*Organometallics* **1997,** *16,* 1702−1713

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Published on April 15, 1997 on http://pubs.acs.org | doi: 10.1021/om960959o

# Reversible C−C Bond Cleavage and Interconversion of the Resulting Hydrocarbyl Ligands on Butterfly Frameworks Derived from Acetylide Complexes $Cp^*WOs_3(\mu_4\text{-}CCR)(CO)_{11}$ (R = Ph, $^n$Bu, $CH_2OMe$, $CH_2OPh$)

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Combination of mononuclear complexes $Cp^*W(CO)_3(CCR)$ ($Cp^* = C_5Me_5$; R = Ph, $^n$Bu, $CH_2OMe$, $CH_2OPh$) with the triosmium cluster $Os_3(CO)_{10}(NCMe)_2$ in toluene affords two isomeric acetylide cluster compounds **a** and **b**, which possess the formula $Cp^*WOs_3(CCR)(CO)_{11}$ (R = Ph (**1**), $^n$Bu (**2**), $CH_2OMe$ (**3**), $CH_2OPh$ (**4**)). Isomers **a** and **b** undergo reversible interconversion by relocating the $Cp^*W(CO)_2$ fragment between the hinge and wingtip positions upon heating in solution. Their reactivities vs the substituents on the acetylide ligand are also investigated and compared. Thus, thermolysis of **1a** furnishes the carbido−alkylidyne cluster $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}CPh)(CO)_{10}$ (**5**) through reversible scission of the C−C bond induced by elimination of CO. By contrast, heating of **2** or **3** gives an isomeric mixture of the carbido−vinylidene clusters $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)(\mu\text{-}CCHR')(CO)_9$ (R′ = $^n$Pr (**6**), OMe (**7**)) through a subsequent C−H activation. The $CH_2OPh$ isomers **4** readily eliminate two CO ligands to give two isomeric carbido−benzofuryl clusters $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)_2(\mu\text{-}C_8H_6O)(CO)_9$ (**9** and **10**), in which the furyl fragments are produced through subsequent ortho-metalation involving the phenyl group, C−C bond formation, and H migration. Hydrogenation of **3** produces the dihydrido−acetylide cluster $Cp^*WOs_3(\mu\text{-}H)_2(CCCH_2OMe)(CO)_{10}$ (**11**) and the carbido−alkylidyne cluster $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)_2(\mu\text{-}CCH_2OMe)(CO)_9$ (**13**) subsequently. The acetylide cluster **11** converts to the tetrahedral alkylidyne complex $Cp^*WOs_3(\mu_3\text{-}CCH_2CH_2OMe)(CO)_{11}$ (**12**) via addition of a CO ligand, whereas the alkylidyne cluster **13** isomerizes upon further heating in solution, giving the alkenyl cluster $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)_2(\mu\text{-}CHCHOMe)(CO)_9$ (**14**) via a 1,2-H shift. Spectroscopic data, X-ray structural analyses, and the possible mechanism leading to the interconversions are presented.

## Introduction

The $C_2$ hydrocarbon ligand holds a key position in the development of organometallic cluster chemistry as such ligands are important intermediates for the catalytic CO hydrogenation reaction.[1] Therefore, much activity has been focused on the synthesis and reactivity of complexes containing alkenyl, vinylidene, dicarbide, acetylene, and acetylide fragments.[2] Among these $C_2$ hydrocarbon derivatives, the chemistry of metal acetylides has attracted considerable attention and has become a flourishing subject in recent years.[3] For example, Carty and co-workers have reported the syntheses and crystal structures of phosphidoruthenium clusters containing various multisite-bound acetylide ligands.[4] In certain cases, the coordinated acetylide is best envisaged as a carbide−alkylidyne linked by a weakened C−C bonding.[5] Other independent investigations, such as the reactivity studies on triosmium acetylide clusters by Deeming et al.,[6] the preparation of heterometallic compounds using mononuclear acetylide precursors by Yamazaki et al.,[7] Vahrenkamp et al.,[8] and Akita et al.,[9]

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

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S0276-7333(96)00959-4 CCC: $14.00 © 1997 American Chemical Society

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Published on April 15, 1997 on http://pubs.acs.org | doi: 10.1021/om960959o

and the generation of acetylide-bridged complexes,[10] provided substantial knowledge about the reactivity and bonding capability of acetylide ligands.

During our investigation of acetylide cluster chemistry, we have synthesized a variety of mixed-metal cluster compounds with the formula CpWOs$_3$(CCR)(CO)$_{11}$ (R = Ph, $^n$Bu),[11] and examined their chemistry toward C$_2$ fragments, such as alkynes or metal acetylides.[12] Recently, we have extended the syntheses by altering the ancillary ligand on the W atom, and this led to the isolation of two butterfly isomers of formula Cp*WOs$_3$(CCCH$_2$OMe)(CO)$_{11}$ (Cp* = C$_5$Me$_5$).[13] The arrangement of metal atoms in these isomers is distinct, one possessing a hinge W atom and the second having the W atom at a wingtip position. Upon heating in solution, the isomers undergo rapid interconversion by shuffling the Cp*W(CO)$_2$ fragment between the hinge and the wingtip sites.

In this article, we address the studies of acetylide C−C bond cleavage through pyrolysis of the species Cp*WOs$_3$(CCR)(CO)$_{11}$ (R = Ph, $^n$Bu, CH$_2$OMe, CH$_2$OPh), which leads to an in-depth understanding of the reversible scission of acetylide in small metal clusters induced by CO elimination. This chemistry supplements our previous report on the reversible interconversion of the acetylide cluster CpWRu$_2$(CCPh)(CO)$_8$ and the carbido−alkylidyne clusters CpWRu$_4$($\mu_5$-C)($\mu$-CPh)(CO)$_{12}$ and CpWRu$_5$($\mu_6$-C)($\mu$-CPh)(CO)$_{14}$, promoted by cluster building and degradation reactions.[14] Portions of this work have been reported as a preliminary communication.[15]

## 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 (400.13 MHz) or a Bruker AMX-300 (300.6 MHz) instrument; all coupling constants are given in hertz. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment mode (FAB). All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. Reactions were monitored by analytical thin-layer chromatography (TLC; 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 mononuclear tungsten acetylide complexes Cp*W(CO)$_3$(C≡CR) (R = Ph, Bu, CH$_2$OMe, CH$_2$OPh) were prepared by treating Cp*W(CO)$_3$Cl with appropriate terminal alkynes in Et$_2$NH solutions in the presence of a catalytic amount of CuI.[16] Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

**Preparation of WOs$_3$ Acetylide Clusters.** To a 100 mL reaction flask were added Os$_3$(CO)$_{10}$(NCMe)$_2$ (500 mg, 0.536 mmol), Cp*W(CO)$_3$(C≡CPh) (330 mg, 0.654 mmol), and toluene (70 mL). The solution was then heated to reflux and continued heating for 40 min, during which time the color changed from yellow-orange to red-brown. After the solution reached room temperature, solvent was removed under vacuum. The residue was subjected to separation by TLC (dichloromethane:hexane = 1:4), giving 75 mg of the red-orange isomer of Cp*WOs$_3$-(CCPh)(CO)$_{11}$ (**1a**, 0.058 mmol, 11%) and a trace amount of isomer **1b**. The corresponding butyl analogues **2a** (19%) and **2b** (14%), CH$_2$OMe analogues **3a** (22%) and **3b** (21%), and CH$_2$OPh analogues **4a** (8%) and **4b** (18%) were prepared under similar conditions.

**Spectral Data for 1a:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1304 (M$^+$); IR (C$_6$H$_{12}$) $\nu$(CO) 2081 (m), 2057 (vs), 2029 (s), 2014 (s), 1997 (w), 1983 (vw), 1972 (vw), 1962 (m), 1956 (w) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 294 K) $\delta$ 8.20−8.18 (m, 2 H), 7.52−5.49 (m, 3 H), 1.70 (s, 15 H, C$_5$*Me*$_5$); $^{13}$C NMR (100 MHz, CDCl$_3$, 294 K) $\delta$ 213.8 (CO, $J_{WC}$ = 155), 210.0 (CO, $J_{WC}$ = 142), 190.8 (*C*CPh), 181.9 (CO), 181.5 (3CO, br), 176.1 (CO), 172.5 (CO), 163.0 (C*C*Ph), 140.9 (*i*-C$_6$H$_5$), 130.9 (*o*,*m*-C$_6$H$_5$), 128.8 (*m*,*o*-C$_6$H$_5$), 128.6 (*p*-C$_6$H$_5$), 103.9 (*C*$_5$Me$_5$), 11.0 (C$_5$*Me*$_5$). Anal. Calcd for C$_{29}$H$_{20}$O$_{11}$Os$_3$W$_1$: C, 26.82; H, 1.55. Found: C, 26.58; H, 1.60.

**Spectral Data for 2a:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1284 (M$^+$); IR (C$_6$H$_{12}$) $\nu$(CO) 2079 (m), 2054 (vs), 2030 (m), 2009 (s), 1993 (w), 1980 (vw), 1963 (m, br) cm$^{-1}$; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 294 K) $\delta$ 3.19−3.16 (m, 1 H), 2.53−2.51 (m, 1 H), 2.01 (s, 15 H, C$_5$*Me*$_5$), 2.05−1.90 (m, 2 H, C*H*$_2$), 1.64−1.52 (m, 2 H, C*H*$_2$), 1.02 (t, *Me*, $J_{HH}$ = 7.4); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 294 K) $\delta$ 213.7 (CO, $J_{WC}$ = 145), 209.2 (CO, $J_{WC}$ = 153), 192.3 ($C_\alpha$), 181.5 (CO, br), 178.8 (3CO, br), 177.5 (3CO, br), 173.2 (2CO, br), 164.1 ($C_\beta$), 104.2 (*C*$_5$Me$_5$), 52.8 (*C*H$_2$), 37.6 (*C*H$_2$), 23.2 (*C*H$_2$), 14.4 (*C*H$_3$), 11.7 (C$_5$*Me*$_5$). Anal. Calcd for C$_{27}$H$_{24}$O$_{11}$Os$_3$W$_1$: C, 25.36; H, 1.89. Found: C, 25.20; H, 1.97.

**Spectral Data for 2b:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1284 (M$^+$); IR(CCl$_4$) $\nu$(CO) 2076 (m), 2040 (s), 2012 (vs), 1998 (m, br), 1982 (w), 1975 (w), 1949 (vw, br), 1927 (vw, br) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 294 K) $\delta$ 3.16 (t, br, CH$_2$, $J_{HH} \approx 8.2$), 2.29 (s, 15 H, C$_5$*Me*$_5$), 1.90 (quintet, br, C*H*$_2$, $J_{HH} \approx 7.4$), 1.63 (sextet, C*H*$_2$, $J_{HH} \approx 7.4$), 1.08 (t, *Me*, $J_{HH}$ = 7.4). Anal. Calcd for C$_{27}$H$_{24}$O$_{11}$Os$_3$W$_1$: C, 25.36; H, 1.89. Found: C, 25.17; H, 1.90.

**Spectral Data for 4a:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1334 (M$^+$); IR (C$_6$H$_{12}$) $\nu$(CO) 2081 (m), 2056 (vs), 2032 (m), 2012 (s), 1994 (w, br), 1983 (vw), 1970 (w, br), 1960 (w) cm$^{-1}$; $^1$H NMR (CDCl$_3$, 294 K) $\delta$ 7.32 (t, 2 H, $J_{HH}$ = 7.8), 7.06 (d, 2 H, $J_{HH}$ = 7.8), 6.99 (t, 1 H, $J_{HH}$ = 7.8), 5.14 (d, 1 H, $J_{HH}$ = 14.2), 4.80 (d, 1 H, $J_{HH}$ = 14.3), 2.01 (s, 15 H, C$_5$*Me*$_5$). Anal. Calcd for C$_{30}$H$_{22}$O$_{12}$-Os$_3$W$_1$: C, 27.11; H, 1.67. Found: C, 27.10; H, 1.63.

