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STRUCTURAL STUDIES ON POLYNUCLEAR OSMIUM CARBONYL HYDRIDES

XXXII *. CRYSTAL AND MOLECULAR STRUCTURE OF $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-tol})]$, A HYDRIDO-VINYLIDENE CLUSTER COMPLEX PRODUCED BY REARRANGEMENT OF A μ_3-ALKYLIDYNE CLUSTER

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Summary

The hydrido-vinylidene complex $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-tol})]$, previously prepared by pyrolysis of $CpWOs_3(CO)_9(\mu\text{-}O)[\mu_3\text{-}CCH_2(p\text{-tol})]$ in boiling toluene, has been investigated crystallographically. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with a 9.522(2), b 22.376(6), c 12.761(3) Å, β 98.276(17)°, V 2690.5(11) Å^3 and $D_{\text{calc'd}}$ 2.97 g/cm^3 for $Z = 4$ and molecular weight 1204.8. Single crystal X-ray diffraction data (Mo-K_α, 2θ 4.0–40.0°) were collected with a Syntex P2$_1$ diffractometer and the structure refined to R 7.9% for all 2529 data [R 5.6% for those 2041 reflections with $|F_0| > 3\sigma(|F_0|)$). The molecule is based upon a tetrahedral WOs_3 core. Each Os is linked to three terminal CO ligands and the W atom is bonded to an η^5-C_5H_5 ligand. The μ-vinylidene fragment spans the W–Os(2) edge (W–C(1) 2.082(40), Os(2)–C(1) 2.148(39) Å) and the μ-oxo ligand spans the W–Os(3) edge of the cluster (W=O 1.791(23) and Os(3)–O 2.131(21) Å). The hydride ligand (which was not directly located) is believed to span the elongated Os(3)–Os(1) edge of the tetrahedron.

Introduction

The reaction of $Cp(CO)_2W{\equiv}C(p\text{-tol})$ ($Cp = \eta^5\text{-}C_5H_5$, $p\text{-tol} = p\text{-}CH_3C_6H_4$) with $(\mu\text{-}H)_2Os_3(CO)_{10}$ yields a variety of mixed-metal clusters [6,7] including the tetranuclear (WOs_3)-μ_3-η^2-acyl complex $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}OCCH_2(p\text{-tol})]$ (**1**). This

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exotic complex has been shown to undergo facile C–O bond scission yielding the oxoalkylidyne species $CpWOs_3(CO)_9(\mu\text{-}O)[\mu_3\text{-}CCH_2(p\text{-}tol)]$ (**2**) [8,9]. This oxoalkylidyne species, has, in turn been shown [8] to undergo hydrogenation yielding the hydridooxoalkylidene species $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}CHCH_2(p\text{-}tol)]$ (**3**); however, when a toluene solution of **2** is boiled under an inert (N_2) atmosphere [8], the hydridooxovinylidene species $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-}tol)]$ (**4**) is produced. The interrelationship of these species is diagrammed in Scheme 1.

We have previously reported X-ray structural analyses of **1** [6,7], **2** [8,9] and **3** [1]. We have now completed a crystallographic analysis of the final product of this reaction sequence (**4**); our results appear below.

Experimental

Crystals of $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-}tol)]$, synthesized as described previously [8] and recrystallized from dichloromethane/hexane, were provided to us by Prof. J.R. Shapley and Mr. J.T. Park of the Chemistry Department, University of Illinois at Urbana-Champaign. The crystal selected for the single-crystal X-ray diffraction study was an opaque dark-red parallelepiped of approximate orthogonal dimensions 0.23 × 0.10 × 0.07 mm^3. It was mounted along its extended direction and centered on our Syntex $P2_1$ automated four-circle diffractometer. All operations were carried out as described previously [10]; details of data collection are provided in Table 1. The diffraction symmetry is $2/m$ (C_{2h}). The systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely indicate the centrosymmetric monoclinic space group $P2_1/c$ [No. 14; C_{2h}^5].

A total of 2727 reflections (one-fourth of the shell with $2\theta = 4.0\text{–}40.0°$) were collected, corrected for the effects of absorption, and were merged to 2529 symmetry-independent data ($R(I)$ 2.1%; $R_w(I)$ 2.2% for averaging statistics). All data were converted to unscaled $|F_0|$ values following correction for Lorentz and polarization factors. Any datum with $I(\text{net}) < 0$ was assigned the value $|F_0| = 0$; no data were rejected.

