

## CRYSTAL STRUCTURE OF $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})^*$ , A TETRAHEDRAL OXO-ALKYLIDYNE COMPLEX DERIVED FROM A PLANAR $\mu_3\text{-}\eta^2\text{-ACYL}$ COMPLEX

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### Summary

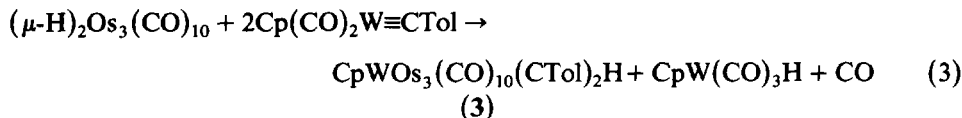
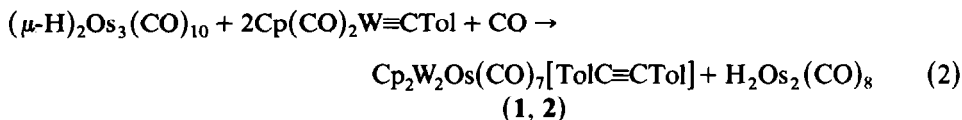
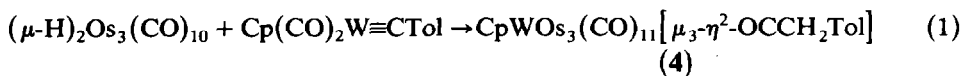
The heterometallic cluster complex  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CCH}_2\text{Tol})$ , previously prepared by pyrolysis of the planar  $\mu_3\text{-}\eta^2\text{-acyl}$  complex  $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-OCCH}_2\text{Tol}]$ , crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  with  $a$  9.7041(25),  $b$  9.7829(27),  $c$  14.5992(39) Å,  $\alpha$  108.106(22),  $\beta$  93.805(21),  $\gamma$  94.565(22)°,  $V$  1307.1(6) Å<sup>3</sup> and  $D(\text{calcd})$  3.06 g cm<sup>-3</sup> for  $Z = 2$  and mol. wt. 1204.8. Single-crystal X-ray diffraction data (Mo- $K_\alpha$ ,  $2\theta$  4.5–45.0°) were collected on a Syntex P2<sub>1</sub> automated four-circle diffractometer and the structure was refined to  $R$  3.9% for all 3438 data ( $R$  3.3% for those 3101 data with  $F_0 > 3\sigma(|F_0|)$ ). The molecule contains a tetrahedral  $\text{WO}_3$  core associated with 60 valence electrons. The  $\mu_3\text{-}\eta^2\text{-acyl}$  fragment of the precursor has undergone scission, leading to separate  $\mu\text{-oxo}$  and  $\mu_3\text{-CCH}_2\text{Tol}$  moieties. The  $\mu\text{-oxo}$  ligand is linked by a double bond to tungsten ( $\text{W}=\text{O}$  1.812(7) Å) and via a single donor bond to Os(1) ( $\text{Os}(1) \leftarrow \text{O}$  2.169(8) Å, with  $\angle\text{W}-\text{O}-\text{Os}(1)$  83.46(31)°. The  $\mu_3\text{-alkylidyne}$  ligand is linked to a  $\text{WO}_2$  face, with  $\text{W}-\text{C}$  2.030(12),  $\text{Os}(1)-\text{C}$  2.291(12) and  $\text{Os}(2)-\text{C}$  2.100(10) Å. The  $\text{O}(\text{oxo}) \cdots \text{C}(\text{alkylidyne})$  separation is now 3.15 Å and is clearly non-bonding.

### Introduction

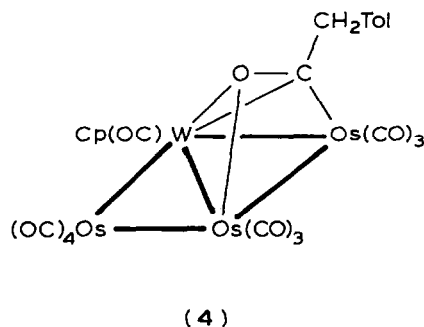
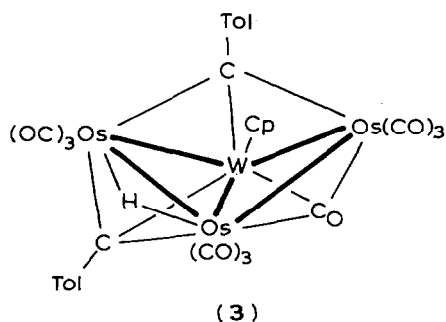
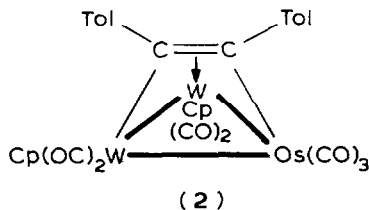
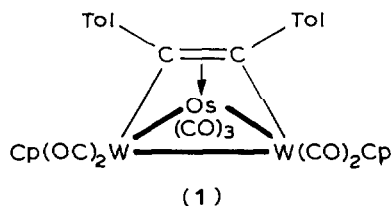
The reaction of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CTol}$  has previously been shown to give rise to three principal mixed-metal cluster complexes [1,2]. The stoichiometry established for the formation of these complexes is indicated by eqs. 1–3.

\* Abbreviations used throughout: Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; Tol = *p*-tolyl.

