Reactions of Cyclotetradeca-1,8-diyne with Triosmium Carbonyl Clusters

Wen-Yann Yeh* and Ming-Ann Hsu

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 804

Shie-Ming Peng† and Gene-Hsiang Lee

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106

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Reaction of $Os_3(CO)_{10}(NCMe)_2$ and cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) affords the alkyne complexes $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**) and $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**). Thermolysis of **1** results in a C−H bond activation to give the hydrido allene complex $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**). Photoirradiation of **1** in the presence of $C_{14}H_{20}$ ligand produces the metallacyclopentadienyl complex $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (**4**). In contrast, $Fe_3(CO)_{12}$ reacts with $C_{14}H_{20}$ to generate $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**5**), which upon heating undergoes cluster fragmentation to give the known complexes $(\eta^4\text{-}C_4(C_{10}H_{20}))Fe(CO)_3$ and $[(\eta^5\text{-}C_5(C_9H_{18}))Fe(CO)_2]_2$. The new compounds **1**−**5** have been characterized by mass, IR, and NMR spectroscopy. The structures of **2**−**4** have been determined by an X-ray diffraction study.

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Introduction

Cycloalkadiynes[1] are versatile starting materials for synthesis of superphanes and cage compounds,[2] which have grown to be an important discipline that is attracting both synthetic and physical chemists. For instance, several metal-capped cyclobutadienophane and cyclobutadienosuperphane complexes were prepared by Gleiter and co-workers from the reactions of cycloalkadiynes with $Fe(CO)_5$, $CpCo(CO)_2$, and $Cp^*Co(C_2H_4)_2$, through a metal-mediated intra- or intermolecular alkyne−alkyne coupling process.[3] However, the coordination chemistry of cyclodiynes with transition-metal clusters has received little attention. Our continuing interest in alkyne−cluster complexes[4] therefore prompted us to investigate the reaction of cyclotetradeca-1,8-diyne with triosmium carbonyl clusters.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques.[5] $Os_3(CO)_{12}$ was prepared from OsO_4 and CO as described in the literature.[6] Cyclotetradeca-1,8-diyne ($C_{14}H_{20}$)[7] and $Os_3(CO)_{10}(NCMe)_2$[8] were prepared by literature methods. $Fe_3(CO)_{12}$ from Strem was used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded with a 0.1 mm pathlength CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra were recorded by using a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Reaction of $C_{14}H_{20}$ and $Os_3(CO)_{10}(NCMe)_2$. $C_{14}H_{20}$ (46 mg, 0.246 mmol), $Os_3(CO)_{10}(NCMe)_2$ (106 mg, 0.113 mmol), and benzene (50 mL) were introduced into a 100 mL Schlenk flask under a dinitrogen atmosphere. The flask was placed in an oil bath at 65−70 °C for 15 min, resulting in a color change from yellow to orange-red. The solution was cooled to room temperature, and the yellow precipitate was filtered. The filtrate was concentrated to ca. 2 mL on a rotary evaporator and subjected to TLC, with petroleum ether as eluent. Isolation of the materials forming the major orange band afforded $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**; 101 mg, 86%).

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† To whom inquiries concerning the X-ray crystallographic work should be addressed.

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The yellow precipitate was extracted with hot THF (10 mL) and filtered. The filtrate was then concentrated to ca. 2 mL, layered with *n*-hexane (10 mL), and placed in a freezer at −15 °C overnight, yielding orange-yellow needle crystals of $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**; 12 mg, 11%).

Characterization of 1. Mass spectrum (FAB): *m/z* 1044 (M^+, ^{192}Os), 1044 − 28*n* (*n* = 1−10). IR (*n*-hexane, ν(CO)): 2104 (w), 2060 (vs), 2048 (sh), 2020 (s), 2000 (m), 1994 (m), 1982 (w), 1850 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 23 °C): δ 2.46 (m, 4H), 2.14 (m, 4H), 2.02 (m, 4H), 1.45 (m, 4H), 1.23 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C): δ 148.4 ($C{\equiv}C{-}Os$), 80.7 ($C{\equiv}C$), 50.7, 33.5, 28.9, 26.8, 18.3 (CH_2). Anal. Calcd for $C_{24}H_{20}O_{10}Os_3$: C, 27.74; H, 1.94. Found: C, 27.78; H, 2.06.

Characterization of 2. Mass spectrum (FAB): *m/z* 1900 (M^+, ^{192}Os). IR (THF, ν(CO)): 2100 (w), 2060 (vs), 2044 (s), 2016 (s), 2000 (s), 1992 (m), 1980 (sh), 1964 (w), 1854 (vw) cm^{-1}. IR (KBr disk, ν(CO)): 2104 (m), 2046 (s, br), 2000 (s, br), 1986 (s, br), 1950 (m), 1840 (m) cm^{-1}. ^1H NMR (THF-d_8, 23 °C): δ 3.20 (m, 8H), 2.09 (m, 8H), 1.88 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_2$, 23 °C): δ 150.0 ($C{\equiv}C{-}Os$), 50.6, 42.2, 34.0 (CH_2). Anal. Calcd for $C_{34}H_{20}O_{20}Os_6$: C, 21.61; H, 1.06. Found: C, 21.68; H, 1.12.

Reaction of 1 with $Os_3(CO)_{10}(NCMe)_2$. $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**; 11 mg, 0.01 mmol) and $Os_3(CO)_{10}(NCMe)_2$ (20 mg, 0.02 mmol) were dissolved in benzene (10 mL) under a dinitrogen atmosphere. The solution was heated at 65−70 °C for 15 min, yielding a yellow precipitate. The precipitate was collected by filtration, washed with benzene, and crystallized from THF/*n*-hexane at −15 °C to give $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**; 10 mg, 53%).

