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Characterization of the Oxo–Alkylidyne Complex $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ Resulting from Acyl Ligand C–O Bond Scission. Interconversion of Alkylidyne, Alkylidene, Vinylidene, and Alkyne Ligand Moieties in a Single Heterometallic Cluster System

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Cleavage of the acyl C—O bond in the mixed-metal cluster $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (1) ($Cp = \eta^5\text{-}C_5H_5$, $Tol = p\text{-}C_6H_4CH_3$) is effected in refluxing toluene, with formation of the oxo—alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (3). Treatment of 3 with carbon monoxide (5 atm) in toluene at 110 °C provides an adduct $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2), which is an observable intermediate in the formation of 3. Complex 3 reacts with dihydrogen to afford a mixture of two isomeric hydrido—oxo—alkylidene complexes, $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (4a,b). A third isomer 4c is produced from a mixture of 4a and 4b either by thermolysis in boiling xylene or by treatment with hydrochloric acid. Pyrolysis of 3 in boiling toluene gives a hydrido–vinylidene complex $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}C{=}CHTol)$ (5), which undergoes further thermal reaction in boiling xylene to produce a hydrido—alkyne complex $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}CHCTol)$ (6). Compounds 2, 3, 4a–c, 5, and 6 have been isolated as crystalline solids and characterized by spectroscopic (IR, MS, and ^1H and ^{13}C NMR) and analytical data. The structure of 2 has been determined by a single crystal X-ray diffraction study. Complex 2 crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 9.988(1) Å, b = 17.673(2) Å, c = 15.940(2) Å, β = 93.00(1)°, V = 2809.9(6) Å^3, and D(calc) = 2.91 g cm^{-3} for Z = 4 and molecular weight = 1232.83. The structure solution was refined to R_f = 5.4% for all 3679 diffraction data (R_f = 2.9% for those 2714 reflections with $|F_o| > 6\sigma(|F_o|)$). The WOs_3 core of the molecule has a "butterfly" arrangement, with a dihedral angle of 138.4° between the W—Os(2)—Os(1) and the W—Os(2)—Os(3) planes and bond lengths of W—Os(1) = 2.755(1), W—Os(2) = 2.842(1), W—Os(3) = 2.710(1), Os(1)—Os(2) = 2.823(1), and Os(2)—Os(3) = 2.755(1) Å. An oxo ligand bridges the W—Os(1) bond, with W—O(1) = 1.801(8) and Os(1)—O(1) = 2.137(8) Å; the angle W—O(1)—Os(1) = 88.4(3)°. The μ_3-alkylidyne ligand caps the W—Os(1)—Os(2) face, with W—C(1) = 1.97(1), Os(1)—C(1) = 2.20(1), and Os(2)—C(1) = 2.18(1) Å.

Introduction

One of the characteristic features of metal cluster chemistry is the promotion of bond scission and bond formation reactions involving attached organic groups.[1] In a preliminary communication[2a] we reported that thermolysis of the heterometallic cluster $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (1)[3] ($Cp = \eta^5\text{-}C_5H_5$; $Tol = p\text{-}C_6H_4CH_3$) in refluxing toluene induces scission of the acyl C—O bond and generates an oxo—alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (3). Complex 3 has been shown to undergo substitution as well as addition reactions with phosphorus donors.[4] Further studies on the reactivity of 3 have led to the isolation of a new species resulting from C—O bond scission, $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2), which can be synthesized directly from carbonylation of 3 (see Scheme 1).

