Competitive Acetylide C−C Bond Scission vs Formation of a Quadruply Bridging Carbonyl Ligand. X-ray Crystal Structures of the Two Pentanuclear Clusters $Cp^*_3W_3Ru_2(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CO)_9$ and $Cp^*_3W_3Ru_2(\mu_3\text{-}CCBu^t)(CO)_9$

Pei-Chiun Su,† Yun Chi,*,† Chi-Jung Su,† Shie-Ming Peng,*,‡ and Gene-Hsiang Lee‡

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, and Department of Chemistry and Instrumentation Center, National Taiwan University, Taipei 10764, Taiwan

Received December 10, 1996⊗

Reactions of $Cp^*WRu_2(CCPh)(CO)_8$ (**1a**) with excess $Cp^*W(CO)_3H$, $Cp^* = C_5Me_5$, affords a carbido−alkylidyne cluster $Cp^*_3W_3Ru_2(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CO)_9$ (**5**) alone with three byproducts, which are identified as hydride cluster $Cp^*WRu_3(\mu\text{-}H)_3(CO)_{11}$ (**2**), vinylidene cluster $Cp^*_2W_2Ru_2(CCHPh)(CO)_9$ (**4**), and a pentanuclear oxo−carbido cluster $Cp^*_2W_2(O)Ru_3(\mu_5\text{-}C)(CO)_{11}$ (**3**). In contrast, the respective condensation using *tert*-butyl derivative $Cp^*WRu_2(CCBu^t)(CO)_8$ (**1b**) gives an acetylide cluster $Cp^*_3W_3Ru_2(\mu_3\text{-}CCBu^t)(CO)_9$ (**6**). The X-ray structural determinations of **5** and **6** reveals the existence of an edge-bridged tetrahedral core, in which the butterfly crater is occupied by a μ_4-carbide in **5** or a quadruply bridging CO ligand in **6**. A plausible mechanism leading to the formation of these two cluster compounds is also presented.

Transition metal clusters containing unsaturated alkyne or acetylide fragments have been an area of intense investigation due to their unique physical and chemical properties[1,2] and their relevance to the transformation of small hydrocarbyl intermediates on metal surfaces. Much work has been devoted to the development of this chemistry in recent years. For example, Carty and co-workers reported the syntheses and crystal structures of phosphido ruthenium clusters containing multisite bound acetylide ligands.[3] Adams and co-workers focused on the hydrogenation of alkyne on the layer-segregated, face-shared bioctahedral clusters.[4] Other investigations, such as the studies on the ruthenium and osmium clusters[5] and the heterometallic counterparts,[6] all provided substantial knowledge about the bonding and reactivity of cluster-bound alkyne and acetylide ligands.

A much less disclosed pattern of reactivity for such complexes is the C−C bond cleavage, which affords two alkylidyne ligands from the coordinated alkynes.[7] Likewise, the related acetylide ligand, which can be envisaged as a carbide−alkylidyne in certain polynuclear systems,[8] has been observed to convert to the well-separated carbide and alkylidyne ligands.[9] In this article, we focus on the irreversible acetylide cleavage through the generation of a Ru_2W_3 mixed-metal cluster, which offers an opportunity to reveal the essence of the acetylide scission vs the competing process involving the generation of the quadruply bridging CO ligand.[10] In addition, this study supplements our previous report on the reversible acetylide cleavage between the parent acetylide cluster $CpWRu_2(CCPh)(CO)_8$ and the polynuclear carbido alkylidyne derivatives $CpWRu_4(\mu_5\text{-}C)(\mu\text{-}CPh)(CO)_{12}$ and $CpWRu_5(\mu_6\text{-}C)(\mu\text{-}CPh)(CO)_{14}$, which is also promoted by a cluster building reaction.[11]

† National Tsing Hua University.
‡ National Taiwan University.
⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Radiochem.* **1985**, *29*, 169. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (c) Kaesz, H. D.; Humphries, A. P. *Prog. Inorg. Chem.* **1979**, *25*, 146. (d) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (e) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (f) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(2) (a) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89. (b) Ma, L.; Williams, G. K.; Shapley, J. R. *Coord. Chem. Rev.* **1993**, *128*, 261. (c) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79. (d) Chi, Y. *J. Chin. Chem. Soc.* **1992**, *39*, 591.

(3) (a) Corrigan, J. F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1769. (b) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293.

(4) (a) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. *Organometallics* **1994**, *13*, 2357. (b) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. *J. Am. Chem. Soc.* **1994**, *116*, 9103.

(5) (a) Boyar, E.; Deeming, A. J.; Felix, M. S. B.; Kabir, S. E.; Adatia, T.; Bhusate, R.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1989**, 5. (b) Deeming, A. J.; Felix, M. S. B.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1987**, 461. (c) Rosenberg, E. *Polyhedron* **1989**, *8*, 383. (d) Ma, L.; Rodgers, D. P. S.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1991**, *30*, 3591. (e) Johnson, D. K.; Rukachaisirikul, T.; Sun, Y.; Taylor, N. J.; Canty, A. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 5544. (f) Haggitt, J. L.; Johnson, B. F. G.; Blake, A. J.; Parsons, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1263. (g) Paw, W.; Lake, C. H.; Churchill, M. R.; Keister, J. B. *Organometallics* **1995**, *14*, 3768. (h) Wong, W.-Y.; Chan, S.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1995**, 1497. (i) Koike, M.; Hamilton, D. H.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1996**, *15*, 4930. (j) Chi, Y.; Hwang, D.-K. In *Comprehensive Organometallics Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 10, Chapter 3.

