

Reactions of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with Conjugated Diynes ($\text{RC}_2\text{C}_2\text{R}'$) Containing Nucleophilic Oxygen in β Position of a Substituent ($\text{R} = \text{Ph}$, $\text{R}' = \text{CH}_2\text{OH}$, $\text{C}(\text{O})\text{Ph}$; $\text{R} = \text{R}' = \text{CMe}_2(\text{OH})$)

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Reactions of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with a series of diynes, $\text{RC}_2\text{C}_2\text{R}'$ (**1**: $\text{R} = \text{Ph}$, $\text{R}' = \text{CH}_2\text{OH}$; **2**: $\text{R} = \text{Ph}$, $\text{R}' = \text{C}(\text{O})\text{Ph}$; **3**: $\text{R} = \text{R}' = \text{C}(\text{OH})\text{Me}_2$), have been studied. It was found that upon coordination to the triosmium cluster, the nucleophilic oxygens of the R' substituents of **1** and **2** take part in intramolecular cyclization reactions to give $[\text{HOs}_3(\text{CO})_{10}\{\mu\text{-}\eta^1\text{-}\eta^2\text{-PhCH}_2\text{-}(\text{C}=\text{CH}-\text{C}=\text{CH}-\text{O})\}]$ (**5**) and $[\text{HOs}_3(\text{CO})_{10}\{\mu\text{-}\eta^1\text{-}\eta^1\text{-Ph}(\text{C}=\text{CH}-\text{C}=\text{C}-\text{O})\text{CPh}\}]$ (**6**), respectively, both of which contain furan rings coordinated to the cluster core. On heating of the latter compound, the furan moiety remains intact, but a carbonyl group dissociates from the cluster, leading to the formation of $[\text{HOs}_3(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^3\text{-}\eta^1\text{-Ph}(\text{C}=\text{CH}-\text{C}=\text{C}-\text{O})\text{CPh}\}]$ (**7**) with a closed “ C_3Os_3 ” pentagonal pyramidal structure. Reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with **3** does not lead to cyclization of the diyne; instead, the clusters $[\text{Os}_3(\text{CO})_{10}\{\mu_3\text{-}\eta^2\text{-}(\text{RCH}=\text{CH}-\text{C}_2\text{R})\}]$ (**8**) and $[\text{Os}_3(\text{CO})_{10}\{\mu_3\text{-}\eta^2\text{-}(\text{RC}_2\text{C}_2\text{R})\}]$ (**9**) are formed. Deuterium labeling of the starting compounds has been used in the reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $\text{HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH}$ in order to investigate possible mechanisms of the cyclization reaction. The crystal and molecular structures of clusters **5**, **7**, and **9** are presented.

Introduction

Because of the synthetic usefulness of 1,3-conjugated diynes, their reactions with transition metal clusters have received increased attention in recent years.^{1–15}

Several studies have shown that coordination of diynes to transition metal carbonyl clusters is often accompanied by rearrangement of these ligands. Such rearrangements include C–C bond rupture,^{1,3} ligand coupling,^{4,10,11,13,14} and intramolecular cyclization reactions.^{7,12,14} Recent results have shown that a cyclized diyne may be decoordinates from a cluster under the

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proper reaction conditions.¹⁶ The elucidation of the reaction mechanisms that occur in these processes may facilitate the development of new rational synthetic strategies aimed at producing novel organic chemicals.

In previous papers,^{6,15,17} we have demonstrated that conjugated diynes containing an electrophilic center in the β position of a substituent readily rearrange to form (coordinated) five-membered cycles in reactions with $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$. General mechanistic schemes have been proposed^{15,17} in order to clarify the trend of the diynes to form five-membered rings upon coordination and to explain variations in coordination modes of the rearranged diynes on the osmium triangle. It has been shown that the cyclization proceeds via nucleophilic attack of the β atom of a substituent on the coordinated diyne chain to give five-membered nitrogen-containing heterocycles¹⁷ or indenyl systems¹⁵ bound to the trinuclear cluster cores in $\mu\text{-}\eta^1\text{:}\eta^2\text{-}$, $\mu\text{-}\eta^1\text{:}\eta^1\text{-}$, or $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}$ modes. In the present study, reactions of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with three conjugated diynes, $\text{RC}_2\text{C}_2\text{R}'$ (**1**: $\text{R} = \text{Ph}$, $\text{R}' = \text{CH}_2\text{OH}$; **2**: $\text{R} = \text{Ph}$, $\text{R}' = \text{C}(\text{O})\text{Ph}$; **3**: $\text{R} = \text{R}' = \text{C}(\text{OH})\text{Me}_2$) are presented.

Experimental Section

General Comments. The starting materials $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$,¹⁸ 5-phenylpenta-2,4-diyne-1-ol (**1**), 4-phenylbutadienylphenyl ketone (**2**), and 2,7-dimethyl-3,5-octadiyne-2,7-diol (**3**) were prepared according to published procedures.¹⁹ Commercial 2,4-hexadiyne-1,6-diol (**4**) (Aldrich) was used as received. D_2 was purchased from AGA Gas. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using solvents that were freshly distilled from appropriate drying agents. Deuterated dichloromethane was carefully dried over molecular sieves directly before the experiments with deuterated compounds in order to avoid isotopic exchange processes due to the adventitious presence of water. Blank experiments in which individual deuterium-labeled components of the reaction mixture were dissolved in dried CD_2Cl_2 showed no change in the deuterium enrichment during 12 h. Infrared spectra were recorded using Nicolet Avatar 360 FTIR and Specord M80 spectrometers. Electron impact and fast atom bombardment (FAB+) mass spectra were obtained on JEOL SX-102 and MX-1321 instruments; 3-nitrobenzyl alcohol was used as a matrix and CsI as the calibrant. ^1H NMR spectra were recorded on Varian Unity 300 MHz and Bruker DX 300 spectrometers; ^{13}C NMR spectra, on a Bruker AM 500 instrument using the solvent resonance as an internal standard and $[\text{Cr}(\text{acac})_3]$ as relaxant. DEPT-135 spectra were used to assign CH, CH_2 , and CH_3 resonances. Thin-layer chromatography was performed on commercial plates precoated with Merck Kieselgel 60 to 0.5 mm thickness, and silica 5–40 mesh was used for flash chromatography separation of the reaction mixtures; the bands obtained are reported in order of elution. Microanalyses were carried out in the Analytical Laboratories of St. Petersburg State University and University of Joensuu.

Deuteration of 2,4-Hexadiyne-1,6-diol and $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$. To prepare deuterium-enriched 2,4-hexadiyne-1,6-diol (**4**) (in the OH positions), the diyne was dissolved in CD_3OD and left overnight. The solvent was then removed and the deuterium enrichment was controlled by EI mass spectrom-

etry, which indicated 80% enrichment. The deuterated cluster $[\text{D}_2\text{Os}_3(\text{CO})_{10}]$ was obtained by direct reaction of gaseous D_2 with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ in dichloromethane at room temperature, which gave ca. 50% deuterium enrichment of the starting cluster.

Reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{OH}$ (1**).** $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ (250 mg, 0.29 mmol) and **1** (99 mg, 0.64 mmol) were dissolved in 10 cm^3 of dichloromethane and left overnight at room temperature. After removal of the solvent, the residue was dissolved in a minimum amount of CHCl_3 and separated by preparative TLC using a hexane/chloroform mixture (2:1, v/v). Orange, solid $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{:}\eta^2\text{-PhCH}_2\text{C}=\text{CH}-\text{C}=\text{CH}-\text{O})]$ (**5**) was isolated as the main product (R_f 0.67, 98.2 mg, 33.3%). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2104w, 2066vs, 2052s, 2018s, 2008m. ^1H NMR (CDCl_3): δ 7.37–6.73 (m, 5H, phenyl), 7.96, 6.27 (1H, 1H, protons of the furan ring), 3.92 (s, 2H, CH_2), –16.10 (s, 1H, $\mu\text{-HOs}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): δ 183.8 (1CO), 179.1 (2CO), 177.8 (1CO), 173.7 (2CO), 173.1 (2CO), 169.1 (2CO); 163.0, 134.1, 137.5 (C(16), C(13), C(15), cf. Figure 1); 124–134 (7C: CH carbons of phenyl ring and C(12), C(14)); 69.6 (s, CH_2). FAB-MS (m/z): 1008 $[\text{M}^+]$ ($\text{Os}_3 = 570$) and $[\text{M}^+ - n\text{CO}]$, $n = 1-10$. Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{O}_1\text{Os}_3$: C, 25.00; H, 1.00. Found: C, 25.30; H, 1.17. Single crystals of **5** suitable for X-ray analysis were grown by slow diffusion of heptane into diethyl ether at 4 °C.

Reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CO})\text{Ph}$ (2**).** $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ (50 mg, 0.06 mmol) and **2** (20 mg, 0.09 mmol) were dissolved in 5 cm^3 of CH_2Cl_2 and stirred for 3 h at room temperature. After removal of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2 and separated by preparative TLC using a hexane/dichloromethane mixture (3:1, v/v) as eluant. Violet solid $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}(\text{C}=\text{CH}-\text{C}=\text{C}-\text{O})\text{CPh})]$ (**6**) was isolated as the main product (R_f 0.6, 64 mg, 98.6%). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2102m, 2054s, 2024m, 2010m, 1842w. ^1H NMR (CDCl_3): δ 7.82–7.28 (m, 11H, two phenyl rings and CH of the furan system), –14.86 (s, 1H, $\mu\text{-HOs}$). FAB-MS (m/z): 1082 $[\text{M}^+]$ ($\text{Os}_3 = 570$) and $[\text{M}^+ - n\text{CO}]$, $n = 1-10$. $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 298 K): δ 211.1 ($\mu\text{-CO}$); 190.5, 184.7, 184.5, 182.5, 178.9, 178.4, 177.9, 177.1, 174.4 (nine terminal CO); 173.9, 172.5, 172.3, 167.8 (three carbons of the furan ring and C(Ph)); 152.5, 127.3 (*ipso*-C of two phenyl rings); 129.4 (2C), 127.9 (2C), 127.7 (2C), 123.3 (2C) (*ortho* and *meta* carbons of two phenyl rings); 129.3 (1C), 127.8 (1C) (*para* carbons of two phenyl rings); 132.6 (1C) furan CH carbon. The latter seven signals appear as positive phase resonances in the DEPT-135 spectrum. Anal. Calcd for $\text{C}_{27}\text{H}_{12}\text{O}_1\text{Os}_3$: C, 29.94; H, 1.12. Found: C, 30.18; H, 1.42. Single crystals of **6** suitable for an X-ray analysis were grown by slow diffusion of hexane in dichloromethane at –20 °C.

Thermolysis of $[\text{HOs}_3(\text{CO})_{10}(\mu_2, \eta^3\text{-Ph}(\text{C}=\text{CH}-\text{C}=\text{C}-\text{O})\text{-CPh})]$ (6**).** Compound **6** (30 mg) was refluxed in hexane for 3 h until a TLC spot test showed complete consumption of the starting compound. Yellow, solid $[\text{HOs}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^1\text{-Ph}(\text{C}=\text{CH}-\text{C}=\text{C}-\text{O})\text{CPh})]$ (**7**) was isolated as the only product of reaction by preparative TLC, using a hexane/dichloromethane mixture (4:1, v/v) as eluant (R_f 0.75, 29.0 mg, 99.2%). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2100m, 2056s, 2024m, 2008m. ^1H NMR (CDCl_3): δ 7.85–7.30 (m, 11H, two phenyl rings and CH of the furan system), –19.59 (s, 1H, $\mu\text{-HOs}$). FAB-MS (m/z): 1054 $[\text{M}^+]$ ($\text{Os}_3 = 570$) and $[\text{M}^+ - n\text{CO}]$, $n = 1-9$. $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 298 K): δ 179.4 (1CO), 178.6 (1CO), 175.2 (1CO), 174.9 (3CO), 173.5 (1CO), 171.8 (2CO); 164.6 (C(12), cf. Figure 3); 147.9, 147.8, 146.2 (C(11), C(13), C(15)); 139.1 (C(16)); 129.1 (C(17)); 131.7, 130.8, 129.4, 129.0, 128.4, 126.2, 121.5 (CH carbons of two phenyl rings and C(14)). Anal. Calcd for $\text{C}_{26}\text{H}_{12}\text{O}_1\text{Os}_3$: C, 29.60; H, 1.15. Found: C, 29.80; H, 1.56. Single crystals of **7** suitable for X-ray analysis were grown from heptane at 25 °C.

Reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $\text{Me}_2(\text{HO})\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}(\text{OH})\text{Me}_2$ (3**).** $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ (250 mg, 0.29 mmol) and **3** (98 mg, 0.59 mmol) were dissolved in 20 cm^3 of dichloromethane. IR spectroscopy indicated that the reaction was

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Table 1. Crystallographic Data for $[HOs_3(CO)_{10}(\mu-\eta^1:\eta^2-PhCH_2C=CH-C=CH-O)]$ (5**), $[HOs_3(CO)_9(\mu_3-\eta^1:\eta^3:\eta^1-Ph(C=CH-C=C-O)CPh)]$ (**7**), and $[Os_3(CO)_{10}(\mu_3-\eta^2-Me_2(HO)C-C\equiv C-C\equiv C-C(OH)Me_2)]$ (**9**)**

	5	7	9
empirical formula	$C_{21}H_{10}O_{11}Os_3$	$C_{26}H_{12}O_{10}Os_3$	$C_{26}H_{20}O_{12}Os_3$
fw	1008.89	1054.96	1095.02
cryst size, mm	$0.07 \times 0.05 \times 0.05$	$0.20 \times 0.10 \times 0.05$	$0.30 \times 0.10 \times 0.10$
temperature, K	100(1)	120(2)	120(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	orthorhombic, $P2_12_12_1$
a, Å	9.3500(4)	8.4266(2)	9.2706(1)
b, Å	22.1418(6)	9.5776(3)	15.1508(4)
c, Å	11.5436(5)	17.2474(5)	20.4703(5)
α , deg	90	83.151(2)	90
β , deg	100.337(2)	83.457(2)	90
γ , deg	90	67.702(2)	90
volume, Å ³	2351.03(16)	1275.12(6) (15)	2875.20(11)
Z, calcd density, Mg/m ³	4, 2.850	2, 2.748	4, 2.530
no. of reflns collected	15820	14510	37545
no. of unique reflns	4780	4452	6265
R_{int}	0.093	0.0513	0.0596
$R_1 [I > 2\sigma(I)]$	0.0368	0.0391	0.0225
$wR_2 [I > 2\sigma(I)]$	0.0714	0.1022	0.0419
largest diff peak and hole, e/Å ⁻³	2.532 and -1.269	2.934 and -2.820	0.811 and -0.784

complete within 3 h. The obtained mixture was "pre-separated" using flash-chromatography (silica 5–40 mesh). Flash elution with hexane/chloroform (1:1, v/v) gave a dark green band containing a very unstable green compound, ca. 50 mg, which could not be isolated in pure form, and minor decomposition products. Further flash elution with pure chloroform gave a mixture of two products, **8** and **9**, which were separated by preparative TLC (chloroform) into two bands and baseline. The IR spectrum of the latter indicated that it contained no carbonyl species, and it was therefore not investigated further. Of the former two bands the first one (yellow, R_f 0.39) gave orange-yellow, solid $[Os_3(CO)_{10}(\mu_3-\eta^2-Me_2(HO)C-CH=CH-C\equiv C-C(OH)Me_2)]$ (**8**) (73 mg, 24.7%). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2100w, 2062vs, 2044s, 2019m, 1994m. 1H NMR ($CDCl_3$): δ 5.55 (d, $^1J = 13$ Hz) and 4.62 (d, $^1J = 13$ Hz) vinylic protons; 3.39 (br s, 2H, OH); 1.41 (br s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 298 K): δ 180–172 (a few broad resonances, CO), 162.0, 146.0, 142.6, 129.5 (diyne carbons), 80.9 ($C(OH)Me_2$), 72.8 ($C(OH)Me_2$), 30.9 ($4CH_3$). FAB-MS (m/z): 1018 [M^+] ($Os_3 = 570$) and [$M^+ - nCO$], $n = 1-3$. Anal. Calcd for $C_{20}H_{16}O_{12}Os_3$: C, 23.57; H, 1.58. Found: C, 23.28; H, 1.64. The second band (R_f 0.22) gave orange, solid $[Os_3(CO)_{10}(Me_2(HO)C-C\equiv C-C\equiv C-C(OH)Me_2)]$ (**9**) (91 mg, 30.9%). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2102w, 2062vs, 2055s,sh, 2020m, 1998m,sh, 1840w,br. 1H NMR ($CDCl_3$): δ 3.08 (br s, 2H, OH), 1.48 (br s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 298 K): δ a broad resonance centered at ca. 176 (10 CO), 164.4, 115.2 (C(11), C(12)), 102.9, 93.4 (C(16), C(17)), 80.1 ($C(OH)Me_2$), 65.6 ($C(OH)Me_2$), ca. 31.6 br ($2CH_3$) 31.4 ($2CH_3$). FAB-MS (m/z): 1016 [M^+] ($Os_3 = 570$) and [$M^+ - nCO$], $n = 1-10$. Anal. Calcd for $C_{20}H_{14}O_{12}Os_3$: C, 23.62; H, 1.39. Found: C, 23.56; H, 1.55. Single crystals of **9** suitable for X-ray analysis were grown from benzene at 4 °C. An EI mass spectrum of the reaction mixture showed the presence of the following signals (m/z), which can be unambiguously assigned to the free enyne $Me_2(HO)C-CH=CH-C\equiv C-C(OH)Me_2$ and products of its fragmentation: 168 [M^+], 153 [$M^+ - CH_3$], 135 [$M^+ - CH_3 - H_2O$].

