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Synthesis of tetranuclear heterometallic cluster complexes via condensation of triosmium alkyne complexes $Os_3(CO)_{10}(C_2R_2)$, R = Tol and Me, and mononuclear tungsten acetylide complexes $LW(CO)_3C{\equiv}CR'$, L = Cp and Cp*, R' = Ph and ^{t}Bu

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Abstract

Condensation of triosmium alkyne complexes $Os_3(CO)_{10}(C_2R_2)$, R = Tol and Me, with mononuclear tungsten acetylide complexes $LW(CO)_3C{\equiv}CR'$, L = Cp and Cp*, R' = Ph and ^{t}Bu generated six WOs_3 cluster complexes via 1:1 combination of the starting materials. The tetrahedral complexes $LWOs_3(CO)_9[CC(R')C(R)C(R)]$ (**1**) formed via coupling of the ligated alkyne with the β-carbon of the acetylide ligand were observed in all cases studied. The planar rhomboidal cluster $CpWOs_3(CO)_{10}[C(Me)C(Me)CC(Ph)]$ (**2**), generated via coupling of the ligated alkyne with the α-carbon of the acetylide ligand, was isolated only from the reaction between $Os_3(CO)_{10}(C_2Me_2)$ and $CpW(CO)_3C{\equiv}CPh$. On thermolysis, complex **2** loses one CO to afford $CpWOs_3(CO)_9(\mu\text{-H})[CMeCMeCC(\mu_2\text{-}\eta^2\text{-}C_6H_4)]$ (**7**) via *ortho*-metallation of the phenyl substituent and $CpWOs_3(CO)_9(CCMeCMe)(\mu_3\text{-CPh})$ (**3a**) via cleavage of the C–C bond of the ligated C_4 hydrocarbon fragment, confirming that the alkylidyne and the coordinated C_3 hydrocarbon ligands in **3a** were generated via alkyne–acetylide coupling followed by cleavage of a C–C bond. For the reaction between $Os_3(CO)_{10}(C_2Me_2)$ and $Cp^*W(CO)_3C{\equiv}CPh$, in addition to the expected complexes **1e** and **3e** (L = Cp*; R' = Ph), we observed the formation of three new complexes $Cp^*WOs_3(CO)_9(C_2Me_2)(\mu_3\text{-CCPh})$ (**4**), $Cp^*WOs_3(CO)_9(C_2Me_2)(\mu_4\text{-CCPh})$ (**5**) and $Cp^*WOs_3(CO)_9(\mu_3\text{-CPh})[CC(Me)C(Me)CO]$ (**6**). The X-ray structural determination reveals that the butyne and acetylide ligands in butterfly complexes **4** and **5** remain as two uncoupled entities. Complexes **4** and **5** are not the precursors for the formation of other cluster complexes, as pyrolysis of these two complexes in refluxing toluene failed to afford substantial amount of butyne–acetylide coupling products. Finally, the tetrahedral complex **6** possesses two triply bridging alkylidyne ligands and a triply bridging CO ligand; the formation of alkylidyne ligands occurs via a C–C bond scission of a ligated CMeCMeCCPh fragment, except that a CO ligand inserts into the linkage

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[1] For inquiries concerning the X-ray crystallographic work.

between the butyne fragment and the transition metal. The structures of complexes **1b**, **4**, **5** and **6** were determined by X-ray analysis. Crystal data for **1b**: space group $P2_1/c$; $a = 18.349(3)$, $b = 11.371(2)$, $c = 19.319(3)$ Å, $\beta = 97.89(1)^\circ$, $Z = 4$; final $R_F = 0.051$, $R_w = 0.077$ for 3392 reflections with $I > 2\sigma(I)$. Crystal data for **4**: space group $P\bar{1}$; $a = 9.982(2)$, $b = 10.153(1)$, $c = 17.410(5)$ Å, $\alpha = 100.94(2)$, $\beta = 90.88(2)$, $\gamma = 111.70(1)^\circ$, $Z = 2$; final $R_F = 0.029$, $R_w = 0.027$ for 4798 reflections with $I > 2\sigma(I)$. Crystal data for **5**: space group $P2_1/c$; $a = 13.721(6)$, $b = 14.791(4)$, $c = 16.880(8)$ Å, $\beta = 111.74(4)^\circ$, $Z = 4$; final $R_F = 0.030$, $R_w = 0.032$ for 4300 reflections with $I > 2\sigma(I)$. Crystal data for **6**: space group $P2_1/c$; $a = 13.910(3)$, $b = 14.375(6)$, $c = 16.490(8)$ Å, $\beta = 95.16(3)^\circ$, $Z = 4$; final $R_F = 0.045$, $R_w = 0.053$ for 4555 reflections with $I > 2\sigma(I)$.

Introduction

The reactivity of heterometallic clusters has been of interest for many years. Research in this area is stimulated by a belief that the combination of metals with different electric and steric properties within one molecule may induce unique chemical transformations. In seeking to develop a systematic method to prepare polynuclear mixed-metal clusters and to exploit the chemistry of the hydrocarbon fragment in the ligand sphere of mixed-metal clusters, we [1] and others [2] have used transition metal acetylide complexes as building blocks to generate various mixed-metal acetylide complexes. For the reaction of $CpW(CO)_3C{\equiv}CR'$ with $Os_3(CO)_{10}(NCMe)_2$, we isolated a tetranuclear acetylide complex $CpWOs_3(CO)_{11}(C{\equiv}CR')$ ($R' =$ Ph and ^nBu) which possesses a novel μ_4-η^2 acetylide ligand [3]. The reactivity of these WOs_3 acetylide clusters toward various disubstituted alkynes has also been studied [4]. Treatment with disubstituted alkynes containing electron-withdrawing groups produces two alkyne–acetylide coupling products $CpWOs_3(CO)_9[CC(Ph)C(R)C(R)]$ and $CpWOs_3(CO)_{10}$-$[C(R)C(R)CC(Ph)]$, $R = CO_2Et$ and CO_2Me. The former is produced via simple coupling of one alkyne molecule with the β-carbon of the coordinated acetylide ligand, and the latter, coupling with the α-carbon. We failed to isolate any product formed by the addition of 2 equiv. of alkyne in these reactions. In contrast to these experimental results, treatment with ditolylacetylene affords a planar complex $CpWOs_3(CO)_8(\mu_3\text{-CPh})[\mu_4\text{-}\eta^5\text{-}C(C_2Tol_2)_2]$ which possesses an alkylidyne ligand and a C_5 alkylidene moiety formed via addition of two ditolylacetylenes, removal of three CO ligands and cleavage of the acetylide C–C bond. One plausible reaction pathway involves a prior addition of one ditolylacetylene to give a C_4 fragment similar to that observed in complexes $CpWOs_3(CO)_{10}[C(R)C(R)CC(Ph)]$, followed by the reaction with a second ditolylacetylene and cleavage of the C–C bond to give the triply bridging alkylidyne and the C_5 alkylidene moiety. However, we failed to confirm this mechanism because we have not yet isolated any complex that was produced via addition of one equivalent of ditolylacetylene to the acetylide complex $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ even under the condition that only an equimolar proportion of ditolylacetylene was employed. In order to synthesize unobserved products of the general structural formula $CpWOs_3(CO)_9[CC(Ph)C(R)C(R)]$ and $CpWOs_3(CO)_{10}[C(R)C(R)CC(Ph)]$ where R is an electron-releasing substituent, and to carry out the subsequent reactivity study with alkyne, we performed the condensation of tungsten acetylide with triosmium alkyne complexes $Os_3(CO)_{10}(C_2R_2)$, $R =$ Tol and Me; by using the triosmium alkyne complexes, we can accurately control the ratio of alkyne and acetylide present in the final product. In this paper, we report full details of these condensation reactions. A portion of the results, concerning the cluster framework rearrangement of $CpWOs_3(CO)_{10}[C(Me)C(Me)CC(Ph)]$ (**2**) [5] and with the treatment of $LWOs_3(CO)_9(CCRCR)(\mu_3\text{-}CPh)$, L = Cp, R = Tol (**3a**); L = Cp*, R = Me (**3e**), with alkyne [6] have appeared in two separate preliminary reports.

Experimental procedure

General information and materials

Infrared spectra were recorded on a Bomen M-100 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz) instrument or a Varian Gemini-300 (300 MHz) instrument. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast-atom bombardment (FAB) mode. All reactions were performed under a dinitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of the reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan. The triosmium alkyne complexes $Os_3(CO)_{10}(C_2R_2)$, R = Me and Tol, were prepared from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 2-butyne or with ditolylacetylene in dichloromethane solution at room temperature [7]. The tungsten acetylide complexes $LW(CO)_3C{\equiv}CR'$, L = Cp and Cp *; R' = Ph and ^tBu, were prepared according to the procedure reported in the literature [8].

Reaction of $Os_3(CO)_{10}(C_2Me_2)$ with $CpW(CO)_3C{\equiv}CPh$

A toluene solution (65 mL) of triosmium alkyne cluster $Os_3(CO)_{10}(C_2Me_2)$ (322 mg, 0.356 mmol) and tungsten acetylide complex $CpW(CO)_3C{\equiv}CPh$ (205 mg, 0.472 mmol) was heated under reflux under nitrogen for 40 min. The color of the solution gradually turned from orange to brown. After evaporation of the solvent *in vacuo*, the residue was separated by thin-layer chromatography (silica gel, dichloromethane/hexane 1:1), giving 140 mg of dark-red $CpWOs_3(CO)_9[CC(Ph)C(Me)C(Me)]$ (**1a**) (0.114 mmol, 32%) and 183 mg of orange-red $CpWOs_3(CO)_{10}[C(Me)C(Me)CC(Ph)]$ (**2**) (0.146 mmol, 41%) in the order of their elution.

Spectral data for **1a**: MS (FAB, ^{184}W, ^{192}Os); m/z 1232(M^+). IR(C_6H_{12}): ν(CO) 2075s, 2047vs, 2004m, 1993vs, 1972vw, 1958w, 1939w, 1850br,vw cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 7.70 (d, 2H, J(H–H) = 7.7 Hz); 7.47 (t, 2H, J(H–H) = 8.4 Hz); 7.39 (t, 1H, J(H–H) = 7.4 Hz); 5.36 (s, 5H); 2.47 (s, 3H); 2.28 (s, 3H). ^{13}C NMR (CD_2Cl_2, 300 K): CO δ 231.2 (J(W–C) = 136 Hz); 187.0, 186.0, 180.8 (br, 3C); 177.3 (3C); δ 237.5 (J(W–C) = 68 Hz); 156.7, 137.3, 135.1 (J(W–C) = 14 Hz); 133.2 (2C); 129.7, 129.2 (2C); 120.3, 92.6 (5C); 30.9 (Me); 19.2 (Me). Anal. Found: C, 25.07; H, 1.38. $C_{26}H_{16}O_9Os_3W_1$ calc.: C, 25.45; H, 1.31%.