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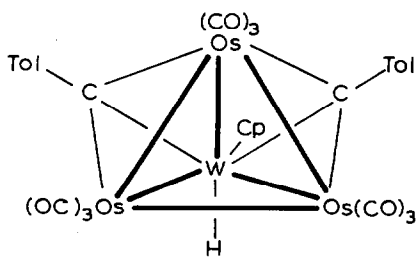


Each of the mixed-metal products has had its structure determined by X-ray diffraction techniques. The trinuclear cluster  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7[\text{TolC}\equiv\text{CTol}]$  exists in two forms related by rotation of the  $\text{TolC}\equiv\text{CTol}$  ligand on the triangular  $\text{W}_2\text{Os}$  face [1,3], (see 1 and 2). The species  $\text{CpWOs}_3(\text{CO})_{10}(\text{CTol})_2\text{H}$  has a "butterfly" shaped metal core with two inequivalent locations for the  $\mu_3\text{-CTol}$  ligands [4] (see 3). The complex  $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-OCCH}_2\text{Tol}]$  has an essentially planar, triangulated,  $\text{WOs}_3$  skeleton with an  $\mu_3\text{-}\eta^2\text{-acyl}$  function bridging a  $\text{WOs}_2$  face [1,2] (see 4).

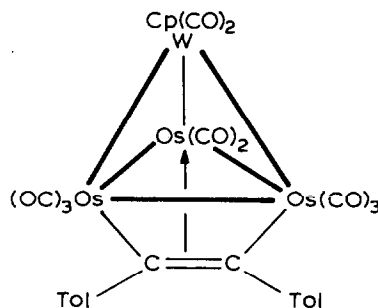


The tetranuclear  $\text{WOs}_3$  clusters show an interesting range of reactions. Thus, the "butterfly"-shaped 62-electron cluster  $\text{CpWOs}_3(\text{CO})_{10}(\text{CTol})_2\text{H}$  (3) can be decarbonylated to form the 60-electron tetrahedral cluster  $\text{CpWOs}_3(\text{CO})_9(\mu_3\text{-CTol})_2\text{H}$  (5) [4,5], a symmetrical bis-alkylidene species also accessible by pyrolytic scission of the  $\mu_3\text{-}\eta^2\text{-bis}(p\text{-tolyl})\text{acetylene}$  moiety of the 60-electron tetrahedral cluster complex  $\text{CpWOs}_3(\text{CO})_{10}(\text{TolC}\equiv\text{CTol})\text{H}$  (6) [5].

It has recently been shown [6] that the  $\mu_3\text{-}\eta^2\text{-acyl}$  complex 4 is transformed (upon heating) into the oxo-alkylidene complex  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ . We now report details of the crystal structure of this unique new complex.



(5)



(6)

## Experimental

### Collection of X-ray diffraction data

Crystals of  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  were provided by Professor J. R. Shapley and Dr. J.T. Park of the Department of Chemistry, University of Illinois at Urbana-Champaign. The crystal selected for the X-ray diffraction study was a well-formed dark red crystalline parallelepiped of approximate dimension  $0.2 \times 0.2 \times 0.05 \text{ mm}^3$ . It was aligned accurately on a Syntex P2<sub>1</sub> automated four-circle diffractometer. Subsequent set-up operations (determination of accurate unit cell dimensions and orientation matrix) and collection of the intensity data were carried

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$

#### Unit cell data.

$a$ 9.7041(25) Å	Crystal system: triclinic
$b$ 9.7829(27) Å	Space group: $P\bar{1}$ ( $C_1^1$ ; No. 2)
$c$ 14.5992(39) Å	$Z = 2$
$\alpha$ 108.106(22)°	Formula: $\text{C}_{23}\text{H}_{14}\text{O}_{10}\text{Os}_3\text{W}$
$\beta$ 93.805(21)°	Mol. wt. 1204.8
$\gamma$ 94.565(22)°	$D(\text{calcd}) 3.06 \text{ g cm}^{-3}$
$V$ 1307.1(6) Å <sup>3</sup>	$T 24^\circ\text{C} (297 \text{ K})$

#### Collection of X-ray diffraction data

Diffractometer: Syntex P2<sub>1</sub>

Radiation: Mo- $K_\alpha$  ( $\lambda$  0.710730 Å)

Monochromator: highly oriented (pyrolytic) graphite; equatorial mode with  $2\theta(m)$  12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction.

Reflections measured:  $+h, \pm k, \pm l$  for  $2\theta$  4.5–45.0°; 3683 total, merged to 3438 symmetry-independent data (file name WOS7, nr. 149).

Scan type: coupled  $\theta(\text{crystal})-2\theta(\text{counter})$ .

Scan width:  $[2\theta(K_{\alpha_1})-1.0]^\circ \rightarrow [2\theta(K_{\alpha_2})+1.0]^\circ$ .

Scan speed: 2.5 deg/min (in  $2\theta$ ).

Backgrounds: stationary-crystal, stationary-counter at the two extremes of the  $2\theta$  scan; each for one-half of total scan time.

Standard reflections: three collected after each batch of 97 reflections; no significant fluctuations observed.

Absorption correction:  $\mu(\text{Mo-}K_\alpha) 200.9 \text{ cm}^{-1}$ ; corrected empirically by interpolation (in  $2\theta$  and  $\phi$ ) between  $\psi$ -scans of close-to-axial reflections.

