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Synthesis and Structure of (η^5-C_5H_5)$WOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$, a Tetrahedral Tungsten–Triosmium Cluster Complex with a Unique Unsymmetrical (W, Os) Edge-Bridging Oxo Ligand[1,2]

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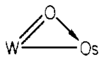
The reaction of $CpWOs_3(CO)_{12}H$ (Cp = η^5-C_5H_5) with (i) Me_3NO and (ii) C_2H_2 produces the species $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2H_2)H$ (**1**) in which the μ_3-η^2-C_2H_2 ligand is believed to bridge the triosmium face of a tetrahedral WOs_3 cluster. Further reaction of **1** with Me_3NO yields the complex $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$ (**2**), a unique species with a



bridge, which has been fully characterized both by spectroscopic methods and via a single-crystal X-ray diffraction study. Complex **2** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with a = 7.526 (2) Å, b = 9.372 (2) Å, c = 14.995 (5) Å, α = 104.17 (2)°, β = 92.06 (2)°, γ = 109.74 (2)°, V = 957.0 (5) Å^3, and Z = 2. Diffraction data (Mo Kα, 2θ = 4.5–45.0°) were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was refined to R_F = 3.4% and R_{wF} = 3.2% for all 2507 independent reflections (none rejected). The molecule contains a tetrahedral WOs_3 core and possesses the following interesting structural features. (1) The μ_3-η^2-C_2H_2 ligand now bridges the W–Os(1)–Os(2) triangular face. (2) The μ-O ligand bridges a tungsten–osmium edge, forming a triangular system in which $W{=}O$ = 1.761 (8) Å, Os(1)–O = 2.200 (8) Å, W–Os(1) = 2.885 (1) Å, and $W{=}O{\rightarrow}Os(1)$ = 92.82 (36)°. (3) The μ-hydride ligand, which was located directly and refined, spans the Os(2)–Os(3) bond.

Introduction

We recently described the synthesis and structures of the alkyne complexes $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Ar_2)H$ (Ar = C_6H_5, p-$C_6H_4CH_3$) together with their conversion to the dialkylidyne complexes $CpWOs_3(CO)_9(\mu_3\text{-}CAr)_2H$ upon decarbonylation.[5] In examining the generality of this alkyne scission reaction, we have prepared an analogous complex of acetylene, $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2H_2)H$ (**1**). However, treatment of this acetylene complex with Me_3NO/CH_3CN does *not* produce the anticipated dimethylidyne complex, $CpWOs_3(CO)_9(\mu_3\text{-}CH)_2H$. Rather, the novel oxo–acetylene compound $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)H$ (**2**) is produced as the major product.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents were rigorously dried before use. The progress of the reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, Silica Gel 60, F-254, E. Merck). Preparative thin-layer plates were prepared from Silica Gel G (Type 60, E. Merck).

Infrared spectra were obtained on a Perkin-Elmer 281B spectrophotometer. Proton NMR spectra were recorded on a Nicolet Model NT-360 spectrometer (360 MHz), which is part of the NSF Regional Instrumentation Facility at the University of Illinois. Mass spectra were obtained with either a Varian MAT CH-5 (electron impact) or a Varian MAT 731 (field desorption) mass spectrometer by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences at the University of Illinois. All m/z values are referenced to ^{192}Os and ^{184}W. Microanalytical data were provided by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

Table I. X-ray Data for $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$

(A) Crystal Parameters at 22 °C

cryst system: triclinic
space group: $P\bar{1}$ (No. 2)
a = 7.526 (2) Å
b = 9.372 (2) Å
c = 14.995 (5) Å
α = 104.17 (2)°
β = 92.06 (2)°
γ = 109.74 (2)°
V = 957.0 (5) Å
Z = 2
mol wt = 1086.7
ρ(calcd) = 3.77 g·cm^{-3}
μ(Mo Kα) = 274.2 cm^{-1}

(B) Measurement of Data

diffractometer: Syntex P2$_1$
radiation: Mo Kα (λ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial mode
reflcns measd: $h,\pm k,\pm l$ for 2θ = 4.5–45.0°
scan type: θ(cryst)–2θ(counter)
scan width: [2θ(Kα_1) − 1.0]° – [2θ(Kα_2) + 1.0]°
scan speed: 2.0°/min (in 2θ)
bkgd meast: stationary cryst and counter at beginning and end of 2θ scan, each for one-fourth of the scan time
reflcns collected: 2739 total, merged to 2507 independent reflcns (none rejected); file name WOS6.
std reflcns: three measd after every 97 reflcns (050, 411, 11$\bar{8}$); no decay obsd

$CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2H_2)H$ (1). A red dichloromethane (50 mL)/acetonitrile (10 mL) solution of $CpWOs_3(CO)_{12}H$[6] (61.0 mg, 0.0527 mmol) was treated with sublimed Me_3NO (4.2 mg, 0.0559 mmol) in a 500-mL glass pressure bottle. After evaporation of the solvent in vacuo, the residue was dissolved in toluene (ca. 100 mL), a partial vacuum was drawn over the greenish blue solution, and the bottle was charged with C_2H_2 to a pressure of 40 psig. The resulting orange solution was heated at 110 °C for 0.5 h. The solvent was evaporated, and **1** was isolated after preparative TLC (pentane:dichloromethane = 3:2). Recrystallization from pentane/dichloromethane gave orange crystals (18.3 mg, 0.0158 mmol, 30%). Minor products (<5% yields) were observed on the TLC plate but were not characterized. IR (CCl_4): ν(CO) 2084 w, 2066 s, 2021 vs, 2005 m, 1992 m, 1960 w cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 9.32 (s, 2 H), 5.40 (s, 5 H), −21.45 (s, 1 H). MS (70 eV): m/z 1132 (M$^+$). Anal.

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(1) Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 28. For previous parts see ref 2.

(2) (a) Part 27, (μ-H)$_3$Os$_3$Rh(CO)$_9$(η^6-C$_6$H$_5$Me): Churchill, M. R.; Bueno, C. *J. Organomet. Chem.* **1983**, *256*, 357–364. (b) Part 26, (μ-H)Os$_3$(CO)$_{10}$[μ-3,4-C$_3$N$_2$H$_2$(2-CH$_3$)]: Churchill, M. R.; Missert, J. R. *Ibid.* **1983**, *256*, 349–356. (c) Part 25, (μ-H)Os$_3$(CO)$_{10}$(μ-η^2-N═NPh): Samkoff, D. E.; Shapley, J. R.; Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1984**, *23*, 397. (d) Part 24: Churchill, M. R.; Bueno, C. *Ibid.* **1983**, *22*, 1510.

(3) SUNY—Buffalo.

(4) University of Illinois.

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(6) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 534.

Table II. Final Atomic Positional Parameters for $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$

atom	*x*	*y*	*z*	B_{iso}, Å^2
Os(1)	0.12289 (6)	0.43241 (5)	0.19387 (3)	
Os(2)	0.23251 (6)	0.16393 (5)	0.16344 (3)	
Os(3)	0.31583 (6)	0.35627 (5)	0.33998 (3)	
W	−0.05678 (6)	0.17472 (5)	0.27193 (3)	
O	−0.1210 (10)	0.3365 (9)	0.2658 (6)	
O(1)	0.4769 (15)	0.5666 (11)	0.1096 (7)	
O(2)	0.2408 (17)	0.7495 (12)	0.3467 (8)	
O(3)	−0.1325 (14)	0.5288 (12)	0.0751 (7)	
O(4)	0.2287 (13)	−0.1627 (10)	0.1449 (7)	
O(5)	0.5246 (17)	0.2089 (13)	0.0282 (9)	
O(6)	0.1946 (13)	0.5624 (11)	0.4944 (7)	
O(7)	0.3894 (14)	0.1782 (12)	0.4711 (7)	
O(8)	0.7170 (13)	0.6000 (11)	0.3529 (7)	
C(1)	0.3426 (21)	0.5142 (15)	0.1396 (10)	
C(2)	0.1987 (18)	0.6288 (15)	0.2946 (10)	
C(3)	−0.0361 (18)	0.4918 (15)	0.1192 (10)	
C(4)	0.2325 (17)	−0.0372 (16)	0.1509 (9)	
C(5)	0.4197 (18)	0.1955 (14)	0.0798 (9)	
C(6)	0.2393 (16)	0.4859 (14)	0.4360 (9)	
C(7)	0.3620 (16)	0.2471 (14)	0.4230 (9)	
C(8)	0.5722 (18)	0.5061 (15)	0.3466 (7)	
C(9)	0.0180 (19)	0.2051 (16)	0.0923 (9)	
C(10)	−0.0777 (17)	0.0829 (16)	0.1314 (9)	
C(11)	−0.1580 (23)	−0.1029 (15)	0.2656 (11)	
C(12)	−0.3115 (21)	−0.0447 (21)	0.2720 (16)	
C(13)	−0.278 (3)	0.0651 (22)	0.3609 (20)	
C(14)	−0.105 (3)	0.0781 (20)	0.4006 (11)	
C(15)	−0.0411 (20)	−0.0276 (20)	0.3474 (13)	
H	0.301 (22)	0.202 (20)	0.269 (13)	10.9 (47)
H(9)	−0.008 (18)	0.186 (16)	0.040 (10)	4.0
H(10)	−0.138 (16)	−0.007 (14)	0.079 (9)	4.0
H(11)	−0.1412	−0.1786	0.2147	6.0
H(12)	−0.4163	−0.0737	0.2255	6.0
H(13)	−0.3580	0.1187	0.3874	6.0
H(14)	−0.0393	0.1509	0.4576	6.0
H(15)	0.0699	−0.0469	0.3641	6.0