X-ray Data Collection and Structure Solution. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and the Collect²⁰ program. The Denzo and Scalepack²¹ programs were used for cell refinements and data reduction. The structures of **5**, **6**, and **9** were solved by direct methods using the SHELXTL v.5.1²² or SHELXS97²³ program packages and the WinGX²⁴ graphical user interface. The structure of **7** was solved by the Patterson method using the DIRDIF-99 program.²⁵ A multiscan absorption correction, based on equivalent reflections, was applied to **5**, **6**, **7**, and **9** (T_{max}/T_{min} were 0.4974/

0.3962 0.3324/0.1644, 0.5215/0.1537, and 0.3500/0.1088, respectively). Structural refinements were carried out with the SHELXTL v.5.1 or SHELXL97 programs.²⁶ All organic hydrogens in **5**, **6**, **7**, and **9**, except the OH hydrogens in **9**, were constrained to ride on their parent atom. The OH hydrogens were located from the difference Fourier map but not refined. The hydride in **6** was located from a difference Fourier map and refined isotropically. The hydride in **7** was placed in idealized positions using the XHYDEX program.²⁷ The structure of **9** was refined as a racemic twin (absolute structure parameter 0.543(9)) in orthorhombic space group $P2_12_12_1$. In the structure of **6**, a carbon in one of the carbonyls bonded to Os was disordered. No acceptable disorder model was found for this structure, which is included in the Supporting Information.²⁸ Crystallographic data for **5**, **7**, and **9** are summarized in Table 1. Selected bond lengths and angles are shown in Table 2, and the molecular structures in Figures 1, 4, and 6.

Results and Discussion

The reactions of $[H_2Os_3(CO)_{10}]$ with the conjugated diynes $PhC_2C_2CH_2OH$ (**1**) and $PhC_2C_2C(O)Ph$ (**2**), which contain oxygen in β position of a substituent, result in rearrangements of the diynes to give coordinated five-membered heterocycles in a way that is very similar to that found earlier for hexa-2,4-diyne-1,6-diol⁶ and some nitrogen-containing diynes.¹⁷ Although $Me_2(HO)C-C\equiv C-C\equiv C-C(OH)Me_2$ (**3**) contains oxygen in β position

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(28) Crystal data for **6**: $C_{27}H_{12}O_{11}Os_3$, monoclinic, $a = 9.9393(3)$ Å, $b = 23.4588(4)$ Å, $c = 11.6438(4)$ Å, $\beta = 95.463(1)^\circ$, $T = 150(2)$, space group $P2_1/c$, $Z = 4$, $D_c = 2.662$ cm^{-1} , 31 506 reflections collected, 4820 unique ($R_{int} = 0.0849$). The final R_1 was 0.0415 [$I > 2\sigma(I)$], $wR_2(F^2) = 0.1020$ [$I > 2\sigma(I)$].

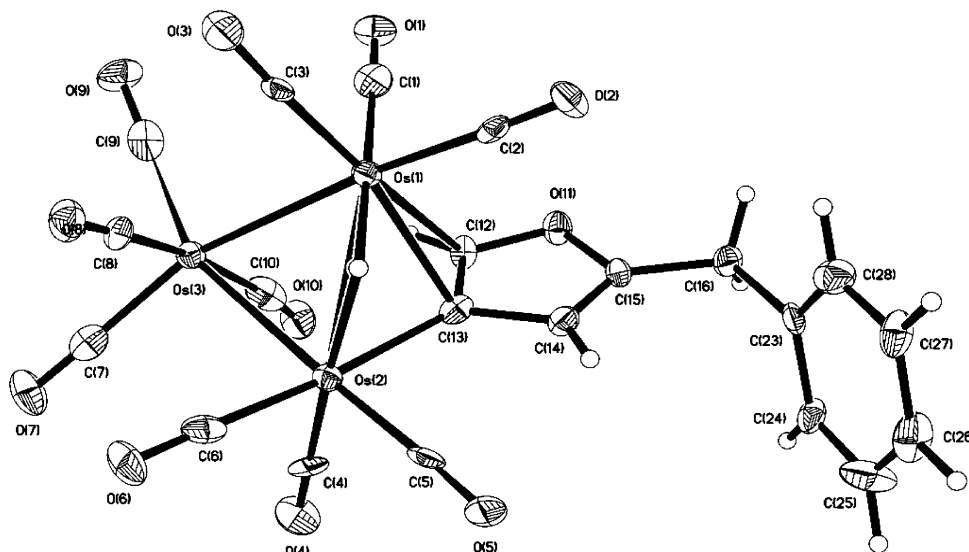


Figure 1. ORTEP view of **5**.

Table 2. Selected Bond Lengths for Clusters **5**, **7**, and **9**^a

	5	7	9
Os(1)–Os(2)	2.8449(5)	2.9899(4)	2.8575(3)
Os(1)–Os(3)	2.8664(6)	2.8325(4)	2.8134(3)
Os(2)–Os(3)	2.8846(5)	2.7925(4)	2.7245(3)
Os(1)–C(13)	2.155(10)	2.068(8)	
Os(1)–C(12)			2.164(6)
Os(2)–C(12)	2.566(9)		
Os(2)–C(13)	2.375(9)		
Os(2)–C(11)		2.106(8)	2.109(6)
Os(3)–C(11)		2.345(7)	2.316(6)
Os(3)–C(12)		2.329(7)	2.234(6)
Os(3)–C(13)		2.357(7)	
C(11)–C(12)		1.415(10)	1.434(8)
C(11)–C(16)			1.426(8)
C(12)–C(13)	1.374(13)	1.436(10)	1.517(8)
C(13)–C(14)	1.469(14)	1.456(11)	1.534(9)
C(14)–C(15)	1.331(13)	1.362(10)	
C(16)–C(17)			1.202(9)
C(17)–C(18)			1.477(8)
O–C(12)	1.380(11)	1.367(9)	
O–C(15)	1.400(12)	1.375(9)	
Os(1)–C(1)	1.898(10)	1.909(8)	1.958(7)
Os(1)–C(2)	1.922(11)	1.896(8)	1.940(8)
Os(1)–C(3)	1.935(11)	1.950(8)	1.975(7)
Os(2)–C(4)	1.924(12)	1.907(9)	1.894(6)
Os(2)–C(5)	1.950(11)	1.894(8)	1.912(6)
Os(2)–C(6)	1.885(10)	1.947(8)	1.963(7)
Os(3)–C(7)	1.940(11)	1.919(8)	1.930(8)
Os(3)–C(8)	1.921(10)	1.907(8)	1.905(6)
Os(3)–C(9)	1.936(12)	1.916(8)	1.883(8)
Os(3)–C(10)	1.963(12)		
Os(1)–C(10)			2.001(7)
Os(2)–C(10)			2.519(6)

^a For numbering scheme see Figures 1, 3, and 5.

relative to the diyne fragment, cyclization of **3** is completely suppressed (*vide infra*). Instead, the two main products of the reaction with **3** represent examples of “regular” $\mu_3\text{-}\eta^2$ triple-bond coordination to an “Os₃–(CO)₁₀” fragment.

Synthesis and Characterization of [HOs₃(CO)₁₀–($\mu\text{-}\eta^1\text{:}\eta^2\text{-PhCH}_2\text{C=CH-C=CH-O}$)] (5**).** Reaction between the triosmium dihydride cluster and ligand **1** affords [HOs₃(CO)₁₀($\mu\text{-}\eta^1\text{:}\eta^2\text{-PhCH}_2\text{C=CH-C=CH-O}$)] (**5**) as the main product along with trace amounts of unidentified compounds. The molecular structure of **5** was determined by an X-ray diffraction study; an

