

Characterization and structures of intermediates in the reactivity of $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ towards dihydrogen and water

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Abstract

Initial decarbonylation of $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (**1**; Cp = $\eta^5\text{-C}_5\text{H}_5$, Tol = $p\text{-C}_6\text{H}_4\text{Me}$) with $\text{Me}_3\text{NO}/\text{MeCN}$ followed by reaction with dihydrogen and water produces a dihydrido complex $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**2**), a 'butterfly' cluster with a 60 valence electron (VE), and an oxo complex $\text{CpWOs}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$ (**4**) respectively. Complex **2** reacts either with carbon monoxide to produce the starting alkylidyne complex **1** by reductive elimination of dihydrogen or with PPh_3 to afford a 62 VE 'butterfly' complex $\text{CpWOs}_3(\text{CO})_{10}(\text{PPh}_3)(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**6**). Thermolysis of **2** in the presence of water gives a hydrido oxo alkylidene complex, *syn*- $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CHTol})(\mu\text{-H})$ (**3a**), in which the tolyl substituent on the alkylidene carbon is oriented *syn* to the μ -oxo ligand. Thermolysis of **4** at 110 °C induces decarbonylation to give a tetrahedral alkylidyne complex $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CTol})$ (**5**), which is reversibly converted back to **4** upon exposure to carbon monoxide. Complex **5** reacts with dihydrogen to afford a mixture of two isomeric hydrido oxo alkylidene complexes, *anti*- $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CHTol})(\mu\text{-H})$ (**3b,c**). The *syn*-isomer **3a** is also produced from a mixture of **3b** and **3c** by thermolysis in boiling toluene. Compounds **2**, **3a,b,c**, **4**, **5** and **6** have been isolated as crystalline solids and characterized by spectroscopic (IR, MS, ¹H and ¹³C NMR) and analytical data. The structures of **2** and **6** have been determined by single crystal X-ray diffraction studies. Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters $a = 14.18(1)$, $b = 28.46(1)$, $c = 13.59(3)$ Å, $V = 5484(13)$ Å³ and $Z = 8$. Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 19.298(2)$, $b = 22.406(4)$, $c = 9.364(1)$ Å, $\beta = 92.83(9)^\circ$, $V = 4044.0(9)$ Å³ and $Z = 4$. Diffraction data were collected on a CAD4 diffractometer, and structures were refined to $R = 0.0957$ and 0.0510 for **2** and **6** respectively. Both **2** and **6** are based upon a 'butterfly' WO_3 metal core with a respective dihedral angle of 114.3(2)° and 113.6(4)° between the $\text{W-Os}(2)\text{-Os}(1)$ and $\text{W-Os}(2)\text{-Os}(3)$ planes. Each molecule consists of three $\text{Os}(\text{CO})_3$ units and a $\text{CpW}(\text{CO})$ fragment, except that the $\text{Os}(1)$ center in **6** is additionally coordinated with PPh_3 . The μ_3 -alkylidyne caps unsymmetrically the respective $\text{W-Os}(2)\text{-Os}(3)$ face of both complexes.

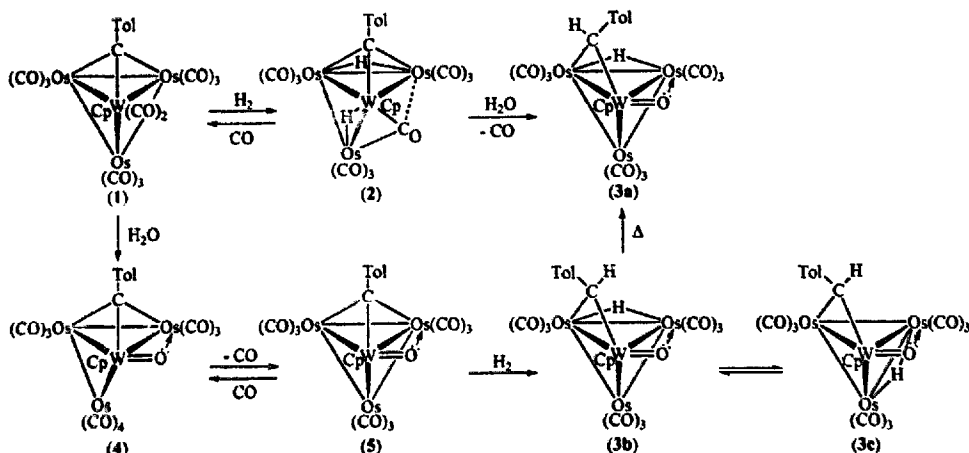
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1. Introduction

In recent years organometallic oxo complexes have attracted considerable attention as both models and potential catalysts for oxygen transfer reactions [1]. The oxo ligand has also been proposed to be essential to the catalyst as a spectator ligand in olefin metathesis [2]. The μ -oxo ligand with a lone pair of electrons is known to promote metal cluster formation, and thus the μ -oxo cluster complexes do not undergo easy cluster degrada-

tion during further reactions [1]. The μ -oxo clusters can generally be prepared by one of three basic processes [1,3]: (1) oxidation by nitrogen oxides (NO , N_2O , Me_3NO , etc.) or dioxygen; (2) hydrolysis; (3) cluster assisted C–O or N–O bond cleavage. In previous work, we have reported the synthesis and solution dynamics of tungsten-triosmium *p*-tolylmethylidyne complex, $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (**1**) [4], and the reactivity of **1** towards dihydrogen leading to formation of an unexpected hydrido-oxo-alkylidene complex *syn*- $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CHTol})(\mu\text{-H})$ (**3a**) (see Scheme 1) [5]. Further studies on the reactivity of **1** towards H_2 and H_2O have resulted in the isolation of intermediates

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Scheme 1.

leading to **3a**, such as a dihydrido complex $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**2**) and several oxo complexes $\text{CpWOs}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$ (**4**), $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CTol})$ (**5**) and two isomers of *anti*- $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CHTol})(\mu\text{-H})$ (**3b,c**). All of the μ -oxo ligands in these clusters were originated from water. The electron deficient nature of the 'butterfly' **2** with a 60 valence electron (VE), based on electron counting rules (ECR) [6], is supported by reaction with PPh_3 to afford the 'butterfly' complex $\text{CpWOs}_3(\text{CO})_{10}(\text{PPh}_3)(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**6**) with a 62 VE. We herein report full details of the two independent synthetic routes to **3a**, $1 \rightarrow 2 \rightarrow 3a$ and $1 \rightarrow 4 \rightarrow 5 \rightarrow 3b,c \rightarrow 3a$, together with structural characterization of two 'butterfly' complexes **2** and **6**.

2. Experimental section

2.1. General comments

All reactions were performed under an atmosphere of nitrogen in oven-dried glasswares. Solvents were dried prior to use. Anhydrous Me_3NO (m.p. 225–230°C) was obtained from $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (97%, Aldrich Chemical Co.) 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, Merck). Preparative thin-layer plates were prepared from silica gel G (Type 60, Merck). Complex **1** was prepared as described in the literature [4,7].

Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. Both ^1H NMR (300 MHz) and ^{13}C NMR (75, 125 MHz) spectra were recorded on either a Bruker AM-300 or a Bruker AMX-500 spectrometer. $\text{Cr}(\text{acac})_3$ (0.02 M) was used as a shiftless relaxation reagent. Mass spectra were recorded by the

staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois using either a Varian MAT CH-5 (EI) or MAT-MAT-731 (FD) mass spectrometer. All m/z values are referenced to ^{184}W and ^{192}Os . Elemental analyses were provided by the Daeduck R&D Center of Daelim Industrial Co., Ltd.

2.2. Synthesis of $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**2**)

A red dichloromethane (30 ml)–acetonitrile (10 ml) solution of **1** (26.9 mg, 0.0219 mmol) was treated with an acetonitrile solution (1.0 ml) of anhydrous Me_3NO (1.7 mg, 0.023 mmol) in a glass pressure bottle and the resulting solution was stirred for 25 min. After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane (30 ml). This solution was degassed by a freeze–pump–thaw cycle and the bottle was charged with dihydrogen gas to a pressure of 50 psig. The reaction mixture was stirred at room temperature for 15 min. Evaporation of the solvent and purification by preparative TLC (hexane/dichloromethane 3:1) produced a greenish red crystalline solid $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**2**, 14.5 mg, 0.012 mmol, 55%, $R_f = 0.39$) together with unreacted $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (**1**, 5.6 mg, 21%). Crystals of **2** suitable for X-ray analysis were grown from dichloromethane–hexane at –10°C. ^1H NMR (CDCl_3 , 25°C): δ 7.15–7.07 (m, 4H), 5.36 (s, 5H), 2.41 (s, 3H), –12.02 (s, br, 1H), –20.55 (s, br, 1H). ^{13}C NMR (CD_2Cl_2 , –80°C): δ (carbonyl carbon) 204.6 ($^1J_{\text{CW}} = 177.6$ Hz), 181.9 (2CO), 179.4, 176.1, 173.9, 173.6 ($^2J_{\text{CH}} = 11.2$ Hz), 172.8, 172.3 ($^2J_{\text{CH}} = 8.0$ Hz), 170.6 ($^2J_{\text{CH}} = 11.3$ Hz). IR (C_6H_{12}): ν (CO) 2087(s), 2056(vs), 2042(w), 2033(m), 2012(s), 2006(s), 1994(s), 1984(sh), 1974(m), 1771(w) cm^{-1} . MS (FD) m/z 1210 (M^+). Anal. Found: C, 23.36; H, 1.36. $\text{C}_{23}\text{H}_{14}\text{O}_{10}\text{WO}_3$. Calc.: C, 22.93; H, 1.17%.

