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Synthesis and Crystal Structure of CpWOs₃ (CO)₁₀(μ-O)(μ₃-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 $Os_4(CO)_{12}$ $(\mu_3-O)_4$[2] was the first oxo carbonyl cluster to be characterized, but the first monomeric oxo carbonyl complex with a terminal oxo group was $WCl_2(PMePh_2)_2(CO)(O)$.[3] In previous work, we have reported the synthesis and solution dynamics of a tungsten-triosmium p-xylylidyne complex, $CpWOs_3(CO)_{11}$ (μ_3-CTol) (**1**, $Cp=\eta^5-C_5H_5$, $Tol=p-C_6H_4Me$),[4a] and the reactivity of **1** toward dihydrogen leading to formation of an unexpected hydrido-oxo-alkylidene complex, $CpWOs_3(CO)_9(\mu-O)(\mu-CHTol)(\mu-H)$ (**2**).[4b] 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, $CpWOs_3(CO)_{10}(\mu-O)(\mu_3-CTol)$ (**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. $CpWOs_3(CO)_{11}(\mu_3-CTol)$ was prepared as described in the literature.[4a] 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 ¹⁸⁴W and ¹⁹²Os. Microanalytical data were provided by the Daeduk R & D Center of Daelim Industrial Co., Ltd.

Reaction of 1 with H₂O. 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	$C_{23}H_{12}O_{11}WOs_3$
fw	1218.79
cryst syst	monoclinic
space group	$P2_1/a$
a, Å	28.263(7)
b, Å	9.358(6)
c, Å	9.986(1)
β, deg	96.75(2)
V, Å³	2622.86(5)
Z	4
ρ(calcd), gcm⁻³	3.09
temp. K	297
λ (Mo Kα), Å	0.71069
μ, mm⁻¹	18.997
R	0.0920
GOF	16.87
$(\Delta/\rho)_{max}$	2.601
$\Delta\rho_{max}/\Delta\rho_{min}$, eÅ⁻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 $CpWOs_3(CO)_{10}(\mu-O)(\mu_3-CTol)$ (**3**, 9.6 mg, 0.0078 mmol, 54%, $R_f=0.28$) as a dark red crystalline solid: ¹H NMR ($CDCl_3$, 25 ℃) 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 $C_{23}H_{12}O_{11}WOs_3$: C, 22.67; H, 0.97; Found: C, 22.05; H, 1.50.

Crystal Structure of 3. A blue-green crystal of approximate dimensions 0.5×0.24×0.6 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 $11.45°<\theta<12.65°$. 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 Kα radiation and ω/2θ scan mode, ω-scan angle$=(0.8+0.34\tan\theta)°$, $\theta_{max}=23°$. All data were converted to E_o values following correction for L-P. The absorption correction was not applied to the data. Space group $P2_1/c$ 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 program[6] 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 $[F_0>3\sigma(F_0)]$ was $R=0.0920$. Crystallographic data and atomic coordinates of compound **3** are given in Tables 1 and 2, respectively.

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Table 2. Final Atomic Coordinates ($\mathring{A} \times 10^4$) and Equivalent Isotropic Thermal Parameters ($\mathring{A} \times 10^3$) 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)^a	4651(2)	8982(9)	8603(7)	74(0)
C(12)^a	4981(2)	6349(8)	8141(8)	90(0)
C(13)	4624(3)	6994(1)	10789(7)	144(7)
C(21)^a	3610(2)	9438(5)	8602(4)	33(0)
C(22)^a	2826(2)	8122(5)	7811(4)	33(0)
C(23)	3382(2)	6929(6)	10327(7)	97(4)
C(31)^a	2492(2)	5234(5)	9046(4)	35(0)
C(32)^a	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)^a	3925(2)	2909(5)	6040(5)	34(0)
C(42)	3536(4)	3381(7)	5311(5)	105(6)
C(43)^a	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)