TABLE 2

FINAL POSITIONAL PARAMETERS FOR  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ 

Atom	x	y	z	B(Å <sup>2</sup> )
W	0.91577(5)	0.91054(5)	0.30360(3)	
Os(1)	0.65322(5)	0.82244(5)	0.31690(3)	
Os(2)	0.77448(5)	0.69167(5)	0.14366(3)	
Os(3)	0.73012(5)	0.98057(5)	0.18849(3)	
O(1)	0.4161(10)	0.6399(10)	0.1752(7)	
O(2)	0.5996(11)	0.6652(11)	0.4664(7)	
O(3)	0.4603(11)	1.0620(11)	0.3766(8)	
O(4)	1.0222(11)	0.6632(10)	0.0293(7)	
O(5)	0.7101(12)	0.3674(12)	0.1036(9)	
O(6)	0.5803(12)	0.6941(13)	-0.0295(7)	
O(7)	0.7456(11)	1.2730(10)	0.3405(7)	
O(8)	0.4347(13)	0.9828(14)	0.0962(8)	
O(9)	0.8930(14)	1.0853(13)	0.0490(9)	
O(10)	0.8191(9)	0.9764(8)	0.4077(5)	
C(1)	0.5110(13)	0.7041(13)	0.2258(9)	
C(2)	0.6219(13)	0.7254(14)	0.4141(9)	
C(3)	0.5294(14)	0.9733(14)	0.3525(9)	
C(4)	0.9264(14)	0.6733(13)	0.0723(9)	
C(5)	0.7299(13)	0.4868(15)	0.1172(9)	
C(6)	0.6516(14)	0.7016(15)	0.0378(9)	
C(7)	0.7353(14)	1.1653(15)	0.2805(10)	
C(8)	0.5509(15)	0.9804(15)	0.1259(9)	
C(9)	0.8340(17)	1.0490(14)	0.1029(11)	
C(10)	1.1468(16)	0.8490(17)	0.2657(10)	4.55(30)
C(11)	1.1199(14)	0.9522(14)	0.2225(10)	4.05(27)
C(12)	1.0978(18)	1.0819(19)	0.2922(11)	5.03(35)
C(13)	1.1145(15)	1.0574(14)	0.3840(9)	4.15(27)
C(14)	1.1444(15)	0.9190(16)	0.3680(10)	4.10(28)
C(15)	0.8461(12)	0.7015(12)	0.2847(7)	2.53(20)
C(16)	0.8796(14)	0.5906(14)	0.3310(9)	3.12(24)
C(17)	1.0208(13)	0.5344(12)	0.3163(8)	3.25(24)
C(18)	1.0550(15)	0.4498(14)	0.2290(9)	3.84(26)
C(19)	1.1807(15)	0.3939(15)	0.2167(10)	3.98(27)
C(20)	1.2793(14)	0.4227(14)	0.2951(9)	3.93(26)
C(21)	1.2498(16)	0.5066(15)	0.3839(10)	4.61(29)
C(22)	1.1177(15)	0.5598(14)	0.3960(10)	4.02(27)
C(23)	1.4155(20)	0.3550(21)	0.2857(12)	5.38(35)
H(10)	1.1633	0.7518	0.2344	6.0
H(11)	1.1168	0.9374	0.1548	6.0
H(12)	1.0761	1.1687	0.2809	6.0
H(13)	1.1062	1.1259	0.4453	6.0
H(14)	1.1610	0.8751	0.4167	6.0
H(16A)	0.8108	0.5101	0.3057	6.0
H(16B)	0.8747	0.6317	0.3986	6.0
H(18)	0.9889	0.4285	0.1741	6.0
H(19)	1.1998	0.3356	0.1544	6.0
H(21)	1.3177	0.5297	0.4378	6.0
H(22)	1.0955	0.6127	0.4587	6.0
H(23A)	1.4696	0.3870	0.3465	6.0
H(23B)	1.4651	0.3829	0.2393	6.0
H(23C)	1.3968	0.2526	0.2652	6.0

out as described previously [7]; details appear in Table 1. The diffraction symmetry is  $\bar{1}$  and there are no systematic absences. The crystal thus belongs to the triclinic system, possible space groups being the noncentrosymmetric  $P1$  ( $C_1^1$ ; No. 1) or the centrosymmetric  $P\bar{1}$  ( $C_1^2$ ; No. 2). With  $Z = 2$ , the latter is more probable and was (later) found to be the appropriate choice.

All data were corrected for the effects of absorption and for Lorentz and polarization factors; they were converted to unscaled  $|F_0|$  values and were placed on an approximately absolute scale by means of a Wilson plot. Any reflection with  $I(\text{net}) < 0$  was assigned the value  $|F_0| = 0$ .

#### *Solution and refinement of the structure*

All subsequent calculations were performed using our locally modified version of the Syntex XTL interactive crystallographic program package [8]. The structure was solved by direct methods using the program MULTAN; the positions of the four heavy atoms were located from an "E-map". All remaining non-hydrogen atoms were located from a difference-Fourier synthesis. The structure was optimized by full-matrix least-squares refinement, minimizing the function  $\sum w(|F_0| - |F_c|)^2$  where  $1/w = [\sigma(|F_0|)]^2 + [0.01|F_0|]^2$ . Hydrogen atoms were included in calculated positions based upon the appropriate idealized geometry, with  $d(\text{C-H})$  0.95 Å [9], and were updated appropriately. Refinement of positional and thermal parameters (anisotropic for the  $\text{WO}_3(\text{CO})_9(\mu\text{-O})$  moiety, isotropic for all other atoms) led to final

TABLE 3

ANISOTROPIC THERMAL PARAMETERS <sup>a</sup> FOR  $\text{CpWO}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ 

