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Reaction of $CpWOs_3(CO)_{11}(\mu_3\text{-CTol})$ with H_2S: μ-alkylidene and μ_3-alkylidyne WOs_3 cluster complexes containing a sulfido ligand

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Abstract

Initial decarbonylation of $CpWOs_3(CO)_{11}(\mu_3\text{-CTol})$ (**1**; $Cp = \eta^5\text{-}C_5H_5$, $Tol = p\text{-}C_6H_4Me$) with $Me_3NO/MeCN$ followed by a reaction with H_2S produces a sulfido–alkylidyne complex as a major product, $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})(\mu_3\text{-S})$ (**2**, 48%), and two hydrido–sulfido–alkylidene complexes as minor products, $CpWOs_3(CO)_{10}(\mu\text{-CHTol})(\mu_3\text{-S})(\mu\text{-H})$ (**3**, 12%) and $CpWOs_3(CO)_9(\mu\text{-CHTol})(\mu\text{-S})(\mu\text{-H})$ (**4**, 14%) by S–H bond activations of H_2S. Decarbonylation of **3** with Me_3NO/CH_2Cl_2 affords complex **4** in 67% yield. Compounds **2**, **3** and **4** have been isolated as crystalline solids and have been characterized by spectroscopic (IR, MS, ^1H and ^{13}C-NMR) and analytical data. The structures of **2**, **3** and **4** have been determined by single-crystal X-ray diffraction studies. Complexes **2** and **3** are based upon a 'butterfly' WOs_3 metal core of a 62 valence electron (VE) with a respective dihedral angle of 100.60(7) and 83.82(8)° between the W–Os(3)–Os(1) and W–Os(3)–Os(2) planes. Each molecule consists of three $Os(CO)_3$ units, a CpW(CO) fragment and a triply bridging sulfido ligand across the open Os(1)–W–Os(2) triangular face. The μ_3-alkylidyne in **2** caps unsymmetrically the outer face of the W–Os(1)–Os(3) 'wing' triangle. For **3**, the μ-alkylidene ligand bridges the 'hinge' W–Os(3) bond and the μ-hydride ligand is supposed to span the W–Os(1) linkage. Complex **4** contains a tetrahedral WOs_3 core associated with a 60 VE. The μ-sulfido and μ-alkylidene ligands bridge the W–Os(2) and W–Os(1) edges, respectively. The μ-sulfido ligand is involved in a $W{=}S{:}\rightarrow Os$ bridge ($W–S = 2.21(2)$ and $Os(2)–S = 2.47(2)$ Å). The μ-hydride ligand is believed to span the elongated Os(2)–Os(3) edge. The tolyl substituent on the alkylidene C is oriented away from the μ-sulfido ligand.

Keywords: Tungsten–triosmium; Metal clusters; Sulfido ligand; Alkylidene; Alkylidyne; X-ray structure

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1. Introduction

There has been considerable current interest in studies of transition metal sulfide complexes due to their relevance to models for metalloproteins in enzymatic catalysis and metal sulfide hydrodesulfurization in homogeneous and heterogeneous catalysis [1]. The transition metal sulfido complexes exhibit a wide variety of an interesting and novel structural chemistry, which stems from the numerous coordination possibilities of the sulfur atom. The μ-sulfido ligand with a lone pair of electrons is known to promote metal cluster formation and thus the μ-sulfido complexes do not undergo easy cluster degradation during further reactions. Adams and coworkers have recently demonstrated the importance of sulfide ligands to form higher nuclearity products either by condensation reactions [2] or by the addition of lightly stabilized clusters [3]. The μ-sulfido clusters can generally be prepared from several sources of sulfide such as elemental sulfur (S_8), hydrogen sulfide (H_2S), carbon disufide (CS_2), or the desulfurization of various organosulfur ligands [4]. Curtis et al. have shown that 'butterfiy' $Cp'_2Mo_2Co_2(\mu_3\text{-S})_2(\mu_4\text{-S})(CO)_4$ ($Cp' = C_5H_4Me$) cluster mediates S atom abstraction from various organosulfur compounds with the concomitant formation of the cubane type cluster

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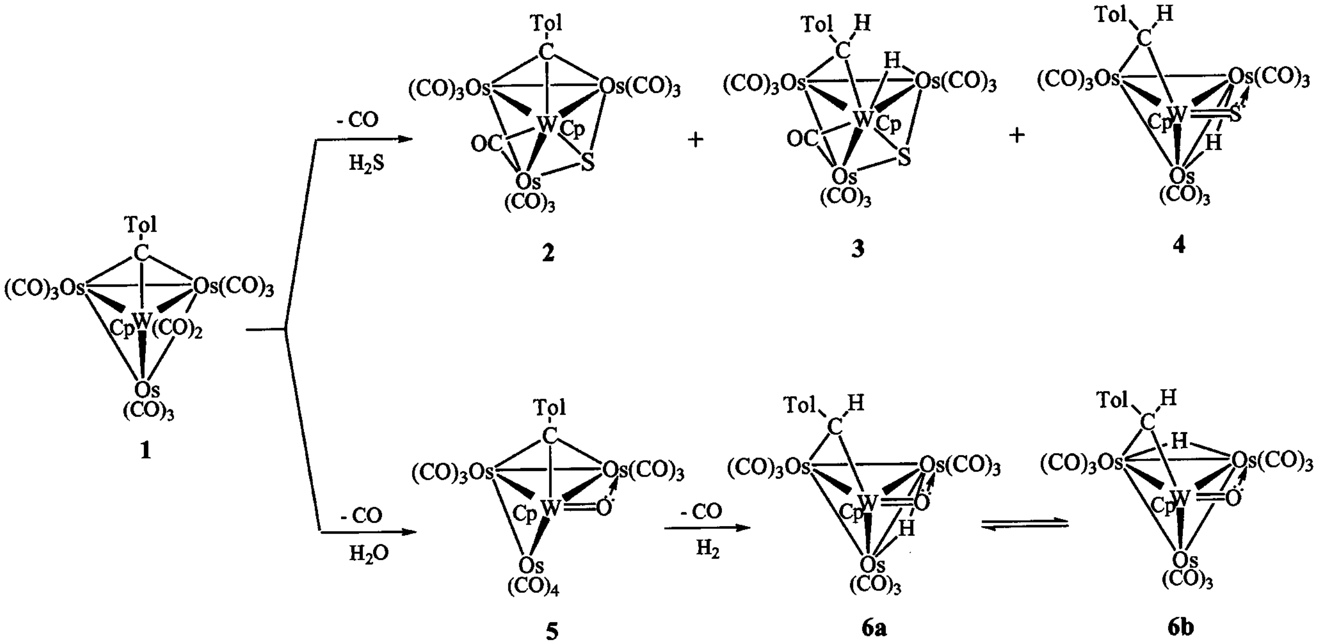

Scheme 1. Reaction scheme for $CpWOs_3(CO)_{11}(\mu_3\text{-CTol})$ (**1**).

$Cp'_2Mo_2Co_2(\mu_4\text{-}S)_4(CO)_2$ and the desulfurized organic hydrocarbon [5].

In previous work, we have reported the synthesis and solution dynamics of a tungsten–triosmium *p*-xylylidyne complex, $CpWOs_3(CO)_{11}(\mu_3\text{-CTol})$ (**1**) [6] and studies on the reactivity of **1** towards H_2O have resulted in the isolation of several μ-oxo complexes, where the μ-oxo ligands were originated from water by O–H bond activations (see Scheme 1) [7]. As a part of this study we have examined the reaction chemistry between complex **1** and H_2S. The reaction of **1** with H_2S under mild conditions affords a sulfido–alkylidyne complex as a major product, $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})(\mu_3\text{-S})$ (**2**) and two hydrido–sulfido–alkylidene complexes as minor products, $CpWOs_3(CO)_{10}(\mu\text{-CHTol})(\mu_3\text{-S})(\mu\text{-H})$ (**3**) and $CpWOs_3(CO)_9(\mu\text{-CHTol})(\mu\text{-S})(\mu\text{-H})$ (**4**), by S–H bond activations of H_2S. Complex **3** is converted to **4** by loss of a carbonyl (C=O) ligand. We herein report full details of synthesis and characterization of **2–4** together with structural studies of two 'butterfly' complexes **2** and **3** and a tetrahedral complex **4**.