Thermolysis of 1. $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**; 156 mg, 0.15 mmol) dissolved in *n*-heptane (50 mL) was heated to reflux (98 °C) under dinitrogen for 1 h. During the reaction, the solution changed from orange to light yellow. The solvent was removed under vacuum, and the residue was subjected to TLC, with CH_2Cl_2/*n*-hexane as eluent (1:9, v/v). $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**; 137 mg, 90%) was isolated from the major yellow band. Mass spectrum (FAB): *m/z* 1016 (M^+, ^{192}Os), 1016−28*n* (*n* = 1−9). IR (C_6H_{12}, ν(CO)): 2099 (m), 2069 (s), 2041 (s), 2019 (s), 2004 (m), 1993 (s), 1987 (m), 1982 (w), 1975 (w) cm^{-1}. ^1H NMR (C_6D_6, 23 °C): δ 2.86−0.86 (m, 19H), −22.03 (s, μ-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C): δ 176.9 (CO), 175.7 ($\mathit{C}{=}C{=}CH$), 173.9 (CO), 173.9 (CO), 170.7 (CO), 170.4 (CO), 167.1 (CO), 162.1 ($C{=}\mathit{C}{=}CH$), 125.0 ($C{=}C{=}\mathit{C}H$), 81.1, 80.2 ($C{\equiv}C$), 48.7, 40.7, 34.4, 31.2, 29.3, 28.4, 26.1, 19.0, 17.9 (CH_2). Anal. Calcd for $C_{23}H_{20}O_9Os_3$: C, 27.33; H, 1.98. Found: C, 27.30; H, 1.88.

Photoirradiation of 1 in the Presence of $C_{14}H_{20}$. This reaction was carried out in an ACE microscale photoreaction vessel equipped with an immersed Pen-Ray 5.5 W low-pressure, cold-cathode, mercury gaseous discharge lamp. $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**; 50 mg, 0.048 mmol), $C_{14}H_{20}$ (40 mg, 0.213 mmol), and *n*-hexane (50 mL) were introduced into the reaction vessel under an atmosphere of dinitrogen. The mixture was irradiated for 1.5 h with dinitrogen slowly bubbling through the solution. During the reaction, the solution changed gradually from orange to gray-yellow. The solvent was removed on a rotary evaporator, and the residue was subjected to TLC, with CH_2Cl_2/*n*-hexane as eluent (1:9, v/v). Compound **1** (24 mg, 48%) was recovered from the first orange band. The major purple-gray band yielded $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (**4**; 28 mg, 48%). Mass spectrum (FAB): *m/z* 1204 (M^+, ^{192}Os). IR (CH_2Cl_2, ν(CO)): 2106 (m), 2054 (vs), 2018 (s), 2000 (s), 1987 (m), 1968 (m), 1922 (m, br) cm^{-1}. ^1H NMR (C_6D_6, 23 °C): δ 3.60−0.90 (m, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C): δ 177.6 (CO), 175.7, 170.4 (C_4Os), 81.9, 80.0 ($C{\equiv}C$), 45.4, 33.1, 32.5, 31.2, 30.2, 28.1, 27.3, 26.4, 19.2, 17.5 (CH_2).

Reaction of $Fe_3(CO)_{12}$ and $C_{14}H_{20}$. $C_{14}H_{20}$ (40 mg, 0.213 mmol) and $Fe_3(CO)_{12}$ (58 mg, 0.115 mmol) were dissolved in *n*-hexane (10 mL) under an atmosphere of dinitrogen. The solution was heated to reflux for 1 h and cooled to room temperature, and the solvent was removed on a rotary evaporator. The residue was subjected to TLC, with petroleum ether as eluent. A major brown band was isolated to give $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**5**; 21 mg, 41%). Mass spectrum (FAB): *m/z* 608 (M^+, ^{56}Fe). IR (*n*-hexane, ν(CO)): 2080 (w), 2062 (vw), 2027 (vs), 2019 (vs), 1998 (s), 1989 (m), 1970 (vw) cm^{-1}. ^1H NMR (C_6D_6, 23 °C): δ 3.29 (m, 2H), 1.97 (m, 6H), 1.45−1.25 (m, 10H), 1.00 (m, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C): δ 212.4 (CO), 208.4, 105.7 ($C{\equiv}C{-}Fe$), 81.8, 79.3 ($C{\equiv}C$), 47.8, 32.5, 30.8, 30.5, 29.9, 29.7, 27.0, 25.4, 18.7, 16.6 (CH_2).

Table 1. Crystallographic Data for $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (2), $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (3), and $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}(C_{14}H_{20})_2)$ (4)

	3	**2**	**4**
chem formula	$C_{23}H_{20}O_9Os_3$	$C_{34}H_{20}O_{20}Os_6$	$C_{37}H_{40}O_9Os_3$
cryst solvent		2 THF	
crysl syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	$Pmn2_1$
fw	1012.00	2033.91	1199.29
a, Å	17.634(5)	9.3471(3)	21.0938(2)
b, Å	9.083(3)	26.7446(7)	10.6494(2)
c, Å	16.756(5)	10.3312(3)	8.4656(1)
α, deg	90	90	90
β, deg	102.06(3)	94.804(1)	90
γ, deg	90	90	90
V, Å^3	2625(1)	2573.6(1)	1901.68(5)
Z	4	2	2
D_{calcd}, g cm^{-3}	2.561	2.625	2.094
μ, cm^{-1}	145.500	148.29	100.48
R/R_w[a]	0.041/0.036		
R1/wR2[b]		0.0443/0.0934	0.0426/0.0886
GOF	1.44		
GOF on F^2		1.076	1.074

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum w|F_o|^2]\}^{1/2}$.
[b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum w|F_o|^4]\}^{1/2}$.

Structure Determination for 3. A yellow crystal of $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**; ca. 0.25 × 0.30 × 0.40 mm) was mounted in a thin-walled glass capillary and aligned on the Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Lattice parameters were determined from 25 randomly selected reflections with 2θ ranging from 19.5 to 24.4°. The data were collected at 298 K using the $\theta/2\theta$ scan technique to maximum 2θ values of 50.0° at a variable speed of 3.30−8.24°/min. The intensities of three representative reflections, which were measured every 60 min of X-ray exposure time, remained constant through data collection; therefore, no decay correction was applied. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-squares cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the NRCSDP-VAX package. A summary of relevant crystallographic data is provided in Table 1.