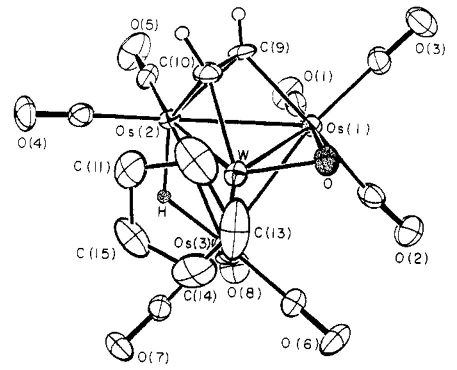

Figure 1. Labeling of atoms in the $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$ molecule (ORTEP-II diagram (30% ellipsoids) with hydride ligand and acetylenic hydrogen atoms reduced for clarity). Atom C(12) of the $\eta^5\text{-}C_5H_5$ ligand is not labeled; also, hydrogen atoms of this system are omitted for clarity.

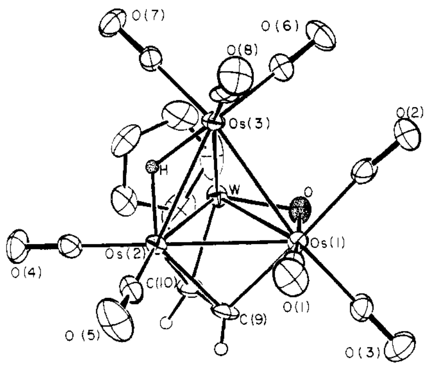

Figure 2. Another view of the $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$ molecule. The molecule is projected onto the Os(1)–Os(2)–Os(3) plane, showing the distribution of ligands relative to the hydride ligand.

Calcd for $C_{17}H_8O_{10}WOs_3$: C, 18.12; H, 0.72. Found: C, 18.14; H, 0.69.

$CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$ (2). Compound **1** (23.2 mg, 0.0206 mmol) was treated with sublimed Me_3NO (1.65 mg, 0.022 mmol) in dichloromethane (30 mL)/acetonitrile (10 mL). After evaporation of the solvent in vacuo, a toluene solution of the residue was refluxed for 0.5 h. Purification by preparative TLC (pentane:dichloromethane = 3:2) and crystallization gave dark red crystals (7.0 mg, 0.0064 mmol, 31%). Other products (<5% yields) were not characterized. IR (C_6H_{12}): ν(CO) 2086 s, 2049 vs, 2022 w, 2011 vs, 1977 m, 1984 m, 1969 m, 1939 m cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.62 (d, 1 H, J = 5.2 Hz), 9.43 (d, 1 H, J = 5.2 Hz), 5.83 (s, 5 H), −9.70 (s, 1 H). MS (field desorption): m/z 1092 (M$^+$). Anal. Calcd for $C_{15}H_8O_9WOs_3$: C, 16.58; H, 0.74. Found: C, 16.78; H, 0.69.

X-ray Structural Study of 2. An opaque dark red crystal of approximate size 0.10 × 0.17 × 0.20 mm was mounted and aligned on the Syntex P2$_1$ diffractometer at SUNY—Buffalo, and data were collected as described previously[7] (see Table I). All data were converted to $|F_o|$ values, following correction for absorption and for Lorentz and polarization factors. Any reflection with I(net) < 0 was assigned a value of $|F_o| = 0$. No data were rejected.

During subsequent calculations the analytical forms for neutral atoms were corrected for both the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[8] The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = [(\sigma(|F_o|))^2 + 0.015|F_o|^2]^{-1}$. All calculations were performed with the SUNY—Buffalo modified Syntex XTL system.

The structure was solved with the program MULTAN[9] and difference-Fourier syntheses. Full-matrix least-squares refinement led smoothly to convergence with R_F = 3.4%, R_{wF} = 3.2%, and GOF = 1.40 for 236 parameters refined against all 2507 reflections.[10] The residuals for those 2266 data with $|F_o| > 3.0\sigma(|F_o|)$ were R_F = 2.8%, R_{wF} = 3.1%, and GOF = 1.45.

A final difference-Fourier synthesis showed no significant features. The function $\sum w(|F_o| - |F_c|)^2$ showed no abnormal dependency on $|F_o|$, (sin θ)/λ, sequency number, identity, or parity class of the crystallographic indices; the weighting scheme is thus satisfactory. Positional and isotropic thermal parameters are collected in Table II; anisotropic thermal parameters can be sought in Table II-S (supplementary material).

Synthetic and Spectroscopic Results

The formulation of compound **1** is established by microanalytical and spectroscopic data. The solution IR (ν(CO)) spectrum of **1** is very similar to that of $CpWOs_3(CO)_{10}[\mu_3\text{-}\eta^2\text{-}C_2(p\text{-}C_6H_4CH_3)_2]H$;[5] the structure of the latter compound involves an intact pseudotetrahedral WOs_3 core with the alkyne bound in $2\sigma + \pi$ fashion to the Os_3 face. An analogous structure for **1** is also consistent with the equivalent acetylenic protons, the chemical shift of which (δ 9.32) is closer to that of the triosmium complex $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2H_2)$ (δ 9.67)[11] than to that of the tetranuclear "butterfly" complex $Os_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2H_2)$ (δ 10.28).[12]

The molecular ion observed in the mass spectrum of **2** differs from that of **1** by 40 mass units, which originally suggested that **2** might have an oxo group (**1** − 2CO + O → **2**) of some

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(9) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(10) $R_F = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$ (%), $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%), and GOF $= [\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO = number of observations and NV = number of refined variables.