The oxo—alkylidyne complex 3 also reacts with dihydrogen to provide a mixture of two isomers of the hydrido—oxo—alkylidene complex, $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (4a,b). Pyrolysis of 3 in boiling toluene (110 °C) results in oxidative addition of a benzylic C—H bond to the metal framework to form a hydrido—vinylidene complex $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}C{=}CHTol)$ (5). This vinylidene complex 5 can be converted to an alkyne complex $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}CHCTol)$ (6) at higher temperatures (140 °C) or hydrogenated to produce the alkylidene complexes 4a,b

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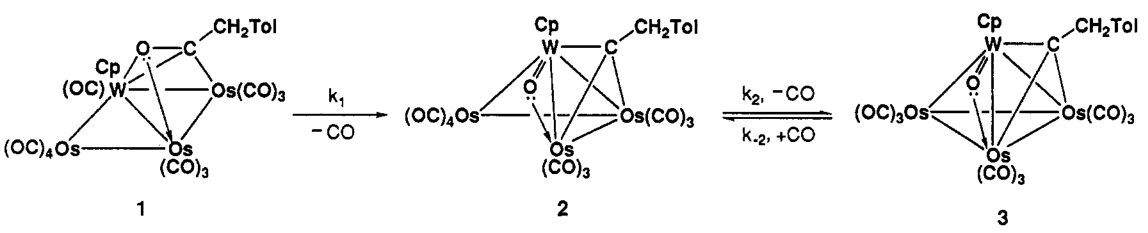
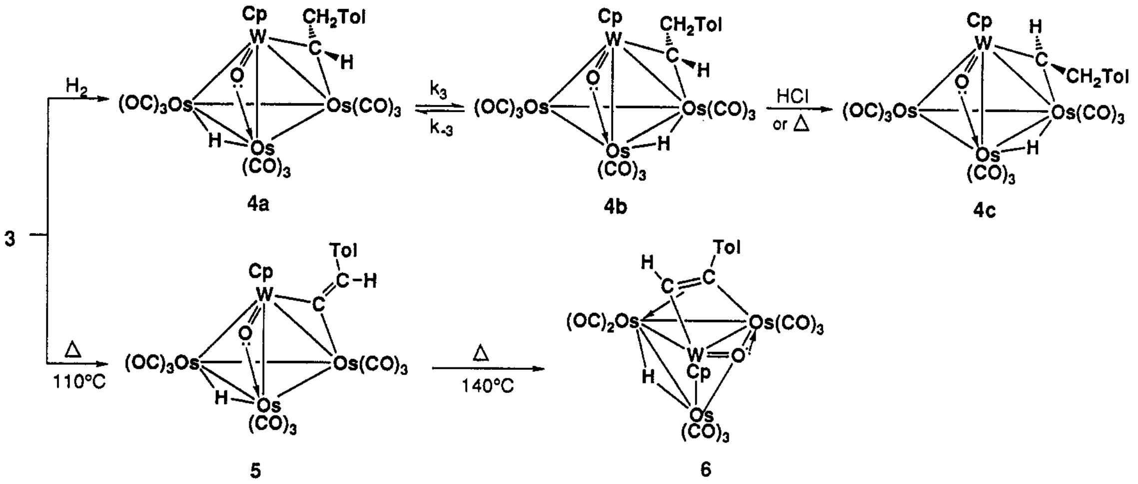
Scheme 1



Scheme 2



(see Scheme 2). We now report the full details of the chemistry shown in Schemes 1 and 2.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware. Solvents were dried appropriately before use. The progress of reactions was monitored by analytical thin-layer chromatography (Silica Gel tlc plates, Eastman). Preparative thin-layer plates were prepared from Silica Gel G (Type 60, E. Merck). Complex 1 was prepared by the procedure described in the literature.[3]

Mass spectra were recorded by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois by using either a Varian-MAT CH-5 (EI) or a Varian MAT-MAT-731 (FD) mass spectrometer. All *m/z* values are referenced to ^{184}W and ^{192}Os. Infrared spectra were obtained on a Perkin-Elmer 281B spectrophotometer. Both ^{1}H NMR (360 MHz) and ^{13}C NMR (90.4 MHz) spectra were recorded on a Nicolet NT-360 spectrometer. Elemental analyses were provided by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

Synthesis of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (3). Dark red compound 1 (59.5 mg, 0.0472 mmol) was dissolved in a mixture of dichloromethane (25 mL) and acetonitrile (10 mL). An acetonitrile solution (10 mL) of anhydrous trimethylamine oxide (3.6 mg, 0.0479 mmol) was added dropwise at room temperature. The solvent was evaporated *in vacuo*, and a toluene solution of the residue was heated to reflux for 15 min. The solvent was evaporated on a rotary evaporator and the crude product was purified by preparative tlc (pentane:dichloromethane, 2:3) to give 3 (46.5 mg, 0.0377 mmol, 80%, R_f = 0.26) as a brownish black solid. Direct pyrolysis of 1 in refluxing toluene (ca. 30 min) also provided 3 in comparable yield (ca. 80%) but contaminated with a second component (<10%) that was very difficult to eliminate by tlc. The minor species was later proved to be 2 by direct synthesis.

