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Synthesis and Characterization of 1,12-Bis(ferrocenyl)-1,3,5,7,9,11-dodecahexayne and Its Coordination to Triosmium and Dicobalt Carbonyls

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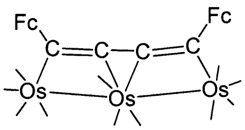
1,12-Bis(ferrocenyl)-1,3,5,7,9,11-dodecahexayne (**1**) was synthesized by in situ oxidative coupling of the terminal triyne FcC≡CC≡CC≡CH (**5**). The reaction of hexayne **1** with $Os_3(CO)_{11}(NCMe)$ (**2**) yielded the new hexaosmium compound $Os_6(CO)_{22}(\mu_6\text{-}\eta^8\text{-}FcC_4C{\equiv}CC{\equiv}CC_4\text{-}Fc)$ (**6**) in 15% yield. Compound **6** contains two open triosmium clusters coordinated parallel to opposite sides of the hexayne chain. Compound **1** also reacted with $Co_2(CO)_8$ to afford $Co_8(CO)_{24}(\mu_8\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FcC_2C{\equiv}CC_4C{\equiv}CC_2Fc)$ (**7**) in 35% yield. In compound **7**, four dicobalt hexacarbonyl groups have been added to the hexayne chain. Compounds **1**, **6**, and **7** were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. Differential pulse voltammograms show only one two-electron oxidation peak for compounds **1**, **6**, and **7**, indicating that there is no detectable electronic communication between the two terminal ferrocenyl groups by this method.

Introduction

Molecules containing long unsaturated carbon atom chains capable of transmitting electrons have been proposed for use as molecular wires for the construction of nanoscale electronic devices.[1,2] Recently, there has been much interest in the coordination of conjugated di- and polyynes to the transition-metal complexes.[3] Conjugated polyynes appear to be especially effective in facilitating electronic exchange.[1] Electronic communication through such potential molecular wires is often evaluated by examining the redox response of electroactive groups placed at their terminii.[1]

We have recently shown that the attachment of a triosmium carbonyl cluster to 1,4-bis(ferrocenyl)-1,3-butadiyne leads to enhancement of the electrocommunication through the butadiyne chain when the osmium atoms are coordinated parallel to the chain in the compound $Os_3(CO)_{11}(\mu_3\text{-}\eta^4\text{-}FcCCCCFc)$ (**A**; Fc = C_5H_4-FeC_5H_5) but leads to a decrease in the electrocommunication when the osmium atoms are coordinated as a triangle to both π-bonds of a single C−C triple bond, as found in the compound $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}FcCCCCFc)$ (**B**).[4] This has been attributed to differing effects of the metal atoms on the π-bonding along the C_4 diyne chain.[4] Similar effects were observed for the triosmium cluster complex of 1,8-bis(ferrocenyl)-1,3,5,7-octatetrayne, $Os_3(CO)_{11}(\mu_3\text{-}\eta^2\text{-}FcC_2C{\equiv}CC{\equiv}CC{\equiv}CFc)$ (**C**).[5]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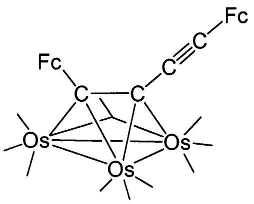
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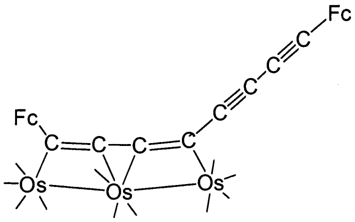
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Here we report the synthesis of the new hexayne 1,12-bis(ferrocenyl)-1,3,5,7,9,11-dodecahexayne (**1**), which was prepared by in situ oxidative coupling of $FcC\equiv CC\equiv CC\equiv CH$ (**5**). The reactions of $Os_3(CO)_{11}(NCMe)$ and $Co_2(CO)_8$ with **1** have yielded two new complexes, $Os_6(CO)_{22}(\mu_6\text{-}\eta^8\text{-}FcC_4C\equiv CC\equiv CC_4Fc)$ (**6**) and $Co_8(CO)_{24}(\mu_8\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FcC_2C\equiv CC_4C\equiv CC_2Fc)$ (**7**), respectively. Compound **6** contains two open triosmium clusters coordinated parallel to the hexayne chain. Compound **7** contains four dicobalt hexacarbonyl groups that are arranged with their metal–metal bonds perpendicular to the hexayne chain. All three compounds have been characterized by crystallography and by electrochemical methods.