(6) (a) Roland, E.; Vahrenkamp, H. *J. Mol. Catal.* **1983**, *21*, 233. (b) Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. *Organometallics* **1984**, *3*, 1595. (c) Bernhardt, W.; Vahrenkamp, H. *J. Organomet. Chem.* **1990**, *383*, 357. (d) Bantel, H.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1990**, *123*, 1607. (e) Adams, K. J.; Barker, J. J.; Charmant, J. P. H.; Ganter, C.; Klatt, G.; Knox, S. A. R.; Orpen, A. G.; Ruile, S. *J. Chem. Soc., Dalton Trans.* **1994**, 477. (f) Adams, R. D.; Barnard, T.; Li, Z.; Wu, W.; Yamamoto, J. H. *J. Cluster Sci.* **1994**, *5*, 551. (g) Akita, M.; Hirakawa, H.; Sakaki, K.; Moro-oka, Y. *Organometallics* **1995**, *14*, 2775. (h) Adams, H.; Bailey, N. A.; Gill, L. J.; Morris, M. J.; Wildgoose, F. A. *J. Chem. Soc., Dalton Trans.* **1996**, 1437. (i) Norton, D. M.; Eveland, R. W.; Hutchison, J. C.; Stern, C.; Shriver, D. F. *Organometallics* **1996**, *15*, 3916.

S0276-7333(96)01041-2 CCC: $14.00

Experimental Section

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400, a Varian Gemini-300, or a Varian Unity-400 instrument. ^{1}H and ^{13}C NMR chemical shifts are quoted with respect to internal standard TMS. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. The acetylide complexes Cp*WRu$_2$(CO)$_8$(CCR), R = Ph and Bu^t, were prepared according to literature procedures.[12] All reactions were performed under nitrogen using deoxygenated solvents dried with an appropriate reagent. Reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F$_{254}$, E. Merck), and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F$_{254}$, E. Merck). Elemental analyses were carried out at the regional instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of 1a with Cp*W(CO)$_3$H. A heptane solution (80 mL) of acetylide complex Cp*WRu$_2$(CCPh)(CO)$_8$ (**1a**; 100 mg, 0.118 mmol) and Cp*W(CO)$_3$H (135 mg, 0.334 mmol) was heated to reflux for 8 h, during which the color gradually changed from orange to dark-brown. After removal of the solvent under vacuum, the residue was redissolved in CH$_2$Cl$_2$ and separated by thin-layer chromatography (silica gel, dichloromethane−hexane 3:7), producing 35 mg of the starting material Cp*WRu$_2$(CCPh)(CO)$_8$ (0.041 mmol, 35%), 2 mg of orange trihydride complex Cp*WRu$_3$(μ-H)$_3$(CO)$_{11}$ (**2**; 0.023 mmol, 2%), 6 mg of orange-red Cp*$_2$W$_2$(O)Ru$_3$(μ_5-C)(CO)$_{11}$ (**3**; 0.0046 mmol, 4%), 3 mg of dark-brown Cp*$_2$W$_2$Ru$_2$(CCHPh)(CO)$_9$ (**4**; 0.0025 mmol, 2%), and 22 mg of black Cp*$_3$W$_3$Ru$_2$(μ_4-C)(μ_3-CPh)(CO)$_9$ (**5**; 0.013 mmol, 12%) in the order of their elution. Crystals of **5** suitable for X-ray diffraction studies were obtained by recrystallization from a layered solution of dichloromethane−methanol at room temperature.

Spectral data of **3**: MS (FAB, ^{102}Ru, ^{184}W) *m/z* 1275 (M$^+$). IR (C$_6$H$_{12}$) ν(CO), 2059 (s), 2022 (vs), 2006 (m), 1990 (s), 1955 (w), 1934 (w), 1802 (vw, br) cm^{-1}; IR (KBr) ν(W≡O), 928 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 294 K) δ 2.14 (s, 15H), 1.72 (s, 15H); ^{13}C NMR (CD$_2$Cl$_2$, 200 K) δ 441.5 (μ_5-C, J_{W-C} = 88 and 101 Hz), 223.0 (2CO, br), 212.0 (2CO, J_{W-C} = 161 Hz), 205.8 (2CO, br), 201.4 (2CO), 199.6 (2CO, br), 192.2 (1CO), 117.1 (*C*$_5$Me$_5$), 102.3 (*C*$_5$Me$_5$), 11.6 (C$_5$*Me*$_5$), 9.7 (C$_5$*Me*$_5$). Anal. Calcd for C$_{32}$H$_{30}$O$_{12}$Ru$_3$W$_2$: C, 30.09; H, 2.37. Found: C, 30.03; H, 2.47.

Spectral data for **4**: MS (FAB, ^{102}Ru, ^{184}W) *m/z* 1196 (M$^+$); IR (C$_6$H$_{12}$) ν(CO), 2049 (s), 2008 (vs), 1990 (m), 1976 (s), 1961 (s), 1920 (w), 1797 (vw, br), 1780 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$, 294 K) δ 7.48 (d, 2H, J_{H-H} = 7.4 Hz), 7.27 (t, 2H, J_{H-H} = 7.4 Hz), 7.12 (t, 1H, J_{H-H} = 7.4 Hz), 6.06 (s, 1H), 2.01 (s, 15H), 1.94 (s, 15H). Anal. Calcd for C$_{37}$H$_{36}$O$_9$Ru$_2$W$_2$: C, 37.20; H, 3.04. Found: C, 37.45; H, 3.16.

