New Triosmium Complexes Containing a Partially Hydrogenated Bis(ferrocenyl)butadiyne Ligand. Their Structures and Electrochemical Responses

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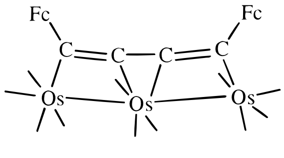
The reaction of $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$ (**3**) ($Fc = C_5H_5FeC_5H_4$) with water in thf solvent at reflux yielded three new cluster complexes: $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}H)$ (**4**) (54%), $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Z\text{-}FcC_3CHFc)(\mu\text{-}OH)$ (**5**) (11%), and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}OH)$ (**6**) (16% yield) in 40 h. The same products were obtained from the reaction of **3** with $Me_3NO{\cdot}2H_2O$ in 35 min at 25 °C, but the yield of **4** was lower (13%), the yield of **5** was higher (34%), and the yield of **6** was about the same (12%). Compounds **4**−**6** were characterized by single-crystal X-ray diffraction analyses. All three compounds contain a triply bridging η^3-bis(ferrocenyl)ynenyl, $FcCCC{=}C(H)Fc$, ligand formed by the addition of one hydrogen atom to the FcC_4Fc ligand in **3**. Compound **4** contains a closed triangular triosmium cluster with one bridging hydride ligand. Compounds **5** and **6** are isomers. Both contain an open triosmium cluster with a bridging hydroxo ligand. The isomers differ by *E*- and *Z*-configurations of the enyl group of the $FcCCC{=}C(H)Fc$ ligand. All three compounds show two resolved one-electron oxidations for the ferrocenyl groups: for **4** at $E° = +0.43$ and $+0.56$ V vs Ag/AgCl, $\Delta E° = 0.13$ V; for **5** at $E° = +0.38$ and $+0.46$ V, $\Delta E° = 0.08$ V; for **6** at $E° = +0.39$ and $+0.49$ V, $\Delta E° = 0.10$ V. The potential differences ΔE are all larger than that in **3**. This may be due in part to increased bonding between the carbon atoms in the C−C triple bond and C−C double bond in the bis(ferrocenyl)ynenyl ligand caused by the coordination to the metal atoms.

Introduction

Bis(ferrocenyl)butadiyne **1** contains two electroactive ferrocenyl groups that can be used to evaluate the electronic communication between the two ends of the molecule.[1,2] In recent studies we have shown that bis(ferrocenyl)butadiyne can coordinate to osmium cluster complexes in significantly different ways, as shown in the triosmium cluster complexes **2** and **3**. We have observed that this coordination can significantly effect the electronic communication between the two ferrocenyl groups.[3] In compound **2** the communication is increased relative to that in **1**, while in compound **3** it is decreased. This has been attributed to the influence of the metal atoms on the π-orbital network of the butadiyne grouping.

$Fc{-}C{\equiv}C{-}C{\equiv}C{-}Fc$

1



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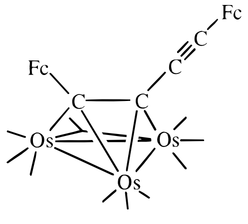

3

To try to learn more about the effects of metal atoms on the electronic communication between the ferrocenyl groups in bis(ferrocenyl)butadiyne metal complexes, we have investigated the reaction of **3** with water and trimethylamine-*N*-oxide dihydrate, $Me_3NO{\cdot}2H_2O$. These reactions yielded three new products: $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}H)$, **4**, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Z\text{-}FcC_3CHFc)(\mu\text{-}OH)$, **5**, and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}OH)$, **6**, $Fc = C_5H_5FeC_5H_4$. Compounds **5** and **6** are isomers formed by the loss of CO and the addition of 1 equiv of water to the cluster. Compound **4** can be viewed as the loss of CO and the addition of 1 equiv of H_2. The syntheses, characterization of these compounds, and results of their electrochemical measurements are reported here.