2. Results and discussion

2.1. Synthesis and characterization of 2, 3 and 4

Initial decarbonylation of **1** with Me_3NO/CH_3CN and subsequent reaction with H_2S gas under mild conditions affords a μ_3-sulfido–alkylidyne complex, $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})(\mu_3\text{-S})$ (**2**) in 48% yield, and two hydrido–sulfido–alkylidene complexes, $CpWOs_3(CO)_{10}(\mu\text{-CHTol})(\mu_3\text{-S})(\mu\text{-H})$ (**3**) and $CpWOs_3(CO)_9(\mu\text{-CHTol})(\mu\text{-S})(\mu\text{-H})$ (**4**) in 12 and 14% yields, respectively (see Scheme 1). Treatment of **3** with Me_3NO/CH_2Cl_2 at room temperature (r.t.) produces complex **4** (67%) by loss of a C=O ligand. The formulations of complexes **2–4** have been established by spectroscopic and analytical data.

The ^{1}H-NMR spectrum of **2** exhibits resonances only for the Cp ligand at δ 5.63 and for the methyl group of the tolyl moiety at δ 2.44, suggesting that the two H atoms of H_2S were eliminated by the S–H bond activations during reaction. The limiting low temperature ^{13}C-NMR spectrum of ^{13}C (*C) enriched $CpWOs_3(^*CO)_{10}(\mu_3\text{-}^*CTol)(\mu_3\text{-S})$ (**2***) at -30°C shows a μ_3-alkylidyne C resonance at δ 239.3 with ^{183}W satellites ($^1J_{CW} = 117.8$ Hz) and ten C=O resonances at δ 232.3, 184.5, 181.3, 180.7, 179.7, 177.5, 177.0, 174.2, 167.9 and 166.8 (each with an intensity of 1). The most downfield signal at δ 232.3 with $^1J_{CW} = 157.7$ Hz is assigned to the C=O group on the W atom [8]. As the temperature is raised to 23°C, one set of three C=O resonances at δ 184.5, 177.0 and 174.2 broadens fast, and another set of three at δ 180.7, 179.7, and 174.2 is beginning to broaden, while the other set at δ 181.3, 177.5, and 166.8 remains sharp. This indicates that each Os center of **2** has a different energy barrier for localized threefold exchange of C=O ligands, although the definitive assignment of each set cannot be made.

The ^{1}H-NMR spectrum of **3** in $CDCl_3$ reveals a μ-hydride resonance at δ -13.5 and a highly deshielded resonance of μ-alkylidene CH at δ 9.64. This observation implies that the two H atoms of H_2S

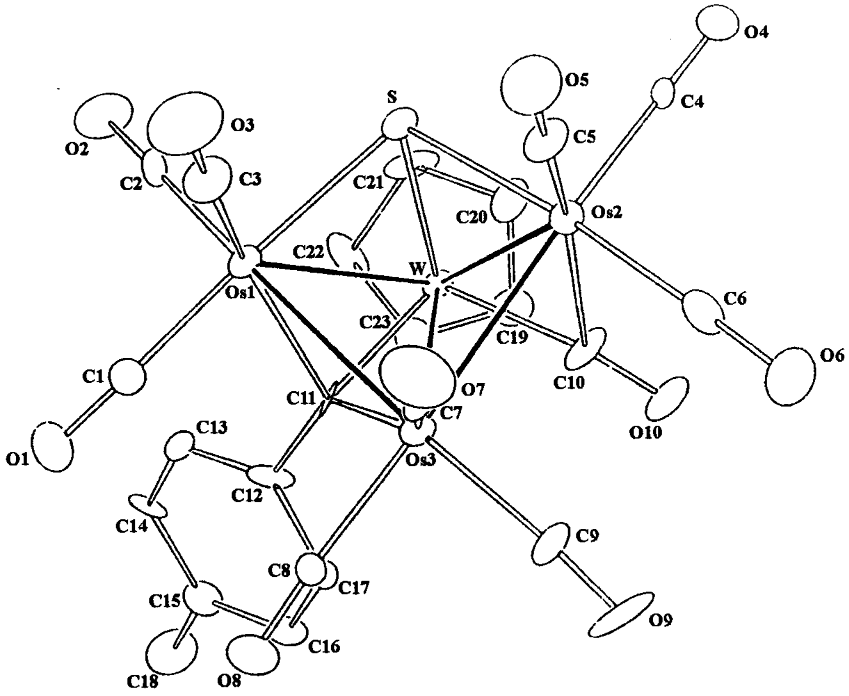

Fig. 1. Molecular geometry and atomic labeling scheme for **2**.

retained in complex **3**. A mutual coupling of $^{3}J_{HH} = 3.2$ Hz has been observed between the μ-hydride and the μ-alkylidene CH, which indicates that the two ligands in **3** bridge the adjacent metal–metal bonds. The μ-hydride resonance exhibits ^{183}W satellites ($^{1}J_{WH} = 36.9$ Hz) and thus the μ-hydride ligand is supposed to be associated with a W–Os edge. The limiting low temperature ^{13}C-NMR spectrum of ^{13}C-enriched $CpWOs_3(*CO)_{10}(\mu\text{-}*CHTol)(\mu_3\text{-}S)(\mu\text{-}H)$ (**3***) is obtained at $-20°C$ in $CDCl_3$. This spectrum shows one μ-alkyli-

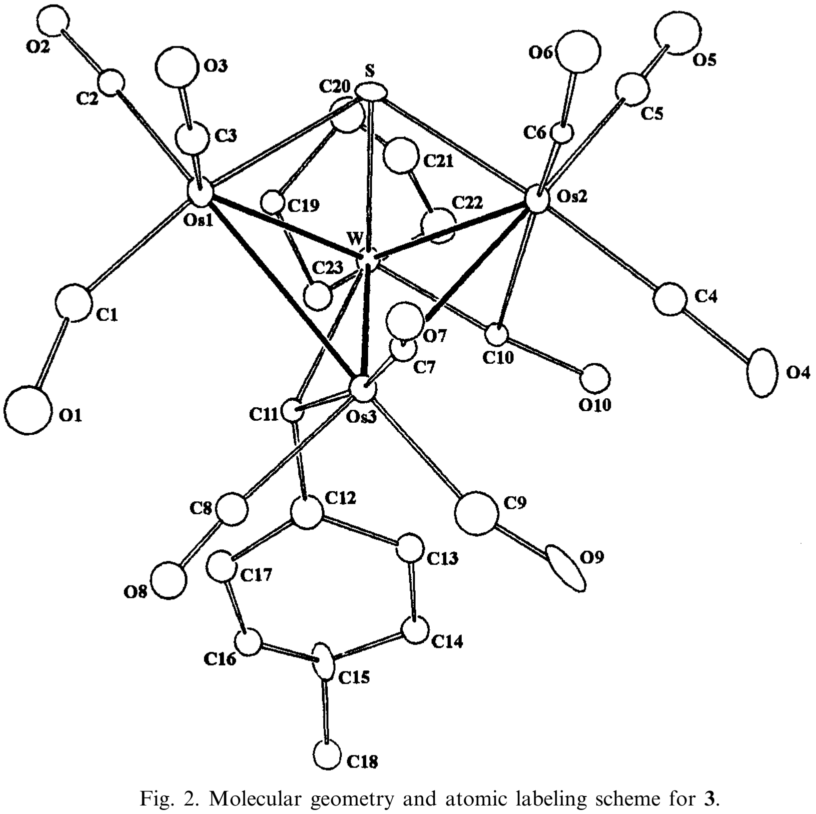

Fig. 2. Molecular geometry and atomic labeling scheme for **3**.

