pattern of alternating single and triple bonds. The distance between two $\{Ru_2(DiMeOap)_4\}$ termini (Ru2···Ru2′) is 18.04 Å.

The cyclic and differential voltammograms (CVs and DPVs) of compounds **1a/b** were examined to gauge the electronic delocalization therein, and the DPV of **1a** shown in Figure 2 reveals a very complex pattern in the window from 1.0 to −2.0 V. To facilitate the analysis of the DPV of **1a**, the DPVs of $[Ru_2(DiMeOap)_4(C_4SiMe_3)]$ (**2′**)[10] and $[Ru_2(m\text{-}MeO\text{-}DMBA)_4(C_4SiMe_3)_2]$ (**3**),[11] both precursors to **1a**, were also included in Figure 2. Compound **2′** exhibits a one-electron oxidation at 0.49 V and a one-electron reduction couple at −0.72 V, and compound **3** exhibits a one-electron oxidation at 0.74 V and a one-electron reduction at −0.88 V. Since the oxidation potential of **3** is far more positive than that of **2′**, the first two one-electron oxidations (+1/0 and +2/+1) in **1a** are attributed to the $\{Ru_2(DiMeOap)_4\}$ termini, and the third oxidation to the central $\{Ru_2(m\text{-}MeO\text{-}DMBA)_4\}$ unit. Similarly, because of the more negative reduction potential of **3**, the first two one-electron reductions (0/−1 and −1/−2) in **1a** are attributed to the Ru_2 termini, and the third reduction to the central Ru_2 unit. Both the pair-wise oxidations and reductions of the $\{Ru_2(DiMeOap)_4\}$ termini in **1a** are the hallmark of electronic couplings in the mixed-valent states (+1 and −1).[1,14] The potential differences within the pair-wise couples are $\Delta E(+1) = E(+2/+1) - E(+1/0) = 91$ mV and $\Delta E(-1) = E(0/-1) - E(-1/-2) = 95$ mV. These values, though small in comparison to strongly coupled compounds such as the Creutz–Taube ion,[14] are still significant considering the large donor–acceptor separation (18 Å). Determination of the intervalence charge-transfer transitions in $\mathbf{1a}^{\pm1}$ would facilitate the quantification of electronic coupling, but the spectroelectrochemical study of **1a** was unsuccessful because of its instability over the timescale required for electrolysis.

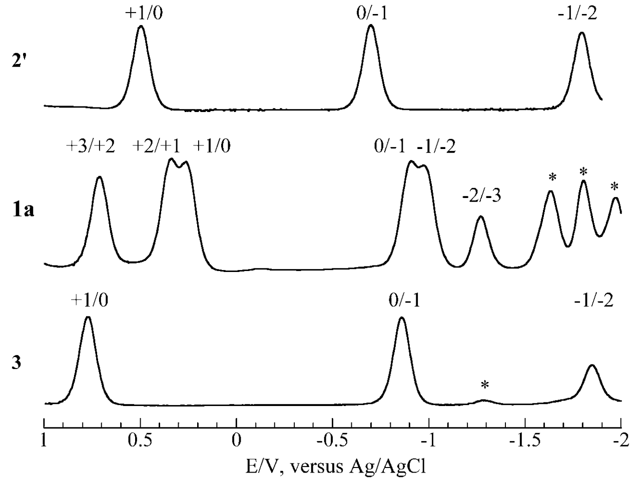

Figure 2. DPVs of compounds **1a**, and its precursors **2′** and **3** recorded in THF. The numbers denote the Ru oxidation states; "*" denotes peaks attributed to the degraded species. A plausible assignment is provided in the Supporting Information.

Additional evidence of significant delocalization comes from the comparison of the electronic absorption spectra of compounds **1a**, **2′**, and **3**, which are shown in Figure 3. The spectrum of **1a** features intense peaks at 931, 770, 618, and 479 nm, and is very different from those of **2′** and **3**. A composite spectrum was calculated as the sum of spectrum **3** and the double of spectrum **2′**, and is included in Figure 3 as well. Should the electronic coupling among three Ru_2 units be negligible, the composite spectrum would be in good agreement with that of **1a**. While the peaks at 770 and 480 nm in compound **1a** were "reproduced" in the composite, the peaks at 618 nm and 931 nm observed for **1a** were absent in the composite. The appearance of these "new" bands must be the consequence of extensive conjugation among three Ru_2 units through the butadiyn-diyl bridges.

