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Rearrangement of acetylide and vinylidene ligands on the coordination spheres of cluster complexes. Reaction of the trinuclear acetylide cluster CpWOs2(CO)8(C.tplbond.CPh) with mononuclear metal hydride complexes LW(CO)3H (L = Cp, Cp*)

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Table IV. Crystal and Experimental Data

formula	$Os_2AgSi_4F_4N_2C_{26}BH_{54}$
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	15.348 (3)
b, Å	18.272 (3)
c, Å	14.114 (2)
β, deg	91.76 (1)
V, Å^3	3956 (2)
Z	4
dens (calc), g/cm^3	1.817
dimens, mm	0.2 × 0.4 × 0.5
μ, cm^{-1}	70.56
transm factor range	0.265–0.052 (numerical)
2θ limit, deg (octants)	46° ($+h,+k,+l$)
no. of intensities (unique, R_i)	6089 (4575, 0.081)
no. of intensities > $2.58\sigma(I)$	3692
R	0.065
R_w (for $w = 1/\sigma^2(F_o) + pF_o^2$)	0.078 (p = 0.03)
max dens in ΔF map, e/Å^3	2.58

with additional details concerning the collection of the data.

Solution and Refinement of the Structure. The structure was solved by direct methods (SHELXS-86);[19] correct positions for the osmium and silver atoms were deduced from an E map. Subsequent least squares-difference Fourier calculation revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for nonhydrogen atoms and a common isotropic thermal parameter was varied for hydrogen atoms. The highest peaks in the final difference map were in the vicinity of the heavy-metal positions. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors.

Synthesis of $[(\eta^5\text{-}C_5H_5)Os(NMe)(CH_2SiMe_3)_2][OSO_2CF_3]$ (5). A solution of 1 (10 mg, 0.023 mmol) in $CDCl_3$ (0.65 mL) was placed in a 5-mm NMR tube along with $MeOSO_2CF_3$ (26 μL, 0.23 mmol). The reaction was monitored by ^1H NMR spectroscopy. After 10 h, the reaction mixture was filtered and solvent and unreacted starting materials were removed in vacuo. The residue consisted of 9 mg (64%) of analytically pure 4. ^1H NMR (500 MHz, CD_2Cl_2, 18 °C): δ 6.06 (s, $C_5\mathbf{H}_5$), 3.05 (d, J = 12.9 Hz, $OsC\mathbf{H}^a\mathbf{H}^b$), 2.78 (s, $NC\mathbf{H}_3$), 2.49 (d, J = 12.9, $OsCH^a\mathbf{H}^b$), 0.19 (s, $Si(C\mathbf{H}_3)_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 18 °C): δ 96.2 ($\mathbf{C}_5H_5$), 61.5 ($N\mathbf{C}H_3$), 1.5 ($Si(\mathbf{C}H_3)_3$), −6.3 ($Os\mathbf{C}H_2$). Anal. Calcd for $C_{15}H_{30}F_3NO_3OsSSi_2$: C, 29.64; H, 4.97; N, 2.30. Found: C, 29.85; H, 4.79; N, 2.37.

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Supplementary Material Available: For $\{[(\eta^5\text{-}C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu\text{-}NAgN)\}\{BF_4\}$, tables of atomic coordinates, thermal parameters, and selected distances and angles (5 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Rearrangement of Acetylide and Vinylidene Ligands on the Coordination Spheres of Cluster Complexes. Reaction of the Trinuclear Acetylide Cluster $CpWOs_2(CO)_8(C{\equiv}CPh)$ with Mononuclear Metal Hydride Complexes $LW(CO)_3H$ (L = Cp, Cp*)

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Reaction of $CpWOs_2(CO)_8(C{\equiv}CPh)$ with 1.2 equiv of Me_3NO in a mixture of dichloromethane–acetonitrile at room temperature followed by in situ reaction with hydride complexes $LW(CO)_3H$, L = Cp and Cp*, in refluxing toluene produced the acetylide cluster complexes $CpLW_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2a**, L = Cp; **2b**, L = Cp*) and vinylidene cluster complexes $CpLW_2Os_2(CO)_9(CCHPh)$ (**3a**, L = Cp; **3b**, L = Cp*). Heating of the acetylide or vinylidene complex in refluxing toluene induced a reversible rearrangement, giving a mixture of both isomeric complexes. The structures of complexes **2b** and **3b** have been determined by single-crystal X-ray diffraction. Crystal data for **2b**: space group $P2_1/c$; a = 34.301 (6), b = 12.319 (4), c = 24.718 (6) Å; β = 103.38 (2)°; Z = 12; final R_F = 0.092, R_w = 0.101 for 8771 reflections with $I > 2\sigma(I)$. Crystal data for **3b**: space group $P4_2/n$; a = 25.486 (6), c = 9.747 (4) Å; Z = 8; final R_F = 0.034, R_w = 0.030 for 3724 reflections with $I > 2\sigma(I)$.

Introduction

The C_2 hydrocarbons hold a key position in the development of organometallic chemistry.[1] Much research has been focused on the synthesis of complexes containing the so-called C_2 hydrocarbon ligands such as acetylene, ethylene, vinyl, vinylidene, or acetylide.[2] The synthesis

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and chemistry of these C_2 hydrocarbon complexes, particularly the acetylide and vinylidene derivatives, have been under intensified examination in recent years. Deeming and co-workers have reported the crystal structure and the reactivities of many acetylide clusters in the triosmium system.[3] Carty and co-workers have studied the trinuclear and polynuclear ruthenium cluster complexes containing both the acetylide and the phosphorus bridging ligands.[4] Vahrenkamp and co-workers have shown some unique examples about the rearrangement of the vinylidene and alkyne ligands in the system of trinuclear and tetranuclear mixed-metal clusters.[5] Recent work by Bullock has demonstrated the ability of mononuclear metal acetylide complexes to accept protons from metal hydride complexes to produce a vinyl or a vinylidene complex.[6]

We have recently reported the systematic synthesis of heterobimetallic acetylide clusters $LWOs_3(CO)_{10}(C\equiv CPh)$, $Cp_2Mo_2Ru_2(CO)_{10}(C\equiv CPh)_2$, and $LWM_2(CO)_8(C\equiv CPh)$ (L = Cp, Cp*; M = Os, Ru).[7] Our studies have also revealed that the acetylide ligand of the trinuclear $LWRu_2(CO)_8(C\equiv CPh)$ complexes undergoes an edge-hopping motion on the face of metal triangle.[8] In addition to the studies of their structures and solution dynamics, another goal of our research is to gain some knowledge about the chemistry of the acetylide ligand in these heterometallic systems. We have therefore carried out the reactions of $CpWOs_2(CO)_8(C\equiv CR)$ with various disubstituted alkynes[9] and with mononuclear transition-metal hydride complexes $LW(CO)_3H$ (L = Cp and Cp*). The reaction with alkynes would not change the nuclearity of the products. On the other hand, the reaction with metal hydrides is classified as a cluster expansion reaction.[10] The latter is of interest because it allows us to increase the nuclearity of the cluster by one unit and, at the same time, to modify the acetylide fragment on the ligand sphere of the newly assembled clusters. In this paper, we report details of the crystal structures and the reactivity studies of the tetranuclear acetylide $CpLW_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ and vinylidene $CpLW_2Os_2(CO)_9(CCHPh)$ complexes isolated.

