ELSEVIER

Journal of Organometallic Chemistry 485 (1995) 219–225

Journal of Organometallic Chemistry

Reactions of diacetylene ligands with trinuclear clusters. I Reactions of 2,4-hexadiyne-1,6-diol and its dicobalthexacarbonyl derivatives with $H_2Os_3(CO)_{10}$

M.G. Karpov [a], S.P. Tunik [a,*], V.R. Denisov [a], G.L. Starova [a], A.B. Nikol'skii [a], F.M. Dolgushin [b], A.I. Yanovsky [b], Yu.T. Struchkov [b]

[a] Department of Chemistry, St. Petersburg University, Universitetskii pr. 2, St. Petersburg, 198904, Russia
[b] A.N. Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Street, Moscow, 117813, Russia

Received 3 May 1994

Abstract

Reactions of $H_2Os_3(CO)_{10}$ with the diyne ligand $HOCH_2C_2C_2CH_2OH$ and its dicobalthexacarbonyl derivatives $\{Co_2(CO)_6\}(\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ and $\{Co_2(CO)_6\}_2(\mu_2,\eta^2:\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ have been studied. The reaction of the uncomplexed ligand yields the cluster $(\mu\text{-H})Os_3(CO)_{10}(\mu_2,\ \eta^3\text{-}\overline{O\text{–}CH\text{=}CH\text{–}C\text{=}C}\text{–}C\text{–}CH_3)$ with the completely rearranged starting ligand. The structure of this compound was determined by a single-crystal X-ray study. The rearranged ligand forms a pseudo-furan ring with the C–CH_3 substituent in the α-position. The reactions of $H_2Os_3(CO)_{10}$ with the both dicobalthexacarbonyl derivatives yield the $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$ cluster as the main osmium-containing product. The structure of this compound was also established by a single-crystal X-ray study.

Keywords: Osmium; Cobalt

1. Introduction

Reactions of alkynes with triosmium clusters have been widely studied over the last two decades [1–3]. It was found that the presence of a terminal hydrogen or CH_2OH groups in the molecule of the parent alkyne makes possible a profound rearrangement of the ligand, including hydride transfer to the ligand with its subsequent dehydration [2,3] and cyclization with the formation of oxygen-containing "C_4O" ring [3]. These rearrangements take place under heating (> 96°C) of the initially formed clusters with the conventional (μ_3, η^2) coordination of alkyne. Reactions of diynes (RC_2C_2R) with the labile $Os_3(CO)_{10}(NCMe)$ cluster [4] afford in the first stage (room temperature) the (μ_3, η^2) coordination of the ligand via one triple bond and subsequent thermolysis of the obtained compound yields (μ_3, η^3) coordination (R = Et) or C–C bond rupture (R = Ph, ^{t}Bu, $SiMe_3$). In the present paper we report the study of $H_2Os_3(CO)_{10}$ reactions with $HOCH_2C_2C_2CH_2OH$ and its $\{Co_2(CO)_6\}$ derivatives under mild conditions.

2. Experimental

$H_2Os_3(CO)_{10}$ was prepared according to the published procedure [5]. Commercial-grade dicobaltoctacarbonyl and 2,4-hexadiyne-1,6-diol were used without additional purification. All solvents were dried over appropriate reagents and distilled prior to use. All reactions were carried out under dry argon. The NMR spectra were recorded on a Bruker AM 500 instrument and the IR spectra on a Specord M80 spectrophotometer. Mass spectra were measured on a MX-1321 instrument (electron impact, ionizing potential 70 eV).

2.1. Reaction of $H_2Os_3(CO)_{10}$ (I) with 2,4-hexadiyne-1,6-diol (II)

The cluster **I** (60 mg, 0.070 mmol) and the ligand **II**, were dissolved in 10 ml of dichloromethane. A TLC

* Corresponding author.

SSDI 0022-328X(94)24753-6

spot test showed the completion of the reaction within 24 h. The mixture obtained was separated on a column (8 × 2.5 cm i.d., silica 5/40) using hexane as the eluent. The main dark-red band afforded 63 mg (95%) of the product $HOs_3(CO)_{10}(C_6H_5O)$ (**III**) as a bright-red crystalline powder. The mass spectrum of **III** exhibits the molecular ion (m/z 947, $Os_3 - 570$), consecutive loss of ten CO groups and the corresponding doubly ionized ions. The IR and ^1H NMR spectra are given in Table 1.