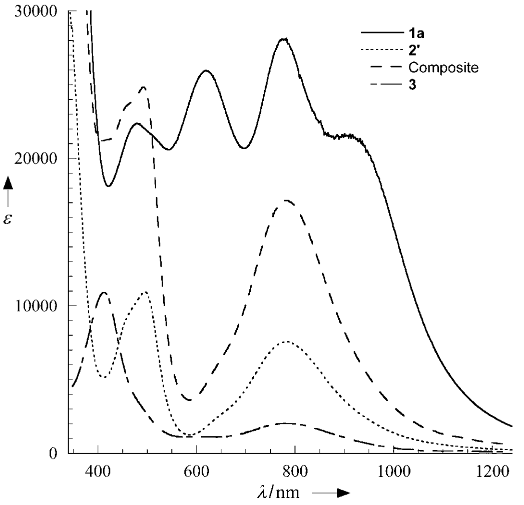

Figure 3. Vis-NIR spectra of compounds **1a**, **2′**, and **3** recorded in THF, along with the composite spectrum $2\varepsilon(\mathbf{2'}) + \varepsilon(\mathbf{3})$.

The magnetic susceptibility of compounds **1a** and **2′** were measured in the temperature range of 1.8–300 K (Figure 4).[15] The $\chi_m T$ characteristics for **2′** are consistent with a $S = 3/2$ ground state that undergoes zero-field splitting. The fitting of $\chi_m T$ data resulted in $g = 2.09$ and $|D| = 56.33$ cm^{-1}, which are

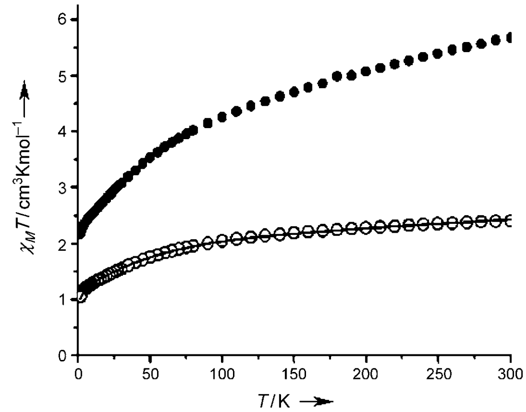

Figure 4. Plots of $\chi_m T$ versus T of compounds **1a** (●) and **2′** (○). The solid line represents the best theoretical fit of the data for **2′**.

in line with studies of related $Ru_2^{II,III}$ species.[16] The [$Ru_2(DMBA)_4(C{\equiv}CR)_2$] type compounds are generally diamagnetic ($S=0$).[3] The magnetic properties of **1a** would be dominated by two {$Ru_2(DiMeOap)_4$} termini ($S=3/2$) with a room temperature $\chi_m T$ value around 3.75 cm^3 K mol^{-1} if the -$(C{\equiv})_2$-$Ru_2(DMBA)_4$-$(C{\equiv}C)_2$- fragment remains $S=0$ and functions as a weak mediator of spin coupling.[17] However, compound **1a** exhibits a significantly higher $\chi_m T$ value of 5.67 cm^3 K mol^{-1} at 300 K, implying the presence of additional unpaired electrons in **1a**. Given the precedent of the $S=1$ state for Ru_2^{6+} compounds with different axial ligands[18] and other examples of spin-admixed diruthenium species,[19] it is possible that the unusually large $\chi_m T$ value of **1a** arises from the contribution of an $S=1$ state of the central Ru_2^{6+} moiety. Hence, the spin distribution in **1a** may be assigned as (3/2)-(1)-(3/2). The theoretical $\chi_m T$ value of this model is 5.28 ($g=2.09$ for Ru_2^{5+}(S=3/2) and g is 2.18 for Ru_2^{6+}(S=1)), and is in agreement with the experimental value at 300 K.[18] On the other hand, the $\chi_m T$ value of **1a** at 1.8 K is 2.17 cm^3 K mol^{-1}, which is twice of that of **2'**. This result suggests that the magnetic centers of **1a** at low temperature consist of two Ru_2^{5+} ($S=3/2$) centers only. The spin state of central Ru_2^{6+} moiety changes from $S=1$ to $S=0$ with decreasing temperature (spin transition). The temperature dependence of the $\chi_m T$ values of **1a** is a combined effect of the zero-field splitting, antiferromagnetic interaction between the Ru_2^{5+} and Ru_2^{6+} centers, and the spin transition at the Ru_2^{6+} center, which is too complicated to be modeled.

