

Synthesis and Crystal Structure of $\text{CpWOS}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$

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In recent years organometallic oxo complexes have attracted much attention due to both models and potential catalysts for the oxygen transfer reactions.¹ The oxo ligand has also been proposed to be essential to the catalyst as a spectator ligand in olefin metathesis. The cluster $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-O})_2$ was the first oxo carbonyl cluster to be characterized, but the first monomeric oxo carbonyl complex with a terminal oxo group was $\text{WCl}_2(\text{PMePh}_2)_2(\text{CO})(\text{O})$.² In previous work, we have reported the synthesis and solution dynamics of a tungsten-triosmium *p*-xylylidyne complex, $\text{CpWOS}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (**1**, $\text{Cp}=\eta^5\text{-C}_5\text{H}_5$, $\text{Tol}=\textit{p}\text{-C}_6\text{H}_4\text{Me}$),^{3a} and the reactivity of **1** toward dihydrogen leading to formation of an unexpected hydrido-oxo-alkylidene complex, $\text{CpWOS}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CHTol})(\mu\text{-H})$ (**2**).^{3b} The μ -oxo ligand of **2** may be derived from a CO ligand by C-O bond scission or from other possible sources (O_2 , H_2O , Me_3NO and etc.). In order to elucidate the source of the μ -oxo ligand, the reactivity of **1** toward H_2O is examined. Initial decarbonylation of **1** and subsequent reaction with H_2O affords a μ -oxo complex, $\text{CpWOS}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$ (**3**), which suggests that the μ -oxo ligand of **2** is originated from water in the reaction solvent. We report herein details of the synthesis and crystal structure of compound **3**.

Experiment Section

General Comments. All reactions were carried out under an atmosphere of nitrogen in oven-dried glasswares. Solvents were dried prior to use. $\text{CpWOS}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ was prepared as described in the literature.^{3a} The progress of reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, Silica Gel 60F-254, E. Merck). Preparative TLC was carried out using glass-backed silica gel plates (20×20 cm) prepared from silica gel (Type 60, E. Merck). Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. ^1H NMR (300 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were recorded by the staff at the Mass Spectrometry Laboratory of University of Illinois by using a Varian MAT-MAT-731 (FD) mass spectrometer. All m/z values are referenced to ^{184}W and ^{192}Os . Microanalytical data were provided by the Daeduk R & D Center of Daelim Industrial Co., Ltd.

Reaction of **1 with H_2O .** Red compound **1** (17.9 mg, 0.0145 mmol) was dissolved in a mixture of dichloromethane (15 mL) and acetonitrile (5 mL). An acetonitrile solution (1 mL) of anhydrous Me_3NO (1.6 mg, 0.0218 mmol) was added

Table 1. Crystal Data for **3**

formula	$\text{C}_{23}\text{H}_{12}\text{O}_{11}\text{WOS}_3$
fw	1218.79
cryst syst	monoclinic
space group	$\text{P}2_1/a$
a, Å	28.263(7)
b, Å	9.358(6)
c, Å	9.986(1)
β , deg	96.75(2)
V, Å ³	2622.86(5)
Z	4
ρ (calcd), gcm^{-3}	3.09
temp. K	297
λ (Mo K α), Å	0.71069
μ , mm^{-1}	18.997
R	0.0920
GOF	16.87
$(\Delta/\rho)_{\text{max}}$	2.601
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, $\text{e}\text{Å}^{-3}$	3.734/−6.556

dropwise at room temperature, and the reaction mixture was stirred for 25 min. After evaporation of the solvent *in vacuo*, the residue was dissolved in dichloromethane (15 mL), and a small quantity (0.2 mL) of water was added. The resulting solution was stirred at room temperature for 10 h. Evaporation of the solvent *in vacuo* and purification by preparative TLC (hexane : dichloromethane, 3 : 2) gave $\text{CpWOS}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$ (**3**, 9.6 mg, 0.0078 mmol, 54%, $R_f=0.28$) as a dark red crystalline solid: ^1H NMR (CDCl_3 , 25 °C) δ 7.12–6.97 (AB pattern, 4H), 5.77 (s, 5H), 2.41 (s, 3H); IR (C_6H_{12}) ν (CO) 2098 (m), 2061 (vs), 2038 (vs), 2027 (s), 2014 (vs), 1998 (w), 1986 (m), 1969 (w), 1944 (w) cm^{-1} ; MS (FD) m/z 1224 (M^+); Anal. Calcd for $\text{C}_{23}\text{H}_{12}\text{O}_{11}\text{WOS}_3$: C, 22.67; H, 0.97; Found: C, 22.05; H, 1.50.

