Reactions of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with 1,8-Bis(ferrocenyl)octatetrayne Yield Products Involving Cyclizations and Trans-Hydrogenation of Alkyne Groups

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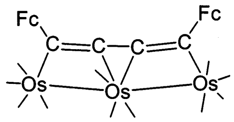
The reaction of 1,8-bis(ferrocenyl)octatetrayne (**1**) with $Os_3(CO)_{10}(\mu\text{-}H)_2$ (**2**) yielded three new osmium cluster complexes containing two electroactive ferrocenyl groups: $Os_3(CO)_9(\mu_3,\eta^3\text{-}FcCCHC_4COC{\equiv}CFc)(\mu\text{-}H)$ (**3**); $Os_3(CO)_{10}(\mu_3,\eta^2\text{-}E\text{-}FcCHCHC_2{-}C{\equiv}C{-}C{\equiv}CFc)$ (**4**); and $Os_6(CO)_{20}(\mu_3,\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}E,E\text{-}FcCHCHC_2{-}C_2CHCHFc)$ (**5**). All three compounds were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. In compound **3**, the tetrayne chain was coupled to a CO ligand and cyclized to form an eight-membered heterobicycle containing two five-membered rings that bridges a closed cluster of three osmium atoms. Compound **4** contains one triangular triosmium cluster. Compound **5** contains two triangular triosmium clusters. In both **4** and **5**, both the hydride ligands were transferred from the cluster to an alkyne group to form an olefinic group with *E*-stereochemistry. A mechanism for trans-hydrogenation at a bimetallic site is proposed. Cyclic and differential pulse voltammetric measurements show two reversible one-electron oxidation peaks for compounds **3** and **4** for their inequivalent ferrocenyl groups. Compound **5** shows only one two-electron oxidation for the two ferrocenyl groups, indicating no significant electrocommunication between them.

Introduction

We have recently shown that the attachment of linear triosmium carbonyl clusters to 1,4-bis(ferrocenyl)butadiyne can lead to enhancement of the electrocommunication through the butadiyne chain as found in the compound $Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-}FcCCCCFc)$ (**A**, Fc = $C_5H_4FeC_5H_5$).[1] This has been explained by the effects of coordination of the metal atoms on the π-bonding of the unsaturated polyyne chain. A structurally similar complex $Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-}Fc\text{-}C_4{-}C{\equiv}C{-}C{\equiv}C{-}Fc)$[2] (**B**), obtained from the reaction of $Os_3(CO)_{11}(NCMe)$ with 1,8-bis(ferrocenyl)octatetrayne (**1**), also contains two alkyne groups of ligand **1** coordinated in a parallel fashion to a linear chain of three osmium atoms. The difference between the redox potentials of the two ferrocenyl groups in this complex is also large, suggesting that there may be electrocommunication between the two ferrocenyl groups in this case too.[2]

In our continuing studies of the coordination chemistry of bis(ferrocenyl)polyynes with osmium complexes, we have now investigated the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ (**2**) with **1**. Three new osmium complexes have been obtained. In one compound, the tetrayne chain was coupled with a CO ligand to form a heterobicycle that bridges all three osmium atoms of the metal cluster. In the other two compounds, the hydride ligands were transferred from the osmium atoms to the carbon atoms of the alkyne groups to form olefinic groups having *E*-stereochemistry. In most cases, the hydrogenation of alkynes by metal hydride complexes proceeds to give olefins with *Z*-stereochemistry by cis-addition of the hydrogen atoms.[3] There have, however, been a few reports showing that trans-hydrogenation can occur when polynuclear metal complexes are involved.[4] This appears to be the case for the complexes that we are describing herein and we have proposed a mechanism to show how this occurs in these complexes. All three new compounds have been characterized by crystallographic and electrochemical methods.



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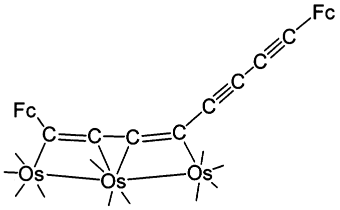

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(1) (a) Adams, R. D.; Qu, B.; Smith, M. D.; Albright, T. A. *Organometallics* **2002**, *21*, 2970. (b) Adams, R. D.; Qu, B. *Organometallics* **2000**, *19*, 2411.

(2) Adams, R. D.; Kwon, O.-S.; Qu, B.; Smith, M. D. *Organometallics* **2001**, *20*, 5225.

(3) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143. (b) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1994**, *116*, 9103. (c) Srebnik, M.; Bhat, N. G.; Brown, H. C. *Tetrahedron Lett.* **1988**, *29*, 2635. (d) Mangaleswaran, S.; Argade, N. P. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1764. (d) Muetteries, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(4) (a) Corrigan, J. F.; Taylor, N. J.; Carty, A. J. *Organometallics* **1994**, *13*, 3779. (b) Burch, R. R.; Shustermann, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546. (c) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090.