**Spectral Data for 4b:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1334 (M$^+$); IR (C$_6$H$_{12}$) $\nu$(CO) 2080 (m), 2043 (vs), 2016 (vs), 2001 (m, br), 1986 (m), 1948 (w, br), 1929 (w), 1915 (vw) cm$^{-1}$; $^1$H NMR (CDCl$_3$, 294 K) $\delta$ 7.29 (t, 2 H, $J_{HH}$ = 8.5), 7.09−6.97 (m, 3 H), 4.97 (s, 2 H, C*H*$_2$), 2.24 (s, 15 H, C$_5$*Me*$_5$); $^{13}$C NMR (CDCl$_3$, 294 K) $\delta$ 220.7 ($C_\alpha$, $J_{WC}$ = 98), 208.1 (2CO, $J_{WC}$ = 173), 181.4 (CO), 178.8, (6CO, br), 170.6 (2CO), 158.7 ($C_\beta$), 153.0 (*i*-C$_6$H$_5$), 130.2 (*o*,*m*-C$_6$H$_5$), 121.8 (*p*-C$_6$H$_5$), 115.3 (*m*,*o*-C$_6$H$_5$), 102.3 (*C*$_5$Me$_5$), 82.7 (*C*H$_2$OPh), 11.6 (C$_5$*Me*$_5$). Anal. Calcd for C$_{30}$H$_{22}$O$_{12}$-Os$_3$W$_1$: C, 27.11; H, 1.67. Found: C, 27.15; H, 1.78.

**Thermolysis of 1a.** The acetylide complex **1a** (74 mg, 0.059 mmol) in a 50 mL round-bottom reaction flask was treated with freshly sublimed Me$_3$NO (4.8 mg, 0.065 mmol) in a mixture of dichloromethane (25 mL) and acetonitrile (10 mL) at room temperature for 30 min. After evaporation of solvent under vacuum, the residue was dissolved in toluene solution (30 mL) and refluxed for 15 min. Solvent was evaporated *in vacuo*, and the residue was taken in CH$_2$Cl$_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 3 mg of **1a** (0.002 mmol) and 58 mg of Cp*WOs$_3$($\mu_4$-C)-($\mu$-CPh)(CO)$_{10}$ (**5**, 0.047 mmol, 80%) as an orange material. Crystals of **5** suitable for X-ray diffraction study were obtained

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by recrystallization from a layered solution of chloroform−methanol at room temperature.

**Reaction of 5 with CO.** A toluene solution (25 mL) of **5** (20 mg, 0.016 mmol) was heated to reflux under CO for 5 min. After solvent was evaporated *in vacuo*, the residue was redissolved in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 15 mg of **1a** (0.011 mmol, 70%) as the major compound isolated.

**Spectral Data for 5:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1276 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2076 (s), 2040 (vs), 2021 (s), 2003 (s), 1981 (m, br), 1976 (vw), 1958 (w), 1950 (vw), 1922 (vw, br) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 251−2.47 (m, 3 H), 7.37 (t, 2 H, $J_{HH}$ = 7.3), 1.99 (s, 15 H, $C_5Me_5$); $^{13}$C NMR ($CDCl_3$, 258 K) $\delta$ 357.0 ($\mu_4$-*C*, $J_{WC}$ = 104), 293.9 ($\mu$-*C*Ph, $J_{WC}$ = 150), 226.7 (CO, $J_{WC}$ = 178), 187.2 (CO, br), 182.1 (2CO), 181.3 (CO), 179.4 (CO), 178.8 (CO, br), 175.1 (CO, br), 173.3 (CO), 164.9 (CO), 155.8 (*i*-$C_6H_5$), 130.1 (*o*,*m*-$C_6H_5$), 129.8 (*m*,*o*-$C_6H_5$), 128.6 (*p*-$C_6H_5$), 107.1 ($C_5$Me$_5$), 11.0 ($C_5Me_5$). Anal. Calcd for $C_{28}H_{20}O_{10}Os_3W_1$: C, 26.46; H, 1.59. Found: C, 26.52; H, 1.63.

**Thermolysis of 2**. In a 50 mL round-bottom reaction flask, complex Cp*WOs$_3$(CC$^n$Bu)(CO)$_{11}$ (**2a**, 133 mg, 0.104 mmol) was treated with $Me_3NO$ (6.4 mg, 0.085 mmol) in a mixture of dichloromethane (25 mL) and acetonitrile (10 mL) at room temperature for 30 min. After evaporation of this solvent mixture under vacuum, the reaction mixture was dissolved in toluene (35 mL) and refluxed for 30 min. The solvent was then evaporated *in vacuo*, and the residue was taken up in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane: hexane = 1:3), giving 95 mg of the vinylidene complexes Cp*WOs$_3$($\mu_4$-C)($\mu$-H)($\mu$-CCH$^n$Pr)(CO)$_9$ (**6a**,**b**, 0.078 mmol, 75%) as a light orange solid and with ca. 6 mg of **2a** and a trace of **2b**. Crystals of **6**, which consists of ca. 57% of **6a** and 43% of **6b**, were grown by recrystallization from a layered solution of dichloromethane−methanol at room temperature.

**Reaction of 6 with CO.** A toluene solution (35 mL) of **6** (22.5 mg, 0.018 mmol) was heated to reflux under CO atmosphere (1 atm) for 40 min. After solvent was evaporated, the residue was redissolved in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving a mixture of **2a**,**b** (9.5 mg, 0.007 mmol, 58%), together with 8 mg of an unreacted mixture of **6a**,**b**.

**Spectral Data for 6:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1228 ($M^+$); IR($C_6H_{12}$) $\nu$(CO) 2075 (m), 2044 (vs), 2008 (s), 2002 (m), 1995 (s), 1976 (w), 1959 (m), 1946 (vw), 1931 (vw, br) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) isomer **a** $\delta$ 4.08 (t, C*H*, $J_{HH}$ = 7.4), 2.10 (s, 15 H, $C_5Me_5$), 1.69 (m, 1 H), 1.56 (m, 1 H), 1.00 (t, *Me*, $J_{HH}$ = 7.4), −24.23 (s, 1 H), isomer **b** $\delta$ 4.15 (t, C*H*, $J_{HH}$ = 7.4), 2.15 (s, 15 H, $C_5Me_5$), 1.68 (m, 1 H), 1.48 (m, 1 H), 1.02 (t, *Me*, $J_{HH}$ = 7.4), −24.29 (s, 1 H); $^{13}$C NMR ($CDCl_3$, 294 K) isomer **a** $\delta$ 343.1 ($\mu_4$-C, $J_{WC}$ = 100), 273.1 (*C*CH$^i$Pr, $J_{WC}$ = 100), 222.6 (CO, $J_{WC}$ = 169), 186.7 (CO), 180.2 (CO), 175.6 (CO), 172.5 (CO), 166.0 (CO), 106.4 ($C_5$Me$_5$), 65.1 (C*C*H$^n$Pr), 36.2 (*C*H$_2$), 26.9 (*C*H$_2$), 13.3 (Me), 11.0 ($C_5Me_5$), isomer **b** $\delta$ 345.7 ($\mu_4$-C, $J_{WC}$ = 100), 269.5 (*C*CH$^n$Pr, $J_{WC}$ = 100), 221.2 (CO, $J_{WC}$ = 169), 187.3 (CO), 179.5 (CO), 175.3 (CO), 173.3 (CO), 166.1 (CO), 106.5 ($C_5$Me$_5$), 65.0 (C*C*H$^n$Pr), 34.2 (*C*H$_2$), 27.4 (*C*H$_2$), 13.5 (Me), 11.2 ($C_5Me_5$). Anal. Calcd for $C_{25}H_{24}O_9Os_3W_1$: C, 24.55; H, 1.98. Found: C, 24.53; H, 2.02.

**Thermolysis of 3**. In a 50 mL reaction flask, the acetylide complex Cp*WOs$_3$(CCCH$_2$OMe)(CO)$_{11}$ (**3a**, 58 mg, 0.0457 mmol) was treated with $Me_3NO$ (4.6 mg, 0.059 mmol) in a mixture of dichloromethane (30 mL) and acetonitrile (15 mL) at room temperature for 30 min. After evaporation of solvent under vacuum, the residue was dissolved in toluene (35 mL) and refluxed for 35 min. After the solution reached room temperature, solvent was evaporated *in vacuo*, and the residue was taken up in $CH_2Cl_2$ and separation by TLC (silica gel, dichloromethane:hexane = 1:5), giving 15 mg of the vinylidene complex Cp*WOs$_3$($\mu_4$-C)($\mu$-H)($\mu$-CCHOMe)(CO)$_9$ (**7a**, 0.012 mmol, 33%), 3 mg of **7b** (0.0025 mmol, 7%), and 12 mg of the starting materials **3a**,**b**. Crystals of **7a** suitable for X-ray diffraction study were obtained by recrystallization from a layered solution of dichloromethane−methanol.

**Reaction of 7 with CO.** A toluene solution (50 mL) of **7a** (50 mg, 0.041 mmol) was heated to reflux under CO atmosphere for 1.5 h. Solvent was then evaporated *in vacuo*, and the residue was taken in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 22 mg of **3a**,**b** (0.017 mmol, 41%), 12 mg of unreacted starting materials **7a**,**b** (24%), and 7 mg of Cp*WOs$_3$($\mu_4$-C)($\mu$-CHCHOMe)(CO)$_{10}$ (**8**, 0.006 mmol, 15%)

**Spectral Data for 7a:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1212 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2075 (s), 2044 (vs), 2008 (s), 2001 (s), 1996 (s), 1977 (m), 1958 (m), 1950 (w), 1941 (vw) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 6.79 (s, 1 H), 3.42 (s, 3 H, O*Me*), 2.18 (s, 15 H, $C_5Me_5$), −24.38 (s, 1 H); $^{13}$C NMR ($CD_2Cl_2$, 240 K) $\delta$ 347.3 ($\mu_4$-C, $J_{WC}$ = 100), 257.2 (*C*CHOMe, $J_{WC}$ = 158), 221.3 (CO, $J_{WC}$ = 167), 190.1 (CO), 188.1 (CO), 181.0 (CO), 180.5 (CO), 177.7 (CO), 176.4 (CO), 172.7 (CO), 166.2 (CO), 107.7 (C*C*HOMe), 107.5 ($C_5$Me$_5$), 61.1 (O*Me*), 11.6 ($C_5Me_5$). Anal. Calcd for $C_{23}H_{20}O_{10}Os_3W_1$: C, 22.81; H, 1.66. Found: C, 22.72; H, 1.71.

**Spectral Data for 7b:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1212 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2076 (s), 2045 (vs), 2009 (s), 2001 (s), 1995 (s), 1976 (w), 1959 (m), 1946 (w), 1923 (vw, br) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 6.85 (s, 1 H), 3.16 (s, 3 H, O*Me*), 2.09 (s, 15 H, $C_5Me_5$), −23.97 (s, 1 H). Anal. Calcd for $C_{23}H_{20}O_{10}Os_3W_1$: C, 22.81; H, 1.66. Found: C, 22.78; H, 1.74.

**Spectral Data for 8:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1240 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2078 (s), 2039 (vs), 2024 (s), 2005 (s), 1981 (s, br), 1969 (w), 1952 (vw), 1869 (w, br) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 6.88 (d, 1 H, $J_{HH}$ = 5.8), 5.05 (d, 1 H, $J_{HH}$ = 5.8), 3.63 (s, 3 H, O*Me*), 1.98 (s, 15 H, $C_5Me_5$); $^{13}$C NMR ($CDCl_3$, 294 K) $\delta$ 346.1 ($\mu_4$-C, $J_{WC}$ = 111), 219.2 (CO, $J_{WC}$ = 167), 182.9 (CO), 178.8 (CO), 169.8 (CO), 107.1 (*C*HCHOMe), 105.2 ($C_5$Me$_5$), 104.8 (CH*C*HOMe, $J_{WC}$ = 42), 59.3 (O*Me*), 10.6 ($C_5Me_5$).

**Thermolysis of 4**. A toluene solution (80 mL) of **4a** (200 mg, 0.15 mmol) was heated to reflux for 2 h. After evaporation of solvent *in vacuo*, the residue was taken up in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 2 mg of red Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-C$_8$H$_5$O)(CO)$_9$ (**10**, 1%, 0.0002 mmol), 105 mg of purple Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-C$_8$H$_5$O)(CO)$_9$ (**9**, 53%, 0.083 mmol), and 5 mg of unreacted starting materials **4**. Crystals of complexes **9** and **10** suitable for X-ray diffraction study were grown at room temperature from layered solutions of chloroform−methanol and chloroform−heptane, respectively. Heating of **4b** afforded a similar result.