2.2. Synthesis of $\{Co_2(CO)_6\}(\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ and $\{Co_2(CO)_6\}_2(\mu_2,\eta^2:\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ complexes

A diethyl ether solution of the ligand **I** (0.75 g, 6.8mmol, 50 ml) and $Co_2(CO)_8$ (0.78 g, 2.3 mmol, 20 ml) were mixed and left for 1 h. The solvent was then removed and the residue was dissolved in chloroform and transferred onto a column (20 × 2.5 cm i.d., silica 40/100). Separation with hexane–diethyl ether mixtures (from 5 : 1 to 2 : 1) gave the following bands in order of elution: (1) red–brown band of $\{Co_2(CO)_6\}_2(\mu_2,\eta^2:\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ (**V**) (0.24 g, 31%), (2) red band of $\{Co_2(CO)_6\}(\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ (**IV**) (0.42 g, 46%).

The mass spectra of compounds **IV** and **V** exhibit the molecular ions (m/z 396 and 682) and the corresponding loss of six and twelve CO groups, respectively. The IR and ^1H NMR spectral characteristics of **IV** and **V** are given in Table 1.

2.3. Reaction of $\{Co_2(CO)_6\}(\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ (IV) with $H_2Os_3(CO)_{10}$ (I).

A mixture of **IV** (93 mg, 0.24 mmol) and **I** (50 mg, 0.058 mmol) in 30 ml of dichloromethane was allowed to stand for 4 days. The precipitate formed was filtered off, hexane (40 ml) was added and the volume of the solution was reduced under vacuum to 20 ml. The solution obtained was transferred onto a column (15 × 2.5 cm i.d., silica 5/40). Separation with hexane–diethyl ether mixtures (from 5 : 1 to 2 : 1) gave the following bands in order of elution: (1) $Os_3(CO)_{12}$ (ca. 5 mg); (2) trace amount of unidentified red product; (3) $(H)(OH)Os_3(CO)_{10}$ (**VI**) (13 mg, 26%); (4) trace amount of unidentified black product; (5) **IV** (2 mg); (6) **V** (ca. 25 mg).

The main osmium-containing product (**VI**) was separated as a yellow crystalline powder on evaporation of the solvent from band 3. The mass spectrum of **VI** exhibits the molecular ion (m/z 868, $Os_3 - 570$) and consecutive loss of ten CO groups. The IR and ^1H NMR spectral characteristics of **VI** are given in Table 1.

2.4. Reaction of $\{Co_2(CO)_6\}_2(\mu_2,\eta^2:\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)$ (V) with $H_2Os_3(CO)_{10}$ (I)

A mixture of **V** (100 mg, 0.15 mmol) and **I** (50 mg, 0.058 mmol) in 20 ml of dichloromethane was allowed to stand for 2 days in air. The reaction mixture was then filtered off the residue formed and the solution was reduced in volume under vacuum to ca. 10 ml and transferred on to a column (12 × 2.5 cm i.d., silica 5/40). Separation with hexane–diethyl ether mixtures (from 10 : 1 to 4 : 1) gave a yellow band of **VI** (34 mg, 68%) and unreacted **V** (45 mg).

2.5. X-ray diffraction studies of III and VI

X-ray diffraction studies of the single crystals of **III** and **VI** were carried out with four circle diffractometers (193 and 293 K, Syntex $P2_1$ and Siemens P3/PC, Mo Kα radiation, graphite monochromator, $\theta/2\theta$ scan, $2\theta < 60°$ for **III** and **VI**, respectively). Crystals of **III** and **VI** are monoclinic, at 193 and 293 K: $a = 9.170(6)$ and 7.379(2) Å, $b = 14.81(1)$ and 24.98(1) Å, $c = 15.15(1)$ and 9.049(3) Å, $\beta = 103.18(2)$ and $107.14(2)^0$, $V = 2003(2)$ and 1594(1) $Å^3$, $d_{calc} = 3.133$ and 3.612 g

Table 1
Spectroscopic data for compounds **III–VI**

Compound	IR, ν CO (cm^{-1}) [a]	^1H NMR, δ (ppm) [a]	Mass spectra
III	(a) 2104_m, 2082_w, 2060_s, 2054_s, 2036_w, 2026_s, 2010_w, 1994_s, 1978_m	(c) 7.97, s (CH); 7.02, s, (CH) 2.64, s (CH_3) − 15.01, s, (OsH)	m/z 947 ($Os_3 - 570$), loss of 10 CO
IV	(b) 2100_m, 2064_s, $2038_{m,br}$	(d) 4.72, s, (CH_2) 4.29, s, (CH_2)	m/z 396, loss of 6 CO
V	(b) 2104_w, 2084_m, 2064_s, $2030_{m,br}$	(d) 4.85, s, (2 CH_2)	m/z 682, loss of 12 CO
VI	(a) 2112_w, 2072_s, 2062_m, 2026_s, 2002_m, 1996_w, 1990_m, 1984_w, 1958_w	(c) 0.21, s (OH) − 12.59, s, (OsH)	m/z 868 ($Os_3 - 570$), loss of 10 CO