10.1021/om020447b CCC: $22.00

Table 1. Crystallographic Data for Compounds 3–5

	3	**4**	**5**
empirical formula	$Os_3Fe_2O_{10}C_{38}H_{20}$	$Os_3Fe_2O_{10}C_{38}H_{20}$	$Os_6Fe_2O_{20}C_{48}H_{22}\cdot{}^1/_2C_6H_{14}$
formula wt	1318.84	1318.84	2214.67
cryst syst	triclinic	orthorhombic	triclinic
lattice parameters			
a (Å)	9.467 (3)	11.1233 (13)	12.182 (2)
b (Å)	13.451 (4)	13.0415 (15)	24.594 (4
c (Å)	14.946 (4)	49.738 (6)	9.616 (2)
α (deg)	68.234 (5)	90	97.06 (2)
β (deg)	87.173 (6)	90	106.82 (1)
γ (deg)	89.462 (6)	90	91.17 (1)
V (Å^3)	1765.3 (9)	7215.3 (14)	2732 (1)
space group	$P\bar{1}$ (no. 2)	$Pbca$ (no. 61)	$P\bar{1}$ (no. 2)
Z value	2	8	2
ρ_{calc} (g/cm^3)	2.481	2.428	2.692
μ(Mo Kα) (mm^{-1})	11.619	11.371	14.473
temp (K)	293	293	293
$2\Theta_{max}$ (deg)	46.6	46.5	44.0
no. of obsd reflns ($I > 2\sigma(I)$)	2960	3749	5066 ($I > 3\sigma(I)$)
no. of variables	482	486	661
goodness of fit (GOF)	1.041	1.051	1.188
max. shift in cycle	0.001	0.001	0.00
residuals: R1; wR2	0.0629; 0.1299	0.0469; 0.0891	R 0.0365; R_w 0.0621
abs corr, max/min	SADABS, 0.801; 0.336	SADABS, 0.458; 0.338	DIFABS 1.000; 0.630
largest peak in the final diff. map (e$^-$/Å^3)	2.312	1.237	2.336

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\sum_{hkl}(w(|F_{obs}| - |F_{calc}|))^2/(n_{data} - n_{vari})]^{1/2}$. $R1 = \sum(||F_{obs}| - |F_{calc}||)/\sum|F_{obs}|$. $wR2 = \{\sum[w(F_{obs}{}^2 - F_{calc}{}^2)^2/\sum[w(F_{obs}{}^2)^2]\}^{1/2}$; $w = 1/\sigma^2(F_{obs}{}^2)$. $GOF = [\sum_{hkl}(w(|F_{obs}{}^2| - |F_{calc2}|))^2/(n_{data} - n_{vari})]^{1/2}$.

Experimental Section

General Data. All the reactions were performed under an atmosphere of nitrogen. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. 1,8-Bisferrocenyloctatetrayne (**1**)[5] and $H_2Os_3(CO)_{10}$ (**2**)[6] were prepared according to literature procedures. Product separation was 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. ^{1}H NMR spectra were run on a Bruker AM-300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of 1 with 2. A 11.0-mg sample of **1** (0.0236 mmol) and 20.0 mg of **2** (0.0235 mmol) were dissolved in 30 mL of CH_2Cl_2 in a 50-mL three-neck round-bottom flask. The reaction mixture was allowed to stir at room temperature for 16 h. The solvent was removed in vacuo. The product mixture was dissolved in a minimum of methylene chloride and separated by TLC with a 4:1 hexane/methylene chloride solvent mixture to yield the following in order of elution: 3.0 mg of unreacted **2**; 1.5 mg of brown $Os_3(H)(CO)_9(\mu_3,\eta^3\text{-FcCCHC}_4\text{COC}{\equiv}\text{CFc})$ (**3**, 5% yield); 6.5 mg of red $Os_3(CO)_{10}(\mu_3,\eta^2\text{-FcCHCHC}_2{-}\text{C}{\equiv}\text{C-C}{\equiv}\text{CFc})$ (**4**, 21% yield). Analytical and spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane) 2097 (s), 2072 (vs), 2046 (s), 2023 (s), 2010 (m), 2003 (s), 1988 (w). ^{1}H NMR (δ in $CDCl_3$) −19.47 (s, 1H, hydride), 4.23 (s, 5H, Cp), 4.29 (s, 5H, Cp), 4.40−4.41 (m, 2H, C_5H_4), 4.48−4.52 (m, 2H, C_5H_4), 4.67 (m, 2H, C_5H_4), 4.82 (m, 1H, C_5H_4), 4.96 (m, 1H, C_5H_4), 6.96 (s, 1H, CH). Anal. Calcd (found): C, 34.61 (34.01); H, 1.51 (1.27). Data for **4**: IR ν_{CO} (cm^{-1} in hexane) 2099 (m), 2067 (vs), 2058 (vs sh), 2029 (s), 2018 (m sh), 2005 (m), 1847 (w). ^{1}H NMR (δ in CD_2Cl_2) 4.08 (s, 5H, Cp), 4.18 (s, 5H, Cp), 4.18 (m, 2H, C_5H_4), 4.27 (m, 2H, C_5H_4), 4.34 (m, 2H, C_5H_4), 4.36 (m, 2H, C_5H_4), 6.40−6.45 (d, 1H, CH), 6.62−6.67 (d, 1H, CH). Anal. Calcd (found): C, 34.61 (34.97); H, 1.52 (1.50).