**Thermolysis of 9**. A xylene solution (35 mL) of the purple complex **9** (31 mg, 0.024 mmol) was heated to reflux for 8 h. After evaporation of solvent *in vacuo*, the residue was redissolved in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 9 mg of red isomer **10** (29%, 0.007 mmol) as the major product.

**Spectral Data for 9:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1278 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2082 (s), 2068 (w), 2054 (vs), 2030 (vs), 2006 (vs), 1982 (m), 1964 (w), 1880 (w) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 7.51 (d, 1 H, $J_{HH}$ = 7.4), 7.30 (t, 1 H, $J_{HH}$ = 7.4), 7.26−7.17 (m, 2 H), 6.21 (s, 1 H, $^2J_{WH}$ = 7.1), 2.00 (s, 15 H), −17.02 (s, 1 H), −22.68 (s, 1 H); $^{13}$C NMR ($CDCl_3$, 294 K) $\delta$ 334.2 ($\mu_4$-C, $J_{WC}$ = 104), 225.7 (CO, $J_{WC}$ = 178), 179.8 (CO), 177.5 (CO), 175.1 (CO), 174.3 (CO), 172.4 (CO), 170.8 (CO), 170.7 (CO), 166.4 (CO), 155.2, 143.5, 136.6, 129.6 (*C*H), 124.7 (*C*H), 121.2 (*C*H), 110.2 (*C*H), 104.2 ($C_\alpha$H, $J_{WC}$ = 25), 102.3 ($C_5$Me$_5$), 10.8 ($C_5Me_5$). Anal. Calcd for $C_{28}H_{22}O_{10}Os_3W_1$: C, 26.42; H, 1.74. Found: C, 26.23; H, 1.77.

**Spectral Data for 10:** MS (FAB, $^{184}$W, $^{192}$Os) *m/z* 1278 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2084 (s), 2054 (vs), 2031 (vs), 2010 (vs), 1984 (s), 1968 (m), 1884 (m, br) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 7.56 (d, 1 H, $J_{HH}$ = 7.4), 7.26−7.18 (m, 2 H), 7.05 (t, 1 H, $J_{HH}$ = 7.4), 5.54 (s, 1 H, $^2J_{WH}$ = 4.8), 1.54 (s, 15 H), −16.47 (s, 1 H), −24.32 (s, 1 H); $^{13}$C NMR ($CDCl_3$, 294 K) $\delta$ 322.9 ($\mu_4$-C, $J_{WC}$ = 117), 222.2 (CO, $J_{WC}$ = 165), 180.5 (CO), 177.5 (CO), 175.4 (CO), 175.3 (CO), 172.0 (CO), 171.8 ($C_\beta$, $J_{WC}$ = 30), 168.8

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(CO), 166.8 (CO), 165.5 (CO), 161.0, 131.8, 125.8 ($C$H), 123.1 ($C$H), 121.7 ($C$H), 110.3 ($C$H), 104.5 ($C_5$Me$_5$), 63.8 ($C_\alpha$H), 10.0 ($C_5Me_5$). Anal. Calcd for $C_{28}H_{19}O_{10}Os_3W_1$: C, 26.42; H, 1.74. Found: C, 26.26; H, 1.77.

**Hydrogenation of 3.** A toluene solution (70 mL) of a mixture of **3** (161 mg, 0.127 mmol) was heated to reflux under hydrogen atmosphere for 2 h. After the solution reached room temperature, solvent was evaporated *in vacuo*, and the residue was taken up in $CH_2Cl_2$ and subjected to TLC separation (silica gel, dichloromethane:hexane = 1:4), giving 49 mg of orange $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)_2(\mu\text{-}CHCHOMe)(CO)_9$ (**14**, 0.040 mmol, 31%), 13 mg of yellow $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)_2(\mu\text{-}CCH_2OMe)(CO)_9$ (**13**, 0.012 mmol, 9%), 7.2 mg of orange $Cp^*WOs_3(\mu\text{-}H)_2(CCCH_2OMe)(CO)_{10}$ (**11**, 0.006 mmol, 5%), and 16 mg of orange $Cp^*WOs_3(\mu_3\text{-}CCH_2CH_2OMe)(CO)_{11}$ (**12**, 0.013 mmol, 10%), together with the recovery of 15 mg of starting materials **3a**,**b**. Single crystals of **11** and **13** suitable for X-ray diffraction studies were grown from mixtures of chloroform−heptane and dichloromethane−methanol, respectively.

**Spectral Data for 11:** MS (FAB, $^{184}$W, $^{192}$Os) $m/z$ 1246 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2080 (s), 2035 (s), 2028 (vs), 2006 (vs), 1991 (w), 1983 (m), 1973 (m), 1950 (w), 1889 (vw, br) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 4.26 (d, 1 H, $J_{HH}$ = 12.6), 4.16 (d, 1 H, $J_{HH}$ = 12.6), 3.46 (s, 3 H, O$Me$), 2.23 (s, 15 H, $C_5Me_5$), −17.95 (d, 1 H, $J_{HH}$ = 2.6), −21.71 (d, 1 H, $J_{HH}$ = 2.6); $^{13}$C NMR ($CDCl_3$, 294 K) $\delta$ 210.7 (CO, $J_{WC}$ = 154), 206.9 (CO, $J_{WC}$ = 183), 197.2 ($C_\alpha$, $J_{WC}$ = 118), 184.7 (CO), 178.5 (CO), 177.5 (CO), 177.3 (CO), 175.4 (CO), 171.0 (CO), 170.6 (CO), 166.8 (CO), 158.5 ($C_\beta$, $J_{WC}$ = 17), 102.9 ($C_5$Me$_5$), 86.7 ($C$H$_2$), 57.9 (O$Me$), 10.6 ($C_5Me_5$). Anal. Calcd for $C_{24}H_{22}O_{11}Os_3W_1$: C, 23.23; H, 1.79. Found: C, 23.33; H, 1.81.

**Spectral Data for 12:** MS (FAB, $^{184}$W, $^{192}$Os) $m/z$ 1274 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2076 (s), 2035 (vs), 2028 (vs), 2004 (m), 1989 (vw), 1981 (w), 1974 (m), 1965 (m), 1951 (vw), 1829 (vw, br) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 4.04 (br, 2 H, C$H_2$), 3.56 (br, 2 H, C$H_2$), 3.50 (s, 3 H, O$Me$), 2.07 (s, 15 H, $C_5Me_5$); $^{13}$C NMR ($CDCl_3$, 220 K) $\delta$ 272.3 ($C_\alpha$, $J_{WC}$ = 52), 223.9 (CO, $J_{WC}$ = 134), 206.6 (CO, $J_{WC}$ = 148), 187.1 (CO), 183.4 (CO), 180.7 (6CO, br), 176.0 (CO), 104.6 ($C_5$Me$_5$), 81.0 ($C_\beta$H$_2$), 62.7 ($C_\gamma$H$_2$), 59.2 (O$Me$), 10.9 ($C_5Me_5$). Anal. Calcd for $C_{25}H_{22}O_{12}Os_3W_1$: C, 23.66; H, 1.75. Found: C, 23.54; H, 1.76.

**Spectral Data for 13:** MS (FAB, $^{184}$W, $^{192}$Os) $m/z$ 1218 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2082 (s), 2051 (vs), 2013 (vs), 2007 (vs), 1981 (w), 1950 (m), 1940 (w) cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$, 294 K) $\delta$ 4.18 (d, 1 H, $J_{HH}$ = 21), 4.07 (d, 1 H, $J_{HH}$ = 21), 3.37 (s, 3 H, O$Me$), 2.02 (s, 15 H, $C_5Me_5$), −15.21 (s, 1 H), −24.42 (s, 1 H); $^{13}$C NMR ($CD_2Cl_2$, 210 K) $\delta$ 337.4 ($\mu_4$-C, $J_{WC}$ = 138), 331.9 ($C$CH$_2$, $J_{WC}$ = 101), 223.6 (CO, $J_{WC}$ = 166), 184.0 (CO), 182.1 (CO), 181.2 (CO), 177.4 (CO), 173.4 (CO), 171.8 (CO), 171.4 (CO), 166.3 (CO), 106.2 ($C_5$Me$_5$), 96.1 ($C$H$_2$), 58.1 (O$Me$), 10.8 ($C_5Me_5$). Anal. Calcd for $C_{23}H_{22}O_{10}Os_3W_1$: C, 22.78; H, 1.83. Found: C, 22.69; H, 1.88.

**Spectral Data for 14:** MS (FAB, $^{184}$W, $^{192}$Os) $m/z$ 1218 ($M^+$); IR ($C_6H_{12}$) $\nu$(CO) 2083 (s), 2052 (vs), 2021 (vs), 2009 (vs), 2002 (vw), 1981 (m), 1954 (m), 1863 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 294 K) $\delta$ 6.32 (d, 1 H, $J_{HH}$ = 7.6), 5.38 (d, 1 H, $J_{HH}$ = 7.6), 3.60 (s, 3 H, O$Me$), 1.98 (s, 15 H, $C_5Me_5$), −16.02 (s, 1 H), −25.43 (s, 1 H); $^{13}$C NMR ($CDCl_3$, 294 K) $\delta$ 321.4 ($\mu_4$-C, $J_{WC}$ = 115), 223.8 (CO, $J_{WC}$ = 164), 180.5 (CO), 178.0 (CO), 177.1 (CO), 175.4 (CO), 171.9 (CO), 168.9 (CO), 168.5 (CO), 165.0 (CO), 115.0 ($C_\beta$H), 104.0 ($C_5$Me$_5$), 97.9 ($C_\alpha$H, $J_{WC}$ = 37), 59.0 (O$Me$), 10.8 ($C_5Me_5$). Anal. Calcd for $C_{23}H_{22}O_{10}Os_3W_1$: C, 22.78; H, 1.83. Found: C, 22.72; H, 1.80.

**Reaction of 11 with CO.** A heptane solution (10 mL) of **11** (8.3 mg, 0.0067 mmol) was heated to reflux under CO atmosphere for 2.5 h. After solvent was evaporated *in vacuo*, the residue was redissolved in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 7.6 mg of orange **12** (0.006 mmol, 90%) as the only isolable cluster compound.

**Hydrogenation of 7.** A toluene solution (20 mL) of a mixture of **7a**,**b** (15.3 mg, 0.0126 mmol) was heated to reflux under $H_2$ for 2.5 h. After solvent was removed under vacuum, the residue was redissolved in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 7 mg of orange **14** (0.007 mmol, 46%), 2.4 mg of yellow **13** (0.003 mmol, 21%), and 3 mg of the starting materials **7a**,**b** (20%). Reaction of **7** with $D_2$ under similar conditions produced the corresponding $D_2$ derivatives $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}D)_2(\mu\text{-}CHCHOMe)(CO)_9$ (**14**-D) and $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}D)_2(\mu\text{-}CCH_2OMe)(CO)_9$ (**13**-D) selectively.

**Thermolysis of 13.** A toluene solution (50 mL) of **13** (50 mg, 0.041 mmol) was heated to reflux under CO for 60 min. After solvent was removed *in vacuo*, the residue was redissolved in $CH_2Cl_2$ and separated by TLC (silica gel, dichloromethane:hexane = 1:3), giving 41 mg of orange **14** (0.034 mmol, 82%) as the only isolated cluster compound. Thermolysis of the deuterium-labeled derivative $Cp^*WOs_3(\mu\text{-}C_4)(\mu\text{-}D)_2(CCH_2OMe)(CO)_9$ (**13**-D) afforded only the corresponding derivative $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}D)_2(\mu\text{-}CHCHOMe)(CO)_9$ (**14**-D), as identified by $^1$H NMR analysis.

**X-ray Crystallography**. The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer at room temperature. 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 ($\psi$ scans). The structure was solved by using the NRCC-SDP-VAX package. All the non-hydrogen atoms had anisotropic temperature factors, while hydrogen atoms were placed at idealized positions with $U_H = U_C + 0.1$. The crystallographic refinement parameters of complexes **5**, **7a**, **8**−**11**, and **13** are given in Table 1, while their selective bond distances and angles are presented in Tables 2−8, respectively.