(11) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

(12) Jackson, R.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1980**, *193*, C1.

Table III. Interatomic Distances (Å) and Esd's for CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C$_2$H$_2$)(μ-H)

(A) Metal-Metal Distances			
W-Os(1)	2.885 (1)	Os(1)-Os(2)	2.844 (1)
W-Os(2)	2.779 (1)	Os(1)-Os(3)	2.942 (1)
W-Os(3)	2.742 (1)	Os(2)-Os(3)	2.726 (1)
(B) Metal-Oxygen Distances			
W-O	1.761 (8)	Os(1)-O	2.200 (8)
(C) Metal-Carbonyl Distances			
Os(1)-C(1)	1.879 (15)	Os(1)···O(1)	3.006 (11)
-C(2)	1.965 (14)	···O(2)	3.100 (11)
-C(3)	1.912 (14)	···O(3)	3.065 (11)
Os(2)-C(4)	1.848 (14)	Os(2)···O(4)	2.996 (10)
-C(5)	1.915 (14)	···O(5)	3.039 (13)
Os(3)-C(6)	1.887 (13)	Os(3)···O(6)	3.014 (10)
-C(7)	1.884 (13)	···O(7)	3.018 (10)
-C(8)	1.947 (14)	···O(8)	3.075 (10)
(D) M-C(acetylene) Distances			
Os(1)-C(9)	2.160 (14)	Os(2)-C(10)	2.191 (14)
Os(2)-C(9)	2.095 (15)	W-C(10)	2.050 (13)
(E) Distances Involved within the Acetylene Ligand			
C(9)-C(10)	1.405 (20)	C(9)-H(9)	0.76 (14)
C(10)-H(10)	0.96 (13)		
(F) W-C(cyclopentadienyl) Distances			
W-C(11)	2.428 (14)	W-C(14)	2.314 (17)
W-C(12)	2.290 (19)	W-C(15)	2.466 (18)
W-C(13)	2.296 (23)	W-Cp	2.045[a]
(G) C-C Distances within the Cyclopentadienyl System			
C(11)-C(12)	1.431 (25)	C(14)-C(15)	1.347 (27)
C(12)-C(13)	1.423 (35)	C(15)-C(11)	1.362 (25)
C(13)-C(14)	1.361 (33)		
(H) C-O Distances			
C(1)-O(1)	1.127 (19)	C(5)-O(5)	1.125 (19)
C(2)-O(2)	1.139 (18)	C(6)-O(6)	1.127 (17)
C(3)-O(3)	1.154 (18)	C(7)-O(7)	1.135 (17)
C(4)-O(4)	1.148 (17)	C(8)-O(8)	1.129 (17)
(I) M-H Distances			
Os(2)-H	1.57 (18)	W···H	2.62 (18)
Os(3)-H	1.53 (18)		

[a] Cp is, here, the centroid of the cyclopentadienyl ring.

sort. The ^{1}H NMR spectrum of **2** shows two 1 H signals at δ 9.43 and 10.62 with J(HH) = 5.2 Hz. The coupling constant suggested that the HCCH group was intact, but the chemical shifts did not eliminate the possibility of methylidyne groups (cf. H$_3$Os$_3$(CO)$_9$(μ_3-CH), δ 9.36,[13] or HOs$_3$(CO)$_{10}$(μ_3-CH), δ 14.16[14]) or a more complex structure.

Description of the X-ray-Determined Molecular Structure of CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C$_2$H$_2$)(μ-H) (2)

The triclinic crystal contains an ordered array of discrete CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C$_2$H$_2$)(μ-H) molecules, which are separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. No crystallographic symmetry is imposed upon the molecule. Indeed, as can clearly be seen in Figures 1 and 2, each metal atom in the tetranuclear cluster has a different ligand connectivity and the isolated CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C$_2$H$_2$)(μ-H) molecule is therefore chiral. However, the complex crystallizes in the centrosymmetric space group $P\bar{1}$ and contains equal quantities of the two enantiomers, which are interrelated by crystallographic inversion centers.