Structure Determination for 2 and 4. A yellow crystal of $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**; ca. 0.20 × 0.25 × 0.35 mm) and a purple crystal of $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}(C_{14}H_{20})_2)$ (**4**; ca. 0.30 × 0.08 × 0.04 mm) were each mounted in a thin-walled glass capillary and aligned on the Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The θ range for data collection is 1.52−27.49° for **2** and 1.91−29.92° for **4**. A total of 11 594 reflections were measured, and 5896 reflections (R_{int} = 0.0598) were unique for **2**, while 14 882 reflections were measured and 4313 reflections (R_{int} = 0.0685) were unique for **4**. Sadabs absorption corrections were made for **2** (T_{min} = 0.0869, T_{max} = 0.2649) and **4** (T_{min} = 0.1459, T_{max} = 0.3576). The structures were solved by the direct method and refined by full-matrix least squares on F^2. The program used was the SHELXTLE package. The data collection and refinement parameters are collected in Table 1. The space group $Pmn2_1$ for **4** is acentric;

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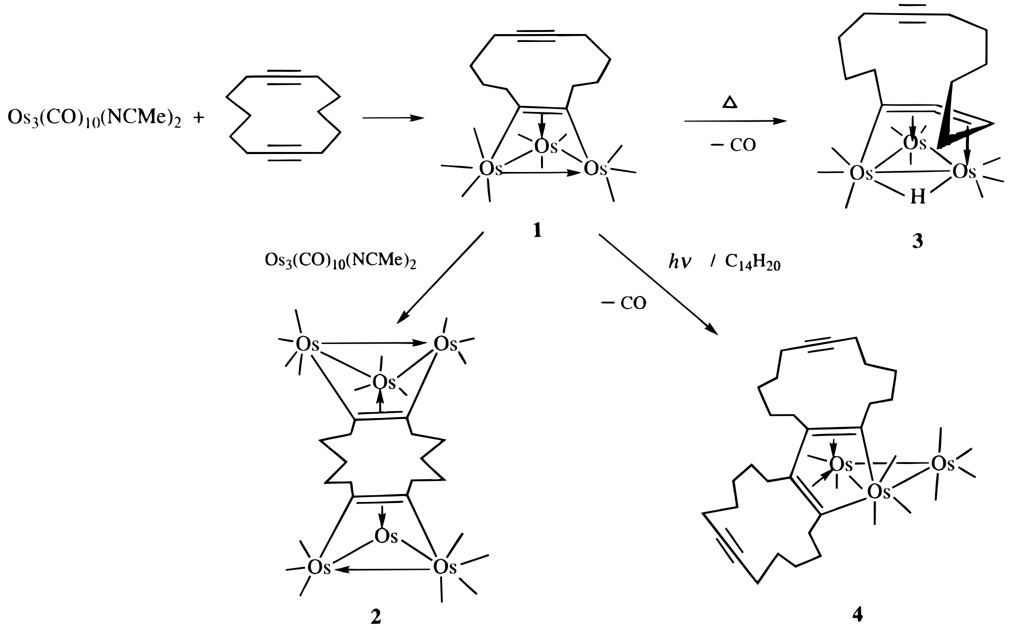
Scheme 1



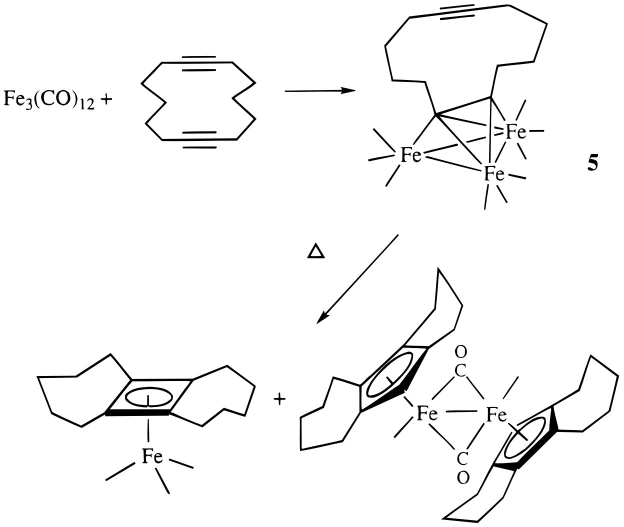
thus, in the course of the final structure factor calculation the program calculates the Flack[9] absolute structure factor *x* and its esd. A comparison of *x* with its esd provides an indication as to whether the refined absolute structure is correct or whether it has to be "inverted". The true value of *x* is close to zero.

Results and Discussion

Synthesis. The reactions of cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) and triosmium clusters are summarized in Scheme 1. $Os_3(CO)_{10}(NCMe)_2$ reacts with $C_{14}H_{20}$ in hot benzene to produce $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**; 86%) and the Os$_6$−diyne cluster $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**; 11%) after purification by TLC and recrystallization. Further treatment of **1** with $Os_3(CO)_{10}(NCMe)_2$ affords **2** in 53% yield, suggesting a stepwise formation of the compounds **1** and **2**. Preparation of $Os_3(CO)_{10}$(alkyne) complexes from $Os_3(CO)_{10}(NCMe)_2$ and the corresponding alkyne ligands is well-established,[10−15] whereas the cyclodiyne-bridged double cluster **2** is unprecedented.

Thermolysis of **1** in refluxing *n*-heptane (98 °C) leads to a CO loss together with an α-C−H bond activation of the alkyne ligand to form the hydrido allene complex $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**) in 90% yield. Analogous transformations were previously observed for thermal reaction of $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Me_2)$ to give $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}MeC{=}C{=}CH_2)$,[16] of $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2(C_2Et)Et)$ to give $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}(C_2Et)C{=}C{=}C(Me)H)$,[13c,17] and of $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Et_2)$ to give $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}EtC{=}C{=}C(Me)H)$,[18] while thermolysis of the diphenylacetylene complex $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)$ led only to decarbonylation to afford the highly reactive species $Os_3(CO)_9(C_2Ph_2)$.[19] On the other hand, $Fe_3(CO)_{12}$ reacts with $C_{14}H_{20}$ to generate $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**5**), which undergoes cluster fragmentation to produce $(\eta^4\text{-}C_4(C_{10}H_{20}))Fe(CO)_3$ and $[(\eta^5\text{-}C_5(C_9H_{18}))Fe(CO)_2]_2$ in refluxing heptane (Scheme 2). The last two compounds were previously reported by King[20] from the thermal

Scheme 2



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reaction of $Fe_3(CO)_{12}$ and cyclotetradeca-1,8-diyne, but the intermediate **5** was not observed in that study.

