

SYNTHESIS AND CRYSTAL STRUCTURE OF A TETRANUCLEAR MIXED-METAL ALKYLIDENE COMPLEX $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-H})(\mu\text{-CHTol})$

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Abstract—The solid-state structure of a tetranuclear mixed-metal cluster $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-H})(\mu\text{-CHTol})$ (**2**) which possesses a bridging hydride, a bridging oxo and a bridging tolylalkylidene ligand is presented. Complex **2** crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.763(5)$, $b = 10.759(4)$, $c = 13.336(3)$ Å, $\alpha = 88.00(3)$, $\beta = 108.56(3)$, $\gamma = 100.44(3)^\circ$, $Z = 2$; 3463 observed reflections with $I > 3\sigma(I)$ were used in the refinement. The R values converged to $R_F = 0.057$, $R_w = 0.058$.

The reactivity of mixed-metal clusters has been of interest for many years.¹ Research in this area is stimulated by a belief that the combination of metals having very different chemical properties within one compound may induce unique chemical transformations. In seeking to develop a systematic way to prepare the mixed-metal clusters of higher nuclearity, Stone and co-workers have used $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CR}$ as a building block to prepare many mixed-metal clusters containing a bridging alkylidyne fragment.² As the number of the mixed-metal alkylidyne clusters has increased dramatically in the past few years, there is increasing interest in examining the chemistry of the alkylidyne clusters because of the possible roles of the alkylidynes as reaction intermediates in, and/or models of various catalytic processes.³ In the present study we have explored the hydrogenation of a tetrahedral mixed-metal alkylidyne complex $\text{CpWOs}_3(\text{CO})_9(\mu_3\text{-CTol})_2(\mu\text{-H})$ (**1**)⁴ which produces an alkylidene complex $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-H})(\mu\text{-CHTol})$ (**2**) in

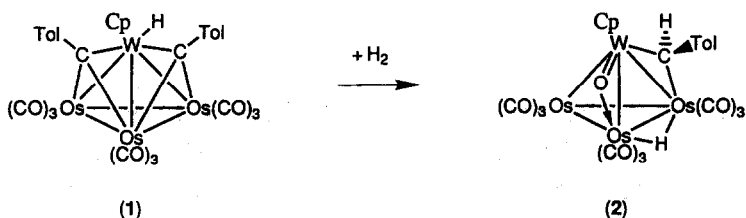
low yield (Scheme 1). The single-crystal X-ray diffraction study on complex **2** suggests that its gross geometry and ligand configuration are complementary to those of the related, structurally characterized WOs_3 clusters $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-H})(\mu\text{-CHCH}_2\text{Tol})$ (**3**)⁵ and $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-Cl})(\mu\text{-CHCH}_2\text{Tol})$ (**4**)⁶ (Scheme 2).

RESULTS AND DISCUSSION

Hydrogenation of complex **1** in refluxing xylenes solution (1 atm, 6 h) produced an orange-brown solution. The solvent was removed *in vacuo* and the product purified by thin-layer chromatography (TLC), giving an orange product in low yield. The mass spectrum indicates a parent ion at m/z 1198, corresponding to a composition $\text{C}_{22}\text{H}_{14}\text{O}_{10}\text{Os}_3\text{W}$. The ¹³C NMR spectrum (CDCl_3 , 100.6 MHz, 213 K) exhibits nine Os—CO signals at δ 194.5, 184.4, 181.4, 180.9, 176.4, 173.2, 169.9, 169.7, 169.1 and the ¹H NMR spectrum (CDCl_3 , 400 MHz, 294 K) shows two singlets at δ 5.52 and -18.05 , in addition to signals corresponding to one Cp ligand and one tolyl fragment. The IR spectrum (C_6H_{12}) in the carbonyl region shows absorption bands at 2090(s), 2965(vs), 2028(vs), 2020(vs), 2014(s), 2007(m),

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Scheme 1.