## Results

**Syntheses of Acetylide Cluster Complexes 1−4.** Treatment of the acetylide complexes $Cp^*W(CO)_3(CCR)$ ($Cp^* = C_5Me_5$; R = Ph, $^n$Bu, $CH_2OMe$, $CH_2OPh$) with the triosmium cluster $Os_3(CO)_{10}(NCMe)_2$ afforded four tetranuclear cluster complexes **1**−**4** (Scheme 1). Only one isomer, **1a**, was isolated and characterized for the CCPh complex, while species **2**−**4** give two isomers which were easily separated by TLC. In the complexes **1a**−**4a**, the $Cp^*W(CO)_2$ fragment is located at the hinge position, while complexes **2b**−**4b** adopt the same type of butterfly framework but with the W atom occupying the wingtip position. The complexes **2a**−**4a** equilibrate with the isomers **2b**−**4b** upon heating in solution.

**Reversible Formation of the Carbido−alkylidyne Cluster.** When a solution of **1a** was treated with anhydrous $Me_3NO$ in dichloromethane−acetonitrile solution at room temperature (30 min), followed by heating in refluxing toluene (10 min), the stable orange product $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}CPh)(CO)_{10}$ (**5**) was formed in 80% yield, purified by chromatography, and recrystallized from a mixture of chloroform and methanol. Its stoichiometry was initially established by FAB mass analysis, which gave a parent ion at $m/z$ 1276, showing that this complex contains one CO less than its precursor **1a**. The loss of a CO ligand strongly suggested the formation of carbide and alkylidyne fragments via the scission of the acetylide C−C bond (Scheme 2). Thus, an X-ray diffraction study was carried out to reveal the structure.

Crystals of **5** contain two crystallographically distinct, but structurally similar, molecules in the asymmetric unit. A perspective view of one of these molecules is

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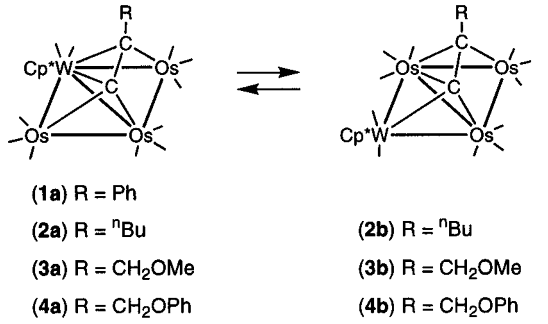
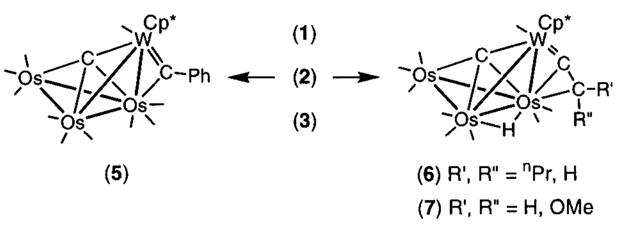
**Table 1. X-ray Structural Data of Complexes 5, 7a, 8−11 and 13**

| | **5** | **7a** | **8** | **9** | **10** | **11** | **13** |
|---|---|---|---|---|---|---|---|
| formula | $C_{28}H_{20}O_{10}Os_3W$ | $C_{23}H_{20}O_{10}Os_3W$ | $C_{24}H_{20}O_{11}Os_3W$ | $C_{28}H_{22}O_{10}Os_3W$ | $C_{28}H_{22}O_{10}Os_3W$ | $C_{24}H_{22}O_{11}Os_3W$ | $C_{23}H_{22}O_{10}Os_3W$ |
| mol wt | 1270.90 | 1210.84 | 1238.85 | 1272.93 | 1272.93 | 1240.89 | 1212.88 |
| crystal system | orthorhombic | monoclinic | triclinic | monoclinic | monoclinic | orthorhombic | triclinic |
| space group | $Pca2_1$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $Pbca$ | $P\bar{1}$ |
| $a$ (Å) | 30.773(5) | 10.666(5) | 9.971(3) | 10.268(3) | 11.219(2) | 9.762(4) | 9.429(2) |
| $b$ (Å) | 9.678(2) | 14.779(3) | 10.758(2) | 17.118(4) | 17.934(3) | 19.091(3) | 9.551(4) |
| $c$ (Å) | 20.561(3) | 18.540(5) | 14.480(5) | 17.080(5) | 15.106(2) | 30.730(5) | 17.183(4) |
| α (deg) | | | 92.11(3) | | | | 101.32(3) |
| $\beta$ (deg) | | 103.62(3) | 91.08(3) | 93.97(2) | 90.21(1) | | 98.55(2) |
| $\gamma$ (deg) | | | 111.88(2) | | | | 105.87(3) |
| $V$ (Å$^3$) | 6124(2) | 2841(2) | 1439.4(7) | 2995(1) | 3039(1) | 5727(3) | 1425.5(7) |
| $Z$ | 8 | 4 | 2 | 4 | 4 | 8 | 2 |
| $D_c$ (g/cm$^3$) | 2.757 | 2.831 | 2.858 | 2.823 | 2.782 | 2.878 | 2.826 |
| $F$(000) | 4518 | 2139 | 1098 | 2288 | 2288 | 4448 | 1084 |
| 2$\theta$(max) | 50° | 55° | 50° | 55° | 50° | 50° | 50° |
| $hkl$ ranges | 0 36, 0 11, 0 24 | −12 12, 0 17, 0 22 | −11 10, 0 12, −17 17 | −13 13, 0 22, 0 22 | −13 13, 0 21, 0 17 | 0 11, 0 22, 0 36 | −11 10, 0 11, −20 20 |
| crystal size (mm) | 0.20 × 0.20 × 0.25 | 0.25 × 0.30 × 0.50 | 0.25 × 0.25 × 0.35 | 0.25 × 0.40 × 0.40 | 0.10 × 0.25 × 0.50 | 0.02 × 0.13 × 0.55 | 0.20 × 0.20 × 0.40 |
| $\mu$(Mo Kα) (cm$^{-1}$) | 163.02 | 175.66 | 173.38 | 166.79 | 164.30 | 174.31 | 175.02 |
| transmission max, min | 1.00, 0.67 | 1.00, 0.53 | 1.00, 0.31 | 1.00, 0.67 | 1.00, 0.17 | 1.00, 0.39 | 1.00, 0.60 |
| no. of unique data | 5546 | 4998 | 5059 | 6862 | 5336 | 5033 | 5005 |
| no. of data with $I > 2\sigma(I)$ | 3139 | 3635 | 3634 | 4835 | 4253 | 3156 | 4081 |
| no. of atoms and params | 124, 757 | 57, 339 | 59, 353 | 61, 380 | 62, 380 | 59, 353 | 60, 342 |
| max $\Delta/\sigma$ ratio | 0.068 | 0.008 | 0.008 | 0.009 | 0.019 | 0.027 | 0.007 |
| $R_F$, $R_w$ | 0.053, 0.047 | 0.037, 0.037 | 0.033, 0.033 | 0.045, 0.052 | 0.043, 0.053 | 0.045, 0.044 | 0.031, 0.032 |
| GOF | 1.21 | 1.83 | 1.38 | 1.11 | 1.57 | 2.28 | 2.17 |
| D-map, max/min (e/Å$^3$) | 2.24/−1.49 | 2.49/−1.38 | 1.81/−1.72 | 2.85/−3.17 | 4.36/−3.13 | 1.83/−1.59 | 1.48/−1.71 |

**Scheme 1**



**Scheme 2**



given in Figure 1, while the bond distances are summarized in Table 2. The overall structure consists of a $WOs_3$ butterfly skeleton with a dihedral angle 99.5(1)°. Each Os atom is coordinated by three CO ligands. The W atom is located at a wingtip position and is coordinated by a Cp* and a CO ligand. Similar skeletal arrangement has been observed in the carbide clusters $CpWRu_3(\mu_4\text{-}C)(\mu\text{-}H)(CO)_{11}$[17] and $CpWOs_3(\mu_4\text{-}C)(\mu\text{-}SMe)(CO)_{11}$[18] and the carbonyl clusters $Cp^*MRu_3(\mu_4\text{-}CO)(\mu\text{-}H)(CO)_{11}$ (M = Mo, W), with a quadruply bridging CO ligand.[19] The carbido atom C(10), which is derived from the acetylide fragment in **1**, is bound to the cluster with short M(wingtip)−C distances (average 1.96(4) Å) and long M(hinge)−C distances (average 2.17 (4) Å), typical for such a carbide in the butterfly environment.[20] The alkylidyne ligand bridges the W−Os(2) edge with angles W−C(12)−C(13) = 142(3)°, Os(1)−C(12)−C(13) = 127(3)°,

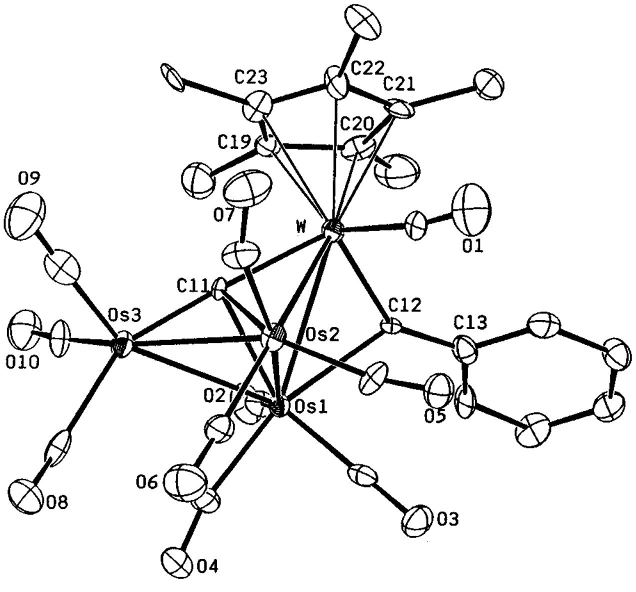


**Figure 1.** Molecular structure of $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}CPh)(CO)_{10}$ (**5**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

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**Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of 5 (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(1) | 2.896(3) | W−Os(2) | 2.974(3) |
| Os(1)−Os(2) | 2.751(2) | Os(1)−Os(3) | 2.899(2) |
| Os(2)−Os(3) | 2.850(3) | W−C(11) | 2.10(4) |
| Os(1)−C(11) | 2.22(4) | Os(2)−C(11) | 2.12(4) |
| Os(3)−C(11) | 1.81(4) | W−C(12) | 1.89(3) |
| Os(1)−C(12) | 2.22(4) | | |
| ∠W−C(11)−Os(3) | 175(3) | ∠Os(1)−C(11)−Os(2) | 79(1) |
| ∠W−C(12)−C(13) | 142(3) | ∠W−C(1)−O(1) | 165(4) |
| ∠Os−C−O (mean) | 176(5) | | |

and W−C(12)−Os(1) = 89(1)°. Since these structural features invoke a trigonal-planar carbon, a substantial degree of W═C double-bond interaction is indicated, W−C(12) = 1.89(3) Å. In accordance with this X-ray structural feature, the $^{13}$C NMR spectrum showed two characteristic signals at $\delta$ 357.0 ($J_{WC}$ = 104 Hz) and 293.9 ($J_{WC}$ = 150 Hz), which were assigned to the carbide and the α-carbon of the bridging alkylidyne ligand, respectively.