Experimental Section

General Data. All the reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques unless indicated otherwise. Reagent grade solvents were dried by the standard procedures and were freshly distilled under nitrogen from appropriate drying agents. $Os_3(CO)_{11}(NCMe)$[6] (**2**), ferrocenylbutadiyne (**3**),[7] and 1,8-bis(ferrocenyl)octatetrayne[7] were prepared according to literature procedures. $Co_2(CO)_8$, *cis*-1,2-dichloroethylene, and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Co. and used as received. 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. ^1H NMR spectra were run on a Bruker AM-300 spectrometer operating at 300 MHz. ^1H chemical shifts were referenced to residual protons in $CDCl_3$ (7.24 ppm) and in CD_2Cl_2 (5.32 ppm) and ^{13}C chemical shifts to $CDCl_3$ (77.0 ppm) and are reported relative to tetramethylsilane. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Synthesis of 1-Chloro-6-ferrocenylhex-1-ene-3,5-diyne (4). Compound **4** was synthesized from **3** and *cis*-1,2-dichloroethylene in 44% yield by analogy to an established procedure.[7] Spectral data for **4** are as follows. ^1H NMR (δ in $CDCl_3$): 4.25 (s, 5H, Cp), 4.25 (m, 2H, C_5H_4), 4.52 (m, 2H, C_5H_4), 5.94 (d, 1H, CH), 6.49 (d, 1H, CH). MS: *m*/*e* 294, with an isotope pattern indicating the presence of one Cl atom.

Synthesis of $Fc(C\equiv C)_6Fc$ (1). A 1.4 mL portion of 1.6 M *n*-butyllithium (2.12 mmol) in hexane was added to a solution of diisopropylamine (0.3 mL, 2.12 mmol) in 15 mL of diethyl ether at −40 °C. The mixture was stirred for 0.5 h and then cooled to −78 °C with a dry ice/acetone bath. To this solution was added 295.0 mg of **4** (1.0 mmol) dissolved in 3 mL of diethyl ether, and the mixture was then stirred for 4 h at −78 °C to generate the intermediate **5**, which was not isolated. A solution of the catalyst was prepared from TMEDA (0.1 mL, 0.66 mmol) and CuCl (41 mg, 0.42 mmol) in 10 mL of acetone by vigorous stirring for 30 min. The catalyst solution was transferred by cannula to the solution of **5** at −78 °C, and the mixture was warmed to room temperature and stirred for 2 h while the flask was slowly purged with O_2. The solution turned dark red during this period. Consumption of the intermediate **5** was monitored by TLC. When complete, the reaction was quenched by addition of a saturated aqueous solution of cold NH_4Cl. The crude product was then extracted with CH_2Cl_2, dried over sodium sulfate, and purified by chromatography over a silica gel column by using a hexane/CH_2Cl_2 (4/1) solvent mixture for elution. The major red product **1** was obtained (65 mg, 0.126 mmol) in 25% yield. Analytical and spectral data for **1** are as follows. IR ($\nu_{C\equiv C}$; cm^{-1} in CH_2Cl_2): 2170 (vs), 2152 (s). ^1H NMR (δ in CD_2Cl_2): 4.20 (s, 10H, 2Cp), 4.28 (m, 4H, $2C_5H_4$), 4.52 (m, 4H, $2C_5H_4$). ^{13}C NMR (δ in $CDCl_3$): 70.5 (η-C_5H_5); η-C_5H_4, 61.8 (C_α), 70.3 (C_β), 73.1 (C_γ); $C\equiv C$, 79.4 (C_1), 71.2 (C_2), 65.2 (C_3), 64.0 (C_4), 63.8 (C_5), 63.4 (C_6). Anal. Calcd (found): C 74.75 (74.75); H, 3.51 (3.16).