Spectral data for **5**: MS (FAB, ^{102}Ru, ^{184}W) *m/z* 1514 (M$^+$); IR (C$_6$H$_{12}$) ν(CO), 1994 (w), 1971 (vs), 1936 (s), 1929 (m), 1918 (w), 1909 (w), 1863 (vw, br), 1762 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 294 K) δ 7.48 (d, 1H, J_{H-H} = 7.5 Hz), 7.25−7.09 (m, 3H), 7.00 (t, 1H, J_{H-H} = 7.0 Hz), 2.14 (s, 15H), 1.81 (s, 15H), 1.74 (s, 15H); ^{13}C NMR (CD$_2$Cl$_2$, 294 K) CO, δ 251.6 (J_{W-C} = 120 Hz), 239.5 (J_{W-C} = 170 Hz), 220.1 (J_{W-C} = 167 Hz), 218.4 (J_{W-C} = 160 Hz), 218.0 (J_{W-C} = 160 Hz), 210.0, 209.6, 208.2, 208.0; δ 402.0 (μ_4-C, J_{W-C} = 119 Hz), 280.3 (μ_3-CPh, J_{W-C} = 96 Hz), 160.9 (*i*-C$_6$H$_5$), 130.1 (*C*H), 128.7 (*C*H), 126.3 (*C*H), 126.0 (*C*H), 124.8 (*C*H), 106.6 (*C*$_5$Me$_5$), 106.0 (*C*$_5$Me$_5$), 101.0 (*C*$_5$Me$_5$), 11.3 (C$_5$*Me*$_5$), 10.8 (C$_5$*Me*$_5$), 10.2 (C$_5$*Me*$_5$). Anal. Calcd for C$_{47}$H$_{50}$O$_9$Ru$_2$W$_3$·$^1/_2$CHCl$_3$: C, 36.29; H, 3.24. Found: C, 36.00; H, 3.23.

Reaction of 2 with Cp*W(CO)$_3$H. A toluene solution (25 mL) of **2** (11.4 mg, 0.0122 mmol) and Cp*W(CO)$_3$H (26 mg, 0.065 mmol) was brought to reflux under nitrogen. The heating was continued for 4 h, during which (20 mg × 3) of Cp*W(CO)$_3$H was added into the mixture on the hour. After removal of the solvent in vacuo, the residue was taken up in CH$_2$Cl$_2$ and separated by thin-layer chromatography (silica gel, dichloromethane−hexane 1:5), producing 5.5 mg of orange-red **3** (0.004 mmol, 30%) and 6 mg of unreacted starting material **2** (52%).

Reaction of 4 with Cp*W(CO)$_3$H. A toluene solution (15 mL) of vinylidene complex **4** (9.3 mg, 0.0078 mmol) and Cp*W(CO)$_3$H (15.7 mg, 0.039 mmol) was heated to reflux for 90 min. After removal of the solvent in vacuo, the residue was separated by thin-layer chromatography (silica gel, dichloromethane−hexane 1:5), producing 8.5 mg of black **5** (0.0056 mmol, 72%).

Reaction of 1b with Cp*W(CO)$_3$H. A heptane solution (60 mL) of acetylide complex CpWRu$_2$(CCBu^t)(CO)$_8$ (**1b**; 50 mg, 0.061 mmol) and Cp*W(CO)$_3$H (73 mg, 0.18 mmol) was heated to reflux for 8 h under nitrogen, during which the color gradually changed from orange to dark-brown. After removal of the solvent in vacuo, the residue was redissolved in CH$_2$Cl$_2$ and separated by thin-layer chromatography (silica gel, dichloromethane−hexane 1:3), producing 16 mg of the starting material **1b** (0.019 mmol, 32%), and 14 mg of black Cp*$_3$W$_3$Ru$_2$(μ_3-CCBu^t)(CO)$_9$ (**6**; 0.0094 mmol, 15%). Crystals of **6** suitable for X-ray diffraction studies were obtained by recrystallization from a layered solution of dichloromethane−methanol at room temperature.

Spectral data for **6**: MS (FAB, ^{102}Ru, ^{184}W) *m/z* 1494 (M$^+$); IR (C$_6$H$_{12}$) ν(CO), 2004 (s), 1972 (vs), 1955 (s), 1930 (vw), 1916 (m), 1871 (vw), 1836 (w, br), 1673 (w, br) cm^{-1}; ^{1}H NMR (CDCl$_3$, 294 K) δ 2.14 (s, 15H), 1.99 (s, 15H), 1.98 (s, 15H), 1.51 (s, 9H); ^{13}C NMR (CD$_2$Cl$_2$, 294 K) CO, δ 287.2 (J_{W-C} = 161 Hz), 285.6 (J_{W-C} = 160 Hz), 234.5 (J_{W-C} = 184 Hz), 230.1 (J_{W-C} = 171 Hz), 219.5 (J_{W-C} = 144 Hz), 207.6, 202.5, 201.4, 198.8; δ 174.9 (*C*CBu^t, J_{W-C} = 134 Hz), 144.1 (C*C*Bu^t), 105.8 (*C*$_5$Me$_5$), 103.6 (*C*$_5$Me$_5$), 103.3 (*C*$_5$Me$_5$), 41.5 (*C*Me$_3$), 37.1 (Me), 12.2 (C$_5$*Me*$_5$), 11.3 (C$_5$*Me*$_5$), 9.6 (C$_5$*Me*$_5$). Anal. Calcd for C$_{46}$H$_{56}$Cl$_2$O$_9$Ru$_2$W$_3$: C, 35.02; H, 3.58. Found: C, 35.14; H, 3.57.