**Formation of Carbido−vinylidene Clusters.** The related *n*-butyl complexes **2** were subjected to the same decarbonylation reaction in attempts to extend the scope of the reaction. Unexpectedly, complexes **2** slowly eliminated two CO ligands in refluxing toluene (30 min) following the treatment with Me$_3$NO, affording two isomeric vinylidene clusters Cp*WOs$_3$($\mu_4$-C)($\mu$-H)($\mu$-CCH$^n$Pr)(CO)$_9$ as an inseparable mixture (**6a**:**6b** = 4:3) in 75% yield (Scheme 2). Both **6a** and **6b** showed almost identical IR $\nu$(CO) spectra in solution, suggesting that they possess a similar cluster skeletal arrangement. Thus, their difference in structure is probably caused by the asymmetric nature of the vinylidene ligand, which is further confirmed by examination of the $^1$H and $^{13}$C NMR data. In the $^1$H NMR spectrum, two set of signals are observed at $\delta$ 4.08 and −24.23 and at $\delta$ 4.15 and −24.29, indicating the presence of a C═CH$^n$Pr vinylidene ligand and a bridging hydride ligand. The $^{13}$C NMR spectrum was similarly interpreted. In addition to the carbide and the W−CO resonances, the resonances due to the α- and $\beta$-carbons of vinylidene in **6a** appeared at $\delta$ 273.1 ($J_{WC}$ = 100 Hz) and 65.1, while those of **6b** occurred at $\delta$ 269.5 ($J_{WC}$ = 100 Hz) and 65.0. We propose that the dominant isomer **6a** contains the *exo* hydrogen, while the less abundant **6b** has the *endo* hydrogen atom, as a positive NOE enhancement (≥3.6%) was observed for the hydride signal of **6b** upon irradiating the respective vinylidene proton signal.

The identification of the vinylidene complexes **6** was further confirmed by the successful isolation of two methoxy derivatives Cp*WOs$_3$($\mu_4$-C)($\mu$-H)($\mu$-CCHOMe)(CO)$_9$ (**7a**,**b**) in 33% and 7% yields, respectively. These products were obtained by treating the CH$_2$OMe derivatives **3a**,**b** with Me$_3$NO, followed by thermolysis. Unlike the $\mu$-CCH$^n$Pr vinylidene complexes **6**, these new complexes **7a**,**b** can be isolated in pure form by repeated TLC separation and recrystallization. Thus, their spectral data can be unambiguously interpreted and confirmed. The diagnostic NMR data for **7a** include the $\mu_4$-carbide signal at $\delta$ 347.3 ($J_{WC}$ = 100 Hz) in the $^{13}$C NMR spectrum and the W-bound CO signal at $\delta$ 221.3 ($J_{WC}$ = 167 Hz), eight Os−CO signals in the range $\delta$ 190.1−166.2, and the vinylidene signals at $\delta$ 257.2 ($C_\alpha$, $J_{WC}$ = 158 Hz) and 107.7 ($C_\beta$). The $^1$H NMR spectra show the expected vinylidene $\beta$-hydrogen signals at $\delta$ 6.79 and 6.85 and the bridging hydrides at $\delta$ −24.38 and −23.57 for **7a**,**b**, respectively.

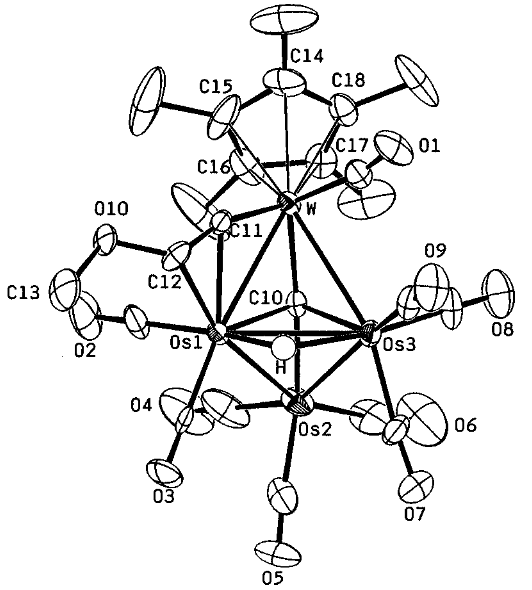

**Figure 2.** Molecular structure of Cp*WOs$_3$($\mu_4$-C)($\mu$-H)($\mu$-CCHOMe)(CO)$_9$ (**7a**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

**Table 3. Selected Bond Distances (Å) and Bond Angles (deg) of 7a (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(1) | 2.840(2) | W−Os(3) | 2.985(1) |
| Os(1)−Os(2) | 2.815(1) | Os(1)−Os(3) | 2.883(1) |
| Os(2)−Os(3) | 2.857(1) | W−C(10) | 2.02(2) |
| Os(1)−C(10) | 2.13(1) | Os(2)−C(10) | 1.91(2) |
| Os(3)−C(10) | 2.18(1) | W−C(11) | 1.93(2) |
| Os(1)−C(11) | 2.18(2) | Os(1)−C(12) | 2.27(2) |
| C(11)−C(12) | 1.36(2) | | |
| ∠W−C(10)−Os(2) | 174.4(8) | Os(1)−C(10)−Os(3) | 84.0(5) |
| ∠W−C(11)−C(12) | 163(1) | ∠W−C(1)−O(1) | 170(2) |
| ∠Os−C−O (mean) | 174(2) | | |

The X-ray diffraction study on one isomer, complex **7a**, confirmed that the molecule possesses the butterfly arrangement of transition-metal atoms with dihedral angle 104.24(3)° (Figure 2 and Table 3). The carbide atom C(10) is encapsulated by all metal atoms with distances in the range 1.91(1)−2.18(1) Å. The hydride ligand was unambiguously located on the electron density map. It spans the slightly elongated hinge Os−Os bond. The vinylidene ligand, which contains a linear W−C−C skeleton and an *endo* hydrogen atom, is best visualized as having a W═C double bond and forming an $\eta^2$-C═C bond with the hinge Os(CO)$_2$ center. These characteristics are in agreement with those of “side-on” coordinated vinylidene ligands observed in dinuclear and polynuclear complexes.[21]

Treatment of **6** with CO in toluene for 40 min led to regeneration of their precursors **2a**,**b** in 58% yield. However, on treatment of **7** with CO, we obtained a mixture of **3a**,**b** in 41% yield, as well as some unreacted **7a**,**b** (24%) and the new alkenyl cluster Cp*WOs$_3$($\mu_4$-C)($\mu$-CHCHOMe)(CO)$_{10}$ (**8**) in 20% yield. As indicated in Figure 3, the molecular structure of **8** is essentially identical with that of **5**, except that the bridging $\mu$-CPh ligand has been replaced by a bridging *trans*-

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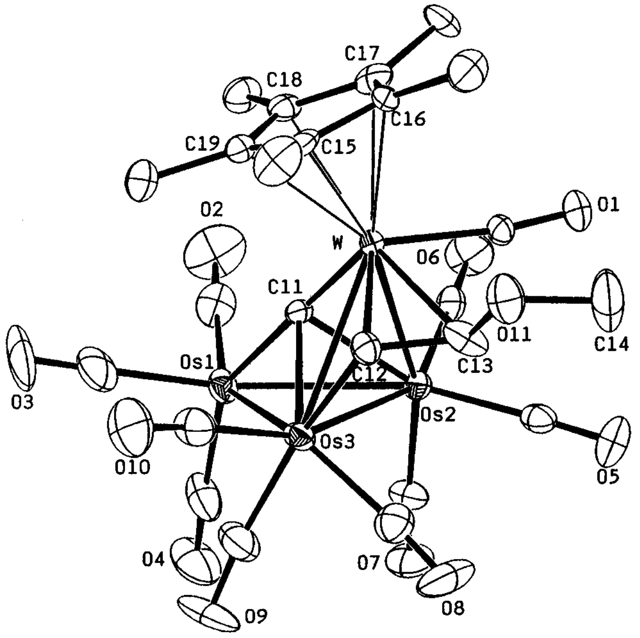

**Figure 3.** Molecular structure of Cp*WOs$_3$(CO)$_9$($\mu_4$-C)($\mu$-CH=CHOMe)(CO)$_9$ (**8**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

**Table 4. Selected Bond Distances (Å) and Bond Angles (deg) of 8 (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(2) | 2.972(1) | W−Os(3) | 2.924(1) |
| Os(1)−Os(2) | 2.829(1) | Os(1)−Os(3) | 2.877(1) |
| Os(2)−Os(3) | 2.773(1) | W−C(11) | 1.98(1) |
| Os(1)−C(11) | 1.94(1) | Os(2)−C(11) | 2.12(1) |
| Os(3)−C(11) | 2.23(1) | W−C(12) | 2.10(1) |
| W−C(13) | 2.40(1) | Os(3)−C(12) | 2.17(1) |
| C(12)−C(13) | 1.44(2) | C(13)−O(11) | 1.31(2) |
| ∠W−C(11)−Os(1) | 174.6(6) | ∠Os(2)−C(11)−Os(3) | 79.2(3) |
| ∠Os(3)−C(12)−C(13) | 118.9(9) | ∠C(12)−C(13)−O(11) | 117.7(12) |
| ∠W−C(1)−O(1) | 171.3(10) | ∠Os−C−O (mean) | 176.7(15) |

CH=CHOMe group, located at exactly the same position and with its C=C double bond coordinated to the W atom. The $^1$H NMR signals due to this alkenyl ligand occur at $\delta$ 6.88 and 5.05 as doublets ($^3J_{HH}$ = 5.8 Hz). The two $^{13}$C NMR signals appearing at $\delta$ 107.1 and 104.8 ($J_{WC}$ = 42 Hz) are assigned to the α- and $\beta$-carbons, respectively.

**Formation of Benzofuryl Clusters.** In contrast with the generation of alkylidyne ligand in **5** or the vinylidene ligand in **6** and **7**, extensive thermolysis of the CH$_2$OPh complexes **4** afforded the purple benzofuryl complex Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-C$_8$H$_5$O)(CO)$_9$ (**9**) in 50% yield, together with a trace amount of the dark red isomeric complex Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-C$_8$H$_5$O)(CO)$_9$ (**10**). The latter can be independently produced in 29% yield by pyrolysis of **9** in xylene solution at 140 °C. A one-pot strategy was employed to prepare larger amounts of these furyl derivatives. In this instance, complexes **9** and **10** was obtained in over 55% and 3% yields, respectively, by heating a 1:1 mixture of Cp*W(CO)$_3$(CCCH$_2$OPh) and Os$_3$(CO)$_{10}$(NCMe)$_2$ in refluxing toluene for 8 h instead of 30 min.

Both complexes **9** and **10** display an identical M$^+$ parent peak in the FAB mass spectra and an essentially identical pattern of CO stretching bands in their IR spectra. However, the $^1$H and $^{13}$C NMR data are distinctive. The $^{13}$C NMR spectra exhibit characteristic carbido and W-bound CO signals at $\delta$ 334.2 ($J_{WC}$ = 104 Hz) and 225.7 ($J_{WC}$ = 178 Hz) for **9** and at $\delta$ 322.9 ($J_{WC}$ = 117 Hz) and 222.2 ($J_{WC}$ = 165 Hz) for **10**, while the corresponding $^1$H NMR spectrum furnishes two hydride signals at $\delta$ −17.02 and −22.68 and $\delta$ −16.47 and −24.32, respectively. Despite these similarities, the $^1$H and $^{13}$C NMR signals in the olefinic and aromatic region are fairly different, suggesting the participation of the phenyl substituent in the generation of these two products. Thus, X-ray diffraction studies were carried out to reveal the true identity of the organic fragment in question.

