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STRUCTURAL STUDIES ON OSMIUM CARBONYL HYDRIDES

XXXI *. CRYSTAL AND MOLECULAR STRUCTURE OF $CpWOs_3(CO)_9(\mu$-$H)(\mu$-$O)(\mu$-$CHCH_2C_6H_4Me)$, A HYDRIDO-ALKYLIDENE PRODUCED BY HYDROGENATION OF A μ_3-ALKYLIDYNE *

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Summary

The complex $CpWOs_3(CO)_9(\mu$-$H)(\mu$-$O)(\mu$-$CHCH_2C_6H_4Me)$, previously prepared by hydrogenation of $CpWOs_3(CO)_9(\mu$-$O)(\mu_3$-$CCH_2C_6H_4Me)$, has been subjected to a single-crystal X-ray diffraction study. The complex crystallizes in the non-centrosymmetric monoclinic space group Cc (C_s^4; No. 9) with a 14.1510(27), b 13.9257(22), c 13.3179(19) Å, β 92.023(13)°, V 2622.8(7) Å^3 and D(calcd) 3.06 g cm^{-3} for $Z = 4$ and mol. wt. 1206.8. Single-crystal X-ray diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer and the structure was refined to R 3.5% for all 2476 independent observations (Mo-K_α radiation, $2\theta = 4.5$–$40.0°$) and R 3.4% for those 2430 data with $|F_0| > 3.0\sigma(|F_0|)$. The molecule contains a tetrahedral WOs_3 core associated with 60 valence electrons. Each osmium atom is associated with three terminal carbonyl ligands and the tungsten atom is linked to an η^5-C_5H_5 ligand. In addition, the μ-oxo ligand is involved in a $W{=}O{:}\rightarrow Os$ bridge (in which W=O(B) 1.737(17), Os(3) ← :O(B) 2.167(16) Å and W–O(B)–Os(3) 96.0(7)°), the μ-hydride ligand spans the Os(1)–Os(3) linkage and the μ-$CHCH_2C_6H_4Me$ ligand bridges the W–Os(2) linkage (W–C(1) 2.068(26) and Os(2)–C(1) 2.281(26) Å).

Introduction

The reaction of $(\mu$-$H)_2Os_3(CO)_{10}$ with $Cp(CO)_2W{\equiv}CTol$ (Cp = η^5-C_5H_5, Tol = p-$CH_3C_6H_4$) has previously been shown to yield mixed-metal clusters [7,8] including

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$$(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}+\text{Cp(CO)}_2\text{W}{\equiv}\text{CTol}\xrightarrow{\Delta}\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-OCCH}_2\text{Tol}]\xrightarrow[-2\text{CO}]{\Delta}$$

$$\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})\xrightarrow{+\text{H}_2}\text{CpWOs}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$$

SCHEME 1

the μ_3-η^2-acyl complex $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-OCCH}_2\text{Tol}]$. This unusual complex has been shown to undergo facile C–O bond scission yielding the oxo-alkylidyne complex $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ [9,10]. This oxo-alkylidyne complex has been shown to undergo hydrogenation [9] yielding the hydrido-oxo-alkylidene complex $\text{CpWOs}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ (see Scheme 1). We have undertaken a single-crystal X-ray diffraction study on this new complex with a view toward determining its precise geometry and connectivity. Our results are reported below.

Experimental

Collection of the X-ray diffraction data

Crystals of $\text{CpWOs}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ were synthesized as described previously [9] and supplied to us 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 single-crystal X-ray diffraction study was a rather irregular opaque dark-red crystal of maximum orthogonal dimensions 0.13 × 0.20 × 0.22 mm. It was inserted into a thin-walled capillary which was flame-sealed, inserted (with bees' wax) into a brass pin, mounted into a eucentric goniometer and accurately centered and aligned on a Syntex $P2_1$ automated four-circle diffractometer. Set-up operations (i.e., determination of accurate unit cell dimensions and the crystal's orientation matrix) and collection of the intensity data were carried out using techniques described in detail previously [11]. Specific information is compiled in Table 1. The diffraction symmetry is $2/m$ (C_{2h}). The systematic absences [hkl for $h+k=2n+1$, $h0l$ for $l=2n+1$ ($h=2n+1$)] are consistent with the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15) or with the non-centrosymmetric monoclinic space group Cc (C_s^4; No. 9). With $Z=4$ and no molecular symmetry, the latter alternative is the most probable and was confirmed by the successful solution of the structure.