Reaction of 4 with 2. A 15.0-mg sample of **4** (0.0114 mmol) and a 11.0-mg sample of **2** (0.0129 mmol) were put into 25 mL of hexane in a 50-mL three-necked round-bottom flask. The mixture was heated to reflux for 2 h. The solvent was then removed in vacuo and the residue was dissolved in a minimal amount of CH_2Cl_2 and separated by TLC on silica gel with a hexane/CH_2Cl_2 (3/1) solvent mixture to yield 6.0 mg of violet-red $Os_6(CO)_{20}(\mu_3,\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}E,E\text{-FcCHCHC}_2{-}\text{C}_2\text{CHCHFc})$ (**5**) in 24% yield. Analytical and spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2102 (w), 2091 (s), 2064 (vs), 2046 (w), 2025 (m), 2020 (s), 2010 (m), 2001 (w), 1994 (m), 1984 (w), 1830 (w). ^{1}H NMR (δ in $CDCl_3$) 4.03 (s, 10H, 2Cp), 4.17 (m, 2H, C_5H_4), 4.24 (m, 4H, C_5H_4), 4.36 (m, 2H, C_5H_4), 6.01−6.06 (d, 2H, 2CH), 6.26−6.31 (d, 2H, 2CH). Anal. Calcd (found): C, 26.55 (26.26); H, 1.01 (0.97).

Crystallographic Analyses. Dark-brown crystals of **3** were grown by slow evaporation of the solvent from a benzene/octane (4:1) solution of the complex at room temperature. Red crystals of **4** were grown by slow evaporation of the solvent from a benzene/octane (4:1) solution of the complex at 5 °C. Red crystals of **5** were grown by slow evaporation of the solvent from a hexane/CH_2Cl_2 (5:1) solution of the complex at room temperature.

X-ray intensity data for **3** and **4** were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer, using Mo Kα radiation ($\lambda = 0.71073$ Å). The raw intensity data frames were integrated with SAINT+,[7] which also applied corrections for Lorentz and polarization effects. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with SADABS.[8] Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Diffraction measurements of **5** were made on a Rigaku AFC6S fully automated four-circle diffractometer, using graphite-monochromated Mo Kα radiation at 20 °C. Crystal data, data collection parameters, and results of this analysis are listed in Table 1. Neutral-atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] The

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(5) Yuan, Z.; Stringer, G.; Jobe, I. R.; Kreller, D.; Scott, K.; Koch, L.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1993**, *452*, 115−120.

(6) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

(7) *SAINT+*, Version 6.02a; Bruker Analytical X-ray System, Inc.: Madison, WI, 1998.

(8) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

Scheme 1

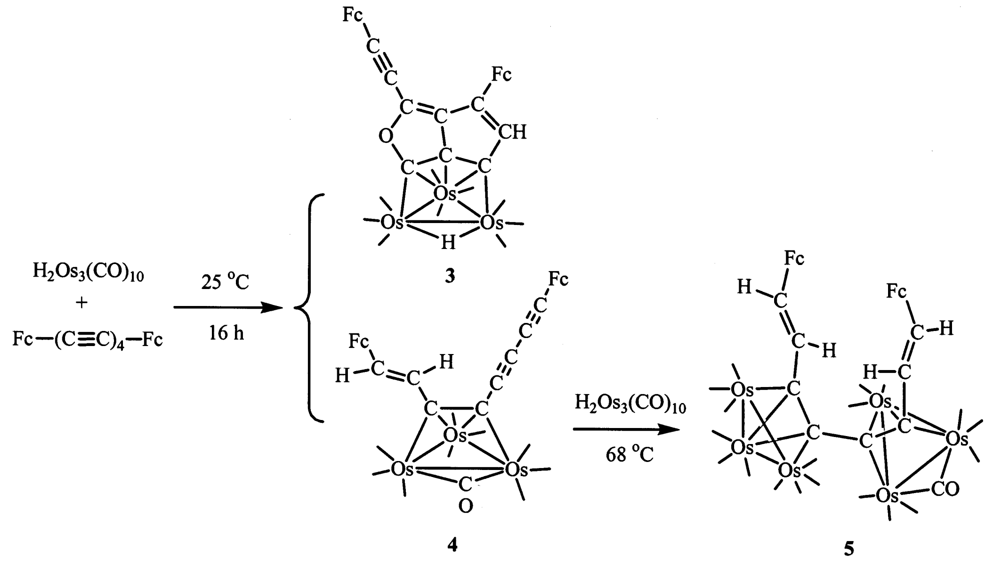

Table 2. Electrochemical Data for Compounds 3−5[a]