Experimental Section

General Data. Although the reagents and products are air-stable, the reactions were performed under an atmosphere of nitrogen. Reagent grade solvents were freshly distilled prior to use. Trimethylamine *N*-oxide dihydrate was purchased from Aldrich Chemical Co. and was used without further purifica-

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[1] Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.

[2] Levanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

[3] Adams, R. D.; Qu, B. *Organometallics* **2000**, *19*, 2411.

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Table 1. Crystallographic Data for Compounds 4−6

	4	5	6
empirical formula	$Os_3Fe_2O_9C_{33}H_{20}$	$Os_3Fe_2O_{10}C_{33}H_{20}$	$Os_3Fe_2O_{10}C_{33}H_{20}$
fw	1242.81	1258.81	1258.81
cryst syst	monoclinic	orthorhombic	monoclinic
lattice params			
a, Å	12.889(2)	17.183(3)	16.60(2)
b, Å	23.916(7)	24.531(4)	11.35(2)
c, Å	12.743(2)	7.832(2)	19.42(2)
β, deg	101.44(1)	90.00	112.31(2)
V, Å^3	3850(1)	3301.4(9)	3382(9)
space group	$P2_1/n$ (14)	$P2_12_12_1$ (19)	$P2_1/c$ (14)
Z value	4	4	4
D_{calc}, g/cm^3	2.14	2.53	2.47
μ(Mo, Kα), cm^{-1}	106.4	124.1	121.1
no. obs., total; $I > 3\sigma(I)$	3485	2384	2395
no. variables	428	434	434
residuals:[a] R; R_w	0.035; 0.052	0.038; 0.045	0.026; 0.030
goodness of fit (GOF)	1.10	1.09	1.04
max shift/final cycle	0.01	0.01	0.01
abs corr, max/min	DIFABS, 0.63−1.00	DIFABS, 0.46−1.00	DIFABS 0.71−1.00
largest resid pk, e$^-$/Å^3	1.29	0.87	0.71

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}(w(|F_{obs}| - |F_{calc}|))^2/(n_{data} - n_{vari})]^{1/2}$.

tion. $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$, **3**, was prepared according to our recently reported procedure.[3] Product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F_{254} glass plates. Infrared spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Differential pulse voltammetric measurements (DPV) were performed by using a three-electrode system consisting of a glassy carbon working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode on a CV-50W voltammetric analyzer purchased from Bioanalytical Systems, West Lafayette, IN. Samples were prepared in 1.0 mM solutions by using a CH_3CN/CH_2Cl_2 (1:1) solvent mixture containing 0.1 M tetrabutylammonium hexafluorophosphate.