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 approximate absolute scale by means of a Wilson plot. Any reflection with $I(\text{net})<0$ was assigned a value of $|F_0|=0$.

Solution and refinement of the structure

All calculations were carried out under our locally-modified version of the Syntex XTL interactive crystallographic program package [12] on our inhouse Data General NOVA 1200 computer. Throughout the analysis the analytical forms of the scattering factors of the neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [13]. The function minimized during

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2C_6H_4Me)$

(A) Crystal parameters at 24° C (297 K)

Crystal system: monoclinic

Space group: $Cc(C_s^4$; No. 9)

Formula: $C_{23}H_{16}O_{10}Os_3W$

Mol. wt.: 1206.8

d(cald): 3.06 g cm^{-3}

$Z = 4$

a 14.1510(27) Å

b 13.9257(22) Å

c 13.3179(19) Å

β 92.023(13)°

V 2622.8(7) $Å^3$

(B) Collection of X-ray diffraction data

Diffractometer: Syntex $P2_1$

Radiation: Mo-K_α(λ 0.710730 Å)

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

Reflections measured: 2476 unique data with $2\theta = 4.5 \rightarrow 40.0°$ (file name WOS8, #150)

Scan type: coupled θ(crystal)—2θ(counter).

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

Scan speed: 2.0 deg/min (in 2θ).

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

Standard reflections: three (600, $02\bar{1}0$, $\bar{1}39$) collected after each batch of 97 reflections; neither significant fluctuations nor steady decay were observed.

Absorption correction: μ(Mo-K_α) 200.3 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) between ψ-scans of close-to-axial reflections.

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least-squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ where $1/w = \{[\sigma(|F_0|)]^2 + [0.01|F_0|]^2\}$. Discrepancy indices used below are defined as follows.

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

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

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

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

The structure was solved by direct methods with the use of the program MULTAN [14]; the positions of the four heavy atoms were determined from an "E-map". (For least-squares refinement processes, the origin was now defined by fixing the x- and z-coordinates or Os(3) at 1/4 and 1/2, respectively.) All remaining non-hydrogen atoms were located from a difference-Fourier map. Hydrogen atoms were included in calculated positions based upon the appropriate idealized geometry and a carbon–hydrogen distance of 0.95 Å [15]; these coordinates were not refined, but were up-dated so as to be consistent with those of their attached carbon atoms. Refinement of positional and thermal parameters (anisotropic for W and Os, isotropic for all others) led to convergence with R_F 3.5%, R_{wF} 4.1% and GOF = 1.92 for 167 parameters refined against all 2476 independent observation ($R_F = 3.4\%$,

$R_{wF} = 4.1\%$ for those 2430 data with $|F_0| > 3.0\sigma(|F_0|)$. Inversion of the coordinates and refinement to convergence once again led to higher residuals; the correct crystal chirality is therefore defined by the initial model and these latter results were discarded.

A final difference-Fourier map showed no unexpected features; the structure is thus both correct and complete. Final positional and thermal parameters are collected in Table 2.

Description of the molecular structure

The crystal contains an ordered arrangement of discrete $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ molecules, which are mutually separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. The overall molecular geometry and the atomic labelling scheme are illustrated in Fig. 1. Interatomic distances and angles are collected in Tables 3 and 4.

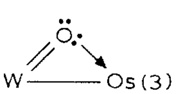
Note that the four metal atoms define a tetrahedral core (vide infra), and that each metal atom is in a different chemical environment. The molecule thus has no improper axes (nor, for that matter, proper axes) and is chiral. However, by virtue of the *c*-glides of space group *Cc*, the crystal contains a racemic mixture of the two chiral enantiomeric molecules.

The metal core is associated with 60 outer valence electrons, as expected for a cluster with a tetrahedral arrangement. If we regard all metal atoms and groups as neutral we have three d^8 Os^0 atoms, one d^6 W^0 atom, 18 electrons from the nine CO ligands, 5 electrons from the Cp ligand, 2 electrons from the μ-$CHCH_2Tol$ ligand, 1 electron from the μ-H ligand and 4 electrons from the μ-O ligand. The present molecule is associated with a number of interesting features.