Compound 3. Anal. Calcd for $C_{23}H_{14}O_{10}WOs_3$: C, 22.93; H, 1.17. Found: C, 22.86; H, 1.30. EI mass spectrum (70 eV): *m/z* 1210 (M$^+$), 1210 − 28*x*, *x* = 1–9 (M$^+$ − *x*CO). IR (C_6H_{12}): ν(CO) 2075 (m) 2040 (s), 2028 (vs), 2008 (vw), 1997 (w), 1989 (m), 1972 (m), 1961 (w), 1954 (vw) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.3–7.1 (4H, m, $C_6H_4CH_3$), 5.75 (5H, s, C_5H_5), 5.25 (1H, d, $^2J_{HH}$ = 15.2 Hz, μ_3-CC*H*HTol), 4.46 (1H, d, $^2J_{HH}$ = 15.2 H, μ_3-CCH*H*Tol), 2.36 (3H, s, $C_6H_4CH_3$). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 220.8 ($^1J_{CW}$ = 105 Hz, μ_3-*C*CH$_2$Tol), 61.9 (t, $^1J_{CH}$ = 129.7 Hz, μ_3-C*C*H$_2$Tol); δ 195.2, 188.7, 187.7, 182.5, 179.9, 179.6, 178.6, 175.0, 166.2 (all Os–*C*O).

Synthesis of $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2). A toluene solution of $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2) (17.9 mg, 0.015 mmol) was placed in a 200-mL pressure bottle. A partial vacuum was drawn over the toluene solution; then the bottle was charged with carbon monoxide to a pressure of 62 psig. After the solution was heated at 110 °C for 1 h, the solvent was evaporated under vacuum. The residue was purified by preparative tlc (pentane:dichloromethane, 2:3) to provide 2 as a dark red crystalline solid (15 mg, 0.0122 mmol, 82%) after recrystallization from carbon tetrachloride–hexane. Crystals of 2 suitable for X-ray diffraction were grown from diethyl ether–hexane at room temperature.

Compound 2. Anal. Calcd for $C_{24}H_{14}O_{11}WOs_3$: C, 23.38; H, 1.14. Found: C, 23.55; H, 1.27. FD mass spectrum: *m/z* 1238 (M$^+$). IR (C_6H_{12}): ν(CO) 2097 (s), 2056 (vs), 2039 (vs), 2021 (vs), 2015 (vs), 1998 (m), 1988 (s), 1974 (m), 1967 (m), 1945 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 18 °C): δ 7.35–7.10 (4H, m, $C_6H_4CH_3$), 6.30 (1H, d, $^2J_{HH}$ = 17.5 Hz, μ_3-CC*H*HTol), 5.86 (5H, s, C_5H_5), 5.35 (1H, d, $^2J_{HH}$ = 17.5 Hz, μ_3-CCH*H*Tol), 2.33 (3H, s, $C_6H_4CH_3$). ^{13}C NMR ($CDCl_3$, 17 °C): δ 220.7 ($^1J_{CW}$ = 105 Hz, μ_3-*C*CH$_2$Tol); δ 185.5, 183.7 ($^2J_{CC}$ = 35.4 Hz), 182.7 ($^2J_{CC}$ = 35.4 Hz), 182.0, 181.3, 178.4, 178.0, 174.7, 173.7 (all Os–*C*O).