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
W	1.859(23)	2.713(22)	2.661(21)	0.048(17)	0.062(16)	0.914(16)
Os(1)	1.804(23)	2.724(21)	2.960(21)	0.477(17)	0.531(16)	1.000(16)
Os(2)	2.034(23)	2.827(22)	2.702(21)	0.569(17)	0.112(16)	0.478(16)
Os(3)	2.736(26)	2.966(22)	3.178(22)	0.845(18)	0.381(17)	1.436(17)
O(1)	2.5(5)	5.2(5)	5.6(5)	-0.8(4)	-0.3(4)	0.8(4)
O(2)	6.3(6)	6.2(6)	5.1(5)	1.1(5)	1.6(4)	4.0(5)
O(3)	4.4(6)	5.0(5)	8.8(7)	3.1(5)	2.5(5)	1.8(5)
O(4)	4.8(6)	5.2(5)	4.9(5)	0.4(4)	1.7(4)	0.7(4)
O(5)	4.7(6)	3.4(5)	11.8(9)	-0.4(5)	0.2(5)	0.8(5)
O(6)	6.7(7)	9.3(7)	3.5(5)	2.1(6)	-1.6(5)	0.4(5)
O(7)	6.8(7)	3.1(4)	6.1(6)	0.6(4)	0.8(5)	0.9(4)
O(8)	5.3(7)	10.8(8)	6.0(6)	3.0(6)	-0.9(5)	2.5(6)
O(9)	8.5(8)	8.5(8)	10.0(8)	3.0(6)	5.7(7)	6.1(7)
O(10)	3.7(4)	3.6(4)	2.33(33)	0.49(33)	0.19(29)	0.51(28)
C(1)	1.7(6)	3.6(6)	4.1(6)	0.2(5)	0.5(5)	0.9(5)
C(2)	2.6(6)	4.3(6)	3.5(6)	1.0(5)	0.5(5)	0.7(5)
C(3)	2.8(7)	3.9(6)	4.3(6)	0.1(6)	0.5(5)	1.3(5)
C(4)	2.7(7)	3.5(6)	3.7(6)	0.5(5)	-0.2(5)	1.0(5)
C(5)	2.0(6)	3.6(7)	5.5(7)	0.1(5)	0.1(5)	0.2(5)
C(6)	2.5(6)	6.2(8)	3.1(6)	2.2(6)	-0.6(5)	0.1(5)
C(7)	3.5(7)	4.2(7)	4.4(7)	0.4(6)	-0.0(5)	2.3(6)
C(8)	3.1(7)	5.9(8)	3.3(6)	1.6(6)	-0.2(5)	1.5(5)
C(9)	6.3(10)	3.5(6)	5.6(8)	2.5(6)	2.2(7)	2.2(6)

<sup>a</sup> The anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form:  $\exp[-0.25(h^2a^{*2}B_{11} + \dots 2hka^{*}b^{*}B_{12} + \dots)]$ .

convergence with the following residuals for all 3488 data (no datum rejected).

$$R_F (\%) = 100 \Sigma ||F_0| - |F_c|| / \Sigma |F_0| = 3.9\%$$

$$R_{wF} (\%) = 100 [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|^2]^{1/2} = 3.5\%$$

$$\text{GOF} = [\Sigma w(|F_0| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2} = 1.95$$

(where NO is the number of observations and NV is the number of variables).

Residuals for those 3101 data with  $|F_0| > 3\sigma(|F_0|)$  were  $R_F$  3.3 and  $R_{wF}$  3.4%.

Throughout the analysis the calculated structure factors were based upon the analytical expression for the neutral atoms' form factors [10a]; both the real ( $\Delta f'$ ) and imaginary ( $i\Delta f''$ ) components of anomalous dispersion [10b] were included for all non-hydrogen atoms. Atomic coordinates are collected in Table 2; anisotropic thermal parameters are listed in Table 3.

### Description of the molecular structure

The crystal contains an ordered arrangement of discrete molecular units of  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  which are separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. The overall molecular geometry and the scheme used for labelling atoms are illustrated in Figs. 1 and 2. Interatomic distances and angles are collected in Tables 4 and 5.

The present molecule is formed from its planar precursor by folding across a W-Os edge in conjunction with scission of the  $\eta^2$ -acyl fragment into  $\mu_2$ -O and  $\mu_3$ -CCH<sub>2</sub>Tol moieties, loss of two carbonyl ligands and formation of an additional Os-Os bond (Scheme 1). The product has a tetrahedral core of metal atoms as expected for a species associated with 60 outer valence electrons. (With all groups regarded as neutral, we have three  $d^8$  Os<sup>0</sup> atoms, one  $d^6$  W<sup>0</sup> atom, 18 electrons

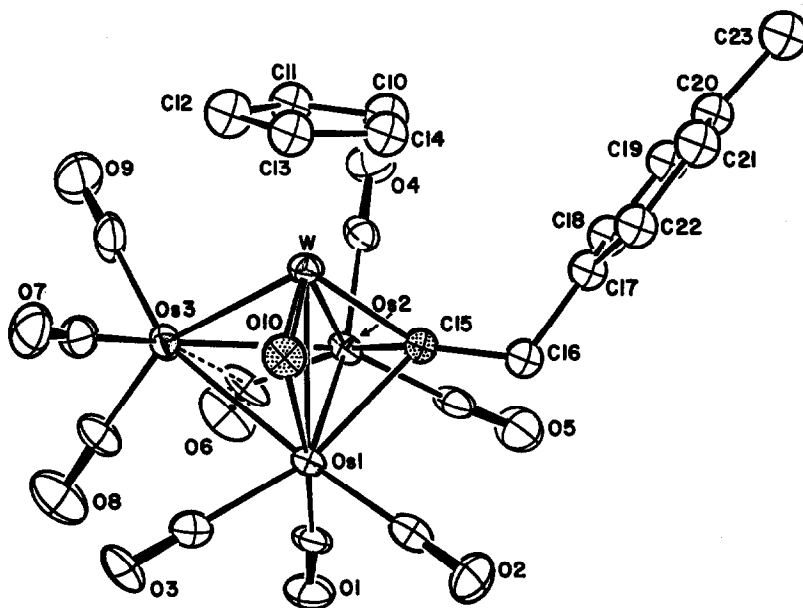


Fig. 1. Overall geometry and atomic labelling for  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ .

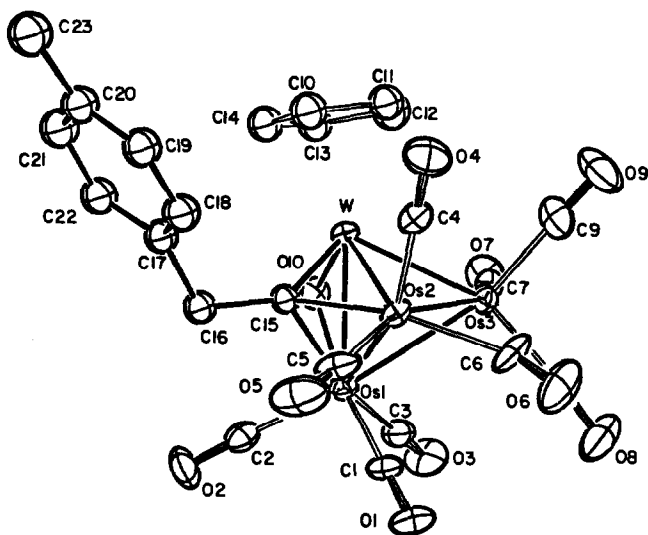
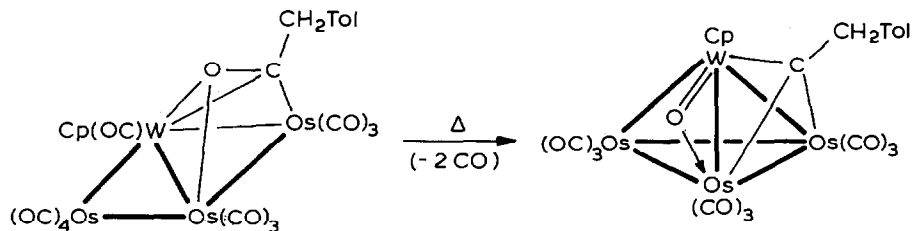


Fig. 2. The other side of the  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  molecule. Note that Os(3) is in an ideal location to form a weak bond to C(6).

from the nine terminal carbonyl ligands, 5 electrons from the Cp ligand, 3 electrons from the  $\mu_3\text{-CCH}_2\text{Tol}$  ligand and 4 electrons from the oxo ligand.) Note that  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  is very closely related structurally to the tetrahedral bis(alkylidyne) complex  $\text{CpWOs}_3(\text{CO})_9(\mu_3\text{-CTol})_2\text{H}$  (**5**) [4,5]. This oxo-alkylidyne complex is associated with a number of interesting features.

#### The tetrahedral metal core

Each of the four metals is in a different chemical environment. The molecule is thus chiral, but the crystal contains an ordered racemic array, with the two enantiomers related to one another by crystallographic inversion centers. Although the tetrahedral cluster as a whole is associated with 60 valence electrons, the formal electron counts at the individual metal atoms are non-uniform, viz., formally  $17 e^-$  at the W atom,  $17 e^-$  at Os(3),  $18 e^-$  at Os(2) and  $20 e^-$  at Os(1). There are hints of some slight "semi-bridging" character in two of the carbonyl ligands (Os(2)–C(6) 1.920(13), Os(3)···C(6) 2.929(14) Å, Os(2)–C(6)–O(6) 173.5(13)°; Os(1)–C(1) 1.886(12), Os(2)···C(1) 2.891(12) Å, Os(1)–C(1)–O(1) 173.7(11)°) and there is much variability in the metal–metal bond lengths. Thus, the individual osmium–osmium distances are Os(2)–Os(3) 2.772(1), Os(1)–Os(2) 2.836(1) and



SCHEME 1

TABLE 4

INTERATOMIC DISTANCES (Å) AND Esd's FOR  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ 

<i>Metal–metal bond lengths</i>			
Os(1)–Os(2)	2.836(1)	Os(1)–W	2.663(1)
Os(1)–Os(3)	2.875(1)	Os(2)–W	2.814(1)
Os(2)–Os(3)	2.772(1)	Os(3)–W	2.655(1)
<i>Metal–alkylidyne bond lengths</i>			
Os(1)–C(15)	2.291(12)	W–C(15)	2.030(12)
Os(2)–C(15)	2.100(10)		
<i>Metal–oxygen bond lengths</i>			
Os(1)–O(10)	2.169(8)	W–O(10)	1.812(7)
<i>Distances within the <math>\mu_3\text{-CCH}_2\text{Tol}</math> ligand</i>			
C(15)–C(16)	1.491(18)		
C(16)–C(17)	1.520(19)	C(20)–C(23)	1.520(24)
C(17)–C(18)	1.366(18)	C(20)–C(21)	1.365(19)
C(18)–C(19)	1.376(20)	C(21)–C(22)	1.422(21)
C(19)–C(20)	1.384(19)	C(22)–C(17)	1.393(18)
<i>Metal–carbonyl distances</i>			
Os(1)–C(1)	1.886(12)	Os(1)···O(1)	3.030(9)
Os(1)–C(2)	1.963(13)	Os(1)···O(2)	3.084(10)
Os(1)–C(3)	1.945(14)	Os(1)···O(3)	3.066(11)
Os(2)–C(4)	1.849(13)	Os(2)···O(4)	2.999(10)
Os(2)–C(5)	1.927(16)	Os(2)···O(5)	3.046(12)
Os(2)–C(6)	1.920(13)	Os(2)···O(6)	3.059(11)
Os(3)–C(7)	1.881(15)	Os(3)···O(7)	3.012(10)
Os(3)–C(8)	1.910(14)	Os(3)···O(8)	3.090(12)
Os(3)–C(9)	1.900(15)	Os(3)···O(9)	3.027(13)
<i>Possible metal–“semi-bridging” carbonyl distances (<math>&lt; 3.0 \text{ \AA}</math>)</i>			
Os(3)···C(6)	2.929(14)	Os(2)···C(1)	2.891(12)
<i>Carbon–oxygen (carbonyl) distances</i>			
C(1)–O(1)	1.148(16)	C(6)–O(6)	1.143(17)
C(2)–O(2)	1.122(17)	C(7)–O(7)	1.134(18)
C(3)–O(3)	1.122(18)	C(8)–O(8)	1.185(19)
C(4)–O(4)	1.150(17)	C(9)–O(9)	1.129(20)
C(5)–O(5)	1.120(20)		
<i>Tungsten–carbon (Cp) distances</i>			
W–C(10)	2.422(16)	W–C(13)	2.318(14)
W–C(11)	2.445(14)	W–C(14)	2.336(14)
W–C(12)	2.388(18)	W···Cent <sup>a</sup>	2.062