^{a} The 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 $Me_3NO/MeCN$ reagent and subsequent reaction with H_2O at room temperature provides a μ-oxo alkylidyne complex, $CpWOs_3(CO)_{10}(μ-O)(μ_3-CTol)$ (**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 $CpWOs_3(CO)_{10}(μ-O)$
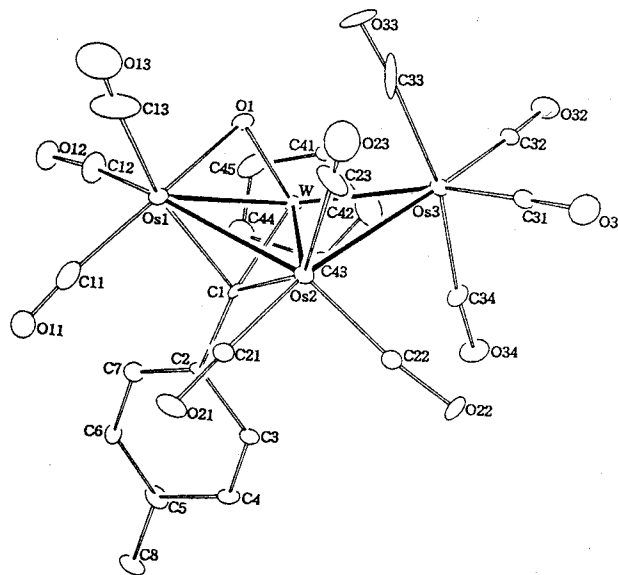
Figure 1. Molecular geometry and atomic labeling scheme for **3**.
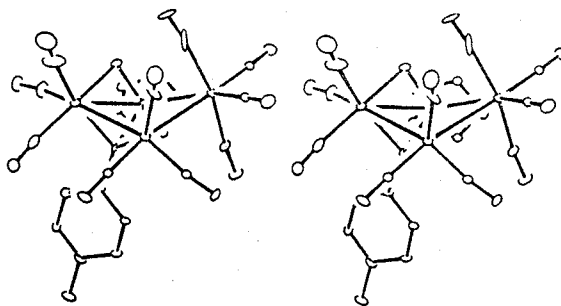
Figure 2. Stereoscopic view of **3**.

(μ₃-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)° 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 Os(1)-Os(2) = 2.813(3) $\mathring{A}$ and Os(2)-Os(3) = 2.899(3) $\mathring{A}$ as compared to the average Os-Os bond distance of 2.877(3) $\mathring{A}$ in the triangular cluster Os_3 $(CO)_{12}$.[8] The individual osmium-tungsten distances vary over a rather larger range, W-Os(3) = 2.698(3), W-Os(1) = 2.750(3) and W-Os(2) = 2.866(3) $\mathring{A}$. 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 W-O(1) = 1.72(3), Os(1)-O(1) = 2.16(3) $\mathring{A}$ and ∠W-O (1)-Os(1) = 89(1)°. If we define unbridged metal-metal bonds in the cluster as normal single bonds, we can calculate an

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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)

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)		

approximate covalent radius of ~1.449 Å for the osmium atom from $1/2[d(Os(2)\text{-}Os(3))]$ and ~1.249 Å for the tungsten atom from $d[W\text{-}Os(3)=2.698\text{ Å}]-r[Os=1.449\text{ Å}]$. 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 $W(=O)(=CHCMe_3)(PEt_3)Cl_2$ [W=O, 1.661(11) Å][9] and $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$ [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(W) 1.25 Å and r(O) 0.66 Å].[11] It compares with typical W-O single bonds as found in $W(C_3Et_3)[OCH(CF_3)_2]_3$ [W-O, 1.932(10)~1.982(11) Å],[12] $W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ [W-O, 1.885(6)~2.008(6) Å],[13] $W[C(t\text{-}Bu)CHC(t\text{-}Bu)][OCH(CF_3)_2]_3$ [W-O, 1.954(7)~1.959(7) Å],[14] $[NH_4]_5[W_3O_4F_9]$ [W-O-W, 1.91-1.99(2) Å][15] and $[Me_4N]_2[W(CO)_3(OEt)]_3$ [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(Os)+r(O)=2.11 Å] and is regarded 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 W=O : →Os. Other examples of the edge-bridging W=O : →Os system have been found previously in μ-oxo tungsten complexes [W=O(av), 1.79 Å and Os-O(av), 2.16