Solution and refinement of the structure

All calculations were performed under the SUNY-Buffalo version of the Syntex XTL crystallographic program package. The F_c values were calculated from the analytical form of the appropriate neutral atom scattering factors; both the real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms [11]. The function $\Sigma w(|F_0| - |F_c|)^2$ was minimized during least-squares refinement, where $w = [\{\sigma(|F_0|)\}^2 + \{0.015|F_0|\}^2]^{-1}$. Discrepancy indices are defined as follows.

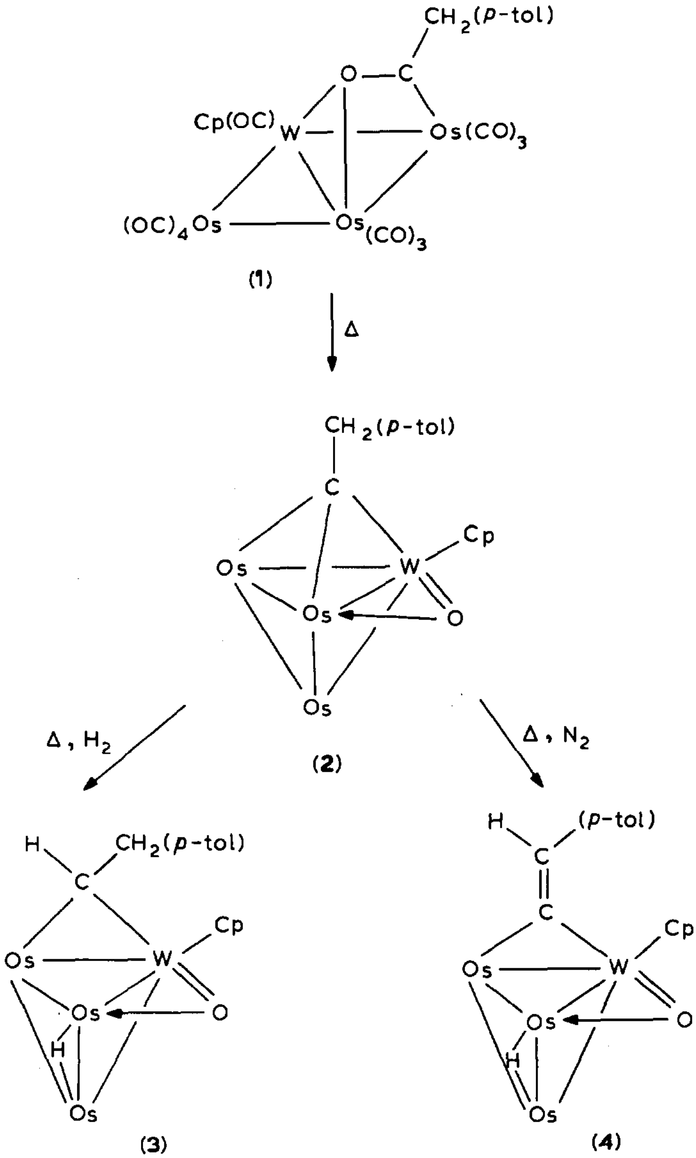
$$R_F(\%) = 100\Sigma||F_0| - |F_c||/\Sigma|F_0|$$

$$R_{wF}(\%) = 100\left[\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\right]^{1/2}$$

$$\text{GOF} = \left[\Sigma w(|F_0| - |F_c|)^2/(NO - NV)\right]^{1/2}.$$

Here, NO is the number of observations and NV is the number of variables.

The structure was solved by direct methods using the program MULTAN76, followed by difference-Fourier syntheses and full-matrix least-squares refinement.



SCHEME 1. Structural formulae of 1–4. (Note that 2, 3, and 4 have three CO ligands per osmium atom; these have been omitted for the sake of clarity).

Hydrogen atoms were included in calculated positions with d(C–H) 0.95 Å [12]. Convergence was reached with R_F 7.9%. R_{wF} 7.0% and GOF = 2.82 for all 2529 data (R_F 5.6% and R_{wF} 6.9% for those 2041 reflections with $|F_0| > 3\sigma(|F_0|)$.) Data were rather weak.

A correction was made for the effects of secondary extinction, using the approximate Zachariasan expression: $|F_{o,corr}| = |F_{o,uncorr}|(1.0 + gI_0)$. The value determined for g was 0.346×10^{-7}.

A final difference-Fourier synthesis showed no unexpected features; the structure is therefore both correct and complete. Atomic parameters are collected in Table 2.