<sup>a</sup> Cent is the centroid of the Cp ring.

Os(1)–Os(3) 2.875(1) Å (as compared to Os–Os 2.877(3) Å in the triangular cluster  $\text{Os}_3(\text{CO})_{12}$  [11] and Os–Os (unbridged) 2.822(1) Å in the tetrahedral cluster  $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{11}(\text{CNMe})$  [12]). The individual osmium–tungsten distances vary over a rather larger range, viz., Os(3)–W 2.655(1), Os(1)–W 2.663(1) and Os(2)–W 2.814(1) Å (cf. Os–W (unbridged) 2.880(3) Å in  $(\mu\text{-H})_3\text{Os}_3\text{W}(\text{CO})_{11}\text{Cp}$  [13] and 2.909(2)–2.934(2) Å in  $(\mu\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}\text{Cp}$  [14]).

#### Nature of the $\text{W}=\text{O} \rightarrow \text{Os}(1)$ linkage

The oxo ligand, defined as O(10), bridges the W–Os(1) edge such that W–O(10) 1.812(7), Os(1)–O(10) 2.169(8) Å and  $\angle\text{W–O(10)–Os(1)}$  83.46(31)°. These distances suggest a tungsten–oxygen double bond (cf. W=O 1.661(11) Å in  $\text{W}(\text{=O})$ -



TABLE 5

INTERATOMIC ANGLES ( $^{\circ}$ ), WITH Esd's FOR  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ 

<i>Intermetallic angles</i>			
Os(1)–W–Os(2)	62.29(2)	Os(1)–Os(2)–W	56.25(2)
Os(1)–W–Os(3)	65.46(2)	Os(1)–Os(2)–Os(3)	61.69(2)
Os(2)–W–Os(3)	60.82(2)	Os(3)–Os(2)–W	56.76(2)
Os(2)–Os(1)–W	61.46(2)	Os(1)–Os(3)–W	57.40(2)
Os(2)–Os(1)–Os(3)	58.06(2)	Os(1)–Os(3)–Os(2)	60.25(2)
Os(3)–Os(1)–W	57.14(2)	Os(2)–Os(3)–W	62.42(2)
<i>M–M–CO Angles</i>			
W–Os(1)–C(1)	133.11(39)	Os(3)–Os(2)–C(4)	104.73(41)
W–Os(1)–C(2)	116.52(38)	Os(3)–Os(2)–C(5)	157.90(42)
W–Os(1)–C(3)	115.89(40)	Os(3)–Os(2)–C(6)	74.81(41)
Os(2)–Os(1)–C(1)	72.36(38)	W–Os(3)–C(7)	89.67(44)
Os(2)–Os(1)–C(2)	122.80(38)	W–Os(3)–C(8)	156.57(42)
Os(2)–Os(1)–C(3)	132.90(40)	W–Os(3)–C(9)	105.67(47)
Os(3)–Os(1)–C(1)	92.44(39)	Os(1)–Os(3)–C(7)	95.83(44)
Os(3)–Os(1)–C(2)	173.05(39)	Os(1)–Os(3)–C(8)	99.36(42)
Os(3)–Os(1)–C(3)	80.67(40)	Os(1)–Os(3)–C(9)	160.42(47)
W–Os(2)–C(4)	93.72(41)	Os(2)–Os(3)–C(7)	149.74(44)
W–Os(2)–C(5)	132.76(42)	Os(2)–Os(3)–C(8)	105.21(42)
W–Os(2)–C(6)	131.20(42)	Os(2)–Os(3)–C(9)	104.49(47)
Os(1)–Os(2)–C(4)	149.95(41)		
Os(1)–Os(2)–C(5)	104.90(42)		
Os(1)–Os(2)–C(6)	107.44(41)		
<i>Os–C–O and C–Os–C angles</i>			
Os(1)–C(1)–O(1)	173.7(11)	C(1)–Os(1)–C(2)	94.3(5)
Os(1)–C(2)–O(2)	176.7(12)	C(1)–Os(1)–C(3)	89.3(6)
Os(1)–C(3)–O(3)	177.4(12)	C(2)–Os(1)–C(3)	101.0(6)
Os(2)–C(4)–O(4)	178.9(12)	C(4)–Os(2)–C(5)	95.0(6)
Os(2)–C(5)–O(5)	176.7(13)	C(4)–Os(2)–C(6)	92.9(6)
Os(2)–C(6)–O(6)	173.5(13)	C(5)–Os(2)–C(6)	94.6(6)
Os(3)–C(7)–O(7)	174.5(13)	C(7)–Os(3)–C(8)	96.3(6)
Os(3)–C(8)–O(8)	173.1(13)	C(7)–Os(3)–C(9)	93.7(6)
Os(3)–C(9)–O(9)	177.3(14)	C(8)–Os(3)–C(9)	96.6(6)
<i>Angles involving O(10) or C(15)</i>			
W–O(10)–Os(1)	83.46(31)	Os(1)–C(15)–C(16)	121.47(81)
W–Os(1)–O(10)	42.52(21)	Os(2)–C(15)–C(16)	133.85(85)
Os(1)–W–O(10)	54.02(25)	C(15)–W–O(10)	92.31(40)
Os(2)–W–O(10)	116.31(25)	C(15)–Os(1)–O(10)	76.88(35)
Os(3)–W–O(10)	92.25(25)	Os(1)–W–C(15)	56.52(32)
Os(3)–Os(1)–O(10)	79.54(21)	Os(1)–Os(2)–C(15)	52.79(31)
Os(2)–Os(1)–O(10)	103.97(21)	Os(2)–W–C(15)	48.10(32)
W–C(15)–Os(1)	75.84(37)	Os(3)–Os(1)–C(15)	89.30(28)
W–C(15)–Os(2)	85.89(42)	Os(3)–Os(2)–C(15)	96.24(31)
W–C(15)–C(16)	136.11(86)	Os(3)–W–C(15)	101.71(32)
<i>Angles from "Cent" (the centroid of the Cp ring)</i>			
Cent–W–Os(1)	173.68	Cent–W–O(10)	122.45
Cent–W–Os(2)	120.80	Cent–W–O(15)	120.60
Cent–W–Os(3)	120.77		
<i>Carbon–carbon–carbon angles within the CCH<sub>2</sub>Tol ligand</i>			
C(15)–C(16)–C(17)	116.6(11)	C(19)–C(20)–C(23)	121.4(13)
C(16)–C(17)–C(18)	123.2(12)	C(20)–C(21)–C(22)	120.3(13)
C(16)–C(17)–C(22)	119.4(11)	C(21)–C(22)–C(17)	120.2(13)
C(17)–C(18)–C(19)	123.1(13)	C(23)–C(20)–C(21)	119.4(13)
C(18)–C(19)–C(20)	119.9(13)		
C(19)–C(20)–C(21)	119.1(13)		