[a] The IR and NMR spectra were recorded at ambient temperature in (a) hexane, (b) $CHCl_3$, (c) $CDCl_3$ and (d) CD_3OD (in the last case the OH groups of the complexes exchange with the solvent and are not observed).

cm^{-3}, $Z = 4$, space group $P2_1c$ and $P2_1/n$ for **III** and **VI**, respectively. The structures were solved by a direct method and refined in the anisotropic approximation (H atoms bound to carbons in **III** were included in calculated positions and refined in the riding model approximation with the common variable $U_{iso} = 0.05(5)$ Å^2; the bridging hydride atom was located in the difference Fourier synthesis and taken into account as a fixed contribution in F_{calc}; H atoms in **VI** were not taken into account). The absorption corrections were applied by the DIFABS method [6] for **III** ($\mu = 190.4$ cm^{-1}) and using the psi-scan technique for **VI** ($\mu = 239.1$ cm^{-1}). The final refinement converged to $R = 0.084$ and 0.036, $R_W = 0.092$ and 0.043 for 2716 and 2566 observed independent reflections with $I > 3\sigma(I)$ and $I > 4\sigma(I)$ for **III** and **VI**, respectively. All calculations were carried out with an IBM PC using the SHELXTL PLUS programs (PC version) [7]. The coordinates of non-hydrogen atoms in the structures **III** and **VI** are given in Tables 2 and 3.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coeffiients (Å$^2 \times 10^3$) in **III**

Atom	*x*	*y*	*z*	U_{eq} [a]
Os(1)	4255(1)	3605(1)	2594(1)	27(1)
Os(2)	1710(1)	2333(1)	2397(1)	21(1)
Os(3)	1879(1)	3923(1)	3524(1)	25(1)
O(1)	5303(31)	5465(20)	3301(22)	57(12)
O(2)	6658(31)	3402(25)	1510(28)	80(16)
O(3)	6166(28)	2480(21)	4196(20)	59(11)
O(4)	−1403(26)	2013(17)	2741(19)	41(10)
O(5)	1348(25)	750(14)	1058(17)	36(8)
O(6)	3329(33)	1105(21)	3958(24)	70(14)
O(7)	−1095(27)	3709(21)	4096(24)	64(13)
O(8)	3570(29)	2807(24)	5154(22)	68(13)
O(9)	2874(33)	5701(22)	4519(29)	90(17)
O(10)	52(37)	4988(19)	1879(17)	56(12)
O(11)	950(30)	4151(18)	107(17)	47(10)
C(1)	4878(32)	4719(30)	3039(22)	34(13)
C(2)	5752(50)	3455(31)	2028(32)	66(18)
C(3)	5597(47)	2863(32)	3655(40)	74(21)
C(4)	−215(41)	2160(21)	2624(21)	30(11)
C(5)	1504(32)	1357(20)	1616(31)	41(13)
C(6)	2727(38)	1538(21)	3405(34)	47(16)
C(7)	127(53)	3776(18)	3888(25)	53(16)
C(8)	3139(48)	3148(25)	4474(33)	59(17)
C(9)	2480(35)	5032(25)	4116(26)	37(12)
C(10)	822(68)	4530(33)	2526(42)	119(28)
C(11)	3058(41)	4184(22)	1471(23)	38(12)
C(12)	1699(34)	3733(24)	962(26)	33(12)
C(13)	1005(30)	3137(24)	1267(19)	23(10)
C(14)	−488(35)	3004(21)	567(23)	27(10)
C(15)	−519(57)	3633(41)	−51(51)	140(34)
C(16)	3491(41)	4957(24)	950(32)	49(16)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coeffiients (Å$^2 \times 10^3$) in **VI**

Atom	*x*	*y*	*z*	U_{eq} [a]
Os(1)	1227(1)	6133(1)	5952(1)	28(1)
Os(2)	−52(1)	5890(1)	2781(1)	28(1)
Os(3)	3171(1)	6546(1)	3925(1)	28(1)
O(1)	−1319(17)	5699(6)	7793(13)	76(6)
O(2)	938(17)	7228(5)	7209(13)	63(5)
O(3)	4966(15)	5983(5)	8461(12)	60(4)
O(4)	−3671(15)	5223(5)	1721(13)	60(5)
O(5)	−1681(20)	6744(6)	411(14)	77(6)
O(6)	1901(16)	5385(5)	601(13)	61(5)
O(7)	3797(21)	6692(5)	748(14)	76(6)
O(8)	6543(17)	7201(6)	5835(16)	82(6)
O(9)	308(17)	7474(5)	3577(13)	58(5)
O(10)	5483(15)	5508(5)	4716(14)	61(5)
O(11)	1277(12)	5397(4)	4745(9)	32(3)
C(1)	−368(19)	5861(6)	7071(13)	40(5)
C(2)	1044(19)	6823(7)	6710(14)	41(5)
C(3)	3592(23)	6037(5)	7533(16)	43(5)
C(4)	−2351(20)	5456(6)	2152(16)	40(5)
C(5)	−1096(18)	6414(7)	1330(16)	46(5)
C(6)	1130(21)	5576(6)	1392(15)	42(5)
C(7)	3553(22)	6646(6)	1941(16)	42(5)
C(8)	5271(22)	6959(7)	5172(18)	49(6)
C(9)	1376(18)	7134(6)	3701(15)	35(4)
C(10)	4626(21)	5880(6)	4417(15)	36(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