Photoirradiation of **1** in the presence of $C_{14}H_{20}$ ligand affords the osmacyclopentadienyl complex $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (**4**) in 48% yield, whereas co-thermolysis of **1** and $C_{14}H_{20}$ produces mainly **2**. Similar metallacyclopentadienyl complexes were obtained from thermal reactions of $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)$ with C_2R_2 (R = Ph, Me)[21−23] and of $Ru_3(CO)_8(\mu\text{-dppm})(\mu_3\text{-}\eta^2\text{-}C_2(CO_2Me)_2)$ with C_2Ph_2.[24]

Recently, the bis(alkyne) complexes $Os_3(CO)_8(C_2R_2)(C_2R'_2)$ (R, R′ = Me, Ph) were prepared by treating a solution of $Os_3(CO)_{10}(C_2R_2)$ in CH_2Cl_2 with Me_3NO/MeCN in the presence of $C_2R'_2$.[25] The molecular structure of $Os_3(CO)_8(C_2Ph_2)_2$[25a] shows the two alkyne ligands capping the opposite triosmium faces in a $\mu_3\text{-}\eta^2\text{-}\|$-mode. Our preliminary investigation on the reaction of **1** with Me_3NO indicates the formation of $[Os_3(CO)_8]_x$ oligomers linked by the cyclodiyne ligands. Further characterization of the products is under way.

Spectroscopic Characterization of New Compounds. Compounds **1**−**5** form air-stable crystalline solids and have been characterized by mass, IR, and NMR spectroscopy.

The FAB mass spectrum of **1** presents the molecular ion peak at *m/z* 1044 for ^{192}Os. The solution IR spectrum in the carbonyl region of **1** (Figure 1a) is in close agreement with those of mono(alkyne) complexes of the type $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C_2R_2)$ (R = Et,[12] CO_2Me[13b]), each of which contains a bridging CO ligand (ν(CO) ca. 1850 cm^{-1}) and has the coordinated alkyne C−C bond approximately parallel to an Os−Os edge. The ^1H and ^{13}C NMR data of **1** are consistent with a molecule of idealized C_s symmetry in solution. The ^{13}C resonances for the coordinated and free alkyne carbons are at δ 148.4 and 80.7, respectively, while the carbonyl ligands are fluxional at 23 °C to give one broad resonance at δ 178.

While **1** has a good solubility in common organic solvents, $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) is sparingly soluble in THF and dichloromethane. The FAB mass spectrum of **2** gives the molecular ion peak at *m/z* 1900 for ^{192}Os. Its NMR spectra displays only three sets of ^1H resonances at δ 2.14, 2.02, and 1.45 in a 2:2:1 ratio and four ^{13}C resonance signals at δ 150 (C≡C), 50.6, 42.2, and 34.0 for the $C_{14}H_{20}$ ligand, suggesting a symmetric structure for **2**. Since the solution IR spectrum does not present a clear absorption for bridging carbonyl, a single-crystal X-ray diffraction study of **2** was conducted.

$(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**) forms yellow crystals. Its FAB mass spectrum displays the molecular ion peak at *m/z*= 1016, which is 28 less than that of **1** to indicate a CO loss during the thermolysis process. The ^1H NMR spectrum of **3** shows a hydride resonance at δ −22.03 and a complex multiplet in the region δ 2.86−0.86 (19H), indicating a C−H activation of the diyne ligand on the cluster. A single-crystal X-ray diffraction study was performed for **3** to establish its structure.

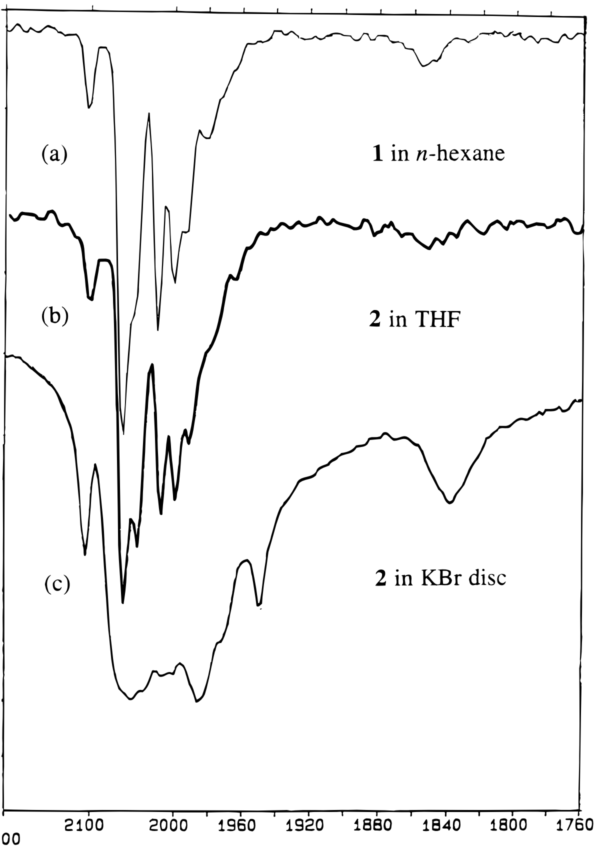

Figure 1. IR spectra in the carbonyl region: (a) $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**) in *n*-hexane solvent; (b) $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) in THF solvent; (c) $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) in a KBr disk.

$Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (**4**) forms purple crystals. Its intense color indicates the presence of a metallacycle.[26] The FAB mass spectrum of **4** displays the molecular ion peak at *m/z* 1204 corresponding to a CO loss (−28) plus a diyne ligand addition (+188) from **1**. The ^{13}C NMR spectrum shows resonances for free alkyne carbons at δ 81.9 and 80.0, while no resonances around δ 150 for coordinated alkyne carbons are observed. A single crystal of **4** was thus subjected to an X-ray diffraction analysis.

Compound **5** forms brown crystalline solids. The FAB spectrum shows the molecular ion peak at *m/z* 608 for ^{56}Fe. The IR absorptions in the carbonyl region shows a pattern similar to that recorded for $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2R_2)$ (R = Et,[27] Ph[28]), in which the alkyne triple bond is disposed above the Fe_3 plane and perpendicular to one of the Fe−Fe edges, with one acetylenic carbon in a μ_3 mode and the other in a μ_2 mode. The ^{13}C NMR spectrum of **5** includes two coordinated alkyne carbon resonances at δ 208.4 and 105.7 and two free alkyne carbon resonances at δ 81.8 and 79.3, consistent with the proposed structure.