Crystal Structure of **3.** A blue-green crystal of approximate dimensions $0.5 \times 0.24 \times 0.6$ mm was used for all X-ray intensity measurements on an Enraf-Nonius CAD-4 diffractometer. The lattice parameters were determined by a least-squares fit to 25 automatically centered reflections in the range $11.45^\circ < \theta < 12.65^\circ$. Three standard reflections were measured every 180 minutes of X-ray exposure and showed maximum variation of 3.29%. One orientation reflection was monitored every 200 reflections. 3845 independent reflections with $0 < h < 30$, $0 < k < 10$, $-10 < l < 10$ were collected using graphite-monochromated Mo K α radiation and $\omega/2\theta$ scan mode, ω -scan angle = $(0.8 + 0.34 \tan \theta)^\circ$, $\theta_{\text{max}} = 23^\circ$. All data were converted to E_o values following correction for L-P. The absorption correction was not applied to the data. Space group $\text{P}2_1/c$ was uniquely defined from the reflection conditions, $h0l : l = 2n$, $0k0 : k = 2n$. The structure was solved by direct methods using SHELX86,⁵ and SHELX76 program⁶ was used for full-matrix least-squares refinement of the structure (use of F magnitude; x, y, z, U_{ij} for W, Os, O and fifteen C atoms; x, y, z, U_{iso} for the rest eight C atoms) with unit weight. Final reliability factor for 2911 reflections [$F_o > 3\sigma(F_o)$] was $R = 0.0920$. Crystallographic data and atomic coordinates of compound **3** are given in Tables 1 and 2, respectively.

Table 2. Final Atomic Coordinates ($\text{\AA} \times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with ESD's for **3**

atom	x	y	z	U_{eq}^b
W	3836(1)	5125(2)	7116(2)	34(1)
Os(1)	4423(1)	6956(2)	8695(2)	36(1)
Os(2)	3437(1)	7477(2)	8440(2)	33(9)
Os(3)	2999(1)	4677(2)	8102(2)	35(1)
O(11)	4737(1)	10089(5)	8517(4)	73(3)
O(12)	5376(1)	6090(5)	7755(5)	87(3)
O(13)	4713(2)	7002(7)	11787(4)	149(5)
O(21)	3714(1)	10660(4)	8659(4)	62(2)
O(22)	2428(1)	8349(4)	7383(5)	72(3)
O(23)	3332(2)	7076(6)	11466(4)	96(3)
O(31)	2165(1)	5593(5)	9594(4)	75(3)
O(32)	2669(2)	1659(4)	7413(4)	69(3)
O(33)	3672(2)	3812(5)	10730(4)	89(3)
O(34)	2530(2)	5853(5)	5356(3)	74(3)
O(1)	4232(1)	4719(3)	8506(3)	46(2)
C(11) ^c	4651(2)	8982(9)	8603(7)	74(0)
C(12) ^c	4981(2)	6349(8)	8141(8)	90(0)
C(13)	4624(3)	6994(1)	10789(7)	144(7)
C(21) ^c	3610(2)	9438(5)	8602(4)	33(0)
C(22) ^c	2826(2)	8122(5)	7811(4)	33(0)
C(23)	3382(2)	6929(6)	10327(7)	97(4)
C(31) ^c	2492(2)	5234(5)	9046(4)	35(0)
C(32) ^c	2778(2)	2788(5)	7674(4)	35(0)
C(33)	3425(2)	4067(8)	9844(8)	95(4)
C(34)	2714(2)	5537(6)	6385(5)	53(3)
C(1)	3905(1)	7153(4)	6876(4)	27(2)
C(2)	3971(2)	8213(5)	5708(4)	33(2)
C(3)	3548(2)	8813(5)	5019(4)	36(2)
C(4)	3576(2)	9522(6)	3870(5)	51(3)
C(5)	4029(2)	9854(7)	3439(5)	60(3)
C(6)	4430(2)	9264(6)	4147(4)	44(3)
C(7)	4390(2)	8492(5)	5296(5)	40(3)
C(8)	4072(2)	10783(6)	2162(5)	68(4)
C(41) ^c	3925(2)	2909(5)	6040(5)	34(0)
C(42)	3536(4)	3381(7)	5311(5)	105(6)
C(43) ^c	3706(2)	4469(5)	4724(4)	34(0)
C(44)	4234(2)	4756(8)	5216(8)	88(5)
C(45)	4336(2)	3591(7)	5936(5)	80(4)