3.1. Reaction of $H_2Os_3(CO)_{10}$ with 2,4-hexadiyne-1,6-diol

The reaction of $H_2Os_3(CO)_{10}$ with the diyne ligand affords the only product (**III**) in high yield:

$$H_2Os_3(CO)_{10} + HOCH_2C_2C_2CH_2OH \xrightarrow{25°C} (\mu\text{-H})Os_3(CO)_{10}(\mu_2,\eta^2\text{-}C_6H_5O) \quad (1)$$

III

The molecular structure of **III**, shown in Fig. 1, was determined by an X-ray diffraction study. Selected bond lengths and angles are given in Table 4. The starting diyne ligand is completely rearranged upon coordination, the reaction with the triosmium cluster being accompanied by the transfer of one hydride from the cluster core to the ligand, its dehydration and cyclization to a pseudo-furan ring with the C–CH_3 substituent in the α-position.

A similar cyclization of but-3-yne-1-ol into a μ_3,η^2-2,3-dihydrofuran-4,5-diyl ligand was observed in the reaction of $Os_3(CO)_{12}$ with the alkynol under rather severe conditions (130°C) and also in the stepwise reaction of the latter ligand with $Os_3(CO)_{10}(NCMe)_2$ (90°C) [3]. In the final complex $Os_3(\mu\text{-H})_2(CO)_9(\mu_3,\eta^3$-

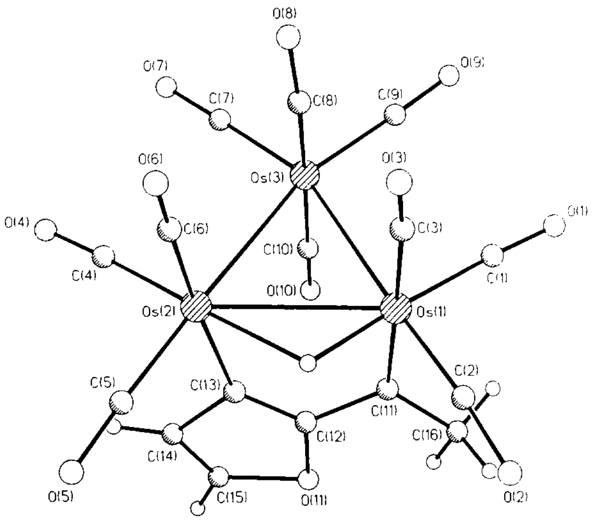


Fig. 1. Molecular structure of **III**.

C=C–CH_2–CH_2–O) (the structure was proposed on the basis of the IR and ^{1}H NMR data), the μ_3, η^3-ligand is evidently coordinated *via* the double bond of the dihydrofuran ring which acts as a four-electron donor. In this case the cluster is a coordinatively saturated 48 electron system. As for the compound **III**, the expected 48 electron shell can be attained if the organic ligand acts as a three-electron donor. In this case the C(11) and C(13) atoms should be bound to Os(1) and Os(2) *via* double and single bonds, respectively. In fact, the Os(1)–C(11), (2.00(3) Å) bond is slightly shorter than Os(2)–C(13) (2.07 Å). A similar Os=C double bond (1.98 Å) has been observed in the structure of (μ_2-acetyl-C,O)-(μ_2-hydrido)(methoxymethylcarbene)nonacarbonyltriosmium [8], whereas the Os=C double bond in the mononuclear complex chloromethylenenitrosobis(triphenylphosphine)osmium is noticeably shorter (1.92 Å) [9]. It should be noted that both of these M–C σ-bonds in **III** display a pronounced *trans*-effect resulting in the elongation of the Os(1)–C(3){O(3)} and Os(2)–C(6){O(6)} bonds to 2.10(5) and 1.98(4) Å, respectively, compared with the average value of 1.86 Å for all other Os–C(O) bonds. The C(12)=C(13) bond in **III** is even shorter (1.24(5) Å) than the "free" double bond of the furan ring (1.32(8) Å),