ORTEP view of the molecule is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The molecule consists of a closed Os₃ triangle with 10 terminal CO ligands, a bridging hydride, and a substituted furan moiety derived from the diyne. The organic furan ring is coordinated to an Os–Os edge in a $\mu\text{-}\eta^1\text{:}\eta^2$ -mode. This $\sigma\text{-}\pi$ coordination mode fits well to the polyhedral skeleton electron pair theory (PSEPT) view of bonding in a closed Os₃ triangle;²⁹ according to this approach, the furan moiety contributes three electrons to give the cluster a 48 valence electron count and thus stabilizes the “HOs₃(CO)₁₀” fragment. The main structural features of **5** are very similar to the structural patterns found for its pyrrolyl analogues, which contain $\mu\text{-}\eta^1\text{:}\eta^2$ -alkenyl coordinated ligands.¹⁷ The Os–Os bond lengths in **5** range from 2.8449(5) to 2.8846(5) Å, the Os(1)–Os(2) bond spanned by the furan moiety and the hydride being the shortest one. It has been shown that the coordination of benzene to a triosmium cluster results in considerable disruption of the aromatic system, so that the bonding between the benzene (“cyclohexatriene”) molecule and the metals may be viewed as localized;³⁰ in the same way, the bonding between the furan moiety and the metals in **5** may be rationalized by a localized approach. Of the three metal to carbon bonds between the alkenyl fragment of the organic moiety and Os(1)/Os(2), the shortest one is the (σ) Os(1)–C(13) bond, which is 2.155(10) Å. The (π) bond between the C(13)=C(12) alkene fragment and Os(2) atom is asymmetric due to the geometrical constraints of the cyclic ligand: the Os(2)–C(13) and Os(2)–C(12) distances are 2.375(9) and 2.566(9) Å, respectively. However, it is worth noting that in **5** the asymmetry is substantially lower than what is found in the related clusters [HOs₃(CO)₁₀($\mu\text{-}\eta^1\text{:}\eta^2\text{-PhCH}_2\text{-(NCHCHCC)CH}_2\text{Ph}$)] and [HOs₃(CO)₁₀($\mu\text{-}\eta^1\text{:}\eta^2\text{-Ph(NCHCHCC)CH}_2\text{Ph}$)], where the corresponding distances are 2.282(8) and 2.985(8) Å; 2.225(5) and 3.111(5) Å, respectively.¹⁷ The more pronounced asymmetry in the latter two clusters may be attributed to steric interactions between substituents of the coordinated

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pyrrolyl rings and the metal cluster cores. Coordination of the C(12)=C(13) double bond in **5** to Os(2) results in its elongation to 1.374(13) Å, which is slightly longer than the uncoordinated double bond of the furane ring, which is 1.331(13) Å. The osmium to carbonyl carbon bond distances in **5** range from 1.885(10) to 1.963(13) Å, with an average value of 1.927 Å, which matches the values found for analogous clusters.^{17,31–33} The coordination mode of all CO ligands in **5** is very close to linear, except C(10)O(10), where the Os(3)–C(10)–O(10) angle is equal to 172.9°. The spectroscopic data for **5** are in agreement with the solid state structure. The C–O stretching pattern is very similar to those observed for related $[HOs_3(CO)_{10}(\mu-\eta^1:\eta^2\text{-alkenyl})]$ clusters.^{17,31–33} Ambient-temperature ¹H, DEPT-135, and ¹³C{¹H} NMR spectra of the coordinated organic ligand in **5** display easily assignable signals corresponding to phenyl and furan rings and the CH₂ group, along with the hydride resonance at –16.1 ppm, typical for a bridging hydride. The room-temperature ¹³C{¹H} NMR spectrum in the carbonyl region consists of six resonances of 1/2/1/2/2/2 relative intensities. This spectral pattern matches completely the fast-exchange limiting spectrum of the $[HOs_3(CO)_{10}(\mu-\eta^1:\eta^2\text{-PhC=CHPh})]$ cluster,³² where the alkenyl bridge oscillates between two osmium atoms, giving rise to an averaged *C_s* symmetry for the {Os₃(CO)₁₀} fragment. In the case of **5** this scrambling results in confluence of the symmetry-related resonances (C(1)O and C(4)O, C(2)O and C(5)O, C(3)O and C(6)O, C(7)O and C(9)O) into double intensity signals, leaving the resonances corresponding to C(8)O and C(10)O unchanged. This type of dynamic behavior is common for osmium and ruthenium clusters containing unsaturated $\mu-\eta^1:\eta^2$ -coordinated organic ligands, such as alkenyl,³⁴ acetylide,^{35–37} allenylidene,³⁶ or allene.³⁸

Synthesis and Characterization of $[HOs_3(CO)_{10}(\mu-\eta^1:\eta^1\text{-Ph(C=CH-C=C-O)CPh)]$ (6**) and Its Thermal Transformation into $[HOs_3(CO)_9(\mu_3-\eta^1:\eta^3:\eta^1\text{-Ph(C=CH-C=C-O)CPh)]$ (**7**).** Reaction of $[H_2Os_3(CO)_{10}]$ with **2**, which contains a keto-oxygen in β position of a substituent, affords the monohydride cluster $[HOs_3(CO)_{10}(\mu-\eta^1:\eta^1\text{-Ph(C=CH-C=C-O)CPh)]$ (**6**) in nearly quantitative yield. The molecular structure of **6** (Figure 2) was proposed on the basis of its spectroscopic (IR, ¹H and ¹³C NMR) and FAB mass spectrometric data. The ¹H NMR spectrum of **6** displays multiplets derived from the two phenyl rings and the furan hydrogen (11H) in the typical 7.82–7.02 ppm range. The hydride signal was observed at –14.86 ppm, which is close to the values found for $[HOs_3(CO)_{10}$

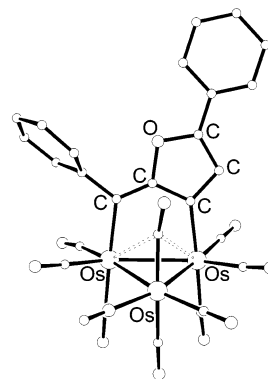


Figure 2. Schematic representation of the structure of **6**.

$(\mu-\eta^1:\eta^1\text{-Me-C-(C-C-CH-CH-O)})]^6$ (–15.01 ppm) and $[HOs_3(CO)_{10}\{\mu-\eta^1:\eta^1\text{-Ph-(NCHCHCC)-C-Me}\}]^{17}$ (–14.31 ppm). The ¹³C{¹H} NMR spectrum provides further arguments in favor of the proposed structure; in this spectrum, as well as in the DEPT-135 spectrum, the CH carbons of the phenyl rings and the hydrogen-bonded furan carbon appear as well-resolved resonances at 129.4 (2C), 127.9 (2C), 127.7 (2C), 123.3 (2C), 129.3 (1C), 127.8 (1C), and 132.6 (1C) ppm. The four signals of relative intensity 2 in this pattern indicate unhindered rotation of the phenyl rings at room temperature. The *ipso* phenyl carbons were found at 136.4 and 161.6 ppm, whereas four low-field signals, 183.1, 181.7, 181.5, and 177.0 ppm, may be assigned to the other bare carbons of the coordinated organic ligand. The low-field shift of these resonances may be attributed to the coordination of the furan fragment to the clusters and the presence of the electrophilic oxygen in the heterocyclic system. The ¹³C spectrum displays 10 signals in the carbonyl region, indicating that the carbonyl environment is completely asymmetric and stereochemically rigid. Nine of the carbonyl resonances appear in the regular range for terminal carbonyl ligands (183–200 ppm), whereas the tenth was found at 211.1 ppm. The latter shift suggests that one carbonyl bridges three metal atoms. Further evidence for this particular feature of the carbonyl envelope structure is provided by a weak 1842 cm^{–1} band in the IR spectrum of **6**.

It was possible to grow single crystals of **6**, and an X-ray analysis confirms the proposed structure of the cluster, in particular the structure of the coordinated organic fragment and the bridging CO. Unfortunately, the poor quality of the crystals precluded the collection of a high-quality data set, and the disorder of one CO ligand could therefore not be fully refined. An indirect confirmation of the proposed structure of **6** is provided by its reactivity, which is very similar to analogous clusters with $\mu-\eta^1:\eta^1$ -coordination modes of the organic moiety.¹⁷ Upon thermolysis, **6** easily loses a CO ligand to give the cluster $[HOs_3(CO)_9(\mu_3-\eta^1:\eta^3:\eta^1\text{-Ph(C=CH-C=C-O)CPh})]$ (**7**), whose crystal and molecular structures have been determined by X-ray diffraction analysis. The molecular structure of **7** is shown in Figure 4, and selected bond lengths and bond distances are listed in Table 2. The cluster framework in **7** consists of three metal and three carbon atoms arranged into a pentagonal pyramid with three carbons and two osmium atoms in the basal plane. This structural motif is frequently observed in products of reactions of iron subgroup carbonyls with alkynes.³⁹ The spectroscopic and struc-

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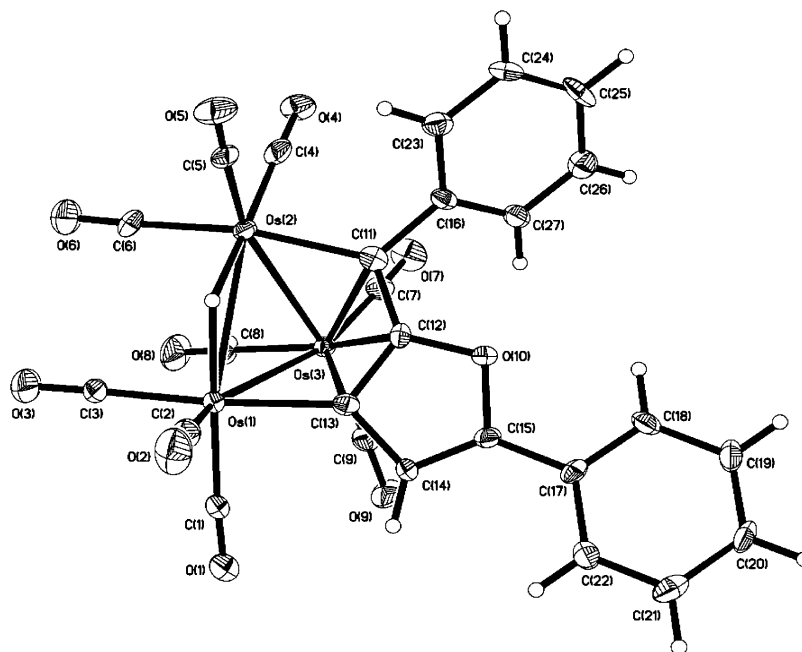


Figure 3. ORTEP view of **7**.