TABLE 5 (continued)

<i>Angles within the Cp ring</i>			
C(10)–C(11)–C(12)	110.5(14)	C(13)–C(14)–C(10)	109.5(13)
C(11)–C(12)–C(13)	106.2(14)	C(14)–C(10)–C(11)	105.8(13)
C(12)–C(13)–C(14)	108.1(13)		

(=CHCMe<sub>3</sub>)(PEt<sub>3</sub>)Cl<sub>2</sub> [15], W=O 1.697(15) Å in W(=O)(=CHCMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> [16] and typical W=O values of ~ 1.75 Å found in such polytungstate derivatives as Na<sub>5</sub>[H<sub>3</sub>PtW<sub>6</sub>O<sub>24</sub>]·20H<sub>2</sub>O [17] and Na<sub>12</sub>[P<sub>4</sub>W<sub>8</sub>O<sub>40</sub>]·20H<sub>2</sub>O [18].

The only other example of an edge-bridging M=O → M' ligand of which we are aware occurs in CpWOS<sub>3</sub>(CO)<sub>8</sub>(μ-O)(μ<sub>3</sub>-η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>)(μ-H) [19], in which W=O 1.761(8), Os←:O 2.200(8) Å and ∠W–O–Os 92.83(36)°.

Both in CpWOS<sub>3</sub>(CO)<sub>8</sub>(μ-O)(μ<sub>3</sub>-η<sup>2</sup>-C<sub>2</sub>H<sub>2</sub>)(μ-H) [19] and in the present CpWOS<sub>3</sub>(CO)<sub>9</sub>(μ-O)(μ<sub>3</sub>-CCH<sub>2</sub>Tol), the oxo ligand is counted as a four-electron donor (neutral atom counting scheme).

#### *The μ<sub>3</sub>-CCH<sub>2</sub>Tol ligand*

This μ<sub>3</sub>-alkylidyne ligand bridges the three atoms of a WOs<sub>2</sub> face of the WOs<sub>3</sub> tetrahedron, with individual metal–C(alkylidyne) distances of W–C(15) 2.030(12), Os(2)–C(15) 2.100(10) and Os(1)–C(15) 2.291(12) Å. In other WOs<sub>3</sub> clusters with μ<sub>3</sub>-alkylidyne ligands on a WOs<sub>2</sub> face, the W–C distances are also uniformly shorter than the Os–C distances: viz., W–C 2.012(12) and 2.012(24) Å and Os–C 2.185(21)–2.270(21) Å in CpWOS<sub>3</sub>(CO)<sub>10</sub>(μ<sub>3</sub>-CTol)<sub>2</sub>H (3) [4]; W–C 1.977(22)–2.013(20) and Os–C 2.135(20)–2.254(21) and Os–C 2.135(20)–2.254(21) Å in CpWOS<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CTol)<sub>2</sub>H (5) [4,5].

#### *Relative positions of the μ-O and μ<sub>3</sub>-CCH<sub>2</sub>Tol ligands*

The relative positions of these two ligands are shown in Fig. 3. The atoms O(10) and C(15) are separated by 3.15 Å; clearly, there is no remaining bond between these two atoms.