Synthesis of $CpWOs_3(CO)_9\text{-}(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (4a,b). Dihydrogen was bubbled with a gas dispersion tube through a red solution (50 mL) of compound 1 (47.2 mg, 0.0374 mmol) in toluene (60 mL) at 110 °C. After 1 h the color of the solution had turned from red to orange and the reaction was stopped. Purification by preparative tlc in pentane–dichloromethane (3:2) provided a mixture of two isomers (4a,b, 40.6 mg, 0.0336 mmol, 90%, R_f = 0.25) as an orange solid. Crystallization of pure 4a was effected by recrystallization of the isomeric mixture from methanol–dichloromethane solution.

Compound 4a. Anal. Calcd for $C_{23}H_{16}O_{10}WOs_3$: C, 22.89; H, 1.34. Found: C, 22.96; H, 1.19. FD mass spectrum: *m/z* 1212

(M^+). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.3–7.1 (4H, m, $C_6H_4CH_3$), 6.08 (5H, s, C_5H_5), 5.80 (1H, dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.4 Hz, μ-$CHCH_2Tol$), 4.06 (1H, dd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 6.4 Hz, μ-CHCHHTol), 3.60 (1H, dd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 8.5 Hz, μ-CHCHHTol), 2.38 (3H, s, $C_6H_4CH_3$), −16.93 (1H, s, Os–H–Os). ^{13}C NMR (CD_2Cl_2, −20 °C): δ 187.6, 186.4, 182.6, 181.1, 178.4 ($^2J_{CH}$ = 4.7 Hz), 176.7, 174.3, 170.7 ($^2J_{CH}$ = 11.1 Hz), 168.1 (all Os–CO); δ 131.6 ($^1J_{CH}$ = 132.6 Hz, μ-$CHCH_2Tol$).

Compound 4b. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.08 (4H, s, $C_6H_4CH_3$), 6.11 (5H, s, C_5H_5), 4.95 (1H, dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.4 Hz, μ-$CHCH_2Tol$), 3.71 (1H, dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 6.4 Hz, μ-CHCHHTol), 3.44 (1H, dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 8.7 Hz, μ-CHCHHTol), 2.37 (s, 3H, $C_6H_4CH_3$), −18.87 (1H, s, Os–H–Os). ^{13}C NMR (CD_2Cl_2, −20 °C): δ 192.2, 183.2, 182.1, 181.7, 176.2, 171.9, 170.2 ($^2J_{CH}$ = 10.9 Hz), 169.6, 169.2 ($^2J_{CH}$ = 7.1 Hz) (all Os–CO); δ 124.7 ($^1J_{CH}$ = 131.5 Hz, μ-$CHCH_2Tol$).

Mixture of 4a,b. IR (C_6H_{12}): ν(CO) 2086 (s), 2059 (m), 2050 (vs), 2031 (m), 2025 (vs), 2009 (m), 2004 (m), 1987 (s), 1958 (m), 1938 (w) cm^{-1}.

Reaction of 4a,b with Aqueous HCl. Orange-red crystals of **4a,b** (12.1 mg, 0.0100 mmol) were dissolved in acetone (25 mL), and then 6 M aqueous hydrochloride acid (0.3 mL) was added. The reaction mixture was heated to reflux for 26 h. The solution was dried and neutralized with anhydrous potassium carbonate. The mixture was filtered, and the solvent was evaporated. Orange crystals of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**4c**, 9.8 mg, 0.0081 mmol, 81%, R_f = 0.6) were isolated after purification by preparative tlc (pentane:dichloromethane, 1:1). EI mass spectrum (70 eV): m/z 1212 (M^+) 1212 − 28x, x = 1–9 ($M^+ - x$CO). IR (C_6H_{12}): ν(CO) 2088 (s), 2059 (vs), 2025 (vs), 2018 (s), 2007 (m), 1999 (w), 1992 (m), 1958 (w), 1940 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.6–7.12 (4H, m, $C_6H_4CH_3$), 6.13 (1H, dd, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 10.8 Hz, μ-$CHCH_2Tol$), 5.55 (5H, s, C_5H_5), 5.48 (1H, dd, $^2J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 5.8 Hz, μ-CHCHHTol), 2.61 (1H, dd, $^2J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 10.8 Hz, μ-CHCHHTol), 2.39 (3H, s, $C_6H_4CH_3$), −18.34 (1H, s, Os–H–Os). ^{13}C NMR (CD_2Cl_2, 20 °C): δ 192.1, 185.3, 184.4, 181.2, 175.4, 174.1, 171.6 ($^2J_{HH}$ = 12.0 Hz), 170.2, 168.2 ($^2J_{CH}$ = 7.9 Hz) (all Os–CO); δ 12.96 ($^1J_{CH}$ = 141.5 Hz, μ-$CHCH_2Tol$).