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-}tol)]$

(A) Unit cell parameters at 24°C (297 K)
Crystal system: monoclinic
Space group: $P2_1/c$ (No. 14)
a 9.522(2) Å
b 22.376(6) Å
c 12.761(3) Å
β 98.276(17)°
V 2690.5(11) $Å^3$

Formula: $C_{23}H_{14}O_{10}Os_3W$
Molecular weight 1204.8
$Z = 4$
D_{calcd} 2.97 g cm^{-3}
μ(Mo-K_α) 195.2 cm^{-1}

(B) Collection of X-ray diffraction data
Diffractometer: Syntex $P2_1$
Radiation: Mo-K_α ($\bar{\lambda}$ 0.710730 Å)
Monochromator: highly oriented (pyrolytic) graphite, 2θ(m) 12.160° for 002 reflection; equatorial mode; assumed 50% perfect/50% ideally mosaic for polarization correction
Reflections measured: $+h$, $+k$, $\pm l$ for $2\theta = 4.0$–40.0°; 2727 reflections merged to 2529 unique data
Scan-type: coupled θ(crystal)–2θ(counter)
Scan-speed: 2.50 deg/min
Scan width: $[2\theta(K_{\alpha_1})-1.0]-[2\theta(K_{\alpha_2})+1.0]$ deg
Backgrounds: stationary-crystal and stationary-counter; measured at each end of the 2θ scan (each for one-half total scan time)
Standards: 3 remeasured after each batch of 97 reflections; no significant fluctuations observed
Absorption correction: empirical, based on interpolation (in ϕ and 2θ) between ψ-scans on close-to-axial reflections; max/min transmission factor 1.7.

The molecular structure

The crystal contains an ordered arrangement of discrete $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-}tol)]$ molecules; there are no unusually close intermolecular contacts. The molecular geometry and the atomic labelling scheme are depicted in Fig. 1. Interatomic distances and angles are listed in Tables 3 and 4.

The tungsten atom and the three osmium atoms define a tetrahedral core of metal which is associated with the expected 60 outer valence electrons. (With all metal atoms and ligands treated as formally neutral we have three d^8 Os^0 atoms, one d^6 W^0 atom, 18 electrons for the nine terminal carbonyl ligands, 5 electrons from the Cp ligand, 2 electrons from the μ-C=CH(p-tol) ligand, 4 electrons from the μ-oxo ligand (vide infra) and 1 electron from the μ-hydride ligand.) Interestingly, each of the four metal atoms is in a different stereochemical environment. The molecule has only $C_1(1)$ symmetry and is chiral; however, the crystal is racemic, with the two enantiomers interrelated by operations of the second kind (i.e., inversion centers and glide-planes).

Although the cluster as a whole is associated with 60 outer valence electrons, the formal electron-counts at the individual metal atoms vary appreciably, being $17\frac{1}{2}$ e^- at Os(1), 18 e^- at Os(2), $19\frac{1}{2}$ e^- at Os(3) and 17 e^- at W. Not surprisingly, there are significant differences in metal–metal bond lengths. Osmium–osmium distances are (in increasing order) Os(1)–Os(2) 2.793(2) Å, Os(2)–Os(3) 2.884(2) Å, and Os(3)–Os(1) 2.930(2) Å. The longest of these is believed to be that associated with the μ-hydride ligand because (a) it is this bond that has been shown to be bridged by a μ-hydride ligand in the very closely related molecule $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}CHCH_2(p\text{-}tol)]$ [1] and (b) a single unsupported bridging hydride ligand typically causes expansion of the bridged metal–metal bond relative to the equiv-

TABLE 2

FINAL ATOMIC PARAMETERS FOR $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)[\mu\text{-}C{=}CH(p\text{-}tol)]$