Direct cleavage of the C≡O bond in carbon monoxide is a process requiring extremely high energy (ca. 255.8 kcal/mol vis à vis 225.0 kcal/mol for N≡N). In the WOs<sub>3</sub> cluster system, the CO ligand is first “inserted” into a M–CTol or M–CH<sub>2</sub>Tol

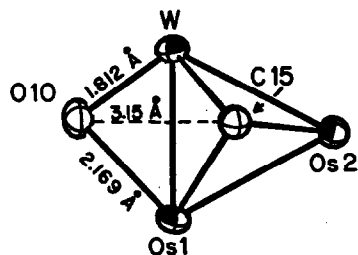
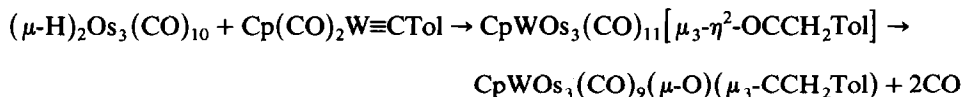


Fig. 3. Geometry and important dimensions involving the oxo ligand (O(10)) and the μ<sub>3</sub>-alkylidyne ligand (C(15)) on the W–Os(1)–Os(2) cluster face.

linkage, then is activated (i.e., the C–O linkage is weakened) by forming a  $\mu_3$ - $\eta^2$ -acyl linkage (in which C–O 1.372(20) Å [2]) and is then cleaved by pyrolysis (see Scheme 1A).

SCHEME 1A



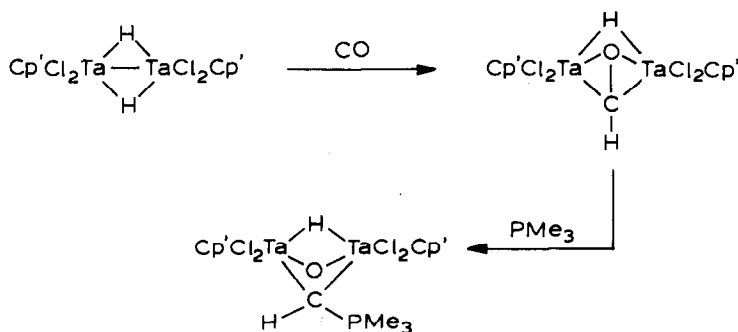
A related set of reactions occurs with dinuclear tantalum complexes [20] as shown in Scheme 2. Here, however, the final cleavage of the C–O bond is accomplished by use of a strong nucleophile and not by thermolysis. Definitive structural studies have led to the unambiguous characterization of both  $[\text{Cp}'\text{TaCl}_2]_2(\mu\text{-H})(\mu\text{-CHO})$  [21,22] and  $[\text{Cp}'\text{TaCl}_2]_2(\mu\text{-H})(\mu\text{-CHPMe}_3)(\mu\text{-O})$  [23,24], where  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$ ; the structure of  $[\text{Cp}'\text{TaCl}_2\text{H}]_2$  is that deduced from a study on the closely related compound  $[\text{Cp}'_2\text{Ta}_2\text{Cl}_3\text{Me}](\mu\text{-H})_2$  [25]. It should be noted, however, that the “side-on” bridging formyl ligand in  $[\text{Cp}'\text{TaCl}_2]_2(\mu\text{-H})(\mu\text{-CHO})$  has a highly activated C–O bond, with C–O 1.496(14) Å.

#### Other features of the structure

Other geometric features of the structure of  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  are quite normal. Individual Os–CO bond lengths range from 1.849(13) through 1.963(13) Å, C–O distances range from 1.120(20) through 1.185(19) Å and Os–C–O angles are from 173.1(13) through 178.9(12)°. Tungsten–carbon (Cp) distances are between 2.318(14) and 2.445(14) Å while  $\text{W} \cdots \text{Cent}$  2.062 Å; these values may be compared with those in such simple complexes as  $\text{CpW}(\text{CO})_3\text{X}$  (e.g.  $\text{CpW}(\text{CO})_3\text{Cl}$ , wherein  $\text{W–C}(\text{Cp})$  2.260(10)–2.376(9) and  $\text{W} \cdots \text{Cent}$  2.001 Å [26]). We note that the Cp ring lies essentially axially (with respect to the  $\text{WOs}_3\text{OC}$  core of the cluster) above the tungsten atom, such that the  $\text{Cent–W–Os}(1)$  angle is 173.68° and remaining cluster angles are close to equivalent, viz.  $\text{Cent–W–Os}(2)$  120.80,  $\text{Cent–W–Os}(3)$  120.77,  $\text{Cent–W–O}(10)$  122.45 and  $\text{Cent–W–C}(15)$  120.60°.

Distances within the  $\text{CCH}_2\text{Tol}$  ligand are in the expected range with  $\text{C}(15)\text{–C}(16)$  1.491(18) Å (ideal  $\text{C}(sp^3)\text{–C}(sp^3)$  1.54 Å),  $\text{C}(16)\text{–C}(17)$  1.520(19) and  $\text{C}(20)\text{–C}(23)$  1.520(24) Å, (ideal  $\text{C}(sp^2)\text{–C}(sp^3)$  1.51 Å) and C–C (aromatic) 1.365(19)–1.422(21) Å (ideal value = 1.39 Å).

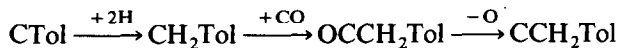
SCHEME 2



## Discussion

The fascinating observation that the  $\mu$ -O and  $\mu_3$ -C fragments in the complex  $\text{CpWOS}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  are derived via cleavage of a carbonyl fragment has been dealt with above. A further interesting observation is that the  $\mu_3\text{-CCH}_2\text{Tol}$  ligand is formed from an initial  $\equiv\text{CTol}$  fragment (cf. Scheme 1A) via the overall homologation sequence shown in Scheme 3. The present system thus constitutes part

### SCHEME 3



of a possible model for hydrocarbon chain growth via intermediate acyl species during Fischer-Tropsch synthesis [27-29].

### Additional material

A table of observed and calculated structure factor amplitudes is available on request from M.R.C.

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