Table IV. Interatomic Angles (Deg) and Esd's for CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C$_2$H$_2$)(μ-H)

(A) Intermetallic Angles			
Os(2)-Os(1)-Os(3)	56.18 (2)	Os(1)-Os(3)-Os(2)	60.09 (2)
Os(2)-Os(1)-W	58.02 (2)	Os(1)-Os(3)-W	60.88 (2)
Os(3)-Os(1)-W	56.15 (2)	Os(2)-Os(3)-W	61.08 (2)
Os(1)-Os(2)-Os(3)	63.73 (2)	Os(1)-W-Os(2)	60.24 (2)
Os(1)-Os(2)-W	61.73 (2)	Os(1)-W-Os(3)	62.98 (2)
Os(3)-Os(2)-W	59.76 (2)	Os(2)-W-Os(3)	59.16 (2)
(B) M-M-CO and M-M-Cp Angles			
Os(2)-Os(1)-C(1)	83.2 (5)	Os(1)-Os(3)-C(6)	93.0 (4)
-C(2)	132.5 (4)	-C(7)	160.3 (4)
-C(3)	132.4 (4)	-C(8)	99.0 (4)
Os(3)-Os(1)-C(1)	95.7 (5)	Os(2)-Os(3)-C(6)	147.5 (4)
-C(2)	77.9 (4)	-C(7)	109.6 (4)
-C(3)	167.6 (4)	-C(8)	105.2 (4)
W-Os(1)-C(1)	140.0 (5)	W-Os(3)-C(6)	90.8 (4)
-C(2)	107.8 (4)	-C(7)	99.7 (4)
-C(3)	118.0 (4)	-C(8)	159.1 (4)
Os(1)-Os(2)-C(4)	163.2 (4)	Os(1)-W-Cp	178.7
-C(5)	105.2 (4)	Os(2)-W-Cp	119.3
Os(3)-Os(2)-C(4)	115.7 (4)	Os(3)-W-Cp	115.7
-C(5)	119.5 (4)		
W-Os(2)-C(4)	102.8 (4)		
-C(5)	166.4 (4)		
(C) M-O-M Angle			
Os(1)-O-W	92.82 (36)		
(D) M-M-O Angles			
Os(2)-Os(1)-O	95.06 (22)	Os(2)-W-O	109.15 (27)
Os(3)-Os(1)-O	80.27 (22)	Os(3)-W-O	94.08 (27)
W-Os(1)-O	37.56 (22)	Os(1)-W-O	49.62 (27)
(E) O-M-C(carbonyl) and O-M-Cp Angles			
O-Os(1)-C(1)	175.9 (5)	O-W-Cp	131.0
-C(2)	87.9 (5)		
-C(3)	89.3 (5)		
(F) M-C-M, M-C-C, M-C-H, and C-C-H Angles Involved with the Acetylene Ligand			
Os(1)-C(9)-Os(2)	83.8 (5)	Os(2)-C(10)-W	81.8 (5)
Os(1)-C(9)-C(10)	112.4 (10)	W-C(10)-C(9)	108.6 (10)
Os(2)-C(9)-C(10)	74.6 (8)	Os(2)-C(10)-C(9)	67.3 (8)
Os(1)-C(9)-H(9)	129 (10)	W-C(10)-H(10)	146 (8)
Os(2)-C(9)-H(9)	128 (10)	Os(2)-C(10)-H(10)	118 (8)
C(10)-C(9)-H(9)	114 (10)	C(9)-C(10)-H(10)	105 (8)
(G) O-M-C(acetylene), C(carbonyl)-M-C(acetylene), and Cp-W-C(acetylene) Angles			
O-Os(1)-C(9)	86.0 (4)	O-W-C(10)	95.8 (5)
C(1)-Os(1)-C(9)	95.5 (6)	C(4)-Os(2)-C(9)	121.8 (6)
C(2)-Os(1)-C(9)	173.8 (6)	C(5)-Os(2)-C(9)	99.6 (6)
C(3)-Os(1)-C(9)	86.1 (6)	C(4)-Os(2)-C(10)	93.3 (6)
Cp-W-C(10)	108.4	C(5)-Os(2)-C(10)	128.1 (5)
(H) C(carbonyl)-M-C(carbonyl) Angles			
C(1)-Os(1)-C(2)	90.5 (6)	C(6)-Os(3)-C(7)	89.9 (6)
C(1)-Os(1)-C(3)	94.6 (6)	C(6)-Os(3)-C(8)	96.3 (6)
C(2)-Os(1)-C(3)	95.0 (6)	C(7)-Os(3)-C(9)	100.0 (6)
C(4)-Os(2)-C(5)	89.8 (6)		
(I) M-C-O Angles			
Os(1)-C(1)-O(1)	177.9 (13)	Os(2)-C(5)-O(5)	177.2 (13)
-C(2)-O(2)	173.5 (13)	Os(3)-C(6)-O(6)	179.0 (12)
-C(3)-O(3)	179.2 (13)	-C(7)-O(7)	178.2 (12)
Os(2)-C(4)-O(4)	178.0 (12)	-C(8)-O(8)	175.9 (12)
(J) M-H-M Angle			
Os(2)-H-Os(3)	123 (10)		

The atomic labeling scheme is shown in Figure 1. Interatomic distances and their estimated standard deviations (esd's) are collected in Table III, while interatomic angles and their esd's are listed in Table IV. The tetrahedral WOs$_3$ cluster *as a whole* is associated with 60 valence electrons. [If we consider, *for electron-counting purposes only*, that all metal atoms are in a formal oxidation state of zero and that all ligands are neutral,[15] then we have one d^6 W(0) atom, three