(A) Positional and isotropic thermal parameters

Atom	x	y	z	B (Å^2)
W	0.15533(15)	0.39964(8)	0.12465(11)	
Os(1)	0.39172(15)	0.40601(8)	0.27445(12)	
Os(2)	0.15840(16)	0.33722(8)	0.30993(12)	
Os(3)	0.13017(16)	0.46548(8)	0.31391(12)	
O(11)	0.5216(34)	0.2914(17)	0.2060(25)	6.83(80)
O(12)	0.5548(34)	0.4810(16)	0.1382(26)	6.91(82)
O(13)	0.5982(36)	0.4262(17)	0.4839(28)	7.23(87)
O(21)	0.1898(31)	0.2145(16)	0.2338(23)	5.83(72)
O(22)	0.3738(32)	0.3178(15)	0.5120(26)	6.24(76)
O(23)	−0.0950(41)	0.3105(18)	0.4257(30)	8.5(10)
O(31)	0.1911(34)	0.4432(17)	0.5506(28)	7.32(85)
O(32)	0.1157(35)	0.6004(18)	0.3421(27)	9.81(84)
O(33)	−0.1726(36)	0.4457(16)	0.3031(25)	6.59(80)
O(B)	0.1015(21)	0.4748(10)	0.1460(16)	2.51(46)
C(11)	0.4868(38)	0.3376(20)	0.2410(30)	3.77(85)
C(12)	0.4839(42)	0.4521(20)	0.1973(32)	4.31(92)
C(13)	0.5164(44)	0.4149(20)	0.4068(33)	4.6(10)
C(21)	0.1943(40)	0.2599(21)	0.2706(32)	3.97(90)
C(22)	0.3036(40)	0.3301(19)	0.4334(32)	3.94(87)
C(23)	−0.0057(58)	0.3205(26)	0.3814(42)	7.0(13)
C(31)	0.1614(36)	0.4509(18)	0.4604(30)	3.32(80)
C(32)	0.1197(50)	0.5540(27)	0.3275(38)	5.9(12)
C(33)	−0.0595(43)	0.4531(20)	0.3192(31)	8.07(89)
C(1)	−0.0033(40)	0.3476(19)	0.1753(30)	3.87(87)
C(2)	−0.1185(40)	0.3269(19)	0.1401(31)	3.95(89)
C(3)	−0.2158(33)	0.3394(16)	0.0452(52)	2.35(69)
C(4)	−0.2213(38)	0.3936(19)	−0.0026(29)	3.59(83)
C(5)	−0.3093(41)	0.4050(20)	−0.0946(32)	4.18(91)
C(6)	−0.4005(40)	0.3625(21)	−0.1422(31)	4.41(92)
C(7)	−0.3954(34)	0.3077(17)	−0.0981(27)	2.69(73)
C(8)	−0.3139(35)	0.2953(18)	0.0008(27)	2.79(75)
C(9)	−0.4949(45)	0.3769(22)	−0.2475(34)	5.0(10)
Cp(1)	0.1049(44)	0.4057(21)	−0.0600(33)	4.7(10)
Cp(2)	0.2432(43)	0.4233(21)	−0.0363(32)	4.6(10)
Cp(3)	0.3225(37)	0.3780(18)	0.0103(28)	3.16(00)
Cp(4)	0.2272(44)	0.3249(22)	0.0072(33)	5.0(10)
Cp(5)	0.1020(42)	0.3465(21)	−0.0377(32)	4.31(92)
H(2)	−0.1505	0.2967	0.1833	3.5
H(4)	−0.1619	0.4247	0.0289	3.5
H(5)	−0.3071	0.4432	−0.1265	3.5
H(7)	−0.4484	0.2762	−0.1350	3.5
H(8)	−0.3244	0.2586	0.0366	3.5
H(91)	−0.4835	0.4177	−0.2649	3.5
H(92)	−0.5942	0.3740	−0.2465	3.5
H(93)	−0.4709	0.3568	−0.3080	3.5
HCp(1)	0.0262	0.4301	−0.0868	3.5
HCp(2)	0.2783	0.4617	−0.0506	3.5
HCp(3)	0.4200	0.3796	0.0394	3.5
HCp(4)	0.2499	0.2854	0.0313	3.5
HCp(5)	0.0189	0.3226	−0.0525	3.5

TABLE 2 (continued)

(B) Anisotropic thermal parameters for the metal atoms [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	3.034(75)	2.633(89)	2.337(75)	0.112(65)	0.536(54)	0.234(65)
Os(1)	2.571(73)	4.23(10)	3.242(81)	0.027(69)	0.606(56)	0.791(73)
Os(2)	3.383(79)	3.35(10)	2.435(77)	−0.297(67)	0.681(56)	0.399(63)
Os(3)	3.233(78)	3.37(10)	3.400(87)	−0.194(67)	0.630(60)	−0.729(68)

[a] The anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})]$.

alent non-bridged bond [13–17]. The heteronuclear tungsten–osmium distances show a similar degree of variation with (in order) W–Os(1) 2.739(2) Å, W–Os(2) 2.743(2) Å and W–Os(3) 2.868(2) Å. A similar pattern is observed in $CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})[\mu\text{-CHCH}_2(p\text{-tol})]$ [1] with W–Os distances of 2.735(2), 2.746(2) and 2.916(1) Å and in $CpWOs_3(CO)_9(\mu\text{-O})[\mu_3\text{-CCH}_2(p\text{-tol})]$ [8,9] with W–Os distances of 2.655(1), 2.663(1) and 2.814(1) Å.

The W(μ-O)Os system

The μ-oxo ligand, defined here as O(B), spans the W–Os(3) edge of the tetrahedral cluster. The W–O(B)–Os(3) plane deviates by only 14.72° from the W–Os(2)–Os(3) triangular face of the cluster (see Table 5, planes C and B). Relevant dimensions are W–O(B) 1.791(23) Å, Os(3)–O(B) 2.131(21) Å and angle W–O(B)–Os(3) 93.6(9)°.