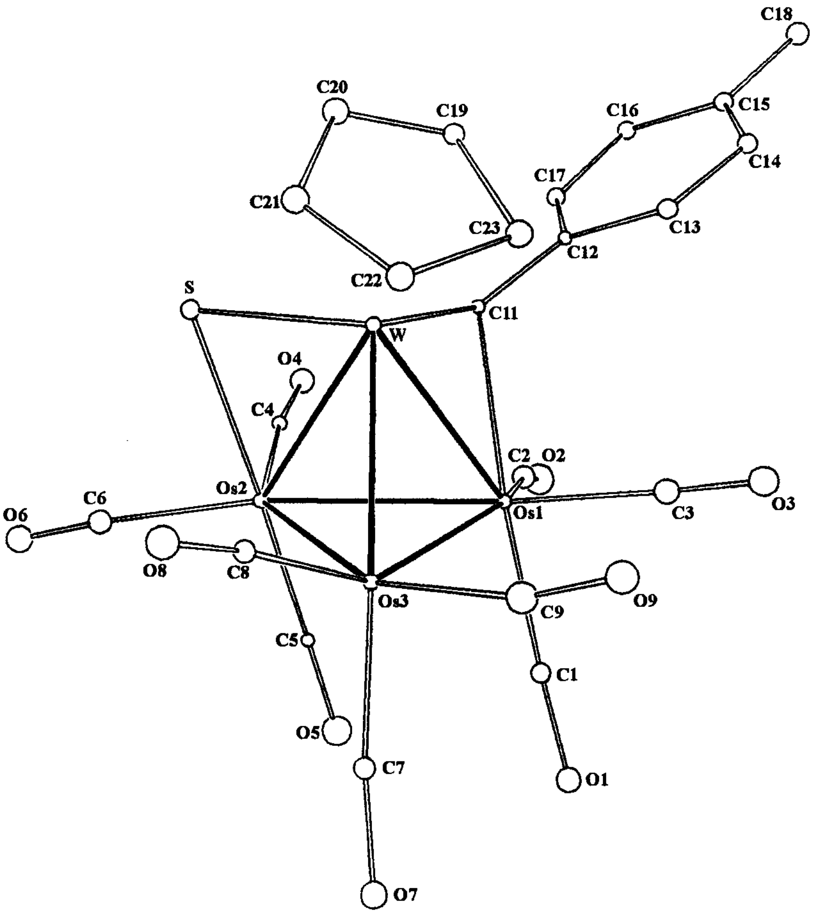

Fig. 3. Molecular geometry and atomic labeling scheme for **4**.

dene C resonance at δ 130.8 (d, $^1J_{CH} = 143.9$ Hz) [9] and ten C=O resonances at δ 225.3, 188.9, 182.4 (2CO), 180.5, 177.9, 176.0, 175.5, 173.6 and 171.1. The C=O resonance at δ 175.5 is a doublet ($^2J_{CH} = 9.8$ Hz) due to a *trans* coupling to the μ-hydride. The resonance at δ 225.3 is assigned to the C=O group on the W atom on the basis of its downfield chemical shift [8]. VT ^{13}C-NMR spectra of **3*** could not be obtained at higher temperatures (> 25°C) due to the thermal instability of **3**. ^{13}C satellites ($^1J_{CH} = 143.9$ Hz) of the μ-alkylidene CH are observed in the ^{1}H-NMR spectrum of **3***.

Mass spectrum of **4** (M^+: *m*/*z* 1214) indicates loss of a C=O ligand from compound **3** (M^+: *m*/*z* 1242). The ^{1}H-NMR spectrum of **4** shows a μ-hydride resonance at δ − 19.8 and a μ-alkylidene CH resonance at δ 5.69 without a mutual coupling, which implies the two ligands are not bridging adjacent metal–metal bonds. The μ-alkylidene CH resonance reveals ^{183}W satellites ($^2J_{WH} = 14.0$ Hz) and thus this ligand in **4** remains bridging the W–Os edge as that in **3**. The limiting low temperature ^{13}C-NMR spectrum of ^{13}C-enriched CpWOs$_3$(*CO)$_9$(μ-*CHTol)(μ-S)(μ-H) (**4***) at 0°C in CD_2Cl_2 shows an alkylidene C resonance at δ 135.8 ($^1J_{CH} = 127.5$ Hz, $^1J_{CW} = 83.3$ Hz) and nine C=O resonances at δ 188.9, 187.3, 185.2, 181.9, 180.9, 179.3, 175.1, 167.7 and 165.0 (each of intensity 1). Of the nine C=O resonances, the two resonances due to C(4)–O(4) and C(9)–O(9) (see Fig. 3) show *trans* couplings to the bridging hydride at δ 179.3 ($^2J_{CH} = 8.9$ Hz) and 165.0 ($^2J_{CH} = 13.6$ Hz). These couplings were verified by obtaining ^{13}C{^{1}H}-NMR spectrum.

H_2S would seem to be an ideal source of sulfide, but it has not been used with wide success. The reaction of H_2S with $Os_3(CO)_{12}$ at 125°C has been reported to produce dihydrido–sulfido cluster $Os_3(CO)_9$(μ-S)(μ-H)$_2$ [10]. Both H atoms of H_2S are transferred from the sulfur atom to the metal atoms, where they bridge adjacent metal–metal bonds and the sulfido ligand serves as a triply bridge on the Os_3 triangle. The oxidative additions of H_2S to $RhCl(PPh_3)_3$ and *trans*-$IrCl(CO)(PPh_3)_2$ have resulted in the formation of respective hydrido–hydrogen–sulfido complexes, $[RhCl(PPh_3)_2$(μ-SH)(H)$]_2$ and $IrCl(CO)(PPh_3)_2(SH)(H)$, in which cases only one H–S bond of H_2S has been activated [11]. A likely pathway for the formation of **2** and **3** seems to be loss of a C=O ligand from **1**, followed by formation of an intermediate, presumably, 'butterfly' dihydrido terminal-sulfido (2e donor as an uncharged atom) complex $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})(S)(\mu\text{-H})_2$ with a 62 VE. This intermediate may undergo two parallel reactions: (a) reductive elimination of H_2 and subsequent conversion of terminal-S to μ_3-S to produce **2** and (b) reduction of the μ_3-alkylidyne C by one of the hydride ligands to form an alkylidene moiety and analogous multiple coordination of the sulfide ligand to afford **3**. In our previous work, the 'butterfly' μ-oxo complex $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})(\mu\text{-O})$ (**5**) has been isolated as an only product from the reaction of **1** with H_2O by O–H bond activations (Scheme 1) [7]. Overall structural features of μ_3-sulfido complex **3** are similar to those of **5**, except that in **5** all the C=O ligands are terminal and the oxo ligand is doubly bridging [7,9]. This structural difference of chalcogen atoms may be attributed to the fact that sulfides tend to be much more covalent than the corresponding oxides [12].