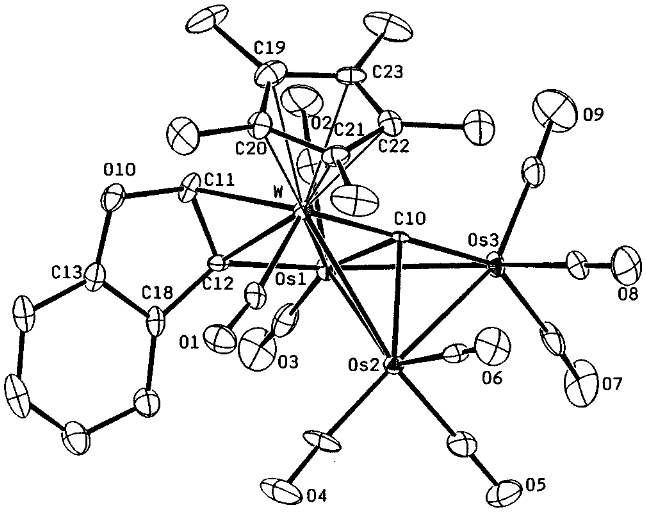

**Figure 4.** Molecular structure of Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-C$_8$H$_6$O)(CO)$_9$ (**9**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

**Table 5. Selected Bond Distances (Å) and Bond Angles (deg) of 9 (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(1) | 2.880(1) | W−Os(2) | 3.030(1) |
| Os(1)−Os(2) | 2.876(1) | Os(1)−Os(3) | 2.891(1) |
| Os(2)−Os(3) | 2.828(1) | W−C(10) | 1.97(2) |
| Os(1)−C(10) | 2.15(2) | Os(2)−C(10) | 2.16(1) |
| Os(3)−C(10) | 1.99(2) | W−C(11) | 2.32(2) |
| W−C(12) | 2.39(1) | Os(1)−C(12) | 2.05(2) |
| C(11)−C(12) | 1.41(2) | C(11)−O(11) | 1.43(2) |
| C(12)−C(18) | 1.48(2) | C(13)−C(18) | 1.40(2) |
| C(13)−O(10) | 1.35(2) | | |
| ∠W−C(10)−Os(3) | 177.0(10) | ∠Os(1)−C(10)−Os(2) | 83.7(6) |
| ∠Os(2)−Os(1)−C(3) | 119.1(6) | ∠Os(1)−Os(2)−C(4) | 114.7(7) |
| ∠Os(1)−Os(2)−C(5) | 109.3(6) | ∠Os(1)−Os(3)−C(7) | 110.9(5) |
| ∠Os(1)−Os(3)−C(9) | 105.1(6) | ∠Os(3)−Os(1)−C(2) | 101.1(6) |
| ∠Os(3)−Os(1)−C(3) | 121.8(6) | ∠W−C(1)−O(1) | 170.5(15) |
| ∠Os−C−O (mean) | 176.1(18) | | |

The molecular structure of **9** is shown in Figure 4, and selected bond distances and angles are listed in Table 5. The WOs$_3$ butterfly core arrangement of **9** is similar to that of the previously discussed complexes **5** and **8**. The Os(1)−Os(2) and Os(1)−Os(3) distances (2.876(1) and 2.891(1) Å) are significantly longer than the third Os−Os bond (Os(2)−Os(3) = 2.828(1) Å), indicating that the hydride ligands are associated with the first two Os−Os vectors, which share the unique Os(1)(CO)$_2$ vertex. The organic segment deriving from the CCH$_2$OPh fragment in **4** now has cyclized to form a benzofuryl ligand, of which the methine atom C(11) of the furyl ring is located adjacent to the unique O(10) atom. The benzofuryl ligand is coordinated to the Os(1) atom via the C(11) atom (Os(1)−C(11) = 2.09(2) Å), while the adjacent C=C double bond involving C(11)−C(12) is linked to the W atom through an elongated $\pi$-interaction (W−C(11) = 2.32(2) Å and W−C(12) =

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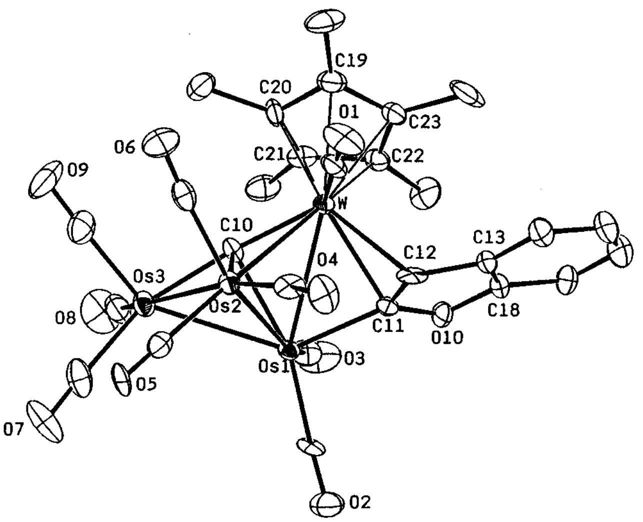

**Figure 5.** Molecular structure of Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-C$_8$H$_6$O)(CO)$_9$ (**10**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

**Table 6. Selected Bond Distances (Å) and Bond Angles (deg) of 10 (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(1) | 2.867(1) | W−Os(2) | 3.002(1) |
| Os(1)−Os(2) | 2.903(1) | Os(1)−Os(3) | 2.908(1) |
| Os(2)−Os(3) | 2.843(1) | W−C(10) | 1.96(2) |
| Os(1)−C(10) | 2.19(2) | Os(2)−C(10) | 2.16(1) |
| Os(3)−C(10) | 1.99(2) | W−C(11) | 2.28(2) |
| W−C(12) | 2.41(2) | Os(1)−C(11) | 2.09(2) |
| C(11)−C(12) | 1.41(3) | C(11)−O(11) | 1.42(2) |
| C(12)−C(13) | 1.49(3) | C(13)−C(18) | 1.39(3) |
| C(18)−O(10) | 1.37(2) | | |

| | | | |
|---|---|---|---|
| ∠W−C(10)−Os(3) | 175.1(11) | ∠Os(1)−C(10)−Os(2) | 83.7(6) |
| ∠Os(2)−Os(1)−C(2) | 116.0(5) | ∠Os(1)−Os(2)−C(4) | 113.8(6) |
| ∠Os(1)−Os(2)−C(5) | 108.8(6) | ∠Os(1)−Os(3)−C(7) | 113.1(7) |
| ∠Os(1)−Os(3)−C(8) | 102.5(7) | ∠Os(3)−Os(1)−C(2) | 120.4(5) |
| ∠Os(3)−Os(1)−C(3) | 101.4(7) | ∠W−C(1)−O(1) | 173.3(17) |
| ∠Os−C−O (mean) | 176.4(17) | | |

2.39(1) Å). Furthermore, this C═C double bond is pointing away from the Os(2) atom of the W−Os(1)−Os(2) triangle. This orientation is related to the orientation observed in the ethoxy-substituted triosmium alkenyl complex Os$_3$($\mu$-H)($\mu$-CH═CHOEt)(CO)$_{10}$.[22]

In contrast, the red benzofuryl derivative **10** (Figure 5 and Table 6) shows an identical butterfly Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$(CO)$_9$ skeletal arrangement. The sole difference is found at the furyl functional group, in which the methine C(12) atom is located one carbon away from the oxygen atom O(10), and the coordinated C═C double bond C(11)-C(12) is now oriented toward the Os(2) atom of the W−Os(1)−Os(2) plane. Thus, the arrangement of the benzofuryl ligand is in agreement with that of the $\mu$,$\eta^2$-furyl complexes Os$_3$($\mu$-H)($\mu$-C$_4$H$_3$O)(CO)$_{10}$, in which both the X-ray structure and the dominant isomer in solution consist of the coordinated C═C double bond bearing the *endo* conformation with respect to the nonbridged Os(CO)$_4$ unit.[23]

**Hydrogenation of Acetylide Clusters 3.** Treatment of **3** with H$_2$ was attempted in order to compare the fate of acetylide with that of the decarbonylation reaction. Four cluster complexes were isolated following hydrogenation of a mixture of **3a**,**b** in toluene (1 atm, 110 °C, 2 h). The first isolated cluster is the acetylide compound Cp*WOs$_3$($\mu$-H)$_2$(CCCH$_2$OMe)(CO)$_{10}$ (**11**, orange, 5%), which is formally produced by replacing one CO with two bridging hydride ligands, while the alkylidyne group in the second compound Cp*WOs$_3$($\mu_3$-CCH$_2$CH$_2$OMe)(CO)$_{11}$ (**12**, orange, 10%) is obtained by transferring both hydrogen atoms to the acetylide C$_\beta$ atom, followed by formation of the tetrahedral metal core. The last two cluster complexes, Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-CCH$_2$OMe)(CO)$_9$ (**13**, yellow, 9%) and Cp*WOs$_3$($\mu_4$-C)($\mu$-H)$_2$($\mu$-CHCHOMe)(CO)$_9$ (**14**, orange, 31%), involve the generation of the $\mu_4$-carbide atom and two hydride ligands during the hydrogenation. These products were characterized by spectroscopic methods and X-ray diffraction studies.

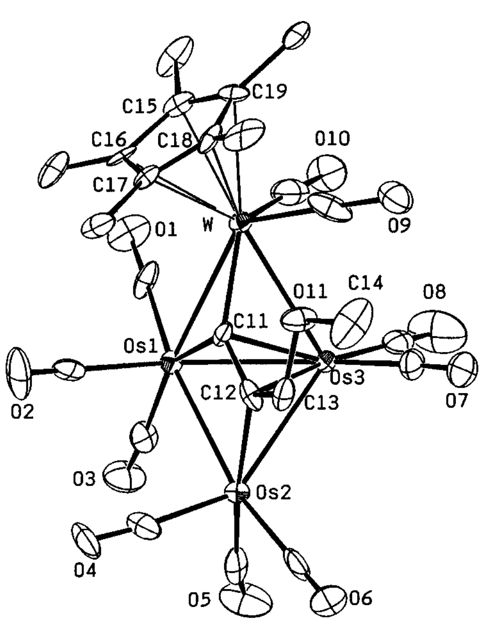

**Figure 6.** Molecular structure of Cp*WOs$_3$($\mu$-H)$_2$(CCCH$_2$-OMe)(CO)$_{10}$ (**11**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

**Table 7. Selected Bond Distances (Å) and Bond Angles (deg) of 11 (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(1) | 3.009(2) | W−Os(3) | 2.905(2) |
| Os(1)−Os(3) | 2.834(2) | Os(1)−Os(2) | 2.880(2) |
| Os(2)−Os(3) | 2.837(2) | W−C(11) | 2.07(3) |
| Os(1)−C(11) | 2.18(2) | Os(3)−C(11) | 2.23(2) |
| Os(2)−C(12) | 2.09(3) | Os(3)−C(12) | 2.31(2) |
| C(11)−C(12) | 1.34(3) | C(12)−C(13) | 1.61(3) |

| | | | |
|---|---|---|---|
| ∠Os(3)−Os(1)−C(1) | 112.5(10) | ∠Os(3)−Os(1)−C(3) | 115.5(8) |
| ∠Os(1)−Os(3)−C(8) | 113.5(7) | ∠Os(2)−Os(3)−C(7) | 106.6(9) |
| ∠Os(2)−Os(3)−C(8) | 129.6(8) | ∠W−C−O (mean) | 176(3) |
| ∠Os−C−O (mean) | 174(2) | | |

For complex **11**, the $^1$H NMR spectrum exhibits two signals at $\delta$ −17.95 and −21.71 in addition to the signals assigned to the Cp* and methoxy groups, showing the presence of two bridging hydride ligands. The acetylide $^{13}$C NMR signals appear at $\delta$ 197.2 ($C_\alpha$, $J_{WC}$ = 118 Hz) and 158.5 ($C_\beta$, $J_{WC}$ = 17 Hz), which fall in the range expected for the $\mu_4$,$\eta^2$-acetylide ligands.[24] As shown in Figure 6 (see also Table 7), the X-ray diffraction analysis confirms that **11** possesses a butterfly WOs$_3$ core

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**Table 8. Selected Bond Distances (Å) and Bond Angles (deg) of 13 (Esd in Parentheses)**

| | | | |
|---|---|---|---|
| W−Os(1) | 2.994(1) | W−Os(2) | 2.827(2) |
| Os(1)−Os(2) | 2.897(1) | Os(1)−Os(3) | 2.8449(9) |
| Os(2)−Os(3) | 2.8836(9) | W−C(10) | 2.00(1) |
| Os(1)−C(10) | 2.13(1) | Os(2)−C(10) | 2.17(1) |
| Os(3)−C(10) | 1.97(1) | W−C(11) | 1.93(1) |
| Os(2)−C(11) | 2.14(1) | C(11)−C(12) | 1.48(2) |
| Os(1)−H(1) | 1.76(10) | Os(2)−H(1) | 1.43(9) |
| Os(2)−H(2) | 1.99(14) | Os(3)−H(2) | 2.02(14) |
| ∠W−C(10)−Os(3) | 173.3(6) | ∠Os(1)−C(10)−Os(2) | 84.7(4) |
| ∠W−C(11)−Os(2) | 88.0(5) | ∠W−C(11)−C(12) | 146.3(9) |
| ∠Os(2)−C(11)−C(12) | 125.7(8) | ∠W−C(1)−O(1) | 171(1) |
| ∠Os−C−O (mean) | 177(1) | | |

geometry, with the W atom located at one wingtip position, similar to the structurally characterized **3b**.[12] The acetylide ligand, which adopts the typical $\mu_4,\eta^2$ bonding mode, occupies the open face of the butterfly framework with its α-carbon residing above the $WOs_2$ triangle (W−C(12) = 2.00(2) Å, Os(1)−C(12) = 2.06(2) Å, and Os(2)−C(12) = 2.15(2) Å), and with the $\beta$-carbon atom linked to Os(2) and Os(3) atoms (Os(2)−C(13) = 2.32(2) Å and Os(3)−C(13) = 2.06(1) Å). The $\mu_4,\eta^2$ mode of bonding resembles that of polynuclear acetylide- or nitrile-capped clusters,[25] in which the acetylide ligand is best considered as $\sigma$-bonded to the W atom via its α-carbon and also interacting with the $Os_3$ triangle via a parallel ($2\sigma + \pi$) mode of typical $\mu_3$-alkyne ligands.[26]

The hydride ligands were not located on a difference Fourier map, but we propose that they span the Os(1)−Os(3) hinge and the adjacent Os(2)−Os(3) edge, which share the common $Os(CO)_2$ unit. Interestingly, the first two Os−Os distances (Os(1)−Os(3) = 2.834(2) Å and Os(2)−Os(3) = 2.837(2) Å) are not longer but are significantly shorter than the third Os−Os bond within the molecule (Os(1)−Os(2) = 2.880(2) Å). This observation contradicts the general belief that the bridging hydride ligand tends to increase metal−metal distances in cluster compounds.[27] We believe that the reversal of Os−Os distances is a consequence of the concomitant acetylide coordination. The observed Os−Os−CO angles are consistent with the assignment of bridging hydride ligands.