Spectral data for **2**: MS (FAB, ^{184}W, ^{192}Os): m/z 1260(M^+). IR(C_6H_{12}): ν(CO) 2077vs, 2055s, 2048vs, 2027m, 2014s, 2010s, 1997m, 1975s, 1968s, 1952vw, 1940m cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 7.45 (d, 2H, J(H–H) = 7.4 Hz); 7.39–7.32 (m, 3H); 5.14 (s, 5H); 2.98 (s, 3H); 1.88 (s, 3H). ^{13}C NMR (CD_2Cl_2, 254 K): CO δ 217.0

(J(W–C) = 149 Hz); 186.0 (br); 183.6, 183.3, 183.2 (br); 182.9, 182.4, 179.1 (br); 179.0, 173.2; δ 193.3, 156.7, 146.6, 144.0, 134.9 (i-C_6H_5); 129.2 (o,m-C_6H_5); 127.7 (p-C_6H_5); 126.5 (m,o-C_6H_5); 90.9 (5C); 39.1 (Me); 23.3 (Me). Anal. Found: C, 25.83; H, 1.30. $C_{27}H_{16}O_{10}Os_3W_1$ calc.: C, 25.84; H, 1.29%.

Pyrolysis of complex 2

In a 100 mL round-bottom reaction flask, complex **2** (183 mg, 0.146 mmol) was treated with sublimed Me_3NO (12.4 mg, 0.165 mmol) in a mixture of dichloromethane (30 mL) and acetonitrile (10 mL) at ambient temperature for 30 min. After evaporation of the solvent on a rotary evaporator, the residue was dissolved in toluene solution (65 mL) and brought to reflux for 5 min. Finally, the solvent was evaporated *in vacuo*, and the residue was separated by thin-layer chromatography (silica gel, dichloromethane/hexane 4:7), giving 32 mg of orange $CpWOs_3(CO)_9(CCMeCMe)(\mu_3\text{-}CPh)$ (**3a**) (0.026 mmol, 18%), 86 mg of $CpWOs_3(CO)_9(\mu\text{-}H)[CMeCMeCC(\mu_2\text{-}\eta^2\text{-}C_6H_4)]$ (**7**) as a wine-red material (0.070 mmol, 48%).

Spectral data for **3a**: MS (FAB, ^{184}W, ^{192}Os); m/z 1232(M^+). IR(C_6H_{12}): ν(CO) 2076s, 2044vs, 2035m, 2018s, 1997vw, 1975m, 1959s, 1914br,w cm^{-1}. ^1H NMR (CD_2Cl_2, 294 K): δ 7.16 (t, 2H, J(H–H) = 7.8 Hz); 7.05 (t, 1H, J(H–H) = 7.3 Hz); 6.80 (d, 2H, J(H–H) = 6.5 Hz); 5.23 (s, 5H); 3.39 (s, 3H); 2.09 (s, 3H). ^{13}C NMR (CD_2Cl_2, 294 K): Os–CO δ 185.6, 183.2, 180.7, 179.8, 178.9, 176.5 (3C); 172.1; δ 236.1, 192.0, 162.2, 136.7, 130.6, 128.8 (2C); 127.2 (2C); 96.5 (5C); 39.2 (Me); 32.1 (Me). Anal. Found: C, 25.47; H, 1.30. $C_{26}H_{16}O_9Os_3W_1$ calc.: C, 25.45; H, 1.31%.

Spectral data for **7**: MS (FAB, ^{184}W, ^{192}Os): m/z 1232(M^+). IR(C_6H_{12}): ν(CO), 2069vw, 2053vs, 2036vs, 1997m, 1987m, 1975s, 1956w cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 8.49 (d, 1H, J(H–H) = 8.2 Hz); 7.59 (d, 1H, J(H–H) = 8.7 Hz); 7.03 (t, 1H, J(H–H) = 7.7 Hz); 6.59 (t, 1H, J(H–H) = 7.3 Hz); 5.23 (s, 5H); 2.53 (s, 3H); 2.46 (s, 3H); –14.26 (s, 1H, J(W–H) = 73.8 Hz). ^{13}C NMR ($CDCl_3$, 253 K): δ 184.9 (3C); 180.5, 179.8 (2C); 177.2, 175.5, 175.3, 174.0, 156.7, 154.1, 147.8, 141.1, 127.0, 122.8, 117.8, 114.3, 107.0 (J(C–W) = 11 Hz); 89.0 (5C); 32.4 (Me); 19.2 (Me). Anal. Found: C, 25.46; H, 1.31. $C_{26}H_{16}O_9Os_3W_1$ calc.: C, 25.45; H, 1.31%.

Reaction of $Os_3(CO)_{10}(C_2Tol_2)$ with $CpW(CO)_3C{\equiv}CPh$

A toluene solution (35 mL) of triosmium alkyne cluster $Os_3(CO)_{10}(C_2Tol_2)$ (92 mg, 0.087 mmol) and tungsten acetylide complex $CpW(CO)_3C{\equiv}CPh$ (76 mg, 0.175 mmol) was heated under nitrogen reflux for 30 min. The color of the solution turned gradually from orange to deep-red. After evaporation of the solvent *in vacuo*, the residue was separated by thin-layer chromatography (silica gel, dichloromethane/hexane 1:1), giving 24 mg of dark-red $CpWOs_3(CO)_9$-[CC(Ph)C(Tol)C(Tol)] (**1b**) (0.017 mmol, 20%) and 26 mg of red $CpWOs_3(CO)_9$-(CCTolCTol)(μ_3-CPh) (**3b**) (0.019 mmol, 22%). Crystals of **1b** suitable for single crystal X-ray diffraction studies were obtained by recrystallization from a layered solution of dichloromethane/methanol at room temperature.

Spectral data of **1b**: MS (FAB, ^{192}Os, ^{184}W): m/z 1384(M^+). IR (C_6H_{12}): ν(CO) 2074s, 2048vs, 2003m, 1994vs, 1973vw, 1960m, 1937m, 1881br, vw cm^{-1}. ^1H NMR ($CDCl_3$, 294 K): δ 7.42–6.15 (m, 13H); 5.31 (s, 5H); 2.16 (s, 3H); 2.14 (s, 3H). Anal. Found: C, 32.89; H, 1.74. $C_{38}H_{24}O_9Os_3W_1$ calc.: C, 33.10; H, 1.75%.

Table 1

Experimental data for the X-ray diffraction studies [a]

	1b	**4**	**5**	**6**
Empirical formula	$C_{38}H_{24}O_9Os_3W_1$	$C_{31}H_{26}O_9Os_3W_1$	$C_{31}H_{26}O_9Os_3W_1$	$C_{32}H_{26}O_{10}Os_3W_1$
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	18.349(3)	9.982(2)	13.721(6)	13.910(3)
b (Å)	11.371(2)	10.153(1)	14.791(4)	14.375(6)
c (Å)	19.319(3)	17.410(5)	16.880(8)	16.490(8)
α (°)		100.94(2)		
β (°)	97.89(1)	90.88(2)	111.74(4)	95.16(3)
γ (°)		111.70(1)		
U (Å^3)	3993(1)	1602.8(6)	3182(2)	3284(2)
Mol. wt.	1379.04	1296.99	1296.99	1325.00
Crystal size (mm)	0.06×0.20×0.45	0.20×0.30×0.40	0.06×0.15×0.50	0.34×0.50×0.50
Z	4	2	4	4
D_c (g/cm^3)	2.294	2.688	2.707	2.680
$F(000)$	2503.08	1171.55	2343.10	2399.09
2θ (max)	45°	50°	50°	50°
Scan parameter	$0.65+0.35 \tan\theta$	$0.70+0.35 \tan\theta$	$0.70+0.35 \tan\theta$	$0.70+0.35 \tan\theta$
Scan speed (deg/min)	16.48/10 to 16.48/2	16.48/10 to 16.48/2	16.48/10 to 16.48/2	16.48/10 to 16.48/2
h, k, l ranges	−19 19, 0 12, 0 20	−11 10, 0 12, −20 20	−16 15, 0 17, 0 20	−16 16, 0 17, 0 19
μ(Mo-K_α) (mm^{-1})	12.51	15.75	15.69	15.21
Transmission factors	1.00, 0.38	1.00, 0.67	1.00, 0.53	1.00, 0.34
No. of standard reflections: 3	Variation $\leq 6\%$, 8σ, every 7200 s	Decay 5%, every 7200 s	Variation $\leq 6\%$, 8σ, every 7200 s	Variation $\leq 4\%$, 6σ, every 7200 s
No. of unique data	5262	5629	5587	5765
Data with $I > 2\sigma(I)$	3392	4798	4300	4555
No. of atoms	75	70	70	72
No. of parameters	460	398	398	416
Weights	Counting-statistics $w^{-1}=\sigma^2(F)$	Counting-statistics $w^{-1}=\sigma^2(F)$	Counting-statistics $w^{-1}=\sigma^2(F)$	Counting-statistics $w^{-1}=\sigma^2(F)+0.0001\times F^2$
R_F; R_w	0.051; 0.077	0.029; 0.027	0.030; 0.032	0.045; 0.053
GOF	4.31	2.53	2.48	2.55
Maximum Δ/σ ratio	0.184	0.004	0.013	0.023
Residual electron (e Å^{-3}) max/min	1.57/−1.79	1.85/−1.55	1.15/−1.46	2.18/−2.80

[a] Features common to all determinations: λ(Mo-K_α) = 0.70930 Å; Nonius CAD-4 diffractometer; temperature, 297 K; scan method, θ–2θ scan mode; absorption correction, psi scan; GOF = $[\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations: N_v = number of variables).

Table 2

Atomic coordinates and equivalent isotropic displacement coefficients for **1b**

	x	y	z	B_{iso}
Os1	0.29763(9)	0.15467(14)	0.20115(7)	4.10(8)
Os2	0.14292(9)	0.17731(13)	0.16456(7)	3.50(7)
Os3	0.21929(8)	0.01654(12)	0.09198(7)	2.73(6)
W	0.19647(8)	−0.02837(14)	0.22889(7)	3.38(7)
C1	0.3868(24)	0.172(4)	0.1669(21)	7.0(26)
C2	0.3424(21)	0.168(3)	0.2952(18)	5.2(21)
C3	0.2867(22)	0.327(4)	0.2034(23)	7.7(27)
C4	0.1630(22)	0.307(3)	0.0991(20)	6.2(24)
C5	0.1179(23)	0.259(3)	0.2458(20)	5.8(24)
C6	0.0463(21)	0.173(3)	0.1311(19)	5.2(21)
C7	0.1371(18)	0.0324(25)	0.0226(16)	3.2(17)
C8	0.2730(19)	0.100(3)	0.0291(17)	3.8(17)
C9	0.0823(21)	−0.016(3)	0.2011(17)	5.2(21)
C10	0.2663(21)	−0.086(3)	0.3365(18)	5.4(22)
C11	0.2257(21)	0.008(3)	0.3542(17)	5.3(22)
C12	0.1538(23)	−0.033(3)	0.3390(18)	5.7(23)
C13	0.1509(23)	−0.141(3)	0.3114(18)	5.9(23)
C14	0.2260(23)	−0.177(3)	0.3130(18)	5.9(23)
C15	0.2969(17)	−0.021(3)	0.1864(17)	3.9(17)
C16	0.3165(18)	−0.100(3)	0.1320(16)	3.5(18)
C17	0.2589(23)	−0.182(3)	0.1085(20)	5.9(22)
C18	0.1924(18)	−0.153(3)	0.1435(15)	3.0(16)
C19	0.3903(19)	−0.113(3)	0.1089(17)	4.2(20)
C20	0.3988(18)	−0.123(3)	0.0418(15)	3.1(17)
C21	0.4665(20)	−0.140(3)	0.0225(17)	4.9(21)
C22	0.5248(25)	−0.141(4)	0.0698(22)	8.5(31)
C23	0.518(3)	−0.121(5)	0.138(3)	12.4(44)
C24	0.4518(24)	−0.112(4)	0.1609(19)	7.5(29)
C25	0.2605(18)	−0.277(3)	0.0531(15)	2.9(15)
C26	0.3063(21)	−0.373(3)	0.0720(18)	4.8(20)
C27	0.3113(25)	−0.460(3)	0.0287(21)	6.3(26)
C28	0.2733(23)	−0.455(3)	−0.0361(21)	6.3(25)
C29	0.2293(23)	−0.366(3)	−0.0582(18)	5.5(22)
C30	0.2216(21)	−0.271(3)	−0.0128(18)	4.5(19)
C31	0.280(3)	−0.554(3)	−0.0864(23)	8.2(29)
C32	0.1306(20)	−0.242(3)	0.1263(17)	3.9(18)
C33	0.1350(22)	−0.354(3)	0.1656(21)	6.1(25)
C34	0.0741(24)	−0.429(3)	0.1562(24)	7.6(29)
C35	0.0120(24)	−0.413(3)	0.1108(20)	6.0(24)
C36	0.0047(24)	−0.304(4)	0.0782(22)	7.3(26)
C37	0.0639(21)	−0.215(3)	0.0845(19)	5.4(21)
C38	−0.066(3)	−0.489(4)	0.101(3)	11.5(38)
O1	0.4389(19)	0.189(3)	0.1348(18)	12.0(25)
O2	0.3690(18)	0.174(3)	0.3530(13)	8.7(19)
O3	0.2802(20)	0.4254(24)	0.2066(20)	12.2(25)
O4	0.1750(18)	0.371(3)	0.0550(15)	9.3(20)
O5	0.1083(20)	0.320(3)	0.2881(14)	11.1(23)
O6	−0.0169(15)	0.1721(22)	0.1019(13)	6.9(16)
O7	0.0846(13)	0.0419(16)	−0.0185(11)	4.0(12)
O8	0.3069(15)	0.1510(22)	−0.0067(11)	6.1(15)
O9	0.0215(13)	−0.0346(19)	0.1850(12)	4.9(13)