Complex **4** is formed upon decarbonylation of **3**. The 'butterfly' μ_3-sulfido complex **3** of a 62 VE is closed to the tetrahedral μ-sulfido complex **4** of a 60 VE by loss of a C=O ligand [13]. Decarbonylation of **2** with Me_3NO/MeCN and subsequent reaction with H_2 did not afford **4**, but resulted in extensive decomposition. Complex **3** can be viewed as a dihydrogenated product of **2**. Complex **3**, however, is not formed from an attempted reaction of **2** with dihydrogen and interestingly is produced in the present reaction of **1** with H_2S, which is used as a source of H_2 and a sulfur atom. In contrast, the μ-oxo complex **5** has been known to be converted to a mixture of two isomeric tetrahedral complexes $CpWOs_3(CO)_9(\mu\text{-CHTol})(\mu\text{-O})(\mu\text{-H})$ (**6a** and **6b**) by initial decarbonylation and subsequent reaction with H_2 as shown in Scheme 1 [7]. The overall structure of μ-sulfido complex **4** is essentially identical to that of one of the isomeric μ-oxo complex **6a** [7,14]. Nevertheless the tautomeric isomerism found in μ-oxo complexes **6a** and **6b** does not take place in μ-sulfido complex **4**.

2.2. Crystal structures of 2–4

The crystal of **2**, **3** or **4** contains an ordered arrangement of discrete molecular units, which are mutually separated by normal van der Waals distances; there are no unusually close intermolecular contacts. The overall molecular geometry and the atomic labeling scheme are illustrated in Fig. 1 for **2**, Fig. 2 for **3** and Fig. 3 for **4**. Crystal data for **2–4** are given in Table 1. Positional and equivalent isotropic thermal parameters of the atoms for **2–4** are listed in Tables 2–4, respectively while the interatomic distances and bond angles of **2–4** are in Tables 5–10, respectively.

Both tetranuclear molecules, **2** and **3**, contain a 'butterfly' arrangement of metal atoms with a respective dihedral angle of 100.60(7) and 83.82(8)° between the W–Os(3)–Os(1) and W–Os(3)–Os(2) planes, typical of a 62 VE tetranuclear array [13]. Each molecule consists of three $Os(CO)_3$ units, a CpW(CO) fragment and a triply bridging sulfido ligand. Complex **2** has a μ_3-alkylidyne ligand (3e donor as an uncharged atom), but complex **3** contains a μ-hydrido (1e donor) and a μ-alkylidene (2e donor) ligands instead. The C=O ligand on the W atom, C(10)–O(10), exhibits a semi bridging nature towards the 'wing-tip' Os(2) atom with W–C(10) = 2.01(3), 1.81(5) Å and Os(2)···C(10) = 2.40(2), 2.47(5) Å for **2** and **3**, respectively. The μ_3-sulfido ligands in **2** and **3** bridge across the open Os(1)–W–Os(2) triangular face such that W–S = 2.322(6), Os–S = 2.388(7), 2.440(5) Å for **2** and W–S = 2.40(2), Os–S = 2.34(2), 2.40(2) Å for **3**. These metal–sulfur bond distances compare with those of W–S = 2.395(8) , Os–S = 2.362(8), 2.418(8) Å for structurally analogous μ_3-sulfido 'butterfly' complex $CpWOs_3(CO)_{11}(\mu\text{-H})(\mu_3\text{-S})$ reported previously [15].

The μ_3-alkylidyne ligand of **2** caps unsymmetrically the outer face of the W–Os(1)–Os(3) 'wing' triangle. The Os–alkylidyne distances (Os(1)–C(11) = 2.22(2) and Os(3)–C(11) = 2.14(2) Å) are longer than the W–C(11) distance of 1.98(2) Å. The longest of the metal–metal bonds, W–Os(1) = 2.941(3) Å of **3**, is assumed to be associated with a single, unsupported μ-hydride ligand [16]. The μ-alkylidene ligand of **3** spans the W–Os(3) 'hinge' bond with W–C(11) = 2.08(5) and Os(3)–C(11) = 2.20(5) Å.

Table 1
Crystal data for **2**, **3**, and **4**

Compound	**2**	**3**	**4**
Formula	$C_{23}H_{12}O_{10}SWOs_3$	$C_{23}H_{14}O_{10}SWOs_3$	$C_{22}H_{14}O_9SWOs_3$
FW	1234.9	1236.5	1208.5
Crystal size (mm)	0.3 × 0.3 × 0.1	0.17 × 0.18 × 0.03	0.2 × 0.2 × 0.2
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P-1$
a (Å)	18.423(2)	19.753(3)	8.995(3)
b (Å)	9.439(2)	9.593(4)	10.271(2)
c (Å)	15.567(2)	16.070(3)	14.592(3)
α (°)			97.29(2)
β (°)	103.08(1)	98.77(1)	106.34(2)
γ (°)			90.66(2)
V (Å^3)	2636.8(7)	3009(1)	1281.5(5)
Z	4	4	2
D (Mg m^{-3})	3.10	2.714	3.096
Temperature (K)	298	293	298
λ (MoK$_\alpha$) (Å)	0.71069	0.71069	0.71069
μ (mm^{-1})	19.00	16.55	19.54

Table 2
Final positional parameters for **2**

Atom	x	y	z	U_{eq}[a]
W	0.9955(1)	−0.1174(1)	0.2447(1)	0.027(1)
Os(1)	0.8599(1)	0.0701(1)	0.1143(1)	0.030(1)
Os(2)	1.0311(1)	0.1577(1)	0.1930(1)	0.032(1)
Os(3)	0.8967(1)	0.1117(1)	0.2576(1)	0.030(1)
S	0.9886(3)	−0.0419(7)	0.1011(4)	0.036(2)
O(1)	0.7013(9)	0.089(2)	0.136(1)	0.070(6)
O(2)	0.850(1)	0.352(2)	0.010(2)	0.070(7)
O(3)	0.817(1)	0.137(2)	0.0372(2)	0.087(8)
O(4)	1.1861(9)	0.136(2)	0.158(1)	0.062(6)
O(5)	0.977(1)	0.365(2)	0.043(1)	0.067(6)
O(6)	1.082(1)	0.383(2)	0.333(2)	0.063(6)
O(7)	0.851(1)	0.376(2)	0.143(2)	0.086(8)
O(8)	0.747(1)	0.103(2)	0.308(1)	0.070(6)
O(9)	0.959(1)	0.247(3)	0.438(1)	0.101(9)
O(10)	1.088(1)	0.067(2)	0.398(1)	0.058(5)
C(1)	0.761(1)	−0.080(3)	0.128(2)	0.048(7)
C(2)	0.855(1)	−0.253(4)	0.050(2)	0.056(9)
C(3)	0.831(1)	0.064(3)	0.018(2)	0.057(8)
C(4)	1.130(1)	0.140(3)	0.172(2)	0.035(6)
C(5)	0.997(1)	0.288(2)	0.100(2)	0.035(6)
C(6)	1.063(1)	0.297(3)	0.278(2)	0.049(8)
C(7)	0.870(1)	0.278(3)	0.188(2)	0.045(7)
C(8)	0.801(1)	0.102(3)	0.288(2)	0.038(7)
C(9)	0.938(1)	0.203(3)	0.371(2)	0.043(7)
C(10)	1.051(1)	0.028(3)	0.329(2)	0.037(6)
C(11)	0.891(1)	−0.115(2)	0.258(1)	0.024(5)
C(12)	0.850(1)	−0.216(2)	0.307(2)	0.041(7)
C(13)	0.814(1)	0.338(2)	0.067(2)	0.032(6)
C(14)	0.790(1)	−0.441(3)	0.319(2)	0.055(9)
C(15)	0.800(1)	−0.415(3)	0.412(2)	0.042(7)
C(16)	0.834(1)	0.292(3)	0.449(2)	0.040(7)
C(17)	0.859(1)	−0.192(2)	0.399(1)	0.028(6)
C(18)	0.778(2)	−0.536(3)	0.470(2)	0.068(9)
C(19)	1.081(1)	−0.258(3)	0.349(2)	0.045(7)
C(20)	1.104(1)	−0.251(3)	0.268(2)	0.049(7)
C(21)	1.053(2)	0.321(3)	0.202(2)	0.053(8)
C(22)	0.992(1)	−0.368(2)	0.241(3)	0.06(1)
C(23)	1.010(2)	−0.320(3)	0.326(2)	0.053(8)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Because of poor crystal quality of **4**, sketchy description of overall molecular framework seems to be appropriate. The μ-hydride ligand is supposed to bridge the longest of the Os–Os bonds, Os(2)–Os(3) = 2.932(4) Å. The μ-sulfido ligand bridges the W–Os(2) edge such that W–S = 2.21(2), Os(2)–S = 2.47(2) Å and ∠W–S–Os(2) = 79.2(6)° and can be best viewed as a W=S: → Os bonding mode. The typical sulfido W=S [17] and W–S [18] distances are ca. 2.14 and 2.45 Å, respectively. The μ-alkylidene ligand spans the W–Os(1) and the tolyl moiety is oriented away from the μ-sulfido ligand.