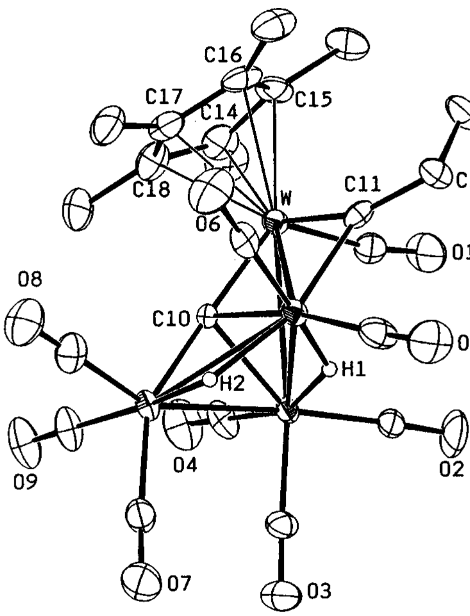
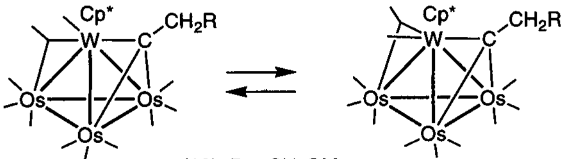


**Figure 7.** Molecular structure of $Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)_2(\mu\text{-}CCH_2OMe)(CO)_9$ (**13**), showing the atomic labeling scheme and the thermal ellipsoids at the 30% probability level.

Treatment of **11** under CO afforded the alkylidyne cluster **12** in 90% yield. The identification of **12** is mainly provided by the IR $\nu$(CO) data, which resemble those of the numerous documented complexes of formulation $LWM_3(\mu\text{-}CR)(CO)_{11}$ (L = Cp, $C_5Me_5$; M = Os, Ru; R = H, Me, $C_5H_{11}$, Ph, OMe).[11,17,28] The $^{13}C$ NMR spectrum at 220 K showed two distinct W−CO signals at $\delta$ 223.9 and 206.6 and four Os−CO signals at $\delta$ 187.1, 183.4, 180.7, and 176.0 in the ratio of 1:1:6:1. The $^1H$ NMR spectrum exhibited four well-resolved multiplets at $\delta$ 4.06, 3.91, 3.55, and 3.46 (AA′BB′ spin system) at the same temperature, due to the methylene protons of the $CCH_2CH_2OMe$ fragment. Upon heatng the sample up to 294 K, the $CH_2CH_2OMe$ multiplets in the $^1H$ NMR spectrum coalesced into two featureless signals centered at $\delta$ 4.04 and 3.56, while the W−CO signal merged into the baseline in the $^{13}C$ NMR spectrum, and the Os−CO signals turned into two broad signals at $\delta$ 181.0 and 179.5 simultaneously. Based on these variable-temperature NMR data and the solid-state structures established,[11,17,28] we propose that the observed dynamics in solution is due to the exchange of the bridging and the terminal CO ligands of the W atom, which generated a time-averaged mirror plane bisecting the $WOs_3$ tetrahedral framework.



**(12)**, R = $CH_2OMe$

Complex **13** is a $WOs_3$ cluster compound containing two hydrides, one carbide, and a $\mu$-$CCH_2OMe$ fragment. The spectroscopic data are within our expectations. The $^1H$ NMR spectrum furnished two hydride signals at $\delta$ −15.21 and −24.42, the Cp* and methoxy signals at $\delta$ 2.02 and 3.37, and two doublets at $\delta$ 4.07 and 4.18 ($J_{HH}$ = 21 Hz) due to the methylene hydrogens. The resonance signals for carbide and the α-carbon of the $\mu$-$CCH_2OMe$ ligand appear at $\delta$ 337.4 ($J_{WC}$ = 138 Hz) and 331.9 ($J_{WC}$ = 101 Hz) in the $^{13}C$ NMR spectrum. These spectral features are further established by X-ray structural analysis, data for which are given in Table 8, with the molecule shown in Figure 7. The structure of **13** consists of a butterfly core arrangement. There is one carbide ligand, nine CO groups, and a $\mu$-$CCH_2OMe$ moiety. The hydride ligands are associated with

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[25] (a) Weatherell, C.; Taylor, N. J.; Carty, A. J.; Sappa, E.; Tiripicchio, A. *J. Organomet. Chem.* **1985**, *291*, C9. (b) Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 1048. (c) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 2456. (d) Lanfranchi, M.; Tiripicchio, A.; Sappa, E.; Maclaughlin, S. A.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 538. (e) Bantel, H.; Hansert, B.; Powell, A. K.; Tasi, M.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1059. (f) Bantel, H.; Suter, P.; Vahrenkamp, H. *Organometallics* **1995**, *14*, 4424.

[26] (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437.

[27] (a) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 534. (b) Churchill, M. R.; Fettinger, J. C.; Hollander. F. J.; Lashewycz-Rubycz, R. A. *J. Organomet. Chem.* **1988**, *340*, 367.

[28] (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) Gong, J.-H.; Chen, C.-C.; Chi, Y.; Wang, S.-L.; Liao, F.-L. *J. Chem. Soc., Dalton Trans.* **1993**, 1829.

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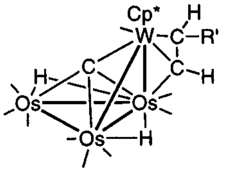
the slightly elongated Os(1)−Os(2) and Os(2)−Os(3) bonds, which are joined at the less sterically congested $Os(CO)_2$ unit at the hinge position. The NMR data are in agreement with the structure established by X-ray diffraction study.

Thermolysis of **13** in toluene at 110 °C affords the alkenyl complex **14** in 82% yield. This molecule was characterized by spectroscopic methods. A single-crystal X-ray diffraction study was attempted, but only primitive structural information was obtained due to poor crystal quality.[29] Nevertheless, this analysis revealed the existence of a $WOs_3(\mu_4\text{-}C)$ butterfly core and a *trans*-CH=CHOMe grouping $\sigma$-bonded to one hinge Os atom and $\pi$-bonded to the wingtip W atom, in a manner similar to that observed in **8**. The proposed structure is depicted below. Other supporting evidence comes from the IR $\nu$(CO) data, which are qualitatively identical with those of benzofuryl complex **10**, and also from the detection of two $^1$H NMR signals at $\delta$ −16.02 and −25.43 due to the bridging hydrides and two doublets at $\delta$ 6.32 and 5.38 ($^3J_{HH}$ = 7.6 Hz) due to the olefinic hydrogen atoms of the *trans*-CH=CHOMe fragment. The $^{13}$C NMR signals of the carbide and the α- and $\beta$-carbons of alkenyl fragment appear at $\delta$ 321.4 ($J_{WC}$ = 115 Hz), 115.0, and 97.9 ($J_{WC}$ = 37 Hz), which offers the final confirmation of such an assignment.



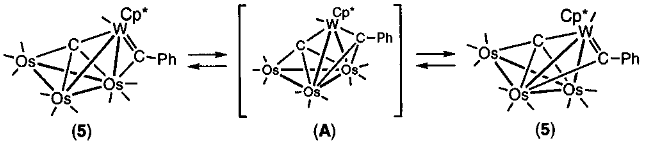
(14) R' = OMe

## Discussion

Treatment of acetylide complexes $Cp^*W(CO)_3(CCR)$ (R = Ph, $^n$Bu, $CH_2OMe$, $CH_2OPh$) with the osmium cluster $Os_3(CO)_{10}(NCMe)_2$ furnishes four tetranuclear clusters **1**−**4** (Scheme 1). Their yields vary from trace amount to up to 22% according to the substituent R on the acetylide ligands. In the isomers **1a**−**4a**, the $Cp^*W(CO)_2$ fragment is located at the hinge position, while the isomers **2b**−**4b** adopt the same framework but with the W atom occupying the wingtip position. The complexes **2a**−**4a** undergo equilibration with the isomers **2b**−**4b** upon heating in solution. To our knowledge, this type of skeletal rearrangement is unprecedented, although a few examples have been reported for framework isomerization in tetrahedral clusters,[30] the transformation between butterfly and tetrahedral clusters,[31] and the polyhedral isomerization in higher nuclearity clusters.[32]

**Interconversion between Acetylide and Carbido−alkylidyne.** The carbido−acetylide cluster **5** was obtained in good yield through treatment of the phenyl derivative **1a** with a slight excess of $Me_3NO$ in acetonitrile followed by pyrolysis, or by direct decarbonylation of **1a** for an extended period of time in toluene. This reaction serves as a model for the cleavage of the multisite-bound acetylide C−C bond, in which the coordinative unsaturation is produced by elimination of a CO ligand. The acetylide complex **1a** can be regenerated from **5** by the addition of one CO ligand. The scrambling of the carbide and carbon atom of the coordinated CO ligands in **5** was not observed, as there was no $^{13}$C incorporation for the $C_\alpha$ atom of acetylide in **1a**, produced by treatment of $^{13}$CO-enriched **5** with $^{13}$CO. This observation is in contrast to the remarkable synthesis of the complex $CpFe_2W(CCTol)(CO)_8$ by Stone and co-workers,[33] in which the acetylide group is clearly derived from a CO ligand and the alkylidyne ligand in precursor $CpW(CO)_2(CTol)$.

**Scheme 3**



In addition, the $\mu$-alkylidyne ligand in **5** undergoes migration at the higher temperature from one W−Os edge to the second W−Os edge through the formation of a $\mu_3$-alkylidyne intermediate on the $WOs_2$ plane (Scheme 3). This fluxionality was revealed by the variable-temperature $^{13}$C NMR spectroscopy. The spectrum of **5** recorded at 253 K showed one W−CO signal at $\delta$ 226.7 and eight Os−CO resonances in the region $\delta$ 187.2−164.9, in which the CO signal at $\delta$ 182.1 possesses double intensity. Upon increasing the temperature to 338 K, the Os−CO signal at $\delta$ 164.9 collapsed to a broad signal, while the rest of the W−CO signal and the other seven Os−CO signals in the range $\delta$ 187.2−173.3 coalesced to generate one very broad signal centered at $\delta$ 181.3, consistent with the generation of a time-averaged mirror plane. However, the high-temperature limiting spectrum cannot be obtained because of rapid decomposition of **5** at the higher temperatures.

Thermolysis of the acetylide derivatives **2** and **3**, which contain an adjacent methylene functional group, afford not the alkylidyne derivatives as does **5** but the vinylidene clusters **6** and **7** as a mixture of two isomers, **a** and **b**. Although complexes **6a**,**b** could not be separated from one another, the isomers **7a**,**b** were isolated by repeated TLC followed by recrystallization. The successful isolation of **7a**,**b** allowed us to make a complete structural identification.