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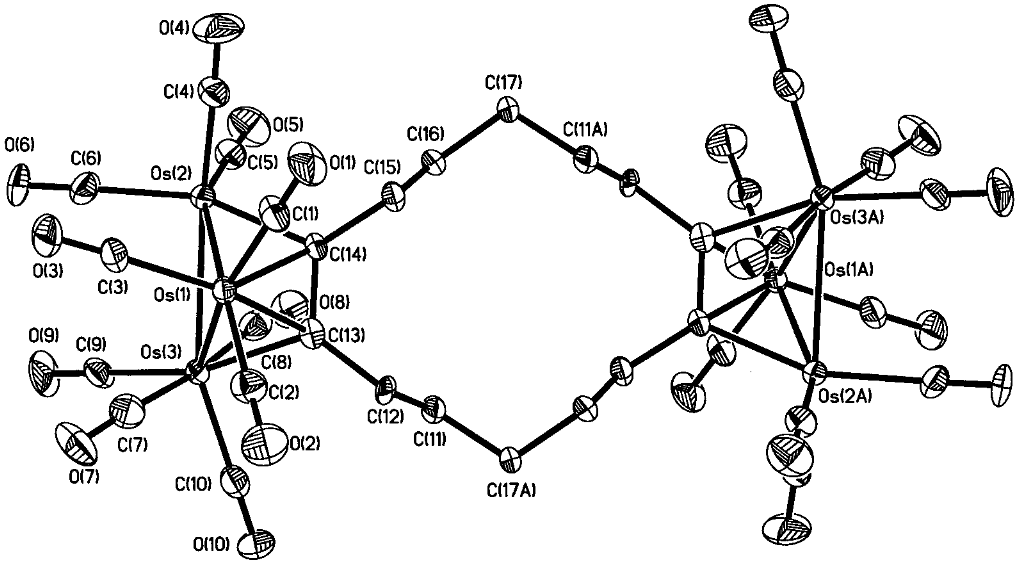

Figure 2. Molecular structure of $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**). The hydrogen atoms have been artificially omitted for clarity.

Crystal Structure of 2. Crystals of $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) contain an ordered array of discrete monomeric molecular units which are mutually separated by normal van der Waals distances. The ORTEP diagram (Figure 2) shows that the two alkyne triple bonds of the $C_{14}H_{20}$ ligand are each bonded to an $Os_3(CO)_{10}$ cluster in a μ_3-η^2 mode. There is a crystallographic center of symmetry imposed on the molecule. Important interatomic distances and intramolecular angles are collected in Table 2.

The metal parts are based upon a triangular array of osmium atoms in which the Os(3)−Os(2) interaction is properly described as a dative bond by donating two nonbonding electrons from Os(3) to Os(2) to satisfy the 18-electron rule for each osmium atom. The distances of the electron-rich Os(3) atom to Os(2) and Os(1) atoms at 2.8776(5) and 2.8570(5) Å, respectively, are significantly longer than the Os(1)−Os(2) distance of 2.7087(6) Å. The alkyne C(13)−C(14) unit is asymmetrically bonded to three osmium atoms, formally forming a π bond to Os(1) and σ bonds to Os(2) and Os(3). The donor ability of the alkyne ligand is weaker to the electron-rich metal Os(3), with a length of 2.21(1) Å to C(13), than to electron-deficient Os(2), with an Os(2)−C(14) length of 2.11(1) Å. In return, the Os(1)−C(13) distance (2.153(9) Å) is significantly shorter than the Os(1)−C(14) distance (2.29(1) Å). The C(13)−C(14) vector is slightly tilted (4.2°) with respect to the Os(3)−Os(2) edge. The C(13), C(14), Os(2), and Os(3) atoms are coplanar to within 0.08 Å, and the dihedral angle between this plane and the triosmium plane is 56.6°.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $(Os_3(CO)_{10})_2(\mu_3,\mu_3\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (2)

Distances			
Os(1)−Os(2)	2.7087(6)	Os(1)−Os(3)	2.8570(5)
Os(2)−Os(3)	2.8776(5)	Os(1)−C(1)	1.88(1)
Os(1)−C(2)	1.94(1)	Os(1)−C(3)	1.91(1)
Os(2)−C(4)	1.90(1)	Os(2)−C(5)	1.87(1)
Os(2)−C(6)	1.97(1)	Os(3)−C(7)	1.95(2)
Os(3)−C(8)	1.98(1)	Os(3)−C(9)	1.97(1)
Os(3)−C(10)	1.94(1)	C(1)−O(1)	1.14(1)
C(2)−O(2)	1.13(1)	C(3)−O(3)	1.13(1)
C(4)−O(4)	1.13(1)	C(5)−O(5)	1.18(2)
C(6)−O(6)	1.10(1)	C(7)−O(7)	1.15(2)
C(8)−O(8)	1.12(1)	C(9)−O(9)	1.12(1)
C(10)−O(10)	1.13(1)	Os(1)−C(13)	2.153(9)
Os(1)−C(14)	2.29(1)	Os(2)−C(14)	2.11(1)
Os(3)−C(13)	2.21(1)	C(11)−C(12)	1.52(1)
C(11)−C(17A)	1.53(1)	C(12)−C(13)	1.52(1)
C(13)−C(14)	1.41(1)	C(14)−C(15)	1.53(1)
C(15)−C(16)	1.54(1)	C(16)−C(17)	1.53(1)
Angles			
Os(1)−Os(2)−Os(3)	61.43(1)	Os(1)−Os(3)−Os(2)	56.37(1)
Os(2)−Os(1)−Os(3)	62.20(1)	Os(1)−C(1)−O(1)	178(1)
Os(1)−C(2)−O(2)	178(1)	Os(1)−C(3)−O(3)	178(1)
Os(2)−C(4)−O(4)	178(1)	Os(2)−C(5)−O(5)	178(1)
Os(2)−C(6)−O(6)	179(1)	Os(3)−C(7)−O(7)	166(1)
Os(3)−C(8)−O(8)	171(1)	Os(3)−C(9)−O(9)	179.8(9)
Os(3)−C(10)−O(10)	179(1)	C(1)−Os(1)−C(3)	90.6(5)
C(1)−Os(1)−C(2)	90.4(5)	C(3)−Os(1)−C(2)	103.1(5)
C(1)−Os(1)−Os(3)	158.0(3)	C(2)−Os(1)−Os(2)	163.2(3)
C(3)−Os(1)−C(13)	152.6(5)	C(3)−Os(1)−C(14)	134.5(5)
C(4)−Os(2)−C(5)	93.0(5)	C(4)−Os(2)−C(6)	94.4(5)
C(5)−Os(2)−C(6)	97.6(5)	C(4)−Os(2)−Os(3)	156.5(4)
C(5)−Os(2)−Os(1)	156.2(4)	C(6)−Os(2)−C(14)	157.2(4)
C(7)−Os(3)−C(8)	172.8(5)	C(7)−Os(3)−C(9)	84.1(5)
C(7)−Os(3)−C(10)	91.5(5)	C(8)−Os(3)−C(9)	90.0(5)
C(8)−Os(3)−C(10)	93.6(5)	C(9)−Os(3)−C(10)	98.9(5)
C(7)−Os(3)−C(13)	103.3(5)	C(7)−Os(3)−Os(1)	65.1(4)
C(8)−Os(3)−Os(2)	71.7(3)	C(8)−Os(3)−C(13)	81.3(4)
C(9)−Os(3)−C(13)	164.0(4)	C(9)−Os(3)−Os(2)	95.5(3)
Os(2)−Os(3)−C(13)	69.0(3)	Os(2)−C(14)−C(13)	111.5(7)
Os(2)−C(14)−C(15)	125.2(7)	Os(3)−Os(2)−C(14)	70.7(3)
Os(3)−C(13)−C(14)	106.9(7)	Os(3)−C(13)−C(12)	124.0(6)
C(13)−C(14)−Os(2)	111.5(7)	C(13)−C(14)−C(15)	123.2(9)
C(13)−Os(1)−C(14)	36.9(4)	C(14)−C(13)−Os(3)	106.9(7)
C(14)−C(13)−C(12)	124.7(9)		