2.3. Synthesis of *syn*-CpW₃O₃(CO)₉(μ-O)(μ-CHTol)(μ-H) (**3a**)

Method 1. A toluene solution of **2** (10 mg, 0.0083 mmol) was placed in a glass pressure bottle. A partial vacuum was drawn over the toluene solution and then the bottle was charged with dihydrogen gas to a pressure of 60 psig. After the solution was heated at 60 °C for 2 h, the solvent was evaporated under vacuum. The residue was purified by preparative TLC (hexane/dichloromethane 3:2) to provide CpW₃O₃(CO)₉(μ-O)(μ-CHTol)(μ-H) (**3a**, 7.3 mg, 0.0061 mmol, 74%, *R_f* = 0.40) as an orange solid [5].

Method 2. Greenish red compound **2** (10.0 mg, 0.0083 mmol) was dissolved in toluene (10 ml), and a small quantity (0.1 ml) of water was added. After the solution was heated at 110 °C for 1.5 h, the solvent was evaporated under vacuum. The residue was purified by preparative TLC (hexane/dichloromethane 3:2) to provide **3a** (7.2 mg, 0.0060 mmol, 72%).

2.4. Synthesis of CpW₃O₃(CO)₁₀(μ-O)(μ₃-CTol) (**4**)

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 Me₃NO (1.6 mg, 0.0218 mmol) was added 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 CpW₃O₃(CO)₁₀(μ-O)(μ₃-CTol) (**4**, 9.6 mg, 0.0078 mmol, 54%, *R_f* = 0.28) as a dark red solid. ¹H NMR (CDCl₃, 25 °C): δ 7.12–6.97 (m, 4H), 5.77 (s, 5H), 2.42 (s, 3H). IR (C₆H₁₂): 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. Found: C, 22.05; H, 1.50. C₂₃H₁₂O₁₁W₃O₃ Calc.: C, 22.67; H, 0.99%.

2.5. Synthesis of CpW₃O₃(CO)₉(μ-O)(μ₃-CTol) (**5**)

A toluene solution (10 ml) of **4** (9.0 mg, 0.0073 mmol) was heated at 90 °C for 1 h. After evaporation of the solvent, purification by preparative TLC (hexane/dichloromethane 1:1) afforded dark brown CpW₃O₃(CO)₉(μ-O)(μ₃-CTol) (**5**, 8.6 mg, 0.0070 mmol, 96%, *R_f* = 0.30). ¹H NMR (CDCl₃, 25 °C): δ 7.14–7.02 (m, 4H), 5.91 (s, 5H), 2.36 (s, 3H). IR (C₆H₁₂): ν(CO) 2078(m), 2044(s), 2032(vs), 2011(vw), 1995(w), 1987(m), 1970(m), 1958(w) cm⁻¹. MS (FD) *m/z* 1196 (M⁺). Anal. Found: C, 22.63; H, 1.48. C₂₂H₁₂O₁₀W₃O₃ Calc.: C, 22.19; H, 1.02%.

2.6. Conversion of **5** to **4**

Carbon monoxide was bubbled with a gas dispersion tube through a brown solution of compound **5** (6.0 mg, 0.0050 mmol) in toluene (10 ml) at 110 °C. After 1.5 h the solution had turned to red and the reaction was stopped. Purification by preparative TLC (hexane/dichloromethane 3:2) provided CpW₃O₃(CO)₁₀(μ-O)(μ₃-CTol) (**4**, 5.7 mg, 0.0047 mmol, 93%).

2.7. Synthesis of CpW₃O₃(CO)₉(μ-O)(μ-CHTol)(μ-H) (**3a,b,c**)

Method 1. Dark red compound **4** (10 mg, 0.082 mmol) was placed in a glass pressure bottle, and dissolved in toluene (20 ml). A partial vacuum was drawn over the toluene solution, and then the bottle was charged with dihydrogen gas to a pressure of 40 psig. After the solution was heated at 110 °C for 2 h, it turned from red to orange and the reaction was stopped. Purification by preparative TLC (hexane/dichloromethane 3:2) provided a mixture of three isomers (**3a,b,c**, 8.5 mg, 0.0071 mmol, 87%) as an orange solid. The ratio of three isomers (**3a,b,c**) was identified by integration of ¹H NMR resonances as 3.1:1.0:1.8 respectively. A mixture of **3b,c** could be isolated from a mixture of three isomers (**3a,b,c**) by preparative TLC with a multiple elution method.

Mixture of **3b,c**. ¹H NMR (CDCl₃, 25 °C): δ 7.09–6.44 (m, 8H, **3b,c**), 5.95 (s, 5H, **3c**), 5.93 (s, 5H, **3b**), 5.82 (s, 1H, **3b**), 4.88 (d, ³*J*_{HH} = 1.9 Hz, 1H, **3c**), 2.30 (s, 6H, **3b,c**), -16.77 (s, 1H, **3b**), -18.52 (d, ³*J*_{HH} = 1.9 Hz, 1H, **3c**). IR (C₆H₁₂): ν(CO) 2086(s), 2061(vs), 2050(s), 2029(sh), 2024(vs), 2011(m), 2005(m), 1984(w), 1954(w), 1934(w) cm⁻¹. MS (70 eV) *m/z* 1198 (M⁺).

Method 2. A toluene solution of CpW₃O₃(CO)₉(μ-O)(μ₃-CTol) (**5**, 10 mg, 0.084 mmol) was treated with dihydrogen gas (40 psig) in a 500 ml glass pressure bottle. After the solution was heated at 110 °C for 30 min, the solution was evaporated under vacuum. The residue was purified by preparative TLC (hexane/dichloromethane 3:2) to provide a mixture of three isomers (**3a,b,c**, 8.6 mg, 0.071 mmol, 85%). The ratio of three isomers (**3a,b,c**) was identified by integration of ¹H NMR resonances as 4.3:1.0:1.8 respectively.

2.8. Conversion of **3b,c** to **3a**

A toluene solution (10 ml) of **3b,c** (5.0 mg, 0.042 mmol) was heated to reflux for 2 h. Evaporation of the solvent and purification by preparative TLC (hexane/dichloromethane 3:2) gave **3a** (3.2 mg, 0.0027 mmol, 64%) as orange-red crystals.

2.9. Reaction of **2** with PPh_3

Greenish red crystals of **2** (15 mg, 0.0125 mmol) were dissolved in dichloromethane (20 ml), and then PPh_3 (32.6 mg, 0.125 mmol) was added. The reaction mixture was stirred for 10 h, and the solvent was evaporated. Green crystals of $\text{CpWO}_3(\text{CO})_{10}(\text{PPh}_3)(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**6**, 10.1 mg, 0.0068 mmol, 54.2%, $R_f = 0.42$) were isolated after purification by preparative TLC (hexane/dichloromethane 1:1). ^1H NMR (CDCl_3 , 25 °C): δ 7.50–6.99 (m, 19H), 4.47 (s, 5H), 2.32 (s, 3H), –14.29 (d, $^2J_{\text{PH}} = 10.4$ Hz, $^1J_{\text{WH}} = 56.7$ Hz, 1H), –20.30 (s, 1H). ^{13}C NMR (toluene- d_8 , 0 °C): δ (carbonyl carbon) 227.9 ($^1J_{\text{CW}} = 147.1$ Hz, $^2J_{\text{CH}} = 7.0$ Hz), 193.2 ($^2J_{\text{CC}} = 35.2$ Hz), 188.2 ($^2J_{\text{CC}} = 35.2$ Hz, $^2J_{\text{CP}} = 5.7$ Hz, $^2J_{\text{CH}} = 6.1$ Hz), 178.9, 174.6 ($^2J_{\text{CH}} = 13.8$ Hz), 174.5, 174.1, 173.7, 171.8 ($^2J_{\text{CH}} = 11.3$ Hz), 170.3. ^{31}P NMR (CDCl_3 , 25 °C): δ 0.09(s). IR (C_6H_{12}): $\nu(\text{CO})$ 2080(s), 2054(vs), 2048(s), 1995(vs), 1983(m), 1973(m), 1740(w) cm^{-1} . MS (FD) m/z 1416 ($\text{M}^+ - 2\text{CO}$). Anal. Found: C, 33.59; H, 2.42. $\text{C}_{41}\text{H}_{29}\text{O}_{10}\text{PWO}_3$. Calc.: C, 33.57; H, 1.99%.