Thermolysis of 4a,b. A xylene (mixed isomers) solution (10 mL) of **4a,b** (19 mg, 0.016 mmol) was heated under reflux for 2 h. After evaporation of the solvent *in vacuo*, the products were purified by preparative tlc (pentane:dichloromethane, 1:1) and recrystallization to provide isomer **4c** (5.8 mg, 0.0048 mmol, 31%) as an orange-red powder. Some $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}C{=}CHTol)$ (**5**) was also observed on the preparative tlc plate but its isolation was not attempted. A better yield of **4c** can be obtained, however, from the solid state pyrolysis of **4a,b** at 185 °C for 5 min. In this case, 10.5 mg of isomer **4c** (57%) was isolated from 18.5 mg of the starting material following the separation.

Synthesis of $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CCHTol)$ (5). A toluene solution of **3** (5.6 mg, 0.0044 mmol) was heated to reflux. After 2 h analytical tlc indicated that compound **3** had completely reacted. Evaporation of the solvent and purification by preparative tlc (pentane:dichloromethane, 1:1) provided compound **5** (2.9 mg, 0.0023 mmol, 52%, R_f = 0.5) as a dark red solid. Compound **5** could also be synthesized in 36% isolated yield from direct pyrolysis of **1** in boiling toluene for 2.5 h. FD mass spectrum: m/z 1210 (M^+). IR (C_6H_{12}): ν(CO) 2089 (m), 2054 (vs), 2032 (vs), 2005 (s), 1988 (s), 1964 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.20 (1H, s, μ-CCHTol), 7.29–7.05 (4H, m, C_6H_4), 5.82 (5H, s, C_5H_5), 2.41 (3H, s, $C_6H_4CH_3$), −17.18 (1H, s, Os–H–Os). ^{13}C NMR (toluene-d_8, 20 °C): δ 187.6, 186.5, 185.0, 181.3, 179.7 ($^2J_{CH}$ = 6.1 Hz), 178.7, 174.8, 168.6 ($^2J_{CH}$ = 11.5 Hz), 168.0 (all (Os–CO).

Reaction of 5 with Dihydrogen. A toluene solution (20 mL) of **5** (13 mg, 0.011 mmol) was heated to reflux under 1 atm of dihydrogen for 15 h, the initial red-purple color turning to light orange. The solvent was evaporated and the crude product was purified by preparative tlc (dichloromethane:pentane, 1:1), followed by crystallization from dichloromethane–hexane to yield orange crystals of $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**4a,b**, 8.8 mg, 0.0072 mmol, 66%). The reaction with deuterium (D_2) was carried out by an identical procedure.

Synthesis of $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}CHCTol)$ (6). Method 1. A toluene solution (15 mL) of **4a** and **4b** (15 mg, 0.0124 mmol) was heated at reflux for 18 h. After evaporation of the solvent under vacuum, the reaction mixture was purified by preparative tlc (pentane:dichloromethane, 1:1). Recrystallization from dichloromethane–pentane provided isomer **4c** (1.2 mg, 0.0010 mmol, 8%) and **6** (2.4 mg, 0.0020 mmol, 16%) as crystalline solids. Pyrolysis under severe conditions, either in refluxing xylene or in the solid state at 180 °C, gave more **4c** and less **6**.