Synthesis of $Os_6(CO)_{22}(\mu_6\text{-}\eta^8\text{-}FcC_4C\equiv CC\equiv CC_4Fc)$ (6). A 30.0 mg amount of $Os_3(CO)_{11}(NCMe)$ (0.0322 mmol) and an 8.3 mg amount of **1** (0.0161 mmol) were dissolved in 40 mL of CH_2Cl_2 in a 100 mL three-necked round-bottom flask. The reaction mixture was stirred at 25 °C for 1 h. The solvent was then removed in vacuo, and the products were separated by TLC using a 3:1 hexane/methylene chloride solvent mixture to yield 5.5 mg of dark gray $Os_6(CO)_{22}(\mu_6\text{-}\eta^8\text{-}FcC_4C\equiv CC\equiv CC_4Fc)$ (**6**; 15% yield). Analytical and spectral data for **6** are as follows. IR (ν_{CO}; cm^{-1} in hexane): 2125 (m), 2100 (s), 2047 (vs), 2041 (s), 2013 (m), 2003 (m), 1972 (m), 1961 (m). ^1H NMR (δ in $CDCl_3$): 4.15 (s, 10H, 2Cp), 4.48 (m, 4H, $2C_5H_4$), 4.57 (m, 4H, $2C_5H_4$). Anal. Calcd (found): C, 28.55 (28.61); H, 0.79 (0.62).

Synthesis of $Co_8(CO)_{24}(\mu_8\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FcC_2C\equiv CC_4C\equiv CC_2Fc)$ (7). A 10 mg amount of **1** (0.0195 mmol) and a 40 mg amount of $Co_2(CO)_8$ (0.1170 mmol) were dissolved in 30 mL of CH_2Cl_2 in a 50 mL three-necked round-bottom flask. The mixture was stirred at 25 °C for 40 min. 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 pure hexane. The major dark gray band was collected to yield 11.3 mg of $Co_8(CO)_{24}(\mu_8\text{-}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FcC_2C\equiv CC_4C\equiv CC_2Fc)$ (**7;** 35% yield). Analytical and spectral data for **7** are as follows. IR (ν_{CO}; cm^{-1} in hexane): 2105 (w), 2092 (sh), 2086 (s), 2069 (vs), 2058 (m), 2035 (s), 2028 (sh). ^1H NMR (δ in $CDCl_3$): 4.25 (s, 10H, 2Cp), 4.36 (m, 4H, $2C_5H_4$), 4.42 (m, 4H, $2C_5H_4$). Anal. Calcd (found): C, 40.57 (40.52); H, 1.08 (1.02).

Crystallographic Analyses. Red crystals of **1** were grown by slow evaporation of the solvent from CH_2Cl_2 at 5 °C. Dark gray crystals of **6** were grown by slow evaporation of the solvent from a benzene/octane (3:1) solution of the complex at 5 °C. Dark gray crystals of **7** were grown by slow evaporation of the solvent from a hexane/CH_2Cl_2 (5:1) solution of the complex at 5 °C.

Crystals of **1**, **6**, and **7** suitable for X-ray diffraction analysis were glued onto the ends of thin glass fibers. X-ray intensity measurements were performed at 293 K on a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Preliminary unit cells were determined on the basis of reflections collected from three sets of frames measured in orthogonal wedges of reciprocal space. The final unit cell parameters are based on the least-squares refinement of all data with $I > 5\sigma(I)$ from each data set. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. The raw intensity data frames were integrated with the SAINT+ program[8] using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied by using the program SAINT. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied with the program SADABS.[9]

Compound **1** crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with the *C*-centered space groups $C2/m$, Cm, and $C2$. The space group $C2/m$ was assumed and confirmed by the successful solution and refinement of the structure. The crystals of **1** were very small; therefore, the data-to-variables ratio in the final refinement was only slightly greater than 6, but we feel that the structure is correct and unambiguous. Compound **6** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refine-

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Table 1. Crystallographic Data for Compounds 1, 6, and 7

	1	**6**	**7**
empirical formula	$Fe_2C_{32}H_{18}$	$Os_6Fe_2O_{22}C_{54}H_{18}\cdot 2C_6H_6$	$Co_8Fe_2O_{24}C_{56}H_{18}$
fw	514.16	2427.80	1657.84
cryst syst	monoclinic	triclinic	orthorhombic
lattice params			
a (Å)	18.114(3)	7.1621(4)	18.9352(7)
b (Å)	8.8812(16)	20.2949 (13)	33.9403(13)
c (Å)	7.3340(13)	23.6103(14)	9.7024(4)
α (deg)	90	78.398(1)	90
β (deg)	103.819(4)	88.010(1)	90
γ (deg)	90	83.550(1)	90
V (Å^3)	1145.7(3)	3340.2(3)	6235.4(4)
space group	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)	$Pccn$ (No. 56)
Z	2	2	4
ρ_{calcd} (g/cm^3)	1.49	2.41	1.77
μ(Mo Kα) (mm^{-1})	1.285	11.860	2.598
temp (K)	293	293	293
$2\theta_{max}$ (deg)	45.2	50.2	48.8
no. of obsd rflns ($I > 2\sigma(I)$)	589	7569	3458
no. of params	91	854	406
goodness of fit[a]	1.008	1.037	1.048
max shift, final cycle	0.000	0.004	0.001
residuals:[b] R1; wR2	0.044; 0.0866	0.0511; 0.0988	0.0544; 0.1154
abs cor, max/min (SADABS)	0.975/0.765	0.694/0.526	1.00/0.798
largest peak in final diff map (e/Å^3)	0.240	2.426	1.085

