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Reaction of Polynuclear Acetylide Clusters. Mixed-Metal Complexes Derived from Reactions of $CpWOs_3(CO)_{11}(C{\equiv}CR)$ ($R = Ph, {}^nBu$) with Disubstituted Alkynes

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Reaction of $CpW(CO)_3(C{\equiv}CR)$ with $Os_3(CO)_{10}(CH_3CN)_2$ in refluxing toluene produces tetranuclear mixed-metal acetylide complexes, $CpWOs_3(CO)_{11}(C{\equiv}CR)$ ($R = Ph$ (**1a**), ${}^nBu$ (**1b**)). Reaction of **1a** with excess ditolylacetylene in refluxing toluene effects the scission of acetylide ligand to give $CpWOs_3(CO)_8(\mu_3\text{-}CPh)[\mu_4\text{-}\eta^5\text{-}C(C_2Tol_2)_2]$ (**3**). In contrast, treatment of complexes **1a** and **1b** with alkynes containing electron-withdrawing groups produces the tetranuclear alkyne-acetylide coupling products $CpWOs_3(CO)_{10}[CR'CR'CCR]$ ($R = Ph$, $R' = CO_2Me$ (**4a**), CO_2Et (**4b**); $R = {}^nBu$, $R' = CO_2Et$ (**4c**)) and $CpWOs_3(CO)_9[CCRCR'CR']$ ($R = Ph$, $R' = CO_2Me$ (**5a**), CO_2Et (**5b**); $R = {}^nBu$, $R' = CO_2Et$ (**5c**)). The structures of complexes **1a**, **3**, **4c**, and **5a** have been determined by single-crystal X-ray diffraction studies. Crystal data for **1a**: space group $P2_1/c$; $a = 9.057$ (2), $b = 9.197$ (1), $c = 29.065$ (4) Å; $\beta = 95.77$ (1)°; $Z = 4$; final $R = 0.055$, $R_w = 0.060$, and GOF = 2.757. Crystal data for **3**: space group $P\bar{1}$; $a = 10.351$ (3), $b = 12.576$ (3), $c = 18.098$ (3) Å; $\alpha = 94.44$ (2), $\beta = 91.07$ (2), $\gamma = 96.00$ (2)°; $Z = 2$; final $R = 0.041$, $R_w = 0.042$, and GOF = 2.397. Crystal data for **4c**: space group $P2_1/n$; $a = 10.025$ (2), $b = 9.550$ (5), $c = 34.708$ (5) Å; $\beta = 91.19$ (2)°; $Z = 4$; final $R = 0.070$, $R_w = 0.072$, and GOF = 2.77. Crystal data for **5a**: space group $P\bar{1}$; $a = 9.203$ (3), $b = 11.580$ (3), $c = 14.937$ (3) Å; $\alpha = 91.57$ (2), $\beta = 100.85$ (2), $\gamma = 102.23$ (2)°; $Z = 2$; final $R = 0.033$, $R_w = 0.034$, and GOF = 1.928.

Introduction

The chemistry of mixed-metal cluster complexes has been the subject of intensive research for many years.[1] Studies in this area are stimulated by a belief that the combination of metals having very different chemical properties in 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 have treated the metal acetylide $CpW(CO)_3(C{\equiv}CR)$ with the triruthenium complexes $Ru_3(CO)_{12}$[2] and $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$[3] with the aim of generating various tetranuclear mixed-metal acetylide complexes. A similar method of using metal acetylide complexes to prepare polynuclear acetylide clusters[4] and dinuclear acetylide complexes[5] has already been reported.

In this paper, we report full details of the preparation and crystal structure of the tetranuclear complexes $CpWOs_3(CO)_{11}(C{\equiv}CR)$ ($R = Ph$ (**1a**), ${}^nBu$ (**1b**)), which possess a novel $\mu_4\text{-}\eta^2$-acetylide ligand.[6] Reactions with various disubstituted alkynes have also been studied. The cluster complex **1a** reacts with ditolylacetylene to induce the scission of the acetylide C-C bond, followed by coupling with two ditolylacetylenes to give a complex possessing a C_1 alkylidyne ligand and a C_5 alkylidene moiety. In contrast, treatment with alkynes containing electron-withdrawing groups produces the alkyne-acetylide coupling products $CpWOs_3(CO)_{10}[CR'CR'CCR]$ ($R = Ph$, $R' = CO_2Me$ (**4a**), CO_2Et (**4b**); $R = {}^nBu$, $R' = CO_2Et$ (**4c**)) and $CpWOs_3(CO)_9[CCRCR'CR']$ ($R = Ph$, $R' = CO_2Me$ (**5a**), CO_2Et (**5b**); $R = {}^nBu$, $R' = CO_2Et$ (**5c**)). Complexes **4** are produced from coupling with the α-carbon of the coordinated acetylide ligand, and complexes **5**, with the β-carbon. Moreover, complex **4** adopts a butterfly geometry with 62 valence electrons, whereas complex **5** undergoes further CO elimination to give a tetrahedral cluster core with only 60 valence electrons.

A portion of these results has appeared in a preliminary report.[7]

Experimental Procedures

General Information. Infrared spectra were recorded with a Perkin-Elmer 580 spectrometer or 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 electron impact, field desorption, or fast atom bombardment modes. All reactions were performed under a nitrogen atmosphere with use of 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 commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). The acetylide complexes $CpW(CO)_3(C{\equiv}CR)$[8] ($R = Ph, {}^nBu$) and the triosmium acetonitrile

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complex $Os_3(CO)_{10}(CH_3CN)_2$[9] were prepared according to the published procedures. Elemental analyses were performed by the staff of the NSC Regional Instrument Center at National Cheng Kung University, Tainan, Taiwan, Republic of China.

Preparation of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$. $Os_3(CO)_{10}(CH_3CN)_2$, prepared from $Os_3(CO)_{12}$ (456 mg, 0.503 mmol) and anhydrous Me_3NO (91 mg, 1.04 mmol) in CH_3CN, and $CpW(CO)_3(C{\equiv}CPh)$ (240 mg, 0.553 mmol) were dissolved in toluene (60 mL) under a nitrogen atmosphere. The solution was then refluxed for 30 min until the color changed from yellow-orange to red-brown. After evaporation of the solvent under vacuum, the residue was separated by thin-layer chromatography (1:1 dichloromethane–hexane) and recrystallization, giving 90 mg of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ (**1a**) as a red crystalline solid (0.073 mmol, 15%) and 35 mg of $CpWOs_2(CO)_8(C{\equiv}CPh)$ (**2a**) as a yellow crystalline solid (0.003 mmol, 8%). Crystals of **1a** suitable for X-ray diffraction study were obtained from a layered solution of dichloromethane–methanol at room temperature. Spectroscopic data for complex **1a**: MS (EI, ^{192}Os, ^{184}W) m/z 1234 (M^+); IR (C_6H_{12}) ν(CO) 2082 (s), 2058 (vs), 2033 (s), 2016 (s), 2000 (m), 1985 (vw), 1972 (s), 1962 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K): δ 7.89 (d, 2 H), 7.46 (m, 3 H), 4.96 (s, 5 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 294 K): δ 208.5 (W–CO), 204.2 (W–CO), 186.9 (CCPh), 180.2 (Os–CO), 176.2 (3 C, Os–CO), 173.8 (Os–CO), 172.8 (Os–CO), 162.8 (CCPh), 146.2 (1 C), 130.0 (1 C), 129.1 (2 C), 126.5 (2 C), 90.5 (Cp). Anal. Calcd for $WOs_3C_{24}H_{10}O_{11}$: C, 23.46; H, 0.82. Found: C, 23.38; H, 0.85.