2.10. Reaction of **2** with CO

A toluene solution of $\text{CpWO}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**2**, 10 mg, 0.0083 mmol) was placed in a pressure bottle. A partial vacuum was drawn over the toluene solution and the bottle was charged with carbon monoxide to a pressure of 30 psig. After the solution was heated at 110 °C for 1 h, the solvent was evaporated under vacuum. The residue was purified by preparative TLC (hexane/dichloromethane 3:1) to provide $\text{CpWO}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (**1**, 9.6 mg, 94%).

2.11. Preparation of ^{13}C O-enriched compounds

The ^{13}C O(^{13}C O)-enriched $\text{CpWO}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (**1**) was prepared from the reaction of ^{13}C O-enriched $\text{Os}_2(\text{CO})_{10}(\text{NCMe})_2$ (ca. 50% enrichment) with $\text{CpW}(\text{CO})_2(\text{CTol})$ by the reported procedure [4]. This complex was then utilized to prepare $\text{CpWO}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**2**) and $\text{CpWO}_3(\text{CO})_{10}(\text{PPh}_3)(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**6**) by procedures similar to those described above.

2.12. X-ray data collection and structure solution of **2**

Crystals of **2** suitable for X-ray analysis were obtained by slow recrystallization from dichloromethane–hexane at –10 °C. A green crystal of approximate dimensions $0.3 \times 0.5 \times 0.2$ mm³ was mounted and aligned on a CAD4 diffractometer. Relevant crystallographic data are given in Table 1. The accurate cell parameters were refined from setting angles of 22 re-

Table 1
Crystal data for **2** and **6**

Compound	2	6
Formula	$\text{C}_{23}\text{H}_{14}\text{O}_{10}\text{WO}_3$	$\text{C}_{41}\text{H}_{29}\text{O}_{10}\text{PWO}_3$
FW	1204.79	1467.10
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a (Å)	14.18(1)	19.298(2)
b (Å)	28.46(1)	22.406(4)
c (Å)	13.59(3)	9.364(1)
β (deg)		92.83(9)
V (Å ³)	5484(13)	4044.0(9)
Z	8	4
D (Mg m^{-3})	2.91	2.42
Temperature (K)	298	291
λ (Mo K α) (Å)	0.71069	0.71069
μ (mm^{-1})	18.09	12.45
Empirical absorption correction	$T_{\text{min}} = 0.4570$	$T_{\text{min}} = 0.4672$
	$T_{\text{max}} = 0.9986$	$T_{\text{max}} = 0.9992$

flections with $11.39^\circ < \theta < 13.91^\circ$. The space group $P2_12_12_1$ was uniquely defined from the reflection conditions $h00: h = 2n; 0k0: k = 2n; 00l: l = 2n$. 4220 independent reflections in the range $0 < h < 15, 0 < k < 30, 0 < l < 14$ were collected using graphite-monochromated Mo K α radiation and the $\omega/2\theta$ scan mode, ω -scan angle $(0.8 + 0.35 \tan \theta)^\circ$, $\theta_{\text{min}} = 23^\circ$. One orientation reflection was checked every 200 reflections and three standard reflections were monitored every 180 min. The intensity variation was less than 5.2% during data collection; the decay correction was not applied to the data. All data were converted to E values following correction for L–P and absorption factors. The four heavy atoms were located using direct methods [8], and non-hydrogen atoms were found on subsequent difference Fourier maps. Hydrogen atoms were not located due to poor quality of the crystal. The whole structure was refined by full-matrix least-squares techniques [use of F magnitude: x, y, z, U_{ij} for Os, W and O atoms; v, y, z, U_{iso} for O(10) atom; all carbon atoms except U_{iso} for fixed C(51), C(52)]. The SHELX93 package [9] was used for all computations and the function minimized was $\sum w(F_o - F_c)^2$, with $w = 1/[\sigma^2 F_o^2 + (0.187P)^2 + 378.76P]$ where $P = (F_o^2 + 2F_c^2)/3$. Neutral atomic scattering factors were used with W and Os (f' and f'') corrected for anomalous dispersion. The number of parameters refined was 213. Final reliability factors for 2367 unique observed reflections [$F_o > 4\sigma(F_o)$] were $R = 0.0957$ and $wR = 0.2369$, with $(\Delta/\sigma)_{\text{max}} = 0.000$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 5.254/-5.533 \text{ e \AA}^{-3}$ in the final $\Delta\rho$ map and $S = 1.046$. Final positional parameters and $U_{\text{eq}}/U_{\text{iso}}$ for non-hydrogen atoms are given in Table 2.

Table 2
Final positional parameters for 2

Atom	x	y	z	U_{eq}^a
W	0.2245(1)	0.1527(1)	0.0167(1)	0.029(1)
Os(1)	0.1824(2)	0.1125(1)	0.1849(1)	0.031(1)
Os(2)	0.0654(1)	0.0883(1)	0.0211(1)	0.029(1)
Os(3)	0.0380(1)	0.1880(1)	-0.0083(1)	0.028(1)
O(1)	0.322(3)	0.154(1)	0.328(3)	0.05(1)
O(2)	0.195(4)	0.014(2)	0.271(3)	0.09(2)
O(3)	0.005(2)	0.130(1)	0.311(3)	0.06(1)
O(4)	-0.058(3)	0.037(2)	0.176(3)	0.08(1)
O(5)	0.195(3)	0.003(2)	-0.007(4)	0.08(1)
O(6)	-0.067(3)	0.066(2)	-0.148(3)	0.08(2)
O(7)	0.101(3)	0.279(1)	-0.105(3)	0.07(1)
O(8)	-0.034(3)	0.235(2)	0.175(3)	0.07(1)
O(9)	-0.138(2)	0.183(1)	-0.132(3)	0.06(1)
O(10)	0.191(3)	0.226(2)	0.176(3)	0.06(1)
C(1)	0.271(3)	0.139(2)	0.285(3)	0.04(1)
C(2)	0.188(4)	0.049(2)	0.246(4)	0.05(1)
C(3)	0.070(3)	0.126(1)	0.262(3)	0.02(1)
C(4)	-0.004(4)	0.054(2)	0.118(4)	0.06(2)
C(5)	0.146(3)	0.035(2)	0.009(3)	0.03(1)
C(6)	-0.023(3)	0.073(2)	-0.088(3)	0.02(1)
C(7)	0.077(4)	0.244(2)	-0.061(4)	0.06(2)
C(8)	-0.007(4)	0.222(2)	0.103(4)	0.05(1)
C(9)	-0.074(4)	0.186(2)	-0.096(4)	0.05(1)
C(10)	0.189(4)	0.197(2)	0.122(4)	0.06(2)
C	0.116(3)	0.147(2)	-0.089(3)	0.03(1)
C(11)	0.129(3)	0.132(2)	-0.195(3)	0.04(1)
C(12)	0.171(3)	0.086(2)	-0.222(3)	0.03(1)
C(13)	0.188(5)	0.082(3)	-0.317(5)	0.08(2)
C(14)	0.156(3)	0.116(2)	-0.397(3)	0.03(1)
C(15)	0.109(4)	0.154(2)	-0.358(4)	0.05(1)
C(16)	0.097(3)	0.161(2)	-0.264(3)	0.03(1)
C(17)	0.177(5)	0.104(3)	-0.503(5)	0.07(2)
C(51) ^b	0.305	0.222	-0.035	0.08(2)
C(52) ^b	0.367	0.195	0.031	0.04(1)
C(53)	0.394(5)	0.148(3)	-0.009(5)	0.08(2)
C(54)	0.347(4)	0.148(2)	-0.101(4)	0.06(2)
C(55)	0.294(3)	0.189(2)	-0.118(3)	0.03(1)

^a Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor. O(10) atom and all carbon atoms were refined isotropically.

^b C(51) and C(52) atoms were kept fixed during refinement.