X-ray Crystallography. The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer.

(7) (a) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182. (b) Gomez-Sal, M. P.; Johnson, B. F. G.; Kamarudin, R. A.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1622. (c) Chi, Y.; Shapley, J. R. *Organometallics* **1985**, *4*, 1900. (d) Eaton, B.; O'Connor, J. M.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 394. (e) Cabrera, E.; Daran, J. C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 607. (f) Stone, F. G. A.; Williams, M. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2467. (g) Park, J. T.; Shapley, J. R.; Bueno, C.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1988**, *7*, 2307. (h) Johnson, B. F. G.; Lewis, J.; Lunniss, J. A.; Braga, D.; Grepioni, F. J. *Chem. Soc., Chem. Commun.* **1988**, 972. (i) Rumin, R.; Robin, F.; Petillon, F. Y.; Muir, K. W.; Stevenson, I. *Organometallics* **1991**, *10*, 2274. (j) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Lunniss, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2223. (k) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Lunniss, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1101. (l) Shaposhnikova, A. D.; Drab, M. V.; Kamalov, G. L.; Pasynskii, A. A.; Eremenko, I. L.; Nefedov, S. E.; Struchkov, Y. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1992**, *429*, 109. (m) Park, J. T.; Woo, B. W.; Chung, J.-H.; Shim, S. C.; Lee, J.-H.; Lim, S.-S.; Suh, I.-H. *Organometallics* **1994**, *13*, 3384. (n) Pasynskii, A. A.; Eremenko, I. L.; Nefedov, S. E.; Kolobkov, B. I.; Shaposhnikova, A. D.; Stadnitchenko, R. A.; Drab, M. V.; Struchkov, Y. T.; Yanovsky, A. I. *New J. Chem.* **1994**, *18*, 69. (o) Quenec'h, P.; Rumin, R.; Pétillon, F. Y. *J. Organomet. Chem.* **1994**, *479*, 93. (p) Adams, H.; Cill, L. J.; Morris, M. J. *Organometallics* **1996**, *15*, 4182. (q) Adams, H.; Cill, L. J.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **1996**, 3909.

(8) (a) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1986**, *5*, 1179. (b) Blenkiron, P.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1995**, 327.

(9) (a) Wu, C.-H.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1990**, 3025. (b) Chi, Y.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 5483. (c) Chi, Y.; Chung, C.; Chou, Y.-C.; Su, P.-C.; Chiang, S.-J.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1997**, *8*, 1702.

(10) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Horwitz, C. P.; Shriver, D. F. *Organometallics* **1984**, *3*, 756.

(11) Chiang, S.-J.; Chi, Y.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *J. Am. Chem. Soc.* **1994**, *116*, 11181.

(12) Hwang, D.-K.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1990**, *9*, 2709.

Table 1. Crystal Data for the X-ray Diffraction Studies of Complexes 5 and 6[a]

compound	**5**	**6**
formula	$C_{47}H_{50}O_9Ru_2W_3 \cdot {}^1/_2CHCl_3$	$C_{45}H_{54}O_9Ru_2W_3 \cdot CH_2Cl_2$
mol wt	1572.30	1577.52
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
a (Å)	12.531(3)	16.949(4)
b (Å)	16.970(4)	17.316(4)
c (Å)	22.086(6)	32.908(6)
β (deg)	99.82(2)	
volume (Å^3)	4628(2)	9658(4)
Z	4	8
D_c (g/cm^3)	2.256	2.170
F(000)	2972	5984
2θ (max) (deg)	50	50
h,k,l ranges	−14 to +14, 0−20, 0−26	0−20, 0−20, 0−39
crystal size, mm	0.10 × 0.22 × 0.50	0.30 × 0.40 × 0.45
μ(Mo Kα) (cm^{-1})	83.59	79.23
transmission: max, min	1.00, 0.51	1.00, 0.68
no. of unique data	8089	9249
no. of data with $I > 2\sigma(I)$	6373	6349
no. of atoms and params	114, 568	236, 1108
weight modifier, g	0.00005	0.00005
max Δ/σ ratio	0.007	0.082
R_F; R_w	0.031; 0.030	0.040; 0.038
GOF	1.61	1.47
D-map, max/min (e/Å^3)	1.49/−1.24	1.42/−1.96

[a] Features common to all determinations: Nonius CAD-4 diffractometer, λ(Mo Kα) = 0.7107 Å; minimize function $\sum(w|F_o - F_c|^2)$, weighting scheme $w^{-1} = \sigma^2(F_o) + |g|\ F_o^2$; GOF = $[\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o, number of observations; N_v, number of variables).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of 5[a]