Preparation of $CpWOs_3(CO)_{11}(C{\equiv}C^nBu)$. $Os_3(CO)_{10}(CH_3CN)_2$, prepared from $Os_3(CO)_{12}$ (780 mg, 0.86 mmol) and anhydrous Me_3NO (137 mg, 1.82 mmol) in CH_3CN, and $CpW(CO)_3(C{\equiv}C^nBu)$ (350 mg, 0.86 mmol) were dissolved in toluene (80 mL) under nitrogen. The solution was then refluxed for 30 min until the color changed from yellow-orange to red-brown. The solvent was then evaporated under vacuum, and the residue was separated by thin-layer chromatography (1:1 dichloromethane–hexane) and recrystallization, giving 200 mg of $CpWOs_3(CO)_{11}(C{\equiv}C^nBu)$ (**1b**) as a red crystalline solid (0.165 mmol, 19%) and 85 mg of $CpWOs_2(CO)_8(C{\equiv}C^nBu)$ (**2b**) as a yellow crystalline solid (0.091 mmol, 11%). The ^{13}CO-enriched samples of complexes **1b** and **2b** were prepared analogously. Selected spectroscopic data for complex **1b**: MS (FAB, ^{192}Os, ^{184}W) m/z 1214 (M^+); IR (C_6H_{12}) ν(CO) 2082 (m), 2057 (vs), 2032 (s), 2009 (s), 2000 (m), 1983 (w), 1977 (s), 1960 (w), 1938 (vw) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K): δ 5.21 (s, 5 H, Cp), 2.99 (m, 1 H, CH), 2.71 (m, 1 H, CH), 1.92 (q, 2 H, CH_2), 1.55 (m, 2 H, CH_2), 1.00 (t, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 294 K): δ 208.9 (J_{W-C} = 145 Hz, W–CO), 205.2 (J_{W-C} = 150 Hz, W–CO), 192.0 (CC^nBu), 181.4 (Os–CO), 178.2 (broad, $Os(CO)_3$), 177.6 ($Os(CO)_3$), 172.6 (Os–CO), 172.2 (Os–CO), 165.8 (CC^nBu), 98.4 (Cp), 55.0 (CH_2), 31.2 (CH_2), 22.0 (CH_2), 13.5 (CH_3). Anal. Calcd for $WOs_3C_{22}H_{14}O_{11}$: C, 21.86; H, 1.17. Found: C, 21.84; H, 1.20.

Reaction of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ with Ditolylacetylene. A toluene solution (25 mL) of a mixture of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ (24 mg, 0.020 mmol) and ditolylacetylene (24 mg, 0.116 mmol) was heated at reflux under nitrogen. The color of the solution turned from orange to green over a period of 3.5 h. Finally, the solvent was evaporated, and the residue was separated by thin-layer chromatography (2:3 dichloromethane–hexane), giving 19 mg of $CpWOs_3(CO)_8(\mu_3\text{-}CPh)[\mu_4\text{-}\eta^5\text{-}C(C_2Tol_2)_2]$ (**3**) as a dark green material (0.0012 mmol, 62%). Crystals of complex **3** suitable for X-ray diffraction study were obtained by recrystallization from a mixture of dichloromethane–hexane at room temperature. Selected spectroscopic data for complex **3**: MS (FAB, ^{192}Os, ^{184}W) m/z 1562 (M^+); IR (C_6H_{12}) ν(CO) 2073 (s, sh), 2070 (vs), 2036 (vs, sh), 2034 (vs), 2019 (m, sh), 2014 (s), 1999 (s), 1991 (m), 1971 (vs), 1960 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 317 K): δ 7.38 (br, 2 H), 7.30 (t, 2 H), 7.10 (t, 1 H), 6.97 (d, 2 H), 6.87 (d, 2 H), 6.78 (m, 4 H), 6.69 (d, 2 H), 6.56 (d, 2 H), 6.34 (d, 2 H), 6.03 (d, 2 H), 5.56 (s, 5 H), 2.26 (s, 3 H), 2.22 (s, 3 H), 2.12 (s, 3 H), 2.03 (s, 3 H). Anal. Calcd for $WOs_3C_{53}H_{38}O_8$: C, 40.88; H, 2.46. Found: C, 40.83; H, 2.50.

Reaction of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ with Dimethyl Acetylenedicarboxylate. A toluene solution (30 mL) of a mixture of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ (42 mg, 0.034 mmol) and dimethyl acetylenedicarboxylate (30 μL, 0.24 mmol) was heated at reflux under nitrogen. The color of the solution turned gradually from orange-red to dark brown. After 25 min, the solvent was evaporated and the residue was separated by thin-layer chromatography (2:1 dichloromethane–hexane), giving 9 mg of $CpWOs_3(CO)_{10}[C(CO_2Me)C(CO_2Me)CCPh]$ (**4a**) as an orange material (0.0067 mmol, 20%) and 11 mg of $CpWOs_3(CO)_9[CC(Ph)C(CO_2Me)C(CO_2Me)]$ (**5a**) as a red-orange material (0.0084 mmol, 25%). Crystals of complex **5a** suitable for X-ray diffraction study were obtained by recrystallization from a mixture of dichloromethane–heptane at room temperature. Selected spectroscopic data for complex **4a**: MS (FAB, ^{192}Os, ^{184}W) m/z 1348 (M^+); IR (C_6H_{12}) ν(CO) 2087 (vs), 2062 (vs), 2032 (m), 2018 (s), 2001 (s), 1975 (w), 1949 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 7.43 (m, 2 H), 7.33 (t, 3 H), 5.51 (s, 5 H), 3.75 (s, 3 H), 3.25 (s, 3 H). Selected spectroscopic data for complex **5a**: MS (FAB, ^{192}Os, ^{184}W) m/z 1320 (M^+); IR (C_6H_{12}) ν(CO) 2080 (vs), 2053 (vs), 2012 (vs), 2005 (s, sh), 1996 (s), 1978 (w), 1965 (m), 1955 (w), 1876 (vw, br) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 7.68 (m, 2 H), 7.38 (t, 3 H), 5.49 (s, 5 H), 3.67 (s, 3 H), 3.61 (s, 3 H). Anal. Calcd for $WOs_3C_{28}H_{16}O_{13}$: C, 25.58; H, 1.23. Found: C, 25.40; H, 1.31.

Reaction of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ with Diethyl Acetylenedicarboxylate. A toluene solution (30 mL) of a mixture of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ (47 mg, 0.039 mmol) and diethyl acetylenedicarboxylate (40 μL, 0.25 mmol) was heated at reflux under nitrogen for 30 min. The color of the solution turned from orange-red to dark brown. After evaporation of the solvent in vacuo, the residue was separated by thin-layer chromatography (2:1 dichloromethane–hexane), giving 5.8 mg of $CpWOs_3(CO)_{10}[C(CO_2Et)CCPh]$ (**4b**) as an orange material (0.0042 mmol, 11%) and 12.7 mg of $CpWOs_3(CO)_9[CC(Ph)C(CO_2Et)C(CO_2Et)]$ (**5b**) as a red-orange material (0.0095 mmol, 24%). Selected spectroscopic data for complex **4b**: MS (FAB, ^{192}Os, ^{184}W) m/z 1376 (M^+); IR (C_6H_{12}) ν(CO) 2086 (vs), 2062 (s), 2056 (vs), 2032 (m), 2020 (s), 1999 (m), 1973 (vw), 1947 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 7.51 (m, 2 H), 7.36 (m, 3 H), 5.44 (s, 5 H), 4.36 (m, 1 H), 4.13 (m, 1 H), 3.65 (m, 1 H), 3.55 (m, 1 H), 1.31 (t, 3 H), 0.90 (t, 3 H). Anal. Calcd for $WOs_3C_{31}H_{20}O_{14}$: C, 27.16; H, 1.47. Found: C, 27.11; H, 1.44. Selected spectroscopic data for complex **5b**: MS (FAB, ^{192}Os, ^{184}W) m/z 1348 (M^+); IR (C_6H_{12}) ν(CO) 2079 (vs), 2050 (vs), 2011 (vs), 2005 (s, sh), 1995 (s), 1982 (w), 1966 (m), 1956 (w), 1878 (vw, br) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K): δ 7.67 (m, 2 H), 7.38 (m, 3 H), 5.48 (s, 5 H), 4.14 (m, 2 H), 4.06 (m, 2 H), 1.10 (t, 3 H), 1.20 (t, 3 H). Anal. Calcd for $WOs_3C_{30}H_{20}O_{13}$: C, 26.83; H, 1.50. Found: C, 26.79; H, 1.47.