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[13] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[14] Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

[15] This is simply one of a number of possible formulations; its principal (and perhaps sole) advantage is simplicity. From a purely intuitive chemical viewpoint the (η^5-C$_5$H$_5$)W=O grouping along with the σ linkage to the acetylene ligand would appear to indicate a W(IV) species.

d^8 Os(0) atoms, sixteen electrons from the eight terminal carbonyl groups, five electrons from the η^5-C_5H_5 system, four electrons from the μ_3-η^2-C_2H_2 ligand, four electrons from the bridging oxo ligand (which is involved in a W=O:→Os mode; vide infra), and one electron from the μ-hydride ligand.] Formal electron counts at the individual metal atoms are as follows: 17 e for W, 20 e for Os(1), $17^1/_2$ e for Os(2), and $17^1/_2$ e for Os(3).

Metal–metal distances within the WOs_3 cluster vary widely, probably as a result of the rather uneven distribution of electrons. Thus the tungsten–osmium distances (in order of increasing distance) are W–Os(3) = 2.742 (1) Å, W–Os(2) = 2.779 (1) Å, and W–Os(1) = 2.885 (1) Å; osmium–osmium distances vary over a wider range, i.e., Os(2)–Os(3) = 2.726 (1) Å, Os(1)–Os(2) = 2.844 (1) Å, and Os(1)–Os(3) = 2.942 (1) Å.

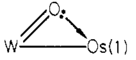
The molecule may be regarded as being composed of one (η^5-C_5H_5)W fragment, two $Os(CO)_3$ fragments (about Os(1), and Os(3)), and one $Os(CO)_2$ fragment (Os(2)), which are linked together by metal–metal bonds and by three bridging ligands. The isolated fragments mentioned above show no unusual features (distances and angles of interest include Os–CO = 1.848 (14)–1.965 (14) Å, C–O = 1.125(19)–1.154 (18) Å, Os–C–O = 173.5 (13)–179.2 (13)°, and W–C(Cp) = 2.290 (19)–2.466 (18) Å). We will therefore confine further discussion principally to the three bridging ligands.

(A) The μ_3-η^2-C_2H_2 Ligand. This ligand is associated with the W–Os(1)–Os(2) triangular face of the tetrahedral metal cluster. Specifically, the ligand, defined by H(9)–C(9)–C(10)–H(10), is σ-bonded to atoms W and Os(1) (with W–C(10) = 2.050 (13) Å and Os(1)–C(9) = 2.160 (14) Å) and is π-bonded to atom Os(2) (with Os(2)–C(9) = 2.095 (15) Å and Os(2)–C(10) = 2.191 (14) Å). The asymmetry of the π-bonding presumably compensates for the asymmetry of the σ-bonding. The C(9)–C(10) distance of 1.404 (20) Å is consistent with the $2\sigma + \pi$ bonding mode as are the (refined) C–C–H angles—i.e., C(10)–C(9)–H(9) = 114 (10)° and C(9)–C(10)–H(10) = 105 (8)°.

The production of the present species from its precursor, $CpWOs_3(CO)_{10}(\mu_3$-η^2-$C_2H_2)(\mu$-H) (**1**), thus involves transfer of the acetylene ligand from an Os_3 to a WOs_2 face of the WOs_3 cluster. A similar rearrangement is observed for certain disubstituted alkyne complexes related to **1**, e.g. $CpWOs_3(CO)_{10}[C_2(CO_2Et)_2]H$, which has also been shown to have the $C_2(CO_2Et)_2$ ligand bonded to one of the WOs_2 faces of a WOs_3 tetrahedral cluster.[16]

(B) The μ-Oxo Ligand. The oxo ligand bridges the tungsten atom and Os(1) such that W–O = 1.761 (8) Å, Os(1)–O = 2.200 (8) Å, and W–O–Os(1) = 92.82 (36)°. These distances and angles suggest the presence of a tungsten–oxygen double bond (cf. W=O = 1.661 (11) Å in the trigonal-bipyramidal species $W(=O)(=CHCMe_3)(PEt_3)Cl_2$,[17,18] W=O = 1.697 (15) Å in the octahedral species $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$,[19,20] and W=O ~ 1.75 Å found in polytungstate ions[21]).

Taken with the W–Os(1) distance of 2.885 (1) Å, the W–O–Os(1) system could be represented by structure I. However, the formal "electron-poor" nature of the tungsten atom, coupled with the formal "electron-rich" nature of Os(1) (vide supra), dictates the closely related structure, II.



I

II

The μ-oxo ligand has a deviation of only 0.251 (9) Å from the Os(1)–Os(2)–W plane (see Figure 2). The dihedral angle between the W–O–Os(1) and Os(1)–Os(2)–W planes is 10.76° (169.24°).[22]

The ligand C(1)–O(1) is directly trans to the oxo ligand, with O–Os(1)–C(1) = 175.9(5)°. The carbonyl ligands C(1)–O(1), C(4)–O(4), and C(5)–O(5) are all nearly coplanar with the W–O–Os(1) plane.