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 (400.13 MHz) instrument or a Varian Gemini-300 (300 MHz) instrument. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment mode (FAB). All reactions were performed under a nitrogen atmosphere by using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck), and the products were separated on the 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 acetylide complexes $CpWOs_2(CO)_8(C\equiv CPh)$ and $CpMoOs_2(CO)_8(C\equiv CPh)$ were prepared from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with the appropriate metal acetylide complexes $CpM(CO)_3C\equiv CPh$ (M = W and Mo).[8b] The acetylide complex $CpWOs_2(CO)_8(C^*CPh)$ with the acetylide α-carbon enriched with approximately 30% ^{13}C carbon was prepared from labeled acetylide complexes $CpW(CO)_3C^*CPh$.[11] The metal hydride complex $CpW(CO)_3H$ was prepared by protonation of the sodium salt of $CpW(CO)_3^-$ anion with acetic acid at ambient temperature, whereas the hydride $Cp^*W(CO)_3H$ was prepared by the reaction of pentamethylcyclopentadiene with $W(CO)_3(NCEt)_3$ in toluene at 100 °C.[12]

Reaction of $CpWOs_2(CO)_8(C\equiv CPh)$ with $CpW(CO)_3H$. In a 50-mL round-bottom reaction flask, the acetylide complex $CpWOs_2(CO)_8(C\equiv CPh)$ (63 mg, 0.066 mmol) was treated with sublimed Me_3NO (6.4 mg, 0.085 mmol) in a mixture of dichloromethane (25 mL) and acetonitrile (10 mL) at ambient temperature for 30 min. After evaporation of the solvent on a rotavapor evaporator and then under vacuum, $CpW(CO)_3H$ (49 mg, 0.148 mmol) was added, and the reaction mixture was then dissolved in a toluene solution (35 mL) and the solution brought to reflux for 30 min. Finally, the solvent was evaporated in vacuo, and the residue was separated by thin-layer chromatography (silica gel, 1:1 dichloromethane–hexane), giving 10 mg of the starting material $CpWOs_2(CO)_8(C\equiv CPh)$ (0.010 mmol, 16%), 27 mg of $Cp_2W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2a**) as a dark brown material (0.022 mmol, 33%), and approximate 1 mg of $Cp_2W_2Os_2(CO)_9(CCHPh)$ (**3a**) as a red material (0.0015 mmol, 2%). Crystals of $Cp_2W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ were obtained by recrystallization from a layered solution of dichloromethane–methanol at room temperature.

Spectral data for **2a**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1236 (M^+); IR (C_6H_{12}) ν(CO) 2071 (vs), 2025 (vs), 2003 (vs), 1977 (w), 1968 (m), 1959 (s), 1953 (m), 1886 (w), 1810 cm^{-1} (vw); ^1H NMR ($CDCl_3$, 294K) δ 7.68 (d, 2 H, J_{H-H} = 7.9 Hz), 7.42 (t, 2 H, J_{H-H} = 7.4 Hz), 7.35 (t, 1 H, J_{H-H} = 7.4 Hz), 5.59 (s, 5 H), 4.62 (s, 5 H), -18.86 (s, 1 H, J_{W-H} = 69.2 Hz). Anal. Calcd for $C_{27}H_{16}O_9Os_2W_2$: C, 26.31; H, 1.31. Found: C, 26.23; H, 1.32.

Spectral data for **3a**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1236 (M^+); IR (C_6H_{12}) ν(CO) 2054 (s), 2006 (vs), 1988 (m), 1975 (s), 1958 (s), 1853 (br, vw), 1953 (m), 1817 cm^{-1} (w); ^1H NMR ($CDCl_3$, 294 K) δ 7.47 (d, 2 H, J_{H-H} = 8.7 Hz), 7.31 (t, 2 H, J_{H-H} = 6.3 Hz), 7.13 (t, 1 H, J_{H-H} = 6.2 Hz), 6.72 (s, 1 H), 5.52 (s, 5 H), 5.45 (s, 5 H).

Reaction of $CpWOs_2(CO)_8(C\equiv CPh)$ with $Cp^*W(CO)_3H$. In a 50-mL round-bottom reaction flask, an acetonitrile solution (8 mL) of freshly sublimed Me_3NO (6.8 mg, 0.091 mmol) was added slowly to a mixed solution of dichloromethane (25 mL) and acetonitrile (5 mL) containing 62 mg of the acetylide complex $CpWOs_2(CO)_8(C\equiv CPh)$ (0.065 mmol) at ambient temperature within 20 min. After removal of the solvent on a rotavapor evaporator and then under vacuum, $Cp^*W(CO)_3H$ (54 mg, 0.134 mmol) was added, and the mixture was then dissolved in a toluene solution (30 mL) and the solution brought to reflux for 30 min. Finally, the solvent was evaporated under vacuum, and the residue was separated by thin-layer chromatography (silica gel, 1:1 dichloromethane–hexane), giving 12 mg of the yellow starting material $CpWOs_2(CO)_8(C\equiv CPh)$ (0.013 mmol, 19%), 8 mg of $CpCp^*W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2b**) as a brown crystalline material (0.006 mmol, 9%) and 10 mg of $CpCp^*W_2Os_2(CO)_9(CCHPh)$ (**3b**) as a red crystalline material (0.008 mmol, 12%). For both

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complexes, crystals suitable for X-ray diffraction studies were obtained by recrystallization from a layered solution of dichloromethane–methanol at room temperature.

Spectral data for **2b**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1306 (M^+); IR (C_6H_{12}) ν(CO) 2068 (vs), 2021 (vs), 1999 (s), 1970 (sh, w), 1964 (m), 1948 (s), 1939 (m), 1873 (w), 1810 cm^{-1} (vw); ^{1}H NMR ($CDCl_3$, 294 K) δ 7.62 (d, 2 H), 7.38 (m, 3 H), 4.57 (s, 5 H), 2.21 (s, 15 H), -18.73 (s, 1 H, J_{W-H} = 69.5 Hz); ^{13}C NMR (CD_2Cl_2, 294 K) δ 233.7 (CO, J_{W-C} = 164 Hz), 219.1 (CO, J_{W-C} = 176 Hz), 214.7 (CO, J_{W-C} = 183 Hz), 207.3 (*C*CPh, J_{W-C} = 117 Hz), 184.1 (CO), 181.3 (CO), 180.2 (CO, J_{C-H} = 4 Hz), 175.9 (CO), 171.3 (CO, J_{C-H} = 10 Hz), 170.6 (CO), 154.2 (ipso-C of C_6H_5), 150.8 (C*C*Ph), 128.2 (*o*,*m*-C of C_6H_5), 127.5 (*p*-C of C_6H_5), 127.1 (*o*,*m*-C of C_6H_5), 102.9 (C_5Me_5), 90.6 (C_5H_5), 10.7 (C_5Me_5). Anal. Calcd for $C_{32}H_{26}O_9Os_2W_2$: C, 29.51; H, 2.01. Found: C, 29.46; H, 2.03.

Spectral data for **3b**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1306 (M^+); IR (C_6H_{12}) ν(CO) 2050 (s), 2001 (vs), 1982 (m), 1971 (s), 1953 (m), 1942 (vw), 1834 (br, vw), 1805 cm^{-1} (br, w); ^{1}H NMR ($CDCl_3$, 294 K) δ 7.51 (d, 2 H, J_{H-H} = 7.5 Hz), 7.29 (t, 2 H, J_{H-H} = 7.6 Hz), 7.14 (t, 1 H, J_{H-H} = 7.4 Hz), 6.83 (s, 1 H), 5.43 (s, 5 H), 2.03 (s, 15 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 294 K) δ 273.5 (CO, J_{W-C} = 96 Hz), 232.2 (CO, J_{W-C} = 162 Hz), 231.9 (*C*CHPh, J_{W-C} = 160 Hz), 219.9 (CO, J_{W-C} = 164 Hz), 206.5 (CO, J_{W-C} = 153 Hz), 185.7 (CO), 184.5 (CO), 181.2 (CO, broad), 179.9 (CO, broad), 176.7 (CO, broad), 148.2 (ipso-C of C_6H_5), 130.6 (*o*,*m*-C of C_6H_5), 128.0 (*o*,*m*-C of C_6H_5), 126.7 (*p*-C of C_6H_5), 103.3 (C_5Me_5), 94.25 (C_5H_5), 71.8 (C*C*HPh), 10.3 (C_5Me_5). Anal. Calcd for $C_{32}H_{26}O_9Os_2W_2$: C, 29.51; H, 2.01. Found: C, 29.42; H, 2.05.