(A) The WOs_3 core. Although the tetrahedral core as a whole is associated with 60 valence electrons (vide supra) the formal electron-counts at the individual metal atoms vary significantly, with 17 1/2 e^- assigned to Os(1), $18e^-$ to Os(2), 19 1/2 e^- to Os(3) and $17e^-$ to W. It seems probable that the differences in metal–metal distances are related, in part, to these variations. The osmium–osmium distances are (in order) Os(1)–Os(2) 2.799(2), Os(2)–Os(3) 2.870(1) and Os(3)–Os(1) 2.951(1) Å and the tungsten–osmium distances are (in order) W–Os(1) 2.735(2), W–Os(2) 2.746(2) and W–Os(3) 2.916(1) Å.

(B) The W(μ-O)Os system. The oxo ligand (defined as O(B)) spans the W–Os(3) edge such that W–O(B) 1.737(17), Os(3)–O(B) 2.167(16) Å and ⟨W–O(B)–Os(3) 96.0(7)°. These distances are compatible with the presence of a tungsten–oxygen double bond and an osmium–oxygen single bond; the appropriate valence-bond description is that in **1**, below. Similar systems have been encountered only in $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$, in which W=O 1.812(7), Os–O 2.169(8) Å and W=O–Os 83.46(31)° [9,10], and in $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$, in which W=O 1.761(8), Os–O 2.200(8) and W=O–Os 92.82(36)° [3].

In each of these cases we regard the oxo ligand as a four-electron donor (neutral atom counting system).



(1)

TABLE 2

FINAL ATOMIC PARAMETERS FOR $CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2C_6H_4Me)$

(A) ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS

Atom	*x*	*y*	*z*	*B* (Å^2)
W	0.29412(9)	0.24633(7)	0.54526(10)	
Os(1)	0.14758(9)	0.32740(7)	0.64353(9)	
Os(2)	0.13073(9)	0.28943(7)	0.43730(9)	
Os(3)	0.25000(0)	0.44661(7)	0.50000(0)	
O(11)	−0.0164(13)	0.4582(15)	0.7097(15)	4.9(4)
O(12)	0.2617(13)	0.3245(14)	0.8391(15)	4.3(4)
O(13)	0.0465(13)	0.1412(15)	0.6832(14)	4.4(4)
O(21)	0.1311(14)	0.3547(15)	0.2171(15)	4.9(4)
O(22)	0.0216(14)	0.1029(16)	0.4315(14)	4.7(4)
O(23)	−0.0581(13)	0.3913(15)	0.4705(14)	4.2(4)
O(31)	0.3580(13)	0.6242(14)	0.5800(14)	4.1(4)
O(32)	0.0846(13)	0.5685(14)	0.4385(14)	4.3(4)
O(33)	0.3321(13)	0.4596(15)	0.2908(15)	4.6(4)
O(B)	0.3635(11)	0.3492(12)	0.5440(12)	2.93(33)
C(11)	0.0459(19)	0.4102(20)	0.6832(20)	3.3(5)
C(12)	0.2203(16)	0.3270(17)	0.7651(17)	2.3(5)
C(13)	0.0797(19)	0.2115(22)	0.6675(20)	3.7(6)
C(21)	0.1320(20)	0.3255(21)	0.3002(23)	3.9(6)
C(22)	0.0633(19)	0.1773(21)	0.4299(20)	3.6(6)
C(23)	0.0170(18)	0.3554(20)	0.4652(20)	3.3(5)
C(31)	0.3211(18)	0.5549(21)	0.5515(21)	3.6(6)
C(32)	0.1512(17)	0.5185(19)	0.4604(18)	2.9(5)
C(33)	0.2978(15)	0.4534(17)	0.3700(17)	2.2(5)
C(1)	0.2667(18)	0.2137(19)	0.3956(19)	3.1(5)
C(2)	0.2556(17)	0.1168(19)	0.3419(18)	2.5(5)
C(3)	0.2145(14)	0.1237(16)	0.2377(15)	1.4(4)
C(4)	0.1270(17)	0.0827(19)	0.2112(18)	2.8(5)
C(5)	0.0877(19)	0.0895(20)	0.1166(20)	3.9(6)
C(6)	0.1364(18)	0.1391(19)	0.0426(19)	2.9(5)
C(7)	0.2244(17)	0.1769(19)	0.0648(19)	3.1(5)
C(8)	0.2602(17)	0.1681(18)	0.1605(19)	2.8(5)
C(9)	0.0900(22)	0.1474(25)	−0.0660(24)	5.2(7)
Cp(1)	0.4337(16)	0.1632(18)	0.5966(18)	2.7(5)
Cp(2)	0.3830(18)	0.1811(21)	0.6818(20)	3.3(6)
Cp(3)	0.2996(16)	0.1353(18)	0.6786(17)	2.4(5)
Cp(4)	0.2949(17)	0.0783(20)	0.5929(18)	3.1(5)
Cp(5)	0.3778(16)	0.0987(19)	0.5391(18)	2.7(5)
H(B)	0.1839	0.4760	0.6198	2.0
H(1)	0.2132	0.2259	0.3474	3.5
H(21)	0.2155	0.0773	0.3800	3.5
H(22)	0.3162	0.0879	0.3390	3.5
H(4)	0.0936	0.0489	0.2608	3.5
H(5)	0.0280	0.0609	0.1008	3.5
H(7)	0.2591	0.2083	0.0147	3.5
H(8)	0.3211	0.1943	0.1751	3.5
H(91)	0.0296	0.1174	−0.0675	3.5
H(92)	0.0828	0.2132	−0.0833	3.5
H(93)	0.1294	0.1168	−0.1126	3.5
Hp(1) [a]	0.4934	0.1890	0.5804	3.5
Hp(2)	0.4047	0.2208	0.7358	3.5
Hp(3)	0.2518	0.1408	0.7267	3.5
Hp(4)	0.2460	0.0344	0.5739	3.5
Hp(5)	0.3926	0.0731	0.4754	3.5