Spectral data of **3b**: MS (FAB, ^{192}Os, ^{184}W): *m/z* 1384(M^+). IR(C_6H_{12}) ν(CO): 2077s, 2048vs, 2036m, 2018s, 1997vw, 1974m, 1969m, 1909w cm^{-1}. ^{1}H NMR ($CDCl_3$, 294 K): δ 7.24–6.75 (m, 13H); 5.49 (s, 5H); 2.33 (s, 3H); 2.19 (s, 3H). Anal. Found: C, 32.91; H, 1.78. $C_{38}H_{24}O_9Os_3W_1$ calc.: C, 33.10, H, 1.75%.

Reaction of $Os_3(CO)_{10}(C_2Tol_2)$ with $Cp^*W(CO)_3C{\equiv}CPh$

A toluene solution (35 mL) of triosmium alkyne cluster $Os_3(CO)_{10}(C_2Tol_2)$ (60 mg, 0.057 mmol) and tungsten acetylide complex $Cp^*W(CO)_3C{\equiv}CPh$ (57 mg, 0.11 mmol) was heated under nitrogen reflux for 30 min. The reaction was stopped when the color of the solution turned from orange to dark brown. Then the solvent was removed *in vacuo*. After separation of the residue by thin-layer chromatography (silica gel, dichloromethane/hexane 1 : 3) and crystallization from a layered solution of dichloromethane/methanol at room temperature, the product $Cp^*WOs_3(CO)_9$[CC(Ph)C(Tol)C(Tol)] (**1c**) was isolated as a red crystalline solid (9 mg, 0.006 mmol, 11%).

Spectral data of **1c**: MS (FAB, ^{192}Os, ^{184}W): *m/z* 1454(M^+). IR (C_6H_{12}) ν(CO): 2071vs, 2045vs, 1999s, 1991vs, 1967w, 1954m, 1935m, 1868br,vw cm^{-1}. ^{1}H NMR ($CDCl_3$, 294 K): δ 7.42 (m, 2H); 7.22 (m, 3H); 6.96 (d, 1H, *J*(H–H) = 7.2 Hz); 6.88 (d, 1H, *J*(H–H) = 7.6 Hz); 6.74 (d, 1H, *J*(H–H) = 6.7 Hz); 6.67 (d, 1H, *J*(H–H) = 7.3 Hz); 6.51 (d, 1H, *J*(H–H) = 7.7 Hz); 6.41 (d, 1H, *J*(H–H) = 7.8 Hz); 6.24 (d, 1H, *J*(H–H) = 6.6 Hz); 6.14 (d, 1H, *J*(H–H) = 7.7 Hz); 2.15 (s, 3H); 2.12 (s, 3H); 1.89 (s, 15H). Anal. Found: C, 34.48; H, 2.47. $C_{43}H_{34}O_9Os_3W_1$ calc.: C, 35.64; H, 2.36%.

Reaction of $Os_3(CO)_{10}(C_2Tol_2)$ with $CpW(CO)_3C{\equiv}C^tBu$

A toluene solution (35 mL) of triosmium alkyne cluster $Os_3(CO)_{10}(C_2Tol_2)$ (80 mg, 0.075 mmol) and $CpW(CO)_3C{\equiv}C^tBu$ (62 mg, 0.15 mmol) was heated under nitrogen reflux for 1.5 h. The solution turned gradually from orange to red brown. After evaporation of the solvent *in vacuo*, separation of the residue by thin-layer chromatography (silica gel, dichloromethane/hexane 1 : 1) and crystallization from a layered solution of dichloromethane/hexane at room temperature, the condensation product $CpWOs_3(CO)_9$[CC(^{t}Bu)C(Tol)C(Tol)] (**1d**) was isolated as a red crystalline solid (35 mg, 0.026 mmol, 34%).

Table 3

Selected bond distances (Å) and bond angles (°) of **1b** (e.s.d. in parentheses)

Os(1)–Os(2)	2.842(2)	Os(1)–Os(3)	2.855(2)
Os(1)–W	2.888(2)	Os(2)–Os(3)	2.795(2)
Os(2)–W	2.765(2)	Os(3)–W	2.782(2)
Os(1)–C(15)	2.02(3)	Os(3)–C(15)	2.20(3)
W–C(15)	2.12(4)	Os(3)–C(16)	2.27(3)
Os(3)–C(17)	2.38(4)	Os(3)–C(18)	2.26(3)
W–C(18)	2.17(3)	C(15)–C(16)	1.46(5)
C(16)–C(17)	1.43(5)	C(17)–C(18)	1.51(5)
Os(2)–C(9)	2.61(4)	W–C(9)	2.09(4)
Os–CO (mean)	1.91(4)		
Os–CO (mean)	174 (4)	W–C(9)–O(9)	165 (3)

Spectral data of **1d**: MS (FAB, ^{192}Os, ^{184}W): *m/z* 1364(M^+). IR (C_6H_{12}) ν(CO): 2073s, 2037vs, 2000sh, 1995vs, 1977w, 1963m, 1933m, 1888br, vw cm^{-1}. ^{1}H NMR ($CDCl_3$, 294 K): δ 7.11 (d, 1H, *J*(H–H) = 8.1 Hz); 6.68 (s, 2H); 6.80 (d, 1H, *J*(H–H) = 8.5 Hz); 6.77 (d, 1H, *J*(H–H) = 8.7 Hz); 6.58 (d, 1H, *J*(H–H) = 7.1 Hz); 6.40 (dd, 1H, *J*(H–H) = 7.9 and 2.1 Hz); 5.84 (dd, 1H, *J*(H–H) = 7.9 and 2.0 Hz);

Table 4

Atomic coordinates and equivalent isotropic displacement coefficients for **4**

	x	y	z	B_{iso}
Os1	0.72791(4)	0.67985(4)	0.221373(24)	1.764(19)
Os2	0.97550(4)	0.75516(5)	0.14901(3)	2.065(18)
Os3	0.76280(4)	0.44844(4)	0.124081(24)	1.765(18)
W	0.66787(4)	0.42065(5)	0.276466(25)	1.761(18)
C1	0.7038(12)	0.8150(12)	0.2999(6)	3.2(6)
C2	0.6561(11)	0.7580(11)	0.1481(7)	3.0(6)
C3	1.0589(10)	0.9509(11)	0.1971(7)	2.6(6)
C4	1.1543(11)	0.7520(11)	0.1192(6)	2.8(5)
C5	0.9218(11)	0.8007(12)	0.0517(7)	3.3(6)
C6	0.9523(12)	0.4571(11)	0.1063(7)	3.5(6)
C7	0.6895(10)	0.4858(10)	0.0319(6)	2.3(5)
C8	0.7066(12)	0.2454(12)	0.0795(7)	3.3(6)
C9	0.6044(12)	0.5440(12)	0.3544(7)	3.1(6)
C10	0.3851(11)	0.5182(12)	0.2271(7)	3.0(6)
C11	0.5261(10)	0.5001(11)	0.2110(6)	2.1(5)
C12	0.5432(10)	0.3878(11)	0.1634(6)	2.2(5)
C13	0.4166(11)	0.2536(11)	0.1199(7)	3.2(6)
C14	0.8509(10)	0.5607(10)	0.2489(5)	1.5(4)
C15	0.9586(10)	0.6871(10)	0.2552(6)	1.9(5)
C16	1.0527(10)	0.7624(11)	0.3312(6)	2.2(5)
C17	1.1954(11)	0.7794(13)	0.3326(7)	3.3(6)
C18	1.2870(12)	0.8347(13)	0.4008(7)	4.0(7)
C19	1.2359(13)	0.8791(13)	0.4690(7)	4.3(7)
C20	1.0937(14)	0.8659(14)	0.4704(7)	4.3(7)
C21	1.0031(12)	0.8087(14)	0.4019(7)	3.8(7)
C22	0.5584(12)	0.2576(11)	0.3562(7)	2.9(6)
C23	0.5844(10)	0.1775(11)	0.2868(6)	2.5(5)
C24	0.7390(11)	0.2237(11)	0.2847(7)	2.6(5)
C25	0.8039(11)	0.3335(12)	0.3504(7)	2.9(6)
C26	0.6980(12)	0.3550(11)	0.3958(6)	3.0(6)
C27	0.4139(13)	0.2311(13)	0.3875(8)	4.3(7)
C28	0.4750(12)	0.0425(11)	0.2335(7)	3.4(6)
C29	0.8174(13)	0.1556(13)	0.2283(8)	4.1(7)
C30	0.9647(12)	0.4052(13)	0.3739(8)	4.4(7)
C31	0.7218(14)	0.4470(14)	0.4772(7)	4.6(8)
O1	0.6924(10)	0.9063(9)	0.3489(5)	5.3(6)
O2	0.6079(8)	0.7982(8)	0.1012(5)	4.2(5)
O3	1.1077(8)	1.0696(9)	0.2282(6)	4.8(5)
O4	1.2698(8)	0.7561(9)	0.1069(5)	4.4(5)
O5	0.8937(10)	0.8317(10)	−0.0037(5)	5.6(5)
O6	1.0595(9)	0.4418(10)	0.0957(6)	6.3(6)
O7	0.6465(8)	0.5069(9)	−0.0228(4)	3.7(5)
O8	0.6787(10)	0.1290(8)	0.0489(5)	5.6(6)
O9	0.5630(9)	0.6122(9)	0.4030(5)	4.7(5)

5.24 (s, 5H); 2.17 (s, 3H); 2.13 (s, 3H); 1.32 (s, 9H). Anal. Found: C, 31.94; H, 2.20. $C_{36}H_{28}O_9Os_3W_1$ calc.: C, 31.82; H, 2.08%.