Reaction of $CpMoOs_2(CO)_8(C{\equiv}CPh)$ with $CpW(CO)_3H$. In a 50-mL round-bottom reaction flask, an acetonitrile solution (8 mL) of freshly sublimed Me_3NO (6.4 mg, 0.085 mmol) was added dropwise into a mixed solution of dichloromethane (25 mL) and acetonitrile (5 mL) containing 70 mg of the acetylide complex $CpMoOs_2(CO)_8(C{\equiv}CPh)$ (0.080 mmol) at ambient temperature within 20 min. After evaporation of the solvent in vacuo, $CpW(CO)_3H$ (27 mg, 0.08 mmol) was added, and the mixture was then dissolved in a toluene solution (30 mL) and the solution refluxed for 15 min. Finally, the solvent was evaporated under vacuum, and the residue was separated by thin-layer chromatography (silica gel, 1:1 dichloromethane–hexane), giving 40 mg of the yellow $CpMoOs_2(CO)_8(C{\equiv}CPh)$ (0.046 mmol, 58%) and 19 mg of $Cp_2MoWOs_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2c**) as a yellowish green crystalline material (0.017 mmol, 21%). Crystalline solids of **2c** were recrystallized from a layered solution of dichloromethane–methanol at room temperature.

Spectral data for **2c**: MS (FAB, ^{98}Mo, ^{192}Os, ^{184}W) *m/z* 1150 (M^+); IR (C_6H_{12}) ν(CO) 2072 (vs), 2028 (vs), 2005 (vs), 1980 (w), 1970 (m), 1958 (s), 1956 (m), 1889 (w), 1812 cm^{-1} (vw); ^{1}H NMR (CD_2Cl_2, 294 K) δ 7.59 (d, 2 H, J_{H-H} = 8.2 Hz), 7.39 (t, 2 H, J_{H-H} = 7.6 Hz), 7.30 (t, 1 H, J_{H-H} = 6.9 Hz), 5.60 (s, 5 H), 4.62 (s, 5 H), -16.08 (s, 1 H). Anal. Calcd for $C_{27}H_{16}MoO_9Os_2W$: C, 28.33; H, 1.41. Found: C, 28.32; H, 1.43.

X-ray Crystallography. Diffraction measurements on complexes **2b** and **3b** were carried out on Nonius CAD-4 and a Rigaku AFC-5R diffractometers, respectively. Lattice parameters of complex **2b** were determined from 25 randomly selected reflections, with 2θ angle in the range 21.05–23.20°, whereas the corresponding cell dimensions of complex **3b** were determined from 20 reflections, with the 2θ angle in the range 39.51–40.51°. Intensities were corrected for Lorentz, polarization, and absorption effects. All data reductions and structural refinements were performed by using the NRCC-SDP-VAX packages. The structures were solved by the heavy-atom method and refined by least-squares cycles; all non-hydrogen atoms were refined with anisotropic thermal parameters. The data collection and refinement parameters for complexes **2b** and **3b** are given in Table I. Atomic positional parameters for complex **2b** are found in Table II, whereas some selected bond angles and lengths are given in Table III. The corresponding parameters for complex **3b** are given in Tables IV and V, respectively.

Table I. Experimental Data for the X-ray Diffraction Studies of Complexes 2b and 3b[a]

compd	**2b**	**3b**
formula	$C_{32}H_{26}O_9Os_2W_2$	$C_{32}H_{26}O_9Os_2W_2$
mol wt	1301.63	1301.63
cryst system	monoclinic	tetragonal
space group	$P2_1/c$	$P4_2/n$
a, Å	34.301 (6)	25.486 (6)
b, Å	12.319 (4)	
c, Å	24.718 (6)	9.747 (4)
β, deg	103.38 (2)	
V, Å^3	10162 (4)	6331 (3)
Z	12	8
D_c, g/cm^3	2.552	2.731
F(000)	7077.29	4718.19
diffractometer	Rigaku (AFC-5R)	Nonius (CAD-4)
radiation (λ, Å)	Cu Kα (1.54056)	Mo Kα (0.70930)
temp, K	297	297
cryst size, mm	0.05 × 0.10 × 0.70	0.15 × 0.20 × 0.55
scan method	$\theta/2\theta$ scan mode	$\theta/2\theta$ scan mode
$2\theta_{max}$, deg	100.0	49.8
scan param	$1.05 + 0.30 \tan\theta$	$0.65 + 0.35 \tan\theta$
scan speed, deg/min	8	16.48/2 to 16.48/10
h,k,l ranges	−34 to 33, 0 to 12, 0 to 24	0 to 30, 0 to 30, 0 to 11
abs cor	ψ scan	ψ scan
μ, mm^{-1}	26.64	15.47
transm factors: max; min	0.101; 1.000	0.7905; 0.9991
standard reflcns (no. 3)	decay 50%; every 150 reflcns	variation < 4%, 4σ; every 7200 s
no. of unique data	10476	5570
no. of data with $I > 2\sigma(I)$	8771	3724
no. of atoms and params refined	210, 1217	71, 407
max Δ/σ ratio	0.169	0.264
R; R_w	0.092; 0.101	0.034; 0.030
GOF	4.10	1.63
max/min resid electron density, e Å^{-3}	4.86/−4.87	1.18/−1.75

[a] Features common to both determinations: $w = 1/\sigma^2(F_o)$; GOF $= [\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables).

Results and Discussion

Synthesis and Spectroscopic Characterization. Treatment of the acetylide complexes $CpWOs_2(CO)_8(C{\equiv}CPh)$ (**1**) with 1.2 equiv of Me_3NO in a mixture of acetonitrile–dichloromethane at room temperature followed by in situ reaction with slightly excess $CpW(CO)_3H$ in refluxing toluene (30 min) produced a dark brown acetylide complex $Cp_2W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2a**, 39%) and a trace amount of a second, red-brown vinylidene complex $Cp_2W_2Os_2(CO)_9(CCHPh)$ (**3a**, 2%). Direct reaction with $CpW(CO)_3H$ in refluxing toluene (1 h) failed to produce any new product, suggesting that the generation of the slightly stabilized[13] acetonitrile substituted precursors is essential for the activation of complex **1**. We have also reacted complex **1** with $Cp^*W(CO)_3H$ under similar conditions in attempt to extend the scope of these cluster expansion reactions and to study both the electronic and steric effects of the Cp* ligand on the formation of clusters of higher nuclearity. Two related acetylide $CpCp^*W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2b**, 11%) and vinylidene $CpCp^*W_2Os_2(CO)_9(CCHPh)$ (**3b**, 15%) clusters were isolated in equal amount (Scheme 1). The yield of the new cluster complexes prepared in this study is reported on the basis of the consumption of complex **1**, as a moderate amount of **1** was recovered from the final reaction mixture in every case, independent to the amount of Me_3NO added.

These new complexes were separated and purified on silica gel TLC plates and were initially characterized by

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(13) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* 1981, 409. (b) Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* 1977, *124*, C19.