^aThe atomic temperature factor was fixed. ^b $U_{eq} = 1/3[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13} \cos\beta)]$.

Results and Discussion

Initial decarbonylation of **1** with the $\text{Me}_3\text{NO}/\text{MeCN}$ reagent and subsequent reaction with H_2O at room temperature provides a μ -oxo alkylidyne complex, $\text{CpWOs}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$ (**3**) in 54% yield. The formulation for compound **3** is established by mass spectroscopic and analytical data. ^1H NMR spectrum of **3** exhibits resonances for the Cp ligand (δ 5.77) and the methyl group (δ 2.41) of the tolyl moiety.

A single crystal X-ray diffraction study of **3** confirmed its characterization as an oxo alkylidyne cluster. The crystal contains an ordered arrangement of discrete $\text{CpWOs}_3(\text{CO})_{10}(\mu\text{-O})$

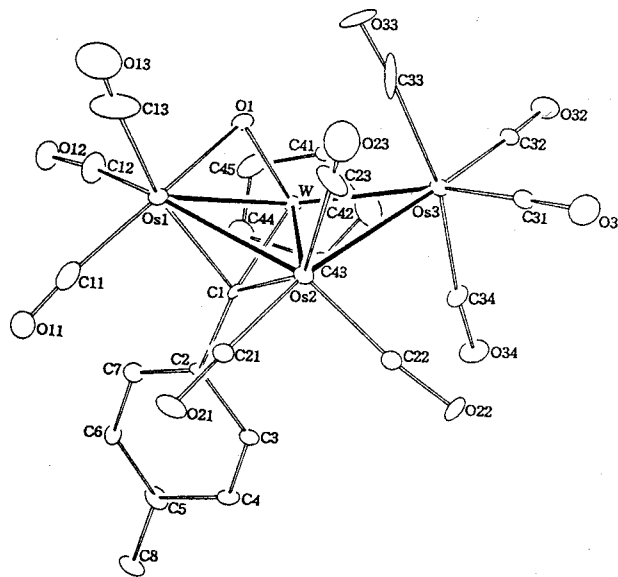


Figure 1. Molecular geometry and atomic labeling scheme for **3**.

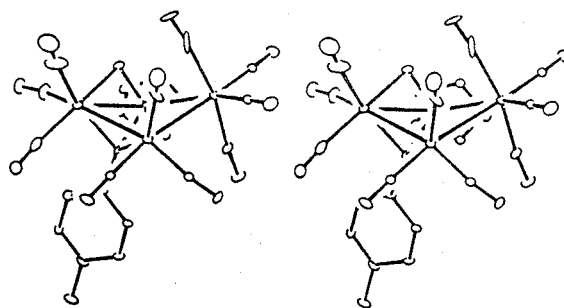


Figure 2. Stereoscopic view of **3**.

($\mu_3\text{-CTol}$) molecules, which are mutually separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. The overall molecular geometry and atomic labelling scheme and stereoview of **3** are illustrated in Figures 1 and 2, respectively. Interatomic distances and angles are listed in Tables 3 and 4.