Reaction of $Os_3(CO)_{10}(C_2Me_2)$ with $Cp^*W(CO)_3C{\equiv}CPh$

For a typical reaction, a toluene solution (70 mL) of triosmium alkyne cluster $Os_3(CO)_{10}(C_2Me_2)$ (450 mg, 0.497 mmol) and tungsten acetylide complex $Cp^*W(CO)_3C{\equiv}CPh$ (251 mg, 0.500 mmol) was heated under nitrogen reflux for 40 min. The color of the solution turned gradually from orange to dark brown. After evaporation of the solvent *in vacuo*, the residue was separated by thin-layer chromatography (silica gel, dichloromethane/hexane 1 : 1), giving 63 mg of dark-red $Cp^*WOs_3(CO)_9[CC(Ph)C(Me)C(Me)]$ (**1e**) (0.046 mmol, 9%), 60 mg of red-orange $Cp^*WOs_3(CO)_9(CCMeCMe)(\mu_3\text{-}CPh)$ (**3e**) (0.049 mmol, 10%), 24 mg of red-orange $Cp^*WOs_3(CO)_9(C_2Me_2)(\mu_3\text{-}CCPh)$ (**5**) (0.019 mmol, 4%), 58 mg of red-orange $Cp^*WOs_3(CO)_9(C_2Me_2)(\mu_4\text{-}CCPh)$ (**4**) (0.045 mmol, 9%) and 21 mg of greenish brown $Cp^*WOs_3(CO)_9(\mu_3\text{-}CPh)[CC(Me)C(Me)CO]$ (**6**) (0.016 mmol, 3%). These complexes are listed in the order of elution. Crystals of complexes **4**, **5** and **6** suitable for single crystal X-ray diffraction studies were obtained by recrystallization from a layered solution of dichloromethane/hexane at room temperature.

Spectral data for **1e**: MS (FAB, ^{184}W, ^{192}Os): m/z 1302(M^+). IR(C_6H_{12}): ν(CO) 2071s, 2044vs, 2032w, 2001m, 1990vs, 1966vw, 1955m, 1937m, 1843br,w cm^{-1}. ^1H NMR (CD_2Cl_2, 294 K): δ 7.74 (d, 2H, J(H–H) = 7.4 Hz); 7.46 (t, 2H, J(H–H) = 7.5 Hz); 7.39 (t, 1H, J(H–H) = 7.3 Hz); 2.41 (s, 3H); 2.07 (s, 3H); 1.99 (s, 15H). Anal. Found: C, 28.68; H, 2.03. $C_{31}H_{26}O_9Os_3W_1$ calc.: C, 28.71; H, 2.02%.

Spectral data for **3e**: MS (FAB, ^{184}W, ^{192}Os): m/z 1302(M^+). IR(C_6H_{12}): ν(CO) 2072s, 2040vs, 2032m, 2012s, 1991vw, 1970m, 1952s, 1912br,w cm^{-1}. ^1H NMR (CD_2Cl_2, 294 K): δ 7.09 (t, 2H, J(H–H) = 6.8 Hz); 6.70 (t, 1H, J(H–H) = 7.2 Hz); 6.91 (d, 1H, J(H–H) = 7.4 Hz); 6.84 (d, 1H, J(H–H) = 7.8 Hz); 3.21 (s, 3H); 2.07 (s, 3H); 1.80 (s, 15H). ^{13}C NMR (CD_2Cl_2, 294 K): Os–CO δ 187.8, 185.6, 181.3, 180.2, 177.2, 176.2 (3C); 172.7; δ 239.5 (J(W–C) = 111 Hz); 195.1, 159.2 (J(W–C) = 15 Hz); 136.6, 136.0, 132.4, 129.8 (J(W–C) = 31 Hz); 128.2, 127.1, 127.0, 107.7 (5C); 37.3 (Me); 26.6 (Me); 13.1 (5Me). Anal. Found: C, 28.69; H, 2.00. $C_{31}H_{26}O_9Os_3W_1$ calc.: C, 28.71; H, 2.02%.

Table 5

Selected bond distances (Å) and bond angles (°) of **4** (e.s.d. in parentheses)

Os(1)–Os(2)	2.7100(9)	Os(1)–Os(3)	2.7612(8)
Os(1)–W	2.8310(7)	Os(2)–Os(3)	2.9942(8)
Os(3)–W	2.860(1)	Os(1)–C(11)	2.14(1)
Os(3)–C(12)	2.205(9)	W–C(11)	2.257(9)
W–C(12)	2.214(9)	Os(1)–C(14)	2.121(8)
Os(1)–C(15)	2.339(9)	Os(2)–C(15)	2.08(1)
Os(3)–C(14)	2.248(9)	W–C(14)	1.989(9)
C(11)–C(12)	1.34(2)	C(14)–C(15)	1.32(1)
W–C(9)	1.94(1)	Mean Os–CO	1.88(2)
W–C(9)–O(9)	176.5(9)	Os–CO (mean)	176 (1)
W–C(14)–C(15)	156.1(8)	Os(1)–C(14)–Os(3)	78.3(3)

Spectral data for **4**: MS (FAB, ^{184}W, ^{192}Os): m/z 1302(M$^+$). IR(C_6H_{12}): ν(CO) 2072vs, 2029vs, 2001vs, 1993vs, 1981w, 1974m, 1949s, 1915vw cm^{-1}. ^{1}H NMR (CD_2Cl_2, 294 K): δ 7.53 (d, 2H, J(H–H) = 7.4 Hz); 7.28 (t, 2H, J(H–H) = 7.3 Hz); 7.24 (t, 1H, J(H–H) = 7.3 Hz); 3.48 (s, 3H); 2.91 (s, 3H); 2.09 (s, 15H). ^{13}C NMR (CD_2Cl_2, 294 K): CO δ 209.4 (J(W–C) = 172 Hz); 188.6, 179.9, 178.7 (broad, 3C);

Table 6

Atomic coordinates and equivalent isotropic displacement coefficients for **5**

	x	y	z	B_{iso}
Os1	0.81592(5)	0.31342(4)	0.07030(3)	2.329(25)
Os2	0.99734(5)	0.20374(4)	0.13402(4)	2.87(3)
Os3	0.84873(5)	0.16989(4)	−0.02370(4)	2.63(3)
W	0.63315(5)	0.24243(4)	−0.04925(4)	2.38(3)
C1	0.8159(11)	0.4283(9)	0.1139(10)	3.8(8)
C2	0.8217(11)	0.2625(9)	0.1751(8)	2.9(7)
C3	1.0745(12)	0.2678(11)	0.2353(9)	4.1(9)
C4	1.1177(13)	0.1442(11)	0.1319(9)	4.8(10)
C5	0.9633(12)	0.1074(10)	0.1924(10)	4.0(8)
C6	0.8894(13)	0.1094(10)	−0.1027(10)	3.9(9)
C7	0.8272(13)	0.0545(10)	0.0145(10)	4.2(9)
C8	0.6568(12)	0.1606(9)	0.0479(9)	3.4(7)
C9	0.5954(11)	0.3330(9)	0.0206(9)	3.3(7)
C10	1.0247(13)	0.4175(11)	0.0844(10)	4.6(9)
C11	0.9645(10)	0.3316(9)	0.0618(8)	2.6(7)
C12	0.9748(11)	0.2623(10)	0.0084(9)	3.7(8)
C13	1.0524(12)	0.2655(12)	−0:0363(10)	4.9(10)
C14	0.7789(11)	0.2794(8)	−0.0714(7)	2.6(7)
C15	0.7396(10)	0.3598(9)	−0.0606(8)	2.5(6)
C16	0.7163(10)	0.4508(8)	−0.1024(8)	2.5(6)
C17	0.7441(11)	0.4636(9)	−0.1739(9)	3.3(7)
C18	0.7266(11)	0.5443(10)	−0.2146(9)	3.3(7)
C19	0.6862(11)	0.6137(10)	−0.1826(10)	4.4(8)
C20	0.6582(13)	0.6017(10)	−0.1135(11)	4.6(9)
C21	0.6735(11)	0.5200(9)	−0.0721(9)	3.2(7)
C22	0.4615(11)	0.1916(10)	−0.1037(8)	3.2(7)
C23	0.5242(11)	0.1251(9)	−0.1253(8)	2.9(7)
C24	0.5669(11)	0.1652(10)	−0.1840(8)	3.3(7)
C25	0.5307(12)	0.2543(11)	−0.2003(9)	4.6(8)
C26	0.4682(11)	0.2750(9)	−0.1486(9)	3.9(8)
C27	0.3955(13)	0.1761(13)	−0.0515(11)	5.7(11)
C28	0.5316(13)	0.0292(9)	−0.1032(10)	4.1(9)
C29	0.6205(14)	0.1155(13)	−0.2312(10)	5.7(11)
C30	0.5433(15)	0.3177(12)	−0.2631(9)	7.1(12)
C31	0.4056(15)	0.3630(13)	−0.1512(12)	7.9(12)
O1	0.8169(10)	0.4999(7)	0.1430(8)	6.6(8)
O2	0.8152(8)	0.2359(7)	0.2360(6)	4.2(6)
O3	1.1226(9)	0.3085(8)	0.2947(7)	6.1(7)
O4	1.1925(9)	0.1101(9)	0.1299(8)	7.4(8)
O5	0.9396(10)	0.0480(8)	0.2264(8)	6.7(8)
O6	0.9142(11)	0.0789(8)	−0.1542(8)	6.7(8)
O7	0.8107(10)	−0.0157(7)	0.0389(8)	6.1(8)
O8	0.6610(9)	0.1110(7)	0.1030(6)	4.9(6)
O9	0.5587(9)	0.3840(8)	0.0554(7)	5.7(7)

178.2, 174.6, 166.2; δ 226.5 (J(W–C) = 145 Hz); 184.3 (J(W–C) = 21 Hz); 151.0, 129.0 (p-C_6H_5); 128.8 (o,m-C_6H_5); 127.5 (o,m-C_6H_5); 121.7 (i-C_6H_5); 104.3 (5C); 88.1 (J(W–C) = 36 Hz); 29.5 (Me); 27.8 (Me); 11.7 (5Me). Anal. Found: C, 28.70; H, 2.04. $C_{31}H_{26}O_9Os_3W_1$ calc.: C, 28.71; H, 2.02%.

Spectral data for **5**: MS (FAB, ^{184}W, ^{192}Os): m/z 1302(M^+). IR(C_6H_{12}): ν(CO) 2078vs, 2015vs, 2001vs, 1989s, 1972vs, 1956s, 1933w, 1918m, 1903m cm^{-1}. ^{1}H NMR (CD_2Cl_2, 294 K): δ 7.77 (d, 2H, J(H–H) = 7.8 Hz); 7.39 (t, 2H, J(H–H) = 6.8 Hz); 7.28 (t, 1H, J(H–H) = 6.9 Hz); 3.06 (s, 3H); 2.64 (s, 3H); 1.95 (s, 15H). ^{13}C NMR ($CDCl_3$, 240 K): CO δ 214.9 (J(W–C) = 164 Hz); 210.5 (J(W–C) = 156 Hz); 197.3, 192.9, 192.6, 184.8 (2C); 171.3, 170.4; δ 148.5, 143.1, 137.5, 136.5 (i-C_6H_5); 131.3 (o-C_6H_5); 129.5 (m-C_6H_5); 128.3 (p-C_6H_5); 103.2 (5C); 78.8, 39.7 (Me); 35.5 (Me); 12.3 (5Me). Anal. Found: C, 28.65; H, 2.02. $C_{31}H_{26}O_9Os_3W_1$ calc.: C, 28.71; H, 2.02%.