(C) The μ-Hydrido Ligand. The μ-hydrido ligand was both located and refined during the X-ray structural analysis. It bridges the Os(2)–Os(3) bond with Os(2)–H = 1.57 (18) Å, Os(3)–H = 1.53 (18) Å, and Os(2)–H–Os(3) = 123 (10)°. The presence of this bridging hydride ligand is confirmed by the enlargement of the adjacent coplanar M–M–CO angles, viz., Os(3)–Os(2)–C(4) = 115.7 (4)°, Os(3)–Os(2)–C(5) = 119.5 (4)°, Os(2)–Os(3)–C(8) = 105.2 (4)°, and Os(2)–Os(3)–C(7) = 109.6 (4)°.

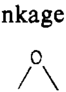
Usually an unsupported μ-hydride ligand is associated with (i) a *lengthened* M–M distance and (ii) abnormally large M–M–L angles for ligands adjacent to, and in the same plane as, the M–H–M system.[23-26] In the present case, the M–M–L angles are expanded, but the Os(2)–Os(3) distance of 2.726 (1) Å is the shortest in the molecule. We attribute this anomaly to the formally "electron-poor" nature of Os(2) and Os(3) ($17^1/_2$ e each; vide supra) which we believe to be compensated by increased bond order in the Os(2)–Os(3) linkage.

Discussion

The complex $CpWOs_3(CO)_8(\mu$-O$)(\mu_3$-η^2-$C_2H_2)(\mu$-H) (**2**) is, to the best of our knowledge, the first metal-cluster molecule found to possess an edge-bridging oxo ligand in an M=O:→M′ bridging mode. As such, it is of possible relevance to the Fischer–Tropsch reaction (eq 1). This reaction is believed

$$CO + H_2 \xrightarrow{\text{Co catalyst}} \text{alkanes, oxygenates, etc.} \qquad (1)$$

to proceed via dissociative chemisorption of CO on the catalytic surface.[27,28] Interest has previously focused on the reactions of the chemisorbed carbon atom, rather than those of oxygen atom. The latter typically is desorbed as H_2O. It has usually been tacitly assumed that the oxygen atom is bound to the surface via an ether-like linkage:



Other features of interest are as follows.

(1) The C_2H_2 ligand in $CpWOs_3(CO)_8(\mu$-O$)(\mu_3$-η^2-$C_2H_2)(\mu$-H) coordinates to a WOs_2 face and has shifted from

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(16) Churchill, M. R.; Ziller, J. W.; Park, J. T.; Shapley, J. R., unpublished results (WOS9).

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(21) (a) $Na_5[H_3PtW_6O_{24}]\cdot 20H_2O$: Lee, K.; Kobayashi, A.; Sasaki, Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 817–819. (b) $Na_{12}[P_4W_8O_{40}]20H_2O$: Gatehouse B. M.; Jozsa, A. J. *Ibid.* **1983**, *C39*, 658–661.

(22) Equations of planes in orthogonalized Cartesian (Å) coordinates are as follows. Os(1)–Os(2)–W plane: $-0.5262x - 0.2370y - 0.8167z + 2.7094 = 0$. W–O–Os(1) plane: $-0.3626x - 0.3017y - 0.8817z + 3.1766 = 0$.

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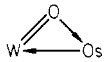
the Os_3 face which it occupies in its precursor, $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$.

(2) The tungsten atom has a coordination shell consisting of $\eta^5\text{-}C_5H_5$, 3Os, σ-C, and =O. This pattern recurs in a number of other WOs_3 clusters that we are currently studying—viz., $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2C_6H_4Me)$,[29] which is formed by pyrolysis of $CpWOs_3(CO)_{11}(\mu_3\text{-}\eta^2\text{-}C(O)CH_2C_6H_4Me)$,[30,31] $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHCH_2C_6H_4Me)(\mu\text{-}H)$,[32] and $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_2\text{-}C{=}CHC_6H_4Me)(\mu\text{-}H)$.[33]

(3) The μ-O ligand must be a four-electron donor in order to satisfy the overall saturation of the compound. The W=O group acts as a two-electron donor to Os(1), which in turn acts as a donor to the tungsten atom in order to supply sufficient electrons to the latter:



The source of the oxo ligand in **2** is not known. In order to determine whether Me_3NO is the source of the oxygen atom, the synthesis of **2** was carried out by using 2 equiv of Me_3NO. This reaction resulted in extensive decomposition and gave a much lower yield (12%) of **2**. The oxo ligand may be derived from a CO ligand by C-O bond scission or from other possible sources (O_2, H_2O, etc.). Note, however, that the oxo-alkylidyne species $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2C_6H_4Me)$ contains a similar oxo ligand acting as a four-electron donor across a tungsten-osmium linkage; in this case the oxo ligand and the alkylidyne ligand are produced from scission of a $\mu_3\text{-}\eta^2$-acyl ligand in the precursor, $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C(O)CH_2C_6H_4Me)$.[29]

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Registry No. **1**, 89065-34-9; **2**, 89044-06-4; $CpWOs_3(CO)_{12}H$, 68796-10-1; W, 7440-33-7; Os, 7440-04-2.