2.13. X-ray data collection and structure solution of 6

Crystals of 6 suitable for X-ray analysis were obtained by slow recrystallization from dichloromethane-hexane at -10°C . A greenish brown crystal of approximate dimensions $0.2 \times 0.3 \times 0.1 \text{ mm}^3$ was mounted and aligned on a CAD4 diffractometer. Relevant crystallographic data are given in Table 1. The accurate cell parameters were refined from setting angles of 25 reflections with $10^\circ < \theta < 15^\circ$. The space group $P2_1/n$ was uniquely defined from the reflection conditions $h0l$: $h + l = 2n$; $0k0$: $k = 2n$. 5789 independent reflections in the range $0 < h < 21$, $0 < k < 24$, $-10 < l < 10$ were collected using graphite-monochromated Mo K α radiation and the $\omega/2\theta$ scan mode, ω -scan angle (0.8

$+ 0.35 \tan \theta$)^o, $\theta_{\text{max}} = 24^\circ$. One orientation reflection was checked every 200 reflections and three standard reflections were monitored every 180 min. The intensity

Table 3
Final positional parameters for 6

Atom	x	y	z	U_{eq}^a
W	0.7564(4)	0.1110(4)	0.2870(1)	0.033(1)
Os(1)	0.6019(4)	0.1322(4)	0.2942(1)	0.040(1)
Os(2)	0.6574(4)	0.0263(4)	0.1532(1)	0.037(1)
Os(3)	0.7541(4)	-0.0099(4)	0.3881(1)	0.034(1)
P	0.573(0)	0.215(0)	0.439(1)	0.04(0)
O(1)	0.635(1)	0.207(1)	0.031(2)	0.07(1)
O(2)	0.453(1)	0.123(1)	0.163(2)	0.10(1)
O(3)	0.573(1)	0.043(1)	0.531(2)	0.06(1)
O(4)	0.505(1)	-0.013(1)	0.161(2)	0.08(1)
O(5)	0.640(1)	0.093(1)	-0.128(2)	0.08(1)
O(6)	0.692(1)	-0.089(1)	-0.004(2)	0.08(1)
O(7)	0.907(1)	-0.002(1)	0.487(2)	0.07(1)
O(8)	0.695(1)	-0.031(1)	0.681(2)	0.09(1)
O(9)	0.767(1)	-0.142(1)	0.303(2)	0.08(1)
O(10)	0.789(1)	0.099(1)	0.611(2)	0.06(1)
C	0.774(1)	0.031(1)	0.194(2)	0.04(1)
C(1)	0.625(1)	0.179(1)	0.129(3)	0.06(1)
C(2)	0.512(1)	0.127(1)	0.218(3)	0.06(1)
C(3)	0.584(1)	0.075(1)	0.448(3)	0.06(1)
C(4)	0.562(1)	0.003(1)	0.156(3)	0.07(1)
C(5)	0.644(1)	0.068(1)	-0.026(3)	0.05(1)
C(6)	0.679(1)	-0.046(1)	0.055(3)	0.05(1)
C(7)	0.849(2)	-0.008(1)	0.456(2)	0.05(1)
C(8)	0.714(1)	-0.021(1)	0.567(2)	0.04(1)
C(9)	0.760(1)	-0.092(1)	0.335(3)	0.06(1)
C(10)	0.775(1)	0.094(1)	0.489(3)	0.04(1)
C(11)	0.822(1)	0.007(1)	0.084(2)	0.03(1)
C(12)	0.875(1)	-0.031(1)	0.120(3)	0.04(1)
C(13)	0.922(1)	-0.049(1)	0.027(3)	0.06(1)
C(14)	0.920(1)	-0.034(1)	-0.112(3)	0.05(1)
C(15)	0.863(1)	0.004(1)	-0.156(2)	0.04(1)
C(16)	0.817(1)	0.025(1)	-0.060(2)	0.04(1)
C(17)	0.968(1)	-0.058(1)	-0.214(3)	0.07(1)
C(21)	0.645(1)	0.250(1)	0.547(3)	0.06(1)
C(22)	0.651(1)	0.313(1)	0.555(3)	0.06(1)
C(23)	0.701(2)	0.334(2)	0.655(4)	0.10(1)
C(24)	0.747(2)	0.299(2)	0.728(4)	0.09(1)
C(25)	0.739(1)	0.239(2)	0.712(3)	0.08(1)
C(26)	0.690(1)	0.214(1)	0.623(3)	0.05(1)
C(31)	0.531(1)	0.275(1)	0.338(3)	0.04(1)
C(32)	0.569(1)	0.305(1)	0.234(3)	0.05(1)
C(33)	0.536(2)	0.350(1)	0.149(3)	0.08(1)
C(34)	0.470(2)	0.367(2)	0.168(4)	0.08(1)
C(35)	0.435(2)	0.341(1)	0.270(4)	0.08(1)
C(36)	0.462(1)	0.293(1)	0.353(3)	0.06(1)
C(41)	0.514(1)	0.198(1)	0.577(3)	0.05(1)
C(42)	0.519(2)	0.221(1)	0.712(3)	0.07(1)
C(43)	0.469(2)	0.214(2)	0.808(3)	0.08(1)
C(44)	0.417(2)	0.172(1)	0.783(5)	0.09(1)
C(45)	0.412(2)	0.148(1)	0.662(3)	0.08(1)
C(46)	0.462(1)	0.161(1)	0.561(4)	0.09(1)
C(51)	0.819(1)	0.196(1)	0.350(3)	0.05(1)
C(52)	0.864(2)	0.155(1)	0.302(3)	0.07(1)
C(53)	0.849(1)	0.142(1)	0.153(3)	0.05(1)
C(54)	0.792(1)	0.180(1)	0.114(5)	0.08(1)
C(55)	0.775(1)	0.213(1)	0.232(4)	0.07(1)

^a Equivalent isotropic U_{eq} defined as $U_{eq} = 1/3[U_{22} + (1/\sin^2 \beta)(U_{11} + U_{33} + 2U_{13} \cos \beta)]$.

variation was less than 1.3% during data collection; the decay correction was not applied to the data. All data were converted to E values following correction for L–P and absorption factors. The four heavy atoms were located using direct methods [8], and non-hydrogen atoms were found on subsequent difference Fourier maps. Hydrogen atoms were put in calculated positions with a bond distance of 1.08 Å. The whole structure was refined by full-matrix least-squares techniques [use of F magnitude with anisotropic thermal factors for all non-H atoms]. All H atoms were refined isotropically at the final cycle. The SHELX93 package [9] was used for all computations and the function minimized was $\sum w(F_o - F_c)^2$, with $w = 1/[\sigma^2 F_o^2 + (0.0632P)^2 + 0.00P]$ where $P = (F_o^2 + 2F_c^2)/3$. Neutral atomic scattering factors were used with W and Os (f' and f'') corrected for anomalous dispersion. The number of parameters refined was 532. Final reliability factors for 3573 unique observed reflections [$F_o > 4\sigma(F_o)$] were $R = 0.0510$ and $wR = 0.1081$, with $(\Delta/\sigma)_{\max} = 2.488$, $\Delta\rho_{\max}/\Delta\rho_{\min} = 1.48/-2.03 e \text{ \AA}^{-3}$ in the final $\Delta\rho$ map and $S = 1.042$. Final positional parameters and U_{eq} for non-hydrogen atoms are given in Table 3.

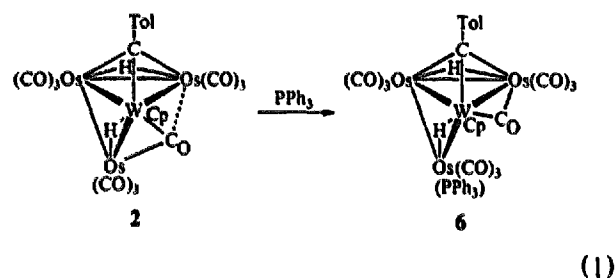
3. Results and discussion

3.1. Synthesis and characterization of 2 and 6

The reaction of $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})$ (1) with dihydrogen under pressure (50 psig) at 110 °C has been reported [5] to provide a hydrido-oxo-alkylidene complex, *syn*-3a, in which the tolyl substituent on the alkylidene carbon is oriented *syn* to the μ -oxo ligand with respect to the WOs_2 face associated with the three edge bridging groups (see Scheme 1). An analogous reaction under milder conditions (room temperature) after decarbonylation of 1 with the $\text{Me}_3\text{NO}/\text{CH}_3\text{CN}$ reagent affords a new cluster 2 in 55% yield. The formulation for 2 is established by mass spectroscopic and analytical data. The ^1H NMR spectrum of 2 reveals that it contains two inequivalent edge-bridging hydride ligands at $\delta = 12.02$ and -20.55 without a mutual H–H coupling. The signal at $\delta = 12.02$ with ^{183}W satellites ($^1J_{\text{WH}} = 100.8 \text{ Hz}$) and that at $\delta = -20.55$ are assigned to be bridging the W–Os(1) and Os(2)–Os(3) edges (vide infra) respectively, which is consistent with the observation that a hydrogen atom bridging a heterometal and an osmium atom has a resonance at lower field than that bridging two osmium atoms [10,11]. The ^{13}C NMR spectrum (CD_2Cl_2 , -80°C) of ^{13}C -enriched 2 shows ten carbonyl groups at δ 204.6 ($^1J_{\text{CW}} = 177.6 \text{ Hz}$), 181.9 (2CO), 179.4, 176.1, 173.9, 173.6 ($^2J_{\text{CH}} \approx 11.2 \text{ Hz}$), 172.8, 172.3 ($^2J_{\text{CH}} = 8.0 \text{ Hz}$), 170.6 ($^2J_{\text{CH}} \approx 11.3 \text{ Hz}$). The most downfield signal at δ 204.6 is assigned to the carbonyl group on the tungsten atom,

on the basis of its chemical shift and ^{183}W satellites [12]. The remaining nine resonances are due to the carbonyl groups on the osmium atoms. The three carbonyl groups [CO(3), CO(5) and CO(7)] *trans* to the bridging hydrides are doublets at δ 173.6, 172.3, and 170.6. The variable temperature (VT) ^{13}C NMR spectra of 2 show that all the carbonyl resonances broaden and coalesce at a similar rate, which precludes definitive assignments of the carbonyl resonances.