Reaction of $CpWOs_3(CO)_{11}(C{\equiv}C^nBu)$ with Diethyl Acetylenedicarboxylate. A toluene solution (30 mL) of a mixture of $CpWOs_3(CO)_{11}(C{\equiv}C^nBu)$ (47 mg, 0.039 mmol) and diethyl acetylenedicarboxylate (40 μL, 0.25 mmol) was heated at reflux for 30 min. The color of the solution turned from orange-red to dark brown. After the evaporation of the solvent under vacuum, the residue was separated by thin-layer chromatography (2:1 dichloromethane–hexane), giving 9 mg of $CpWOs_3(CO)_{10}[C(CO_2Et)C(CO_2Et)CC^nBu]$ (**4c**) as an orange material (0.0067 mmol, 17%) and 9 mg of $CpWOs_3(CO)_9[CC(^nBu)C(CO_2Et)C(CO_2Et)]$ (**5c**) as a red-orange material (0.0068 mmol, 18%). Crystals of complex **4c** suitable for X-ray diffraction study were obtained by recrystallization from a mixture of dichloromethane–methanol at room temperature. Selected spectroscopic data for complex **4c**: MS (FAB, ^{192}Os, ^{184}W) m/z 1356 (M^+); IR (C_6H_{12}) ν(CO) 2086 (s), 2060 (vs), 2028 (m), 2016 (s), 1998 (s), 1974 (w), 1953 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K): δ 5.56 (s, 5 H), 4.37 (m, 2 H), 4.12 (m, 2 H), 2.81 (m, 1 H), 2.48 (m, 1 H), 1.93 (m, 1 H), 1.82 (m, 1 H), 1.44 (q, 2 H), 1.40 (t, 3 H), 1.30 (t, 3 H), 0.99 (t, 3 H). Anal. Calcd for $WOs_3C_{29}H_{24}O_{14}$: C, 25.78; H, 1.79. Found: C, 25.75; H, 1.79. Selected spectroscopic data for complex **5c**: MS (FAB, ^{192}Os, ^{184}W) m/z 1328 (M^+); IR (C_6H_{12}) ν(CO) 2079 (vs), 2047 (vs), 2011 (vs), 2005 (s, sh), 1993 (m), 1983 (w), 1971 (m), 1957 (w), 1873 (vw, br) cm^{-1}; ^1H NMR ($CDCl_3$, 294 K) δ 5.40 (s, 5 H), 4.28 (m, 2 H), 4.05 (q, 2 H), 3.69 (m, 1 H), 2.71 (m, 1 H), 1.91 (m, 1 H), 1.58 (m, 2 H), 1.31 (t, 3 H), 1.18 (t, 3 H), 1.05 (t, 3 H). Anal. Calcd for $WOs_3C_{28}H_{24}O_{13}$: C, 25.42; H, 1.83. Found: C, 25.40; H, 1.85.

X-ray Crystallography. Diffraction measurements were carried out on a Nonius CAD-4 fully automated four-circle diffractometer. In general, the space group and parameters of unit

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Table I. Selected Interatomic Distances (Å) and Bond Angles (deg) of Complex 1 (Esd's in Parentheses)

(A) Intermetallic Distances and Angles			
Os(1)–Os(2)	2.866 (1)	Os(1)–Os(3)	2.819 (1)
Os(1)–W	2.833 (1)	Os(2)–W	2.906 (1)
Os(3)–W	2.968 (1)		
∠Os(2)–Os(1)–W	61.32 (3)	∠Os(2)–Os(1)–Os(3)	107.65 (3)
∠Os(1)–Os(2)–W	58.79 (3)	∠Os(3)–Os(1)–W	63.36 (3)
∠Os(1)–W–Os(2)	59.89 (3)	∠Os(1)–Os(3)–W	58.56 (3)
∠Os(2)–W–Os(3)	102.73 (3)	∠Os(1)–W–Os(3)	58.08 (3)
(B) Parameters Associated with the Acetylide Fragment			
Os(1)–C(23)	2.13 (2)	Os(3)–C(23)	1.95 (2)
W–C(23)	2.27 (2)	Os(2)–C(24)	2.09 (2)
W–C(24)	2.49 (2)	C(23)–C(24)	1.38 (2)
∠Os(1)–C(23)–Os(3)	87.2 (6)	∠Os(1)–C(23)–W	80.2 (6)
∠Os(3)–C(23)–W	89.1 (8)	∠Os(3)–C(23)–C(24)	153 (1)
∠Os(2)–C(24)–W	78.2 (7)	∠C(17)–C(24)–C(23)	121 (2)
(C) Parameters Associated with the Carbonyl Ligands			
W–C(10)	1.99 (2)	W–C(11)	2.01 (2)
Os(2)···C(10)	2.71 (2)	Os(3)···C(11)	2.91 (2)
∠Os(1)–C(1)–O(1)	178 (2)	∠Os(1)–C(2)–O(2)	171 (2)
∠Os(1)–C(3)–O(3)	179 (2)	∠Os(2)–C(4)–O(4)	178 (2)
∠Os(2)–C(5)–O(5)	179 (2)	∠Os(2)–C(6)–O(6)	178 (2)
∠Os(3)–C(7)–O(7)	177 (2)	∠Os(3)–C(8)–O(8)	176 (2)
∠Os(3)–C(9)–O(9)	178 (2)	∠W–C(10)–O(10)	164 (2)
∠W–C(11)–O(11)	167 (2)	∠Os(2)···C(10)–O(10)	121 (2)
∠Os(3)···C(11)–O(11)	119 (1)		

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

(A) Intermetallic Distances and Angles			
Os(1)–Os(3)	2.784 (1)	Os(1)–W	3.004 (1)
Os(2)–Os(3)	2.743 (1)	Os(2)–W	2.807 (1)
Os(3)–W	2.766 (1)		
∠Os(3)–Os(2)–W	59.76 (3)	∠Os(3)–Os(1)–W	56.93 (3)
∠Os(1)–Os(3)–W	65.54 (3)	∠Os(1)–Os(3)–Os(2)	126.72 (3)
∠Os(1)–W–Os(2)	116.42 (3)	∠Os(2)–Os(3)–W	61.28 (3)
∠Os(2)–W–Os(3)	58.97 (3)	∠Os(1)–W–Os(3)	57.53 (3)
(B) Parameters Associated with the C_5 Hydrocarbon Fragment			
Os(2)–C(14)	2.14 (2)	Os(3)–C(14)	2.15 (1)
W–C(14)	1.95 (2)	Os(1)–C(29)	2.23 (1)
Os(3)–C(29)	2.08 (1)	Os(1)–C(21)	2.25 (1)
W–C(37)	2.30 (1)	Os(3)–C(37)	2.14 (1)
W–C(38)	2.36 (1)	Os(2)–C(46)	2.19 (2)
W–C(46)	2.09 (2)	C(21)–C(29)	1.44 (2)
C(21)–C(37)	1.54 (2)	C(37)–C(38)	1.33 (2)
C(38)–C(46)	1.51 (2)		
∠Os(3)–C(37)–W	77.0 (4)	∠Os(2)–C(46)–W	82.0 (5)
∠C(29)–C(21)–C(37)	101 (1)	∠Os(1)–C(29)–Os(3)	80.6 (5)
∠C(37)–C(38)–C(46)	116 (1)	∠C(21)–C(37)–C(38)	135 (1)
(C) Bond Angles of the Carbonyl Ligands			
∠Os(1)–C(1)–O(1)	177 (1)	∠Os(1)–C(2)–O(2)	178 (1)
∠Os(1)–C(3)–O(3)	172 (1)	∠Os(2)–C(4)–O(4)	178 (1)
∠Os(2)–C(5)–O(5)	178 (2)	∠Os(2)–C(6)–O(6)	176 (1)
∠Os(3)–C(7)–O(7)	173 (1)	∠Os(3)–C(8)–O(8)	176 (1)

Table III. Experimental Data for the X-ray Diffraction Study of Complex 4c

(A) Crystal Data			
a	10.025 (2) Å	Laue symmetry	monoclinic
b	9.550 (5) Å	space group	$P2_1/n$
c	34.708 (5) Å	Z	4
β	91.19 (2)°	formula	$C_{29}H_{24}O_{14}Os_3W$
V	3322.1 (2) Å^3	mol wt	1350.94
$F(000)$	2355.10	density (calcd)	2.701 g/cm^3
temp	297 K		

(B) Data Collection, Reduction, Solution, and Refinement	
data collecn instrument	Nonius CAD-4
radiation (monochromated in incident beam)	Cu Kα (λ = 1.54056 Å)
scan method	$\theta/2\theta$ scan mode
scan param	0.7 + 0.14 tan θ
h,k,l ranges	−9 to 9, 0 to 9, 0 to 34
cryst size	0.15 × 0.15 × 0.45 mm
linear abs coeff	28.00 mm^{-1}
transmission factors: max, min	0.99871, 0.64827
no. of unique data, total with $I > 2\sigma(I)$	3406, 2989
no. of atoms and params refined	71, 425
max Δ/σ ratio	0.290
R; R_w[a]	0.070; 0.072
GOF[b]	2.77
residual electron density: max/min	2.17/−2.12 e/Å^3

[a] $w = 1/\sigma^2(F_o)$. [b] $S = [\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables).