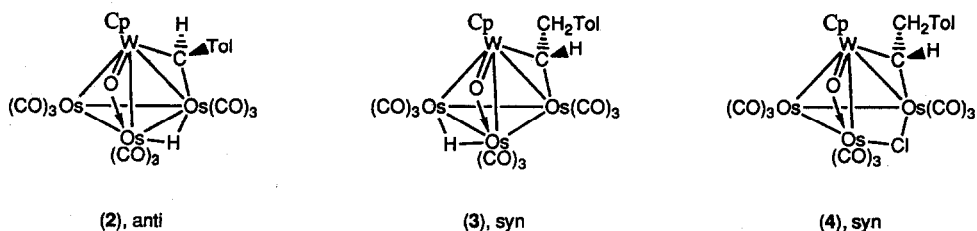
1991(w), 1958(w), 1940(m) cm^{-1} , indicating that the molecule is analogous to the recently reported dioxo cluster $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})_2(\mu\text{-H})$.⁷ Based on these spectroscopic data, a formulation $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-H})(\mu\text{-CHTol})$ is proposed for this complex. The exact source of the oxo ligand in **2** and the fate of the second alkyldiene in **1** are unknown. However, based on reports in the literature, we speculate that the oxo ligand may be derived from a CO ligand by C—O bond scission or from other possible sources (O_2 or H_2O)⁸ in the solution and that the alkyldiene may be eliminated as a *para*-xylene molecule.⁹

The molecular structure of **2** was determined by a single-crystal X-ray diffraction study. The ORTEP diagram and the scheme used for labelling the atoms are shown in Fig. 1. The bond distances and angles are listed in Tables 1 and 2, respectively. The molecule consists of one tungsten atom and three osmium atoms which define a tetrahedral core associated with the expected 60 outer valence electrons. The tungsten atom is coordinated to a Cp, a bridging oxo and a bridging alkyldiene ligand, whereas each of the three basal osmium atoms is associated with three terminal CO ligands arranged in a pseudo-octahedral geometry.

The oxo ligand O(10) bridges the W—Os(2) edge and the W—O(10)—Os(2) interaction is characterized by the short tungsten—oxygen bond distance (W—O(1) = 1.77 Å), the comparatively long Os(2)—O(10) bond length (2.13 Å) and the small W—O(10)—Os(2) angle (94.6°). These data are compatible with the parameters for the typical

W=O→Os bonding interaction as has been found previously in the related WOs_3 complexes.¹⁰ In addition, there is also a doubly bridging alkyldiene ligand ($\mu\text{-CHTol}$) which is associated with the second W—Os edge of the triangular face defined by the atoms W, Os(1) and Os(2). The W—C(22) distance (2.08 Å) is slightly shorter than the Os(1)—C(22) distance (2.24 Å) and the tolyl substituent is oriented toward the bridging oxo ligand. Finally, the structurally undetermined bridging hydride ligand is proposed to be associated with the third Os—Os edge of this WOs_2 triangle. Consistent with our postulate, this metal—metal vector displays a relatively large Os(1)—Os(2) distance (2.997 Å) and possesses two enlarged Os—Os—CO angles (113–114°) and two regular Os—Os—CO angles (89–94°). The other two Os—Os distances within the molecule are slightly smaller, with Os(1)—Os(3) = 2.844(2) and Os(2)—Os(3) = 2.846(2) Å. After the position of the bridging hydride ligand is established, the formal electron counts for the W, Os(1), Os(2) and Os(3) atoms are calculated to be 17, 18.5, 19.5 and 17e⁻, respectively.

The structure of **2** is different from those of the analogous hydrido-alkyldiene complex **3** and the chloro-alkyldiene complex **4** in terms of the location of the bridging hydride and the configuration of the bridging alkyldiene ligand (Scheme 2). In complex **3**, the bridging hydride is located on the Os—Os edge eclipsed to the W—Os edge which is associated with the alkyldiene fragment; therefore, the metal—metal edges supporting the bridging hydride, oxo and alkyldiene ligands are aligned in a zigzag



Scheme 2.