Table 4
Selected bond lengths and angles in **III**

Bond lengths (Å)		Bond angles (°)			
Os(1)–Os(2)	2.961(3)	Os(2)Os(1)Os(3)	59.2(1)	Os(2)Os(3)C(8)	84(1)
Os(1)–Os(3)	2.890(3)	Os(2)Os(1)C(1)	142(1)	C(7)Os(3)C(8)	97(2)
Os(3)–Os(2)	2.892(3)	Os(3)Os(1)C(1)	83(1)	Os(1)Os(3)C(9)	102(1)
Os(1)–C(11)	2.00(3)	Os(2)Os(1)C(2)	123(1)	Os(2)Os(3)C(9)	163(1)
Os(2)–C(13)	2.07(3)	Os(3)Os(1)C(2)	178(1)	C(7)Os(3)C(9)	98(2)
C(11)–C(12)	1.47(5)	C(1)Os(1)C(2)	95(2)	C(8)Os(3)C(9)	96(2)
C(11)–C(16)	1.50(6)	Os(2)Os(1)C(3)	93(1)	Os(1)Os(3)C(10)	90(2)
C(12)–C(13)	1.24(5)	Os(3)Os(1)C(3)	95(2)	Os(2)Os(3)C(10)	88(2)
C(13)–C(14)	1.54(4)	C(1)Os(1)C(3)	96(2)	C(7)Os(3)C(10)	88(2)
C(14)–C(15)	1.32(8)	C(2)Os(1)C(3)	86(2)	C(8)Os(3)C(10)	171(2)
C(12)–O(11)	1.46(4)	Os(2)Os(1)C(11)	85(1)	C(9)Os(3)C(10)	91(2)
C(15)–O(11)	1.52(6)	Os(3)Os(1)C(11)	91(1)	Os(1)H(1)Os(2)	102
Os(1)–H(1)	1.7	C(1)Os(1)C(11)	90(1)	C(12)O(11)C(15)	98(3)
Os(2)–H(1)	2.1	C(2)Os(1)C(11)	89(2)	Os(1)C(11)C(12)	119(3)
Os(1)–C(1)	1.82(4)	C(3)Os(1)C(11)	172(2)	Os(1)C(11)C(16)	128(3)
Os(1)–C(2)	1.79(5)	Os(1)Os(2)Os(3)	59.2(1)	C(12)C(11)C(16)	112(3)
Os(1)–C(3)	2.10(5)	Os(1)Os(2)C(4)	145(1)	O(11)C(12)C(11)	116(3)
Os(2)–C(4)	1.89(4)	Os(3)Os(2)C(4)	86(1)	O(11)C(12)C(13)	117(3)
Os(2)–C(5)	1.85(4)	Os(1)Os(2)C(5)	122(1)	C(11)C(12)C(13)	125(3)
Os(2)–C(6)	1.98(4)	Os(3)Os(2)C(5)	176(1)	Os(2)C(13)C(12)	129(2)
Os(3)–C(7)	1.83(5)	C(4)Os(2)C(5)	93(1)	Os(2)C(13)C(14)	124(2)
Os(3)–C(8)	1.99(4)	Os(1)Os(2)C(6)	95(1)	C(12)C(13)C(14)	107(3)
Os(3)–C(9)	1.89(4)	Os(3)Os(2)C(6)	94(1)	C(13)C(14)C(15)	106(3)
Os(3)–C(10)	1.83(6)	C(4)Os(2)C(6)	94(2)	O(11)C(15)C(14)	112(4)
C(1)–O(1)	1.21(5)	C(5)Os(2)C(6)	89(2)	Mean Os–C–O	174
C(2)–O(2)	1.27(7)	Os(1)Os(2)C(13)	78.9(8)		
C(3)–O(3)	1.04(6)	Os(3)Os(2)C(13)	89.1(9)		
C(4)–O(4)	1.16(5)	C(4)Os(2)C(13)	96(1)		
C(5)–O(5)	1.22(4)	C(5)Os(2)C(13)	87(1)		
C(6)–O(6)	1.10(5)	C(6)Os(2)C(13)	170(2)		
C(7)–O(7)	1.24(6)	Os(1)Os(3)Os(2)	61.6(1)		
C(8)–O(8)	1.13(6)	Os(1)Os(3)C(7)	160(1)		
C(9)–O(9)	1.18(5)	Os(2)Os(3)C(7)	98.5(9)		
C(10)–O(10)	1.27(6)	Os(1)Os(3)C(8)	83(1)		