A 'butterfly' structure of 2 (vide infra) with 60 VE is apparently 2e-deficient based on ECR [6]. Analogous deviations from the rule have been encountered in several 'butterfly' complexes with 60 VE [13]. It is therefore of interest to investigate reactions of 2 with donor molecules in order to establish whether a 62 VE 'butterfly' species is readily attained. As expected, it undergoes facile reaction with PPh_3 to produce a saturated 'butterfly' complex with 62 VE, $\text{CpWOs}_3(\text{CO})_{10}(\text{PPh}_3)(\mu_3\text{-CTol})(\mu\text{-H})_2$ (6) (Eq. (1)).



Reaction of 2 with CO (30 psig), however, unexpectedly leads to reformation of the starting complex 1, presumably by reductive elimination of H_2 and subsequent coordination of CO from 2, which reveals a reversible interconversion between tetrahedral 1 and 'butterfly' 2, as shown in Scheme 1. The reversible skeletal isomerism between tetrahedral (60 VE) and 'butterfly' (62 VE) clusters has previously been reported in tetrametallic complexes such as $[\text{Fe}_4(\mu\text{-AlCO})_3]^-$ (A = Lewis acid ligands) [14] and $\text{LWRu}_3(\text{CO})_{12}\text{H}$ (L = $\eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5\text{Me}_5$) [15], in which the isomerization is accompanied by a change in the total electron count due to the conversion of an $\eta^1\text{-CO}$ to a $\mu_3\text{-}\eta^2\text{-CO}$ ligand. A similar skeletal rearrangement has been observed in platinum clusters with 58 VE, $\text{Cp}_2\text{Pt}_3\text{M}_2(\text{CO})_6(\text{PR}_3)_2$ (M = Mo, W) due to steric reasons [16]. The reaction of 2 with CO under H_2 at room temperature does not produce a 'butterfly' complex of $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})(\mu\text{-H})_2$ analogous to 6. It is not clear at the moment why the reaction of 2 with PPh_3 produces a simple adduct 6 but that with CO induces reductive elimination of H_2 to afford 1. Thermolysis of 2 in a wet toluene solvent leads to the formation of *syn*-3a by loss of a carbonyl ligand in a low yield (30%), a better yield (74%) being obtained by reaction under a pressure

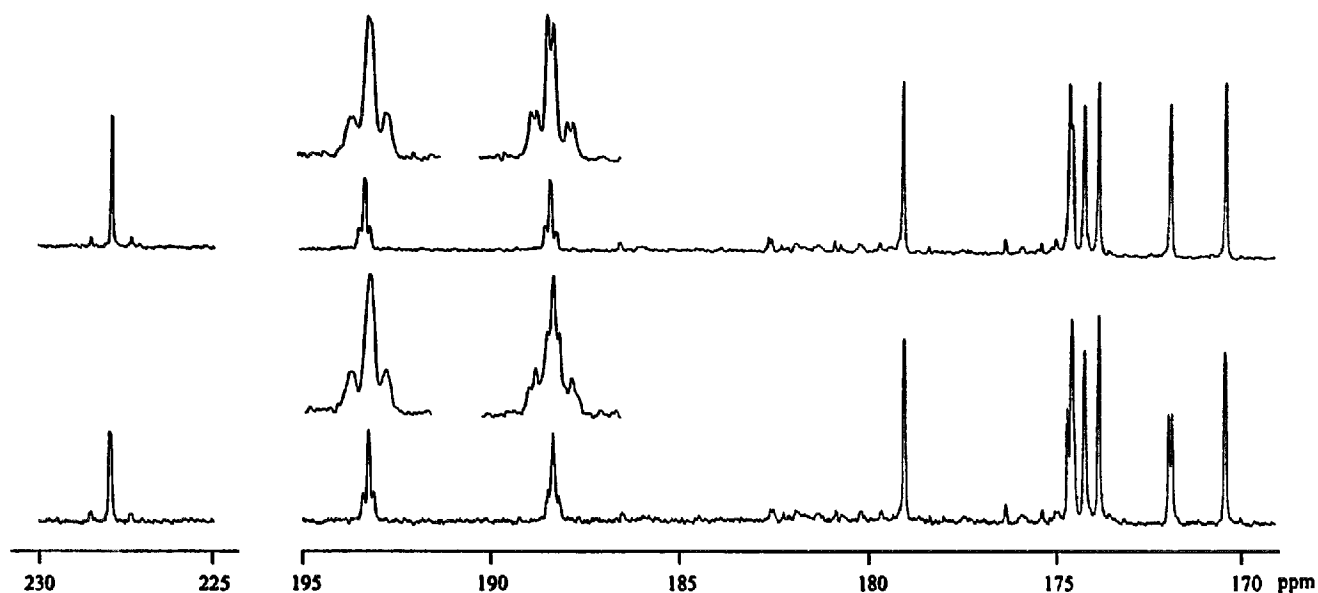


Fig. 1. ^{13}C NMR spectra (125 MHz, toluene- d_6 , carbonyl region) of $\text{CpWOS}_3(\text{}^* \text{CO})_{10}(\text{PPh}_3)_2(\mu_3\text{-CTol})(\mu\text{-H})_2$ (**6**) at 0°C : (upper) ^1H -decoupled; (lower) ^1H -coupled. Inserts are resonances due to inequivalent *trans* diaxial carbonyls.

(60 psig) of dihydrogen. The external dihydrogen may inhibit the reductive elimination of H_2 from **2**, resulting in the better yield of **3a**. Thermolysis of **2** at 110°C in the presence of water also gives a better yield (72%) of **3a**, indicating that the unsaturated cluster **2** reacts with water to afford **3a**.

The ^1H NMR spectrum of **6** also shows the two μ -hydride resonances at $\delta -14.29$ (d, $^2J_{\text{PH}} = 10.4$ Hz, $J_{\text{WH}} = 56.7$ Hz) and -20.30 (s). The former resonance at $\delta -14.29$ with both W–H and P–H couplings is assigned to the μ -hydride on the W–Os(1) edge, which indicates that the PPh_3 ligand is coordinated on the ‘wing-tip’ Os(1) atom associated with the μ -H ligand. The latter resonance at $\delta -20.30$ is due to the μ -hydride on the Os(2)–Os(3) edge. The limiting low temperature ^{13}C NMR spectrum of ^{13}C -enriched **6** (see Fig. 1) was obtained at 0°C and is consistent with the molecular structure observed in the solid state (vide infra). The spectrum shows ten carbonyl resonances at δ 227.9, 193.2, 188.2, 178.9, 174.6, 174.5, 174.1, 173.7, 171.8, and 170.3 (each of intensity 1). The most downfield signal at 227.9 with $^1J_{\text{CW}} = 147.1$ Hz is assigned to the carbonyl group [CO(10)] on the tungsten atom. The resonances at δ 193.2 and 188.2 reveal an AB pattern of ^{13}C satellites ($^2J_{\text{CC}} = 35.2$ Hz), characteristic of inequivalent *trans* diaxial carbonyls CO(1) and CO(3) [11,17]. The latter resonance is further split into a doublet due to a coupling to the phosphorus atom, six peaks with $^2J_{\text{CP}} = 5.7$ Hz, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (see the inset to the upper spectrum). This C–P coupling between mutually *cis* carbonyl and phosphine ligands is rather unusual, but preceded in other complexes such as ‘butterfly’ $\text{CpWOS}_3(\text{CO})_9[\text{P}(\text{OMe})_3](\mu_3\text{-CCH}_2\text{Tol})$ and tetrahedral $\text{CpWOS}_3(\text{CO})_8[\text{P}(\text{OMe})_3](\mu$