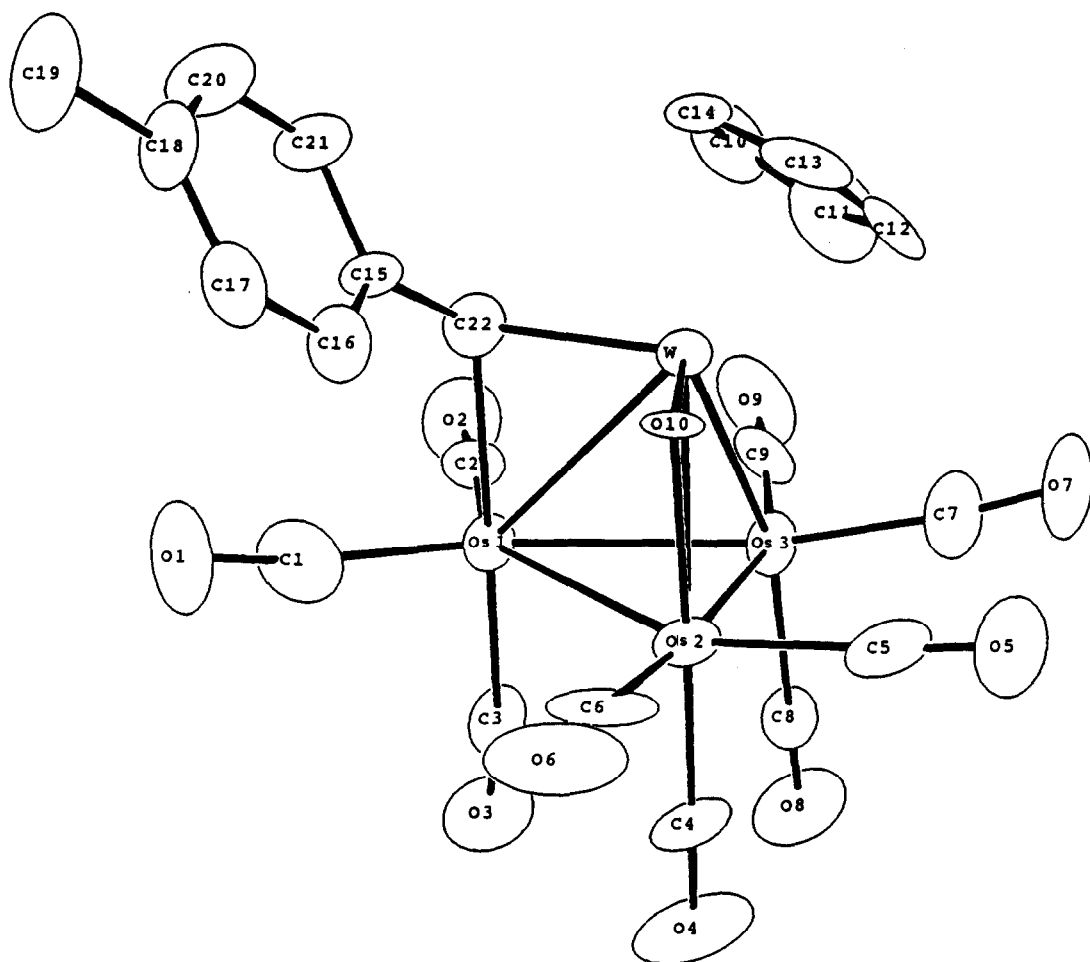


Fig. 1. The molecular structure of CpWOs₃(CO)₉(μ-O)(μ-H)(μ-CHTol) (**2**) showing the atomic numbering scheme.

Table 1. Selected interatomic distances (Å) of complex **2** (ESADs in parentheses)

Os(1)—Os(2)	2.977(2)	Os(1)—Os(3)	2.844(2)
Os(2)—Os(3)	2.846(2)	W—Os(1)	2.857(2)
W—Os(2)	2.874(2)	W—Os(3)	2.629(2)
W—O(10)	1.77(2)	Os(2)—O(10)	2.13(?)
W—C(22)	2.08(2)	Os(1)—C(22)	2.24(2)
Os(1)—C(1)	1.92(3)	Os(1)—C(2)	1.95(3)
Os(1)—C(3)	1.96(3)	Os(2)—C(4)	1.86(3)
Os(2)—C(5)	1.94(3)	Os(2)—C(6)	1.68(4)
Os(3)—C(7)	1.87(3)	Os(3)—C(8)	1.95(3)
Os(3)—C(9)	1.80(3)	C(1)—O(1)	1.13(3)
C(2)—O(2)	1.08(4)	C(3)—O(3)	1.10(4)
C(4)—O(4)	1.11(4)	C(5)—O(5)	1.15(3)
C(6)—O(6)	1.30(5)	C(7)—O(7)	1.17(3)
C(8)—O(8)	1.08(4)	C(9)—O(9)	1.19(4)
W—C(10)	2.34(4)	W—C(11)	2.39(4)
W—C(12)	2.35(2)	W—C(13)	2.37(3)
W—C(14)	2.31(3)	C(22)—C(15)	1.53(3)