	peak positions				
compd	E_p(+/0),[b] V	E_p(2+/+),[b] V	$E_{1/2}$(+/0),[c] V	$E_{1/2}$(2+/+),[c] V	ΔE_p,[d] V
3	0.46	0.56	0.48	0.58	0.10
4	0.38	0.51	0.40	0.53	0.13
5	0.42		0.44		-

[a] The data were recorded on a CV-50W votammetric analyzer with 1.0 mM sample in a 0.1 M $^nBu_4NPF_6$ solution (CH_2Cl_2/NCMe 1:1) with carbon working and Pt counter electrodes and a Ag/AgCl reference electrode. [b] E_p is the peak position in DPV. [c] $E_{1/2} = E_p + E_{pul}/2$,[10] E_{pul} = 50 mV in DPV for **3**−**5**. [d] $\Delta E_p = E_p(2+/+) - E_p(+/0)$.

structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares on F^2, using SHELXTL. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries and were included in the structure factor calculations without refinement.

Electrochemical Measurements. Cyclic and differential pulse voltammetric measurements (DPV) were performed by using a three-electrode system consisting of a glassy carbon working electrode, a platinum counter, 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_2Cl_2:MeCN (1:1) solvent containing 0.1 M tetrabutylammonium hexafluorophosphate. The scan rate was 100 mV/s for CV and 20 mV/s for DPV. The pulse amplitude was 50 mV for all the DPV measurements. The DPV potential values are reported as the peak positions E_p. The relationship between the peak potentials in DPV and $E_{1/2}$ values has been described by Richardson et al.[10] Under these conditions E_p for ferrocene is 0.32 V (using a pulse amplitude of 10 mV). Electrochemical data for compounds **3** and **4** are listed in Table 2. The DPV spectrum of compound **3** shows two one-electron oxidations for the ferrocenyl groups at E_p = +0.46 and +0.56 V vs Ag/AgCl, ΔE_p = 0.10 V. Compound **4** shows two one-electron oxidations for the ferrocenyl groups at E_p = +0.38 and +0.51 V vs Ag/AgCl, ΔE_p = 0.13 V. Compound **5** shows one two-electron oxidation for the ferrocenyl groups at E_p = +0.42 V vs Ag/AgCl. The cyclic voltammograms of **3**, **4**, and **5** show that these redox processes are completely reversible.

Results

The reaction of **1** with **2** at room temperature yielded two products: $Os_3(H)(CO)_9(\mu_3,\eta^3$-FcCCHC$_4$COC≡CFc) (**3**) and $Os_3(CO)_{10}(\mu_3,\eta^2$-*E*-FcCHCHC$_2$−C≡CC≡CFc) (**4**), in 5% and 21% yields, respectively, see Scheme 1. When **4** was treated with an additional quantity of **2** and heated to reflux in hexane solvent, the compound $Os_6(CO)_{20}(\mu_3,\mu_3$-$\eta^2$-$\eta^2$-*E*,*E*-FcCHCHC$_2$−C$_2$CHCHFc) (**5**) was obtained in 24% yield, see Scheme 1. Compounds **3**−**5** were characterized by IR, ^{1}H NMR, and single-crystal diffraction analyses. ORTEP diagrams of the molecular structures of **3**, **4**, and **5** are shown in Figures 1, 2, and 3, respectively. Selected interatomic distances and angles are listed in Table 3.

Compound **3** contains a triangular triosmium cluster and three linear terminal carbonyl ligands on each metal atom. The tetrayne chain was converted into a heterobicycle consisting of two five-membered rings by a cyclization process that includes coupling to one of the CO ligands and the transfer of one of the hydride ligands from the cluster to the carbon atom C(2) shown in Figure 1. The bicycle is coordinated to the three osmium atoms by the carbon atoms C(3), C(4), and C(9). One of the two hydride ligands remains on the cluster as a bridging ligand across the Os(1)−Os(3) bond, and exhibits a highly shielded resonance at δ −19.47 ppm in the ^{1}H NMR spectrum. The hydrogen atom on carbon C(2) exhibits a strongly deshielded resonance at δ 6.96 ppm. This bicycle formally donates five electrons to the cluster, and all the metal atoms achieve 18-electron configurations. There are formal double bonds in the bicycle between atoms C(1) and C(2) (1.37 (3) Å) and C(5) and C(6) (1.38(3) Å).