Table IV. Experimental Data for the X-ray Diffraction Study of Complex 5a

(A) Crystal Data			
a	9.203 (3) Å	cryst syst	triclinic
b	11.580 (3) Å	space group	$P\bar{1}$
c	14.937 (3) Å	Z	2
α	91.57 (2)°	formula	$C_{28}H_{16}O_{13}Os_3W$
β	100.85 (2)°	V	1524.06 Å^3
γ	102.23 (2)°	mol wt	1314.88
$F(000)$	1209.55	density (calcd)	2.865 g/cm^3
temp	297 K		

(B) Data Collection, Reduction, Solution and Refinement	
data collecn instrument	Nonius CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.70930 Å)
scan method	$2\theta-\theta$ scan mode
scan range	0.65 + 0.35 tan θ
h,k,l ranges	−10 to 10, 0 to 13, −17 to 17
cryst size	0.20 × 0.20 × 0.30 mm
linear abs coeff	16.39 mm^{-1}
transmission factors: max, min	0.99873, 0.41463
no. of unique data, total with $I > 2\sigma(I)$	5350, 3956
no. of atoms and params refined	61, 407
R; R_w[a]	0.033; 0.034
GOF[b]	1.928
max Δ/σ ratio	0.411
residual electron density: max/min	2.38/−1.66 e/Å^3

[a] $w^{-1} = \sigma^2(F)$. [b] $S = [\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables).

cell dimensions were determined and refined from 25 randomly selected reflections, with a 2θ angle around 20°, obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The normalized absorption corrections, based on ϕ scans of 111 suitable reflections with χ values close to 90°, were applied to all intensity data. All data reduction and structure refinements were performed with use of the NRCC-SDP-VAX packages. The structures were solved by the Patterson method and refined by least-squares cycles; all non-hydrogen atoms were refined with anisotropic thermal parameters.

The data collection and atomic positional and anisotropic parameters for complexes **1a** and **3** have been published previously in the format of notes and supplementary material;[7] therefore, only the tables of bond distances and angles (Tables I and II), which summarize the crucial structural information, are reported. The data collection and refinement parameters for complexes **4c** and **5a** are given in Tables III and IV, respectively. Atomic positional parameters for complex **4c** are presented in Table V, while some selected bond angles and lengths are given in Table VI. The corresponding parameters for complex **5a** are given in Tables VII and VIII, respectively.

Results and Discussion

Preparation and Characterization of $CpWOs_3(CO)_{11}(C\equiv CR)$. Treatment of $CpW(CO)_3(C\equiv CR)$ with the lightly stabilized triosmium species $Os_3(CO)_{10}(CH_3CN)_2$ in refluxing toluene (110 °C, 30 min) provides the red tetranuclear acetylide complexes $CpWOs_3(CO)_{11}(C\equiv CR)$ (R = Ph (**1a**), ^{n}Bu (**1b**)) in low yield, in addition to the yellow trinuclear complexes $CpWOs_2(CO)_8(C\equiv CR)$ (R =

Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) of Complex 4c (Esd's in Parentheses)

(A) Intermetallic Distances and Angles			
Os(1)–Os(2)	2.819 (2)	Os(1)–W	2.881 (2)
Os(2)–Os(3)	2.814 (2)	Os(2)–W	2.849 (2)
Os(3)–W	2.902 (2)		
∠Os(1)–Os(2)–Os(3)	120.47 (7)	∠Os(2)–Os(1)–W	59.95 (2)
∠Os(3)–Os(2)–W	61.65 (5)	∠Os(1)–Os(2)–W	61.10 (5)
∠Os(1)–W–Os(3)	115.48 (7)	∠Os(2)–Os(3)–W	59.76 (5)
∠Os(2)–W–Os(3)	58.59 (5)	∠Os(1)–W–Os(2)	58.94 (5)
(B) Parameters Associated with the C_4 Hydrocarbon Fragment			
Os(3)–C(17)	2.10 (13)	W–C(17)	2.35 (3)
Os(2)–C(16)	2.20 (5)	W–C(16)	2.23 (4)
W–C(22)	2.34 (3)	W–C(26)	2.37 (3)
Os(1)–C(26)	2.09 (3)	C(16)–C(17)	1.48 (6)
C(16)–C(22)	1.36 (6)	C(22)–C(26)	1.33 (5)
∠Os(3)–C(17)–W	81 (1)	∠Os(2)–C(16)–W	80 (2)
∠Os(1)–C(26)–W	80 (1)	∠C(17)–C(16)–C(22)	123 (4)
∠C(16)–C(22)–C(26)	129 (4)		
(C) Parameters Associated with the Carbonyl Ligands			
Os(1)···C(10)	2.70 (3)	Os(2)···C(10)	2.66 (3)
∠Os(1)–C(1)–O(1)	175 (3)	∠Os(1)–C(2)–O(2)	175 (4)
∠Os(1)–C(3)–O(3)	176 (3)	∠Os(2)–C(4)–O(4)	173 (4)
∠Os(2)–C(5)–O(5)	173 (3)	∠Os(2)–C(6)–O(6)	176 (3)
∠Os(3)–C(7)–O(7)	169 (5)	∠Os(3)–C(8)–O(8)	173 (3)
∠Os(3)–C(9)–O(9)	174 (3)	∠W–C(10)–O(10)	159 (3)
∠Os(1)···C(10)–O(10)	122 (2)	∠Os(2)···C(10)–O(10)	122 (2)

Table VI. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Complex 4c

	x	*y*	*z*	B_{iso}, Å^2
Os(1)	0.60087 (13)	0.22569 (16)	0.19901 (3)	3.42 (6)
Os(2)	0.49282 (13)	0.00053 (15)	0.15609 (3)	2.98 (6)
Os(3)	0.22668 (13)	0.00909 (17)	0.12875 (4)	3.82 (7)
W	0.36038 (13)	0.26438 (15)	0.15335 (3)	3.03 (6)
C(1)	0.780 (4)	0.218 (4)	0.2018 (10)	6.1 (20)
C(2)	0.605 (4)	0.383 (4)	0.2225 (11)	6.0 (19)
C(3)	0.579 (3)	0.124 (4)	0.2450 (10)	5.2 (17)
C(4)	0.672 (4)	−0.022 (4)	0.1585 (11)	6.5 (21)
C(5)	0.466 (3)	−0.123 (4)	0.1974 (9)	4.5 (16)
C(6)	0.485 (3)	−0.136 (3)	0.1177 (9)	4.1 (15)
C(7)	0.166 (4)	−0.079 (5)	0.1739 (10)	6.2 (20)
C(8)	0.205 (4)	−0.142 (4)	0.1001 (11)	5.6 (19)
C(9)	0.062 (5)	0.077 (6)	0.1173 (15)	9.3 (29)
C(10)	0.339 (3)	0.158 (4)	0.2006 (9)	4.9 (17)
C(11)	0.305 (4)	0.490 (4)	0.1328 (11)	6.4 (20)
C(12)	0.203 (4)	0.417 (5)	0.1256 (13)	7.5 (23)
C(13)	0.164 (4)	0.365 (4)	0.1606 (14)	7.2 (24)
C(14)	0.276 (6)	0.446 (5)	0.1907 (14)	9.5 (30)
C(15)	0.350 (5)	0.504 (6)	0.1676 (15)	9.0 (29)
C(16)	0.467 (5)	0.147 (5)	0.1078 (14)	8.9 (27)
C(17)	0.326 (4)	0.152 (4)	0.0935 (9)	4.9 (17)
C(18)	0.269 (5)	0.197 (5)	0.0556 (12)	8.8 (30)
C(19)	0.282 (4)	0.110 (5)	0.0261 (11)	6.8 (23)
C(20)	0.230 (7)	0.155 (6)	−0.0146 (15)	11.7 (40)
C(21)	0.235 (10)	0.061 (10)	−0.0398 (25)	19.1 (74)
C(22)	0.543 (4)	0.263 (4)	0.1127 (10)	5.6 (19)
C(23)	0.504 (11)	0.330 (9)	0.064 (3)	20.7 (75)
C(24)	0.637 (5)	0.341 (6)	0.0087 (12)	9.4 (31)
C(25)	0.768 (6)	0.383 (7)	0.0097 (16)	11.8 (38)
C(26)	0.588 (3)	0.323 (3)	0.1450 (8)	3.9 (15)
C(27)	0.654 (4)	0.462 (4)	0.1414 (12)	6.5 (20)
C(28)	0.863 (8)	0.622 (8)	0.1297 (21)	14.6 (52)
C(29)	0.868 (10)	0.616 (12)	0.095 (3)	21.4 (87)
O(1)	0.899 (3)	0.217 (3)	0.2012 (7)	6.9 (14)
O(2)	0.601 (3)	0.491 (4)	0.2404 (10)	10.0 (20)
O(3)	0.564 (3)	0.054 (3)	0.2724 (7)	7.0 (15)
O(4)	0.790 (3)	−0.051 (3)	0.1608 (10)	9.1 (19)
O(5)	0.435 (3)	−0.202 (3)	0.2223 (7)	6.8 (14)
O(6)	0.4861 (24)	−0.223 (3)	0.0942 (7)	6.2 (13)
O(7)	0.116 (3)	−0.134 (4)	0.2009 (9)	10.3 (21)
O(8)	0.183 (3)	−0.241 (4)	0.0770 (9)	9.5 (19)
O(9)	−0.040 (4)	0.128 (5)	0.1040 (12)	12.3 (25)
O(10)	0.2870 (21)	0.1101 (22)	0.2294 (6)	4.3 (10)
O(11)	0.533 (4)	0.471 (5)	0.0701 (11)	13.1 (28)
O(12)	0.606 (3)	0.269 (3)	0.0457 (7)	6.7 (14)
O(13)	0.611 (4)	0.574 (4)	0.1617 (10)	10.8 (22)
O(14)	0.776 (3)	0.455 (4)	0.1235 (10)	10.0 (20)

Ph (**2a**), ^{n}Bu (**2b**)). For the trinuclear complexes **2a** and **2b**, the crystal structure as well as some chemical reactions with disubstituted alkynes have been reported recently;[2,10] therefore, discussion is limited here to the preparation and the reaction of the tetranuclear acetylide complexes **1a** and **1b**.