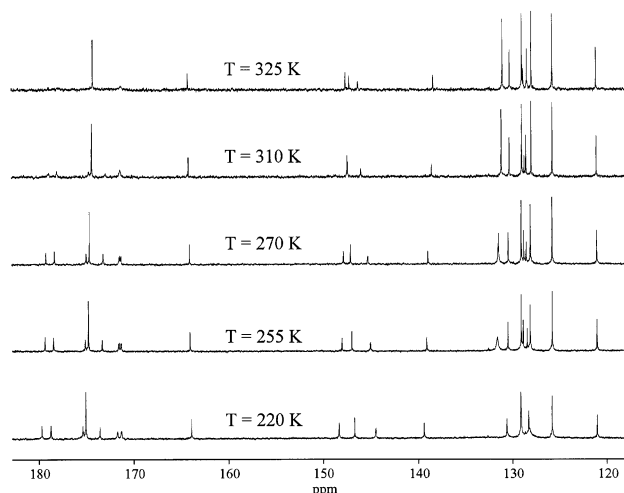


Figure 4. Variable-temperature ^{13}C NMR spectra of **7**.

tural characteristics of this compound (cf. Experimental Section and Table 2) are very similar to the corresponding parameters found for pentagonal pyramidal clusters formed in analogous thermal reactions.¹⁷ The Os–Os bond lengths in **7** range from 2.7925(4) to 2.9899(4) Å; the longest bond is located in the basal plane (cf. Figure 3) and is bridged by the hydride ligand. The Os–C bond lengths in the basal plane of the pentagonal pyramid are equal to 2.106(8) and 2.068(8) Å, which is very close to the values found in the analogous clusters $[\text{HOs}_3(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^3\text{-}\eta^1\text{-MeC=C=C-CH=CH-NPh}\}]$ (2.106(5) and 2.078(4) Å) and $[\text{HOs}_3(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^3\text{-}\eta^1\text{-(OCH=CHC=C-CMe)}\}]$ (2.087(11) and 2.064(11) Å).¹⁷ The three other metal–carbon bonds, which link the apical Os(3) with the carbon atoms of the basal plane, are 2.329(7), 2.345(7), and 2.357(7) Å, which is substantially longer (by approximately 0.2 Å) than those in the basal plane. The relatively large apical metal–carbon bond lengths may be a result of the strain caused when the two apical to basal (Os–Os) bonds, which are inherently

longer than the Os–C bonds, are incorporated into the pentagonal pyramidal framework. The ^1H and ^{13}C NMR spectra of **7** fit well to the structure found in the solid state. The NMR data indicate a fixed orientation of the ligand both at 325 and at 220 K, which may be expected since three ligand carbons are incorporated into the pentagonal “ Os_3C_3 ” pyramid. However, VT ^{13}C NMR spectra show that, in contrast to the parent cluster **6**, the carbonyl environment of **7** is not rigid. At least two independent scrambling pathways, relevant to two groups of carbonyl ligands, may be discerned in the temperature range 220–325 K, cf. Figure 4. In the low-temperature (220 K) spectrum, six resonances of relative intensity 1 and one resonance of triple intensity can be observed. The former six resonances account for the nonequivalent carbonyl ligands coordinated to Os(1) and Os(2) atoms. This assignment is confirmed by the presence of typical $^2J(\text{H}_{\text{hydride}}\text{-C})_{\text{trans}}$ couplings^{32,34,35,38,40} (11 Hz) for two resonances (C(1)O and C(4)O). The resonance at 174.8 ppm of triple intensity is assigned to the three carbonyls of the Os(3) atom, which undergo a tripodal “turnstile” rotation about the Os center that is not frozen even at 220 K. This resonance does not display any broadening on warming up to 325 K, indicating an absence of carbonyl ligand exchange between Os(3) and the other osmium atoms. However, the other six individual CO signals start to broaden on heating and degrade to the baseline at 325 K. We propose that this fluxional process is also due to localized turnstile rotations of the carbonyl ligands without intermetal exchange. This type of localized tripodal fluxionality has been observed for several ruthenium and osmium carbonyl clusters containing coordinated η^2 and η^3 organic moieties.^{34,35,38,41,42} Moreover, a fluxional behavior identical to that described above for **7** has been verified in the analogous $[\text{HRu}_3\text{-}$

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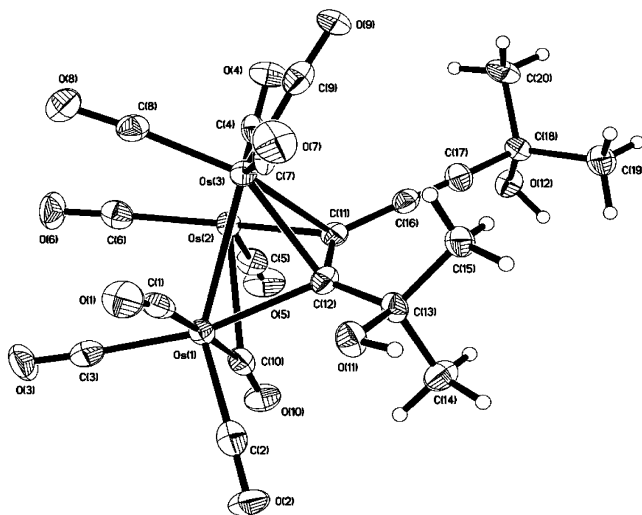


Figure 5. ORTEP view of **9**.

$(CO)_9(\mu_3, \eta^3\text{-MeCCHCMe})$ cluster^{38,41} by variable-temperature ^{13}C NMR and ^{13}C – ^{13}C EXSY studies.

Synthesis and Characterization of the Products of the Reaction of $[H_2Os_3(CO)_{10}]$ with the Diyne **3.** We also examined the reaction of $[H_2Os_3(CO)_{10}]$ with the diyne **3**. No cyclization of **3** could be observed, which is in accordance with our proposed general mechanism for diyne cyclization (vide infra).¹⁷ Instead, **3** reacts as a “normal” alkyne; thus, the two nonhydride clusters $[Os_3(CO)_{10}(\mu_3, \eta^2\text{-Me}_2(\text{HO})\text{C}=\text{CH}=\text{C}\equiv\text{C}(\text{OH})\text{Me}_2)]$ (**8**) and $[Os_3(CO)_{10}(\mu_3, \eta^2\text{-Me}_2(\text{HO})\text{C}\equiv\text{C}=\text{C}(\text{OH})\text{Me}_2)]$ (**9**) are formed in the reaction of **3** with $[H_2Os_3(CO)_{10}]$. Single crystals of **9** suitable for X-ray analysis were grown, and its crystal structure was determined in order to verify the identity of **9**. The molecular structure of **9** is shown in Figure 5; it is closely related to previously determined structures of $[Os_3(CO)_{10}(\mu_3, \eta^2\text{-alkyne})]$ clusters containing one bridging CO ligand.^{43–45} For **9** and related clusters, there is an idealized C_s symmetry for the alkyne-containing “ Os_3C_2 ” fragment, where the vector of the coordinated triple bond is parallel to the edge of the Os_3 triangle, which is bridged by a CO ligand. However, there are significant deviations from this idealized structure in **9**. In particular, the $Os(1)\text{--}Os(2)\text{--}C(11)\text{--}C(12)$ torsion angle is equal to $-7.8(4)^\circ$. Moreover, substantial structural differences between the alkyne carbons are also observed. The $Os(1)\text{--}C(12)$ and $Os(2)\text{--}C(11)$ bond lengths are different [2.109(6) and 2.164(6) Å, respectively] and substantially shorter than those that arise from the π -interaction between the alkyne and $Os(3)$ [$Os(3)\text{--}C(11) = 2.316(6)$ Å, $Os(3)\text{--}C(12) = 2.334(6)$ Å]. Similar deviations from the idealized C_s symmetry have been detected earlier for related clusters.^{44,45} The C–C bond distance of the coordinated alkyne moiety in **9** is substantially elongated [$C(11)\text{--}C(12) = 1.434(8)$ Å], whereas the C–C distance of the noncoordinated triple bond is typical for alkynes, 1.202(9) Å. In accord with the unperturbed nature of noncoordinated triple bond,

the $C(11)\text{--}C(16)\text{--}C(17)\text{--}C(18)$ chain is almost linear: the $C(11)\text{--}C(16)\text{--}C(17)$ and $C(16)\text{--}C(17)\text{--}C(18)$ angles are equal to $169.1(7)^\circ$ and 176.7° , respectively.