Reaction of 3 with H_2O. A 20.0 mg sample of $Os_3(CO)_{10}(FcC_4Fc)$ (0.0158 mmol) and 5.67 mL of distilled H_2O (0.315 mol) were put in a 50 mL three-neck flask and stirred, and then 20 mL of THF was added to the flask. The solution was heated to reflux for 40 h. The solvent and excess H_2O were then removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and separated by TLC using a hexanes/CH_2Cl_2 (2:1) solvent mixture to yield in order of elution 10.5 mg of yellow orange $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-H})$, **4**, 54%; 2.2 mg of red $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Z\text{-}FcC_3CHFc)(\mu\text{-OH})$, **5**, 11%; and 3.2 mg of orange $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-OH})$, **6**, 16%. Longer elution times were needed to separate the isomers **5** and **6**. For **4**: IR ν_{CO} (cm^{-1} in hexane): 2094 (s), 2068 (vs), 2044 (vs), 2024 (s), 2014 (m), 1999 (s), 1989 (m), 1983 (w), 1976 (m). ^{1}H NMR (δ in $CDCl_3$): 6.75, s, 1H, CH; 4.57, m, 1H, C_5H_4; 4.47, m, 1H, C_5H_4; 4.41, m, 2H, C_5H_4; 4.35, m, 2H, C_5H_4, 4.27, m, 1H, C_5H_4; 4.21, s, 5H, Cp; 4.18, m, 1H, C_5H_4; 3.90, s, 5H, Cp; −21.06, s, 1H, μ-H. Anal. Calcd (found): C, 31.89 (32.05); H, 1.62 (1.56). For **5**: IR ν_{CO} (cm^{-1} in hexane): 2093 (s), 2067 (vs), 2043 (vs), 2023 (s), 2009 (m), 1996 (s), 1984 (w), 1968 (m). ^{1}H NMR (δ in $CDCl_3$): 8.02, s, 1H, CH; 4.74, m, 1H, C_5H_4; 4.60, m, 1H, C_5H_4; 4.57, m, 2H, C_5H_4, 4.50, m, 1H, C_5H_4, 4.46, m, 1H, C_5H_4, 4.45, m, 1H, C_5H_4, 4.37−4.42, m, 1H, C_5H_4, 4.36, s, 5H, Cp, 4.22, s, 5H, Cp, −4.21, s, 1H, OH. Anal. Calcd (found): C, 31.49 (31.72); H, 1.60 (1.45). For **6**: IR ν_{CO} (cm^{-1} in hexane): 2091 (s), 2066 (vs), 2041 (vs), 2019 (s), 2004 (m), 1995 (s), 1980 (w), 1968 (m). ^{1}H NMR (δ in $CDCl_3$): 7.15, s, 1H, CH; 4.90, m, 1H, C_5H_4; 4.80, m, 1H, C_5H_4; 4.60, m, 1H, C_5H_4, 4.57, m, 1H, C_5H_4, 4.50, m, 1H, C_5H_4, 4.42−4.44, m, 1H, C_5H_4, 4.27−4.28, m, 2H, C_5H_4, 4.19, s, 5H, Cp, 4.10, s, 5H, Cp, −4.05, s, 1H, OH. Anal. Calcd (found): C, 31.49 (30.98); H, 1.60 (1.48).

Reaction of 3 with $Me_3NO{\cdot}2H_2O$. A 44.0 mg amount of $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$ (0.0347 mmol) and 5.8 mg amount of $Me_3NO{\cdot}2H_2O$ (0.0522 mmol) were dissolved in 50 mL of CH_2Cl_2 in a 100 mL three-necked flask. The solution was stirred at 25 °C for 35 min. The solvent was then removed, and the residue was dissolved in a minimal amount of CH_2Cl_2 and was separated by TLC on silica gel with a hexane/CH_2Cl_2 (2:1) solvent mixture. The principal products (in order of elution) are yellow-orange **4**, 5.6 mg (13%); red **5**, 15.0 mg (34%); and orange **6**, 5.2 mg (12%).

Isomerization of Compound 5 to 6. A 7.7 mg amount of **5** (0.0061 mmol) was dissolved in benzene-d_6 in a NMR tube. The NMR tube was then placed in an oil bath and heated to 60 °C. NMR spectra of this solution were recorded daily until the ratio of **5** to **6** no longer changed. This required a total of 4 days. The ratio of **5**/**6** at equilibrium as determined by NMR peak integration was 2.22.

Crystallographic Analyses. Orange crystals of **4**, dark red crystals of **5**, and red crystals of **6** were grown by slow evaporation of the solvent from solutions in hexane/CH_2Cl_2 (5:1) mixtures at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Ka radiation at 20 °C. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. The data were processed on a Silicon-Graphics INDIGO^2 Workstation by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[4a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[4b] Lorentz/polarization (*Lp*) corrections were applied to the data. Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.06\ I_{net})^2]^{1/2}/Lp$.