$\text{O})(\mu_3\text{-CCH}_2\text{Tol})$ [18]. The remaining seven resonances are assigned to the rest of the carbonyl ligands on the osmium atoms. Of the ten carbonyl resonances, four signals show couplings to the bridging hydrides at δ 227.9 ($^2J_{\text{CH}} = 7.0$ Hz), 188.2 ($^2J_{\text{CH}} = 6.1$ Hz), 174.6 ($^2J_{\text{CH}} = 13.8$ Hz) and 171.8 ($^2J_{\text{CH}} = 11.3$ Hz). These couplings were verified by obtaining the ^1H -coupled spectrum as shown in Fig. 1. The doublet of an AB pattern at δ 188.2 exhibits a triplet of an AB pattern, a superimposition of a dd splitting of the AB pattern with $^2J_{\text{CP}} \approx ^2J_{\text{CH}}$, in the ^1H -coupled spectrum of **6** (see the insert to the bottom spectrum). The carbonyl ligand on the tungsten atom [CO(10)] and either one [presumably CO(3)] of the *trans* diaxial ligands on the Os(1) atom appear to couple to the μ -H on the W–Os(1) edge. The two carbonyl groups CO(5) and CO(7), *trans* to the μ -H on the Os(2)–Os(3) edge, are doublets at δ 174.6 and 171.8. The VT ^{13}C NMR spectra of **6** cannot be obtained at higher temperatures ($> 50^\circ\text{C}$) due to the thermal instability of **6**.

3.2. Crystal structures of **2** and **6**

The crystal of **2** or **6** 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. 2 for **2** and Fig. 3 for **6**. Interatomic distances and bond angles of **2** and **6** are listed in Tables 4–7 respectively.

Both tetranuclear molecules, **2** and **6**, contain a ‘butterfly’ arrangement of metal atoms with a respective dihedral angle of $114.3(2)^\circ$ and $113.6(4)^\circ$ between the

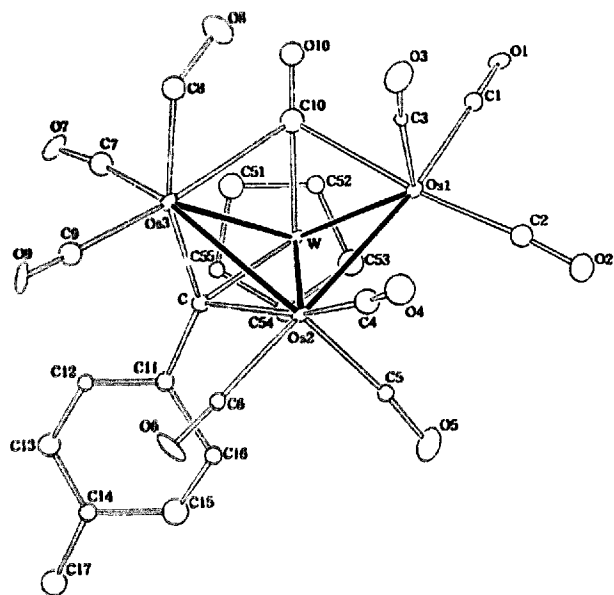


Fig. 2. Molecular geometry and atomic labeling scheme for 2.

W–Os(2)–Os(1) and W–Os(2)–Os(3) planes, typical of a 62 VE tetranuclear array [6]. Compound 2, however, is associated with 60 VE and 2e-deficient based on ECR [6]. Each molecule consists of three Os(CO)₃ units and a CpW(CO) fragment, except that the Os(1) center in 6 is additionally coordinated with a triphenylphosphine ligand resulting in a 62 VE of 6. Complex 6 is derived from complex 2 by an addition of the PPh₃ ligand to the Os(1) center. The unusually short W–Os(1) distance of 2.624(5) Å of 2 is believed to be due to the formally electron-poor nature of the W (17.5e) and Os(1) (16.5e) centers, which could be compensated for by an increased bond order in the W–Os(1) linkage [19]. The longest of the metal–metal bonds, W–Os(1) = 3.024(3) Å of 6, is assumed to be associated with a single, unsup-

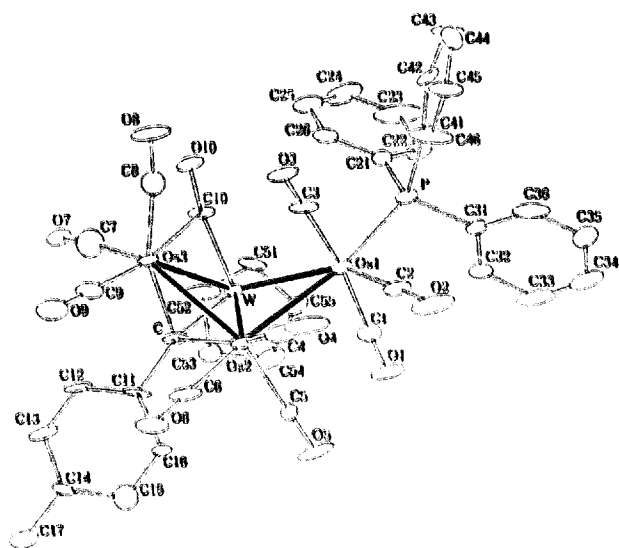


Fig. 3. Molecular geometry and atomic labeling scheme for 6.

Table 4
Interatomic distances (Å) and e.s.d.s for 2

(A) Metal–metal distances			
Os(1)–Os(2)	2.859(3)	Os(1)–W	2.625(5)
Os(2)–Os(3)	2.890(3)	Os(2)–W	2.907(3)
Os(3)–W	2.849(3)		
(B) Metal–alkylidyne distances			
W–C	2.11(4)	Os(2)–C	2.35(5)
Os(3)–C	1.95(4)		
(C) Distances within the μ_3 -CTol ligand			
C–C(11)	1.51(6)	C(11)–C(12)	1.48(7)
C(12)–C(13)	1.32(8)	C(13)–C(14)	1.51(8)
C(14)–C(15)	1.38(7)	C(14)–C(17)	1.51(8)
C(15)–C(16)	1.31(7)	C(16)–C(11)	1.33(6)
(D) Metal–carbon (carbonyl) distances			
Os(1)–C(1)	2.00(5)	Os(2)–C(4)	1.91(6)
Os(1)–C(2)	1.99(6)	Os(2)–C(5)	1.92(5)
Os(1)–C(3)	1.94(4)	Os(2)–C(6)	2.00(4)
Os(3)–C(7)	1.83(7)	W–C(10)	1.98(6)
Os(3)–C(8)	1.90(6)	Os(1)–C(10)	2.55(7)
Os(3)–C(9)	1.99(6)	Os(3)–C(10)	2.76(7)
(E) Carbon–oxygen (carbonyl) distances			
C(1)–O(1)	1.02(5)	C(2)–O(2)	1.07(7)
C(3)–O(3)	1.14(5)	C(4)–O(4)	1.20(6)
C(5)–O(5)	1.16(6)	C(6)–O(6)	1.04(5)
C(7)–O(7)	1.22(7)	C(8)–O(8)	1.12(6)
C(9)–O(9)	1.03(6)	C(10)–O(10)	1.10(7)
(F) Metal–carbon (Cp) distances			
W–C(51)	2.39(2)	W–C(52)	2.35(2)
W–C(53)	2.43(7)	W–C(54)	2.36(6)
W–C(55)	2.32(4)		
(G) Distances within the Cp ligand			
C(51)–C(52)	1.48(1)	C(51)–C(55)	1.47(4)
C(52)–C(53)	1.50(8)	C(53)–C(54)	1.41(8)
C(54)–C(55)	1.42(8)		

ported μ -hydride ligand [20]. The PPh₃ ligand takes up a position *trans* to the Os(1)–Os(2) bond and the Os(1)–P distance is 2.371(7) Å. The carbonyl ligand C(10)–O(10) on the tungsten atom of 2 is semi-triple bridging [W–C(10) = 1.96(7), Os(1) \cdots C(10) = 2.52(7), and Os(3) \cdots C(10) = 2.76(7) Å], but that of 6 is semi-double bridging [W–C(10) = 1.94(3) and Os(3) \cdots C(10) = 2.54(2) Å]. The μ_3 -alkylidyne ligand caps unsymmetrically the respective W–Os(2)–Os(3) face of 2 and 6. All other distances and angles observed for 2 and 6 are in the normally accepted ranges.