W(1)−Ru(1)	2.889(1)	W(1)−Ru(2)	2.910(1)
W(2)−W(3)	3.0560(7)	W(2)−Ru(1)	2.742(1)
W(2)−Ru(2)	2.873(1)	W(3)−Ru(1)	2.887(1)
W(3)−Ru(2)	2.767(1)	Ru(1)−Ru(2)	2.739(1)
W(1)−C(10)	2.037(7)	W(3)−C(10)	1.992(7)
Ru(1)−C(10)	2.125(8)	Ru(2)−C(10)	2.141(7)
W(2)−C(11)	2.128(8)	W(3)−C(11)	2.104(8)
Ru(2)−C(11)	2.120(7)	W(1)−C(1)	1.980(9)
W(1)−C(2)	1.979(9)	W(2)−C(3)	2.094(8)
W(2)−C(4)	1.979(9)	W(3)−C(5)	1.980(9)
Ru(1)−C(6)	1.894(8)	Ru(1)−C(7)	1.874(9)
Ru(1)−C(3)	2.145(8)	Ru(2)−C(8)	1.907(8)
Ru(2)−C(9)	1.902(9)		
W(1)−C(10)−W(6)	172.0(4)	Ru(1)−C(10)−Ru(2)	79.9(3)
W(2)−C(3)−O(3)	145.2(7)	Ru-CO(terminal)	175.7(8)
W-CO(terminal)	170.0(8)		

[a] Esd in parentheses.

Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant change in intensities, due to crystal decay, was observed over the course of all data collection. Intensities of the diffraction signals were corrected for Lorentz, polarization, and absorption effects (ψ scans). The structure was solved by using the NRCC-SDP-VAX package. All the non-hydrogen atoms had anisotropic temperature factors, and the hydrogen atoms of the organic functional groups were placed at idealized positions with $U_H = U_C + 0.1$. The crystallographic refinement parameters of complexes **5** and **6** are given in Table 1, while their selective bond distances and angles are presented in Tables 2 and 3, respectively.

Results

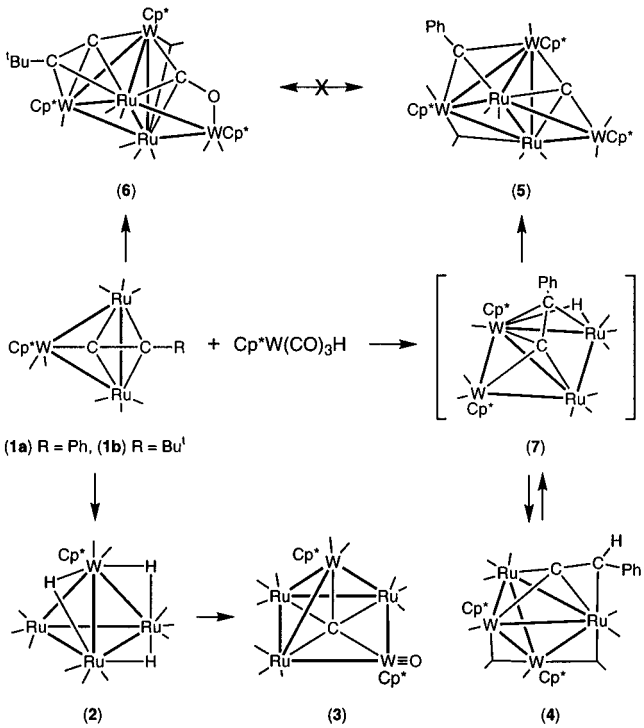
Treatment of acetylide cluster Cp*WRu$_2$(CCPh)(CO)$_8$ (**1a**) with excess Cp*W(CO)$_3$H in refluxing heptane solution for 8 h afforded four cluster complexes in low to moderate yields. These complexes included orange trihydride complex **2** (2%), orange-red, oxo−carbido cluster **3** (4%), dark-brown vinylidene cluster **4** (2%) and black carbido−alkylidyne cluster **5** (12%) (see Scheme 1). Each cluster complex was separated by thin-layer chromatography on silica gel and was further purified by recrystallization. The first two complexes **2** and **3** were immediately identified by comparing their IR and ^{1}H NMR data with the authentic samples prepared from the reaction of Ru$_3$(CO)$_{12}$ and Cp*W(CO)$_3$H,[13] and from the condensation of the cluster Cp*WRu$_3$(μ-H)(CO)$_{12}$ or **2** with Cp*W(CO)$_3$H, respectively.[14] This reactivity pattern strongly suggests that the oxo−carbido complex **3** is produced by the prior formation of the cluster Cp*WRu$_3$(μ-H)(CO)$_{12}$ or **2**, while the latter is generated from a parallel reaction of Cp*W(CO)$_3$H with Ru$_3$(CO)$_{12}$, and the Ru$_3$(CO)$_{12}$ existed in the solution is most likely produced from the thermally induced decomposition of

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) of 6

W(1)−Ru(1)	2.854(2)	W(1)−Ru(2)	2.921(2)
W(2)−W(3)	3.007(1)	W(2)−Ru(1)	2.883(2)
W(2)−Ru(2)	2.824(2)	W(3)−Ru(1)	2.830(2)
W(3)−Ru(2)	2.811(2)	Ru(1)−Ru(2)	2.782(2)
W(2)−C(10)	1.97(2)	W(3)−C(10)	2.13(2)
Ru(2)−C(10)	2.26(2)	W(3)−C(11)	2.22(2)
Ru(2)−C(11)	2.31(2)	C(10)−C(11)	1.35(3)
W(1)−C(1)	2.49(2)	W(2)−C(1)	2.00(2)
Ru(1)−C(1)	2.18(2)	Ru(2)−C(1)	2.29(2)
W(1)−O(1)	2.10(1)	C(1)−O(1)	1.28(2)
W(1)−C(2)	1.97(2)	W(1)−C(3)	2.11(2)
W(2)−C(4)	2.00(2)	W(3)−C(5)	1.95(2)
Ru(1)−C(4)	2.33(2)	Ru(1)−C(6)	1.79(2)
Ru(1)−C(7)	1.92(2)	Ru(2)−C(8)	1.90(2)
Ru(2)−C(9)	1.90(2)		
W(2)−C(10)−C(11)	157.3(15)	C(10)−C(11)−C(12)	141.5(19)
W(2)−C(1)−O(1)	148.0(14)	W(2)−C(4)−O(4)	150.4(17)
Ru(1)−C(4)−O(4)	121.9(15)	Ru-CO(terminal)	174.5(20)
W-CO(terminal)	167.0(20)		

[a] Esd in parentheses.