The formulation for the W–Os_3 acetylide complexes has been established by spectroscopic and analytical data. Infrared spectra of **1a** and **1b** indicated the presence of only terminal CO ligands. The solution ^{13}C NMR spectrum of a ^{13}CO-enriched sample of complex **1b** in CD_2Cl_2 shows six signals at δ 208.9, 205.2, 181.4, 177.6, 172.6, and 172.2 in the relative ratio 1:1:1:3:1:1, in addition to a very broad signal centered at δ 178.2. The first two signals at δ 208.9 and 205.2 are assigned to the CO ligands on the tungsten atom on the basis of the chemical shift and the presence of ^{183}W satellites. The signals at δ 181.4, 172.6, and 172.2 in the ratio 1:1:1 are assigned to a $Os(CO)_3$ fragment that undergoes relatively slow rotational motion, and the signal at δ 177.6, of intensity corresponding to three carbons, is assigned to a second $Os(CO)_3$ unit undergoing rapid rotation. As expected, an increase of temperature to 370 K in *o*-xylene-d_{10} solution caused the broad signal at δ 178.2 to sharpen and the three signals at δ 181.4, 172.6, and 172.2 to coalesce, giving a broad signal at δ 175.2. Similarly, the ^{13}C NMR spectrum of **1a** (CD_2Cl_2) shows two W–CO signals at δ 208.5 and 204.2 and four Os–CO signals at δ 180.2, 176.2, 173.8, and 172.8 in the ratio 1:3:1:1.

After completion of the assignment of CO resonance signals, the signals of the acetylide α-carbon at δ 192.0 and β-carbon at δ 165.8 can be assigned unambiguously in the spectrum of a regular sample of complex **1b**. For the phenyl derivative **1a**, the signals at δ 186.9 and 169.8 are assigned to the acetylide α- and β-carbons, respectively. The chemical shifts observed for both α- and β-carbons are in good agreement with the data summarized by Carty and co-workers.[11] The downfield shift also suggests that the acetylide ligand is very electron-deficient.

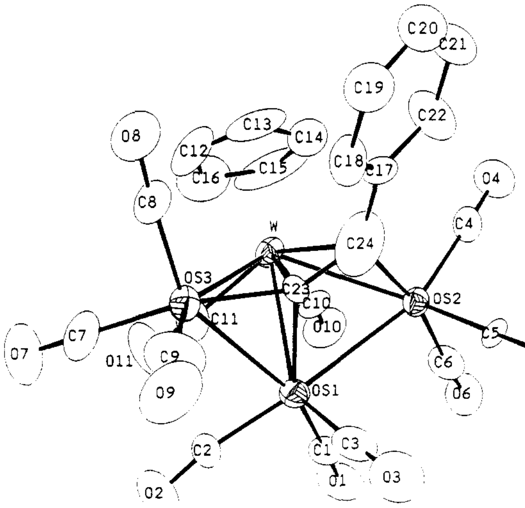

Figure 1. ORTEP diagram of complex **1a** showing the atomic numbering scheme.

Description of the Structure of $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ (1a). The structure of **1a** has been determined

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(10) Chi, Y.; Huttner, G.; Imhof, W. *J. Organomet. Chem.* **1990**, *384*, 93.

(11) Carty, A. J.; Cherkas, A. A.; Randall, L. H. *Polyhedron* **1988**, *7*, 1045.

Table VII. Selected Interatomic Distances (Å) and Bond Angles (deg) of Complex 5a (Esd's in Parentheses)

(A) Intermetallic Distances and Angles			
Os(1)–Os(2)	2.841 (1)	Os(1)–Os(3)	2.815 (1)
Os(1)–W	2.740 (1)	Os(2)–W	2.902 (1)
Os(3)–W	2.773 (1)	Os(2)–Os(3)	2.876 (1)
∠Os(2)–Os(1)–Os(3)	61.11 (3)	∠Os(2)–Os(1)–W	62.63 (3)
∠Os(3)–Os(1)–W	59.87 (3)	∠Os(1)Os(2)–Os(3)	58.99 (3)
∠Os(1)–Os(2)–W	56.97 (3)	∠Os(3)–Os(2)–W	57.35 (3)
∠Os(1)–Os(3)–Os(2)	59.90 (3)	∠Os(1)–Os(3)–W	58.72 (3)
∠Os(2)–Os(3)–W	61.80 (3)	∠Os(1)–W–Os(2)	60.40 (3)
∠Os(1)–W–Os(3)	61.41 (3)	∠Os(2)–W–Os(3)	60.84 (3)
(B) Parameters Associated with the C_4 Hydrocarbon Fragment			
Os(2)–C(15)	2.00 (1)	Os(3)–C(15)	2.20 (1)
W–C(15)	2.05 (1)	Os(3)–C(16)	2.25 (1)
Os(3)–C(25)	2.26 (1)	Os(3)–C(26)	2.28 (1)
W–C(26)	2.12 (1)	C(15)–C(16)	1.44 (2)
C(16)–C(25)	1.45 (2)	C(25)–C(26)	1.46 (2)
∠Os(2)–C(15)–Os(3)	86.3 (4)	∠Os(2)–C(15)–W	91.5 (5)
∠Os(3)–C(15)–W	81.5 (4)	∠Os(3)–C(16)–C(15)	69.0 (7)
∠C(15)–C(16)–C(25)	109 (1)	∠W–C(26)–C(25)	121.0 (9)
∠Os(3)–C(26)–W	78.1 (4)		
(C) Parameters Associated with the Carbonyl Ligands			
W–C(9)	1.99 (1)	Os(1)⋯C(9)	2.49 (2)
∠Os(1)–C(1)–O(1)	176 (2)	∠Os(1)–C(2)–O(2)	175 (1)
∠Os(1)–C(3)–O(3)	180 (2)	∠Os(2)–C(4)–O(4)	174 (2)
∠Os(2)–C(5)–O(5)	178 (1)	∠Os(2)–C(6)–O(6)	174 (2)
∠Os(3)–C(7)–O(7)	180 (1)	∠Os(3)–C(8)–O(8)	180 (1)
∠W–C(9)–O(9)	163 (1)	∠Os(1)⋯C(9)–O(9)	xxx (2)

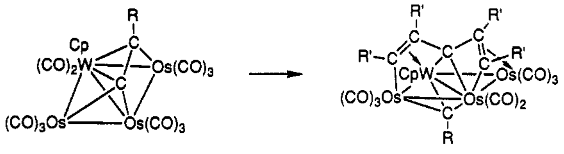
by a single-crystal X-ray diffraction study. As shown in Figure 1, the molecule consists of a W–Os_3 core of a "butterfly" arrangement, with Os(2) and Os(3) defining the "wingtip" positions and W and Os(1) atoms the "hinge" positions. Each osmium atom associates with three CO ligands and the tungsten, with two CO ligands and a Cp ligand. The dihedral angle between the triangular wings W–Os(1)–Os(2) and W–Os(1)–Os(3) is 131.4 (3)°. All the CO ligands on the osmium atoms are linear with the Os–C–O angles in the range 171 (2)–179 (2)°, whereas both CO ligands on the tungsten atom, C(10)–O(10) and C(11)–O(11), are bent slightly with ∠W–C(10)–O(10) = 164 (2)° and ∠W–C(11)–O(11) = 167 (2)°. The formation of these semibridging CO ligands[12] can be regarded as a natural consequence of redistribution of the formal valence electrons between the adjacent metal atoms. Formal electron counts at the individual metal atoms (neutral ligands and metal assumed) are 18e at Os(1), 17e at Os(2) and Os(3), and 20e at the W atom. Therefore, the electron deficiency at Os(2) and Os(3) is compensated by the formation of some bonding interaction with the CO ligands of the electron-rich tungsten atom.