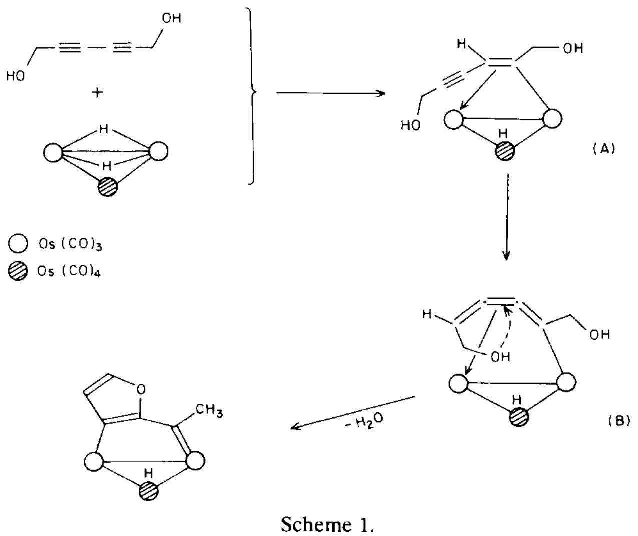
which is in agreement with the absence of the additional π-interaction of the cluster core with the C_{12}=C_{13} bond. In the related compound $Os_3(\mu\text{-}H)(CO)_9(\mu_3,\eta^3\text{-}CH{=}CH{=}C{=}CHO)$ [2] the organic ligand acts as a five-electron donor involving three carbon atoms in the interaction with the Os_3 core and the corresponding bond lengths between three coordinated carbon atoms of the ligand are substantially longer (1.44 (3) and 1.52 (3) Å).

A possible mechanism of the diyne ligand rearrangement is given in Scheme 1. In the first stage of the process the ligand coordinates to the Os_3 framework with the transfer of a hydride onto a coordinated triple bond affording the intermediate **A** well known for the reactions of $H_2Os_3(CO)_{10}$ with alkynes [10,11]. The formation of the cumulene structure (intermediate **B**) is a natural step in this reaction sequence owing to high conjugation of adjacent multiple bonds in **A**. Moreover, the $HOCH_2C_2CH_2OH$ ligand was shown to rearrange into a similar allene in the reaction with $H_2Os_3(CO)_{10}$ [2]. The coordinated cumulene **B** can easily rearrange into a furan ring with the elimination of a water molecule and simultaneous transfer of a hydrogen atom to the terminal position of the ligand to give the final product (**III**).

The cyclization of the alkyne ligand on coordination is evidently due to the presence of two unsaturated triple bonds in the molecule. Once the ligand bears the protecting $Co_2(CO)_6$ group(s) on its triple bond(s), the reaction with $H_2Os_3(CO)_{10}$ proceeds in a different way.

Corresponding $Co_2(CO)_6$-substituted compounds were obtained using a procedure similar to that described in [12] (Eq. (2)).

$$Co_2(CO)_8 + HOCH_2C_2C_2CH_2OH \longrightarrow \{Co_2(CO)_6\}(\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)\ \textbf{IV} + \{Co_2(CO)_6\}_2(\mu_2,\eta^2:\mu_2,\eta^2\text{-}HOCH_2C_2C_2CH_2OH)\ \textbf{V} \quad (2)$$



Scheme 1.

The spectroscopic characteristics of **IV** and **V** given in Table 1 are in agreement with $Co_2(CO)_6$ coordination to one and two triple bonds of the diyne, respectively.

The reactions of these compounds with $H_2Os_3(CO)_{10}$ yields the cluster $(\mu\text{-}H)(\mu\text{-}OH)Os_3(CO)_{10}$ (**VI**) as the main osmium-containing product:

$$H_2Os_3(CO)_{10} + \textbf{IV} \xrightarrow[\text{Ar, 96 h}]{25°C} Os_3(CO)_{12} + (\mu\text{-}H)(\mu\text{-}OH)OS_3(CO)_{10}\ \textbf{VI}(26\%) \quad (3)$$

$$H_2Os_3(CO)_{10} + \textbf{V} \xrightarrow[\text{in air, 48 h}]{25°C} (\mu\text{-}H)(\mu\text{-}OH)Os_3(CO)_{10}\ \textbf{VI}(68\%) \quad (4)$$

It should be noted that **V** is completely inactive in reaction (4) under anaerobic conditions. The role of an oxygen-containing atmosphere in this process is evidently associated with the oxidation of the $Co_2(CO)_6$ protecting group and the deshielding of the completely protecting compound **V** into **IV** with a free triple bond. Thus, the coordination of **IV** to $H_2Os_3(CO)_{10}$ is apparently a common stage of the both reactions (3) and (4):

$$H_2Os_3(CO)_{10} + (\text{IV}) \longrightarrow [HOCH_2{-}C{\equiv}C(H){-}C{\equiv}C{-}CH_2OH]\ \text{with}\ HOs_3(CO)_{10}\ \text{and}\ Co_2(CO)_6\ \textbf{VII} \quad (5)$$