[a] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$; n = no. of reflections, p = total no. of parameters refined. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2, 0)]/3$.

Table 2. Electrochemical Data for the Compounds $Fc(C\equiv C)_2Fc$, $Fc(C\equiv C)_4Fc$, 1, 6, and 7[a]

compd	$E_p(+/0)/E_p(2+/+)$, mV[c]	$E_{1/2}(+/0)/E_{1/2}(2+/+)$, mV[d]	ΔE_p, mV[e]
$Fc(C\equiv C)_2Fc$[4]	476/576	486/586	100
$Fc(C\equiv C)_4Fc$[b]	576	601	
1[b]	652	677	
6[b]	380	405	
7[b]	428	453	

[a] The data were recorded on a CV-50W voltammetric 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. The scan rate is 100 mV/s for CV and 20 mV/s for DPV. Under these same conditions the oxidation of ferrocene occurs at 320 mV. [b] Only one redox peak observed for this compound. [c] E_p is the peak position in DPV. [d] $E_{1/2} = E_p + E_{pul}/2$,[10] E_{pul} = 20 mV from DPV for $Fc(C\equiv C)_2Fc$; E_{pul} = 50 mV for $Fc(C\equiv C)_4Fc$, **1**, **6**, and **7**. [e] $\Delta E_p = E_p(2+/+) - E_p(+/0)$.

ment of the structure. Compound **7** crystallized in the orthorhombic crystal system. The space group *Pccn* was established on the basis of the systematic absences observed in the data. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares on F^2, using the SHELXTL software.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms on the ferrocenyl groups were calculated by assuming idealized tetrahedral geometries.

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 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_2Cl_2/CH_3CN (1:1) solvent mixture containing 0.1 M tetrabutylammonium hexafluorophosphate. 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 320 mV (using a pulse amplitude of 10 mV). The DP voltammogram of 1,4-bis(ferrocenyl)butadiyne shows two one-electron oxidations for the ferrocenyl groups at E_p = 0.476 and 0.576 V vs Ag/AgCl. 1,8-Bis(ferrocenyl)octatetrayne, **1**, **6**, and **7** each show only one two-electron oxidation for the ferrocenyl groups at E_p = +0.576, +0.652, +0.380, and +0.428 V vs Ag/AgCl, respectively, as listed in Table 2. The two-electron oxidation for **1** at E_p = +0.652 V was confirmed by using a known amount of ferrocene reference as an internal standard. The cyclic voltammograms showed that the redox processes for all compounds were reversible.

Results

The synthesis of the new compound 1,12-bis(ferrocenyl)-1,3,5,7,9,11-dodecahexayne (**1**) followed the conventional synthetic procedures for the preparation of polyynediyl complexes by copper-catalyzed oxidative coupling and is summarized in Scheme 1. 1-Chloro-6-ferrocenylhex-1-ene-3,5-diyne (**4**) was prepared in good yield by a slight modification of the published procedure:[7] reaction of ferrocenylbutadiyne with *cis*-1,2-dichloroethylene in toluene in the presence of a Pd catalyst, CuI, and $^nBuNH_2$. Dechlorination of **4** in the presence of lithium diisopropylamine (LDA) yielded the terminal triyne $FcC\equiv CC\equiv CC\equiv CH$ (**5**), which was then converted in situ into 1,12-bis(ferrocenyl)dodecahexayne (**1**) in 25% yield by oxidative coupling by using TMEDA·CuCl catalyst. Isolation of the terminal triyne **5** was not possible, as the compound rapidly decomposed when warmed above −78 °C. The instability of simple and higher terminal polyynes is a major challenge in their preparation, because they are highly sensitive to polymerization and rapid decomposition.[11] Compound **1** was characterized by ^1H NMR, single-crystal X-ray diffraction analysis, and differential pulse voltammetry (DPV). An ORTEP diagram of the molecular structure of compound **1** is shown in Figure 1. Selected inter-