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) for 2b

	x	y	z	B_{iso}
Os(1A)	0.11122 (4)	0.76882 (14)	0.15826 (7)	4.34 (8)
Os(2A)	0.07848 (4)	0.91795 (14)	0.22361 (7)	4.28 (8)
W(1A)	0.09457 (4)	0.84197 (14)	0.33888 (7)	3.98 (8)
W(2A)	0.15637 (4)	0.84586 (14)	0.26708 (7)	4.04 (8)
C(1A)	0.1328 (10)	0.745 (3)	0.3746 (17)	5.3 (21)
C(2A)	0.1329 (9)	0.955 (3)	0.3633 (14)	4.2 (18)
C(3A)	0.1495 (10)	0.996 (3)	0.2510 (16)	4.8 (18)
C(4A)	0.1461 (12)	0.679 (4)	0.1305 (19)	6.8 (25)
C(5A)	0.1041 (12)	0.860 (3)	0.0925 (18)	6.0 (23)
C(6A)	0.0641 (10)	0.695 (3)	0.1269 (16)	5.3 (20)
C(7A)	0.0256 (10)	0.866 (3)	0.1934 (17)	5.3 (20)
C(8A)	0.0715 (10)	1.030 (3)	0.2703 (16)	5.1 (20)
C(9A)	0.0762 (11)	1.014 (3)	0.1648 (18)	5.9 (22)
C(10A)	0.0558 (11)	0.925 (4)	0.3931 (18)	6.6 (24)
C(11A)	0.0287 (9)	0.891 (3)	0.3462 (14)	4.2 (17)
C(12A)	0.0304 (9)	0.783 (3)	0.3429 (14)	3.9 (16)
C(13A)	0.0585 (11)	0.741 (3)	0.3909 (17)	5.4 (21)
C(14A)	0.0750 (12)	0.832 (4)	0.4208 (20)	7.3 (27)
C(15A)	0.0619 (11)	1.037 (3)	0.4187 (19)	6.4 (23)
C(16A)	–0.0036 (12)	0.958 (4)	0.3132 (20)	7.6 (27)
C(17A)	0.0034 (10)	0.714 (4)	0.3049 (18)	6.4 (24)
C(18A)	0.0646 (13)	0.630 (3)	0.4104 (20)	7.2 (26)
C(19A)	0.1020 (9)	0.836 (3)	0.4799 (17)	4.8 (19)
C(20A)	0.2072 (10)	0.724 (3)	0.3104 (18)	5.5 (21)
C(21A)	0.2143 (10)	0.760 (3)	0.2596 (19)	6.3 (24)
C(22A)	0.2211 (9)	0.870 (3)	0.2640 (18)	5.7 (22)
C(23A)	0.2183 (10)	0.904 (3)	0.3173 (18)	5.5 (21)
C(24A)	0.2094 (10)	0.812 (3)	0.3437 (16)	5.1 (20)
C(25A)	0.0977 (9)	0.770 (3)	0.2674 (14)	3.9 (16)
C(26A)	0.1116 (8)	0.6996 (25)	0.2339 (14)	3.3 (15)
C(27A)	0.1217 (10)	0.578 (3)	0.2516 (16)	5.2 (20)
C(28A)	0.1503 (11)	0.518 (3)	0.2340 (18)	5.7 (21)
C(29A)	0.1531 (13)	0.405 (3)	0.2472 (20)	7.3 (26)
C(30A)	0.1303 (12)	0.357 (3)	0.2767 (19)	6.7 (25)
C(31A)	0.1016 (12)	0.418 (4)	0.2924 (20)	7.6 (27)
C(32A)	0.0964 (10)	0.530 (3)	0.2824 (16)	5.0 (20)
O(1A)	0.1534 (7)	0.6772 (21)	0.4036 (12)	6.4 (15)
O(2A)	0.1549 (7)	1.0291 (20)	0.3829 (11)	5.7 (13)
O(3A)	0.1557 (7)	1.0930 (21)	0.2461 (13)	6.8 (16)
O(4A)	0.1684 (7)	0.6293 (23)	0.1111 (13)	7.3 (17)
O(5A)	0.1001 (9)	0.9071 (25)	0.0532 (14)	8.9 (21)
O(6A)	0.0375 (8)	0.645 (3)	0.1062 (15)	9.1 (21)
O(7A)	–0.0058 (8)	0.8428 (25)	0.1709 (14)	8.2 (19)
O(8A)	0.0707 (7)	1.1214 (20)	0.2915 (12)	6.1 (14)
O(9A)	0.0773 (9)	1.0826 (25)	0.1329 (14)	8.5 (19)
Os(1B)	0.27254 (4)	0.51983 (13)	0.04581 (7)	4.33 (8)
Os(2B)	0.23703 (4)	0.34571 (13)	0.09310 (7)	4.27 (8)
W(1B)	0.24560 (5)	0.14565 (14)	0.03284 (8)	4.25 (8)
W(2B)	0.31260 (5)	0.30932 (14)	0.07263 (7)	4.26 (8)
C(1B)	0.2819 (9)	0.117 (3)	–0.0141 (15)	4.0 (17)
C(2B)	0.2865 (10)	0.083 (3)	0.0963 (19)	5.9 (22)
C(3B)	0.3091 (11)	0.298 (3)	0.1497 (17)	5.9 (22)
C(4B)	0.3054 (11)	0.612 (3)	0.0105 (20)	6.5 (24)
C(5B)	0.2752 (11)	0.620 (3)	0.1060 (18)	6.0 (22)
C(6B)	0.2238 (9)	0.581 (3)	0.0050 (17)	5.0 (20)
C(7B)	0.1859 (9)	0.392 (3)	0.0581 (16)	4.4 (18)
C(8B)	0.2276 (9)	0.230 (3)	0.1366 (15)	4.3 (18)
C(9B)	0.2409 (11)	0.442 (3)	0.1542 (17)	5.8 (21)
C(10B)	0.2038 (10)	0.002 (3)	0.0503 (17)	5.7 (21)
C(11B)	0.1783 (9)	0.094 (3)	0.0318 (16)	4.4 (18)
C(12B)	0.1796 (10)	0.118 (3)	–0.0215 (16)	4.9 (18)
C(13B)	0.2063 (9)	0.047 (3)	–0.0384 (15)	4.4 (17)
C(14B)	0.2207 (11)	–0.023 (3)	0.0050 (19)	6.2 (23)
C(15B)	0.2075 (10)	–0.065 (3)	0.0994 (20)	6.7 (25)
C(16B)	0.1483 (11)	0.134 (3)	0.0649 (21)	7.1 (27)
C(17B)	0.1512 (12)	0.206 (4)	–0.0579 (22)	7.8 (27)
C(18B)	0.2119 (11)	0.042 (3)	–0.0999 (18)	6.0 (23)