arrangement. In contrast, the bridging chloro ligand of complex **4** is located at a position similar to that of the bridging hydride in complex **2**; therefore, the respective metal–metal edges are arranged in a triangular pattern. In addition, because the bridging chloro ligand is a three-electron-donor, the bond distance between the osmium atoms linked by chloro ligand is not in the range of a typical Os—Os single bond.

On the other hand, the α -hydrogen of the alkylidene ligand in both complexes **3** and **4** is oriented toward the bridging oxo ligand; therefore, the configuration of the bridging alkylidene (denoted as *syn*) is in contrast to that of complex **2** (denoted as *anti*). We propose that the formation of the *anti* configuration for complex **2** is due to its greater thermodynamic stability with respect to the unobserved *syn* configuration, and the latter is destabilized because of the unfavourable steric repulsion between the tolyl substituent and the Cp ligand.

Table 2. Selected bond angles (°) of complex **2** (ESADs in parentheses)

W—Os(1)—Os(2)	58.98(4)	W—Os(2)—Os(1)	58.43(4)
Os(1)—W—Os(2)	62.58(4)	W—Os(1)—Os(3)	54.91(4)
W—Os(3)—Os(1)	62.79(4)	Os(1)—W—Os(3)	62.29(4)
W—Os(2)—Os(3)	54.72(5)	W—Os(3)—Os(2)	63.17(5)
Os(2)—W—Os(3)	62.11(5)	Os(1)—Os(2)—Os(3)	58.42(4)
Os(2)—Os(3)—Os(1)	63.08(5)	Os(3)—Os(1)—Os(2)	58.49(4)
Os(1)—C(1)—O(1)	172(3)	Os(1)—C(2)—O(2)	178(2)
Os(1)—C(3)—O(3)	172(3)	Os(2)—C(4)—O(4)	177(4)
Os(2)—C(5)—O(5)	176(3)	Os(2)—C(6)—O(6)	169(3)
Os(3)—C(7)—O(7)	174(3)	Os(3)—C(8)—O(8)	175(4)
Os(3)—C(9)—O(9)	178(2)	Os(1)—C(22)—W	82.7(8)
W—Os(1)—C(22)	46.3(5)	Os(1)—W—C(22)	51.1(6)
Os(2)—O(10)—W	94.6(7)	Os(2)—W—O(10)	47.5(5)
W—Os(2)—O(10)	37.9(5)	W—C(22)—C(15)	119(2)
Os(1)—C(22)—C(15)	123(2)	Os(1)—Os(2)—C(4)	94.4(9)
Os(1)—Os(2)—C(6)	113(1)	Os(2)—Os(1)—C(1)	114(1)
Os(2)—Os(1)—C(3)	89(1)		

EXPERIMENTAL

IR spectra were recorded using a Perkin–Elmer 580 spectrometer calibrated using the absorption of cyclohexane at 2138.5 cm^{-1} and the absorption of polystyrene film at 1944.5 cm^{-1} . Both ^1H and ^{13}C NMR spectra were recorded using a Bruker AM-400 instrument. Mass spectra were obtained on a JEOL-HX110 instrument operating in electron impact, field desorption or fast atom bombardment modes. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical TLC (5735 Kieselgel 60 F₂₅₄, E. Merck) and the products were separated on the commercially available preparative TLC plates (Kieselgel 60 F₂₅₄, E. Merck). The mixed-metal complexes CpWOs₃(CO)₉(μ₃-CTol)₂(μ-H) (**1**) were prepared according to the literature method.⁴