To rationalize the unusual magnetism of **1a**, DFT/B3LYP calculations were performed.[20] The computed ground state of **1a** is a singlet state that results from weak antiferromagnetic interaction between two $S=3/2$ Ru_2^{5+} termini (Figure 5). The computed coupling constant (J) between the two Ru_2^{5+} moieties (-0.18 cm^{-1}) is so small that the ferromagnetic (3/2)-(3/2) and antiferromagnetic (3/2)-($-$3/2) states are nearly degenerate. The two Ru_2^{5+} termini are thus independent, which is consistent with the observed $\chi_m T$ at 1.8 K. Two excited states, (3/2)-(1)-(3/2) and (3/2)-($-$1)-(3/2) derived from the spin flip at the Ru_2^{6+} center, lie at approximately 0.50 and 0.44 eV above the ground state. The computed coupling constant between the Ru_2^{5+} and Ru_2^{6+} centers is -72.26 cm^{-1}, implying moderate antiferromagnetic interaction.

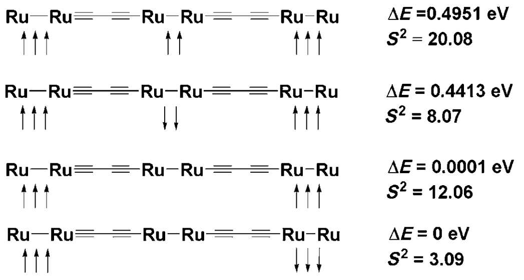

Figure 5. Relative energies of four energy states with possible spin alignment of **1a**. S denotes the calculated spin angular momentum.

To further understand the spin flip in **1a**, a companion calculation was performed for the model compound **4**, [{$Ru_2(DMBA)_4$}$(C_4H)_2$], which retains the central Ru_2 unit of **1a** with two Ru_2^{5+} termini being replaced by hydrogen atoms.[20] The two unpaired electrons in **4** ($S=1$) occupy the π* and δ* orbitals with a 1.01 eV energy difference. Correspondingly, the SOMO and SOMO-3 in **1a** exhibit the π* and δ* characters of the central Ru_2^{6+} moiety, respectively. Comparing the π* orbital of **4** with that of **1a**, shows the latter exhibits a pronounced contribution from two Ru_2^{5+}–butadiynyl fragments (Figure 6). Clearly, the presence of Ru_2^{5+} termini results in an enhanced π–π antibonding interaction between the butadiynyl ligand and the Ru_2^{6+} core, which destabilizes the π*(Ru_2^{6+}) in **1a** and reduces the π*(SOMO-3)–δ*(SOMO) gap from 1.01 (in **4**) to 0.72 eV. The actual π*–δ* gap could be much smaller than the computed one, which would facilitate the spin transition at elevated temperature. Moreover, the spin population of the central Ru atoms in **1a** is 0.77, which is slightly higher than that in **4** (0.72). The increase in the spin population of the central Ru atoms may qualitatively indicate that the unpaired electrons in **1a** delocalize from the terminal Ru_2^{5+} moieties to the central Ru_2^{6+} unit.[21]