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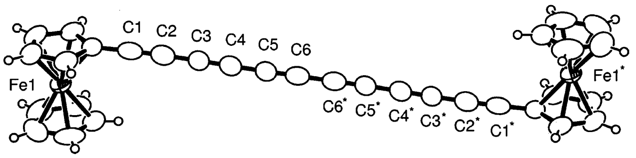
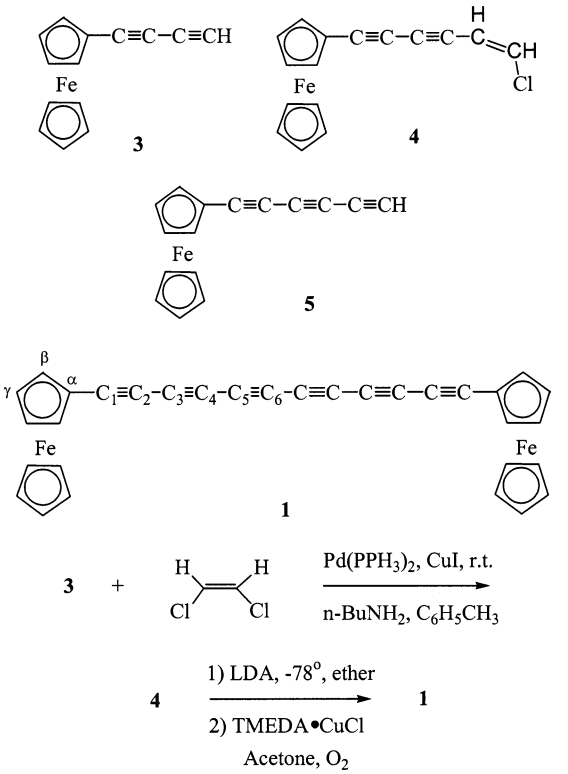


Figure 1. ORTEP diagram of 1,12-bis(ferrocenyl)-1,3,5,7,9,11-dodecahexayne, $Fc(C\equiv C)_6Fc$ (**1**), showing 40% probability thermal ellipsoids.

Scheme 1



atomic distances and angles are listed in Table 3. The hexayne chain is linear, as expected. The linearity can be estimated by the sum and average of the deviation of the bond angles from 180°, which are 11.8/1.0°. Three other hexayne compounds that have been reported recently are the (dodecahexaynediyl)diiron compound $Fp^*(C\equiv C)_6Fp^*$ ($Fp^* = Fe(\eta^5\text{-}C_5Me_5)(CO)_2$)[11a] and the C_{12} complexes $(p\text{-tol})(p\text{-tol}_3P)_2Pt(C\equiv C)_6Pt(P\text{-}p\text{-tol}_3)_2(p\text{-tol})$[11b] and $(F_5C_6)(p\text{-tol}_3P)_2Pt(C\equiv C)_6Pt(P\text{-}p\text{-tol}_3)_2(C_6F_5)$.[11c] In these three compounds, the hexayne chains are considerably twisted and show distinct nonlinearity. The sum and average of deviation of the bond angles for the hexayne chains are 57.5/4.8°, 36.4/3.0°, and 58.0/6.3°, respectively. In compound **1**, short (triple) and long (single) bond alternation is clearly observed. The averaged values for the C≡C and C–C bond lengths along the chain are 1.22 and 1.35 Å.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 6, and 7