Scheme 1



(13) (a) Chi, Y.; Cheng, C.-Y.; Wang, S.-L. *J. Organomet. Chem.* **1989**, *378*, 45. (b) Chen, C.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1993**, 1823.

(14) Su, C.-J.; Su, P.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Am. Chem. Soc.* **1996**, *118*, 3289.

1a. In agreement with this postulation, treatment of **2** with excess $Cp^*W(CO)_3H$ in toluene affords the expected Ru_3W_2 complex **3** in moderate yield.

The vinylidene complex **4** was established principally from its spectroscopic data. The FAB mass spectrum gave molecular ion M^+ due to the formula $Cp^*_2W_2Ru_2(CCHPh)(CO)_9$ and the peaks corresponding to successful loss of nine CO ligands. The IR ν(CO) spectrum shows a pattern similar to that of the structurally characterized W_2Os_2 analogue,[15] consisting of five Ru−CO absorptions in the range 2050−1960 cm^{-1} and three broader peaks at 1920, 1797, and 1780 cm^{-1}, which we attributed to W-bound CO and bridging CO ligands. The presence of vinylidene ligand is evident form the ^1H NMR data, which exhibits a singlet at δ 6.06 characteristic of a C=C*H*Ph group, in addition to the signals of phenyl and two Cp* ligands.

Complex **5** exhibited three Cp* signals at δ 2.14, 1.81, and 1.74 in the ^1H NMR spectrum, suggesting the incorporation of three Cp*W fragments. The ^{13}C NMR spectrum showed four Ru−CO resonances between the narrow range δ 210.0 and 208.0 and five W−CO resonances between δ 251.6 and 218.0; the latter were established by their characteristic J_{W-C} couplings. In addition, we observed one signal at δ 402.0 and a second one at δ 280.3, which are best assigned to a carbido and an alkylidyne ligand, respectively. In order to confirm this hypothesis, we performed single-crystal X-ray crystallography.

According to the X-ray structural study, complex **5** is as a CH_2Cl_2 solvate. It possesses a pentametallic core of three W atoms and two Ru atoms coordinated by nine CO ligands, one face-bridging alkylidyne ligand and a carbide atom (Figure 1). The metal skeleton consists of an edge-bridged tetrahedral arrangement with a pendant Cp*W(1) unit attached to the Ru_2W_2 tetrahedron. Alternatively, it can be considered to adopt a face-bridged butterfly geometry with the Cp*W(2) fragment coordinated to a Ru_2W metal triangle. In this molecule, all metal−metal bonds are normal with the W(2)−W(3) distance being the longest 3.0560(7) Å and the Ru(1)−Ru(2) distance being the shortest 2.7391(11) Å. Other W−Ru distances are within the intermediate range 2.7423(10)−2.9097(10) Å. The variation of metal−metal bond distances is consistent with the fact that the atomic radii of the group 6 metals are slightly greater than that of the group 8 elements. A further shortening of the W(2)−Ru(1) and the W(3)−Ru(2) distances (2.7423(10) and 2.7674(10) Å) with respect to the rest of W−Ru distances (2.8734(10)−2.9097(10) Å) is probably due to the influence of bridging CO and alkylidyne ligands.

The most important features of **5** are the carbide and alkylidyne ligands which are separated by a distance (3.13(1) Å). The carbide atom C(10) occupied the Ru_2W_2 butterfly crater; the environment around the carbide atom is analogous to that of the tetranuclear carbide clusters reported in the literature.[16] On the other hand, the alkylidyne ligand lies on the adjacent RuW_2 metal triangle in a virtually symmetrical fashion, W(2)−C(11) = 2.128(8) Å, W(3)−C(11) = 2.104(8) Å, and Ru(2)−C(11) = 2.120(7) Å. Its bonding is akin to that of the alkylidyne clusters $LWM_3(\mu_3\text{-CR})(CO)_{11}$, L = Cp, Cp*; M = Os, Ru; R = H, Ph, OMe.[16e,17] In these alkylidyne complexes, the face-capping alkylidyne ligand and the edge-bridging CO ligand are all connected to the common $LW(CO)_2$ vertex. Moreover, the hexagonal face of phenyl substituent appears to possess some contact with two neighboring Cp* ligands. Consistent with this observation, the ^{13}C NMR spectrum at room temperature showed six well-separated signals for the phenyl group, showing the preservation of such highly congested conformation even in solution state.