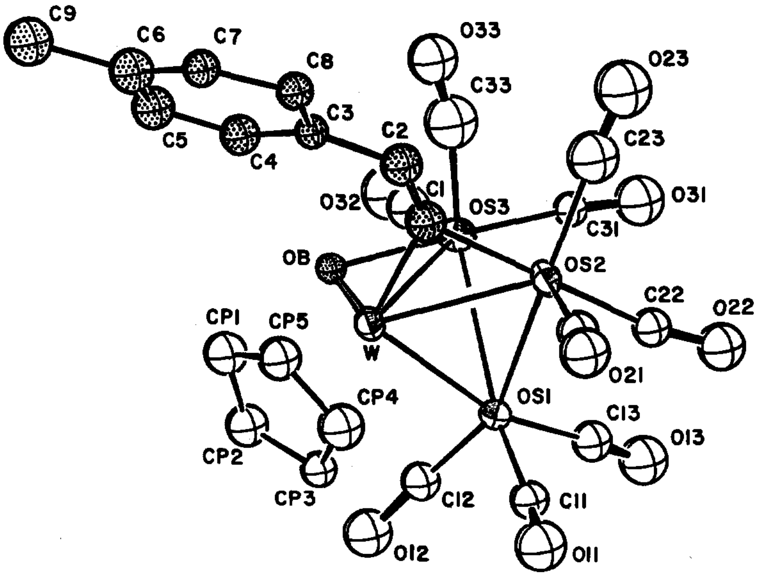


Fig. 1. Labelling of non-hydrogen atoms within the $CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})[\mu\text{-C=CH}(p\text{-tol})]$ molecule. The μ-hydride ligand is believed to occupy a position about the Os(1)–Os(3) vector. Both the μ-O and μ-C=CH(p-tol) ligands are stipped for clarity [ORTEP-II diagram].

TABLE 3

INTERATOMIC DISTANCES (Å), WITH Esd's, FOR $CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})[\mu\text{-C=CH}(p\text{-tol})]$

(A) Metal–metal distances			
W–Os(1)	2.739(2)	Os(1)–Os(2)	2.793(2)
W–Os(2)	2.743(2)	Os(2)–Os(3)	2.884(2)
W–Os(3)	2.868(2)	Os(3)–Os(1)	2.930(2)
(B) Metal–(bridging ligand) distances			
W–O(B)	1.791(23)	W–C(1)	2.082(40)
Os(3)–O(B)	2.131(21)	Os(2)–C(1)	2.148(39)
(C) Osmium-carbonyl distances (including all Os... C distances < 3 Å)			
Os(1)–C(11)	1.86(4)	Os(1)...O(11)	3.03(4)
Os(1)–C(12)	1.75(4)	Os(1)...O(12)	3.01(3)
Os(1)–C(13)	1.93(4)	Os(1)...O(13)	3.11(4)
Os(2)–C(21)	1.85(5)	Os(2)...O(21)	2.94(4)
Os(2)–C(22)	1.95(4)	Os(2)...O(22)	3.09(3)
Os(2)–C(23)	1.96(6)	Os(2)...O(23)	3.06(4)
Os(3)–C(31)	1.88(4)	Os(3)...O(31)	3.03(4)
Os(3)–C(32)	1.99(6)	Os(3)...O(32)	3.05(4)
Os(3)–C(33)	1.84(4)	Os(3)...O(33)	2.90(3)
Os(1)–C(22)	2.86(4)		
(D) Distances with η^5-C_5H_5W moiety			
W–Cp(1)	2.34(4)	Cp(1)–Cp(2)	1.37(6)
W–Cp(2)	2.39(4)	Cp(2)–Cp(3)	1.35(6)
W–Cp(3)	2.36(4)	Cp(3)–Cp(4)	1.49(6)
W–Cp(4)	2.41(5)	Cp(4)–Cp(5)	1.34(6)
W–Cp(5)	2.38(4)	Cp(5)–Cp(1)	1.36(7)
W...Cent	2.065		
(E) Carbon–oxygen distances			
C(11)–O(11)	1.19(6)	C(23)–O(23)	1.11(7)
C(12)–O(12)	1.26(5)	C(31)–O(31)	1.16(5)
C(13)–O(13)	1.19(6)	C(32)–O(32)	1.06(7)
C(21)–O(21)	1.12(6)	C(33)–O(33)	1.08(5)
C(22)–O(22)	1.16(5)		
(F) Distances within C=CH(p-tol) ligand			
C(1)–C(2)	1.22(6)	C(6)–C(7)	1.35(6)
C(2)–C(3)	1.44(5)	C(7)–C(8)	1.41(5)
C(3)–C(4)	1.36(5)	C(8)–C(3)	1.42(5)
C(4)–C(5)	1.37(5)	C(6)–C(9)	1.54(6)
C(5)–C(6)	1.37(6)		