The cluster in **4** contains ten carbonyl ligands: nine are terminal and one is a bridging ligand (C(23)−O(23)). Both hydride ligands were transferred to one of the alkyne groups to form an olefinic group having *E*-stereochemistry. The C−C distance of the hydrogenated

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

(10) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds 3−5

	3	4	5
	distances[a]		
C1−C2	1.37 (3)	1.311 (18)	1.34 (3)
C2−C3	1.42 (3)	1.470 (18)	1.49 (3)
C3−C4	1.47 (3)	1.428 (18)	1.39 (3)
C4−C5	1.39 (3)	1.432 (18)	1.49 (3)
C4−C9	1.37 (3)		
C5−C6	1.38 (3)	1.190 (18)	1.44 (3)
C6−C7	1.38 (3)	1.39 (2)	1.43 (3)
C7−C8	1.26 (3)	1.197 (18)	1.33 (3)
C9−O9	1.46 (3)		
Os1−C9	2.01 (2)		
Os1−Os2	2.8058 (14)	2.7574 (8)	2.750 (1)
Os1−Os3	3.1002 (16)	2.7659 (8)	2.762 (1)
Os1−H1	1.80 (2)		
Os2−C9	2.35 (2)		
Os2−C4	2.31 (2)		2.25 (2)
Os2−C3	2.42 (2)		
Os2−Os3	2.8060 (15)	2.8472 (8)	
Os3−H1	1.80 (2)		
Os1−C3		2.331 (12)	2.30 (2)
Os1−C4		2.261 (12)	2.37 (2)
Os3−C3		2.114 (13)	2.12 (2)
Os2−C4		2.115 (12)	2.25 (2)
Os4−Os5			2.853 (1)
Os5−Os6			2.847 (1)
Os4−Os6			2.726 (1)
Os4−C5			2.21 (2)
Os4−C6			2.34 (2)
Os5−C5			2.25 (2)
Os6−C6			2.13 (2)
	angles[a]		
C1−C2−C3	114 (2)	127.3 (14)	127 (2)
C2−C3−C4	100.7 (19)	122.4 (12)	120 (2)
C3−C4−C5	111 (2)	123.2 (11)	125 (2)
C4−C5−C6	103 (2)	175.5 (14)	129 (2)
C5−C6−C7	137 (2)	173.7 (15)	123 (2)
C6−C7−C8	173 (3)	176.0 (16)	128 (2)
C7−C8−C50	176 (3)	172.4 (15)	
C1−C5−C6	149 (2)		
C40−C1−C2	129 (2)	124.8 (13)	
C2−C1−C70			125 (2)
C7−C8−C80			130 (2)
Os1−Os2−Os3	67.07 (4)	59.12 (2)	59.43 (3)
Os1−Os3−Os2	56.46 (3)	58.82 (2)	59.03 (3)
Os2−Os1−Os3	56.47 (3)	62.06 (2)	61.55 (3)
Os4−Os5−Os6			57.14 (3)
Os4−Os6−Os5			61.54 (3)
Os5−Os4−Os6			61.32 (3)

[a] Estimated Standard deviation in the least significant figure is given in parentheses.

alkyne is elongated C(1)−C(2) = 1.311(18) Å, which is typical for a double bond. The ligand is coordinated to the triosmium cluster through the alkyne group C(3)−C(4) that is adjacent to the newly formed olefinic group in the usual di-($\sigma + \pi$) coordination mode and bridges all three metal atoms.

The hexaosmium compound **5** contains two independent triangular triosmium clusters that are coordinated by the two inner alkyne groups of the original molecule **1**. The C−C distances of these alkynes (C(3)−C(4) = 1.39(3) Å and C(5)−C(6) = 1.44(3) Å) are elongated as a result of the coordination. The two triangular triosmium clusters in compound **5** have slightly different arrangements of the CO ligands: one cluster (Os(1)−Os2−Os(3)) contains nine linear terminal CO ligands and one bridging CO, similar to that in **4**, and the other (Os(4)−Os5−Os(6)) contains nine linear terminal COs and one semibridging CO. Both hydride ligands from each of the clusters in **5** were transferred to the two outer alkyne groups to form olefinic groups with *E*-stereochemistry. The C−C distances of the two olefinic groups are typical of C−C double bonds, C(1)−C(2) = 1.34(3) Å and C(7)−C(8) = 1.33(3) Å.