C(19B)	0.2472 (13)	–0.120 (4)	0.0010 (21)	8.0 (28)
C(20B)	0.3607 (10)	0.266 (4)	0.0217 (18)	6.4 (24)
C(21B)	0.3712 (11)	0.361 (3)	0.0508 (19)	6.5 (25)
C(22B)	0.3793 (10)	0.345 (3)	0.1065 (18)	5.6 (22)
C(23B)	0.3734 (9)	0.232 (3)	0.1136 (16)	5.0 (19)
C(24B)	0.3625 (10)	0.184 (3)	0.0610 (20)	6.2 (24)
C(25B)	0.2513 (9)	0.2998 (25)	0.0164 (15)	3.9 (16)
C(26B)	0.2679 (8)	0.3892 (24)	–0.0084 (13)	3.1 (15)
C(27B)	0.2756 (9)	0.380 (3)	–0.0634 (15)	4.3 (17)
C(28B)	0.3091 (10)	0.430 (3)	–0.0811 (16)	5.2 (20)
C(29B)	0.3152 (12)	0.416 (4)	–0.1346 (19)	7.0 (25)
C(30B)	0.2877 (13)	0.368 (3)	–0.1740 (21)	7.5 (27)
C(31B)	0.2561 (10)	0.314 (3)	–0.1576 (16)	5.3 (21)
C(32B)	0.2503 (11)	0.325 (3)	–0.1041 (16)	5.4 (21)
O(1B)	0.3031 (7)	0.0906 (23)	–0.0427 (12)	6.9 (16)
O(2B)	0.3088 (7)	0.0378 (23)	0.1291 (13)	7.3 (17)
O(3B)	0.3149 (7)	0.2840 (21)	0.1971 (12)	6.2 (14)
O(4B)	0.3243 (9)	0.6703 (25)	–0.0044 (15)	8.9 (20)
O(5B)	0.2734 (9)	0.696 (3)	0.1336 (15)	8.9 (20)
O(6B)	0.1955 (7)	0.6138 (21)	–0.0206 (13)	6.9 (15)
O(7B)	0.1543 (8)	0.4202 (22)	0.0360 (14)	7.5 (17)
O(8B)	0.2241 (8)	0.1697 (22)	0.1727 (13)	7.1 (16)
O(9B)	0.2428 (7)	0.4979 (23)	0.1919 (12)	6.9 (16)
Os(1C)	0.40088 (5)	0.89456 (16)	0.25234 (8)	5.50 (9)
Os(2C)	0.38584 (4)	0.66731 (16)	0.25243 (7)	4.89 (9)
W(1C)	0.41322 (5)	0.58359 (14)	0.36550 (7)	4.32 (8)
W(2C)	0.46136 (4)	0.73788 (14)	0.30932 (8)	4.34 (8)
C(1C)	0.4521 (9)	0.650 (3)	0.4266 (16)	4.3 (17)
C(2C)	0.4580 (11)	0.508 (3)	0.3439 (19)	6.3 (23)
C(3C)	0.4569 (11)	0.654 (3)	0.2457 (18)	6.0 (22)
C(4C)	0.4174 (12)	1.039 (3)	0.2647 (20)	7.0 (25)
C(5C)	0.3969 (12)	0.909 (4)	0.1757 (19)	7.4 (25)
C(6C)	0.3505 (12)	0.925 (4)	0.2485 (17)	6.9 (24)
C(7C)	0.3334 (11)	0.687 (3)	0.2525 (16)	5.6 (21)
C(8C)	0.3910 (11)	0.513 (3)	0.2458 (20)	6.6 (24)
C(9C)	0.3780 (10)	0.672 (4)	0.1735 (21)	7.6 (28)
C(10C)	0.3863 (10)	0.409 (3)	0.3790 (18)	5.6 (21)
C(11C)	0.3535 (10)	0.477 (3)	0.3566 (17)	5.3 (20)
C(12C)	0.3536 (8)	0.563 (3)	0.3938 (15)	3.9 (17)
C(13C)	0.3824 (11)	0.550 (3)	0.4388 (18)	5.9 (21)
C(14C)	0.4061 (9)	0.453 (3)	0.4314 (17)	5.2 (19)
C(15C)	0.3964 (14)	0.298 (4)	0.354 (3)	9.4 (35)
C(16C)	0.3205 (12)	0.441 (4)	0.3108 (22)	7.7 (28)
C(17C)	0.3201 (10)	0.644 (3)	0.3888 (18)	6.0 (21)
C(18C)	0.3886 (11)	0.608 (3)	0.4945 (19)	6.9 (24)
C(19C)	0.4395 (12)	0.402 (4)	0.4717 (22)	7.9 (29)
C(20C)	0.5118 (10)	0.804 (3)	0.3839 (20)	6.5 (23)
C(21C)	0.5130 (11)	0.855 (4)	0.3352 (22)	7.5 (27)
C(22C)	0.5230 (10)	0.784 (3)	0.2963 (17)	5.7 (21)
C(23C)	0.5265 (11)	0.681 (3)	0.3221 (18)	5.9 (22)
C(24C)	0.5196 (10)	0.692 (3)	0.3733 (18)	6.3 (23)
C(25C)	0.4027 (9)	0.736 (3)	0.3341 (14)	3.9 (17)
C(26C)	0.4103 (8)	0.853 (3)	0.3333 (14)	3.7 (17)
C(27C)	0.4188 (9)	0.909 (3)	0.3889 (15)	4.2 (17)
C(28C)	0.4437 (11)	1.001 (3)	0.3954 (18)	5.8 (22)
C(29C)	0.4547 (12)	1.050 (3)	0.4470 (22)	7.6 (27)
C(30C)	0.4391 (12)	1.014 (4)	0.4900 (21)	7.6 (26)
C(31C)	0.4149 (12)	0.928 (4)	0.4832 (20)	7.2 (26)
C(32C)	0.4058 (9)	0.878 (3)	0.4330 (16)	4.5 (18)
O(1C)	0.4726 (7)	0.6837 (21)	0.4665 (11)	6.0 (14)
O(2C)	0.4825 (8)	0.4508 (22)	0.3359 (14)	7.4 (17)
O(3C)	0.4656 (8)	0.5941 (24)	0.2093 (13)	7.7 (17)
O(4C)	0.4248 (10)	1.129 (3)	0.2719 (17)	10.5 (24)
O(5C)	0.3957 (11)	0.929 (3)	0.1279 (16)	12.0 (27)
O(6C)	0.3145 (8)	0.946 (3)	0.2428 (14)	8.5 (19)
O(7C)	0.2993 (8)	0.701 (3)	0.2530 (13)	8.0 (19)
O(8C)	0.3931 (7)	0.4247 (22)	0.2378 (13)	7.2 (16)
O(9C)	0.3743 (8)	0.682 (3)	0.1249 (13)	7.9 (19)