The presence of a $Co_2(CO)_6$ protecting group in the intermediate **VII** prevents the diyne moiety from undergoing subsequent cyclization. In this case, instead of the ligand rearrangement, α-hydroxyl group transfer onto the Os_3 framework is observed. Similarly, the formation of the cluster **VI** was found to occur in the reaction of $H_2Os_3(CO)_{10}$ with $HOCH_2C_2CH_2OH$, in which the possibility of the ligand rearrangement was limited by the nature of the alkyne used [2].

The molecular structure of **VI** (Fig. 2) was determined by an X-ray diffraction study. Selected bond lengths and angles are given in Table 5. The main structural features of **VI** are similar to those of the closely related compound $(\mu\text{-}H)(\mu\text{-}OMe)Os_3(CO)_{10}$ studied in [13]. Metal–metal distances in the osmium triangle of **VI** (2.810(1), 2.834(2) and 2.820(2) Å) are

Table 5
Selected bond lengths and angles in **VI**

Bond lengths (Å)		Bond angles (°)			
Os(1)–Os(2)	2.810(1)	Os(1)Os(2)Os(3)	60.5(1)	C(7)Os(3)C(9)	95.0(6)
Os(1)–Os(3)	2.834(2)	Os(1)Os(3)Os(2)	59.6(1)	Os(1)Os(3)C(10)	83.8(5)
Os(3)–Os(2)	2.820(2)	Os(2)Os(1)Os(3)	60.0(1)	C(7)Os(3)C(10)	95.8(6)
Os(1)–O(11)	2.145(9)	Os(2)Os(1)O(11)	49.2(2)	C(9)Os(3)C(10)	167.0(7)
Os(2)–O(11)	2.148(8)	Os(1)Os(2)O(11)	49.1(2)	Os(2)Os(3)C(10)	86.4(4)
Os(1)–C(1)	1.89(2)	Os(3)Os(1)O(11)	83.9(3)	C(8)Os(3)C(10)	91.7(6)
Os(1)–C(2)	1.87(2)	Os(1)O(11)Os(2)	81.8(3)	O(11)Os(1)C(1)	94.1(5)
Os(1)–C(3)	1.92(1)	Os(2)Os(1)C(1)	113.2(4)	Os(3)Os(1)C(2)	90.4(5)
Os(2)–C(4)	1.95(2)	Os(3)Os(1)C(1)	172.2(3)	C(1)Os(1)C(2)	90.6(7)
Os(2)–C(5)	1.85(2)	Os(2)Os(1)C(2)	122.3(4)	Os(3)Os(1)C(3)	90.3(5)
Os(2)–C(6)	1.90(2)	O(11)Os(1)C(2)	171.4(4)	C(1)Os(1)C(3)	97.4(6)
Os(3)–C(7)	1.91(1)	Os(2)Os(1)C(3)	133.8(5)	Os(1)Os(2)Os(3)	60.5(1)
Os(3)–C(8)	1.93(2)	O(11)Os(1)C(3)	97.1(5)	Os(3)Os(2)O(11)	84.3(2)
Os(3)–C(9)	1.95(1)	C(2)Os(1)(3)	89.4(6)	Os(3)Os(2)C(4)	174.8(5)
Os(3)–C(10)	1.96(1)	Os(1)Os(2)O(11)	49.1(2)	Os(1)Os(2)C(5)	121.0(5)
C(1)–O(1)	1.16(2)	Os(1)Os(2)C(4)	114.8(4)	O(11)Os(2)C(5)	170.0(5)
C(2)–O(2)	1.12(2)	O(11)Os(2)C(4)	93.9(5)	Os(1)Os(2)C(6)	133.1(4)
C(3)–O(3)	1.12(2)	Os(3)Os(2)C(5)	88.8(4)	O(11)Os(2)C(6)	97.1(5)
C(4)–O(4)	1.10(2)	C(4)Os(2)C(5)	92.4(6)	C(5)Os(2)C(6)	89.9(6)
C(5)–O(5)	1.16(2)	Os(3)Os(2)C(6)	88.9(4)	Os(1)Os(3)C(7)	153.8(4)
C(6)–O(6)	1.14(2)	C(4)Os(2)C(6)	96.1(6)	Os(1)Os(3)C(8)	106.8(5)
C(7)–O(7)	1.15(2)	Os(1)Os(3)Os(2)	59.6(1)	C(7)Os(3)C(8)	99.5(7)
C(8)–O(8)	1.13(2)	Os(2)Os(3)C(7)	94.2(4)	Os(2)Os(3)C(9)	85.7(4)
C(9)–O(9)	1.14(2)	Os(2)Os(3)C(8)	166.3(5)	C(8)Os(3)C(9)	93.5(6)
C(10)–O(10)	1.11(2)	Os(1)Os(3)C(9)	83.3(4)	mean Os–C–O	177.8