Spectral data for **6**: MS (FAB, ^{184}W, ^{192}Os): m/z 1330(M^+). IR(C_6H_{12}): ν(CO) 2076s, 2041vs, 2005w, 1992m, 1988m, 1977s cm^{-1}. ^{1}H NMR (CD_2Cl_2, 230 K): δ 7.24 (m, 2H); 7.14 (m, 2H); 7.06 (m, 1H); 2.30 (s, 3H); 1.70 (s, 15H); 1.62 (s, 3H). ^{13}C NMR (CD_2Cl_2, 254 K): CO δ 280.6 (J(W–C) = 150 Hz); 204.6, 187.9, 178.8, 174.0 (br, 3C); 173.8 (3C); δ 282.1 (J(W–C) = 122 Hz); 250.6 (J(W–C) = 107 Hz); 181.1 (J(W–C) = 15 Hz); 163.4 (J(W–C) = 15 Hz); 146.3, 131.7, 128.8, 128.7, 128.5, 127.0, 109.5 (5C); 22.5 (Me); 11.7 (Me); 10.5 (5Me). Anal. Found: C, 28.95; H, 1.97. $C_{32}H_{26}O_{10}Os_3W_1$ calc.: C, 29.01; H, 1.98%.

Pyrolysis of complex 6

A toluene solution of complex **6** (12 mg, 0.009 mmol) was heated under reflux at 1 atm of CO atmosphere for 3 h. After evaporation of the solvent on a rotary evaporator, the residue was separated by thin layer chromatography (silica gel, dichloromethane/hexane 1:2), giving 6.4 mg of orange **3e** (0.0049 mmol, 54%) and 1.9 mg of unreacted **6** (0.0014 mmol, 16%).

X-Ray crystallography

Diffraction measurements were carried out on a Nonius CAD-4 diffractometer. Lattice parameters of **1b** were determined from 25 randomly selected high angle reflections with 2θ angles in the range 18.82–26.38°, whereas the corresponding

Table 7

Selected bond distances (Å) and bond angles (°) of **5** (e.s.d. in parentheses)

Os(1)–Os(2)	2.829(1)	Os(1)–Os(3)	2.785(1)
Os(1)–W	2.778(2)	Os(2)–Os(3)	2.734(2)
Os(3)–W	3.024(2)	Os(1)–C(11)	2.284(2)
Os(2)–C(11)	2.21(1)	Os(2)–C(12)	2.20(1)
Os(3)–C(12)	2.11(1)	Os(1)–C(14)	2.31(1)
Os(1)–C(15)	2.18(1)	Os(3)–C(14)	1.90(1)
W–C(14)	2.23(1)	W–C(15)	2.32(1)
C(11)–C(12)	1.41(2)	C(14)–C(15)	1.35(2)
Mean W–CO	1.97(2)	Mean Os–CO	1.88(2)
W–CO (mean)	172 (1)	Os–CO (mean)	177 (1)
Os(3)–C(14)–C(15)	165 (3)		

cell dimensions of complexes **4**, **5** and **6** were determined from 25 reflections, with 2θ angles in the range 19.00–24.50°, 20.68–22.82° and 20.74–26.34°, respectively. For complexes **1b**, **5** and **6**, the space group $P2_1/c$ was identified on the basis of

Table 8

Atomic coordinates and equivalent isotropic displacement coefficients for **6**

	x	y	z	B_{iso}
Os1	0.12847(5)	0.96861(4)	0.19161(3)	1.996(23)
Os2	0.28390(5)	0.87519(4)	0.12641(3)	2.350(25)
Os3	0.24889(5)	0.85162(4)	0.29459(3)	2.32(3)
W	0.32200(5)	1.02365(5)	0.23883(3)	2.143(25)
C1	0.0647(14)	1.0839(13)	0.1802(12)	4.1(9)
C2	0.0235(12)	0.9184(15)	0.2427(11)	4.2(9)
C3	0.0739(12)	0.9174(12)	0.0926(10)	3.2(7)
C4	0.4070(14)	0.8542(14)	0.0920(11)	4.5(9)
C5	0.2356(16)	0.7538(11)	0.0918(9)	3.9(9)
C6	0.2468(23)	0.7246(13)	0.2594(11)	7.2(15)
C7	0.1472(14)	0.8240(11)	0.3635(9)	3.2(7)
C8	0.3340(13)	0.8267(13)	0.3819(9)	3.6(8)
C9	0.3916(12)	0.9042(14)	0.2460(9)	3.6(8)
C10	0.2540(11)	1.0187(10)	0.1305(8)	2.1(6)
C11	0.2294(14)	1.0602(12)	0.0463(9)	3.2(7)
C12	0.2345(13)	1.0051(12)	−0.0175(8)	3.1(8)
C13	0.2582(14)	0.9089(11)	0.0027(9)	3.1(7)
C14	0.1935(18)	1.1595(13)	0.0422(11)	5.1(10)
C15	0.2083(18)	1.0354(14)	−0.1055(10)	4.9(11)
C16	0.2104(11)	0.9972(11)	0.3069(9)	2.6(7)
C17	0.1708(11)	1.0357(10)	0.3823(8)	1.9(6)
C18	0.1022(14)	1.1000(15)	0.3814(10)	4.4(9)
C19	0.0686(17)	1.1365(16)	0.4493(12)	5.6(11)
C20	0.1049(17)	1.1076(15)	0.5218(12)	5.3(11)
C21	0.1780(17)	1.0428(13)	0.5315(10)	4.6(10)
C22	0.2112(17)	1.0081(13)	0.4612(10)	4.5(10)
C23	0.3457(17)	1.1856(13)	0.2548(12)	5.1(10)
C24	0.3859(16)	1.1385(14)	0.3309(11)	5.2(10)
C25	0.4578(16)	1.0853(15)	0.3154(11)	5.3(10)
C26	0.4720(14)	1.0907(17)	0.2309(11)	5.4(11)
C27	0.4060(14)	1.1547(14)	0.1966(10)	4.4(9)
C28	0.2742(24)	1.2621(15)	0.2490(17)	8.5(18)
C29	0.3561(23)	1.1678(18)	0.4146(13)	8.3(15)
C30	0.520(3)	1.0334(23)	0.3792(21)	11.6(21)
C31	0.5538(18)	1.0449(24)	0.1893(17)	9.4(18)
C32	0.4102(22)	1.1951(22)	0.1107(13)	10.3(18)
O1	0.0224(13)	1.1535(10)	0.1695(9)	6.9(9)
O2	−0.0436(10)	0.8935(13)	0.2737(8)	6.8(9)
O3	0.0388(11)	0.8899(11)	0.0306(8)	6.0(8)
O4	0.4813(11)	0.8416(12)	0.0694(8)	7.0(9)
O5	0.2090(15)	0.6856(10)	0.0670(8)	7.7(11)
O6	0.2294(19)	0.6459(9)	0.2434(8)	9.6(14)
O7	0.0938(10)	0.8085(9)	0.4065(7)	4.6(6)
O8	0.3978(11)	0.8211(10)	0.4384(7)	5.7(7)
O9	0.4678(10)	0.8604(10)	0.2576(7)	4.9(7)
O10	0.2573(12)	0.8516(9)	−0.0526(6)	5.1(7)

Table 9

Selected bond distances (Å) and bond angles (deg) of **6** (e.s.d. in parentheses)

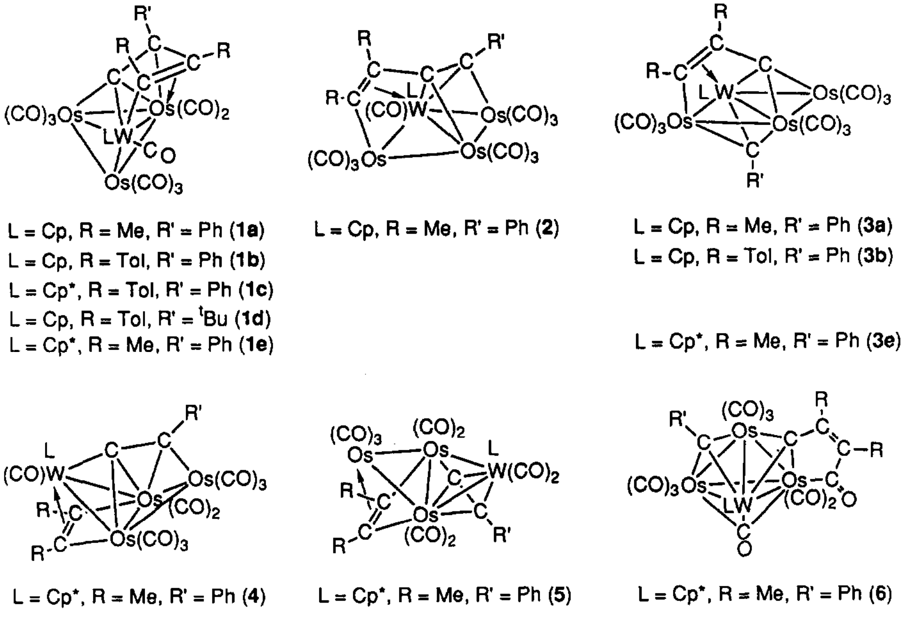
Os(1)–Os(2)	2.838(1)	Os(1)–Os(3)	2.829(1)
Os(1)–W	2.846(1)	Os(2)–Os(3)	2.879(2)
Os(2)–W	2.845(1)	Os(3)–W	2.857(1)
Os(2)–C(9)	2.40(2)	Os(3)–C(9)	2.33(2)
W–C(9)	1.97(2)	Os(1)–C(10)	2.21(1)
Os(2)–C(10)	2.11(2)	W–C(10)	1.95(1)
Os(2)–C(13)	2.10(2)	C(10)–C(11)	1.52(2)
C(11)–C(12)	1.32(2)	C(12)–C(13)	1.45(2)
Os(1)–C(16)	2.17(2)	Os(3)–C(16)	2.17(2)
W–C(16)	1.94(1)	Mean Os–CO (terminal)	1.88(2)
W–C(9)–O(9)	176.5(9)	Mean Os–CO (terminal)	176 (1)
W–C(14)–C(15)	156.1(8)	Os(1)–C(14)–Os(3)	78.3(3)

systematic absences, whereas complex **4** crystallized in a triclinic space system. All reflections were corrected for Lorentz, polarization and absorption effects. All data reduction and refinement were performed using the NRCC-SDP-VAX packages. The structures were solved by the direct method and refined by least squares cycle, all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The combined data collection and refinement parameters are given in Table 1. Atomic positional parameters for complex **1b** are found in Table 2, whereas some selected bond angles and lengths are given in Table 3. The corresponding parameters for complexes **4**, **5** and **6** are given in Tables 4 and 5, Tables 6 and 7, and Tables 8 and 9, respectively. Tables of bond distances and angles, tables of positional parameters and anisotropic thermal parameters and listings of the observed and calculated structural factors are available from one of the authors (Y.C.).