The carbonyl environment of **9** consists of nine terminal and one bridging ligand. It is worth noting that the longest metal to carbon distances, 1.975(7) and 1.963(7) Å, are observed for the $C(3)O$ and $C(6)O$ ligands disposed in *trans* positions with respect to the $Os\text{--}C_{\text{alkyne}}\sigma$ -bonds, indicating a substantial *trans* influence from these bonds. The terminal ligands are nearly linear with the $Os\text{--}C\text{--}O$ angles, falling in the interval $174.3(6)\text{--}179.4(6)^\circ$, the only exception being $C(1)O$, where the metal–carbonyl angle is $170.2(6)^\circ$. This slight distortion is probably caused by steric interaction with the $C(OH)\text{Me}_2$ group of the coordinated diyne. The bridging $C(10)O$ ligand is coordinated to the $Os(1)\text{--}Os(2)$ edge in a highly asymmetric manner, with the $C(10)\text{--}Os(1)$ and $C(10)\text{--}Os(2)$ distances being equal to 2.001(7) and 2.519(6) Å, respectively. Such asymmetry has also been found in other $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-RC}_2\text{R}')]_n$ clusters, where the corresponding distances equal 2.086, 2.302 Å ($R = R' = \text{Et}$)⁴⁴ and 1.96, 2.6 Å ($R = \text{H}$, $R' = C_2\{Co_2(CO)_6\}SiMe_3$).⁴⁵

The spectroscopic data obtained for **9** indicate that the molecular structure found in the solid state is maintained in solution. The room-temperature ^1H NMR spectrum displays two broad resonances at 1.48 and 3.08 ppm, which correspond to the inequivalent Me and OH groups of the coordinated diyne, respectively. The ν_{CO} band at 1840 cm^{-1} in the IR spectrum of **9** indicates the presence of a bridging carbonyl group.

Variable-temperature ^{13}C NMR studies of **9** (Figure 6) showed that the molecule is stereochemically nonrigid in solution in the temperature range 300–180 K. The room-temperature ^{13}C NMR spectrum of **9** displays a broad resonance for the 10 carbonyl ligands at ca. 175 ppm and a set of signals corresponding to the coordinated diyne (165–30 ppm). The assignment of the latter signals was in part based on the spectroscopic data obtained for the analogous ruthenium cluster $[Ru_3(CO)_{10}(\mu_3, \eta^2\text{-HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH})]$:¹⁰ low-field resonances at 164.4 and 115.2 ppm correspond to $C(11)$ and $C(12)$ of the coordinated triple bond, while the resonances for the uncoordinated triple bond occur at 102.9 and 93.4 ppm ($C(16)$ and $C(17)$, respectively). All alkyne resonances are shifted downfield as compared to the resonance for the free ligand **3** (84.4 and 66.2 ppm); the shift of the resonances for the uncoordinated alkyne moiety may be attributed to the disappearance of the conjugated diyne system. The resonances at 80.1 and 65.6 ppm were assigned to the $C(13)$ and $C(18)$ atoms, respectively. At room temperature, the methyl substituents in **9** appear as a sharp resonance at 31.4 ppm superposed on a very broad signal, which is resolved into two singlets at 31.8 and 31.2 ppm upon cooling to 260 K. The signal at 31.4 ppm is assigned to the methyl groups bonded to $C(18)$, which are equivalent because of free rotation around the $C(17)\text{--}C(18)$ bond. The broad resonance observed at room temperature is due to restricted rotation of the $C(13)(OH)\text{Me}_2$ moiety at room temperature, which is frozen out at 260 K to yield the two observed singlets. The room-temperature ^{13}C spectrum is compatible with exposure of the diyne ligand to the influence of an averaged “ $Os_3(CO)_{10}$ ” cluster core,

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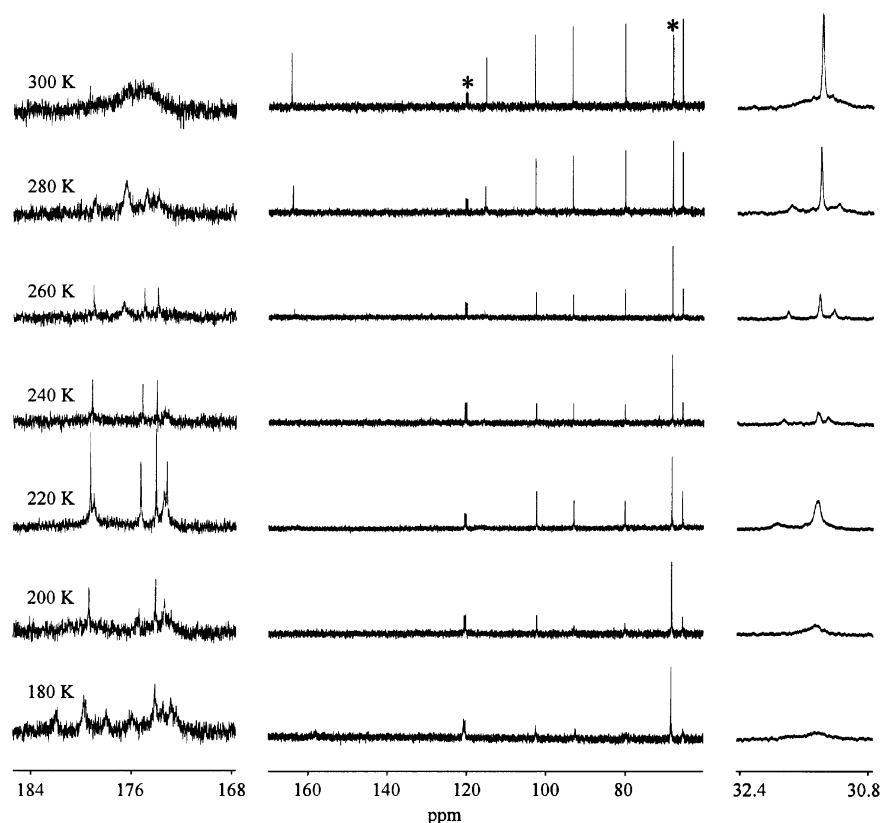


Figure 6. Variable-temperature ^{13}C NMR spectra of **9**, asterisks denote impurities.

where the averaging process is a fast exchange of all 10 carbonyls over the Os_3 framework (vide infra).

The further changes in the ^{13}C spectrum that are observed at lower temperatures may be explained by the scrambling model proposed⁴⁴ for the dynamic behavior of the closely related $[\text{M}_3(\mu\text{-CO})(\text{CO})_9(\mu_3, \eta^2\text{-RC}_2\text{R})]$ clusters ($\text{M} = \text{Os}$,⁴⁴ Ru ⁴⁶). For example, upon cooling to 260 K, the broad carbonyl resonance observed at room temperature splits into three sharp lines of equal intensity and another relatively broad signal. The spectroscopic changes that are observed upon cooling of the sample are in agreement with a rigid structure of the $\text{Os}_3(\text{CO})_3$ moiety and continuous scrambling inside the $\text{Os}(1)\text{Os}(2)(\text{CO})_6(\mu_2\text{-CO})$ fragment as proposed by Aime and co-workers.^{44,46} In the case of **9**, the dynamics of the carbonyl environment result in simultaneous broadening of the signals due to the diyne ligand. The signals corresponding to the coordinated triple bond, which are inherently the most sensitive to the dynamics occurring in the “ $\text{Os}_3(\text{CO})_{10}$ ” unit, disappear into the baseline at temperatures above ca. 260 K, whereas C(13), C(16), C(17), C(18), and the methyl resonances display lower sensitivity and slower broadening because these atoms are farther away from the metal–carbonyl cluster core. Unfortunately, a fully resolved spectrum of **9** could not be obtained, as it was not possible to freeze out the dynamics of the low-temperature fluxional process even at 180 K.