Complex **3** adopts a "butterfly" arrangement of four metal atoms with a dihedral angle of $142.7(1)^\circ$ between W-Os(1)-Os(2) and W-Os(2)-Os(3) planes. This is the usual arrangement for a species associated with 62 valence electrons.⁷ The osmium-osmium distances are $\text{Os(1)-Os(2)} = 2.813(3) \text{ \AA}$ and $\text{Os(2)-Os(3)} = 2.899(3) \text{ \AA}$ as compared to the average Os-Os bond distance of $2.877(3) \text{ \AA}$ in the triangular cluster $\text{Os}_3(\text{CO})_{12}$.⁸ The individual osmium-tungsten distances vary over a rather larger range, $\text{W-Os(3)} = 2.698(3)$, $\text{W-Os(1)} = 2.750(3)$ and $\text{W-Os(2)} = 2.866(3) \text{ \AA}$. The formal electron counts at the individual metal atoms are non-uniform, formally 17e- at W, 19e- at Os(1), 18e- at Os(2), and 18e- at Os(3). It seems probable that the differences in metal-metal distances are related, in part, to these variations.

The μ -oxo ligand, defined as O(1), spans the W-Os(1) edge such that $\text{W-O(1)} = 1.72(3)$, $\text{Os(1)-O(1)} = 2.16(3) \text{ \AA}$ and $\angle \text{W-O(1)-Os(1)} = 89(1)^\circ$. If we define unbridged metal-metal bonds in the cluster as normal single bonds, we can calculate an

Table 3. Interatomic Distances (Å) and Esd's for 3

(A) Metal-Metal Distances					
W-Os(1)	2.750(3)	Os(1)-Os(2)	2.813(3)		
W-Os(2)	2.866(3)	Os(2)-Os(3)	2.899(3)		
W-Os(3)	2.698(3)				
(B) Metal-Alkylidyne Distances					
W-C(1)	1.93(4)	Os(1)-C(1)	2.20(4)	Os(2)-C(1)	2.18(4)
(C) Metal-Oxygen Distances					
W-O(1)	1.72(3)	Os(1)-O(1)	2.16(3)		
(D) Distances within the μ_3 -CTol Ligand					
C(1)-C(2)	1.56(5)	C(2)-C(3)	1.42(6)		
C(2)-C(7)	1.32(6)	C(3)-C(4)	1.34(6)		
C(4)-C(5)	1.43(7)	C(5)-C(6)	1.38(7)		
C(5)-C(8)	1.56(6)	C(6)-C(7)	1.37(6)		
(E) Metal-Carbon (Carbonyl) Distances					
Os(1)-C(11)	2.01(8)	Os(2)-C(21)	1.90(5)		
Os(1)-C(12)	1.82(6)	Os(2)-C(22)	1.87(4)		
Os(1)-C(13)	2.11(7)	Os(2)-C(23)	1.98(6)		
Os(3)-C(31)	1.88(4)	Os(3)-C(32)	1.91(5)		
Os(3)-C(33)	2.08(8)	Os(3)-C(34)	1.98(5)		
(F) Carbon-Oxygen (Carbonyl) Distances					
C(11)-O(11)	1.07(8)	C(12)-O(12)	1.25(7)		
C(13)-O(13)	0.99(7)	C(21)-O(21)	1.18(5)		
C(22)-O(22)	1.18(5)	C(23)-O(23)	1.17(7)		
C(31)-O(31)	1.18(5)	C(32)-O(32)	1.12(6)		
C(33)-O(33)	1.09(7)	C(34)-O(34)	1.14(5)		
(G) Distances involving the Cp Ligand					
W-C(41)	2.36(4)	C(41)-C(42)	1.30(1)		
W-C(42)	2.51(6)	C(41)-C(45)	1.34(8)		
W-C(43)	2.45(4)	C(42)-C(43)	1.30(7)		
W-C(44)	2.34(6)	C(43)-C(44)	1.54(8)		
W-C(45)	2.42(6)	C(44)-C(45)	1.32(9)		