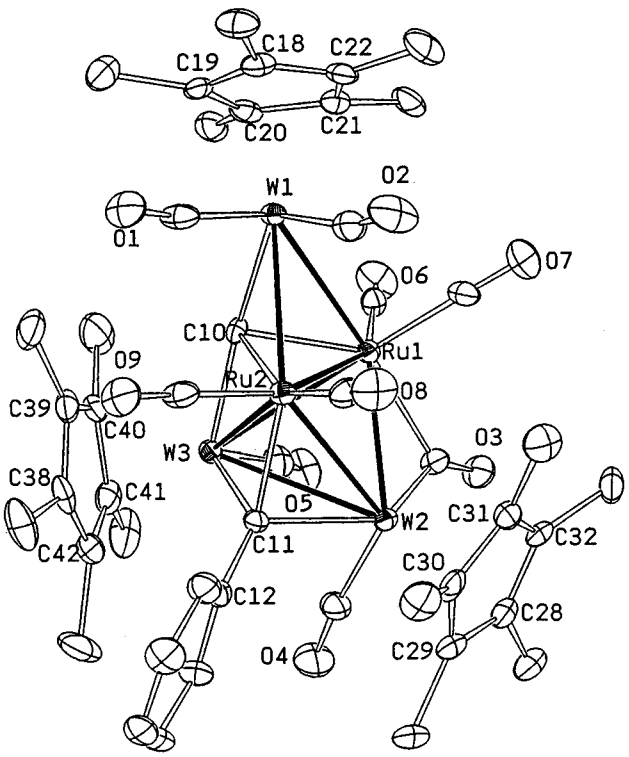


Figure 1. Molecular structure of $Cp^*_3W_3Ru_2(\mu_4\text{-C})(\mu_3\text{-CPh})(CO)_9$ (**5**) showing the atomic labeling scheme and the thermal ellipsoids at 30% probability level.

On the contrary, the reaction of *tert*-butyl derivative **1b** and $Cp^*W(CO)_3H$ led to the formation of acetylide complex **6** (Scheme 1). The ^1H NMR spectrum showed one *tert*-butyl group at δ 1.51 and three Cp*W fragments at δ 2.14, 1.99, and 1.98, which agrees with the formula revealed by the FAB mass analysis. In contrast, the ^{13}C NMR spectrum exhibited two high-field signals at δ 174.9 (J_{W-C} = 134 Hz) and 144.1, which are attributed to the μ_3-acetylide ligand[12,18] but not the carbide and the alkylidyne as observed in **5**.

The structure of **6** was confirmed by X-ray diffraction study. It crystallizes in an orthorhombic space group $P2_12_12_1$ with a disordered $CHCl_3$ solvent molecule and

(15) Chi, Y.; Wu, C.-H.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1991**, *10*, 1676.

(16) (a) Bradley, J. S. *Adv. Organomet. Chem.* **1982**, *22*, 1. (b) Harris, S.; Bradley, J. S. *Organometallics* **1984**, *3*, 1086. (c) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158. (d) Hriljac, J. A.; Harris, S.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 816. (e) Chi, Y.; Chuang, S.-H.; Chen, B.-F.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1990**, 3033. (f) Gong, J.-H.; Tsay, C.-W.; Tu, W.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Cluster Sci.* **1995**, *6*, 289.

(17) (a) Busetto, L.; Green, M.; Hesser, B.; Howard, J. A. K.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519. (b) Chi, Y.; Lee, G.-H.; Peng, S.-M.; Wu, C.-H. *Organometallics* **1989**, *8*, 1574. (c) Gong, J.-H.; Chen, C.-C.; Chi, Y.; Wang, S.-L.; Liao, F.-L. *J. Chem. Soc., Dalton Trans.* **1993**, 1829. (d) Gong, J.-H.; Hwang, D.-K.; Tsay, C.-W.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1994**, *13*, 1720.

(18) (a) Hwang, D.-K.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Organomet. Chem.* **1990**, *389*, C7. (b) Chi, Y.; Lee, G.-H.; Peng, S.-M.; Liu, B.-J. *Polyhedron* **1989**, *8*, 2003. (c) Carty, A. J.; Cherkas, A. A.; Randall, L. H. *Polyhedron* **1988**, *7*, 1045.

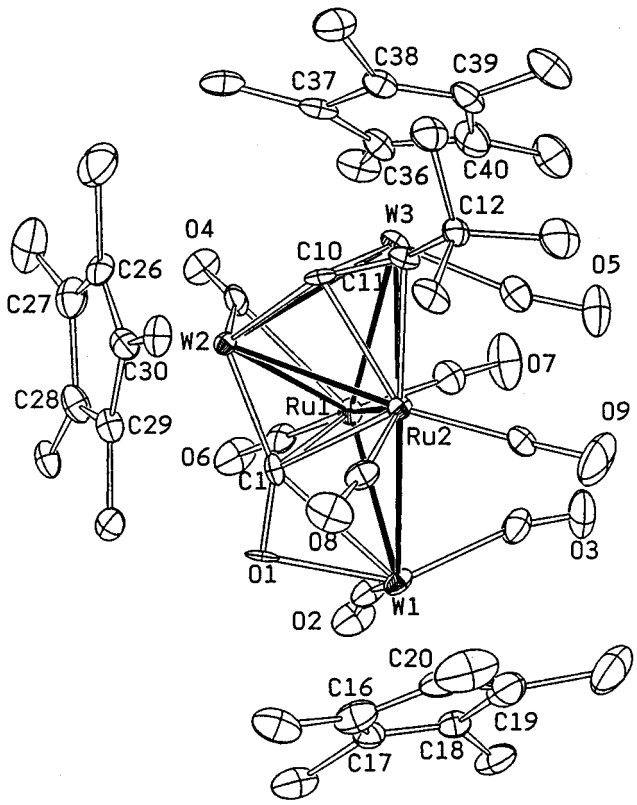


Figure 2. Molecular structure of $Cp^*_3W_3Ru_2(\mu_3\text{-}CCBu^t)(CO)_9$ (**6**) showing the atomic labeling scheme and the thermal ellipsoids at 30% probability level.