Results and discussion

Reaction of $Os_3(CO)_{10}(C_2Me_2)$ with $CpW(CO)_3C{\equiv}CPh$

Treatment of triosmium complex $Os_3(CO)_{10}(C_2Me_2)$ and tungsten acetylide complex $CpW(CO)_3C{\equiv}CPh$ gave two heterometallic complexes $CpWOs_3(CO)_9$-[CC(Ph)C(Me)C(Me)] (**1a**) and $CpWOs_3(CO)_{10}$[C(Me)C(Me)CC(Ph)] (**2**). These two complexes have been characterized by spectroscopic methods and by microanalysis. The molecular ions observed in FAB mass spectra suggest that complex **1a** possesses nine CO ligands and complex **2**, ten CO ligands. The ^{1}H NMR spectra show the presence of C_2Me_2 and CCPh fragments, indicating that these two complexes were generated via a 1:1 condensation reaction. This pattern of reactivity agrees with that of the reactions of tetranuclear acetylide complexes $CpWOs_3(CO)_{11}$(CCR) with internal alkyne containing electron-withdrawing substituents, suggesting that the products isolated should adopt similar structure (Scheme 1). Based on these arguments, we propose that complex **1a** was produced by coupling of the ligated butyne with the β-carbon of the acetylide ligand,



L = Cp, R = Me, R' = Ph (**1a**)
L = Cp, R = Tol, R' = Ph (**1b**)
L = Cp*, R = Tol, R' = Ph (**1c**)
L = Cp, R = Tol, R' = ^{t}Bu (**1d**)
L = Cp*, R = Me, R' = Ph (**1e**)

L = Cp, R = Me, R' = Ph (**2**)

L = Cp, R = Me, R' = Ph (**3a**)
L = Cp, R = Tol, R' = Ph (**3b**)
L = Cp*, R = Me, R' = Ph (**3e**)

L = Cp*, R = Me, R' = Ph (**4**)

L = Cp*, R = Me, R' = Ph (**5**)

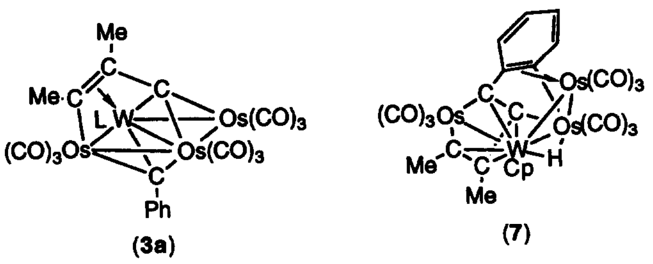
L = Cp*, R = Me, R' = Ph (**6**)

Scheme 1.

whereas complex **2** was generated by coupling with the α-carbon of the acetylide ligand.

These assignments are supported by ^{13}C NMR studies. The ^{13}C NMR data of **1a** show five CO resonances at δ 231.2 (J(W–C) = 136 Hz), 187.0, 186.0, 180.8 (br, 3C) and 177.3 (3C) consistent with the proposed structure. The signal at δ 231.2 is due to the semi-bridging CO linked to the tungsten atom, the signals at δ 187.0 and 186.0 are due to the CO of an Os(CO)$_2$ unit, whereas the CO resonances at δ 180.8 and 177.3 with ratio three are assigned to two Os(CO)$_3$ units that undergo rapid threefold rotation. The ligated carbon atoms appear at δ 237.5 (J(W–C) = 68 Hz), 156.7, 135.1 (J(W–C) = 14 Hz) and 120.3, which are assigned with the assistance of their tungsten satellites and the data of chemical shifts. The signal at δ 237.5 is due to the α-carbon of the C$_4$ ligand because the chemical shift is in the range expected for a triply bridging alkylidyne carbon; the signal at δ 135.1 which exhibits the tungsten–carbon coupling is assigned to the ω-carbon because this carbon is directly linked to the tungsten atom. The signals at δ 156.7 and 120.3 are due to the signals of β- and γ-carbons by default. For complex **2**, the ^{13}C data of a ^{13}CO enriched sample present one W–CO resonance at δ 217.0 with J(W–C) = 149 Hz and nine Os–CO resonances (six sharp and three very broad signals) in the range 186.0–173.2 at 254 K. The signals of the ligated C$_4$ hydrocarbon are observed at δ 193.3, 156.7, 146.6 and 144.0; no tungsten coupling was seen for all four resonances.

The reactivity of complex **2** was examined. Treatment of **2** with 1.1 molar equiv. of Me$_3$NO in a mixture of acetonitrile/dichloromethane at ambient temperature followed by heating in refluxing toluene produced a burgundy solution within 10 min. Following TLC separation (hexane/dichloromethane 4:1) and purification by recrystallization, we obtained an orange cluster CpWOs$_3$(CO)$_9$(CCMeCMe)(μ_3-



Scheme 2.

CPh) (**3a**, 18%), in addition to a wine-red cluster $CpWOs_3(CO)_9(\mu\text{-}H)[CMeCMeCC(\mu_2\text{-}\eta^2\text{-}C_6H_4)]$ (**7**, 48%) (Scheme 2). This observation strongly indicates that the alkylidyne and the coordinated C_3 hydrocarbon ligands in **3** were generated via alkyne–acetylide coupling followed by cleavage of a C–C bond. The characterization of **3a** was achieved by comparing the IR and ^{13}C NMR spectral data with those of complex **3b**, whereas complex **7** was determined by conventional spectroscopic methods and X-ray diffraction [5].

Reaction of $Os_3(CO)_{10}(C_2Tol_2)$ with $LW(CO)_3C{\equiv}CR'$

When the triosmium alkyne complex $Os_3(CO)_{10}(C_2Tol_2)$ was treated with another tungsten acetylide complex $CpW(CO)_3C{\equiv}CPh$ under similar conditions, two heterometallic complexes $CpWOs_3(CO)_9[CC(Ph)C(Tol)C(Tol)]$ (**1b**) and $CpWOs_3(CO)_9(CCTolCTol)(\mu_3\text{-}CPh)$ (**3b**) were isolated after purification by preparative TLC and recrystallization. In contrast, the corresponding reactions of $Os_3(CO)_{10}(C_2Tol_2)$ with acetylide complexes $LW(CO)_3C{\equiv}CR'$ in refluxing toluene afforded only one heterometallic cluster complex $LWOs_3(CO)_9[CC(R')C(Tol)C(Tol)]$ ($L = Cp^\star$, $R' = Ph$, **1c** and $L = Cp$, $R' = {}^tBu$, **1d**). The identification of complexes **1b**, **1c** and **1d** was achieved by analysis of their spectroscopic data. In particular, IR spectroscopy is the most valuable technique because the $\nu(CO)$ spectra in solution are almost identical to that of complex **1a**. Complex **3b** was initially characterized by IR, mass and ^1H NMR data; the structure was confirmed by X-ray diffraction studies. The crystal structure of **3b** has been discussed previously [6]. The ^{13}C NMR spectrum of **3b** was not recorded because of poor solubility. We present the ^{13}C NMR data of the related $Cp^\star$ derivative **3e** on p. 363.

Crystal structure of complex 1b

Although the spectroscopic data of **1b** fairly well define its molecular structure, nevertheless X-ray diffraction studies were performed in order to confirm our structural assignment. The ORTEP diagram of complex **1b** and the scheme used to label the atoms are illustrated in Fig. 1, while selected bond distances and angles are listed in Table 6. The structure is essentially identical to that of the related $CpWOs_3(CO)_9[CC(Ph)C(CO_2Et)C(CO_2Et)]$. For complex **1b**, the tungsten atom and three osmium atoms form a slightly distorted tetrahedral skeleton with metal–metal distances in the range 2.765–2.888 Å. The W atom is capped by a Cp ligand and a semibridging CO ligand (W–C(9)–O(9) = 165°), the Os(3) atom is coordinated by all four carbon atoms of the ligated C_4 fragment and two extra

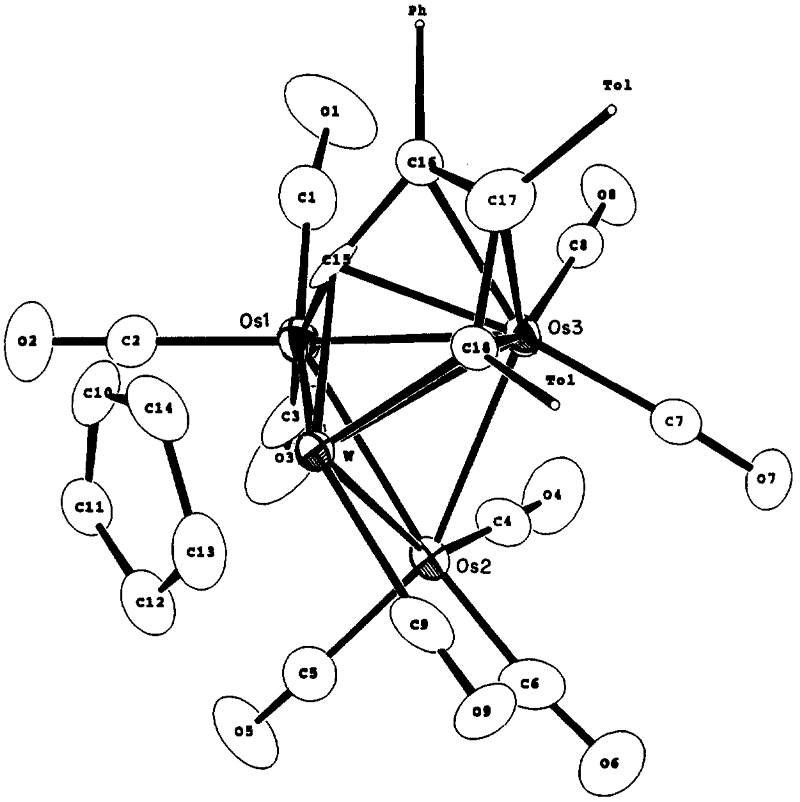


Fig. 1. Molecular structure of **1b**, showing the atomic numbering scheme; the tolyl substituent on atoms C(17) and C(18) and the phenyl group on C(16) are removed for clarity.

terminal CO ligands, whereas the Os(1) and the Os(2) atoms are each linked to three terminal CO ligands. The ligated C_4 ligand C(15)–C(16)–C(17)–C(18), which is associated with a WOs_2 triangle via an η^4 interaction, can also be viewed as a derivative of a μ_3-η^2 vinylidene. Therefore the vinylidene C(15)–C(16) backbone, derived from the acetylide ligand, is coordinated to the Os(1)–W edge via a σ-bond and π-bonded to the Os(3) atom via an η^2 interaction. The C_2 substituent C(17)–C(18), derived from the alkyne, is linked to the β-carbon of the vinylidene and the W atom via a σ-bond and coordinated to the Os(3) atom via a π-bond. Alternatively, the molecule can be considered to adopt a M_4C *closo* trigonal bipyramidal geometry with atoms Os(2) and C(15) located at the axial positions, and atoms Os(1), Os(3) and W on the equatorial plane. In this case, the C_4 hydrocarbyl ligand is considered to be a 1,3-disubstituted allyl moiety linked to C(15) and W atoms via two σ-bonds and π-bonded to the third Os(3) atom by an η^3 interaction.