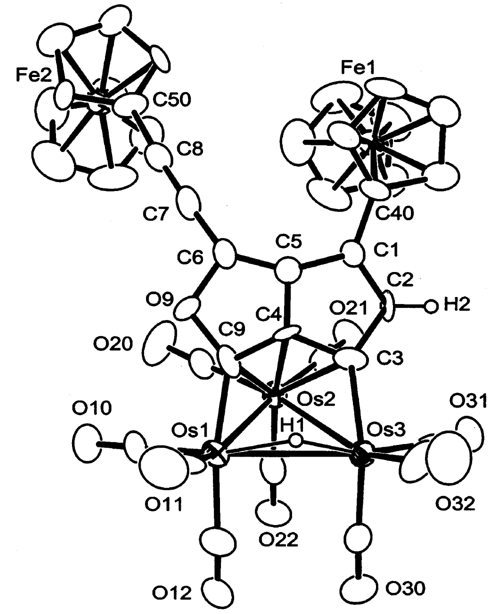
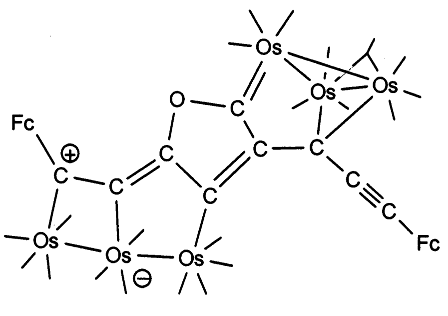


Figure 1. An ORTEP diagram of $Os_3(CO)_9(\mu_3,\eta^3\text{-}FcCCHC_4\text{-}COC{\equiv}CFc)(\mu\text{-}H)$ (**3**) showing 40% probability thermal ellipsoids.

Discussion

Compound **3** was obtained by an intramolecular cyclization involving three of the C−C triple bonds of the tetrayne chain, a coupling to one of the CO ligands, and the transfer of one of the hydride ligands to a carbon atom. The mechanism for the formation of this heterobicyclic ligand was not established in this study. Carbocyclization reactions of alkynes are important and useful methods for the synthesis of a variety of carbocyclic and heterocyclic compounds,[11] and a wide range of new organic compounds;[12] however, the coupling of CO to polyynes has been explored very little. We have recently observed formation of a five-membered heterocycle by the coupling of a CO ligand to the tetrayne grouping of **2** in another triosmium complex **C**.[2] This seems to be an area of great potential for the synthesis of novel heterocycles.



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[11] Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635.

The observation of the formation of *E*-olefinic groups in **4** and **5** was an unexpected result since metal-mediated hydrogenation of alkynes generally proceeds by cis-addition of the hydrogen atoms.[3] Years ago, Muetterties reported some examples of unusual trans-hydrogenation for some alkynes when metal complexes containing two or more metal atoms were involved.[4] In one case, this was shown to occur via an insertion of the alkyne into the metal−hydrogen bond to give a $\sigma-\pi$ alkenyl intermediate containing trans-stereochemistry.[4c]

The formation of the olefinic groups with *E*-stereochemistry in the case of **4** and **5** could be the result of three possible processes: (1) trans-insertion, such as observed by Muetterties,[4c] (2) a two-step process involving first cis-addition of both hydrogen atoms followed by an independent *Z*- to *E*-isomerization, or (3) direct formation of an *E*-olefinic group via a cis-insertion followed by a trans-addition of the second hydrogen atom.

Previous studies have shown that the insertion of alkynes into osmium−hydrogen bonds proceed with cis-insertion in hydride containing osmium clusters,[13,14] so we think that option (1) above is unlikely. We found no evidence of products having olefinic groups with *Z*-stereochemistry. Since the olefinic group in these complexes has moved away from the metal atoms after the hydrogen atoms were transferred to it, it seems unlikely that these metal atoms would be able to induce a *Z*- to *E*-isomerization, at least not intramolecularly, and so we think that the absence of products with *Z*-stereochemistry indicates that option (2) above is also probably not the correct one.

There are some attractive features to the third possibility. For example, the formation of the closely related compound $Os_4(CO)_{11}(\mu\text{-}\eta^2\text{-FcCC(H)C}_2\text{Fc})(\mu\text{-H})_3$ (**6**) occurs by cis-insertion of bis(ferrocenyl)butadiyne into an osmium−hydrogen bond (i.e. the first hydrogen transfer step).[13] Compound **6** was obtained from the reaction of 1,4-bis(ferrocenyl)butadiyne with $Os_4(CO)_{12}(\mu\text{-H})_4$ in the presence of an Me_3NO activator. A view of the molecular structure of **6** in Figure 4 shows the stereochemistry of the $FcCC(H)C_2Fc$ ligand resulting from cis-insertion of the diyne into the metal−hydrogen bond. The $FcCC(H)C_2Fc$ ligand is coordinated to two osmium atoms in a μ-η^2-fashion. This is similar to that found for the partially hydrogenated diphenylacetylene ligand in the complex $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-PhCC(H)Ph})(\mu\text{-H})$ that was obtained from the reaction of **2** with diphenylacetylene.[14]