	1	6	7
	Distances[a]		
C1–C2	1.224(10)	1.336(19)	1.357(8)
C2–C3	1.349(11)	1.28(2)	1.394(8)
C3–C4	1.204(10)	1.33(2)	1.210(7)
C4–C5	1.347(11)	1.429(19)	1.393(7)
C5–C6	1.196(9)	1.214(19)	1.347(7)
C6–C6*	1.404(16)		1.420(10)
C6–C7		1.37(2)	
C7–C8		1.215(19)	
C8–C9		1.385(19)	
C9–C10		1.32(2)	
C10–C11		1.32(2)	
C11–C12		1.29(2)	
Os1–Os2		2.9225(9)	
Os2–Os3		2.9131(9)	
Os1–C1		2.151(12)	
Os2–C2		2.335(13)	
Os2–C3		2.334(12)	
Os3–C4		2.130(14)	
Os4–Os5		2.9263(9)	
Os5–Os6		2.9258(9)	
Os4–C9		2.166(13)	
Os5–C10		2.314(14)	
Os5–C11		2.313(14)	
Os6–C12		2.128(14)	
Co1–Co2			2.4608(14)
Co1–C1			1.979(6)
Co1–C2			1.940(6)
Co2–C1			1.950(6)
Co2–C2			1.975(6)
Co3–Co4			2.4702(12)
Co3–C5			1.952(5)
Co3–C6			1.947(5)
Co4–C5			1.966(6)
Co4–C6			1.962(5)
	Angles[a]		
C1–C2–C3	178.5(7)	172.2(13)	139.8(6)
C2–C3–C4	179.3(7)	177.5(14)	177.1(7)
C3–C4–C5	179.7(7)	124.0(13)	175.5(6)
C4–C5–C6	178.8(7)	165.9(18)	140.2(5)
C5–C6–C6*	179.5(8)		141.7(6)
C5–C6–C7		178.4(17)	
C6–C7–C8		174.4(18)	
C7–C8–C9		178.1(16)	
C8–C9–C10		122.9(14)	
C9–C10–C11		172.9(15)	
C10–C11–C12		171.3(15)	
Os1–Os2–Os3		163.11(3)	
Os4–Os5–Os6		162.36(3)	
C1–Co1–C2			40.5(2)
C1–Co2–C2			40.4(2)
C5–Co3–C6			40.4(2)
C5–Co4–C6			40.1(2)

[a] The estimated standard deviation in the least significant figure is given in parentheses.

The reaction of **1** with $Os_3(CO)_{11}(NCMe)$ at 25 °C yielded the new compound $Os_6(CO)_{22}(\mu_6\text{-}\eta^8\text{-}FcC_4C\equiv CC\equiv CC_4Fc)$ (**6**) in 15% yield, as shown in Scheme 2. Compound **6** was characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analysis and by DP voltammetry. An ORTEP diagram of the molecular structure of **6** is shown in Figure 2. Selected interatomic distances and angles are listed in Table 3. Compound **6** contains six osmium atoms arranged in the form of two open triosmium clusters coordinated to the two outer alkyne groups of **1**, C(1)–C(2), C(3)–C(4) and C(9)–C(10), C(11)–C(12), in a linear parallel mode. The molecule is crystallographically centrosymmetrical, and the two $Os_3(CO)_{11}$ groupings lie on opposite sides of the hexayne chain to minimize their steric interactions. Each metal cluster contains 11 terminal carbonyl groups. The coordinated triple bonds are lengthened as a result of the coordination: C(1)–C(2) = 1.336(19) Å, C(3)–C(4) = 1.33(2) Å and C(9)–C(10) = 1.32(2), C(11)–C(12) = 1.29(2) Å, while the C–C single bonds between the two triple bonds have decreased in length, C(2)–C(3) = 1.28(2) Å and C(10)–C(11) = 1.32(2) Å. Similar effects on the C–C bond distances were observed upon coordination of the open triosmium clusters to the 1,4-bis(ferrocenyl)butadiyne compound **A** and the 1,8-bis-