The acetylide ligand occupies the open face of the butterfly framework and is coordinated in multisite fashion with its α-carbon bound to the three metal atoms W, Os(1), and Os(3) with bond distances W–C(23) = 2.27 (2) Å, Os(1)–C(23) = 2.13 (2) Å, and Os(3)–C(23) = 1.95 (2) Å and with the β-carbon atom linked to W and Os(2) atoms with bond distances W–C(24) = 2.49 (2) Å and Os(2)–C(24) = 2.09 (2) Å. The bonding mode of this acetylide ligand is of particular interest.[13] The μ_4-η^2 bonding mode has been documented in spiked-triangular Ni_2Fe_2 and $FeRuCo_2$ complexes,[14] a square-pyramidal Ru_5 complex,[15] and a wingtip-bridged butterfly $NiRu_4$ complex.[16] Complex **1a** is the first example in the butterfly system in which the acetylide ligand can be considered as σ-bonded to one wingtip atom, Os(3), via its α-carbon and also as interacting with the second metal triangle, Os(1)–Os(2)–W, via a parallel ($2\sigma + \pi$) bonding mode of a typical μ_3-alkyne ligand.[17] Alternatively, if we consider both acetylide carbons as a part of the polyhedral skeleton, the geometry of this molecule can be considered to be a M_4C_2 capped trigonal bipyramid with the acetylide β-carbon serving as

Table VIII. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Complex 5a

	x	y	z	B_{iso}, Å^2
Os(1)	0.35001 (6)	0.67633 (5)	0.09879 (4)	2.273 (23)
Os(2)	0.45377 (6)	0.62318 (5)	0.28117 (4)	2.159 (22)
Os(3)	0.21149 (5)	0.74611 (4)	0.23771 (4)	1.805 (21)
W	0.50062 (6)	0.86250 (5)	0.22190 (4)	1.947 (21)
C(1)	0.5169 (18)	0.6496 (14)	0.0547 (11)	3.8 (8)
C(2)	0.2214 (17)	0.5253 (14)	0.0864 (10)	3.2 (7)
C(3)	0.2549 (18)	0.7027 (14)	−0.0178 (11)	3.9 (8)
C(4)	0.4645 (20)	0.4847 (13)	0.2086 (11)	4.0 (8)
C(5)	0.3756 (17)	0.5302 (13)	0.3732 (10)	3.2 (7)
C(6)	0.6550 (19)	0.6340 (13)	0.3388 (14)	4.3 (9)
C(7)	0.0577 (15)	0.7631 (12)	0.1380 (10)	2.5 (6)
C(8)	0.0783 (16)	0.6089 (13)	0.2610 (9)	3.0 (7)
C(9)	0.3966 (15)	0.8959 (13)	0.0993 (9)	2.9 (7)
C(10)	0.7363 (15)	0.9298 (15)	0.3217 (12)	4.0 (8)
C(11)	0.6748 (16)	1.0287 (14)	0.2954 (14)	4.6 (9)
C(12)	0.6645 (16)	1.0337 (13)	0.1977 (13)	3.8 (8)
C(13)	0.7189 (17)	0.9381 (15)	0.1662 (12)	4.2 (8)
C(14)	0.7644 (16)	0.8774 (14)	0.2420 (13)	4.1 (8)
C(15)	0.4332 (13)	0.7798 (11)	0.3314 (8)	2.0 (5)
C(16)	0.3274 (12)	0.8119 (10)	0.3823 (8)	1.5 (5)
C(17)	0.2989 (13)	0.7594 (11)	0.4677 (9)	2.0 (5)
C(18)	0.4243 (15)	0.7580 (12)	0.5352 (10)	2.8 (6)
C(19)	0.4119 (17)	0.7073 (13)	0.6160 (10)	3.4 (7)
C(20)	0.2643 (21)	0.6552 (14)	0.6269 (11)	4.2 (9)
C(21)	0.1418 (17)	0.6547 (13)	0.5634 (11)	3.6 (7)
C(22)	0.1557 (15)	0.7052 (12)	0.4817 (10)	2.8 (6)
C(23)	0.1055 (21)	1.1521 (15)	0.4008 (16)	5.9 (12)
C(24)	0.1709 (15)	0.9708 (13)	0.3786 (11)	2.9 (7)
C(25)	0.2653 (14)	0.9061 (11)	0.3381 (9)	2.1 (5)
C(26)	0.3305 (14)	0.9412 (11)	0.2586 (9)	2.3 (6)
C(27)	0.2842 (15)	1.0442 (12)	0.2109 (9)	2.6 (6)
C(28)	0.0924 (22)	1.1163 (18)	0.1254 (17)	7.9 (13)
O(1)	0.6235 (13)	0.6319 (11)	0.0330 (10)	6.1 (7)
O(2)	0.1344 (12)	0.4349 (10)	0.0745 (9)	5.1 (6)
O(3)	0.1970 (14)	0.7213 (12)	−0.0884 (8)	6.1 (7)
O(4)	0.4793 (19)	0.4016 (11)	0.1724 (9)	7.5 (9)
O(5)	0.3275 (15)	0.4724 (10)	0.4248 (9)	6.1 (7)
O(6)	0.7783 (13)	0.6498 (11)	0.3795 (11)	6.8 (8)
O(7)	−0.0350 (12)	0.7722 (10)	0.0798 (8)	4.4 (6)
O(8)	−0.0043 (14)	0.5239 (10)	0.2753 (9)	6.2 (7)
O(9)	0.3525 (12)	0.9449 (9)	0.0356 (7)	4.1 (6)
O(10)	0.1991 (14)	1.0805 (10)	0.3698 (10)	6.3 (8)
O(11)	0.0628 (15)	0.9214 (11)	0.4089 (11)	7.0 (8)
O(12)	0.1417 (12)	1.0207 (9)	0.1719 (8)	4.4 (6)
O(13)	0.3692 (11)	1.1355 (9)	0.2057 (9)	4.7 (6)

Scheme I



R = Ph, (**1a**)

R = Ph, R' = Tol, (**3**), 62%

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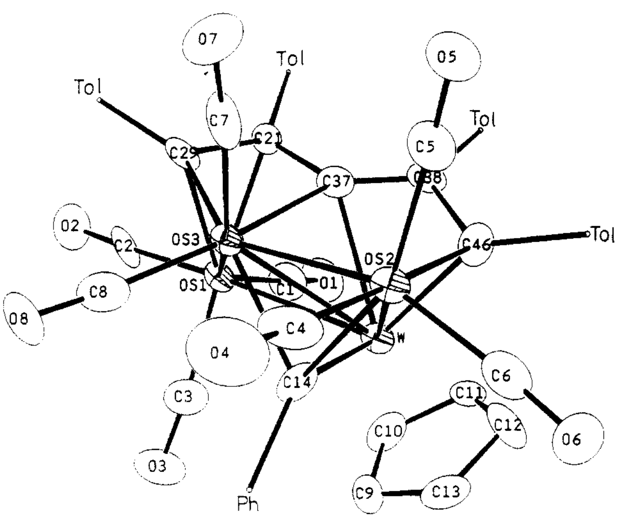


Figure 2. ORTEP diagram of complex 3 showing the atomic numbering scheme. The phenyl and tolyl substituents have been omitted for clarity.

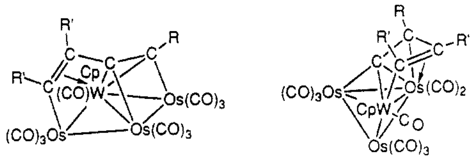
a cap.[18] Clusters that exhibit this capped-trigonal-bipyramidal geometry include several mixed-metal vinylidene complexes[19] and a Fe_4 nitrile complex,[20] the crystal structures of which have all been previously reported.

Reaction with Ditolylacetylene. Reaction of **1a** with excess ditolylacetylene in refluxing toluene (110 °C, 2 h) produces a dark green complex, $CpWOs_3(CO)_8(\mu_3\text{-}CPh)[\mu_4\text{-}\eta^5\text{-}C(C_2Tol_2)_2]$ (**3**), in 62% yield, as the only isolable cluster product (Scheme I). Decreasing the reaction time to 1 h or using exactly 1 equiv of ditolylacetylene gave only partial conversion to **3**, in addition to some unreacted **1a**. No intermediate was observed under these reaction conditions.