3.3. Synthesis and characterization of intermediates 4, 5, and 3b,c for the formation of 3a

The unexpected formation of the μ -oxo ligand has been observed in the conversion of 1 \rightarrow 3a [5]. Similarly, the oxo-alkyne complexes CpWOs₃(CO)₈(μ -O)(μ_3 - η^2 -C₂R₂)(μ -H) (R = H, Ph, Tol) have been re-

Table 5
Interatomic angles (deg) and e.s.d.s for 2

(A) Intermetallic angles			
Os(1)–W–Os(2)	62.0(1)	Os(2)–W–Os(3)	60.3(1)
Os(1)–W–Os(3)	92.7(1)	Os(2)–Os(1)–W	63.9(1)
Os(2)–Os(3)–W	60.9(1)	W–Os(2)–Os(1)	54.2(1)
W–Os(2)–Os(3)	58.9(1)	Os(1)–Os(2)–Os(3)	87.1(1)
(B) M–M–CO angles			
W–Os(1)–C(1)	107(1)	Os(2)–Os(1)–C(1)	170(1)
W–Os(1)–C(2)	139(2)	Os(2)–Os(1)–C(2)	98(2)
W–Os(1)–C(3)	125(2)	Os(2)–Os(1)–C(3)	90(1)
W–Os(2)–C(4)	138(2)	Os(1)–Os(2)–C(4)	84(2)
W–Os(2)–C(5)	92(1)	Os(1)–Os(2)–C(5)	85(1)
W–Os(2)–C(6)	128(1)	Os(1)–Os(2)–C(6)	176(1)
Os(3)–Os(2)–C(4)	122(2)	W–Os(3)–C(7)	94(2)
Os(3)–Os(2)–C(5)	148(1)	W–Os(3)–C(8)	113(2)
Os(3)–Os(2)–C(6)	92(1)	W–Os(3)–C(9)	143(2)
Os(2)–Os(3)–C(7)	150(2)	Os(1)–W–C(10)	66(2)
Os(2)–Os(3)–C(8)	116(2)	Os(2)–W–C(10)	100(2)
Os(2)–Os(3)–C(9)	99(2)	Os(3)–W–C(10)	68(2)
Os(2)–Os(1)–C(10)	89(1)	W–Os(1)–C(10)	45(1)
(C) Os–C–O and C–Os–C angles			
Os(1)–C(1)–O(1)	172(4)	C(1)–Os(1)–C(10)	81(2)
Os(1)–C(2)–O(2)	173(5)	C(2)–Os(1)–C(10)	173(2)
Os(1)–C(3)–O(3)	175(4)	C(3)–Os(1)–C(10)	92(2)
Os(2)–C(4)–O(4)	171(5)	C(1)–Os(1)–C(2)	92(2)
Os(2)–C(5)–O(5)	174(4)	C(1)–Os(1)–C(3)	94(2)
Os(2)–C(6)–O(6)	176(4)	C(2)–Os(1)–C(3)	89(2)
Os(3)–C(7)–O(7)	173(5)	C(4)–Os(2)–C(5)	88(2)
Os(3)–C(8)–O(8)	169(5)	C(4)–Os(2)–C(6)	94(2)
Os(3)–C(9)–O(9)	171(5)	C(5)–Os(2)–C(6)	98(2)
W–C(10)–O(10)	161(5)	C(7)–Os(3)–C(8)	88(3)
Os(1)–C(10)–O(10)	119(5)	C(7)–Os(3)–C(9)	92(2)
C(10)–Os(1)–C(1)	81(2)	C(8)–Os(3)–C(9)	103(2)
C(10)–Os(1)–C(2)	173(2)	C(10)–Os(1)–C(3)	92(2)
(D) Angles involving C			
Os(1)–W–C	113(1)	Os(3)–Os(2)–C	42(1)
Os(2)–W–C	53(1)	Os(1)–Os(2)–C	99(1)
Os(3)–W–C	43(1)	Os(2)–Os(3)–C	54(1)
W–Os(3)–C	48(1)	C(4)–Os(2)–C	163(2)
C(5)–Os(2)–C	109(2)	C(6)–Os(2)–C	83(2)
C(7)–Os(3)–C	98(2)	C(8)–Os(3)–C	160(2)
C(9)–Os(3)–C	96(2)	W–Os(2)–C	46(1)
C(10)–W–C	112(2)		
(E) Angles within the μ_3-CTol ligand			
C–C(11)–C(12)	122(4)	C–C(11)–C(16)	117(4)
C(11)–C(12)–C(13)	114(5)	C(12)–C(13)–C(14)	126(6)
C(13)–C(14)–C(15)	112(5)	C(14)–C(15)–C(16)	124(5)
C(15)–C(14)–C(17)	129(5)	C(13)–C(14)–C(17)	119(5)
C(11)–C(16)–C(15)	123(5)	C(12)–C(11)–C(16)	120(4)
(F) Angles within the Cp ligand			
C(51)–C(52)–C(53)	114(3)	C(52)–C(51)–C(55)	101(2)
C(52)–C(53)–C(54)	101(5)	C(53)–C(54)–C(55)	114(6)
C(51)–C(55)–C(54)	110(4)		

ported to be produced in the thermolysis of alkyne complexes, $\text{CpWOS}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{R}_2)(\mu\text{-H})$. The μ -oxo ligand may be derived from a CO ligand by a C–O bond scission or from other possible sources (H_2O , O_2 , Me_3NO , etc.) [21]. It has been reported that

the μ -oxo ligands in $\text{CpWOS}_3(\text{CO})_9(\mu\text{-O})_2(\mu\text{-H})$ clearly have not been originated from Me_3NO used for decarbonylation and have not been formed in a carefully dried solvent [22]. In order to elucidate the source of the μ -oxo ligand, the reactivity of **1** towards H_2O is examined. Initial decarbonylation of **1** and subsequent reaction with H_2O affords a μ -oxo alkyldyne complex $\text{CpWOS}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CTol})$ (**4**) in 54% yield. The IR spectrum of **4** is identical to that of its homologue (**4** + CH_2), $\text{CpWOS}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ (**7**) [23], which has been structurally characterized previously. The μ -oxo ligand in **7** is originated from the thermal acyl C–O bond scission of $\text{CpWOS}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C}(\text{O})\text{CH}_2\text{Tol}]$ [24]. Complex **4** is isostructural [25] with **7** and has a 'butterfly' arrangement (62 VE) of

Table 6
Interatomic distances (Å) and e.s.d.s for 6

(A) Metal–metal distances			
Os(1)–Os(2)	2.942(2)	Os(1)–W	3.024(3)
Os(2)–Os(3)	2.928(3)	Os(2)–W	2.930(2)
Os(3)–W	2.870(3)		
(B) Metal–alkyldyne distances			
W–C	2.04(2)	Os(3)–C	2.08(2)
Os(2)–C	2.26(2)		
(C) Metal–phosphorus distances			
Os(1)–P	2.371(7)		
(D) Distances within the μ_3-CTol ligand			
C–C(11)	1.52(3)	C(11)–C(12)	1.35(3)
C(12)–C(13)	1.36(3)	C(13)–C(14)	1.34(3)
C(14)–C(15)	1.44(3)	C(14)–C(17)	1.46(3)
C(15)–C(16)	1.38(3)	C(11)–C(16)	1.40(3)
(E) Metal–carbon (carbonyl) distances			
Os(1)–C(1)	1.94(3)	Os(1)–C(2)	1.84(2)
Os(1)–C(3)	1.96(3)	Os(2)–C(4)	1.92(2)
Os(2)–C(5)	1.92(3)	Os(2)–C(6)	1.92(3)
Os(3)–C(7)	1.90(3)	Os(3)–C(8)	1.90(2)
Os(3)–C(9)	1.91(3)	Os(3)–C(10)	2.54(2)
W–C(10)	1.94(3)		
(F) Carbon–oxygen (carbonyl) distances			
C(1)–O(1)	1.13(3)	C(2)–O(2)	1.24(3)
C(3)–O(3)	1.10(3)	C(4)–O(4)	1.15(2)
C(5)–O(5)	1.11(3)	C(6)–O(6)	1.14(3)
C(7)–O(7)	1.16(3)	C(8)–O(8)	1.17(2)
C(9)–O(9)	1.16(3)	C(10)–O(10)	1.17(3)
(G) Metal–carbon (Cp) distances			
W–C(51)	2.32(2)	W–C(52)	2.30(2)
W–C(53)	2.35(2)	W–C(54)	2.36(3)
W–C(55)	2.37(2)		
(H) Distances within the Cp ligand			
C(51)–C(52)	1.36(3)	C(51)–C(55)	1.41(4)
C(52)–C(53)	1.45(3)	C(53)–C(54)	1.42(3)
C(54)–C(55)	1.40(4)		
(I) Phosphorus–carbon distances			
P–C(21)	1.85(3)	P–C(31)	1.81(2)
P–C(41)	1.81(2)		