If we define the unbridged metal–metal bonds in the cluster as normal single bonds we can calculate approximate covalent radii of ~ 1.42 Å for osmium (from $\frac{1}{4}[d(\text{Os(1)–Os(2)}) + d(\text{Os(2)–Os(3)})]$) and ~ 1.32 Å for tungsten (from $d(\text{W–Os(1)}) - r(\text{Os})$). The W–O(B) bond lenghts of 1.791(23) Å is substantially shorter than the predicted W–O single bond length of ~ 1.98 Å (from r(W) 1.32 Å and r(O) 0.66 Å [18]). It is slightly longer than well-defined tungsten-oxygen double bonds in such discrete mononuclear species as $W(=O)(=CHCMe_3)(PEt_3)Cl_2$ (W=O 1.661(11) Å) [19] and $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$ (W=O 1.697(15) Å) [20]. It is substantially shorter than typical tungsten–alkoxide bonds as found in $W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ (W–O 1.885(6)–2.008(6) Å) [21], $W(C_3Et_3)[OCH(CF_3)_2]_3$ (W–O

TABLE 4

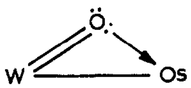
INTERATOMIC ANGLES (deg.) FOR CpWOs$_3$(CO)$_9$(μ-H)(μ-O)[μ-C=CH(p-tol)]

(A) Interatomic angles			
Os(1)–W–Os(2)	61.26(6)	W–Os(2)–Os(1)	59.31(6)
Os(2)–W–Os(3)	61.81(6)	Os(1)–Os(2)–Os(3)	62.14(6)
Os(3)–W–Os(1)	62.97(6)	Os(3)–Os(2)–W	61.24(6)
W–Os(1)–Os(2)	59.43(6)	W–Os(3)–Os(1)	56.36(5)
Os(2)–Os(1)–Os(3)	60.45(6)	Os(1)–Os(3)–Os(2)	57.41(5)
Os(3)–Os(1)–W	60.67(6)	Os(2)–Os(3)–W	56.95(5)
(B) M–M–CO angles			
W–Os(1)–C(11)	100.1(12)	W–Os(2)–C(21)	102.9(13)
W–Os(1)–C(12)	93.8(14)	W–Os(2)–C(22)	131.1(12)
W–Os(1)–C(13)	163.0(13)	W–Os(2)–C(23)	126.1(16)
Os(2)–Os(1)–C(11)	90.5(12)	Os(1)–Os(2)–C(21)	106.9(13)
Os(2)–Os(1)–C(12)	153.2(14)	Os(1)–Os(2)–C(22)	71.8(12)
Os(2)–Os(1)–C(13)	108.6(13)	Os(1)–Os(2)–C(23)	152.7(16)
Os(3)–Os(1)–C(11)	150.2(12)	Os(3)–Os(2)–C(21)	163.4(13)
Os(3)–Os(1)–C(12)	109.7(14)	Os(3)–Os(2)–C(22)	97.1(12)
Os(3)–Os(1)–C(13)	103.5(13)	Os(3)–Os(2)–C(23)	95.7(16)
W–Os(3)–C(31)	136.7(11)	Os(2)–Os(3)–C(31)	81.0(12)
W–Os(3)–C(32)	126.5(15)	Os(2)–Os(3)–C(32)	175.6(15)
W–Os(3)–C(33)	98.9(13)	Os(2)–Os(3)–C(33)	86.9(13)
Os(1)–Os(3)–C(31)	94.3(12)		
Os(1)–Os(3)–C(32)	121.4(15)		
Os(1)–Os(3)–C(33)	143.3(13)		
(C) Os–C–O and OC–Os–CO angles			
Os(1)–C(11)–O(11)	166(4)	C(11)–Os(1)–C(12)	93.2(19)
Os(1)–C(12)–O(12)	175(4)	C(12)–Os(1)–C(13)	97.8(19)
Os(1)–C(13)–O(13)	173(4)	C(13)–Os(1)–C(11)	91.6(18)
Os(2)–C(21)–O(21)	166(4)	C(21)–Os(2)–C(22)	90.3(18)
Os(2)–C(22)–O(22)	167(4)	C(22)–Os(2)–C(23)	97.4(20)
Os(2)–C(23)–O(23)	177(5)	C(23)–Os(2)–C(21)	98.0(12)
Os(3)–C(31)–O(31)	175(4)	C(31)–Os(3)–C(32)	95.1(19)
Os(3)–C(32)–O(32)	175(5)	C(32)–Os(3)–C(33)	94.9(20)
Os(3)–C(33)–O(33)	167(4)	C(33)–Os(3)–C(31)	87.3(17)
(D) Angles involving the C(1), the vinylidene carbon atom			
W–C(1)–Os(2)	80.8(14)	W–Os(2)–C(1)	48.6(11)
W–C(1)–C(2)	139.0(34)	Os(2)–W–C(1)	50.7(11)
Os(2)–C(1)–C(2)	139.4(34)		
(E) Angles involving O(B), the bridging oxide ligand			
W–O(B)–Os(3)	93.6(9)	Os(1)–W–O(B)	94.0(7)
W–Os(3)–O(B)	38.6(6)	Os(2)–W–O(B)	108.4(7)
Os(3)–W–O(B)	47.9(7)	C(31)–Os(3)–O(B)	175.3(13)
(F) C–C–C angles within the C=CH(p-tol) ligand			
C(1)–C(2)–C(3)	132(4)	C(8)–C(3)–C(4)	118(3)
C(2)–C(3)–C(4)	122(3)	C(3)–C(4)–C(5)	122(4)
C(2)–C(3)–C(8)	120(3)	C(4)–C(5)–C(6)	122(4)
C(5)–C(6)–C(9)	120(4)	C(5)–C(6)–C(7)	118(4)
C(7)–C(6)–C(9)	122(4)	C(5)–C(7)–C(8)	122(3)
		C(7)–C(8)–C(3)	118(3)