Reaction of $Os_3(CO)_{10}(C_2Me_2)$ with $Cp^*W(CO)_3C{\equiv}CPh$

When triosmium complex $Os_3(CO)_{10}(C_2Me_2)$ was reacted with acetylide complex $Cp^*W(CO)_3C{\equiv}CPh$ under similar conditions, we isolated five heterometallic complexes generated via 1:1 combination of starting materials. As indicated by the IR, ^1H and ^{13}C NMR data, the first two complexes, $Cp^*WOs_3(CO)_9[CC(Ph)C(Me)C(Me)]$ (**1e**) and $Cp^*WOs_3(CO)_9(CCMeCMe)(\mu_3\text{-}CPh)$ (**3e**), are analogous to the derivatives **1** and **3** mentioned previously. The other three complexes $Cp^*WOs_3(CO)_9(C_2Me_2)(\mu_3\text{-}CCPh)$ (**4**), $Cp^*WOs_3(CO)_9(C_2Me_2)(\mu_4\text{-}CCPh)$ (**5**) and $Cp^*WOs_3(CO)_9(\mu_3\text{-}CPh)[CC(Me)C(Me)CO]$ (**6**) were newly observed in this system. Complex **1e** was identified by its IR spectrum, whereas complex **3e** is assigned according to the IR and ^{13}C NMR data. Consistent with the established structure of **3a** and **3b**, the ^{13}C NMR spectrum of **3e** shows seven Os–CO resonances at δ 187.8, 185.6, 181.3, 180.2, 177.2, 176.2 (3C), 172.7 but no signal for W–CO ligand. The four ligated carbon atoms appear at δ 239.5 (J(W–C) = 111 Hz), 195.1, 159.2 (J(W–C) = 15 Hz), and 129.8 (J(W–C) = 31 Hz) which are assigned to the alkylidyne (μ_3-CPh) carbon [9] and α, γ and β-carbons of the C_3 hydrocarbon ligand (CCMeCMe), respectively. The ^{13}C NMR spectra of **4**, **5** and **6** were also measured but discussion of the results is deferred until after the X-ray diffraction data, described below. The ^1H NMR data of **4**, **5** and **6** confirm only the presence of equimolar ligated butyne and acetylide but are unable to delineate the detailed structure of these complexes.

Crystal structure and ^{13}C NMR identification of 4

The structure of **4** was determined by a single-crystal X-ray diffraction study. As shown in Fig. 2, the molecule consists of a WOs_3 core of a butterfly arrangement, with Os(2) and W defining the wing-tip positions and Os(1) and Os(3) atoms, the hinge positions; the dihedral angle of the butterfly framework is 135.59(2)°. The acetylide and the butyne moieties are not coupled. The acetylide ligand occupies the open face via a μ_4-η^2-bonding interaction with its α-carbon bound to the WOs_2 triangle with bond distances W–C(14) = 1.989(9) Å, Os(1)–C(14) = 2.121(8) Å and Os(3)–C(14) = 2.248(8) Å, and with the β-carbon atom linked to Os(1) and Os(2) atoms with bond distances Os(1)–C(15) = 2.339(9) Å and Os(2)–C(15) = 2.08(1) Å. The μ_4-η^2-bonding mode of this acetylide ligand is similar to that of the parent acetylide complex $CpWOs_3(CO)_{11}(CCPh)$, the mixed-metal vinylidene complexes [10] and a Fe_4 nitrile complex [11], the crystal structures of which have been previously reported. The ligated butyne moiety, however, is coordinated to the same WOs_2 face opposite the acetylide ligand via a conventional μ_3-η^2-mode. As expected, metal–carbon distances of the π-interactions (W–C(11) = 2.257(9) and W–C(12) = 2.214(9) Å) are slightly longer than the respective σ-interactions (Os(1)–C(11) = 2.14(1) and Os(3)–C(12) = 2.205(9) Å). In accordance with the solid state structure, the ^{13}C NMR spectrum shows, in addition to a signal at δ 209.9 (J(W–C) = 172 Hz) due to the terminal W–CO ligand, six Os–CO signals at δ 188.6, 179.9, 178.7, 178.2, 174.6 and 166.2 with ratio 1:1:3:1:1:1. The μ_4-η^2 acetylide gives two signals at δ 226.5 (J(W–C) = 145 Hz) and 151.0; the observed chemical shifts agree with data summarized by Carty *et al.* [12]. Two additional signals at δ 184.3 (J(W–C) = 21 Hz) and 88.1 (J(W–C) = 36 Hz) with the characteristics of tungsten satellites were also observed; they are assigned to the ligated butyne ligand, because these two carbon atoms are linked directly to the tungsten atom. The large separation of the chemical shift for the ligated alkyne carbons is presumably due to the deshielding effect of the nearby Cp* ring.

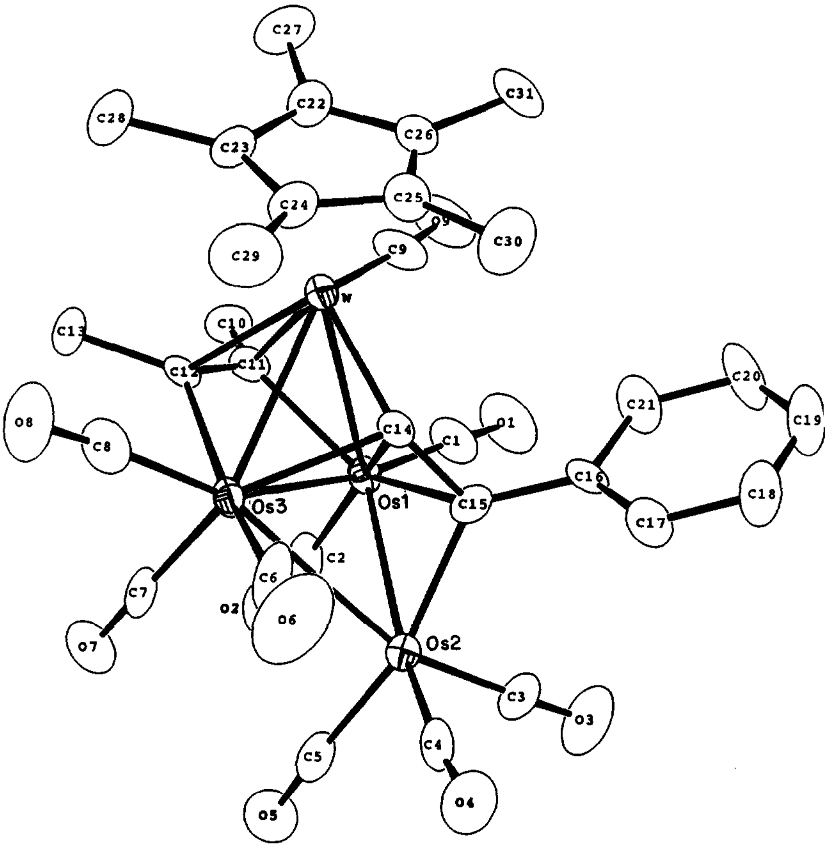


Fig. 2. Molecular structure of **4**, showing the atomic numbering scheme.

Crystal structure of complex 5

The second new product of the reaction with Cp*W(CO)$_3$C≡CPh is a red-orange complex **5**; its molecular formula is identical to that of **4** but the crystal structure is different. Needle-shaped crystals were obtained from a layered solution of dichloromethane/hexane at room temperature. The molecular structure and the atomic numbering scheme are presented in Fig. 3 and selected parameters of bond lengths and angles are summarized in Table 7. As indicated in Fig. 3, the molecule has a butterfly WOs$_3$ core arrangement in which the wing-tip tungsten and osmium atoms Os(2) are capped by a Cp ring and two terminal CO ligands and by three terminal CO ligands, respectively, whereas the atoms Os(1) and Os(3) located at the hinge positions are coordinated by only two terminal CO ligands, the dihedral angle of the butterfly core is 155.28(3)°. All metal–metal bonds are normal, showing metal–metal single-bond lengths in the range 3.024(2)–2.734(2) Å. All CO ligands on the osmium atoms are essentially linear (Os–C–O(mean) = 177(1)°), while the W–CO ligands have an average angle W–C–O = 172(1)°.

The arrangement of ligands in **5** is in contrast to that of the ligated acetylide and butyne fragments of complex **4**. The carbon atoms of the butyne ligand are linked to the wing-tip Os(2) atom via π-bonds and connected to both hinge Os(1)

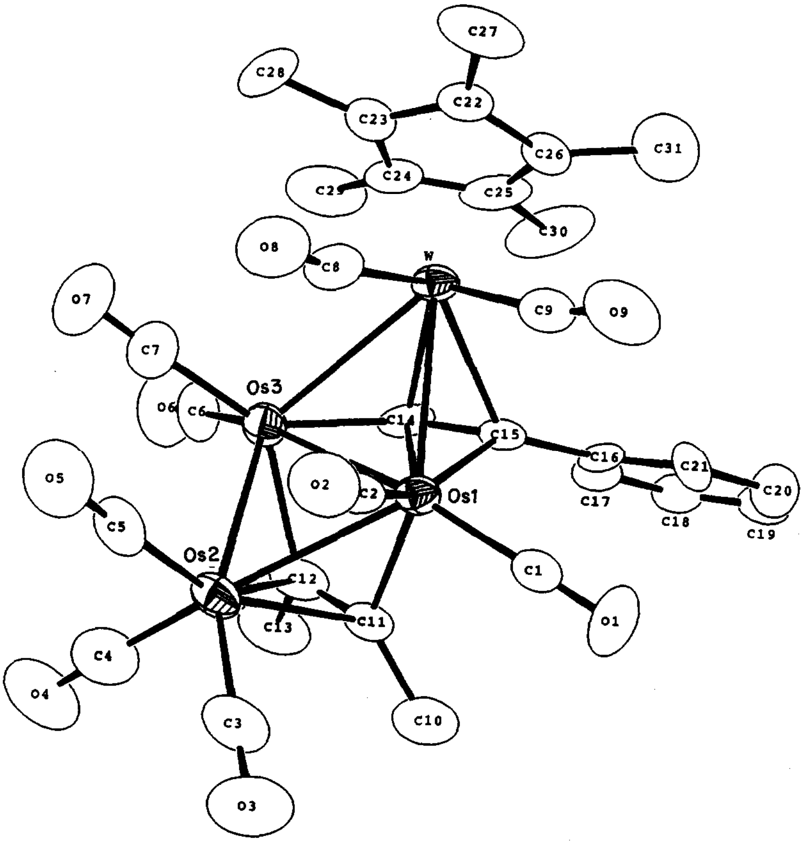


Fig. 3. Molecular structure of 5, showing the atomic numbering scheme.

and Os(3) atoms via σ-bonds, indicating the existence of the common $2\sigma + \pi$ bonding mode. The bonding modes of the butyne ligand are formally identical but the transition metal atoms that support the butyne ligand are different, *i.e.* the butyne ligand in **5** is coordinated to a triosmium triangle whereas the butyne ligand in **4** resides over the WOs_2 face. The acetylide ligand is found to coordinate to the unique WOs_2 face with metal–carbon distances W–C(14) = 2.23(1), Os(1)–C(14) = 2.31(1), Os(3)–C(14) = 1.90(1), Os(1)–C(15) = 2.18(1) and W–C(15) = 2.32(1) Å; therefore, the mode is best described as a μ_3-η^2 mode, different from the μ_4-mode of **4**. The phenyl substituent is perpendicular to the Os(1)–W vector, presumably due to minimization of the steric interaction with the adjacent CO ligands. The arrangement of this μ_3-η^2 acetylide is similar to that of the related, structurally characterized trinuclear derivative $CpWOs_2(CO)_8(CCPh)$ [13].