We have not been able to obtain single crystals of **8** suitable for crystallographic analysis. The proposed structure of **8** is therefore based on mass, IR, and ^1H , ^{13}C NMR spectroscopic studies. A schematic representa-

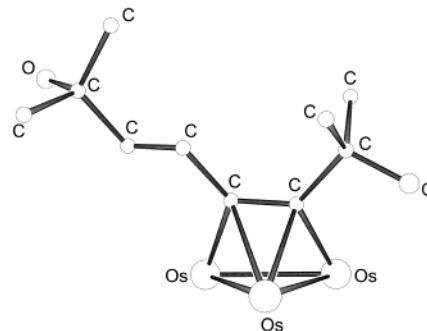
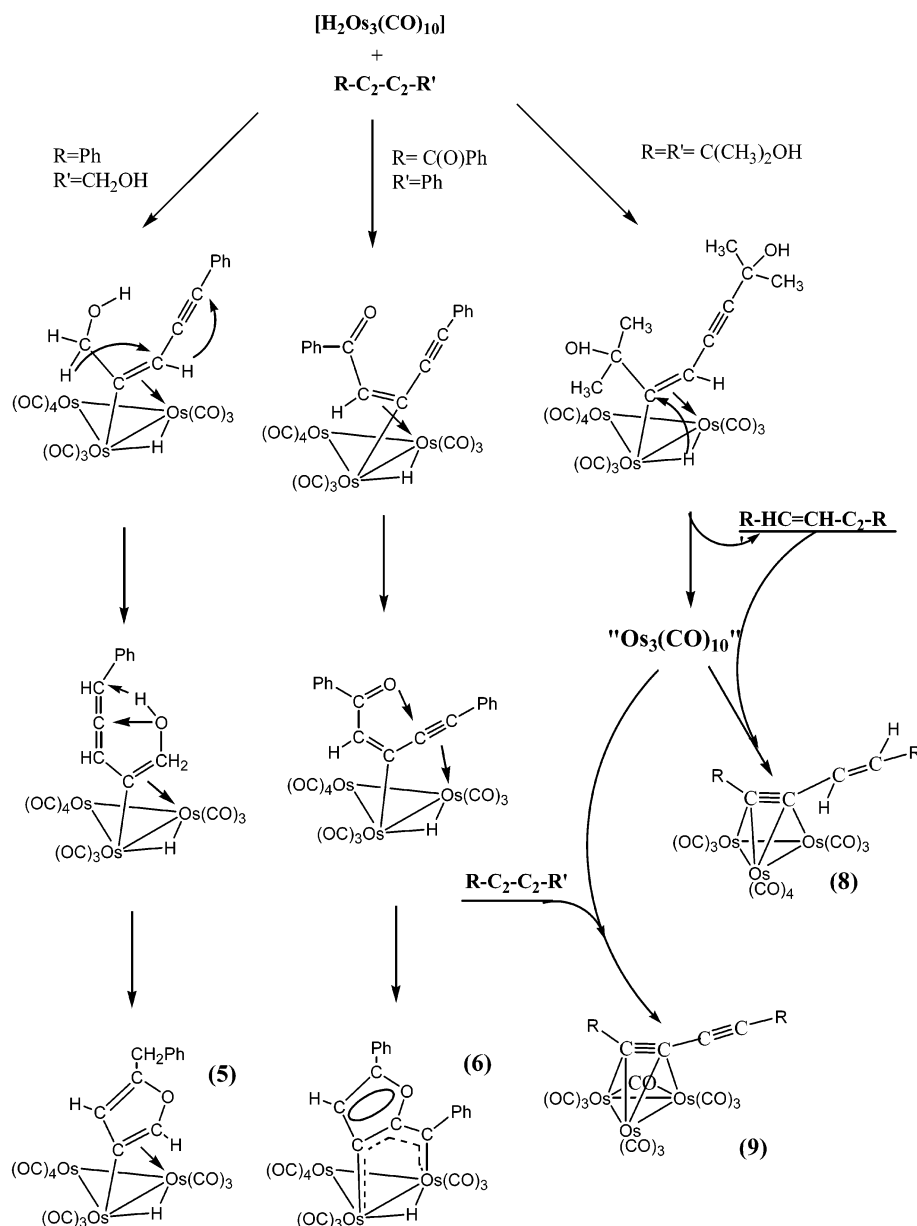


Figure 7. Schematic representation of the structure of **8**.

tion of the proposed structure of **8** is shown in Figure 7. The mass spectrum of **8** displays a peak for the molecular ion that matches the proposed formula $[\text{Os}_3(\text{CO})_{10}\{\text{Me}_2(\text{HO})\text{C}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{C}(\text{OH})\text{Me}_2\}]$ and a fragmentation pattern corresponding to the loss of seven CO ligands. The ^1H NMR spectrum shows broad signals for the methyl and OH groups (1.41 and 3.39 ppm, respectively) along with two doublets of the vinyl protons at 5.55 and 4.62 ppm. The value of the coupling constant for the latter resonances, 13 Hz, is typical for the *trans* double-bond configuration. No hydride signal could be detected; this suggests that **8** and **9** are similar but quite distinct from the other clusters described above. A group of resonances at typical shifts of terminal carbonyl ligands could be observed at 172–180 ppm in the room-temperature $^{13}\text{C}\{^1\text{H}\}$ spectrum, and two signals for CH carbons at 162.0 and 146.0 ppm were unambiguously assigned from a DEPT-135 spectrum. Two other low-field resonances (142.6 and 129.5 ppm) are assigned to the carbons of the coordinated triple bond. A set of high-field resonances at 80.9 (2 C), 72.8

(46) Aime, S.; Gobetto, R.; Milone, L.; Osella, D.; Violano, L.; Arce, A. J.; Desanctis, Y. *Organometallics* **1991**, *10*, 2854.

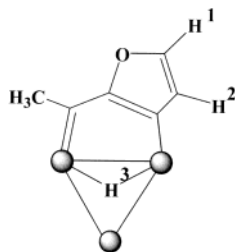
Scheme 1. Possible Mechanisms of $[H_2Os_3(CO)_{10}]$ Interaction with Oxygen-Containing Conjugated Diynes

(2 C), and 30.9 (4 C) ppm were assigned as quaternary carbons of the ligand substituents and Me groups, respectively, on the basis of a DEPT-135 spectrum. The shifts are very similar to those observed for the analogous carbons in the spectrum of **9**. The data obtained are in agreement with the structure of **8** that is schematically shown in Figure 7, in which an enyne ligand is coordinated to the $Os_3(CO)_{10}$ fragment through its triple bond in a $\mu_3-\eta^2$ manner. The carbonyl environment of **8** does not contain bridging ligands, as both the IR and NMR spectra clearly show. This is in contrast to the ligand sphere of **9**, but is not unusual in the chemistry of $[Os_3(CO)_{10}(\text{alkyne})]$ clusters.⁴⁷ It is likely that the enyne ligand found in **8** is formed by reduction of coordinated diyne triple bonds via transfer of two hydrides from $[H_2Os_3(CO)_{10}]$. The presence of signals corresponding to the enyne in the mass spectrum of the reaction mixture (cf. Experimental Section) suggests that this ligand may dissociate from the cluster.

Discussion of the Reaction Mechanisms. The reactions described above afforded products whose structures are in full agreement with previously suggested mechanistic schemes;^{15,17} the proposed mechanism(s) for cyclization of β -oxygen-containing diynes to produce five-membered furan type rings in the reaction with $[H_2Os_3(CO)_{10}]$ is shown in Scheme 1. The first reaction pathway shown in Scheme 1 is very similar to that suggested earlier for the corresponding transformation of the $PhC_2C_2CH_2NHCH_2Ph$ ligand.¹⁷ In ligand **1**, both of the *ortho* carbons of the phenyl substituent and the oxygen atom are in β position relative to the diyne moiety. Nucleophilic attack by either center can, in principle, lead to formation of a five-membered ring; this has, for example, been observed for symmetrically substituted diynes containing either two alcohol or two phenyl substituents.^{6,15} The nature of the formed ring system and its coordination mode depend on which of the two triple bonds of the asymmetric diyne that is initially coordinated to the cluster core and on the

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Table 3. Relative Intensities of the Proton Signals in the Cluster $[\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_6\text{O}_2)]$ Obtained in the Course of Experiments: (A) $4 + [\text{H}_2\text{Os}_3(\text{CO})_{10}]^{\text{Deuterated}}$, (B) $4^{\text{Deuterated}} + [\text{H}_2\text{Os}_3(\text{CO})_{10}]$, and (C) $4 + [\text{H}_2\text{Os}_3(\text{CO})_{10}]$



time, h	relative ^a intensities of proton signals in								
	experiment A			experiment B			experiment C		
	H ₂ /H ₁	H ₃ /H ₁	CH ₃ /H ₁	H ₂ /H ₁	H ₃ /H ₁	CH ₃ /H ₁	H ₂ /H ₁	H ₃ /H ₁	CH ₃ /H ₁
1	0.43	0.45	3.04	1.00	0.99	3.03	1.01	1.03	3.02
12	0.46	0.47	3.02	1.01	1.03	3.02	1.01	1.01	2.98
24	0.48	0.46	3.01	1.04	1.01	3.02	1.03	0.99	2.98
average values of the integrals, uncertainty in parentheses	0.46 (0.02)	0.46 (0.01)	3.02 (0.01)	1.02 (0.02)	1.01 (0.02)	3.02 (0.01)	1.02 (0.01)	1.01 (0.02)	2.99 (0.02)

^a With respect to the integral of H¹.