approximate covalent radius of ~ 1.449 Å for the osmium atom from $1/2[d(\text{Os}(2)-\text{Os}(3))]$ and ~ 1.249 Å for the tungsten atom from $d[\text{W}-\text{Os}(3)] - r[\text{Os} = 1.449 \text{ Å}]$. The W-O(1) bond length of 1.72(3) Å is slightly longer than well-defined tungsten-oxygen double bonds in such discrete mononuclear species as $\text{W}(=\text{O})(=\text{CHCMe}_3)(\text{PEt}_3)\text{Cl}_2$ [W=O, 1.661(11) Å]⁹ and $\text{W}(=\text{O})(=\text{CHCMe}_3)(\text{PMe}_3)_2\text{Cl}_2$ [W=O, 1.697(15) Å].¹⁰ It is substantially shorter than the predicted W-O single bond length of ~ 1.91 Å [from $r(\text{W}) 1.25$ Å and $r(\text{O}) 0.66$ Å].¹¹ It compares with typical W-O single bonds as found in $\text{W}(\text{C}_2\text{Et}_3)[\text{OCH}(\text{CF}_3)_2]_3$ [W-O, 1.932(10)–1.982(11) Å],¹² $\text{W}(\text{C}_2\text{Et}_3)[\text{O}-2,6-\text{C}_6\text{H}_3(i-\text{Pr})_2]_3$ [W-O, 1.885(6)–2.008(6) Å],¹³ $\text{W}[\text{C}(t-\text{Bu})\text{CHC}(t-\text{Bu})][\text{OCH}(\text{CF}_3)_2]_3$ [W-O, 1.954(7)–1.959(7) Å],¹⁴ $[\text{NH}_4]_5[\text{W}_3\text{O}_4\text{F}_6]$ [W-O-W, 1.91–1.99(2) Å]¹⁵ and $[\text{Me}_4\text{N}]_3[\text{W}(\text{CO})_3(\text{OEt})_3]$ [W-O-W, 2.11–2.14 Å].¹⁶ All indications are that the W-O(1) linkage is a formal double bond. The Os(1)-O(1) distance of 2.16(3) Å is slightly longer than expected for a single bond [$r(\text{Os}) + r(\text{O}) = 2.11$ Å] and is regarded as a "coordinate-covalent" or donor bond, *i.e.*, $\text{O} : \rightarrow \text{Os}$. The μ -oxo ligand is thus a 4-electron donor (neutral atom counting scheme). The W(μ -O)Os system is best depicted as $\text{W}=\text{O} : \rightarrow \text{Os}$. Other examples of the edge-bridging $\text{W}=\text{O} : \rightarrow \text{Os}$ system have been found previously in μ -oxo tungsten complexes [W=O(av), 1.79 Å and Os-O(av), 2.16