Table 7
Interatomic angles (deg) and e.s.d.s for 6

(A) <i>Intermetallic angles</i>			
Os(1)–W–Os(2)	59.2(1)	Os(2)–W–Os(3)	60.6(1)
Os(1)–W–Os(3)	96.3(0)	Os(2)–Os(1)–W	58.8(0)
Os(2)–Os(3)–W	60.7(0)	W–Os(2)–Os(1)	62.0(1)
W–Os(2)–Os(3)	58.7(1)	Os(1)–Os(2)–Os(3)	96.8(1)
(B) <i>M–M–CO angles</i>			
W–Os(1)–C(1)	78.6(7)	Os(2)–Os(1)–C(1)	88.3(7)
W–Os(1)–C(2)	152.8(8)	Os(2)–Os(1)–C(2)	97.6(8)
W–Os(1)–C(3)	97.2(7)	Os(2)–Os(1)–C(3)	83.6(7)
W–Os(2)–C(4)	141.2(9)	Os(1)–Os(2)–C(4)	81.0(8)
W–Os(2)–C(5)	96.7(7)	Os(1)–Os(2)–C(5)	88.3(6)
W–Os(2)–C(6)	126.6(6)	Os(1)–Os(2)–C(6)	171.4(6)
Os(3)–Os(2)–C(4)	119.6(8)	W–Os(3)–C(7)	93.5(7)
Os(3)–Os(2)–C(5)	147.2(6)	W–Os(3)–C(8)	115.4(7)
Os(3)–Os(2)–C(6)	88.8(7)	W–Os(3)–C(9)	145.1(8)
Os(2)–Os(3)–C(7)	144.3(6)	Os(1)–W–C(10)	97.9(6)
Os(2)–Os(3)–C(8)	115.1(6)	Os(2)–W–C(10)	111.8(6)
Os(2)–Os(3)–C(9)	96.7(8)	Os(3)–W–C(10)	60.0(6)
(C) <i>C–Os–C angles</i>			
C(1)–Os(1)–C(2)	89(1)	C(7)–Os(3)–C(8)	97(1)
C(1)–Os(1)–C(3)	171(1)	C(7)–Os(3)–C(9)	92(1)
C(2)–Os(1)–C(3)	92(1)	C(8)–Os(3)–C(9)	97(1)
C(4)–Os(2)–C(5)	93(1)	C(10)–Os(3)–C(7)	75(1)
C(4)–Os(2)–C(6)	91(1)	C(10)–Os(3)–C(8)	83(1)
C(5)–Os(2)–C(6)	91(1)	C(10)–Os(3)–C(9)	166(1)
(D) <i>Angles involving C</i>			
Os(1)–W–C	109(1)	Os(3)–Os(2)–C	45(1)
Os(2)–W–C	50(1)	Os(1)–Os(2)–C	106(1)
Os(3)–W–C	46(1)	Os(2)–Os(3)–C	50(1)
W–Os(3)–C	45(1)	C(4)–Os(2)–C	163(1)
C(5)–Os(2)–C	102(1)	C(6)–Os(2)–C	83(1)
C(7)–Os(3)–C	94(1)	C(8)–Os(3)–C	158(1)
C(9)–Os(3)–C	100(1)	W–C–Os(2)	86(1)
C(10)–Os(3)–C	84(1)	Os(2)–C–Os(3)	85(1)
(E) <i>Angles within the μ_3-CTol ligand</i>			
C–C(11)–C(12)	122(2)	C(13)–C(14)–C(15)	115(2)
C–C(11)–C(16)	122(2)	C(13)–C(14)–C(17)	123(2)
C(12)–C(11)–C(16)	116(2)	C(15)–C(14)–C(17)	122(2)
C(11)–C(12)–C(13)	123(2)	C(14)–C(15)–C(16)	121(2)
C(12)–C(13)–C(14)	124(2)	C(11)–C(16)–C(15)	120(2)
(F) <i>Angles within the Cp ligand</i>			
C(51)–C(52)–C(53)	111(3)	C(52)–C(51)–C(55)	107(3)
C(52)–C(53)–C(54)	104(3)	C(53)–C(54)–C(55)	109(3)
C(51)–C(55)–C(54)	109(3)		
(G) <i>P–M–C angles</i>			
P–Os(1)–C(1)	96.2(8)	P–Os(1)–C(3)	91.7(7)
P–Os(1)–C(2)	91.6(8)		
(H) <i>M–P–C and P–C–C angles</i>			
Os(1)–P–C(21)	117(1)	C(21)–P–C(31)	105(1)
Os(1)–P–C(31)	113(1)	C(21)–P–C(41)	101(1)
Os(1)–P–C(41)	115(1)	C(31)–P–C(41)	104(1)
P–C(21)–C(22)	122(2)	P–C(31)–C(36)	124(2)
P–C(21)–C(26)	118(2)	P–C(41)–C(42)	124(2)
P–C(31)–C(32)	119(2)	P–C(41)–C(46)	124(2)

metal atoms with the μ -oxo ligand bridging the W–Os(CO)₃ ('wing-tip') edge as a well-documented, bent W=O; \rightarrow Os system [19]. The formation of μ -oxo

complex 4 unambiguously proves that the μ -oxo ligand comes from water in the solvent. A likely pathway for the formation of 4 may be loss of a carbonyl ligand from 1, followed by formation of the 'butterfly' hydrido hydroxo complex CpWOs₃(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 H₂. A facile conversion of hydroxo complex Re(OH)(C₂Et₂)₃ to oxo hydride complex Re(O)(H)(C₂Et₂)₂ has appeared in the literature [26].

Thermolysis of 4 at 110°C induces decarbonylation to give a tetrahedral alkylidyne complex CpWOs₃(CO)₉(μ -O)(μ_3 -CTol) (5), which is reversibly converted back to 4 upon exposure to CO at 110°C in a quantitative yield. The transformation from 4 to 5 reveals another reversible 'butterfly' to tetrahedral cluster rearrangement. Complex 5 reacts readily with dihydrogen in refluxing toluene to afford a mixture of three isomeric hydrido-oxo-alkylidene clusters CpWOs₃(CO)₉(μ -O)(μ -CHTol)(μ -H) (*anti*-3b,c and *syn*-3a). The ratio of three isomers (3a,b,c) is identified by integration of ¹H NMR resonances as 3.1:1.0:1.8 respectively, after reaction of 5 with H₂ for 2 h.

A mixture of 3b,c is not chromatographically separable, but can be separated from 3a by preparative TLC with a multiple elution method. Complexes 5 and 3b,c show essentially the same spectroscopic data as those of homologues CpWOs₃(CO)₉(μ -O)(μ_3 -CCH₂Tol) (8) [24] and *anti*-CpWOs₃(CO)₉(μ -O)(μ -CHCH₂Tol)(μ -H) (9a,b) [27,28], and therefore are isostructural with 8 and 9a,b respectively. The key stereochemical feature of 3b,c is that the tolyl substituent is oriented away (*anti*) from the μ -oxo group. The ¹H NMR spectrum of 3b,c in CDCl₃ exhibits two hydride resonances at δ = 16.77 (s, 3b) and –18.52 (d, ¹J_{HM} = 1.9 Hz, 3c) and two alkylidene hydrogen resonances at δ 5.82 (s, 3b) and 4.88 (d, ¹J_{HM} = 1.9 Hz, 3c). The resonance at δ 4.88 with ¹J_{HM} = 1.9 Hz is assigned to the alkylidene hydrogen of 3c, which implies that the hydride and the alkylidene ligands in 3c bridge the adjacent metal–metal bonds. Complex 3a also reveals a coupling (³J_{HM} = 1.7 Hz) between μ -H (δ –18.05) and μ -CH (δ 5.52) hydrogens.

Analogous conversions of 4 \rightleftharpoons 5 \rightarrow 3b,c \rightarrow 3a have also been reported for their homologues [23,27,28] and molybdenum homologues [29]. The hydride migration interconvert 3b and 3c with $K_{cy} = [3c]/[3b] = 1.65(6)$ which compares with $K_{cy} = [9b]/[9a] = 0.67(5)$ of their homologues [27] at room temperature. The rate of *anti* \rightarrow *syn* isomerization of 3b,c \rightarrow 3a (110°C) is faster than that of its homologues (140°C) [30]. The relative thermodynamic stability of the *anti*- and *syn*-isomers has been explained by steric interactions of the bulky substituent on the alkylidene carbon with the Cp ligand [29], which implies that the steric repulsion is larger in the present tolyl group compared with the CH₂Tol

group. The $-\text{CH}_2-$ moiety between the alkylidene carbon and tolyl group in the homologue complexes may relieve the direct steric interaction of the tolyl group with the Cp ligand.

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** and **6** are available from the authors.

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