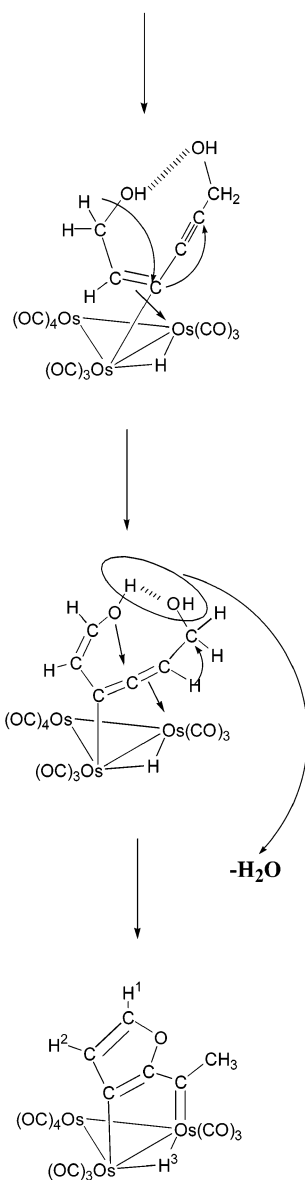
relative nucleophilicity of the β -centers. The structure of **5** indicates that initial coordination of the diyne occurs through the triple bond adjacent to the alcohol substituent, followed by nucleophilic attack of the β -oxygen on a carbon atom of the diyne chain to afford a μ - η^1 : η^2 -alkenyl type coordination of the furan ring. This is in agreement with the expected higher nucleophilicity of the β -oxygen (and the lower pK_a of the OH moiety), as compared to the β -CH group in ligand **1**. In contrast to the rearrangement of the symmetric ligand $\text{HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH}$,⁶ the closure of the furan ring in the case of **1** is not accompanied by ligand fragmentation, most likely because such elimination of a ligand fragment would involve disruption of the aromatic phenyl ring. As a result, the furan ring in **5** is coordinated in a μ - η^1 : η^2 -alkenyl coordination mode rather than the μ - η^1 : η^1 bonding mode observed for $[\text{HOs}_3(\text{CO})_{10}\{\mu$ - η^1 : η^1 -MeC=C=C-CH=CHO $\}]$.⁶

The proposed reaction sequence for the reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with ligand **2** is shown in the second reaction sequence of Scheme 1. Again, the first step of the reaction consists of the formation of a μ - η^1 : η^2 -alkenyl intermediate through ligand coordination and hydride transfer. Subsequent nucleophilic attack of the keto-oxygen onto the coordinated alkenyl fragment results in closure of the furan ring with the concomitant formation of a formal Os-carbene fragment involving the fourth carbon of the erstwhile diyne, resulting in μ - η^1 : η^1 coordination of the ligand to afford a "diosmacyclopentadien(yl)" ring {Os(1)Os(2)C(11)C(12)C(13)}. The Os(1)–Os(2) bond may thus be viewed as part of a conjugated ring system involving the furan moiety; this type of bonding mode has been observed previously in the case of $[\text{HOs}_3(\text{CO})_{10}\{\mu$ - η^1 : η^1 -MeC=C=C-CH=CHO $\}]$ ⁶ and $[\text{HOs}_3(\text{CO})_{10}\{\mu$ - η^1 : η^1 -MeC=C=C-CH=CH-NPh $\}]$.¹⁷ The high yield (98.6%) of **6**, which is the sole identifiable product of the reaction, indicates that the initial hydride transfer occurs with high regioselectivity. (The same degree of regioselectivity cannot be inferred for the formation of **5** because there are several minor unidentified products formed in that reaction.)

Deuterium Labeling. To get further insight into possible reaction mechanisms, we studied the reactions between the deuterated ligand $\text{DOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OD}$ (**4**) and $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$, as well as between **4** and the deuterated cluster $[\text{D}_2\text{Os}_3(\text{CO})_{10}]$, using ¹H NMR. The results are listed in Table 3. Deuteration of the diyne does not affect the relative intensities of the hydride and ligand protons in the reaction product, indicating that the protons (deuterons) of the hydroxyl groups are not incorporated into the cyclized product, $[\text{HOs}_3(\text{CO})_{10}\{\mu$, η^1 : η^1 -(OCH=CHC=C-CMe $\})]$.⁶ Further evidence for the lack of incorporation of the deuterium of the OD groups into the product cluster was obtained from the mass spectrum of the product: the isotopic distribution pattern of the molecular ion peak was identical to that of the product obtained from the reaction with unlabeled ligand. These observations are in agreement with our proposal that a molecule of (deuterated) water is eliminated in the cyclization of the diyne-diol (cf. Scheme 2). An analogous reaction takes place when $\text{PhNH}_2\text{CH}_2\text{C}_2\text{-C}_2\text{CH}_2\text{NH}_2\text{Ph}$ is reacted with $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$;¹⁷ in this case, a molecule of aniline (which has been experimentally detected) is eliminated and the cyclized diyne is coordinated in the same μ - η^1 : η^1 mode that is observed for $[\text{HOs}_3(\text{CO})_{10}\{\mu$, η^1 : η^1 -(OCH=CHC=C-CMe $\})]$. On the other hand, the reaction of the deuterium-enriched cluster with unlabeled ligand showed that the deuterium label is exclusively incorporated into the 2-H position of the coordinated ligand, in agreement with Scheme 2.

The products obtained from the reaction of the diyne **3** with $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ are fundamentally different from **5**, **6**, and related clusters,^{6,15,17} but we believe that the formation of clusters **8** and **9** is nevertheless compatible with the proposed reaction mechanisms^{15,17} (vide supra). It is possible that formation of **8** involves initial hydride transfer to yield a μ - η^1 : η^2 -alkenyl intermediate but that cyclization of the ligand is prevented by the fact that the methyl substituents are not liable to undergo 1,3-shifts (cf. Scheme 1). Possible steric hindrance exerted by the methyl substituents, which would prevent nu-

Scheme 2. Mechanism of 2,4-Diyne-1,6-diol Rearrangement in the Reaction with $H_2Os_3(CO)_{10}$



cleophilic attack of the oxygen on the diyne moiety, cannot be excluded. Thus, the second cluster hydride may be transferred to the alkenyl fragment to produce an “en-yne” ligand coordinated through its double bond. The further development of the reaction is completely in accord with the reactivity patterns found for a large variety of monoalkynes^{32,43,44,48} where the transfer of the second hydride results in dissociation of the alkene formed to afford coordinatively unsaturated and highly reactive “ $Os_3(CO)_{10}$ ” species. An indirect confirmation of such ligand dissociation was provided by the detection of the free en-yne in the reaction mixture via mass spectrometry (vide supra). In the reaction involving

ligand **3**, the latter species easily reacts with either the excess of starting ligand to give the nonhydride cluster **9** or with the liberated “en-yne” to give **8**. In both products, the well-known μ_3, η^2 alkyne coordination mode is observed.

Conclusions

This study has shown the following:

1. Conjugated diynes containing an oxygen atom in β position of a substituent undergo facile rearrangements to give furan rings (provided that the other β substituents are mobile, see **3** below).

2. It is likely that the mechanism(s) of the diyne rearrangements consist of initial formation of a vinyl intermediate, subsequent nucleophilic attack of the oxygen onto the third atom of the diyne chain, and (if necessary/possible) hydrogen shifts along the coordinated organic moiety to give either $\mu\text{-}\eta^1\text{:}\eta^2\text{-}$ or $\mu\text{-}\eta^1\text{:}\eta^1\text{-}$ coordinated furan ligands, depending on the nature of the ligand substituents.

3. It appears that the β methyl groups in ligand **3** prevent cyclization due to their inability to take part in (1,3-) shifts along the hydrocarbon chain. Instead, products containing the coordinated diyne, or its partially reduced enyne derivative, are formed.

The results of the studies presented here and published earlier^{6,15,17} indicate that $[H_2Os_3(CO)_{10}]$ is uniquely suited as a template for diyne cyclizations, probably due to the presence of hydrides in its coordination sphere and its particular electronic and geometrical characteristics. Along with its ruthenium analogue, $[H_2Os_3(CO)_{10}]$ is the only hydride-containing transition metal carbonyl cluster that is electronically unsaturated and thus a good electrophile. It should be noted that reaction of diynes with nonhydride trinuclear ruthenium and osmium clusters^{1,8–10} does not lead to cyclizations. The same is true for the reaction of diphenyldiacetylene ligand with another dihydride cluster of the iron subgroup, $[H_2Ru_4(PPh)(CO)_{12}]$,⁴ which results in 1,2- and 1,4-insertion of two hydrides to give coordinated “en-yne” and diallyl organic fragments; in contrast, the same ligand is readily cyclized in the reaction with $[H_2Os_3(CO)_{10}]$.¹⁵

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Supporting Information Available: Tables S1–S23, giving a summary of X-ray analysis, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for the structures of **4** clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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