Compounds **4** and **6** crystallized in the monoclinic crystal system. Compound **5** crystallized in the orthorhombic crystal system. The space groups $P2_1/n$, $P2_12_12_1$, and $P2_1/c$ were established for **4**, **5**, and **6**, respectively, on the basis of the systematic absences observed during the collection of the data. All the structures were solved by a combination of direct methods (SIR92) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal pa-

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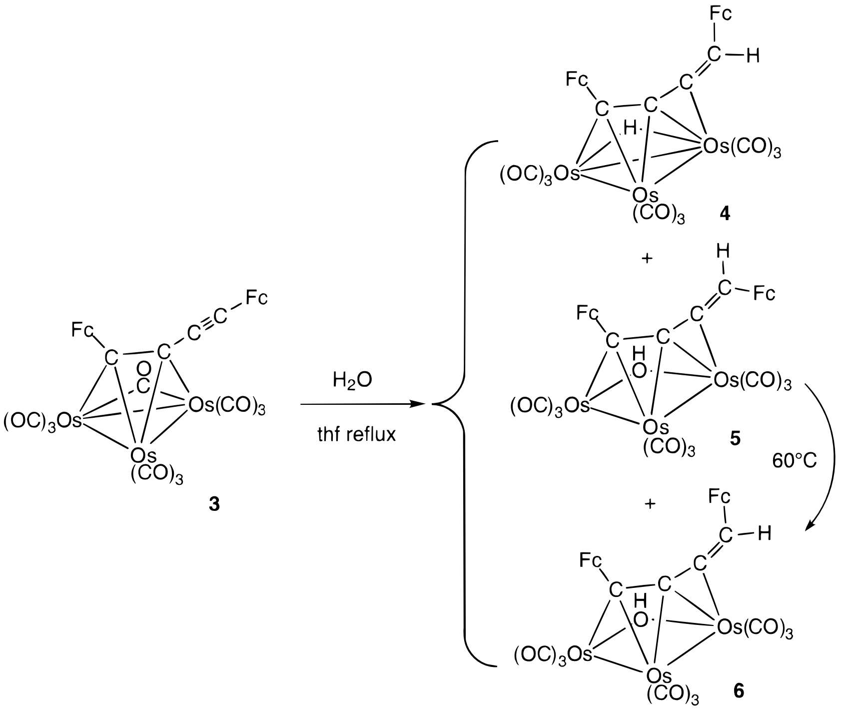
(4) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99−101. (b) *Ibid*., Table 2.3.1, pp 149−150.

Scheme 1



rameters. The positions of the hydrogen atoms on the ferrocenyl groups were calculated by assuming idealized tetrahedral geometries at the carbon atoms with C−H distances of 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined. A test for the correctness of the enantiomorph of compound **5** was made by inverting the coordinates of all atoms and refining again, but this did not produce an improvement in the *R*-factors, and the original set of positional parameters was thus retained.

Results

Three new triosmium cluster complexes, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}H)$ (**4**) (54%), $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Z\text{-}FcC_3CHFc)(\mu\text{-}OH)$ (**5**) (11%), and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}OH)$ (**6**) (16%), were obtained from the reaction of $Os_3(CO)_{10}(\mu_3\text{-}FcC_4Fc)$ (**3**) ($Fc = C_5H_5FeC_5H_4$) with H_2O in refluxing THF solvent for 40 h; see Scheme 1. The same products were also obtained from the reaction of **3** with $Me_3NO{\cdot}2H_2O$ in CH_2Cl_2 in 35 min at 25 °C, but the yield of **4** was decreased to 13%; the yield of **5** was increased to 34%, and the yield of **6** was not significantly different at 12%. Compounds **4**−**6** were characterized by IR and ^1H NMR spectroscopy, single-crystal X-ray diffraction analyses, and differential pulse voltammetry (DPV). ORTEP diagrams of the molecular structures of **4**−**6** are shown in Figures 1−3, respectively. All three compounds contain a triply bridging η^3-bis(ferrocenyl)ynenyl (FcCCC=C(H)Fc) ligand and nine linear terminal carbonyl ligands coordinated to a triosmium cluster. In each compound the FcCCC=C(H)Fc ligand exhibits one strongly deshielded singlet due to the single proton on the C_4 chain. For **4** this resonance lies at 6.75 ppm; for **5**, 8.02 ppm; and for **6**, 7.15 ppm. Compounds **5** and **6** are isomers. These isomers differ only by the configuration of the enyl grouping, *E* vs *Z*, of the bridging bis(ferrocenyl)ynenyl ligand.