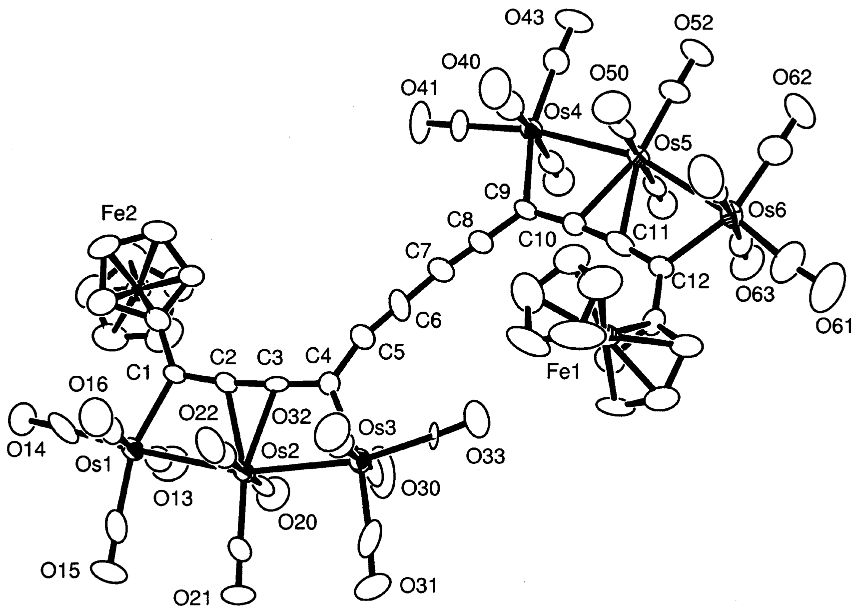
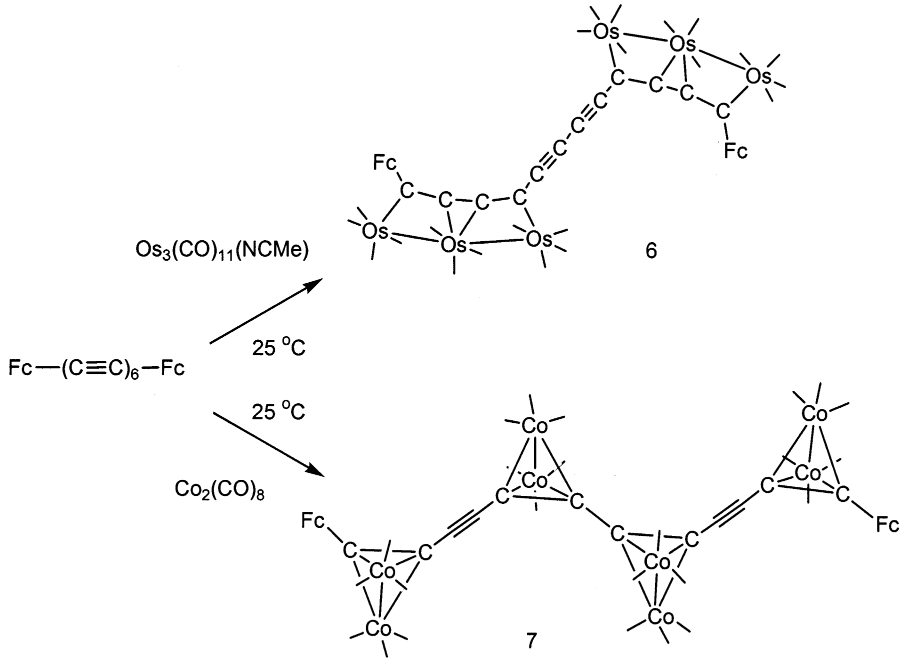


Figure 2. ORTEP diagram of $Os_6(CO)_{22}(\mu_6\text{-}\eta^8\text{-}FcC_4C{\equiv}CC{\equiv}CC_4Fc)$ (**6**), showing 40% probability thermal ellipsoids.

Scheme 2



(ferrocenyl)octatetrayne species **C**. This has been explained by a butatrienediyl-induced character into the two coordinated triple bonds by the cluster.[4a] The uncoordinated C−C triple bonds in **6** exhibit normal bond distances: C(5)−C(6) = 1.214(19) Å and C(7)−C(8) = 1.215(19) Å. The triosmium groups are not exactly linear but are slightly bent at the central osmium atom: Os1−Os2−Os3 = 163.11(3)° and Os4−Os5−Os6 = 162.36(3)°. Similar bending was observed in compounds **A** and **C**.

The reaction of excess $Co_2(CO)_8$ with **1** at 25 °C provided the quadruple-addition product $Co_8(CO)_{24}(\mu_8\text{-}\eta^8\text{-}FcC_2C{\equiv}CC_4C{\equiv}CC_2Fc)$ (**7**) in 35% yield. Compound **7** was characterized by a combination of IR, ^1H NMR, and single-crystal X-ray diffraction analyses and by DP voltammetry. An ORTEP diagram of the molecular structure of **7** is shown in Figure 3. Selected interatomic distances and angles are listed in Table 3. Compound **7** contains four dicobalt hexacarbonyl groupings coordinated to four separate C−C triple bonds along the hexayne chain of **1**. The molecule is crystallographically centrosymmetrical. The four $Co_2(CO)_6$ groupings are arranged on opposite sides of the hexayne chain to minimize their steric interactions, and Co−Co vectors are perpendicular to the direction of the hexayne chain. The length of the Co−Co bonds, 2.4608(14) and 2.4702(12) Å, and the coordinated C−C triple bonds, 1.357(8) and 1.347(7) Å, are similar to those previously reported for bridging alkyne ligands in $Co_2(CO)_6(\mu\text{-}RC_2R)$ complexes[13] and in cyclic polyynes of the dicobalt complexes.[14] The two central $Co_2(CO)_6$ groups lie on adjacent