The ^1H NMR spectrum of complex **3** exhibits one Cp signal at δ 5.55 and four methyl signals at δ 2.26, 2.22, 2.16, and 2.03 in $CDCl_3$ solution at room temperature, suggesting that 2 equiv of ditolylacetylene has added to the acetylide cluster. In addition, the region of the aromatic proton signals is very complex: some signals are broad, and the total integration is less than that for one phenyl and four tolyl groups. We regard this observation as due to the hindered rotation of the aromatic rings. Sharp signals and a good integration ratio for the aromatic protons were obtained when the spectrum was recorded at 317 K.

Description of the Structure of $CpWOs_3(CO)_8(\mu_3\text{-}CPh)[C(C_2Tol_2)_2]$ (3). The cluster core of complex **3** is depicted in Figure 2 with all the phenyl and tolyl rings removed for clarity. The molecule adopts a flat butterfly geometry or a planar triangulated rhomboidal arrangement as expected for cluster species characterized by 62 valence electrons. The W and Os(3) atoms are located at the hinge positions and the Os(1) and Os(2) atoms at the wingtip positions; the angle between the W–Os(1)–Os(3) and W–Os(2)–Os(3) planes is 3.32 (3)°. The W atom and the Os(3) atoms associate with a Cp ligand and with two terminal CO ligands, respectively, while each terminal Os(1) and Os(2) atom is linked to three terminal CO ligands. Formal electron counts at the metal centers in this complex reveal that all metal atoms are electron-precise.

Chart I



R = Ph, R' = CO_2Me	(**4a**), 20%	(**5a**), 25%
R = Ph, R' = CO_2Et	(**4b**), 11%	(**5b**), 25%
R = ^nBu, R' = CO_2Et	(**4c**), 17%	(**5c**), 18%

There is a triply bridging alkylidyne group capped on the W–Os(2)–Os(3) triangle with the bond distances W–C(14) = 1.95 (1) Å, Os(2)–C(14) = 2.14 (2) Å, and Os(3)–C(14) = 2.15 (1) Å. On the opposite side of the WOs_3 square plane, there is a C_5 hydrocarbyl moiety that interacts with all four transition-metal atoms with M–C distances in the range 2.07–2.36 Å. This C_5 ligand is best described as a bis(2-metallovinyl)alkylidene ligand. The center alkylidene carbon atom C(37) is bridged across the bridgehead W–Os(3) bond with bond angles ∠Os(3)–C(37)–W = 77.0 (4)° and ∠C(21)–C(37)–C(38) = 135 (1)°. The metallovinyl fragment C(21)–C(29) is bound to the Os(3) atom via a σ-bond and to the Os(1) atom via a π-bond, and the metallovinyl fragment C(38)–C(46) is bound to the Os(2) atom and the W atom via a σ-bond and a π-bond, respectively. In order to support the π-bonding for both metallovinyl fragments, the distance between the adjacent Os(1) and W atoms is increased to 3.004 (1) Å, which is the longest metal–metal bond within the molecule. The shortest metal–metal interaction of bond distance 2.743 (1) Å is parallel to the longest Os(1)–W bond.

Reaction with Electron-Withdrawing Alkynes. When complexes **1a** and **1b** were treated with excess dialkyl acetylenedicarboxylate (R' = CO_2Me and CO_2Et) in refluxing toluene (110 °C, 30 min), more than four different complexes were observed on the analytical TLC plates. From the reaction mixture, the major products $CpWOs_3(CO)_{10}[CR'CR'CCR]$ (R = Ph, R' = CO_2Me (**4a**), CO_2Et (**4b**); R = ^nBu, R' = CO_2Et (**4c**)) and $CpWOs_3(CO)_9[CCRCR'CR']$ (R = Ph, R' = CO_2Me (**5a**), CO_2Et (**5b**); R = ^nBu, R' = CO_2Et (**5c**)) have been isolated by preparative TLC on silica gel followed by recrystallization. These complexes have all been characterized by spectroscopic methods and by microanalysis. The molecular ions observed in FAB mass spectra suggest that complex **4** possesses 10 CO ligands and complex **5** possesses 9 CO ligands. The ^1H NMR spectra of complexes **4** and **5** reveal, in contrast to that of complex **3**, the presence of only two inequivalent CO_2R groups. As such, it is clear that these complexes are formed by coordination of one alkyne molecule. In order to solve the structural relationship between these two isomers, X-ray diffraction studies have been carried out on complexes **4c** and **5a**. Both the structural solution and the relative yield of these two isomers are indicated in Chart I.

When we varied the reaction conditions slightly, we observed that the isolated yields for complexes 4 and 5 are independent of the amount of alkyne added (6–20 equiv) and the reaction period (15–60 min). Attempts to extend the scope of reaction by using other electron-withdrawing alkynes were unsuccessful; treatment of **1a** (120 °C, 2 h) with excess hexafluoro-2-butyne in a sealed tube under similar conditions, however, failed to produce any new complexes.

Description of the Structure of $CpWOs_3(CO)_{10}[C(CO_2Et)C(CO_2Et)CC(^nBu)]$ (4c). The structure of **4c** is

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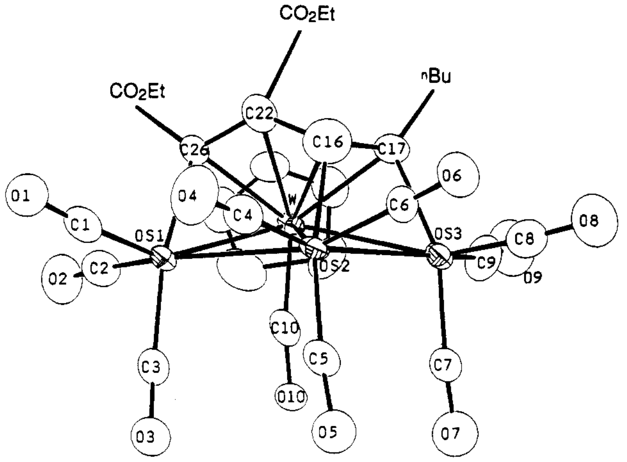

Figure 3. ORTEP diagram of complex **4c** showing the atomic numbering scheme. The CO_2Et and the ^nBu substituents have been removed for clarity.

illustrated in Figure 3. Selected bond distances and angles are given in Table VI. The molecule can be regarded as possessing a planar triangular rhomboidal arrangement with W and Os(2) atoms at the bridgehead position, the angle between the W–Os(1)–Os(2) and W–Os(2)–Os(3) planes being 197.06 (6)°. The W atom and the Os(2) atom of the bridgehead position are coordinated to a Cp and a CO ligand and to three CO ligands, respectively, whereas each terminal Os(1) and Os(3) atom is linked to three terminal CO ligands. All the CO ligands are linear (169–176°), except that the CO ligand on the tungsten atom is bent slightly with ∠W–C(10)–O(10) = 159°. Again, the formation of a semibridging CO ligand can partially compensate the electron deficiency at the Os(1) atom. If we consider all hydrocarbon ligands and metals to be neutral, the formal electron count for each metal vertex is 18 valence electrons for the Os(2) atom, 17 electrons for the Os(1) and Os(3) atoms, and 20 electrons for the W atom.

The bonding interaction of the newly formed C_4 hydrocarbyl fragment C(17)–C(16)–C(22)–C(26) in complex **4c** is best described as a modified μ_4-η^2-acetylide ligand similar to that of complex **1a**. Insertion of the alkyne into the M–C_α bond of the acetylide ligand in **1a**, followed by elimination of a CO ligand and coordination of the alkyne π-bond to the W atom, would generate the structure suggested by complex **4c**. In fact, there is no significant difference of the structural parameters of the W–Os_3 core between complexes **1a** and **4c**. An interesting feature of **4c** is the presence of a larger dihedral angle between the two W–Os_2 triangles (197.06 (6)°) than for complex **1a** (131.4 (3)°). The reason for the excessively large dihedral angle must be related to the fact that **4c** contains a parallel and rigid C_4 fragment, whereas the C_2 acetylide ligand in **1a** is much smaller and more adaptable to a butterfly geometry.

Description of the Structure of $CpWOs_3(CO)_9[CC(Ph)C(CO_2Me)C(CO_2Me)]$ (5a). The ORTEP diagram of complex **5a** and the scheme used for labeling the atoms are illustrated in Figure 4. Selected bond distances and angles are listed in Table VII. In this molecule, the tungsten atom and three osmium atoms form a slightly distorted tetrahedral core with the metal–metal distances in the range 2.704–2.904 Å; these distances are comparable to those in complexes **1a**, **3**, and **4c**. The W atom is associated with a semibridging CO ligand (∠W–C(9)–O(9) = 163°) and a Cp ligand, whereas the Os(2) atom is linked to two terminal CO ligands and the Os(1) and the Os(3) atoms are coordinated to three terminal CO ligands.