close to the osmium–osmium bond lengths in the methoxy derivative (2.813, 2.822 and 2.812 Å). The elongation of the H-bridged Os–Os edge discussed above is not observed in this case, which is obviously due to the contrasting effect of the bridging OH group. This group is bound symmetrically to the Os(1)–Os(2) bond as the OME ligand in (μ-H)(μ-OMe)$Os_3(CO)_{10}$. A difference can be pointed out in the lengths of Os–O(H) and Os–O(Me) bonds: 2.145(9) and 2.148(8) Å as compared with 2.112(9) and 2.093(9) Å, respectively. A more interesting peculiarity is displayed by the Os–C(O) bonds in **VI**: mean values of the bond lengths for bridged Os(1) and Os(2) atoms are 1.895 and 1.901 Å, respectively, whereas the corresponding value for the Os(3) atom is 1.937 Å. This difference is evidently associated with the absence of a π-acceptor ability of the μ-H and μ-OH ligands bound to the Os(1) and Os(2) atoms.

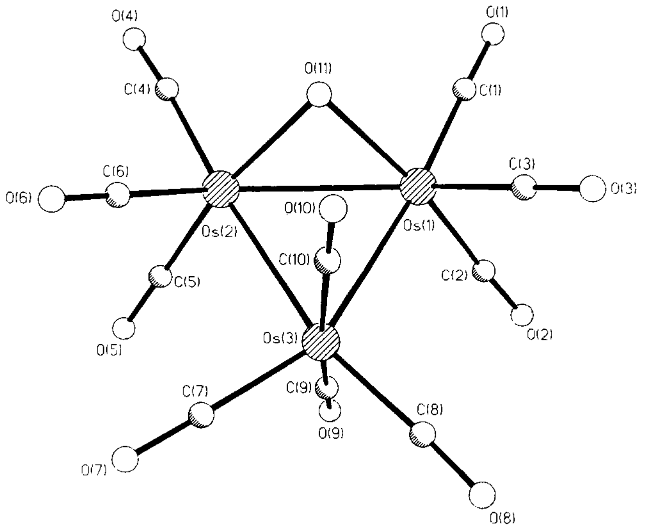


Fig. 2. Molecular structure of **VI**. The H atoms bridging the Os(1)–Os(2) bond and at O(11) hydroxyl oxygen are not located.

Acknowledgements

We thank Johnson-Matthey for the generous loan of the starting osmium material. One of the authors (A.I.Y.) acknowledges support from the American Crystallographic Association within the framework of the ACA/USNCCr programme.

References

[1] E. Sappa, A. Tiripicchio and P. Brounstein, *Chem. Rev.*, *83* (1983) 203.
[2] S. Aime, A. Tiripicchio, M. Tiripicchio-Camellini Camellin and A.J. Deeming, *Inorg. Chem.*, *20* (1981) 2027.
[3] S. Aime and A.J. Deeming, *J. Chem. Soc, Dalton Trans.*, (1983) 1807.

[4] A.J. Deeming, M.S.B. Felix, P.A. Bates and M.B. Hursthouse, *J. Chem. Soc, Dalton Trans.*, (1987) 461.
[5] S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, *J. Am. Chem. Soc.*, *97* (1975) 3942
[6] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, *39* (1983) 158.
[7] W. Robinson and G.M. Sheldrick, SHELX in N.W. Isaacs and M.R. Taylor (eds.), *Crystallographic Computing – Techniques and New Technologies*, Oxford University Press, Oxford, 1988, p. 366.
[8] C.M. Jensen, C.B. Knobler and H.D. Kaesz, *J. Am. Chem. Soc.*, *106* (1984) 5926.
[9] A.F. Hill, W.R. Roper, J.M. Waters and A.H. Wright, *J. Am. Chem. Soc.*, *105* (1983) 5939.
[10] A.D. Clauss, M. Tachikawa, J.R. Shapley and C.G. Pierpoint, *Inorg. Chem.*, *20* (1981) 1528.
[11] E. Sappa, A. Tiripicchio and A.M.M. Lanfredi, *J. Organomet. Chem.*, *249* (1983) 391.
[12] W. Hubel and R. Merenyi, *Chem. Ber.*, *96* (1963) 930.
[13] M.R. Churchill and H.J. Wasserman, *Inorg. Chem.*, *19* (1980) 2391..