spectroscopic methods. The molecular ion observed in the FAB mass spectra for complexes **2** and **3** indicates that all these complexes have identical molecular masses, being heterometallic W_2Os_2 clusters with nine CO ligands and one coordinated C_2Ph moiety.

The ^1H NMR spectra of **2a** and **2b** each display a high-field resonance signal at δ −18.86 (J_{W-H} = 69.2 Hz) and at δ -18.73 (J_{W-H} = 69.5 Hz), respectively, indicating the presence of bridging hydride, which is associated with a Os–W bond. Therefore, the bonding mode of the original C_2 acetylide ligand is retained in complex **2**. Consistent with this assignment, the ^{13}C NMR spectrum of **2b** showed nine CO signals in the region between δ 233.7 and 170.6 and two acetylide signals at δ 207.3 (J_{W-C} = 117 Hz) and

Table III. Selected Bond Distances (Å) and Angles (deg) of Complex 2b (Esd's in Parentheses)

(A) Intermetallic Parameters			
Os(1A)–Os(2A)	2.844 (2)	Os(1A)–W(2A)	2.934 (3)
Os(2A)–W(1A)	2.928 (2)	Os(2A)–W(2A)	2.784 (2)
W(1A)–W(2A)	3.064 (2)		
∠Os(2A)–Os(1A)–W(2A)	57.60 (5)	∠Os(1A)–Os(2A)–W(1A)	109.64 (7)
∠Os(1A)–Os(2A)–W(2A)	62.82 (6)	∠W(1A)–Os(2A)–W(2A)	64.82 (6)
∠Os(2A)–W(1A)–W(2A)	55.33 (5)	∠Os(1A)–W(2A)–Os(2A)	59.58 (6)
∠Os(1A)–W(2A)–W(1A)	103.71 (6)	∠Os(2A)–W(2A)–Os(1A)	59.85 (5)
(B) Parameters Associated with the Acetylide Fragment			
Os(2A)–C(25A)	2.14 (3)	W(1A)–C(25A)	2.00 (3)
W(2A)–C(25A)	2.22 (3)	Os(1A)–C(26A)	2.05 (3)
W(2A)–C(26A)	2.39 (3)	C(25A)–C(26A)	1.36 (4)
∠W(1A)–C(25A)–C(26A)	156 (3)	∠C(25A)–C(26A)–C(27A)	121 (3)
(C) Selected Parameters of the Carbonyl Ligands			
W(1A)–C(1A)	1.84 (4)	W(1A)–C(2A)	1.91 (3)
W(2A)–C(3A)	1.89 (3)	Os(1A)–C(4A)	1.87 (4)
Os(1A)–C(5A)	1.95 (4)	Os(1A)–C(6A)	1.86 (4)
Os(2A)–C(7A)	1.91 (3)	Os(2A)–C(8A)	1.85 (4)
Os(2A)–C(9A)	1.86 (4)		
∠W(1A)–C(1A)–O(1A)	168 (3)	∠W(1A)–C(2A)–O(2A)	172 (3)
∠W(2A)–C(3A)–O(3A)	163 (3)	∠Os(1A)–C(4A)–O(4A)	175 (4)
∠Os(1A)–C(5A)–O(5A)	175 (3)	∠Os(1A)–C(6A)–C(6A)	174 (4)
∠Os(2A)–C(7A)–O(7A)	172 (3)	∠Os(2A)–C(8A)–O(8A)	162 (3)
∠Os(2A)–C(9A)–O(9A)	171 (4)	∠Os(2A)–W(2A)–C(3A)	63 (1)
∠W(2A)–Os(2A)–C(8A)	104 (1)	∠W(2A)–Os(2A)–C(9A)	112 (1)
∠Os(1A)–W(2A)–C(3A)	96 (1)	∠W(2A)–Os(1A)–C(4A)	106 (1)
∠W(2A)–Os(1A)–C(5A)	121 (1)		

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for 3b

	x	y	z	B_{iso}
Os(1)	0.009661 (23)	0.773568 (21)	0.09576 (6)	2.388 (24)
Os(2)	–0.011886 (22)	0.743695 (22)	–0.18614 (6)	2.344 (24)
W(1)	–0.093734 (23)	0.76569 (22)	0.01983 (6)	2.501 (24)
W(2)	–0.020907 (21)	0.666527 (21)	0.02633 (6)	2.048 (22)
C(1)	–0.0683 (6)	0.7980 (5)	0.1944 (16)	3.8 (8)
C(2)	0.0318 (6)	0.7702 (7)	0.2869 (17)	5.0 (9)
C(3)	0.0298 (7)	0.8416 (6)	0.0792 (14)	4.5 (8)
C(4)	0.0200 (6)	0.7001 (6)	–0.3229 (18)	4.2 (8)
C(5)	0.0229 (6)	0.8050 (6)	–0.2454 (15)	3.8 (7)
C(6)	–0.0721 (6)	0.7561 (6)	–0.3010 (16)	4.3 (8)
C(7)	–0.0756 (6)	0.8352 (5)	–0.0530 (15)	3.8 (8)
C(8)	–0.0596 (5)	0.6918 (5)	0.1909 (16)	3.2 (7)
C(9)	–0.0769 (5)	0.6637 (5)	–0.1133 (15)	3.2 (7)
C(10)	–0.1714 (6)	0.8055 (6)	0.0748 (17)	4.2 (8)
C(11)	–0.1705 (6)	0.7557 (6)	0.1379 (16)	4.4 (8)
C(12)	–0.1706 (6)	0.7152 (5)	0.0458 (16)	3.7 (7)
C(13)	–0.1721 (6)	0.7385 (6)	–0.0823 (18)	4.6 (8)
C(14)	–0.1731 (6)	0.7941 (6)	–0.0670 (19)	5.0 (8)
C(15)	–0.0174 (5)	0.5900 (5)	0.1645 (14)	2.4 (6)
C(16)	–0.0337 (5)	0.5751 (5)	0.0301 (14)	2.8 (6)
C(17)	0.0077 (5)	0.5866 (5)	–0.0618 (14)	2.9 (7)
C(18)	0.0495 (5)	0.6061 (5)	0.0134 (14)	2.5 (6)
C(19)	0.0347 (5)	0.6105 (5)	0.1518 (14)	2.5 (6)
C(20)	–0.0453 (6)	0.5780 (6)	0.2967 (15)	4.1 (8)
C(21)	–0.0834 (7)	0.5461 (6)	–0.0037 (17)	5.1 (9)
C(22)	0.0072 (6)	0.5679 (6)	–0.2102 (17)	4.6 (9)
C(23)	0.1048 (6)	0.6138 (5)	–0.0453 (16)	3.9 (8)
C(24)	0.0684 (6)	0.6265 (6)	0.2735 (15)	3.9 (7)
C(25)	0.0397 (5)	0.7151 (5)	–0.0338 (14)	2.7 (6)
C(26)	0.0845 (5)	0.7357 (6)	0.0235 (13)	3.2 (7)
C(27)	0.1264 (5)	0.7684 (5)	–0.0448 (15)	3.1 (7)
C(28)	0.1544 (5)	0.8061 (5)	0.0242 (15)	3.3 (7)
C(29)	0.1954 (6)	0.8325 (6)	–0.0361 (17)	4.3 (8)
C(30)	0.2119 (5)	0.8184 (6)	–0.1674 (17)	3.9 (8)
C(31)	0.1857 (6)	0.7815 (6)	–0.2391 (16)	4.2 (8)
C(32)	0.1428 (6)	0.7557 (6)	–0.1820 (16)	3.9 (7)
O(1)	–0.0783 (4)	0.8180 (4)	0.3015 (10)	4.7 (6)
O(2)	0.0414 (5)	0.7675 (5)	0.3969 (11)	6.5 (7)
O(3)	0.0445 (4)	0.8858 (4)	0.0665 (12)	5.2 (6)
O(4)	0.0405 (5)	0.6742 (4)	–0.3975 (12)	6.3 (7)
O(5)	0.0410 (5)	0.8428 (4)	–0.2838 (12)	6.1 (7)
O(6)	–0.1078 (4)	0.7629 (5)	–0.3729 (11)	5.8 (7)
O(7)	–0.0681 (4)	0.8774 (4)	–0.0931 (12)	4.9 (6)
O(8)	–0.0755 (4)	0.6922 (4)	0.3037 (10)	3.8 (5)
O(9)	–0.1089 (4)	0.6495 (4)	–0.1909 (11)	4.2 (5)

Table V. Selected Bond Distances (Å) and Angles (deg) of Complex 3b (Esd's in Parentheses)