Å] such as $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$,[17] $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$,[18] $Cp^*WOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_3)$ $(Cp^*=\eta^5\text{-}C_5Me_5)$,[19] $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$,[20] *anti*-CpWOs$_3$

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$(CO)_9(\mu-O)(\mu-CHCH_2Tol)(\mu-H)$,[21] syn-$CpWOs_3(CO)_9(\mu-O)(\mu-CHTol)(\mu-H)$,[4b] and $CpWOs_3(CO)_9(\mu-O)(\mu-C=CHTol)(\mu-H)$.[22]

The μ_3-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-(μ_3-C) bond lengths being shorter than Os-(μ_3-C) bond lengths has also been observed in CpWOs$_3$(CO)$_9$(μ_3-CTol)$_2$H[23] [W-C=1.98(2)~2.01(2) Å and Os-C =2.14(2)~2.25(2) Å] and CpWOs$_3$(CO)$_{10}$(μ_3-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(sp^2)-C(sp^3)=1.51 Å] and C-C(aromatic)=1.32(6)~1.43(7) Å [ideal C(sp^2)-C(sp^2)=1.39 Å]. The structure of **3** is essentially identical to that of its homologue (**3**+CH$_2$), CpWOs$_3$(CO)$_{10}$(μ-O)(μ_3-CCH$_2$Tol) (**4**),[18] which was structurally characterized. The μ-oxo ligand in **4**, however, is originated from the thermal acyl C-O bond scission of CpWOs$_3$(CO)$_{11}$[μ_3-η^2-C(O)CH$_2$Tol].

The reaction of **1** with H$_2$O produces an oxo alkylidyne "butterfly" complex **3** as shown in eq. 1. This reaction un-

(1)
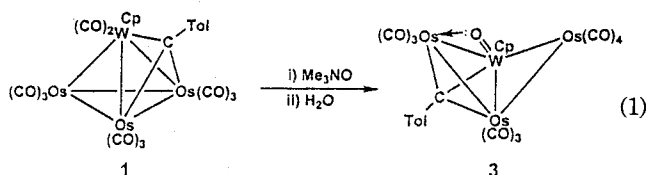
ambiguously proves that the μ-oxo ligand of **3** comes from water in the solvent. Complex **3** can be converted to compound **2** by thermolysis and reaction with dihydrogen.[25] A likely pathway for the formation of **3** may be loss of a carbonyl ligand from **1** followed by formation of "butterfly" hydrido hydroxo complex CpWOs$_3$(CO)$_{10}$(μ-OH)(μ-H)(μ_3-CTol) by O-H bond activation of water, further O-H bond activation to form an oxo dihydrido species, and subsequent loss of H$_2$. A facile conversion of hydroxo complex Re(OH)(C$_2$Et$_2$)$_3$ to oxo hydride complex Re(O)(H)(C$_2$Et$_2$)$_2$ has been appeared in the literature.[26] It has been reported that the μ-oxo ligands in CpWOs$_3$(CO)$_9$(μ-O)$_2$(μ-H) clearly have not been originated from Me$_3$NO used for decarbonylation and have not been formed in a carefully dried solvent.[27] Similarly, the oxo complexes CpWOs$_3$(CO)$_8$(μ-O)(μ_3-η^2-C$_2$R$_2$)(μ-H) (R=H, Ph, Tol) were also reported to be produced by initial decarbonylation of the alkyne complexes CpWOs$_3$(CO)$_{10}$(μ-O)(μ_3-η^2-C$_2$R$_2$)(μ-H) with Me$_3$NO/MeCN followed by thermolysis at 110 ℃.[28] The μ-oxo ligand in these alkyne complexes seems to be derived also from water in the reaction solvent based on our observation.

Supplementary Material Available. Details of the crystallographic study of **3** are available from the authors (I.-H. S.).

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