two crystallographically distinct, but structurally similar, molecules. A prospective view of one of these molecules is depicted in Figure 2. In this compound, the Ru_2W_2 cluster core assumes a closely related edge-bridged tetrahedral skeleton, on which the *tert*-butyl acetylide resides on the same RuW_2 face supporting the alkylidyne in **5**. The acetylide α-carbon is found to link to W(2) atom via α-bonding, while the C_2 vector is bisecting the opposing W(3)−Ru(2) edge. The butterfly cavity is occupied by a μ_4-CO ligand with its oxygen atom linking to the $Cp^*W(CO)_2$ pendent. The formation of μ_4-CO ligand is rare in metal clusters, and only a few examples have been reported since it was first documented.[19,20] Other important features of **6** involve the relocating of the bridging CO to the W(2)−Ru(1) edge and the removal of terminal CO ligand from the W(2) atom. Such reshuffling of CO ligands is in response to the change of donor capacity from the alkylidyne ligand in **5** (3-electron donor) to the acetylide ligand in **6** (5-electron donor). Finally, the electron counting for both complexes gives 74 valence electrons, which is consistent with the prediction of pentanuclear clusters possessing eight M−M bondings.

Discussion

This work has demonstrated that the formation of the μ_4-CO ligand and the scission of acetylide are two competing processes which can be controlled by changing the substituents on acetylide ligand. We do not understand the actual driving force associated with change of substituents. However, it is obvious that both clusters **5** and **6** are produced through a tetranuclear Ru_2W_2 intermediate **7** as shown in Scheme 1, which contains a hydride and an acetylide ligand. Evidence in support of this hypothesis is derived from the isolation of the Ru_2W_2 cluster **4** in trace amount and from the observation of the thermally induced, reversible interconversion between the vinylidene and the hydrido−acetylide isomers of its W_2Os_2 analogue.[15] Moreover, treatment of **4** with excess $Cp^*W(CO)_3H$ in refluxing toluene afforded the expected pentanuclear complex **5** in high yield, which offers the ultimate confirmation. Unfortunately, we are unable to isolate the corresponding *tert*-butyl derivatives of **4** or **7**, in a finite attempt to illustrate their involvement in the stepwise formation of the acetylide cluster **6**.

The generation of the less congested, edge-bridged tetrahedral cluster core also deserves special attention. It can be tracked back to our previous studies on the synthesis of two pentanuclear complexes $LWRu_4(\mu_3\text{-}H)(CO)_{14}$[20e] and $L_2W_2Ru_3(CO)_{13}$, L = Cp and Cp*.[14] In both cases, the Cp derivatives exhibit the closely packed, trigonal-bipyramidal geometry. However, the Cp* derivatives show the formation of the same kind of edge-bridged tetrahedral geometry with one μ_4-CO ligand[20e] or the wingtip-bridged butterfly structure containing one carbide and one oxo ligand generating by C−O bond cleavage.[14]

On the basis of these experiments, one would instinctively expect that the dominant factor in controlling the cluster core arrangement is due to the reduction of interligand repulsion imposed by the Cp* ligand. The coordinative unsaturation generated by changing from the trigonal-bipyramidal to the edge-bridged tetrahedral geometry is thus compensated by forming the μ_4-CO ligand as observed in **6**. In the presence of ligated acetylide, such as in **5**, it would give rise to the carbide and alkylidyne ligands. Clearly, study of the related Cp derivatives of **5** or **6** is vital to the confirmation of this assumption. However, attempts to generate the Cp derivatives via combining $CpWRu_2(CCR)(CO)_8$, R = Ph, Bu^t, and $CpW(CO)_3H$ under similar conditions gave no stable products at all.

Acknowledgment. We thank the National Science Council of Taiwan, Republic of China for financial support (Grant NSC 85-2113-M007-008).

Supporting Information Available: Tables giving all bond distances and angles, atomic coordinates, and anisotropic thermal parameters for complexes **5** and **6** (26 pages). Ordering information is given on any current masthead page.

OM9610410

(19) (a) Manassero, M.; Sansoni, M.; Longoni, G.; *J. Chem. Soc., Chem. Commun.* **1976**, 919. (b) Brun, P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 926. (c) Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Pearsall, M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1089. (d) Horwitz, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8147. (e) Horwitz, C. P.; Holt, E. M.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8136. (f) Adams, R. D.; Babin, J. E.; Tasi, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 685. (g) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1988**, *27*, 2618. (h) Wang, J.; Sabat, M.; Horwitz, C. P.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 552. (i) Anson, C. E.; Bailey, P. J.; Conole, G.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Chem. Commun.* **1989**, 442.

(20) (a) Chi, Y.; Wu, F.-J.; Liu, B.-J.; Wang, C.-C.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 873. (b) Chi, Y.; Chuang, S.-H.; Liu, L.-K.; Wen, Y.-S. *Organometallics* **1991**, *10*, 2485. (c) Wang, J.-C.; Lin, R.-C.; Chi, Y.; Peng, S.-H.; Lee, G.-H. *Organometallics* **1993**, *12*, 4061. (d) Chi, Y.; Su, C.-J.; Farrugia, L. J.; Peng, S.-H.; Lee, G.-H. *Organometallics* **1994**, *13*, 4167. (e) Su, C.-J.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 4286.