Table 4. Interatomic Angles (deg) and Esd's for 3

(A) Intermetallic Angles			
Os(1)-W-Os(2)	60.1(1)	W-Os(1)-Os(2)	62.0(1)
Os(2)-W-Os(3)	62.7(1)	W-Os(2)-Os(3)	55.8(1)
Os(1)-W-Os(3)	112.6(1)	W-Os(3)-Os(2)	61.5(1)
Os(1)-Os(2)-Os(3)	105.0(1)	W-Os(2)-Os(1)	57.9(1)
(B) M-M-CO Angles			
W-Os(1)-C(11)	138(2)	Os(1)-Os(2)-C(21)	85(1)
W-Os(1)-C(12)	97(2)	Os(1)-Os(2)-C(22)	163(1)
W-Os(1)-C(13)	132(3)	Os(1)-Os(2)-C(23)	93(2)
W-Os(2)-C(21)	132(1)	Os(2)-Os(1)-C(11)	99(2)
W-Os(2)-C(22)	119(1)	Os(2)-Os(1)-C(12)	156(2)
W-Os(2)-C(23)	109(2)	Os(2)-Os(1)-C(13)	105(3)
W-Os(3)-C(31)	153(1)	Os(3)-Os(2)-C(21)	170(1)
W-Os(3)-C(32)	110(1)	Os(3)-Os(2)-C(22)	84(1)
W-Os(3)-C(33)	84(2)	Os(3)-Os(2)-C(23)	78(2)
W-Os(3)-C(34)	85(1)	Os(2)-Os(3)-C(31)	92(1)
Os(2)-Os(3)-C(33)	87(2)	Os(2)-Os(3)-C(32)	171(1)
Os(2)-Os(3)-C(34)	82(2)		
(C) OC-Os-CO Angles			
C(11)-Os(1)-C(12)	89(3)	C(11)-Os(1)-C(13)	88(3)
C(12)-Os(1)-C(13)	98(4)	C(21)-Os(2)-C(22)	86(2)
C(21)-Os(2)-C(23)	103(2)	C(22)-Os(2)-C(23)	103(2)
C(31)-Os(3)-C(32)	97(2)	C(31)-Os(3)-C(33)	93(2)
C(31)-Os(3)-C(34)	94(2)	C(32)-Os(3)-C(34)	95(2)
C(33)-Os(3)-C(34)	167(2)	C(32)-Os(3)-C(33)	94(2)
(D) Os-C-O Angles			
Os(1)-C(11)-O(11)	175(5)	Os(2)-C(21)-O(21)	178(4)
Os(1)-C(12)-O(12)	173(7)	Os(2)-C(22)-O(22)	172(4)
Os(1)-C(13)-O(13)	176(0)	Os(2)-C(23)-O(23)	158(6)
Os(3)-C(31)-O(31)	178(4)	Os(3)-C(32)-O(32)	177(5)
Os(3)-C(33)-O(33)	175(6)	Os(3)-C(34)-O(34)	171(5)
(E) Angles within the μ_3 -CTol Ligand			
C(1)-C(2)-C(3)	117(3)	C(2)-C(3)-C(4)	119(4)
C(3)-C(4)-C(5)	121(5)	C(4)-C(5)-C(6)	118(4)
C(2)-C(7)-C(6)	122(5)	C(1)-C(2)-C(7)	123(4)
C(3)-C(2)-C(7)	120(4)	C(5)-C(6)-C(7)	120(5)
C(4)-C(5)-C(8)	122(5)	C(6)-C(5)-C(8)	120(5)
(F) Angles involving O(1) or C(1)			
Os(1)-W-O(1)	52(1)	Os(2)-W-O(1)	93(1)
Os(1)-W-C(1)	53(1)	Os(2)-W-C(1)	50(1)
O(1)-W-C(1)	105(2)	Os(3)-W-O(1)	101(1)
Os(3)-W-C(1)	108(1)	W-Os(1)-O(1)	39(8)
Os(2)-Os(1)-O(1)	86(8)	W-Os(1)-C(1)	44(1)
Os(2)-Os(1)-C(1)	50(1)	O(1)-Os(1)-C(1)	83(1)
W-Os(2)-C(1)	42(1)	Os(1)-Os(2)-C(1)	50(1)
Os(3)-Os(2)-C(1)	94(1)	W-O(1)-Os(1)	89(1)
W-C(1)-Os(2)	88(2)	W-C(1)-Os(1)	83(1)
(G) Angles within the Cp Ligand			
C(41)-C(42)-C(43)	101(8)	C(42)-C(43)-C(44)	113(6)
C(41)-C(45)-C(44)	108(6)	C(42)-C(41)-C(45)	118(5)
C(43)-C(44)-C(45)	100(6)		

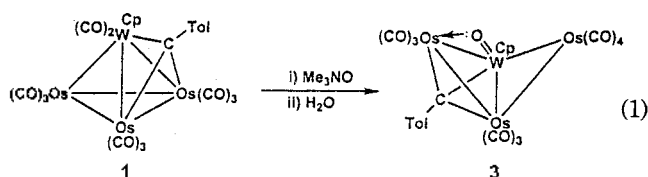
Å] such as $\text{CpWOS}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$,¹⁷ $\text{CpWOS}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$,¹⁸ $\text{Cp}^*\text{WOS}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_3)$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$),¹⁹ $\text{CpWOS}_3(\text{CO})_8(\mu\text{-O})(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)(\mu\text{-H})$,²⁰ *anti*- CpWOS_3