The Os(1) and Os(2) atoms are each linked to three terminal carbonyl ligands, with the Os−CO lengths in the range 1.87(1)−1.97(1) Å and the Os−C−O angles in the range 178(1)−179(1)°. Four carbonyl ligands are bonded to the Os(3) atom with slightly longer Os−C lengths, ranging from 1.94(1) to 1.98(1) Å. The Os(3)−C(9)−C(9) and Os(3)−C(10)−C(10) angles are 179(1)°, while the Os(3)−C(7)−O(7) and Os(3)−C(8)−O(8) angles are 166(1) and 171(1)°, respectively. The last two Os−C−O angles deviate slightly but significantly from linearity and show weak bonding with the adjacent Os atoms, such as Os(1)···C(7) = 2.65(1) Å and Os(2)···C(8) = 2.95(1) Å, clearly indicating a semibridging interaction.[29] The crystal structure of the diphenylacetylene

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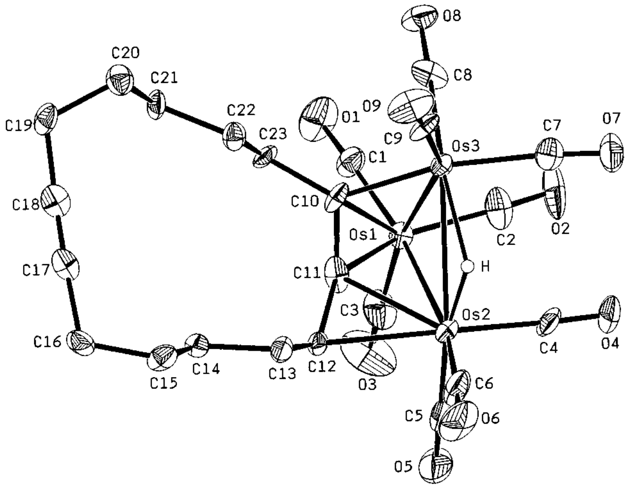

Figure 3. Molecular structure of $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**). The hydrogen atoms, except the bridging hydride, have been artificially omitted for clarity.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (3)

Distances			
Os(1)−Os(2)	2.807(1)	Os(1)−Os(3)	2.793(3)
Os(2)−Os(3)	2.992(1)	Os(1)−C(1)	1.89(2)
Os(1)−C(2)	1.95(2)	Os(1)−C(3)	1.91(2)
Os(2)−C(4)	1.89(1)	Os(2)−C(5)	1.89(2)
Os(2)−C(6)	1.92(2)	Os(3)−C(7)	1.96(2)
Os(3)−C(8)	1.85(2)	Os(3)−C(9)	1.91(2)
Os(2)−H	1.4(1)	Os(3)−H	1.9(1)
C(1)−O(1)	1.14(2)	C(2)−O(2)	1.11(2)
C(3)−O(3)	1.12(2)	C(4)−O(4)	1.13(2)
C(5)−O(5)	1.18(2)	C(6)−O(6)	1.11(2)
C(7)−O(7)	1.13(2)	C(8)−O(8)	1.15(2)
C(9)−O(9)	1.12(2)	Os(1)−C(10)	2.30(1)
Os(1)−C(11)	2.10(1)	Os(2)−C(11)	2.27(2)
Os(2)−C(12)	2.34(1)	Os(3)−C(10)	2.05(1)
C(10)−C(11)	1.41(2)	C(10)−C(23)	1.49(2)
C(11)−C(12)	1.40(2)	C(12)−C(13)	1.45(2)
C(17)−C(18)	1.17(2)		
Angles			
Os(2)−Os(1)−Os(3)	64.61(3)	Os(1)−Os(2)−Os(3)	57.47(3)
Os(1)−Os(3)−Os(2)	57.92(2)	Os(2)−Os(1)−C(1)	163.8(5)
Os(3)−Os(1)−C(3)	162.4(6)	C(1)−Os(1)−C(2)	94.6(7)
C(1)−Os(1)−C(3)	91.4(8)	C(2)−Os(1)−C(3)	97.1(7)
C(10)−Os(1)−C(11)	36.9(6)	Os(1)−Os(2)−C(6)	166.1(5)
Os(1)−Os(2)−C(11)	47.5(3)	Os(1)−Os(2)−C(12)	78.5(4)
Os(3)−Os(2)−C(4)	87.9(4)	Os(3)−Os(2)−C(5)	148.9(6)
Os(3)−Os(2)−C(11)	63.5(4)	Os(3)−Os(2)−C(12)	93.6(3)
Os(3)−Os(2)−H	28(5)	C(4)−Os(2)−C(5)	91.4(6)
C(4)−Os(2)−C(6)	96.7(7)	C(4)−Os(2)−C(11)	140.9(6)
C(4)−Os(2)−C(12)	171.6(6)	C(5)−Os(2)−C(6)	94.9(8)
C(11)−Os(2)−C(12)	35.4(5)	Os(1)−Os(3)−C(9)	154.2(4)
Os(1)−Os(3)−C(10)	54.1(4)	Os(2)−Os(3)−C(10)	73.7(4)
Os(2)−Os(3)−H	20(4)	C(7)−Os(3)−C(8)	92.5(7)
C(7)−Os(3)−C(9)	95.1(7)	C(7)−Os(3)−C(10)	163.8(6)
C(8)−Os(3)−C(9)	95.0(6)	Os(1)−C(1)−O(1)	178(1)
Os(1)−C(2)−O(2)	178(2)	Os(1)−C(3)−O(3)	179(2)
Os(2)−C(4)−O(4)	177(1)	Os(2)−C(5)−O(5)	178(2)
Os(2)−C(6)−O(6)	176(1)	Os(3)−C(7)−O(7)	175(1)
Os(3)−C(8)−O(8)	178(1)	Os(3)−C(9)−O(9)	177(1)
Os(3)−C(10)−C(23)	133(1)	C(11)−C(10)−C(23)	118(1)
C(10)−C(11)−C(12)	143(1)	Os(2)−C(12)−C(11)	69.7(8)
Os(2)−C(12)−C(13)	120(1)	C(11)−C(12)−C(13)	122(1)
C(16)−C(17)−C(18)	178(2)	C(17)−C(18)−C(19)	177(2)
Os(2)−H−Os(3)	130(8)		