(B) ANISOTROPIC THERMAL PARAMETERS (in Å^2) [b] FOR THE METAL ATOMS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	1.53(4)	2.08(5)	1.67(4)	0.451(35)	−0.125(30)	0.03(4)
Os(1)	2.06(4)	2.26(5)	1.58(4)	0.23(4)	0.261(31)	−0.00(4)
Os(2)	1.50(4)	2.40(5)	1.80(4)	0.33(4)	−0.119(31)	−0.25(4)
Os(3)	1.96(4)	2.15(5)	1.60(4)	0.11(4)	0.163(31)	0.05(4)

[a] Hp(1) is the hydrogen atom linked to atom Cp(1) etc. [b] The anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form: $\exp[-1/4(h^2a^{*2}B_{11} + \ldots 2hka^*b^*B_{12} + \ldots)]$.

(C) The μ-CHCH$_2$Tol ligand. The μ-alkylidene ligand bridges the W–Os(2) bond with W–C(1) 2.068(26) and Os(2)–C(1) 2.281(26) Å. It was formed from the μ_3-alkylidyne precursor by hydrogenation of C(1) in conjunction with cleavage of a Os–C linkage (see eq. 1); specifically, relative to Fig. 1, it appears that the Os(3)–C(1) linkage of the alkylidyne precursor is cleaved. The W–C and Os–C distances in the alkylidyne precursor are W–C 2.030(12), Os–C 2.100(10) and 2.291(12) Å; interestingly, it is the shorter of the two Os–C bonds that is cleaved (i.e., that one associated with the oxo-linked osmium atom).