Interestingly, heating pure sample of either **7a** or **7b** in toluene at 50 °C over a period of 6 h furnishes an approximately 1:1 mixture, as revealed by $^1$H NMR study. These observations indicate that the interconversion is slow but feasible at the higher temperature. Two possible pathways are proposed to account for this isomerization reaction.

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(29) Selected cell constants: monoclinic, space group $P2_1/n$, $a$ = 14.723(1), $b$ = 10.743(1), and $c$ = 18.016(1) Å, $b$ = 102.22(1)°, $V$ = 2785.0(2) Å$^3$.

(30) Müller, M.; Schacht, H.-T.; Fischer, K.; Ensling, J.; Gütlich, P.; Vahrenkamp, H. *Inorg. Chem.* **1986**, *25*, 4032.

(31) (a) Müller, M.; Schacht, H.-T.; Fischer, K.; Ensling, J.; Gütlich, P.; Vahrenkamp, H. *Inorg. Chem.* **1986**, *25*, 4032. (b) Bernhardt, W.; Vahrenkamp, H. *J. Organomet. Chem.* **1988**, *355*, 427. (c) Horwitz, C. P.; Shriver, D. F.; *Organometallics* **1984**, *3*, 756. (d) Chi, Y.; Shu, H.-Y.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Chem. Commun.* **1991**, 1023.

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(33) Green, M.; Marsden, K.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1983**, 446.

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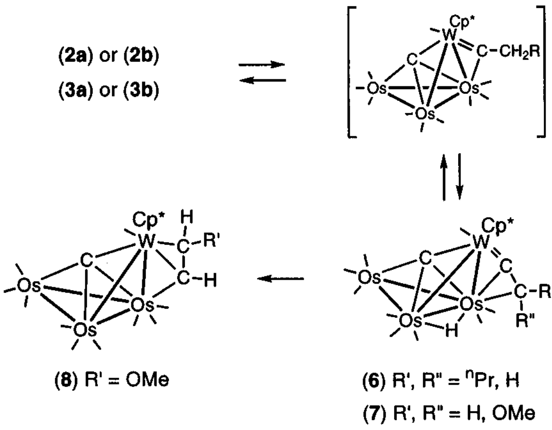
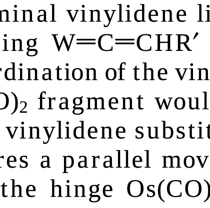
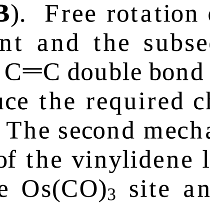
**Scheme 4**



The first one possesses a transition state containing a terminal vinylidene ligand (**B**). Free rotation of the resulting W=C=CHR′ fragment and the subsequent recoordination of the vinylidene C=C double bond to the $Os(CO)_2$ fragment would produce the required change of the vinylidene substituents. The second mechanism requires a parallel movement of the vinylidene ligand from the hinge $Os(CO)_2$ to the $Os(CO)_3$ site and the concurrent shifting of one CO ligand from the hinge $Os(CO)_3$ to the $Os(CO)_2$ site to balance the distribution of electron density (**C**). Both reaction pathways are possible, and we cannot eliminate either one of them.



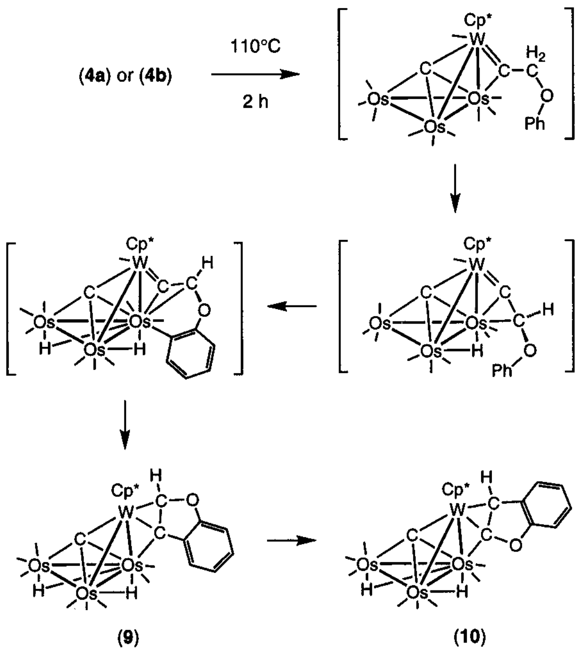
**(B)**



**(C)**

The pathways leading to the formation of vinylidene from **2** and **3** were also established (Scheme 4), involving the C−C bond cleavage and a subsequent C−H bond activation. This mechanism is consistent with our previous discussion that the acetylide complex **1a** can liberate one CO ligand to induce the scission of C−C bond, giving the carbide and alkylidyne fragments. The reaction proceeds further to produce vinylidene via C−H activation, a process which is akin to those observed in the metal clusters and the metal surfaces.[34] Two isomers are anticipated due to the poor selectivity in abstracting the diastereotopic hydrogen atoms. Finally, heating of either **6** or **7** in toluene regenerated the acetylide complexes **2** or **3**, respectively. Although these reactions seem to be reversible, they require extended heating in refluxing toluene for over 1.5 h, indicating a slowing down of the reaction rate as compared with that of the carbido−alkylidyne to acetylide conversion. A further unusual feature is that a small amount of carbido−alkenyl complex **8** was isolated during the treatment of **7** with CO in toluene for 1.5 h. There is no doubt that the alkenyl ligand is produced via a direct transfer of hydride to the α-carbon, not the β-carbon of the vinylidene ligand, as required for the regeneration of acetylide precursor **3**.

**Scheme 5**



Replacing the $CH_2OMe$ substituent in **3** by the $CH_2OPh$ substituent in **4** leads to the introduction of an additional reactive site, e.g., the *ortho* hydrogens of the phenyl substituent. The expected carbido−vinylidene clusters were not isolated in this case, but the reaction proceeds until the benzofuryl derivative **9** is formed. One possible pathway is summarized in Scheme 5, which clearly shows the initial involvement of acetylide C−C bond cleavage and C−H bond activation. Because of the presence of the phenyl functional group, the reaction proceeds further through an orthometalation step, followed by an immediate C−C bond formation with the α-carbon of the vinylidene fragment by reductive elimination, affording the second hydride ligand and the benzofuryl ligand. Formation of the stable five-membered benzofuryl ring appears to be the major driving force to induce the C−C bond formation.

Generation of the thermodynamically more stable benzofuryl derivative **10** during the initial thermolysis of **4** appears to be due a formal 1,2-hydrogen migration on the benzofuryl segment. The isolation of **10** by heating of **9** in xylenes provides the necessary support for this postulation. It should be stressed that the $\sigma + \pi$ mode of the alkenyl (furyl) ligand is retained during the conversion from **9** to **10**. The electron-withdrawing effect of the oxygen atom in **9** appears to increase the acidity of the nearby C−H group and makes the hydrogen atom more susceptible to migration. Steric effect is less influential because there is no visible interligand repulsion between the benzofuryl fragment and the Os−CO ligands in **9**.

**Hydrogenation of the Acetylide Complexes 3.** Hydrogenation of the $CH_2OMe$ derivatives **3** has been conducted to show the fate of the acetylide in the presence of $H_2$. This reaction affords four compounds which are produced through two distinct pathways based on their molecular structures (Scheme 6). The first pathway comprises the clusters **11** and **12**, while complexes **13** and **14**, both possessing the $\mu_4$-carbide

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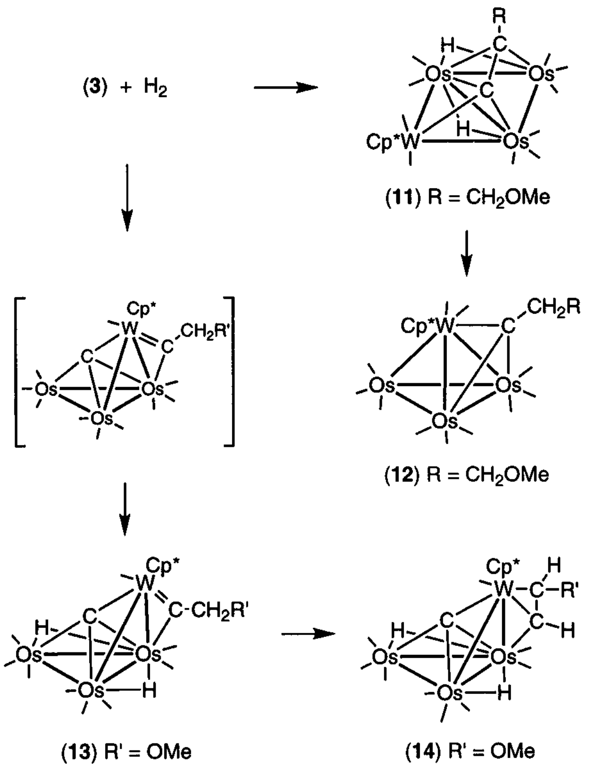
[34] (a) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Ziller, J. W.; Beannan, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1144. (b) Park, J. T.; Chi, Y.; Shapley, J. R.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1994**, *13*, 813. (c) Dutta, T. K.; Vites, J. C.; Fehlner, T. P. *Organometallics* **1986**, *5*, 385. (d) Hills, M. M.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597.

**Scheme 6**



atom, are involved in the second. It is clear that the formation of **11** through addition of $H_2$ molecule to the cluster framework is required, as heating **11** under CO afforded **12** in high yields. The vinylidene intermediate has been invoked to account for the similar transformation.[35]

In contrast, the second pathway requires prior C−C bond cleavage to afford a carbido−alkylidyne intermediate, which is identical with that observed for **5**, as observed in the previous section. This intermediate then reacts to give **13** by removal of a CO ligand and addition of $H_2$. In accordance with this postulation, treatment of **7a** with $D_2$ led to the clean transformation to the deuteride-labeled clusters Cp*WOs$_3$($\mu_4$-C)($\mu$-D)$_2$($\mu$-CCH$_2$OMe)(CO)$_9$ (**13**-D) and Cp*WOs$_3$($\mu_4$-C)($\mu$-D)$_2$($\mu$-CHCHOMe)(CO)$_9$ (**14**-D), respectively.

The conversion from **13** to **14** demands a formal H migration from the methylene group to the α-carbon of the alkylidyne ligand. The participation of hydrides in this alkylidyne to alkenyl transformation is safely excluded, as heating the $D_2$-substituted derivative **13**-D produced only the corresponding **14**-D; no scrambling of deuteride and the hydrogen of alkenyl ligand was detected by $^1$H NMR spectroscopy. This isomerization proceeded in the absence of CO in much lower yield. Moreover, the 1,2-H migration in the alkylidyne ligand resembles a few precedents in the literature.[36]

**Summary.** In this article, we report the synthesis of a variety of WOs$_3$ complexes bearing acetylide ligands. We also show that the acetylide groups can undergo the novel C−C bond cleavage to afford carbide and alkylidyne ligands. In the presence of $H_2$, the formation of alkylidyne through transfer of hydrides to the acetylide group is as important as the direct C−C bond scission. The latter is analogous to the scission of coordinated alkyne, taking place on metal cluster complexes, giving two alkylidyne fragments.[37] The reactivity and the destination of the resulting alkylidyne ligand in our system can be altered profoundly by variation of the substituent R. For example, the CCPh fragment undergoes reversible C−C bond cleavage. The incorporation of methylene and phenyl functional groups premits the conversion to the vinylidene or the furyl fragments via subsequent C−H activation, orthometalation, and reductive coupling. The vinylidene complexes produced display a reduced reactivity with the carbide in re-forming the acetylide ligand. In the extreme case of benzofuryl complexes **9** and **10**, there is absolutely no coupling with the carbide atom, even under pressurized CO atmosphere. This result will be discussed in a forthcoming paper.

**Acknowledgment.** We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 85-2113-M007-008).

**Supporting Information Available:** Tables of atomic coordinates and the corresponding anisotropic thermal parameters for complexes **8**−**11** and **13** (20 pages). Ordering information is given on any current masthead page.

OM960959O

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