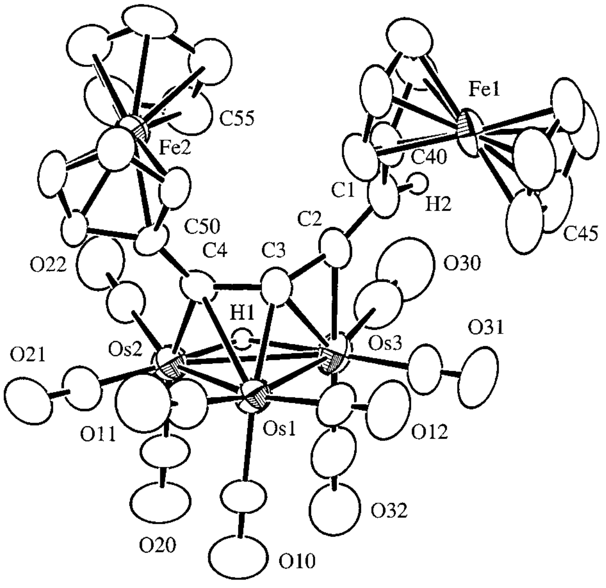


Figure 1. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3CHFc)(\mu\text{-}H)$, **4**, showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Os(1)−Os(2) = 2.8128(8), Os(1)−Os(3) = 2.824(1), Os(1)−C(3) = 2.12(1), Os(1)−C(4) = 2.37(1), Os(2)−Os(3) = 3.0144(9), Os(2)−C(4) = 2.08(1), Os(3)−C(2) = 2.24(1), Os(3)−C(3) = 2.29(1), C(1)−C(2) = 1.31(2), C(2)−C(3) = 1.35(2), C(3)−C(4) = 1.43(2); C(1)−C(2)−C(3) = 152(1), C(2)−C(3)−C(4) = 139(1).

The three metal atoms in **4** form a closed cluster that contains one bridging hydride ligand, located crystallographically, ^1H NMR −21.06 ppm. The clusters of compounds **5** and **6** are both open and contain a bridging hydroxo ligand across the open osmium−osmium bond. It is notable that the resonance of the hydroxyl proton is strongly shielded, −4.21 ppm for **5** and −4.05 for **6**. The strongly shielded resonances of the protons of bridging hydroxo ligands have been observed previously.[5]