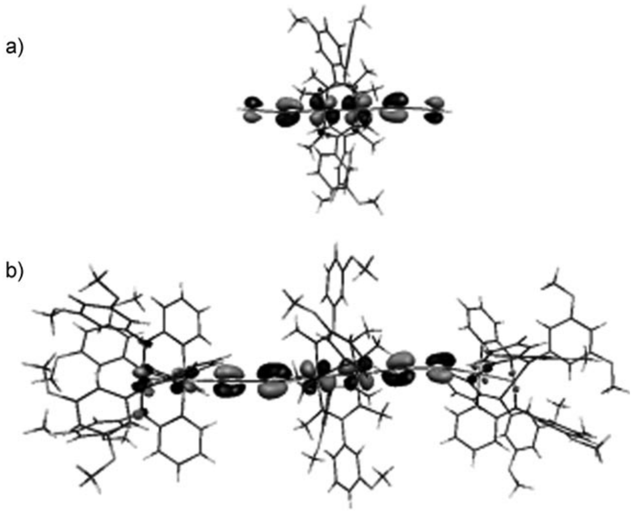

Figure 6. π* orbitals of a) **4** (SOMO) and b) **1a** (SOMO-3).

In summary, we report very unusual trimeric compounds, **1**, based on Ru_2 species linked by the butadiyn-diyl bridges, for which both the voltammetric and spectroscopic data are consistent with an extensive delocalization over a span of 20 Å. A spin transition was also observed for **1a** and rationalized on the basis of DFT calculations by the existence of low-lying triplet states that are very close in energy to the singlet ground state.

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[12] Compound **1a** was prepared from the reaction between [Ru_2(*m*-MeO-DMBA)$_4$(NO_3)$_2$] (0.84 g, 0.080 mmol) and **2** (0.188 g, 0.16 mmol) in THF/Et_2NH (3:1, v:v) at room temperature for 1 h. The blue solid obtained upon solvent removal was recrystallized from THF/hexanes to afford 0.200 g (77 %) **1a** as a brown powder. Data: MS-MALDI (m/z, based on ^{101}Ru): 3259 [M^+]; elemental analysis (%) calcd for $C_{152}H_{156}N_{24}O_{20}Ru_6$: C 56.25, H 4.84, N 10.36; Found C 56.01, H 4.88, N 9.85. Electrochemistry, $E_{1/2}$/V, ΔE_p/V, $i_{\text{backward}}/i_{\text{forward}}$: $\pm 3/\pm 2$, 0.686, 0.063, 1.029; $\pm 2/\pm 1$, 0.328, 0.057, 0.696; $\pm 1/0$, 0.237, 0.062, 1.167; $0/-1$, −0.881, 0.095, 0.939; $-1/-2$, −0.976, 0.117, 0.703; $-2/-3$, −1.292, 0.074, 0.137. Preparation of **1b** is similar to that of **1a**.

[13] Crystallographic data for **1a**: space group $C2/c$, $a = 56.642(3)$ Å, $b = 16.6840(8)$, $c = 16.0750(8)$ Å, $\beta = 95.001(3)°$ $V = 15\,133(1)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.438$ Mg m^{-3}, $\mu = 5.329$ mm^{-1}. X-ray intensity data of **1a** were measured at 100 K on a Bruker AXS SMART APEX II CCD-based diffractometer using $Cu_{K\alpha}$ ($\lambda = 1.54178$ Å), and the structure was solved using direct method; 34 497 reflections collected, 12 505 unique reflections ($R_{\text{int}} = 0.0936$), data/restraints/parameters 12505/0/933, final R indices ($I > 2\sigma$(I)) $R1 = 0.0977$ and $wR2 = 0.248$. CCDC 745048 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[15] Magnetic susceptibility measurements for both compounds **1a** and **2′** were obtained with the use of a Quantum Design MPMS-XL7 SQUID magnetometer at temperature range of 1.8–300 K.

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[20] Single point calculations on compounds **1a** and **4** were carried out using the DFT formalism with the spin unrestricted option as implemented in the Gaussian 03 program with the B3LYP functional. 6-31G basis sets were used to describe the H atoms. 6-31G* basis sets were used to describe the C, N, and O atoms. For more details, see the Supporting Information.

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