From these two examples it seems reasonable to expect that the first step in the formation of the *E*-olefinic groups in **5** and **6** is an insertion of one of the external alkyne groups of the tetrayne chain of **1** into an osmium−hydrogen bond to form an intermediate containing a $FcCC(H)(C_2)_3Fc$ ligand having a μ-η^2-coordination with a cis-stereochemistry for the substitutents, see intermediate **A** in Scheme 2. For steric reasons, see Figure 4, it seems unlikely that *E*- to *Z*-isomerization will occur in this intermediate.[15] The second hydrogen transfer can then occur in either of two ways (see Scheme 2): Step 1 would result in cleavage of the Os(1)−C(1) bond in **A** and would result in an olefin having *Z*-stereochemistry (not the observed result). The other possibility (Step 2) would result in cleavage of the Os(2)−C(1) bond. In this case, the formation of the C(1)−H bond would lower the C(1)−C bond order toward one and would facilitate the formation of an olefinic group with *E*-stereochemistry after a slight rotation about the C(1)−C bond. We believe that the transfer of this second hydrogen atom will be induced by the neighboring uncoordinated alkyne that

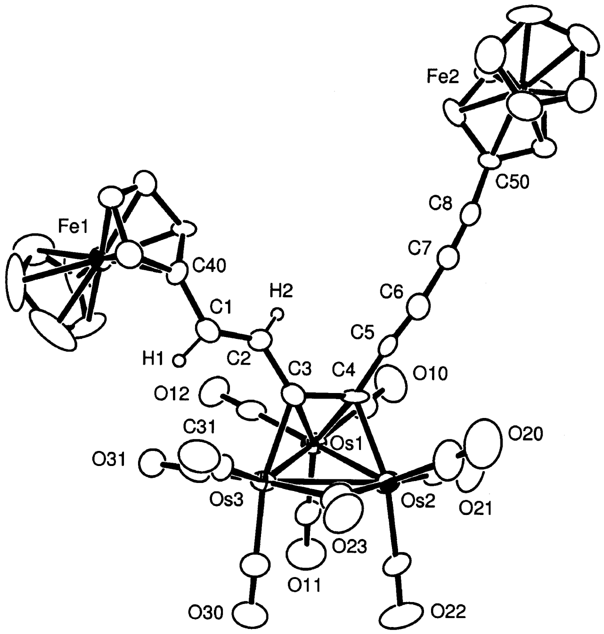

Figure 2. An ORTEP diagram of $Os_3(CO)_{10}(\mu_3,\eta^2\text{-}E\text{-FcCHCHC}_2\text{−C≡C−C≡CFc})$ (**4**) showing 40% probability thermal ellipsoids.

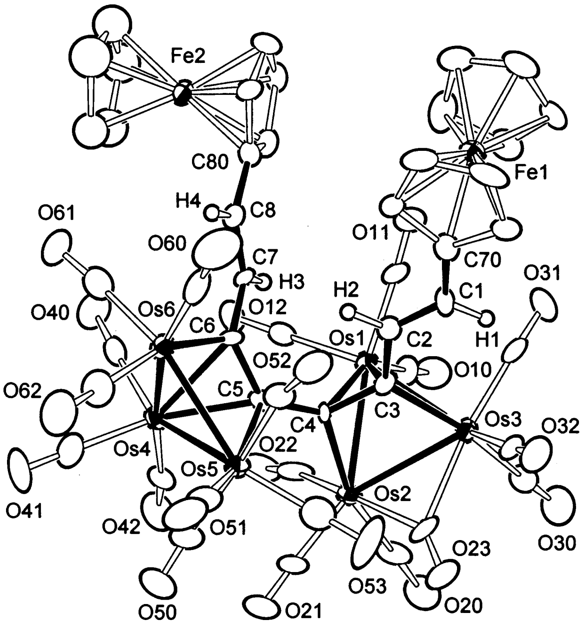

Figure 3. An ORTEP diagram of $Os_6(CO)_{20}(\mu_3,\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}E,E\text{-FcCHCHC}_2\text{C}_2\text{CHCHFc})$ (**5**) showing 40% probability thermal ellipsoids.

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(12) (a) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Casalnuovo, J. A.; Shore, N. E. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH Pub., Weinheim, Germany, 1995; Chapter 5.

(13) Adams, R. D.; Qu, B. *J. Organomet. Chem.* **2001**, *619*, 271.

(14) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

(15) Hart, D. W.; Schwartz, J. *J. Organomet. Chem.* **1975**, *87*, C11.