(A) Intermetallic Parameters			
Os(1)–Os(2)	2.904 (1)	Os(1)–W(2)	2.744 (1)
Os(1)–W(2)	2.917 (1)	Os(2)–W(1)	2.949 (1)
Os(2)–W(2)	2.865 (1)	W(1)–W(2)	3.138 (1)
∠Os(2)–Os(1)–W(1)	62.89 (2)	∠Os(2)–Os(1)–W(2)	58.98 (2)
∠W(1)–Os(1)–W(2)	67.25 (2)	∠Os(1)–Os(2)–W(1)	55.92 (3)
∠Os(1)–Os(2)–W(2)	60.74 (3)	∠W(1)–Os(2)–W(2)	65.30 (3)
∠Os(1)–W(1)–Os(2)	61.20 (3)	∠Os(1)–W(1)–W(2)	59.00 (2)
∠Os(2)–W(1)–W(2)	56.06 (2)	∠Os(1)–W(2)–Os(2)	60.28 (3)
∠Os(1)–W(2)–W(1)	53.76 (2)	∠Os(2)–W(2)–W(1)	58.64 (2)
(B) Parameters Associated with the Vinylidene Fragment			
Os(1)–C(25)	2.10 (1)	Os(2)–C(25)	2.11 (1)
W(2)–C(25)	2.06 (1)	Os(1)–C(26)	2.25 (1)
C(25)–C(26)	1.38 (2)		
∠Os(1)–C(25)–Os(2)	87.2 (4)	∠Os(1)–C(25)–W(2)	89.0 (5)
∠Os(2)–C(25)–W(2)	86.6 (5)	∠Os(1)–C(25)–C(26)	77.8 (8)
∠Os(1)–C(26)–C(25)	65.6 (7)	∠C(25)–Os(1)–C(26)	36.7 (5)
(C) Selected Parameters of the Carbonyl Ligands			
Os(1)–C(1)	2.29 (2)	Os(1)–C(2)	1.95 (2)
Os(1)–C(3)	1.81 (2)	Os(2)–C(4)	1.92 (2)
Os(2)–C(5)	1.89 (2)	Os(2)–C(6)	1.93 (2)
W(1)–C(7)	1.96 (2)	W(2)–C(8)	1.99 (2)
W(2)–C(9)	1.97 (2)	W(1)–C(1)	2.00 (2)
Os(1)···C(8)	2.89 (1)	W(1)···C(8)	2.66 (2)
∠Os(1)–C(1)–O(1)	132 (1)	∠Os(1)–C(2)–O(2)	176 (1)
∠Os(2)–C(3)–O(3)	178 (1)	∠Os(2)–C(4)–O(4)	176 (1)
∠Os(2)–C(5)–O(5)	176 (1)	∠Os(2)–C(6)–C(6)	178 (1)
∠W(1)–C(7)–O(7)	175 (1)	∠W(2)–C(8)–O(8)	159 (1)
∠W(2)–C(9)–O(9)	164 (1)	∠W(1)–C(1)–O(1)	149 (1)
∠Os(1)···C(8)–O(8)	121 (1)	∠W(1)···C(8)–O(8)	118 (1)

150.8, assigned to the α- and β-carbons, respectively. The observed chemical shifts for both α- and β-carbons are in good agreement with the data of tetranuclear WOs$_3$ acetylide clusters previously prepared in our research group[14] and with the data summarized by Carty and co-workers.[15] The identification of the acetylide α-carbon was achieved by a selective ^{13}C labeling experiment.

The ^{1}H NMR spectra of **3a** and **3b** each show a singlet resonance signal at δ 6.72 and at 6.83, respectively, in addition to the signals assigned to the phenyl group and the respective signals of the Cp and Cp* ligands. We propose that the hydride ligand has migrated to one of the acetylide carbons of **1** during the formation of complexes **3**, producing either an alkyne (CH=CPh) fragment or a vinylidene (C=CHPh) fragment. The ^{13}C NMR spectrum of **3b**, which exhibits two signals at δ 231.9 (J_{W-C} = 160 Hz) and 71.8 for the C$_2$ fragment, is more helpful in terms of differentiating these two possibilities. We can rule out the possibility of the formation of an alkyne fragment because the downfield signal at δ 231.9 fails to display direct proton coupling and to exhibit NOE enhancement upon proton decoupling; therefore this signal must be due to the vinylidene α-carbon. On the other hand, the chemical shifts of the signals observed are in the expected range of the μ_3-η^2-vinylidene ligands.[16] After completion of the assignment of the vinylidene resonance signals, the signals of four W–CO ligands and five Os–CO ligands can be assigned unambiguously with the assistance of the observed characteristic tungsten satellites and their chemical shifts. Finally, among these four W–CO signals, one occurs at a very downfield position δ 273.5 (J_{W-C} = 96 Hz), which is assigned to a bridging CO ligand.

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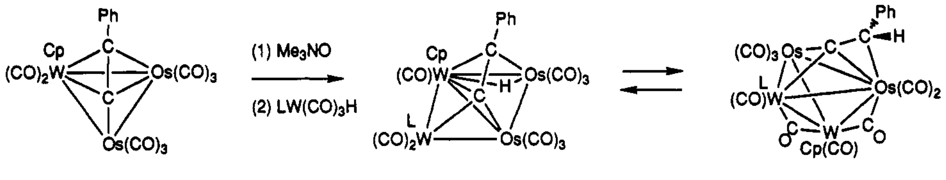
Scheme I



(1) (2a), L = Cp (3a), L = Cp

(2b), L = Cp* (3b), L = Cp*

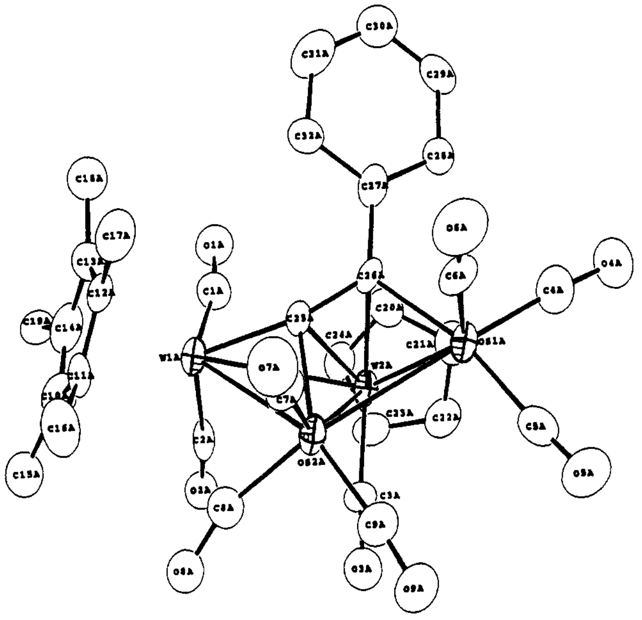
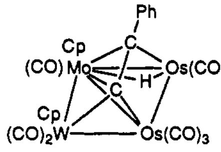


Figure 1. Molecular structure of $CpCp^*W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2b**), showing the atomic numbering scheme.

Crystal Structure of $CpCp^*W_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ (2b). A single-crystal structural determination was carried out on **2b** to confirm the structure of the W_2Os_2 acetylide complexes. Suitable crystals were obtained from a layered solution of CH_2Cl_2–MeOH at room temperature. According to the results of the structural determination, the asymmetric unit contains three crystallographically distinct, but structuraly similar, molecules. An ORTEP diagram of one of these molecules is shown in Figure 1, whereas selected bond distances and angles are given in Table III. As shown in Figure 1, the molecule consists of a W_2Os_2 core of a butterfly arrangement, with Os(1A) and W(1A) defining the wing-tip positions and Os(2A) and W(2A) the hinge positions. Each osmium atom is associated with three CO ligands, the tungsten W(1A) atom is linked to two CO ligands and a Cp* ligand, and the tungsten W(2A) atom is connected to one CO and a Cp ligand. The dihedral angle between the triangular wings W(2A)–Os(1A)–Os(2A) and W(1A)–W(2A)–Os(2A) is 131.2 (1)°, and the corresponding dihedral angles for the molecules B and C are 130.5 (1) and 130.6 (1)°, respectively.