Supplementary Material Available: A table of anisotropic thermal parameters (Table II-S) and a list of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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(33) Churchill, M. R.; Li, Y. J.; Park, J. T.; Shapley, J. R., unpublished work (WOS10-FRAN).

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Reactions of Metal-Metal Multiple Bonds. 10.[1] Reactions of $Mo_2(OR)_6$ (M≡M) and $[Mo(OR)_4]_x$ Compounds with Molecular Oxygen. Preparation and Characterization of Oxo Alkoxides of Molybdenum: $MoO_2(OR)_2$, $MoO_2(OR)_2(bpy)$, $MoO(OR)_4$, $Mo_3O(OR)_{10}$, $Mo_4O_8(OR)_4(py)_4$, and $Mo_6O_{10}(OR)_{12}$

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$Mo_2(OR)_6$ (M≡M) compounds and molecular oxygen react in hydrocarbon solvents to give $MoO_2(OR)_2$ compounds and alkoxy radicals. For R = *t*-Bu, the reaction is rapid with no isolable intermediates; for R = *i*-Pr and CH_2-*t*-Bu, intermediates of formulas $Mo_3O(OR)_{10}$ and $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ have been isolated and characterized. $[Mo(OR)_4]_x$ compounds react with O_2 to give $MoO(OR)_4$ compounds where R = *t*-Bu and $x = 1$, R = *i*-Pr and $x = 2$, and R = CH_2-*t*-Bu and $x \geq 2$. $Mo(O\text{-}t\text{-}Bu)_4$ and O_2 also react to yield $MoO_2(O\text{-}t\text{-}Bu)_2$ and *t*-BuO· in a 1:2 ratio. A general scheme for the reaction of $Mo_2(OR)_6$ compounds with O_2 is proposed involving an initial facile cleavage of the Mo≡Mo bond to give $MoO_2(OR)_2$ and $Mo(OR)_4$ compounds. The subsequent course of the reaction depends on the reactivity of $Mo(OR)_4$ compounds. The new oxo alkoxides $MoO_2(O\text{-}t\text{-}Bu)_2$, $MoO_2(OR)_2(bpy)$ (where R = *i*-Pr and CH_2-*t*-Bu), $Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6$ (where R = *i*-Pr and CH_2-*t*-Bu), $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_2$, and $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ have been characterized by a variety of physicochemical techniques. The oxo groups are formed from the added molecular oxygen. Crystal data: (i) $MoO_2(O\text{-}i\text{-}Pr)_2(bpy)_2\cdot{}^1/_2$(toluene) at -161 °C, $a = 13.907$ (6) Å, $b = 8.413$ (3) Å, $c = 19.999$ (8) Å, $\alpha = 111.02$ (1)°, $\beta = 71.37$ (2)°, $\gamma = 88.98$ (1)°, $Z = 4$, $d_{calcd} = 1.455$ g cm^{-3}, space group $P\bar{1}$; (ii) $Mo_3O(OCH_2\text{-}t\text{-}Bu)_{10}\cdot{}^1/_3CH_2Cl_2$ at -161 °C, $a = 35.557$ (19) Å, $b = 18.969$ (9) Å, $c = 19.342$ (9) Å, $Z = 8$, $d_{calcd} = 1.283$ g cm^{-3}, space group *Pbcn*; (iii) $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ at -162 °C, $a = 21.274$ (6) Å, $b = 21.808$ (5) Å, $c = 10.207$ (2) Å, $\alpha = 98.69$ (1)°, $\beta = 92.92$ (1)°, $\gamma = 118.03$ (1)°, $Z = 4$, $d_{calcd} = 1.452$ g cm^{-3}, space group $P\bar{1}$; (iv) $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ at -162 °C, $a = 13.082$ (3) Å, $b = 11.478$ (2) Å, $c = 9.760$ (2) Å, $\alpha = 106.40$ (1)°, $\beta = 91.85$ (1)°, $\gamma = 99.81$ (1)°, $Z = 1$, $d_{calcd} = 1.738$ g cm^{-3}, space group $P\bar{1}$.

Introduction

We have shown that the Mo≡Mo bond in $Mo_2(OR)_6$ compounds is labile toward a number of oxidative-addition reactions. Treatment with halogens leads to the formation of $Mo_2(OR)_6X_4$ (M-M) compounds (R = *i*-Pr; X = Cl, Br, I), and addition of ROOR to formation of $Mo_2(OR)_8$ (R = *i*-Pr).[2] Reaction with benzoyl peroxide gave[3] a compound $Mo_2(OR)_6(O_2CPh)_2$ (R = *i*-Pr), believed to contain a Mo=Mo bond. These earlier findings prompted us to continue to in-

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