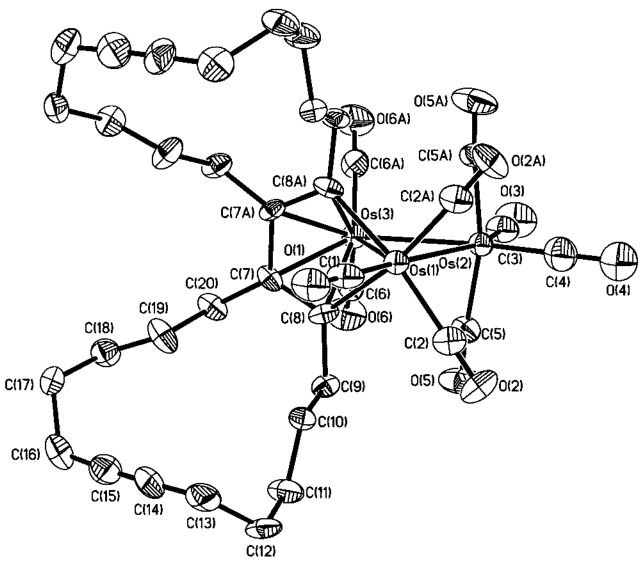

Figure 4. Molecular structure of $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (**4**). The hydrogen atoms have been artificially omitted for clarity.

complex $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)$ has been illustrated[11] to exhibit two semibridging CO ligands but with the two long Os···C distances being roughly equal (2.77 and 2.75 Å). , In contrast, the analogous 3-hexyne complex $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Et_2)$ displays only one symmetrically bridging CO ligand.

However, it is noteworthy that the IR spectrum of **2** in THF solvent shows a very weak absorption at 1854 cm^{-1}, while its solid-state spectrum in a KBr disk displays a broad peak at 1840 cm^{-1} (Figure 1c), characteristic of a bridging CO ligand. In contrast, the IR spectrum of $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)$ in the solid state shows no CO absorptions below 1920 cm^{-1}.[11,13b] It is likely that two energetically comparable structures, with one containing two semibridging CO ligands as determined and the other containing one bridging CO ligand as $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Et_2)$, are present for **2** to account for the IR data, while a single crystal of **2** with the former structure was chosen by chance for analysis. We have recently prepared the analogous complex $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_{14}H_{20}(Cp_2Mo_2(CO)_4))$, the crystal structure of which shows one CO ligand bridging an Os−Os edge.[30]

Crystal Structure of 3. The ORTEP drawing of $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{14}H_{19})$ (**3**) is shown in Figure 3. Selected bond distances and bond angles are given in Table 3.

The molecule is based on a triangular array of osmium atoms in which the dibridged Os(2)−Os(3) distance of 2.992(1) Å is significantly longer than the other two intermetallic distances (*i.e.* an Os(1)−Os(3) distance of 2.793(1) Å and an Os(1)−Os(2) distance of 2.807(1) Å). Each osmium atom is associated with three terminal carbonyl ligands. The Os−CO distances range from 1.85(2) Å (Os(3)−C(8)) through 1.96(2) Å (Os(3)−C(7)), while the Os−C−O angles are in the range 175(1)−179(2)°. The Os(2)−Os(3) edge is bridged by a hydride ligand, which is tilted 19° out of the triosmium plane away from the allene ligand.

The allene unit C(10)~C(12) can be described as forming a σ bond to the Os(3) atom (Os(3)−C(10) = 2.05-

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Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (4)