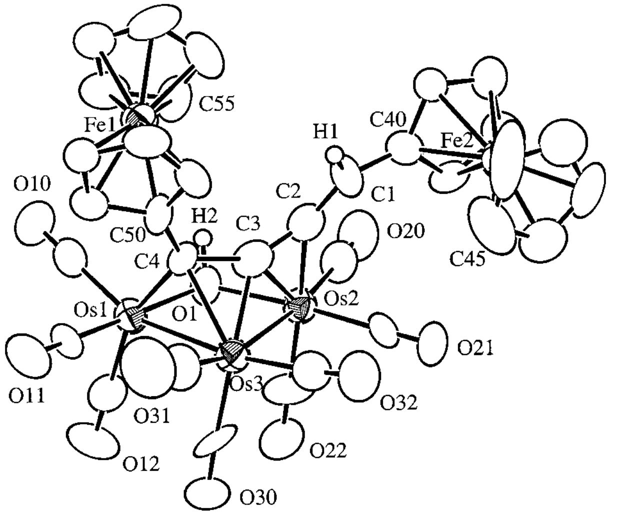


Figure 2. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Z\text{-}FcC_3\text{-}CHFc)(\mu\text{-}OH)$, **5**, showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Os(1)−Os(3) = 2.812(1), Os(1)−O(1) = 2.15(1), Os(1)−C(4) = 2.06(2), Os(2)−Os(3) = 2.876(1), Os(2)−O(1) = 2.12(1), Os(2)−C(2) = 2.25(2), Os(2)−C(3) = 2.24(2), Os(3)−C(3) = 2.09(2), Os(3)−C(4) = 2.28(2), C(1)−C(2) = 1.33(3), C(2)−C(3) = 1.37(3), C(3)−C(4) = 1.45(3); C(1)−C(2)−C(3) = 146(2), C(2)−C(3)−C(4) = 145(2).

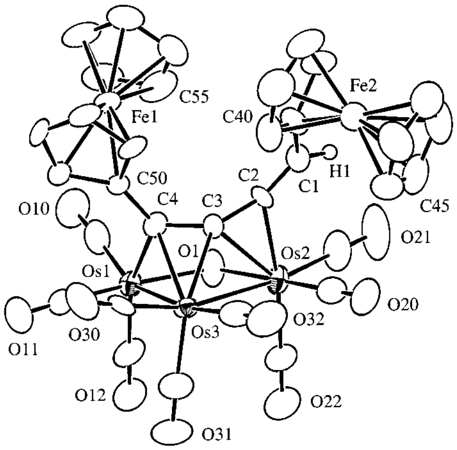


Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}E\text{-}FcC_3\text{-}CHFc)(\mu\text{-}OH)$, **6**, showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Os(1)−Os(3) = 2.816(4), Os(1)−O(1) = 2.105(9), Os(1)−C(4) = 2.10(1), Os(2)−Os(3) = 2.8648(8), Os(2)−O(1) = 2.114(9), Os(2)−C(2) = 2.24(1), Os(2)−C(3) = 2.30(1), Os(3)−C(3) = 2.11(1), Os(3)−C(4) = 2.30(1), C(1)−C(2) = 1.28(2), C(2)−C(3) = 1.34(2), C(3)−C(4) = 1.41(2); C(1)−C(2)−C(3) = 154(1), C(2)−C(3)−C(4) = 142(1).

The $Os_3(\mu\text{-}C_4)$ structural arrangement in three complexes appears to be heretofore unprecedented. In each compound, the C−C triple bond, atoms C(3) and C(4), of the bis(ferrocenyl)ynenyl ligand are coordinated to all three metal atoms of the cluster in the μ-|| arrangement. The three C(3)−C(4) distances are not significantly different, 1.43(2) Å for **4**, 1.45(3) Å for **5**, and 1.41(2) Å for **6**. The C−C distance of the coordinated triple bond in **3** is 1.40(2) Å. The neighboring C−C bond, C(2)−C(3), is formally single, but in each case this C−C distance is unusually short, 1.35(2) Å for **4**, 1.37(3) Å for **5**, and 1.34(3) Å for **6**, and must certainly contain some multiple-bond character. For comparison, the C−C distance of the bond connecting the two triple bonds in **3** is 1.47(2) Å. The shortening of the C(2)−C(3) bond is probably due to coordination of C(2) to the one of the osmium atoms. This atom is not coordinated in **3**. The C(1)−C(2) bond is formally double, and this is strongly supported by the short distances: 1.31(2) Å for **4**, 1.33(3) Å for **5**, and 1.28(2) Å for **6**.