The acetylide ligand occupies the open face of the butterfly framework and is coordinated in multisite fashion with its α-carbon bound to three metal atoms W(1A), W(2A), and Os(2A) with bond distances Os(2A)–C(25A) = 2.14 (3) Å, W(1A)–C(25A) = 2.00 (3) Å, and W(2A)–C(25A) = 2.22 (3) Å and with the β-carbon atom linked to W(2A) and Os(1A) atoms with bond distances Os(1A)–C(26A) = 2.05 (3) Å and W(2A)–C(26A) = 2.39 (3) Å. The bonding interaction of this acetylide ligand is of interest because it can be considered as a model for the chemisorption of acetylide on the steps of metal and alloy surfaces.[17] Furthermore, complex **2b** also is a rare example of a tetranuclear acetylide complex,[18] in which the acetylide can be considered as σ-bonded to one wing-tip atom, W(1A), via its α-carbon and also interacting with the second metal triangle, Os(1A)–Os(2A)–W(2A), via a parallel (2σ + π) bonding mode of a typical μ_3-alkyne ligand.[19]

The bridging hydride was not located on the Fourier map. We speculate that the hydride is associated with the W(2A)–Os(1A) bond because of the observation of tungsten–hydride coupling in its ^1H NMR spectrum. The bridging hydride is definitely not associated with the hinge W(2A)–Os(2A) bond because ∠Os(2A)–W(2A)–C(3A) is extremely small (63 (1)°), contrary to the general belief that the presence of a bridging hydride would enlarge the adjacent coplanar M–M–CO angles to a value greater than 105°.[20] In good agreement with our suggestion, the W(2A)–Os(1A) (2.934 (3) Å) vector is longer than the hinge W(2A)–Os(2A) vector (2.784 (2) Å). Examination of the spectroscopic properties of an analogous cluster $Cp_2MoWOs_2(CO)_9(CCPh)(\mu\text{-}H)$ (**2c**) prepared from reaction of $CpMoOs_2(CO)_8(C{\equiv}CPh)$ with $CpW(CO)_3H$ also provides some additional support. The pattern of the IR (ν(CO)) spectra of **2c** is very similar to that of **2a** and **2b**, indicating that its structure can be shown as



2c

As expected, no tungsten satellites were observed for the hydride signal at δ -16.08 in its ^1H NMR spectrum, indicating that the hydride is associated with a Mo–Os edge. Finally, calculation of the formal electron counts at the individual metal atoms (neutral ligands and metal assumed) gives 17.5e at Os(1A), 18e at W(1A) and Os(2A), and 18.5e at W(2A).

Crystal Structure of $CpCp^*W_2Os_2(CO)_9(CCHPh)$ (3b). The molecular structure of **3b** was determined by single-crystal X-ray diffraction. The ORTEP diagram and the scheme used for labeling the atoms are shown in Figure 2. The bond distances and the bond angles are listed in Table V. The four transition-metal atoms of the molecule define a slightly distorted tetrahedral core structure with the metal–metal distances in the range 2.865–3.138 Å. The

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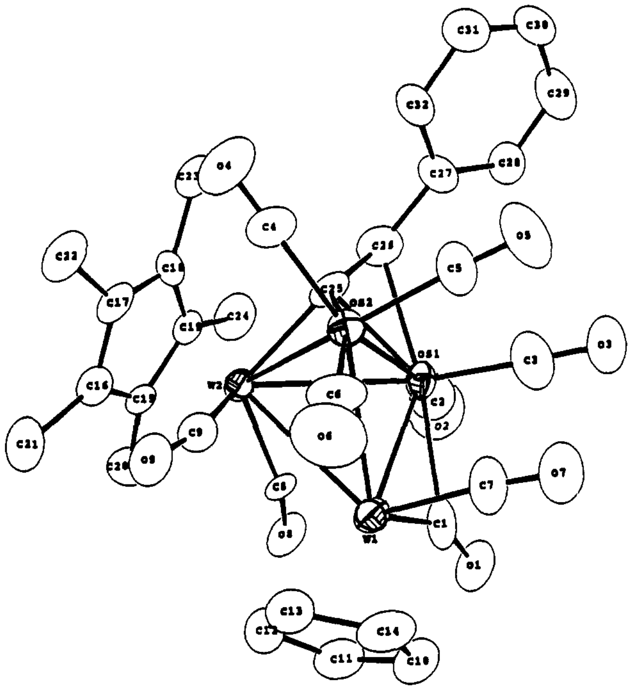

Figure 2. Molecular structure of $CpCp^{*}W_2Os_2(CO)_9(CCHPh)$ (**3b**), showing the atomic numbering scheme.

atoms W(1) and W(2) are connected to one terminal and one bridging CO ligand in addition to the respective Cp and Cp* ligands, whereas osmium Os(1) links to two terminal CO ligands and one bridging CO ligand and the Os(2) atom links to three terminal CO ligands. The vinylidene ligand is coordinated to a triangular face defined by atoms Os(1), Os(2), and W(2) with its β-carbon connected to atom Os(1). Therefore, the bonding mode of the vinylidene ligand can be considered to be σ-bonded to the atoms Os(2) and W(1) and π-bonded to Os(1) atom via an η^2 interaction. This type of vinylidene bonding interaction is not uncommon and has already been well documented in the literature.[21] Finally, the cluster is associated with the expected 60 valence electrons, and calculation of the formal electron counts gives 18e for all the individual metal atoms.

Isomerization between Acetylide and Vinylidene Complexes. Thermolysis of either **2b** or **3b** in refluxing toluene under a carbon monoxide atmosphere (1 atm, 2 h) produced about 45% of **2b** and 50% of **3b**. We are unable to study the kinetics of the equilibration reaction because of the low solubility in toluene-d_8 at about 95 °C. When the reaction was done under nitrogen at 1 atm, we obtained similar results but with much lower yield due to decomposition. These observation indicate that the observed rearrangement between acetylide and vinylidene involves a concerted and reversible hydride migration from a W–Os edge to the β-carbon of the acetylide ligand (Scheme I). The unsaturation generated by the hydride migration is compensated by the folding of the butterfly framework and the formation of a new W–Os bond, leading to the observed tetrahedral arrangement. Therefore, the reversible formation and cleavage of the metal–metal bond is crucial for the facile acetylide to vinylidene rearrangement. This isomerization reaction can also provide some understanding of the reaction mechanism of the transformation of acetylide (μ_4-η^2-CCR) to an alkylidyne (μ_3-CCH_2R) in the system of the related WOs_3 cluster.[7] Unfortunately, hydrogenation of either **2b** and **3b** under hydrogen at 1 atm (110 °C, 3 h) fails to generate any new cluster complexes.

Finally, pyrolysis of acetylide complex **2a** provides only trace amounts of vinylidene complex **3a** ($\leq 4\%$) under similar conditions, indicating that the auxiliary ligand on the transition-metal atom can also change the thermodynamic preference of the acetylide–vinylidene isomerization.

Acknowledgment. We are grateful to the National Science Council of the Republic of China for financial support (Grant No. NSC80-0208-M007-60).

Note Added in Proof. Recently, Farrugia and coworkers have reported the facile transformation between the spiked-triangular hydrido acetylide and the butterfly vinylidene clusters as well as the characterization of a derivative with an intermediate molecular geometry in the acetylide–vinylidene tautomerization.[22]

Supplementary Material Available: ORTEP diagrams of the molecules B and C of complex **2b** with complete atomic labeling schemes and tables of nonessential bond distances and angles and anisotropic thermal parameters for **2b** and **3b** (18 pages); listings of the observed and calculated structure factors for **2b** and **3b** (53 pages). Ordering information is given on any current masthead page.

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