(CO)₉(μ-O)(μ-CHCH₂Tol)(μ-H),²¹ syn-CpWOS₃(CO)₉(μ-O)(μ-CHTol)(μ-H),^{4b} and CpWOS₃(CO)₉(μ-O)(μ-C=CHTol)(μ-H).²²

The μ₃-alkylidyne ligand caps the outer face of the W-Os (1)-Os(2) "wing" triangle, with individual metal-carbon distances W-C(1)=1.93(4), Os(1)-C(1)=2.20(4) and Os(2)-C(1)=2.18(4) Å. The pattern of W-(μ₃-C) bond lengths being shorter than Os-(μ₃-C) bond lengths has also been observed in CpWOS₃(CO)₉(μ₃-CTol)₂H²³ [W-C=1.98(2)~2.01(2) Å and Os-C=2.14(2)~2.25(2) Å] and CpWOS₃(CO)₁₀(μ₃-CTol)₂(μ-H)²⁴ [W-C=2.01(1) Å and Os-C=2.19(2)~2.27(2) Å]; this presumably occurs to compensate for the electron-poor nature of tungsten in all these species.

All other structural features of complex 3 are within the expected range. Individual Os-CO range from 1.82(6) through 2.11(7) Å, C-O bond lengths range from 0.99(7) through 1.25(7) Å and Os-C-O angles are in the range 158(6)~178(4)°. Tungsten-Carbon(Cp) distances are between 2.34(6) and 2.51(6) Å. Distances within the CTol ligand are in the expected range with C(1)-C(2)=1.56(5) and C(5)-C(8)=1.56(6) Å, [ideal C(sp²)-C(sp²)=1.51 Å] and C-C(aromatic)=1.32(6)~1.43(7) Å [ideal C(sp²)-C(sp²)=1.39 Å]. The structure of 3 is essentially identical to that of its homologue (3+CH₂), CpWOS₃(CO)₁₀(μ-O)(μ₃-CCH₂Tol) (4),¹⁸ which was structurally characterized. The μ-oxo ligand in 4, however, is originated from the thermal acyl C-O bond scission of CpWOS₃(CO)₁₁[μ₃-η²-C(O)CH₂Tol].

The reaction of 1 with H₂O produces an oxo alkylidyne "butterfly" complex 3 as shown in eq. 1. This reaction un-



ambiguously proves that the μ-oxo ligand of 3 comes from water in the solvent. Complex 3 can be converted to compound 2 by thermolysis and reaction with dihydrogen.²⁵ A likely pathway for the formation of 3 may be loss of a carbonyl ligand from 1 followed by formation of "butterfly" hydrido hydroxo complex CpWOS₃(CO)₁₀(μ-OH)(μ-H)(μ₃-CTol) by O-H bond activation of water, further O-H bond activation to form an oxo dihydrido species, and subsequent loss of H₂. A facile conversion of hydroxo complex Re(OH)(C₂Et)₂ to oxo hydride complex Re(O)(H)(C₂Et)₂ has been appeared in the literature.²⁶ It has been reported that the μ-oxo ligands in CpWOS₃(CO)₉(μ-O)₂(μ-H) clearly have not been originated from Me₃NO used for decarbonylation and have not been formed in a carefully dried solvent.²⁷ Similarly, the oxo complexes CpWOS₃(CO)₈(μ-O)(μ₃-η²-C₂R₂)(μ-H) (R=H, Ph, Tol) were also reported to be produced by initial decarbonylation of the alkyne complexes CpWOS₃(CO)₁₀(μ-O)(μ₃-η²-C₂R₂)(μ-H) with Me₃NO/MeCN followed by thermolysis at 110 °C.²⁸ The μ-oxo ligand in these alkyne complexes seems to be derived also from water in the reaction solvent based on our observation.

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