The DPV voltammogram of each product shows two resolved one-electron oxidations for the ferrocenyl groups: for **4** at $E° = +0.43$ and $+0.56$ V vs Ag/AgCl, $\Delta E° = 0.13$ V; for **5** at $E° = +0.38$ and $+0.46$ V, $\Delta E° = 0.08$ V; for **6** at $E° = +0.39$ and $+0.49$ V, $\Delta E° = 0.10$ V. For comparison, compound **3** shows two poorly resolved one-electron oxidations centered at $E = +0.512$ V with the difference between them $\Delta E° \approx 0.06$ V, **2** shows two well-resolved oxidations at $E° = +0.30$ and $+0.48$ V, $\Delta E° = 0.18$ V, and the free molecule 1,4-bis(ferrocenyl)-butadiyne shows two one-electron oxidations for the ferrocenyl groups, $E_1° = +0.48$ V and $E_2° = +0.58$ V with $\Delta E° = 0.10$ V.[2,3]

Discussion

It is known that H_2O will react with $Os_3(CO)_{12}$ to form the hydroxo−hydrido complex $Os_3(CO)_{10}(\mu\text{-}OH)(\mu\text{-}H)$ by loss of two CO ligands and the addition of 1 equiv of H_2O and a cleavage of one of the OH bonds.[6] The loss of a CO ligand and the addition of 1 equiv of H_2O to the cluster must be the first step in the formation of compounds **5** and **6** from **3**. A transient species containing a hydride ligand might be traversed en route to **5** and **6**, but the hydride ligand is ultimately shifted to a carbon atom of the bis(ferrocenyl)butadiyne ligand to form the FcCCC=C(H)Fc ligand to complete the reaction.

The formation of **4** may involve the attack of H_2O at one of the carbonyl ligands. It is known that these reactions lead to the formation of CO_2 and metal hydride ligands by transfer of the hydrogen atoms to the metal atoms.[7] If this were the case here, a transfer of one of the hydride ligands to the carbon atom of the bis(ferrocenyl)butadiyne ligand would then complete the formation of **4**.

It is known that Me_3NO promotes decarbonylation of metal carbonyls by conversion of a CO ligand into CO_2.[8] Thus, treatment of **3** with $Me_3NO{\cdot}2H_2O$ would faciliate the removal of CO and also the addition of H_2O to the metal atoms.[5] Accordingly, it seems reasonable to expect that this reagent would increase the yields of the compounds **5** and **6**. Indeed, the rate of formation of **5** and its yield were increased considerably at the expense of the formation of **4** in this reaction. We have observed in an independent experiment that compound **5** is converted to **6** when heated to 60 °C. The **5**/**6** equilibrium at this temperature is 2.22 and required 4 days to be achieved.

Today, there is considerable interest in unsaturated carbon chains for their potential to serve as molecular

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wires.[9] These materials are frequently evaluated by examining the electrochemical response when electroactive groups are placed at the termini. In compounds **4**−**6** we have found that the difference between the oxidation potentials of the ferrrocenyl groups is larger than it is in compound **3**. We have recently shown that the electronic communication between the ferrocenyl groups in **2** is also increased considerably compared with that of **3**.[3] This was attributed to the unusual coordination of the bis(ferrocenyl)butadiyne ligand in **2**. In compound **2** the coordination of the metal atoms led to a shortening of the C−C single bond between the two C−C triple bonds. It was proposed that this produced an increased electronic interaction between the π-bonds of the two triple bonds and, in turn, a greater transmission of the electronic effects between the two ferrocenyl groups when one of them is oxidized. Interestingly, we have also observed that the C−C single bond between the coordinated triple in the bis(ferrocenyl)ynenyl ligand in each of the compounds **4**−**6** is also shorter than the C−C single bond in the bis(ferrocenyl)butadiyne ligand in **3**. The resultant increased interaction between the yne and enyl groups could be partially responsible for the greater electronic communication between the two ferrocenyl groups in compounds **4**−**6**. One must remember however that the ferrocenyl groups in the compounds **4**−**6** are intrinsically inequivalent, and this also contributes to the difference in the electrode potentials of these two groupings. It is not possible to separate the combined effects of chemical inequivalence and electronic communication through the carbon chain to determine the relative contribution of each factor to the total.

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Supporting Information Available: Tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters are available for the structural analyses of **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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