TABLE 4 (continued)

(G) Angles within the η^5-C_5H_5 ligand			
Cp(5)–Cp(1)–Cp(2)	106(4)	Cp(3)–Cp(4)–Cp(5)	103(4)
Cp(1)–Cp(2)–Cp(3)	110(4)	Cp(4)–Cp(5)–Cp(1)	113(4)
Cp(2)–Cp(3)–Cp(4)	107(3)		
(H) Angles about "Cent" (the centroid of the η^5-C_5H_5 Ligand)			
Cent–W–Os(1)	113.3	Cent–W–O(B)	118.9
Cent–W–Os(2)	132.7	Cent–W–C(1)	113.1
Cent–W–Os(3)	163.0		

1.932(10)–1.982(11) Å [22] and W[C(t-Bu)CHC(t-Bu)][OCH$(CF_3)_2$]$_3$ (W–O 1.954(7)–1.959(7) Å [23], even though there is some oxygen–tungsten π-donation in these species. All indications are that the W–O(B) linkage is a formal double bond. The Os(3)–O(B) distance of 2.131(21) Å is slightly longer than expected for a single bond (r(Os) + r(O) = 1.42 + 0.66 = 2.08 Å) and we treat this as a "coordinate-covalent" or donor bond, i.e., O: → Os. The μ-oxo ligand is thus a 4-electron donor (neutral atom counting scheme). The W(μ-O)Os system is best depicted as in



(5)

structure 5. The present molecule joins the three others with this feature, viz.: CpWOs$_3$(CO)$_9$(μ-O)[μ_3-CCH$_2$(p-tol)] (2) [8,9], CpWOs$_3$(CO)$_9$(μ-H)(μ-O)[μ-CHCH$_2$(p-tol)] (3) [1] and CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C_2H_2)(μ-H), [4]. Dimensions within these species are compared in Table 6. As can readily be seen, dimensions for the last three entries are completely self-consistent. The W–Os distance and the W–O–Os angle are anomalously small in CpWOs$_3$(CO)$_9$(μ-O)[μ_3-CCH$_2$(p-tol)] (2), simply because this W–Os vector is now part of the WOs$_2$ face capped by the μ_3-CCH$_2$(p-tol) ligand; in complexes 3 and 4 the μ_2-CHCH$_2$(p-tol) or μ_2-C=CH(p-tol) ligands are linked only to the tungsten atom of the W(μ-O)Os system and in CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C_2H_2)(μ-H) this W–Os vector is part of the triangular WOs$_2$ face capped by the sterically undemanding μ_3-η^2-C_2H_2 ligand.