All other features of the molecular geometry observed for **2–4** are within the normally accepted ranges.

3. Experimental section

3.1. General comments

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents were dried appropriately before use. Anhydrous Me_3NO (m.p. 225–230°C) was obtained from $Me_3NO \cdot 2H_2O$ (97% Aldrich) by sublimation (three times) at 90–100°C under vacuum. The progress of reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, silica gel 60 F-254, E. Merck). Preparative thin-layer plates were prepared from silica gel (Type 60, E. Merck). Complex **1** was prepared as described in the literature [6].

Table 3
Final positional parameters for **3**

Atom	x	y	z	U_{eq}[a]
W	0.7947(1)	0.0092(2)	0.2000(1)	0.033(1)
Os(1)	0.8321(1)	−0.0668(2)	0.0355(1)	0.038(1)
Os(2)	0.9045(1)	0.2034(2)	0.1978(1)	0.036(1)
Os(3)	0.7820(1)	0.2039(2)	0.0731(1)	0.036(1)
S	0.9072(8)	−0.035(2)	0.1662(9)	0.040(4)
O(1)	0.712(4)	0.086(5)	−0.114(3)	0.11(3)
O(2)[b]	0.861(2)	−0.375(5)	0.033(3)	0.06(1)
O(3)[b]	0.939(3)	0.033(5)	−0.074(3)	0.07(1)
O(4)	0.887(3)	0.513(5)	0.236(3)	0.08(2)
O(5)	0.996(3)	0.135(6)	0.369(2)	0.11(2)
O(6)	1.022(3)	0.265(4)	0.105(3)	0.07(2)
O(7)	0.886(2)	0.327(4)	0.028(3)	0.06(1)
O(8)[b]	0.667(2)	0.207(5)	−0.073(3)	0.06(1)
O(9)	0.749(3)	0.480(7)	0.133(3)	0.09(2)
O(10)[b]	0.789(2)	0.286(4)	0.299(2)	0.05(1)
C(1)	0.756(4)	−0.078(6)	−0.053(5)	0.07(2)
C(2)[b]	0.851(3)	−0.256(6)	0.037(3)	0.04(1)
C(3)[b]	0.892(4)	−0.002(7)	−0.036(4)	0.05(2)
C(4)[b]	0.894(3)	0.386(7)	0.224(4)	0.05(2)
C(5)[b]	0.965(4)	0.164(7)	0.306(4)	0.06(2)
C(6)[b]	0.969(2)	0.257(5)	0.135(3)	0.02(1)
C(7)[b]	0.851(3)	0.292(5)	0.016(3)	0.03(1)
C(8)[b]	0.704(4)	0.194(6)	−0.020(4)	0.05(2)
C(9)[b]	0.750(5)	0.372(9)	0.108(6)	0.09(3)
C(10)[b]	0.792(3)	0.181(5)	0.246(3)	0.03(1)
C(11)[b]	0.706(3)	0.068(5)	0.120(3)	0.03(1)
C(12)[b]	0.637(4)	0.117(8)	0.144(4)	0.07(2)
C(13)[b]	0.636(3)	0.220(6)	0.209(4)	0.05(2)
C(14)[b]	0.570(4)	0.252(7)	0.236(4)	0.05(2)
C(15)	0.510(4)	0.169(9)	0.202(4)	0.07(2)
C(16)	0.517(3)	0.108(6)	0.140(4)	0.05(2)
C(17)[b]	0.573(4)	0.061(8)	0.108(4)	0.06(2)
C(18)[b]	0.439(4)	0.219(7)	0.215(4)	0.06(2)
C(19)[b]	0.762(3)	−0.218(6)	0.240(3)	0.04(1)
C(20)[b]	0.837(5)	−0.20(1)	0.285(6)	0.09(3)
C(21)[b]	0.828(9)	−0.12(2)	0.31(1)	0.16(6)
C(22)[b]	0.790(5)	0.053(9)	0.340(5)	0.09(3)
C(23)[b]	0.714(4)	−0.120(8)	0.264(4)	0.06(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Atoms were refined isotropically.

Table 4
Final positional parameters for **4**[a]

Atom	x	y	z	U_{eq}^{b}
W	0.7567(3)	0.3621(3)	0.2521(2)	0.0113(6)
Os(1)	0.9927(3)	0.2089(3)	0.2229(2)	0.0107(6)
Os(2)	0.8410(3)	0.1339(3)	0.3614(2)	0.0128(6)
Os(3)	0.6849(3)	0.1116(3)	0.1541(2)	0.0111(6)
S	0.683(2)	0.325(2)	0.379(1)	0.019(4)
C(1)	1.007(9)	0.039(8)	0.157(6)	0.02(1)
O(1)	1.027(7)	0.063(6)	0.118(4)	0.03(1)
C(2)	1.18(1)	0.230(9)	0.307(6)	0.03(2)
O(2)	1.315(9)	0.225(8)	0.358(6)	0.06(2)
C(3)	1.04(1)	0.271(9)	0.113(7)	0.03(2)
O(3)	1.057(7)	0.310(6)	0.049(5)	0.04(1)
C(4)	0.998(6)	0.213(5)	0.459(4)	0.013(9)
O(4)	1.117(7)	0.265(6)	0.519(5)	0.04(1)
C(5)	0.943(8)	−0.015(7)	0.340(5)	0.01(1)
O(5)	1.012(9)	−0.115(7)	0.327(5)	0.05(2)
C(6)	0.73(1)	0.059(9)	0.446(7)	0.03(2)
O(6)	0.684(8)	0.012(7)	0.495(5)	0.04(1)
C(7)	0.686(9)	0.069(8)	0.118(6)	0.02(1)
O(7)	0.690(7)	−0.184(6)	0.085(4)	0.03(1)
C(8)	0.480(9)	0.124(7)	0.145(5)	0.02(1)
O(8)	0.343(7)	0.124(6)	0.127(5)	0.04(1)
C(9)	0.678(7)	0.15(1)	0.030(5)	0.04(2)
O(9)	0.678(7)	0.200(6)	−0.037(5)	0.04(1)
C(11)	0.993(7)	0.412(6)	0.295(4)	0.01(1)
C(12)	1.101(8)	0.516(7)	0.290(5)	0.01(1)
C(13)	1.090(9)	0.573(7)	0.203(5)	0.02(1)
C(14)	1.197(8)	0.672(7)	0.203(5)	0.02(1)
C(15)	1.307(9)	0.729(8)	0.285(6)	0.02(1)
C(16)	1.319(9)	0.676(8)	0.372(6)	0.02(2)
C(17)	1.215(9)	0.569(8)	0.368(6)	0.02(1)
C(18)	1.412(1)	0.840(9)	0.286(7)	0.03(2)
C(19)	0.737(8)	0.575(7)	0.217(5)	0.02(1)
C(20)	0.64(1)	0.565(9)	0.266(6)	0.03(2)
C(21)	0.51(1)	0.462(8)	0.199(6)	0.03(2)
C(22)	0.54(1)	0.415(9)	0.116(7)	0.03(2)
C(23)	0.70(1)	0.488(9)	0.121(6)	0.03(2)

[a] Atoms were refined isotropically.