Preparation of CpWOs₃(CO)₉(μ-O)(μ-H)(μ-CHTol) (**2**)

A xylene solution (45 cm³) of CpWOs₃(CO)₉(μ₃-CTol)₂(μ-H) (**1**) (56 mg, 0.043 mmol) was heated at reflux under 1 atm of hydrogen. After refluxing for 6 h, the solvent was evaporated *in vacuo* and the residue was separated on a preparative TLC plate (hexane–dichloromethane, 3:2), giving the alkylidene complex **2** (6 mg, 0.005 mmol, 12%) as red–orange crystals after recrystallization from dichloromethane–methanol. In addition, some starting materials (10 mg, 0.008 mmol, 18%) were also recovered from the residue of the reaction mixture.

Spectroscopic data for complex 2. MS (EI, ^{192}Os , ^{184}W), m/z 1198(M⁺); IR(C₆H₁₂): ν(CO), 2090(s), 2065(vs), 2028(vs), 2020(vs), 2014(s), 2007(m), 1991(w), 1958(w), 1940(m) cm⁻¹; ^1H NMR (400 MHz, CDCl₃, 294 K): δ 7.05–6.45 (m, 4H), 5.94 (s, 5H), 5.52 (s, 1H), 2.39 (s, 3H), –18.05 (s, 1H); ^{13}C -{H} NMR (100.4 MHz, CDCl₃, 213 K): Os—CO, δ 194.5, 184.4, 181.4, 180.9, 176.4, 173.2, 169.9, 169.7, 169.1.

Structural determination of complex **2**

Crystals suitable for diffraction analysis were obtained from a dichloromethane–methanol solution. A crystal was mounted on a glass fibre. Diffraction measurements were carried out on a Nonius CAD-4 fully automated four-circle diffractometer. The unit cell was determined and refined using setting angles of 25 randomly selected reflections, with 2θ angles in the range of 2.5–50°, obtained by using the CAD-4 automatic search, centre, index and least-squares routines. All data reduction and structure refinement were performed using the NRCC-SDP-VAX packages. The structure was solved by the Patterson method and refined by least-squares; all non-hydrogen atoms were refined with anisotropic thermal parameters. The data collection parameters are summarized in Table 3. Tables of atomic coordinates, anisotropic thermal parameters, structure factor amplitudes, and non-essential bond distance and angle parameters have been deposited as supplementary data and are available from the authors (S.M.P.).

Table 3. Experimental data for the X-ray diffraction study of complex 2

(A) Crystal data	
<i>a</i> (Å)	9.763(5)
<i>b</i> (Å)	10.759(4)
<i>c</i> (Å)	13.336(3)
α (°)	88.00(3)
β (°)	108.56(3)
γ (°)	100.44(3)
<i>F</i> (000)	1056
Temperature (K)	297
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>Z</i>	2
Formula	C ₂₂ H ₁₄ O ₁₀ Os ₃ W ₁
<i>V</i> (Å ³)	1305.6(9)
Molecular weight	1192.8
Density (calc.) (g cm ⁻³)	3.034
(B) Data collection, reduction, solution and refinement	
Data collection instrument	Nonius CAD-4
Radiation (monochromated in incident beam)	Mo- <i>K</i> _α (λ = 0.71073 Å)
Scan method	2θ-θ scan mode
Scan range	0.65+0.35 tan θ
Scan speed	Variable; 1.10–8.24°/min
Crystal size (mm)	0.25 × 0.40 × 0.40
Linear absorption coefficient (mm ⁻¹)	19.10
Transmission factors: max, min.	0.99, 0.55
Number of unique data, total with <i>I</i> > 3σ(<i>I</i>)	4574, 3463
Number of atoms and parameters refined	36, 326
Largest and mean Δ/σ	0.228, 0.001
<i>R</i> ; <i>R</i> _w ^a (%)	5.7; 5.8
G.O.F. ^b	3.71
Residual electron density (e Å ⁻³): max./min.	4.43/–2.88

$$^a w^{-1} = \sigma^2(F).$$

^b $S = [\sum w|F_o - F_c|^2 / (N_o - N_v)]^{1/2}$ (*N*_o = number of observations; *N*_v = number of variables).

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