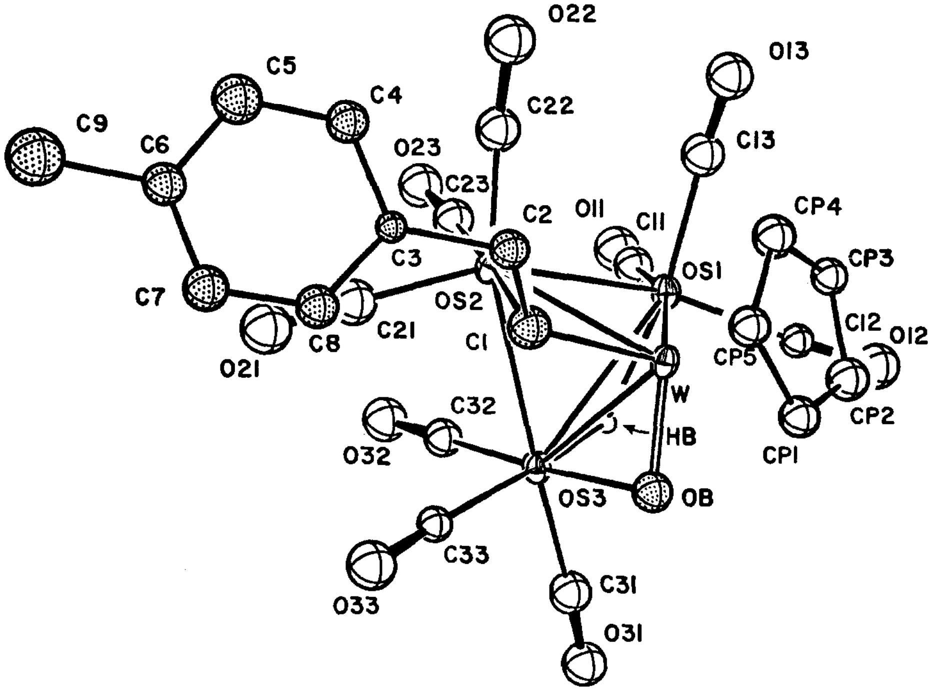
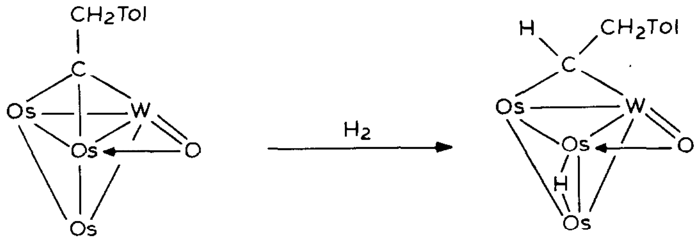


Fig. 1. Molecular geometry and atomic labelling scheme for CpWOs$_3$(CO)$_9$(μ-H)(μ-O)(μ-CHCH$_2$Tol). All organic hydrogens have been omitted for clarity's sake. The μ-oxo and μ-CHCH$_2$Tol ligands are stippled. (ORTEP-II diagram; 30% probability ellipsoids).

TABLE 3

INTERATOMIC DISTANCES (Å) WITH Esd's FOR $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2C_6H_4Me)$

(A) Metal-metal Bond Lengths			
Os(1)–Os(2)	2.799(2)	W–Os(1)	2.735(2)
Os(2)–Os(3)	2.870(1)	W–Os(2)	2.746(2)
Os(3)–Os(1)	2.951(1)	W–Os(3)	2.916(1)
(B) Metal-(Bridging Ligand) Distances			
W–C(1)	2.068(26)	Os(2)–C(1)	2.281(26)
W–O(B)	1.737(17)	Os(3)–O(B)	2.167(16)
Os(1)–H(B)	2.16	Os(3)–H(B)	1.92
(C) Distances within the μ*-*$CHCH_2Tol$ *ligand*			
C(1)–C(2)	1.53(4)	C(6)–C(7)	1.37(4)
C(2)–C(3)	1.49(3)	C(7)–C(8)	1.36(4)
C(3)–C(4)	1.40(3)	C(8)–C(3)	1.38(3)
C(4)–C(5)	1.36(4)	C(6)–C(9)	1.57(4)
C(5)–C(6)	1.40(4)		
(D) Osmium-Carbonyl Distances			
Os(1)–C(11)	1.932(27)	Os(1) ··· O(11)	3.102(20)
Os(1)–C(12)	1.887(23)	Os(1) ··· O(12)	3.016(19)
Os(1)–C(13)	1.910(30)	Os(1) ··· O(13)	3.017(20)
Os(2)–C(21)	1.894(30)	Os(2) ··· O(21)	3.070(20)
Os(2)–C(22)	1.830(29)	Os(2) ··· O(22)	3.022(21)
Os(2)–C(23)	1.901(26)	Os(2) ··· O(23)	3.070(19)
Os(3)–C(31)	1.926(28)	Os(3) ··· O(31)	3.078(19)
Os(3)–C(32)	1.784(25)	Os(3) ··· O(32)	2.982(19)
Os(3)–C(33)	1.884(22)	Os(3) ··· O(33)	3.061(20)
Os(1) ··· C(23)	2.983(26)		
(E) Carbon-Oxygen Distances in Carbonyl Ligands			
C(11)–O(11)	1.17(3)	C(23)–O(23)	1.18(3)
C(12)–O(12)	1.13(3)	C(31)–O(31)	1.16(3)
C(13)–O(13)	1.11(4)	C(32)–O(32)	1.20(3)
C(21)–O(21)	1.18(4)	C(33)–O(33)	1.18(3)
C(22)–O(22)	1.19(4)		
(F) Tungsten-Cyclopentadienyl Distances			
W–Cp(1)	2.369(24)	Cp(1)–Cp(2)	1.39(4)
W–Cp(2)	2.357(26)	Cp(2)–Cp(3)	1.34(4)
W–Cp(3)	2.354(24)	Cp(3)–Cp(4)	1.39(4)
W–Cp(4)	2.424(27)	Cp(4)–Cp(5)	1.42(3)
W–Cp(5)	2.375(25)	Cp(5)–Cp(1)	1.41(4)



