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Effect of Metals on the Electronic Communication through a Molecular Wire Model

Richard D. Adams* and Bo Qu

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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*Summary: Two triosmium complexes of 1,4-bis(ferrocenyl)-1,3-butadiyne, $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$ (**2**) and $Os_3(CO)_{11}(\mu_3\text{-}FcC_4Fc)$ (**3**) ($Fc = (C_5H_5)Fe(C_5H_4)$), have been prepared and structurally characterized. In **2** one of the triple bonds of the butadiyne grouping is coordinated as a triple bridge to a triangle of three osmium atoms. In **3** the triosmium cluster is opened and is coordinated as a linear chain to both triple bonds. The electronic communication measured via redox potentials of the ferrocenyl groups indicates that the metal atoms increase the electronic communication in **3** and decrease it in **2**.*

There is great interest in developing molecular components for use in the construction of nanoscale electronic devices.[1] Recent efforts to prepare and evaluate the properties of "molecular wires" have provided some very promising results.[2] Conjugated polyynes have attracted attention as a potentially important class of molecular wire materials.[3] One of the most popular methods for testing electronic communication through a potential molecular wire is to examine the interaction between redox active groups located at its termini.[3] We have now obtained some important new results on the effects that metal groupings placed along the "wire" exert on the electronic communication between the two ends of the model molecular wire 1,4-bis(ferrocenyl)-1,3-butadiyne (**1**).

A solution of **1** and $Os_3(CO)_{11}(NCMe)$ in hexane solvent heated to reflux for 20 min yielded two products: orange $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$ (**2**; 18% yield) and red $Os_3(CO)_{11}(\mu_3\text{-}FcC_4Fc)$ (**3**; 31% yield) ($Fc = (C_5H_5)Fe(C_5H_4)$).[4] Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.[5,6]

An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. The molecule contains an $Os_3(CO)_{10}$ cluster attached to one of the two C−C triple bonds of **1**. This alkyne grouping is coordinated by using both of its π-bonds to donate four electrons to the three metal atoms. This triple-bridging di-$(\sigma + \pi)$ coordination mode is similar to that found in other trimetallic alkyne complexes.[7] As expected, the coordinated triple bond C(1)−C(2) is significantly longer than the uncoordinated triple bond C(3)−C(4): C(1)−C(2) = 1.40(2) Å and C(3)−C(4) = 1.19(2) Å. The C(2)−C(3) bond is long (1.47(2) Å) and single. The C−C triple-bond and single-bond distances in the free molecule of **1** are 1.203(3) and 1.373(4) Å, respectively.[8]

An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. This molecule contains an open linear $Os_3(CO)_{11}$ cluster attached both of the C−C triple

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[4] A 20.0 mg amount of $Os_3(CO)_{11}(NCMe)$ (0.0217 mmol) and 9.5 mg of **1** (0.0227 mmol) dissolved in 30 mL of hexane were heated to reflux for 20 min. The products were separated by TLC on silica gel using a hexane/CH_2Cl_2 (3/1) solvent mixture to yield in order of elution: orange $Os_3(CO)_{10}$(Fc-C_4-Fc) (**2**; 5.1 mg, 18%) and red $Os_3(CO)_{11}$(Fc-C_4-Fc) (**3**; 8.8 mg, 31%).

[5] Data for **2** are as follows. IR ν_{CO} (cm^{-1}, in hexane): 2097 (s), 2065 (vs), 2055 (vs), 2026 (s), 2014 (sh), 2007 (s), 1982 (w) 1840 (w). ^1H NMR (δ in $CDCl_3$): 4.42, m, 2H, C_5H_4; 4.30, m, 2H, C_5H_4; 4.23−4.27, m, 4H, C_5H_4; 4.28, s, 5H, Cp; 4.24, s, 5H, Cp. Anal. Calcd (found): C, 32.19 (31.88); H, 1.42 (1.04). Data for **3** are as follows. IR ν_{CO} (cm^{-1}, in hexane): 2123 (m), 2095 (s), 2044 (vs), 2040 (sh), 2000 (s), 1969 (w), 1957 (m). ^1H NMR (δ in $CDCl_3$): 4.61, m, 2H, C_5H_4; 4.44, m, 2H, C_5H_4; 4.17, s, 5H, Cp. Anal. Calcd (found): C, 32.42 (32.01); H, 1.39 (1.15).