Distances			
Os(1)−Os(2)	2.9286(9)	Os(1)−Os(3)	2.7431(9)
Os(2)−Os(3)	2.7318(9)	Os(1)−C(1)	1.86(2)
Os(1)−C(2)	1.96(2)	Os(1)−C(8)	2.18(1)
Os(2)−C(3)	1.87(2)	Os(2)−C(4)	1.82(3)
Os(2)−C(5)	1.91(1)	Os(3)−C(6)	1.86(1)
Os(3)−C(7)	2.263(9)	Os(3)−C(8)	2.25(1)
C(1)−O(1)	1.18(2)	C(2)−O(2)	1.12(2)
C(3)−O(3)	1.17(2)	C(4)−O(4)	1.30(3)
C(5)−O(5)	1.15(1)	C(6)−O(6)	1.14(2)
C(7)−C(8)	1.40(2)	C(7)−C(7A)	1.47(2)
C(7)−C(20)	1.56(2)	C(8)−C(9)	1.53(1)
C(14)−C(15)	1.23(2)		
Angles			
Os(2)−Os(1)−Os(3)	57.47(2)	Os(1)−Os(2)−Os(3)	57.85(2)
Os(1)−Os(3)−Os(2)	64.68(3)	C(1)−Os(1)−C(2)	94.9(6)
C(2)−Os(1)−C(2A)	98.2(8)	C(2)−Os(1)−C(8A)	168.5(4)
C(1)−Os(1)−C(8)	88.0(6)	C(2)−Os(1)−C(8)	92.7(5)
C(8)−Os(1)−C(8A)	76.3(5)	C(2)−Os(1)−Os(3)	117.7(4)
C(8)−Os(1)−Os(3)	52.8(3)	C(1)−Os(1)−Os(2)	175.3(7)
C(2)−Os(1)−Os(2)	82.0(3)	C(8)−Os(1)−Os(2)	95.8(3)
C(4)−Os(2)−C(3)	97(1)	C(4)−Os(2)−C(5)	97.1(5)
C(3)−Os(2)−C(5)	90.1(4)	C(5A)−Os(2)−C(5)	165.8(9)
C(4)−Os(2)−Os(3)	162.8(7)	C(3)−Os(2)−Os(3)	100.4(8)
C(5)−Os(2)−Os(3)	83.0(4)	C(4)−Os(2)−Os(1)	104.9(7)
C(3)−Os(2)−Os(1)	158.3(8)	C(5)−Os(2)−Os(1)	87.3(4)
C(6A)−Os(3)−C(6)	93.2(9)	C(6A)−Os(3)−C(8)	161.9(5)
C(6)−Os(3)−C(8)	94.6(5)	C(8)−Os(3)−C(8A)	73.6(5)
C(6)−Os(3)−C(7)	97.0(4)	C(8)−Os(3)−C(7)	36.2(4)
C(8A)−Os(3)−C(7)	65.4(4)	C(6)−Os(3)−C(7A)	126.5(5)
C(6)−Os(3)−Os(2)	95.6(4)	C(8)−Os(3)−Os(2)	99.9(3)
C(7)−Os(3)−Os(2)	135.0(3)	C(6)−Os(3)−Os(1)	131.0(5)
C(8)−Os(3)−Os(1)	50.7(3)	C(7)−Os(3)−Os(1)	74.6(3)
Os(1)−C(1)−O(1)	179(2)	Os(1)−C(2)−O(2)	179(1)
Os(2)−C(3)−O(3)	180(2)	Os(2)−C(4)−O(4)	180(2)
Os(2)−C(5)−O(5)	175(1)	Os(3)−C(6)−O(6)	178(1)
C(8)−C(7)−C(7A)	115.8(6)	C(8)−C(7)−C(20)	124(1)
C(7A)−C(7)−C(20)	120.5(6)	C(8)−C(7)−Os(3)	71.3(6)
C(7)−C(8)−C(9)	123(1)	C(7)−C(8)−Os(1)	115.4(7)
C(9)−C(8)−Os(1)	119.0(8)	C(15)−C(14)−C(13)	179(2)
C(14)−C(15)−C(16)	176(2)		

(1) Å) and two π bonds from C(10)═C(11) to Os(1) and C(11)═C(12) to Os(2) with Os(1)−C(10) = 2.30(1) Å, Os(1)−C(11) = 2.10(1) Å, Os(2)−C(11) = 2.27(2) Å, and Os(2)−C(12) = 2.34(1) Å. The atoms C(10), C(11), Os(2), and Os(3) are coplanar to within 0.05 Å (plane 1). The dihedral angle between plane 1 and the Os(1), Os(2), Os(3) plane is 56.1°, and that between plane 1 and the C(11), C(12), Os(2)plane is 34.0°. The C(10)−C(11) and C(11)−C(12) distances of 1.41(2) and 1.40(2) Å are characteristic of an alkene C═C bond π-coordinated to a transition metal. The uncoordinated alkyne C(17)−C(18) length is 1.17(2) Å.

Crystal Structure of 4. An ORTEP diagram of $Os_3(CO)_9(\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2)$ (**4**) is shown in Figure 4. There are no abnormally short intermolecular contacts. A plane of symmetry is passing through the triosmium framework. Selected bond distances and bond angles are collected in Table 4.

The molecule is formally derived from $Os_3(CO)_{12}$, but with three carbonyls being replaced by a six-electron-donating $\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2$ ligand (yielding an osmacyclopentadienyl fragment). The Os−Os distances show substantial variation, with Os(1)−Os(2) = 2.9286(9) Å, Os(1)−Os(3) = 2.7431(9) Å, and Os(2)−Os(3) = 2.7318(9) Å. The Os(1), Os(2), and Os(3) atoms are each linked to three, four, and two terminal CO ligands, respectively. The average of the Os−CO distances is 1.90 ± 0.08 Å, with C−O = 1.21 ± 0.09 Å; all Os−C−O systems are close to linear (175(1)−180(2)°).

The $\mu\text{-}\eta^4\text{-}C_4(C_{12}H_{20})_2$ ligand forms a σ-bond to Os(1) (Os(1)−C(8) = 2.18(1) Å) and two π-bonds to Os(3) (Os(3)−C(7) = 2.263(9) Å and Os(3)−C(8) = 2.25(1) Å). The C(7), C(7A), C(8), C(8A), and Os(1) atoms are coplanar to within 0.06 Å. The carbon atoms connected to the metallacyclic ring are not eclipsed, as evidenced by the torsional angle C(9)−C(8)-C(7)−C(20) = 12.8°. The carbon−carbon distances within the metallacycle are C(7)−C(8) = 1.40(2) Å and C(7)−C(7A) = 1.47(2) Å. The uncoordinated alkyne C(14)−C(15) distance is 1.23(2) Å.

Conclusions

Several interesting triosmium carbonyl clusters containing cyclotetradeca-1,8-diyne ligands have been prepared and structurally characterized. A unique feature of **1**, **3**, **4**, and **5** is their pendant alkyne moieties which are capable of binding other metal fragments, such as $Cp_2Mo_2(CO)_4$, $Co_2(CO)_6$, and $Os_3(CO)_{10}$, to form higher nuclearity mixed-metal clusters or cluster oligomers. Further studies aimed at investigating these reactions are in progress.

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Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond lengths, and bond angles of **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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