The ^{13}C NMR data are in accordance with the arrangement of CO and acetylide and butyne ligands. The ^{13}C NMR spectrum at 240 K shows two terminal W–CO signals at δ 214.9 (J(W–C) = 164 Hz) and 210.5 (J(W–C) = 156 Hz), and six terminal Os–CO resonances at δ 197.3, 192.9, 192.6, 184.8 (2C), 171.3 and 170.4 as required for the established structure. The signals at δ 184.8 with ratio two may be caused by either an accidental degeneracy or a localized pairwise exchange of

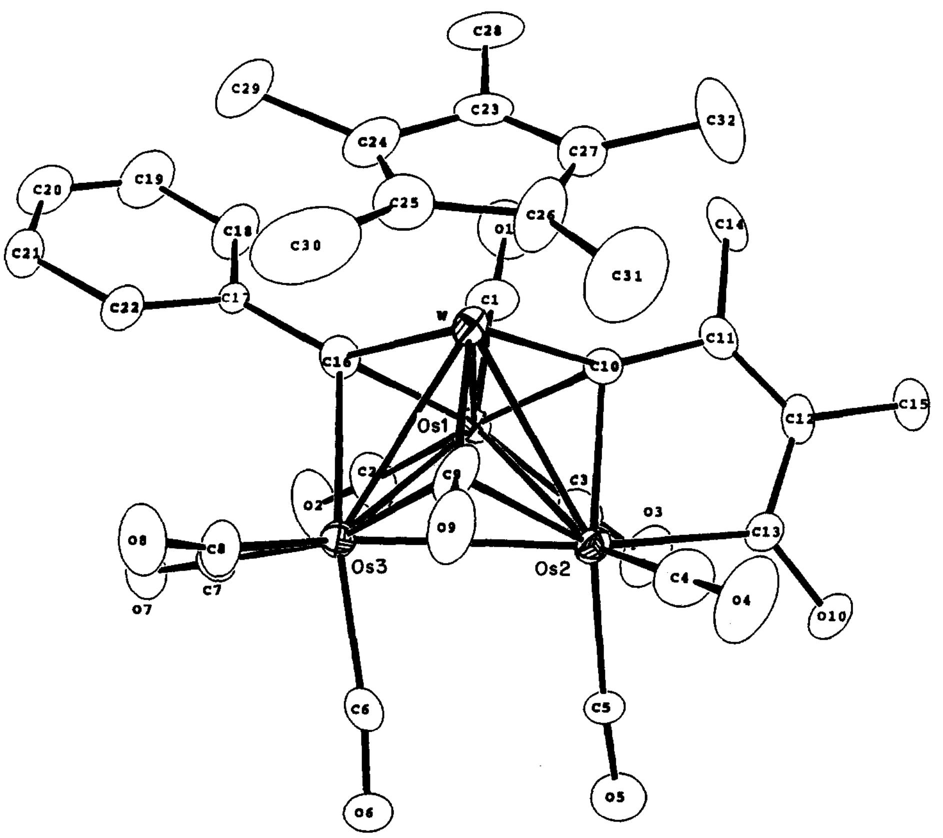
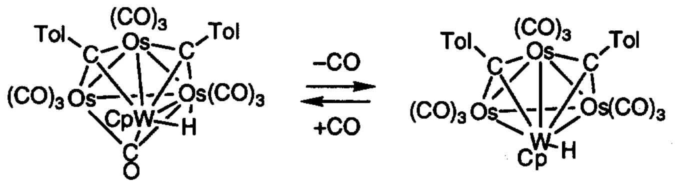


Fig. 4. Molecular structure of **6**, showing the atomic numbering scheme.

the $Os(CO)_2$ center. The signals for the acetylide and butyne ligands occur at δ 148.5, 78.8, 143.1 and 137.5, respectively. The assignment of the peaks due to the α-carbon of acetylide, *ipso*-carbon of the phenyl group and the butyne carbons, is questionable because of the small difference of chemical shifts and lack of tungsten–carbon coupling.

Crystal structure of complex 6

Green single crystals obtained from dichloromethane/hexane at room temperature were suitable for an X-ray diffraction study; the molecular structure is shown in Fig. 4 and selected bond lengths and angles appear in Table 9. The metal framework of this molecule is constituted of a slightly distorted WOs_3 tetrahedron, with metal–metal distances ranging from 2.879(2) to 2.829(1) Å. The tungsten atom is coordinated by a Cp and triply bridging CO ligand and the osmium atoms are each coordinated by three, three and two terminal CO ligands, respectively. Two substantially different alkylidyne ligands occupy similar locations. The first, centered on atom C(16), is bonded to a WOs_2 triangle and considered as a normal alkylidyne ligand. This alkylidyne ligand originated from the coordinated acetylide ligand via C–C bond scission; the osmium–alkylidyne distances, Os(1)–C(16) = 2.17(2) and Os(3)–C(16) = 2.17(2) Å, are equivalent but longer than the tungsten–



Scheme 3.

alkylidyne distance, W–C(16) = 1.94(1) Å. The observed W–C(16) distance is in turn comparable to that of the bridging CO ligand (W–C(9) = 1.97(2) Å) located on the adjacent WOs_2 triangle, indicating the existence of some multiple bond character. The second alkylidyne ligand, produced by coupling of the α-carbon of the acetylide, the butyne and a carbonyl group, is centered on atom C(10), spans the third WOs_2 face and links to Os(2) via an additional Os–C(13) σ-interaction to complete a metallocyclic arrangement. Irregularities around C(10) in this ligand are more pronounced than those around C(16) of the normal alkylidyne ligand. The W–C(10) distance is the shortest (1.95(1) Å) and the Os(2)–C(10) distance is 0.1 Å shorter than the Os(1)–C(10) distance. The Os(2)–C(10) distance is almost equivalent to that of the Os(2)–C(13) vector located at a *cis*, equatorial position, the C(10)–Os(2)–C(13) angle being 77.7(6)°.

From the viewpoint of the WOs_3 core arrangement and the distribution of the ligated alkylidynes, complex **6** is related to the butterfly complex $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2(\mu\text{-H})$, synthesized by the reaction of $H_2Os_3(CO)_{10}$ and $Cp(CO)_2W(CTol)$, and the tetrahedral complex $CpWOs_3(CO)_9(\mu_3\text{-CTol})_2H$, prepared via subsequent thermally induced CO elimination (Scheme 3) [14]. The complex $CpWOs_3(CO)_9(\mu_3\text{-CTol})_2H$ undergoes reversible tetrahedral to butterfly transformation via addition of CO across an open face of the WOs_3 cluster core, *i.e.* the third WOs_2 face not occupied by bridging alkylidyne ligands. Unlike these bis-alkylidyne complexes, complex **6** fails to add CO in refluxing toluene to afford a butterfly geometry similar to that of $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2(\mu\text{-H})$, because addition of CO across a W–Os edge must require the migration of the acyl ligand from the $Os(CO)_2$ center to the tungsten atom. Thermolysis of **6** under 1 atm CO in toluene solution gave complex **3e** (54%) by de-insertion of the acyl CO ligand instead. This negative result suggests that the proposed acyl migration process is thermodynamically unfavored.

For complex **6**, the ^{13}C NMR data of these ligated hydrocarbons have been assigned unambiguously because their chemical shifts are distinct from the other ^{13}C signals. The Os–CO resonances emerge at δ 187.9, 178.8, 174.0 (broad) and 173.8 of ratio 1:1:3:3; the last two signals are due to two $Os(CO)_3$ units undergoing rapid rotation. The resonances for the alkylidyne carbons appear at δ 282.1 (J(W–C) = 122 Hz) and 250.6 (J(W–C) = 107 Hz). The carbon atoms of the butyne fragment appear at δ 181.1 (J(W–C) = 15 Hz) and 163.4 (J(W–C) = 15 Hz), whereas the signals for the triply bridging CO ligand and the unique acyl CO ligand appear at δ 280.6 (J(W–C) = 150 Hz) and 204.6, respectively.

Summary

Condensation of triosmium alkyne complexes $Os_3(CO)_{10}(C_2R_2)$, R = Tol and Me, with mononuclear tungsten acetylide complexes $LW(CO)_3C{\equiv}CR'$, L = Cp and

Cp*, R′ = Ph and ^{t}Bu generated six heterometallic cluster complexes **1–6** via 1:1 combination of the starting materials. The tetrahedral complexes **1** were formed via coupling of the ligated alkyne with the β-carbon of the acetylide ligand and were observed in all the cases studied. In contrast, the planar rhomboidal cluster **2**, generated via coupling of the ligated alkyne with the α-carbon of the acetylide ligand, was isolated only in the reaction between $Os_3(CO)_{10}(C_2Me_2)$ and $CpW(CO)_3C{\equiv}CPh$ in about 41% yield. The reactivity of **2** differs greatly from that of the analogous $CpWOs_3(CO)_{10}[C(R)C(R)CC(Ph)]$, R = CO_2Et and CO_2Me containing the electron-withdrawing substituents [4]. On thermolysis, complex **2** loses one CO and affords complex **7** via *ortho*-metallation of the phenyl substituent and complex **3a** via cleavage of the C–C bond of the ligated C_4 hydrocarbon fragment, confirming that the alkylidyne and the coordinated C_3 hydrocarbon ligand in **3a** was generated via prior alkyne–acetylide coupling following by cleavage of a C–C bond. This reaction is the only case where we have unambiguously confirmed the origination of **3a**. The related derivatives **3b** and **3e** were isolated in low yield from the respective condensation reaction, although we failed to isolate the complexes **2a** and **2e** as intermediates in these two reactions. The reactions of $Os_3(CO)_{10}(C_2Tol_2)$ with acetylide complexes $LW(CO)_3C{\equiv}CR'$ containing a bulky substituent (L = Cp*, R′ = Ph; L = Cp, R′ = ^{t}Bu), in refluxing toluene afforded only one cluster complex **1c** and **1d**, respectively.

For the reaction between $Os_3(CO)_{10}(C_2Me_2)$ and $Cp^*W(CO)_3C{\equiv}CPh$, in addition to the expected complexes **1e** and **3e**, we observed the formation of three new complexes **4**, **5** and **6**. The X-ray structural determination reveals that the butyne and acetylide ligands in butterfly complexes **4** and **5** remain as two uncoupled entities. Complexes **4** and **5** are not the precursors for the formation of other cluster complexes, since pyrolysis of these two complexes in refluxing toluene failed to produce **1e** or **2e**, but we have isolated a trace amount of **3e** (about 2%) during the thermolysis of **4** in refluxing toluene for 2 h. The major, isolable cluster complexes are the unreacted starting material **4** (50%) and an unknown decarbonylation product (36%). Finally, complex **6** possesses a tetrahedral metal skeleton with two triply bridging alkylidyne ligands and a triply bridging CO ligand coordinated to the WOs_2 triangles. We believe that the formation of alkylidyne ligands occurs via a C–C bond scission process, except that a CO ligand has to insert into the Os–C linkage of the ligated butyne fragment, affording the observed, cyclic CC(Me)C(Me)CO arrangement. Consequently, complex **6** may be formed via the formation of an intermediate with a linear CPhCCMeCMe or CPhCCMeCMeCO linkage similar to that observed in complex **2**. However, this possibility remains an unconfirmed hypothesis because pyrolsis of **2** in refluxing toluene gave only **3b** and **7** as the isolable products. Furthermore, thermolysis of **6** under 1 atm of CO atmosphere, fails to afford the expected CO addition reaction but leads to the de-insertion of the acyl CO fragment and formation of **3e** in 54% yield, suggesting that complex **3e** is a thermodynamic product of the reaction.

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