[6] Crystal data for **2**: $Os_3Fe_2O_{10}C_{34}H_{18}$, $M_r = 1268.80$, space group $P2_1/a$, $a = 15.074(3)$ Å, $b = 10.254(3)$ Å, $c = 23.055(5)$ Å, $\beta = 103.75(4)°$, $V = 3461.7(7)$ Å^3, $Z = 4$, $\mu = 118.4$ cm^{-1}, λ(Mo Kα) = 0.710 73 Å, T = 20 °C, 3233 reflections ($I > 3.00\sigma(I)$), Lorentz/polarization and absorption corrections (DIFABS) applied, solved by direct methods (SIR92), refined 438 variables, full matrix on F, R1 = 0.041, wR2 = 0.052, GOF = 1.11. Crystal data for **3**: $Os_3Fe_2O_{11}C_{35}H_{18}$, $M_r = 1296.77$, space group $C2/c$, $a = 22.529(2)$ Å, $b = 7.369(2)$ Å, $c = 43.609(4)$ Å, $\beta = 95.806(8)°$, $V = 7203(2)$ Å^3, Z = 8, $\mu = 114.6$ cm^{-1}, Mo Kα = 0.71073 Å, T = 20 °C, 2984 reflections ($I > 3.00\sigma(I)$), Lorentz/polarization and absorption corrections (DIFABS) applied, solved by direct methods (SIR92), refined 438 variables, full matrix on F, R1 = 0.037, wR2 = 0.058, GOF = 1.25.

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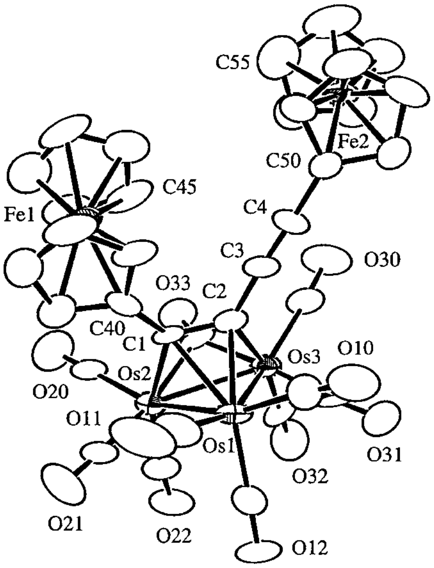

Figure 1. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$ (**2**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)–Os(2) = 2.7465(9), Os(1)–Os(3) = 2.7965(8), Os(2)–Os(3) = 2.8328(8), Os(1)–C(1) = 2.33(1), Os(1)–C(2) = 2.21(1), Os(2)–C(1) = 2.13(1), Os(3)–C(2) = 2.12(2), C(1)–C(2) = 1.40(2), C(3)–C(4) = 1.19(2).

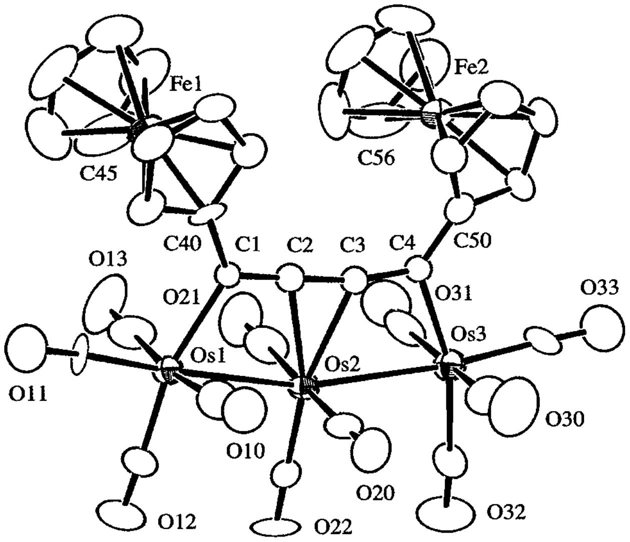

Figure 2. ORTEP diagram of the molecular structure of $Os_3(CO)_{11}(\mu_3\text{-}FcC_4Fc)$ (**3**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Os(1)–Os(2) = 2.909(1), Os(2)–Os(3) = 2.909(1), Os(1)–C(1) = 2.15(1), Os(2)–C(2) = 2.38(2), Os(2)–C(3) = 2.31(2), Os(3)–C(4) = 2.17(1), C(1)–C(2) = 1.29(2), C(2)–C(3) = 1.33(2), C(3)–C(4) = 1.33(2); Os(1)–Os(2)–Os(3) = 162.65(4), C(1)–C(2)–C(3) = 178(2), C(2)–C(3)–C(4) = 168(2).

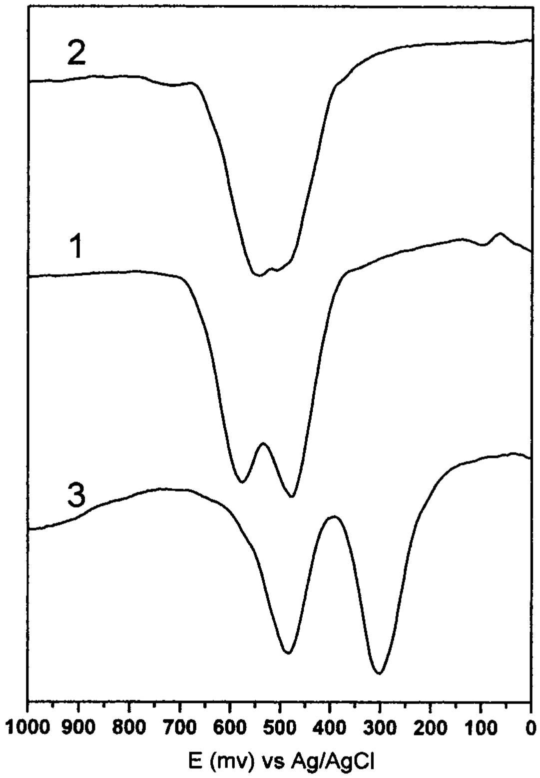

Figure 3. Differential pulse voltammograms of compounds **1**–**3** at 1.0 mM concentration recorded in a 1:1 CH_2Cl_2/NCMe solvent mixture containing 0.1 M $[NBu_4][PF_6]$ using a Ag/AgCl reference electrode.