[b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

IR spectra were obtained on a Nicolet 5-MX FT-JR spectrophotometer. Both ^{1}H-NMR (300 MHz) and ^{13}C-NMR (125 and 75 MHz) spectra were recorded on either a Bruker AMX-500 or AM-300 spectrometer. Mass spectra were recorded by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois by using a Varian MAT-731 mass spectrometer. All m/z values are referenced to ^{184}W and ^{192}Os. Elemental analyses were provided by the Agency for Defense Development.

*3.2. Reaction of **1** with H_2S*

Dark red compound 1 (43.0 mg, 0.0350 mmol) was dissolved in a mixture of dichloromethane (30 ml) and acetonitrile (10 ml). An acetonitrile solution (2 ml) of anhydrous Me_3NO (4.0 mg, 0.052 mmol) was added dropwise at r.t. and the resulting solution was stirred for 25 min. After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane (30 ml) and was bubbled with H_2S gas for 10 min, and the reaction mixture was stirred at r.t. for 2 h. Evaporation of the solvent and purification by preparative TLC (hexane/dichloromethane 1:1) provided red $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})(\mu_3\text{-S})$ (**2**, 20.8 mg, 0.168 mmol, 48%, $R_f = 0.65$), red $CpWOs_3(CO)_{10}(\mu\text{-CHTol})(\mu_3\text{-S})(\mu\text{-H})$ (**3**, 5.2 mg, 0.0042 mmol, 12%, $R_f = 0.72$) and dark red $CpWOs_3(CO)_9(\mu\text{-CHTol})(\mu\text{-S})(\mu\text{-H})$ (**4**, 5.8 mg, 0.0048 mmol, 14%, $R_f = 0.81$) as crystalline solids.

*3.2.1. Compound **2***

^{1}H-NMR ($CDCl_3$, 25°C) δ 7.12 (d, 2H), 6.88 (br, 2H), 5.63 (s, 5H), 2.44 (s, 3H). ^{13}C-NMR ($CDCl_3$, -30°C) δ 239.3 ($J_{CW} = 117.8$ Hz, μ_3-**C**), 232.3 ($^1J_{CW} = 157.5$ Hz, W–**C**O), 184.5, 181.3, 180.7, 179.7, 177.5, 177.0, 174.2, 167.9, 166.8 (Os–**C**O). IR (C_6H_{12}) ν(CO) 2084(s), 2056(vs), 2032(vs), 2018(m), 2005(w), 1989(w), 1979(w), 1968(w), 1957(vw) cm^{-1}. MS (FD) m/z 1240 (M^+). Anal. Calc. for $C_{23}H_{12}O_{10}SWOs_3$: C, 22.37; H, 0.98, Found: C, 22.20; H, 0.98.

*3.2.2. Compound **3***

^{1}H-NMR ($CDCl_3$, 25°C) δ 9.64 (d, $J_{HH} = 3.2$ Hz, μ-C**H**) 7.12–7.35 (AB pattern, 4H), 5.53 (s, 5H), 2.32 (s, 3H), -13.5 (d, $J_{HH} = 3.2$ Hz, $J_{WH} = 36.9$ Hz, μ-**H**). ^{13}C-NMR ($CDCl_3$, -20°C) δ 225.3, 188.9, 182.4 (2**C**O), 180.5, 177.9, 176.0, 175.5 ($J_{CH} = 9.8$ Hz), 173.6, 171.1, 130.8 ($J_{CH} = 143.9$ Hz, $^1J_{CW} = 66.4$ Hz, μ-**C**H).

Table 5
Interatomic distances (Å) and estimated standard deviations for **2**

(A) Metal–metal distances			
W–Os(1)	2.875(1)	Os(1)–Os(3)	2.775(2)
W–Os(2)	2.838(1)	Os(2)–Os(3)	2.908(1)
W–Os(3)	2.865(1)		
(B) Metal–sulfur distances			
W–S	2.322(6)	Os(1)–S	2.440(5)
Os(2)–S	2.388(7)		
(C) Metal–alkylidyne distances			
W–C(11)	1.98(2)	Os(1)–C(11)	2.22(2)
Os(3)–C(11)	2.14(2)		
(D) Metal–carbon (carbonyl) distances			
Os(1)–C(1)	1.88(3)	Os(2)–C(10)	2.40(2)
Os(1)–C(2)	1.99(4)	Os(3)–C(7)	1.91(3)
Os(1)–C(3)	1.94(3)	Os(3)–C(8)	1.93(2)
Os(2)–C(4)	1.93(2)	Os(3)–C(9)	1.95(3)
Os(2)–C(5)	1.90(3)	W–C(10)	2.01(3)
Os(2)–C(6)	1.86(3)		
(E) Carbon–oxygen distances			
C(1)–O(1)	1.14(3)	C(6)–O(6)	1.18(3)
C(2)–O(2)	1.12(3)	C(7)–O(7)	1.16(3)
C(3)–O(3)	1.08(3)	C(8)–O(8)	1.11(2)
C(4)–O(4)	1.11(2)	C(9)–O(9)	1.12(3)
C(5)–O(5)	1.14(3)	C(10)–O(10)	1.19(3)

Table 6
Interatomic angles (°) and estimated standard deviations for **2**

(A) Intermetallic angles			
Os(2)–W–Os(3)	61.31(3)	W–Os(3)–Os(1)	61.27(3)
W–Os(3)–Os(2)	58.89(3)	Os(1)–Os(3)–Os(2)	83.44(4)
W–Os(2)–Os(3)	59.80(3)	Os(3)–W–Os(1)	57.82(3)
Os(2)–W–Os(1)	82.93(4)	Os(3)–Os(1)–W	60.91(3)
(B) M–M–CO angles			
W–Os(2)–C(10)	44.1(6)	Os(2)–W–C(10)	56.4(7)
Os(1)–W–C(10)	126.0(6)	Os(3)–W–C(10)	71.1(6)
Os(3)–Os(2)–C(10)	65.9(6)		
(C) M–C–O and C–M–C angles			
Os(2)–C(10)–O(10)	125(2)	W–C(10)–O(10)	155(2)
(D) M–S–M and M–M–S angles			
Os(1)–S–Os(2)	103.2(2)	Os(1)–S–W	74.2(2)
Os(2)–S–W	74.1(2)	W–Os(1)–S	51.0(2)
Os(3)–Os(1)–S	86.3(2)	W–Os(2)–S	51.9(2)
Os(1)–W–S	54.8(1)	Os(2)–W–S	54.0(2)
Os(3)–W–S	86.5(2)	Os(3)–Os(2)–S	84.3(1)
(E) S–M–C angles			
S–W–C(10)	109.2(7)	S–Os(2)–C(6)	172.1(8)
S–W–C(11)	104.6(6)	S–Os(1)–C(1)	176.3(9)
S–Os(2)–C(10)	95.1(6)	S–Os(1)–C(2)	89.3(7)
S–Os(2)–C(4)	91.3(7)	S–Os(1)–C(3)	87.9(8)
S–Os(2)–C(5)	92.7(7)	S–Os(1)–C(11)	94.2(5)
(F) Angles involving alkylidyne C			
W–C(11)–C(12)	130(2)	Os(1)–C(11)–C(12)	125(2)
Os(3)–C(11)–C(12)	131(1)		

IR (C_6H_{12}) ν(CO) 2088(s), 2061(vs), 2036(vs), 2019(w), 2007(m), 1989(w), 1974(vw), 1962(vw) cm^{-1}. MS (FD) m/z 1242 (M^+). Anal. Calc. for $C_{23}H_{14}O_{10}SWOs_3$: C, 22.34; H, 1.14, Found: C, 22.30; H, 0.98.