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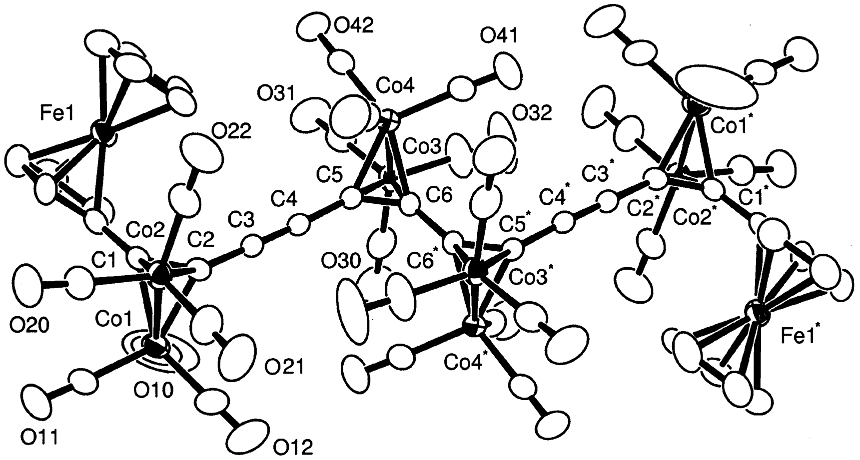

Figure 3. ORTEP diagram of $Co_8(CO)_{24}(\mu_8\text{-}\eta^8\text{-}FcC_2C{\equiv}CC_4C{\equiv}CC_2Fc)$ (**7**), showing 40% probability thermal ellipsoids.

C−C triple bonds, which have been observed in di- and tetraynes.[15] Two of the original six C−C triple bonds, C(3)−C(4) = 1.210(7) Å, are uncoordinated. Compound **7** is stable in the air at 25 °C for weeks.

The DP voltammograms of **1**, **6**, and **7** show only one two-electron oxidation for the ferrocenyl groups at E_p = +0.652, +0.380, and +0.428 V vs Ag/AgCl, respectively.

Discussion

In previous studies we have shown that the coordination of open triosmium clusters parallel to the carbon chains of bis(ferrocenyl)polyyne complexes enhances the electrocommunication between the ferrocenyl groups through the carbon chain.[4,5] It is known that, as conjugated carbon chains become longer, communication from one end to the other decreases.[16] To test this effect further and also to test the potential of the triosmium coordination to promote electrocommunication, we have prepared a new longer chain bis(ferrocenyl)hexayne, **1**. This was accomplished by in situ oxidative coupling of the terminal triyne **5** using standard Hay conditions (TMEDA·CuCl, O_2, acetone, room temperature).[17] The DP voltammogram of **1** was found to exhibit only one two-electron redox process at E_p = + 0.65 V, indicating no detectable electrocommunication between the ferrocenyl groups by this method. Next, we prepared the compound **6**, the hexaosmium complex of **1**, which we have shown contains two open triosmium clusters coordinated parallel to the chain at opposite ends. The DP voltammogram of **6** also shows only one two-electron redox process at E_p = + 0.38 V, indicating again that there is no detectable electrocommunication between the ferrocenyl groups. Apparently, the chain in **1** is so long that even in the presence of two triosmium enhancers, the DPV method is still not able to detect any electrocommunication between the ferrocenyl groups.

We have been able to add four $Co_2(CO)_6$ groups to **1** to form compound **7**. Each $Co_2(CO)_6$ group is coordinated to the two π-bonds of the alkyne group to which it is attached. This should disrupt the π-bonding along the hexayne chain; therefore, any electrocommunication between the ferrocenyl groups would be expected to decrease. As expected, only a single redox process was observed, E_p = +0.43 V.

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Supporting Information Available: Tables giving crystallographic data for the structural analyses of **1**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020270L

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