bonds of the ligand **1** in a novel di-μ-|| coordination mode. The μ-|| coordination mode has been observed previously for alkynes bridging *two* metal atoms.[9] An alkyne group in the μ-|| coordination mode donates only two electrons to the metal atoms by using only one of its two π-bonds. With two such ligand groupings in **3**, the cluster thus receives four electrons from the ligand **1**. Both C–C triple bonds are lengthened in the diyne unit in **3** (C(1)–C(2) = 1.29(2) Å and C(3)–C(4) = 1.33(2) Å), but most interestingly the C(2)–C(3) single bond is significantly shortened to 1.33(2) Å.

Electrochemical measurements show that the metal atoms have a profound effect on the electronic communication between the two redox active ferrocenyl groups. The redox potentials for **1**–**3** were measured by differential pulse voltammetry (DPV).[10] The DPV voltammograms of all three compounds are shown in Figure 3. Each compound shows two peaks corresponding to two reversible one-electron oxidations: for **1**, $E_1 = +476$ mV and $E_2 = +576$ mV, for **2**, $E_1 = +483$ mV and $E_2 = +540$ mV, and for **3**, $E_1 = +300$ mV and $E_2 = +484$ mV vs the Ag/AgCl electrode, although the peaks for **2** are just barely resolved. The difference in the two potentials ΔE ($E_2 - E_1$) is of special interest and is clearly the greatest for **3** (184 mV) and the smallest for **2** (57 mV). ΔE for **1** is approximately midway between that of the two complexes (100 mV).[11,12] Because the ferrocenyl groups are equivalent in **1** and **3**, the difference in the two potentials is a direct measure of the

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[10] Electrochemical analyses were performed on a CV-50W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN) with 1.0 mM sample in a 1:1 CH_2Cl_2/NCMe solution containing 0.1 M tetrabutylammonium hexafluorophosphate. A three-electrode system was employed, consisting of a glassy-carbon working electrode, a platinum counter, and a Ag/AgCl reference electrode.

[11] This value for **1** is essentially identical with the value measured by Levanda et al. by cyclic voltammetry.[12]

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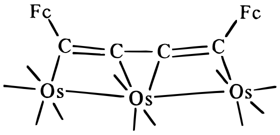
communication between the two redox centers. For **2** the difference in the two potentials is a combination of their communication and their intrinsic inequivalence, so the measure of electronic communication between the two redox centers in **2** must be less than that measured by the potential difference.[13] On the basis of the differences in redox potentials, it can be concluded that the metal grouping in **3** significantly enhances the communication between the two redox centers, while the arrangement of metal atoms in **2** significantly decreases the communication.

This can be explained by the effect of the coordination of the metal atoms on the π orbitals of the diyne connecter. In **2** both π orbitals of one C−C triple bond grouping are engaged in bonding to the metal atoms. This causes a decrease in the interaction of these orbitals with those of the second triple bond and results in an increase in length of the C(2)−C(3) single bond that connects them. On the other hand, in **3** the metal atoms are simultaneously bonded to both triple bonds by using only one π bond in each triple bond grouping. There is still one free π bond in each triple bond for use in electron exchange interactions. In addition, one of the metal atoms Os(2) actually bridges the C(2)−C(3) single bond and this results in a shortening of that distance. This leads to an increase in the π-orbital interactions between the two triple bonds, and in turn an increase in the electronic communication between the two ferrocenyl redox centers. The structure **A** shows one representation of the bonding in Os_3C_4 grouping in **3**. On the other hand, in **2** the C−C π-interactions between the triple bonds are decreased by the coordination of both π bonds of the one C−C triple bond to the triangle of metal atoms, **B**.



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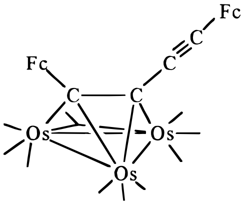

B

Our results show clearly that metal atoms can have a significant effect on the communication between redox centers linked by a model molecular wire. This suggests that if one could selectively add and properly arrange metal atoms along a molecular wire, it might be possible to modify and control the electronic communication through the wire in a systematic way.

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Supporting Information Available: Text giving experimental details of the syntheses and tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The contribution to Δ*E* due to the intrinsic inequivalence of the two ferrocenyl groups in **2** cannot be measured independently.