3.2.3. Compound **4**

^{1}H-NMR ($CDCl_3$, 25°C) δ 7.05 (d, 2H) 6.68 (br, 2H), 5.75 (s, 5H), 5.69 (s, $J_{CW} = 14$ Hz, μ-**CH**), 2.30 (s, 3H), -19.8 (s, μ-**H**). ^{13}C-NMR (CD_2Cl_2, 0°C)δ 188.9, 187.3, 185.2, 181.9, 180.9, 179.3 (d, $J_{CH} = 8.9$ Hz), 175.1, 167.7, 165.0 (d, $J_{CH} = 13.6$ Hz), 135.8 ($J_{CH} = 127.5$ Hz, $J_{CW} = 83.3$ Hz, μ-**C**H). IR (C_6H_{12}) ν(CO) 2082(m), 2049(vs), 2030(vs), 2014(vw), 2005(w), 1980(m), 1957(w) cm^{-1}. MS (FD) m/z 1214 (M^+). Anal. Calc. for $C_{22}H_{14}O_9SWOs_3$: C, 21.86; H, 1.68, Found: C, 21.86; H, 1.93.

3.3. Conversion of **3** to **4**

Red compound **3** (20.0 mg, 0.0162 mmol) was dissolved in a dichloromethane (20 ml). A dichloromethane solution of anhydrous Me_3NO (1.2 mg, 0.016 mmol) was added dropwise at r.t. and the reaction mixture was stirred for 30 min. Evaporation of the solvent in vacuo and purification by preparative TLC (hexane/dichloromethane 3:2) gave compound **4** (13.4 mg, 0.0108 mmol, 67%).

Table 7
Interatomic distances (Å) and estimated standard deviations for **3**

(A) Metal–metal distances			
W–Os(1)	2.941(3)	Os(1)–Os(3)	2.873(3)
W–Os(2)	2.866(3)	Os(2)–Os(3)	2.896(3)
W–Os(3)	2.749(3)		
(B) Metal–sulfur distances			
W–S	2.40(2)	Os(1)–S	2.40(2)
Os(2)–S	2.34(2)		
(C) Metal–alkylidene distances			
W–C(11)	2.08(5)	Os(3)–C(11)	2.20(5)
(D) Metal–carbon (carbonyl) distances			
Os(1)–C(1)	1.91(8)	Os(2)–C(5)	2.00(6)
Os(1)–C(2)	1.85(6)	Os(2)–C(6)	1.82(4)
Os(1)–C(3)	1.88(7)	Os(3)–C(7)	1.94(5)
Os(2)–C(4)	1.82(7)	Os(3)–C(8)	1.98(7)
Os(2)–C(10)	2.47(5)	Os(3)–C(9)	1.85(1)
W–C(10)	1.81(5)		
(E) Carbon–oxygen distances			
C(1)–O(1)	1.21(9)	C(6)–O(6)	1.22(6)
C(2)–O(2)	1.16(7)	C(7)–O(7)	1.13(6)
C(3)–O(3)	1.22(7)	C(8)–O(8)	1.05(7)
C(4)–O(4)	1.24(7)	C(9)–O(9)	1.11(9)
C(5)–O(5)	1.13(7)	C(10)–O(10)	1.32(6)

3.4. Preparation of ^{13}C-enriched compounds

The ^{13}C (*C)-enriched $CpWOs_3(*CO)_{11}(\mu_3\text{-}*CTol)$ (**1***) was prepared from the reaction of ^{13}C-enriched $Cp(*CO)_2W(*CTol)$ (ca. 60% enrichment) [8] with $Os_3(CO)_{10}(NCMe)_2$ [19] by the reported procedure [6].

Table 8
Interatomic angles (°) and estimated standard deviations for **3**

(A) Intermetallic angles			
Os(2)–W–Os(3)	62.07(8)	W–Os(3)–Os(1)	63.03(8)
W–Os(3)–Os(2)	60.95(8)	Os(1)–Os(3)–Os(2)	82.35(9)
W–Os(2)–Os(3)	56.98(8)	Os(3)–W–Os(1)	60.55(8)
Os(2)–W–Os(1)	81.70(8)	Os(3)–Os(1)–W	56.42(7)
(B) M–M–CO angles			
W–Os(2)–C(10)	38.9(1)	Os(1)–W–C(10)	128.0(2)
Os(2)–W–C(10)	59.0(2)	Os(3)–Os(2)–C(10)	61.6(1)
(C) M–C–O and C–M–C angles			
W–C(10)–O(10)	164.0(4)	Os(2)–C(10)–O(10)	106.0(3)
(D) M–S–M and M–M–S angles			
Os(1)–S–Os(2)	106.4(6)	Os(1)–S–W	75.5(4)
Os(2)–S–W	74.3(5)	W–Os(1)–S	52.3(4)
Os(3)–Os(1)–S	83.5(4)	W–Os(2)–S	53.8(4)
Os(1)–W–S	52.2(4)	Os(2)–W–S	51.9(4)
Os(3)–W–S	86.2(4)	Os(3)–Os(2)–S	84.0(4)
(E) S–M–C angles			
S–W–C(10)	110.0(2)	S–Os(2)–C(6)	97.0(2)
S–W–C(11)	128.5(1)	S–Os(1)–C(1)	166.0(2)
S–Os(2)–C(10)	91.9(1)	S–Os(1)–C(2)	91.0(2)
S–Os(2)–C(4)	174.0(2)	S–Os(1)–C(3)	98.0(2)
S–Os(2)–C(5)	88.0(2)		
(F) Angles involving alkylidene C			
W–C(11)–C(12)	128.0(4)	Os(3)–C(11)–C(12)	125.0(4)

Table 9
Interatomic distances (Å) and estimated standard deviations for **4**

(A) Metal–metal distances			
W–Os(1)	2.753(4)	Os(1)–Os(3)	2.791(4)
W–Os(2)	2.987(4)	Os(2)–Os(3)	2.932(4)
W–Os(3)	2.755(4)	Os(1)–Os(2)	2.909(4)
(B) Metal–sulfur distances			
W–S	2.21(2)	Os(2)–S	2.47(2)
(C) Metal–alkylidene distances			
Os(1)–C(11)	2.21(6)	W–C(11)	2.08(6)
(D) Metal–carbon (carbonyl) distances			
Os(1)–C(1)	1.91(8)	Os(2)–C(5)	1.83(7)
Os(1)–C(2)	1.78(9)	Os(2)–C(6)	2.01(9)
Os(1)–C(3)	1.95(9)	Os(3)–C(7)	1.87(8)
Os(2)–C(4)	1.80(5)	Os(3)–C(8)	1.81(7)
Os(3)–C(9)	1.9(1)		

This complex was then utilized to prepare Cp-$WOs_3(^*CO)_{10}(\mu_3$-$^*CTol)(\mu_3$-S) (**2***), $CpWOs_3(^*CO)_{10}(\mu$-$^*CHTol)(\mu_3$-S)(μ-H) (**3***) and $CpWOs_3(^*CO)_9(\mu$-$^*CHTol)(\mu$-S)(μ-H) (**4***) by the procedure described above.