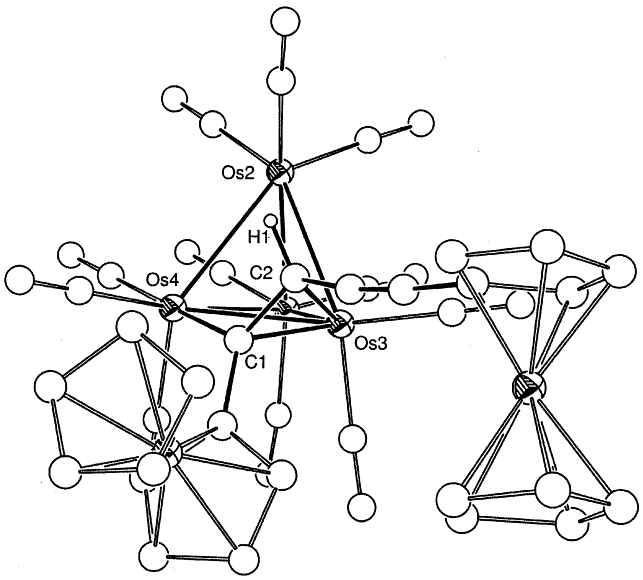
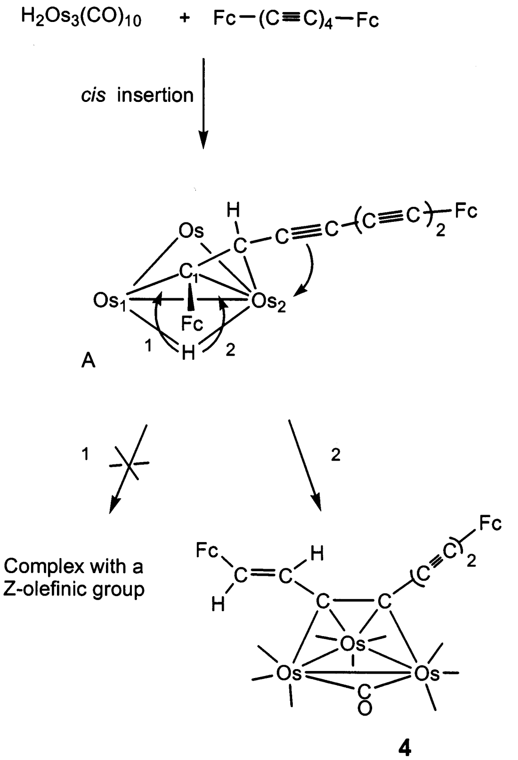


Figure 4. An ORTEP diagram of $Os_4(CO)_{11}(\mu\text{-}\eta^2\text{-}FcCC(H)C_2Fc)(\mu\text{-}H)_3$ (**6**).

Scheme 2



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must add at the metal atom Os(2) because of the geometry of the coordinated μ-η^2-alkenyl group. Formally, this alkyne addition will increase the number of electrons at Os(2) to 20, two beyond the accepted 18-electron configuration. Thus, the reductive-elimination step that leads to formation of the CH bond should also occur at Os(2) in order to return Os(2) to the 18-electron configuration. In other words, the proximity and geometry of the ligand is such that the uncoordinated alkyne group can interact only with the metal atom Os(2) and will thus promote the formation of the second C−H bond via cleavage of the Os(2)−C(1) bond. This is exactly the Os−C bond whose cleavage would lead to the formation of an olefin with *E*-stereochemistry, Scheme 2. Finally, the olefinic group is displaced by the alkyne group that becomes coordinated to all three osmium atoms. In the case of the formation of **5** this entire process actually happens twice.

The difference between the oxidation potentials of the ferrocenyl groups in compounds **3** ($\Delta E_p = 100$ mV) and **4** ($\Delta E_p = 130$ mV) is significantly larger than that in compound **2**, where there is no detectable communication between the two terminal ferrocenyl groups. This can be attributed to the intrinsic inequivalence of the two terminal ferrocenyl groups. In compounds **3** and **4** the two ferrocenyl groups are chemically inequivalent. It is impossible to separate the combined effects of chemical inequivalence and electrocommunication, and so it is not possible to confirm the existence of electrocommunication between the ferrocenyl groups by this method. In compound **5**, however, the two ferrocenyl groups are equivalent assuming the differences in ligand geometry on the clusters are insignificant or time averaged. However, only a single two-electron oxidation peak was observed for the ferrocenyl groups at $E_p = 0.42$ V in **5**; thus, in this case there is no evidence for communication between the ferrocenyl groups by this method.

Summary

The addition of **2** to **1** yielded three new cluster complexes in which hydrogen was transferred from the cluster to the polyyne ligand. In the case of compound **3** this was accompanied by cyclization processes that produced a heterobicycle by incorporating a CO ligand into one of the rings. In compounds **4** and **5** both hydride ligands from the triosmium clusters were transferred to the alkynes to produce olefinic groups which possessed *E*-stereochemistry. A mechanism has been proposed to account for the trans-hydrogenation process by taking advantage of the binuclear coordination of the partially hydrogenated intermediate.

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Supporting Information Available: Experimental procedures and tables of data for the structural analyses of **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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