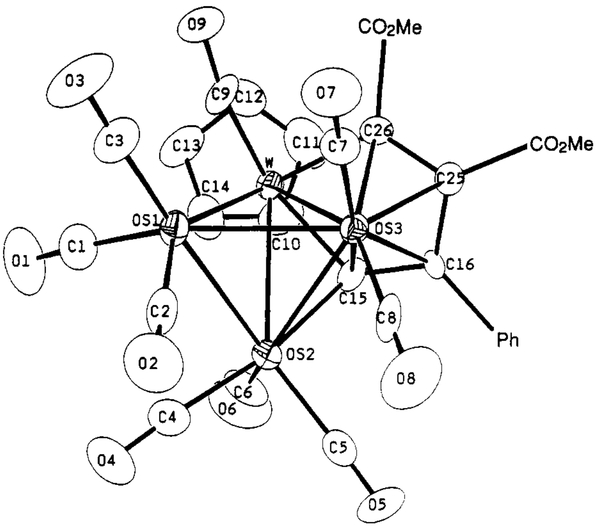

Figure 4. ORTEP diagram of complex **5a** showing the atomic numbering scheme. The CO_2Me and the phenyl substituents have been removed for clarity.

The most interesting ligand in the cluster is the η^4 triply bridging C_4 hydrocarbyl fragment C(15)–C(16)–C(25)–C(26). The skeleton of this C_4 fragment can be viewed as a derivative of a μ_3-η^2-vinylidene. The vinylidene C(15)–C(16) backbone, derived from the acetylide ligand, is coordinated to the Os(2)–W edge via two σ-bonds and is π-bonded to the Os(3) atom via a η^2 interaction. The C_2 substituent C(25)–C(26), derived from the alkyne, is linked to the β-carbon of the vinylidene and the W atom via two σ-bonds and is coordinated to the Os(3) atom via a π-bond. Alternatively, the molecule can also be considered to adopt a M_4C closo trigonal-bipyramidal geometry with atoms Os(1) and C(15) located at the axial positions and atoms Os(2), Os(3), and W on the equatorial plane. In this case, the C_4 hydrocarbyl ligand could be considered to be a 1,3-disubstituted allyl moiety that is linked to C(15) and W atoms via two σ-bonds and is π-bonded to the third Os(3) atom by a η^3 interaction.

Finally, the cluster is associated with 60 outer valence electrons and the formal electron count for each metal vertex is 18 valence electrons for the Os(2) and W atoms, 17 electrons for Os(1), and 19 electrons for Os(3).

Possible Mechanism of the Scission of the Acetylide Ligand. The substituents on the alkylidyne and the alkylidene moieties of **3** indicate that the α-carbon of the newly formed alkylidyne originates from the acetylide β-carbon of complex **1a**. Therefore, the coordinated acetylide ligand of **1a** undergoes a C–C bond cleavage during the reaction with ditolylacetylene. We propose two different pathways for this unique reaction. The first involves a scission of the acetylide C–C bond to form an alkylidyne and a carbide initially; the carbide then couples with two molecules of ditolylacetylene to generate the observed C_5 alkylidene moiety. Studies of the scission of the coordinated alkyne ligand,[21] the coupling of a coordinated carbide and alkyne,[22] and the consideration of acetylides as alkylidyne carbides[23] provide precedents for this postulated

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reaction pathway. The second pathway, however, involves a prior coupling of one ditolylacetylene and acetylide to give a C_4 fragment similar to that observed in complex **4c**, 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.

We prefer the alkylidyne carbide pathway because the time period required for the reaction with ditolylacetylene (2.5 h) is much greater than that with dialkyl acetylenedicarboxylate (30 min), suggesting that the structure of the intermediate of the ditolylacetylene reaction (carbide + alkylidyne) may differ from that of complex 4 produced from reactions with dialkyl acetylenedicarboxylate. The greater reaction period also implies that the activation barrier of inducing the cleavage of the acetylide C–C bond is slightly higher than that of the coupling with dialkyl acetylenedicarboxylate. Furthermore, reactions of **4b** with excess ditolylacetylene or diethyl acetylenedicarboxylate under conditions similar (110 °C, 2.5 h) to those for the ditolylacetylene reaction have also been carried out; only decomposition was observed for these two reactions.

Although the alkylidyne carbide mechanism seems preferable, we still cannot completely eliminate the second possibility, because one may argue that the electron-withdrawing substituents of complex 4 would inhibit the reaction with the second alkyne and the following C–C bond cleavage reaction. Therefore, it would be useful if we could synthesize an analogous cluster complex that possesses the basic structure of **4c** but lacks the electron-withdrawing groups. The direct reaction of **1a** with exactly 1 equiv of ditolylacetylene has proved useless for this propose; therefore, we decided to approach the synthesis of this target molecule by using a triosmium alkyne complex and a metal acetylide. Unfortunately, the designated reaction between the unsaturated $Os_3(CO)_9(C_2Tol_2)$[24] and $CpW(CO)_3(C{\equiv}CPh)$ gives two new $W–Os_3$ clusters, neither of which has the expected geometry of complex **4c**. The results of these studies will be reported separately.

Acknowledgment. We are grateful to the National Science Council of the Republic of China for financial support (Grant No. NSC 79-2008-M007-52).

Supplementary Material Available: ORTEP diagrams for complexes **4c** and **5a** with a complete atomic labeling scheme and tables of nonessential bond distances and angles and anisotropic thermal parameters for **4c** and **5a** (14 pages); listings of the observed and calculated structure factors for **4c** and **5a** (29 pages). Ordering information is given on any current masthead page.

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Mechanism of Hydride Fluxionality as Intramolecular Proton Transfer between Metal–Metal Bonds. Kinetics of Hydride Fluxionality for $(\mu\text{-H})_nRu_3(\mu_3\text{-X})(CO)_8L$ (n = 1, X = CH_2SEt, L = CO; n = 2, X = $CHCO_2Me$, $MeOC_2Me$, L = CO; n = 2, X = $CHCO_2Me$, L = PPh_3)

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The kinetics of hydride fluxionality have been measured for the structurally analogous series of clusters $(\mu\text{-H})_nRu_3(\mu_3\text{-X})(CO)_8L$, in which the number of hydride ligands and the nature of the capping ligand can be varied. For $(\mu\text{-H})_2Ru_3(\mu_3\text{-CHCO}_2Me)(CO)_9$, the lower energy process ($\Delta H^{\ddagger}$ = 49.5 ± 7.6 kJ, $\Delta S^{\ddagger}$ = −4 ± 29 J/(K mol)) involves movement of one hydride to the Ru–Ru bond and the higher energy process ($\Delta H^{\ddagger}$ = 56.9 ± 5.9 kJ, $\Delta S^{\ddagger}$ = −33 ± 18 J/(K mol)), which exchanges the hydrides, is proposed to occur through a two-step pathway. Only hydride exchange is observed for $(\mu\text{-H})_2Ru_3(\mu_3\text{-CHCO}_2Me)(CO)_8(PPh_3)$ ($\Delta H^{\ddagger}$ = 53.9 ± 3.8 kJ, $\Delta S^{\ddagger}$ = −41 ± 12 J/(K mol)) and $(\mu\text{-H})_2Ru_3(\mu_3\text{-MeOC}_2Me)(CO)_9$ ($\Delta H^{\ddagger}$ = 54.0 ± 5.2 kJ, $\Delta S^{\ddagger}$ = −37 ± 19 J/(K mol)). The fluxional process for $(\mu\text{-H})Ru_3(\mu_3\text{-CH}_2SEt)(CO)_9$ consists of hydride exchange between the two metal–metal vectors which are bridged by carbon and sulfur ($\Delta G^{\ddagger}$ = 51 kJ at 248 K); the deuterium kinetic isotope effect was determined to be 1.6 (79% deuterium enrichment). Activation parameters and deuterium isotope effects for these compounds, in combination with literature values for a number of Ru_3 clusters, are rationalized in terms of the model of intramolecular proton transfer between metal–metal bonds via a transition state that contains a single terminal hydride ligand.

Introduction

It has been recognized for many years that hydride ligands on metal clusters are frequently involved in intramolecular migrations with rates on the order of the NMR time scale.[1] Although numerous studies of this dynamic behavior have been performed, it has not been possible to determine the relationship between the rate of hydride migration and the structure of the cluster. In fact, for clusters of greater than two metal atoms, in no case has it been possible to determine whether hydride migration proceeds through terminal or μ_3 coordination of the hydride ligand in the transition state.[39] The dynamics of hydride migration on metal clusters may be presumed to

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