*3.5. X-ray data collections and structure solutions of **2**, **3** and **4***

Crystals of **2**, **3** and **4** suitable for structural determination were obtained from a layered solution of dichloromethane/hexane. Red crystals of approximate dimensions $0.3 \times 0.3 \times 0.1$ mm (**2**), $0.17 \times 0.18 \times 0.03$ mm (**3**) and $0.2 \times 0.2 \times 0.2$ mm (**4**) were mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated MoK_α radiation, and accurate cell parameters were determined from the least-squares fit of 25 accurately centered reflections with θ range of 10–14°. The asymmetric units of intensities for **2–4** were collected in the $\omega - 2\theta$ scan mode, ω-scan angle $= (0.8 + 0.35 \tan\theta)°$, $2\theta_{max} = 48$, 46 and 45°, respectively. Three standard reflections for each crystal were measured every 4 h and the intensities of the standards remained constant within experimental error throughout data collection. All data were corrected for $L - P$ and absorption factors.

Table 10
Interatomic angles (°) and estimated standard deviations for **4**

(A) Intermetallic angles			
Os(2)–Os(1)–W	63.6(1)	Os(1)–W–Os(2)	60.7(1)
Os(1)–Os(3)–W	59.5(1)	Os(1)–W–Os(3)	60.9(1)
Os(2)–Os(3)–W	63.3(1)	Os(2)–W–Os(3)	61.3(1)
Os(1)–Os(2)–Os(3)	57.1(1)	W–Os(2)–Os(3)	55.5(1)
Os(2)–Os(1)–Os(3)	61.9(1)	W–Os(1)–Os(3)	59.6(1)
Os(1)–Os(3)–Os(2)	61.0(1)	Os(1)–Os(2)–W	55.5(1)
(B) M–S–M and M–M–S angles			
Os(2)–S–W	79.2(6)	Os(3)–Os(2)–S	86.4(5)
Os(1)–Os(2)–S	101.2(5)	W–Os(2)–S	46.6(5)
Os(1)–W–S	113.6(5)	Os(2)–W–S	54.1(5)
Os(3)–W–S	96.0(5)		

The structures of **2** and **3** were solved by locating W and Os atoms by use of direct methods [20]. All remaining non-H atoms were found by iterative cycles of full-matrix least-squares refinement and difference-Fourier syntheses. Thermal parameters were treated anisotropically for all atoms of **2** and all but four O atoms (2, 3, 8, 10) and most C atoms of **3**. H atoms were not located. SHELX93 package [21] was used for all computation and function minimized $\Sigma\omega(|F_o| - |F_c|)^2$, with $\omega = 1/[\sigma^2(F_o^2) + (0.0521 \times P)^2]$ for **2** and $\omega = 1/[\sigma^2(F_o^2) + (0.1327 \times P)^2]$ for **3**, where $P = (F_o^2 + 2 \times F_c^2)/3$. Neutral atomic scattering factors were used with W and Os corrected for anomalous dispersion. Numbers of parameters refined were 343 for **2** and 227 for 3. Final reliability factors for 2402 (**2**) and 2040 (**3**) unique observed reflections $[F_o > 4\sigma(F_o)]$ were $R = 0.048$, $\omega R = 0.097$ and $S = 1.1038$ for **2**, and $R = 0.087$, $\omega R = 0.253$ and $S = 0.710$ for **3**. The maximum and minimum $\Delta\rho$ in the final difference Fourier maps were $1.74/-1.59$ and $3.34/-3.29$ e A^{-3} for **2** and **3**, respectively.

The structure of **4** was solved by direct and difference Fourier methods and refined by the full-matrix least-squares methods employing unit weights. All non-H atoms were refined isotropically and H atoms were not located. Calculations were carried out with the NRC-VAX program [22]. Number of parameters refined was 145. Final reliability factors for 2916 unique observed reflections $[F_o > 3\sigma(F_o)]$ were $R = 0.144$, $\omega R = 0.179$ and $S = 5.92$. The high R value of **4** may be due to poor crystal quality. The maximum and minimum $\Delta\rho$ in the final difference Fourier maps were -16.4 and 13.4 e A^{-3}. Crystal data for **2–4** are given in Table 1. Positional and equivalent isotropic thermal parameters of the atoms for **2–4** are listed in Tables 2–4, respectively.

4. Supplementary material available

A full listing of positional and thermal parameters, complete lists of bond distances and angles, and structure factor tables of complexes **2**, **3** and **4** are available from the authors.

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References

[1] (a) J. Wachter, Angew. Chem. Int. Ed. Engl. 28 (1989) 1613. (b) R.J. Angelici, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, vol. 3, Wiley, New York, 1994, pp. 1433–1443.

[2] (a) R.D. Adams, I.T. Horvath, B.E. Segmuller, L.W. Yang, Organometallics 2 (1983) 144. (b) R.D. Adams, I.T. Horvath, H.S. Kim, Organometallics 3 (1984) 548. (c) R.D. Adams, I.T. Horvath, P. Mathur, J. Am. Chem. Soc. 106 (1984) 6292.

[3] R.D. Adams, I.T. Horvath, L.W. Yang, J. Am. Chem. Soc. 105 (1983) 1533.

[4] R.D. Adams, Polyhedron 4 (1985) 2003.

[5] U. Riaz, O.J. Curnow, M.D. Curtis, J. Am. Chem. Soc. 116 (1994) 4357.

[6] J.T. Park, J.R. Shapley, Bull. Korean Chem. Soc. (1990) 531.

[7] J.T. Park, J.-H. Chung, H. Song, K.Y. Lee, J.-H. Lee, J.-R. Park, I.-H. Suh, J. Organomet. Chem. 526 (1996) 215.

[8] J.T. Park, J.R. Shapley, M.R. Churchill, C. Bueno, Inorg. Chem. 22 (1983) 1579.

[9] J.T. Park, Y. Chi, J.R. Shapley, M.R. Churchill, J.W. Ziller, Organometallics 13 (1994) 813.

[10] A.J. Deeming, M Underhill, J. Organomet. Chem. 42 (1972) 60.

[11] A.M. Mueting, P. Boyle, L.H. Pignolet, Inorg. Chem. 23 (1984) 44.

[12] J.K. Burdett, E.L. Miller, J. Am. Chem. Soc. 109 (1987) 4081.

[13] (a) K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1. (b) D.M. Mingos, D.J. Wales, Introduction To Cluster Chemistry, Prentice Hall, Englewood Cliffs, NJ, 1990, Chap. 2.

[14] (a) M.R. Churchill, Y.-J. Li, J. Organomet. Chem. 291 (1985) 61. (b) J.T. Park, M.-K. Chung, K.M. Chun, S.S. Yun, S. Kim, Organometallics 11 (1992) 3313.

[15] G. Suss-Fink, U. Thewalt, K. Heinz-Peter, J. Organomet. Chem. 262 (1984) 315.

[16] (a) M.R. Churchill, B.G. Deboer, F.T. Rotella, Inorg. Chem. 14 (1976) 1843. (b) M.R. Churchill, Adv. Chem. Ser. 167 (1978) 36.

[17] (a) A. Muller, W. Hellmann, H. Bigge, M. Rimer, U. Schimanski, Angew. Chem. Int. Ed. Engl. 21 (1982) 860. (b) H. Brunner, W. Meier, J. Wachter, E. Guggolz, T. Zahn, M.L. Ziegler, Organometallics 1 (1982) 1107. (c) A. Muller, Polyhedron 5 (1986) 323.

[18] S. Thomas, E.R.T. Tieink, C.G. Young, Organometallics 15 (1996) 2428.

[19] B.F.G. Johnson, J. Lewis, D.A. Pippard, J. Chem. Soc., Dalton Trans. (1981) 407.

[20] G.M. Sheldrick, SHELX 86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1985.

[21] G.M. Sheldrick, SHELX 93, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1993.

[22] E.J. Gabe, Y.L. Page, J.P. Charland, F.L. Lee, P.S. White, J. Appl. Crystallogr. 22 (1989) 384.