(1)

TABLE 4

INTERATOMIC ANGLES (°) FOR CpWOs$_3$(CO)$_9$(μ-H)(μ-O)(μ-CHCH$_2$C$_6$H$_4$Me)

(A) Intermetallic Angles			
Os(1)–W–Os(2)	61.42(4)	W–Os(2)–Os(1)	59.10(4)
Os(2)–W–Os(3)	60.83(4)	Os(1)–Os(2)–Os(3)	62.71(4)
Os(3)–W–Os(1)	62.85(4)	Os(3)–Os(2)–W	62.53(4)
W–Os(1)–Os(2)	59.48(4)	W–Os(3)–Os(1)	55.56(3)
Os(2)–Os(1)–Os(3)	59.52(4)	Os(1)–Os(3)–Os(2)	57.46(3)
Os(3)–Os(1)–W	61.58(4)	Os(2)–Os(3)–W	56.65(3)
(B) M–M–CO Angles			
W–Os(1)–C(11)	164.1(8)	W–Os(2)–C(21)	121.8(9)
W–Os(1)–C(12)	90.5(7)	W–Os(2)–C(22)	105.6(9)
W–Os(1)–C(13)	97.2(9)	W–Os(2)–C(23)	134.9(8)
Os(2)–Os(1)–C(11)	110.0(8)	Os(1)–Os(2)–C(21)	153.2(9)
Os(2)–Os(1)–C(12)	150.0(7)	Os(1)–Os(2)–C(22)	103.9(9)
Os(2)–Os(1)–C(13)	88.8(9)	Os(1)–Os(2)–C(23)	76.1(8)
Os(3)–Os(1)–C(11)	103.3(8)	Os(3)–Os(2)–C(21)	93.0(9)
Os(3)–Os(1)–C(12)	107.0(7)	Os(3)–Os(2)–C(22)	165.0(9)
Os(3)–Os(1)–C(13)	147.6(9)	Os(3)–Os(2)–C(23)	93.9(8)
W–Os(3)–C(31)	124.7(8)	Os(1)–Os(3)–C(33)	145.5(7)
W–Os(3)–C(32)	139.2(8)	Os(2)–Os(3)–C(31)	174.5(8)
W–Os(3)–C(33)	99.0(7)	Os(2)–Os(3)–C(32)	84.0(8)
Os(1)–Os(3)–C(31)	118.2(8)	Os(2)–Os(3)–C(33)	89.8(7)
Os(1)–Os(3)–C(32)	96.3(8)		
(C) Os–C–O and OC–Os–CO Angles			
Os(1)–C(11)–O(11)	177.8(23)	C(11)–Os(1)–C(12)	99.0(11)
Os(1)–C(12)–O(12)	177.6(21)	C(12)–Os(1)–C(13)	96.7(11)
Os(1)–C(13)–O(13)	175.0(25)	C(13)–Os(1)–C(11)	94.3(12)
Os(2)–C(21)–O(21)	175.0(25)	C(21)–Os(2)–C(22)	101.4(12)
Os(2)–C(22)–O(22)	175.6(24)	C(22)–Os(2)–C(23)	88.8(12)
Os(2)–C(23)–O(23)	171.0(23)	C(23)–Os(2)–C(21)	95.6(12)
Os(3)–C(31)–O(31)	174.8(23)	C(31)–Os(3)–C(32)	93.5(11)
Os(3)–C(32)–O(32)	176.8(22)	C(32)–Os(3)–C(33)	90.2(11)
Os(3)–C(33)–O(33)	176.5(20)	C(33)–Os(3)–C(31)	95.1(11)
Os(1) ··· C(23)–O(23)	122.9(19)		
(D) Angles involving C(1), the Alkylidene Carbon			
W–C(1)–Os(2)	78.2(8)	W–Os(2)–C(1)	47.5(7)
W–C(1)–C(2)	131.0(18)	Os(2)–W–C(1)	54.4(7)
Os(2)–C(1)–C(2)	116.6(17)		
(E) Angles involving O(B) or H(B)			
W–O(B)–Os(3)	96.0(7)	Os(1)–H(B)–Os(3)	92 (–)
W–Os(3)–O(B)	36.3(4)	C(13)–Os(1)–H(B)	163 (–)
Os(3)–W–O(B)	47.7(5)	C(33)–Os(3)–H(B)	163 (–)
Os(1)–W–O(B)	95.9(5)		
Os(2)–W–O(B)	106.3(5)		
C(32)–Os(3)–O(B)	175.9(6)		
(F) C–C–C Angles within the CHCH$_2$C$_6$H$_4$Me Ligand			
C(1)–C(2)–C(3)	114.2(20)	C(8)–C(3)–C(4)	115.4(20)
C(2)–C(3)–C(4)	121.6(20)	C(3)–C(4)–C(5)	122.3(23)
C(2)–C(3)–C(8)	123.0(20)	C(4)–C(5)–C(6)	119.3(24)
C(5)–C(6)–C(9)	118.9(24)	C(5)–C(6)–C(7)	120.0(24)
C(7)–C(6)–C(9)	121.0(24)	C(6)–C(7)–C(8)	118.2(24)
		C(7)–C(8)–C(3)	124.7(23)