Other features of the molecule

All other features of the molecular geometry are within the expected ranges. Individual Os–CO distances are 1.75(4)–1.99(6) Å, C–O distance are 1.06(7)–1.26(5) Å and Os–C–O angles are 166(4)–177(5)°. The p-tolylvinylidene fragment spans the W–Os(2) vector, with W–C(1) 2.08(4) Å and Os(2)–C(1) 2.15(4) Å; carbon–carbon bond lengths are consistent with the formulation C=CH(p-tol).

The vinylidene ligand (as defined by W–Os(2)–C(1)–C(2)) is essentially coplanar with the cluster face W–Os(1)–Os(2), the dihedral angle between these planes being only 0.05° (see Table 5, planes A and B). The p-tolyl moiety is twisted by 35.03° from coplanarity with the W–Os(2)–C(1)–C(2) system.

The η^5-C_5H_5 ligand is planar within experimental error and the W...Cent distance is 2.065 Å.

TABLE 5

IMPORTANT PLANES (AND ATOMIC DEVIATIONS THEREFROM, IN Å) WITHIN THE CpWOs$_3$(CO)$_9$(μ-H)(μ-O)[μ-C=CH(p-tol)] MOLECULE [a]

Atom	Dev.	Atom	Dev.
Plane A: Plane of W-Os(1)-Os(2)			
$0.4518x - 0.7911y - 0.4123z = -7.1589$			
W*	0.000	C(1)	−0.066(41)
Os(1)*	0.000	C(2)	0.017(42)
Os(2)*	0.000	C(3)	−0.051(35)
Plane B: Plane of W-Os(2)-Os(3)			
$0.9786x - 0.0909y - 0.1844z = -2.3268$			
W*	0.000	O(B)	0.337(20)
Os(2)*	0.000		
Os(3)*	0.000		
Plane C: Plane of W-O(B)-Os(3)			
$-0.9513x - 0.3047y - 0.0459z = -3.9865$			
W*	0.000	Os(2)	0.614(2)
Os(3)*	0.000	Os(1)	−2.010(2)
O(B)*	0.000		
Plane D: Plane of W-Os(2)-C(1)-C(2)			
$0.4511x - 0.7914y - 0.4126z = -7.1740$			
W*	0.012(2)	Os(1)	0.009(2)
Os(2)*	0.011(2)	Os(3)	−2.405(2)
C(1)*	−0.053(42)	C(3)	−0.036(35)
C(2)*	0.030(42)	C(6)	−0.107(44)
Plane E: Plane of C(3)-C(8)			
$0.7945x - 0.3094y - 0.5226z = -4.3761$			
C(3)*	0.029(32)	C(2)	0.088(40)
C(4)*	−0.002(37)	C(9)	0.017(44)
C(5)*	−0.005(40)	C(1)	0.532(39)
C(6)*	−0.018(40)		
C(7)*	0.046(34)		
C(8)*	−0.050(34)		
Plane F: Plane of η^5-C_5H_5 *ring*			
$0.3406x - 0.2483y - 0.9068z = -1.1574$			
Cp(1)*	−0.032(42)	W	−2.064(1)
Cp(2)*	0.033(41)	O(B)	−2.915(21)
Cp(3)*	−0.022(36)	Os(1)	−3.142(2)
Cp(4)*	0.002(42)	Os(2)	−3.945(2)
Cp(5)*	0.018(41)	Os(3)	−4.797(2)
Selected interplanar angles			
Plane A/Plane D	0.05°	(179.95°)	
Plane B/Plane C	14.72°	(165.28°)	
Plane D/Plane E	35.03°	(144.97°)	

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[a] Atoms marked with an asterisk are those used in calculating the appropriate plane. Equations for planes are in orthonormalized coordinates.

Additional material. A table of observed and calculated structure factors is available on request (from M.R.C.)

TABLE 6

DIMENSIONS OF THE W(μ-O)Os SYSTEM IN WOs_3 CLUSTERS

Complex	d(W=O)	d(Os–O)	d(W–Os)	Angle W–O–Os	Ref.
$CpWOs_3(CO)_9(\mu\text{-O})[\mu_3\text{-CCH}_2(p\text{-tol})]$ (**2**)	1.812(7)	2.169(8)	2.663(1)	83.5(3)	8, 9
$CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})[\mu\text{-CHCH}_2(p\text{-tol})]$ (**3**)	1.737(17)	2.167(16)	2.916(1)	96.0(7)	1
$CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})[\mu\text{-C=CH}(p\text{-tol})]$ (**4**)	1.791(23)	2.131(21)	2.868(2)	93.6(9)	Present work
$CpWOs_3(CO)_8(\mu\text{-O})(\mu_3\text{-}\eta^2\text{-C}_2H_2)(\mu\text{-H})$	1.761(8)	2.200(8)	2.885(1)	92.8(4)	4

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