TABLE 4 (continued)

(G) Angles within the Cp Ligand			
Cp(5)–Cp(1)–Cp(2)	105.2(22)	Cp(3)–Cp(4)–Cp(5)	106.5(22)
Cp(1)–Cp(2)–Cp(3)	111.7(24)	Cp(4)–Cp(5)–Cp(1)	108.1(21)
Cp(2)–Cp(3)–Cp(4)	108.3(23)		

Note that O(B) occupies a site trans to C(32)–O(32) in the pseudo-octahedral coordination sphere of Os(3).

(D) The μ-hydride ligand. The bridging hydride ligand was located from a difference-Fourier map, but was not refined. It is associated with imprecise distances of Os(1)–H(B) 2.16 and Os(3)–H(B) 1.92 Å and spans the longest osmium–osmium bond (Os(3)–Os(1) 2.951(1) Å) as is typical of unsupported μ-hydride ligands [16–18]. It occupies a position *trans* to C(13)–O(13) on Os(1) and *trans* to C(33)–O(33) on Os(3). The μ-hydride ligand thus completes the pseudo-octahedral geometry about both Os(1) and Os(3).

(e) Other features of the structure. All other features of the structure of $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ are normal. Individual Os–CO distances range from 1.784(25) through 1.932(27) Å, C–O bond lengths range from 1.11(4) through 1.20(3) Å and Os–C–O angles are in the range 171.0(23)–177.8(23)°. Tungsten–carbon (Cp) distances vary from 2.354(24) through 2.424(27) Å and carbon–carbon (Cp) distances are in the range 1.34(4)–1.42(3) Å.

Discussion

The present structural study provides a further step in the homologation and reduction of the CTol ligand. As may be seen from Scheme 1, the initial CTol ligand is transformed step-wise to, finally, the present μ-$CHCH_2Tol$ ligand. The individual reactions are indicated by eqs. 2–5.

$$CTol + 2H \rightarrow CH_2Tol \qquad (2)$$

$$CH_2Tol + CO \rightarrow OCCH_2Tol \qquad (3)$$

$$OCCH_2Tol \xrightarrow{\Delta} CCH_2Tol + O \qquad (4)$$

$$CCH_2Tol + 1/2\ H_2 \rightarrow CHCH_2Tol \qquad (5)$$

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Additional material

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

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