Method 2. A xylene solution (10 mL) of $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CCHTol)$ (**5**, 10 mg, 0.0083 mmol) was heated to reflux for 90 min with dinitrogen passing through the solution to remove carbon monoxide. The solvent was evaporated *in vacuo*, and the residue was purified by preparative tlc (dichloromethane:pentane, 1:1) to give a red-purple band followed by a light orange band. The latter band was extracted into dichloromethane, and evaporation gave the red-orange alkyne complex **6** (2.3 mg, 0.0020 mmol, 24%). Anal. Calcd for $WOs_3C_{22}H_{14}O_9$: C, 22.45; H, 1.20. Found: C, 22.61; H, 1.02. FD mass spectrum: m/z 1182 (M^+). IR (CCl_4): ν(CO) 2085 (s), 2050 (vs), 2024 (w), 2007 (vs), 1995 (w), 1983 (w), 1979 (w), 1940 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 18 °C): δ 10.63 (^1H, s, HCCTol), 7.27–7.12 (4H, m, $C_6H_4CH_3$), 5.88 (5H, s, C_5H_5), 2.34 (3H, s, $C_6H_4CH_3$), −10.29 (^1H, s, Os–H–Os). ^{13}C NMR ($CDCl_3$, 18 °C): δ 194.1, 182.6, 181.9, 181.0, 178.7, 176.4 ($^1J_{CH}$ = 9.8 Hz), 173.5, 166.9 (all Os–CO); δ 140.9 ($^1J_{CH}$ = 168 HZ, $^1J_{CW}$ = 110 Hz, HCCTol).

Synthesis of ^{13}C-Enriched Compounds. The ^{13}C-enriched $CpWOs(^*CO)_{11}[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ (**1***) was prepared from the reaction of ^{13}CO-enriched $H_2Os_3(^*CO)_{10}$ (ca. 50% enrichment) with $Cp(CO)_2W(CTol)$ by the reported procedure.[3] This complex was then utilized to prepare $CpWOs_3(^*CO)_{10}(\mu\text{-}O)(\mu_3\text{-}^*CCH_2Tol)$ (**2***), $CpWOs_3(^*CO)_9(\mu\text{-}O)(\mu_3\text{-}^*CCH_2Tol)$ (**3***), $CpWOs_3(^*CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}^*CHCH_2Tol)$ (**4a*–4c***), $CpWOs(^*CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}^*CCHTol)$ (**5***), and $CpWOs_3(^*CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}^*CHCTol)$ (**6***) by the procedures described above.

Kinetic Studies of C–O Bond Scission in 1. Sample solutions in toluene-d_8 were sealed in NMR tubes under vacuum. The tubes were placed in a constant temperature bath maintained at 105 °C. Tubes were withdrawn from the bath and cooled quickly to room temperature for periodic examination by ^1H NMR spectroscopy. Reactions were followed by measuring the signal intensity (I) of the cyclopentadienyl resonance of the starting complex. Plots of $\log(I_o/I_t)$ vs time were linear, and k_{obs} is the slope of this line as determined by least-squares fitting.

Collection of X-ray Diffraction Data for 2. A bright red crystal of complex **2** was sealed in a thin walled glass capillary and accurately aligned on the Syntex $P2_1$ automated four-circle diffractometer. Subsequent set-up operations (determination of accurate cell dimensions and orientation matrix) and collection of the intensity data were carried out according to the previously described procedures of this laboratory;[5] details appear in Table 1. The systematic absences for $h0l$ reflections ($h + l = 2n + 1$) and $0k0$ reflections ($k = 2n + 1$) uniquely define the space group as $P2_1/n$ with equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

All data were corrected for the effects of absorption and for Lorentz and polarization factors, were converted to unscaled $|F_o|$ values, and were placed on an approximate absolute scale by means of a Wilson plot. Those reflections with I(net) < 0 were assigned the value $|F_o| = 0$.

Structure and Refinements. All crystallographic calculations were performed using a locally modified version of the Syntex XTL program package.[6] The structure was solved by

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[5] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, *16*, 265.

[6] Syntex XTL Operations Manual, Syntex Analytical Instruments, Cupertino, California, 1976.

Table 1. Experimental Data for the X-ray Diffraction Study of $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2)

(A) Unit Cell Data

crystal system: monoclinic	space group $P2_1/n$
$a = 9.988(1)$ Å	$Z = 4$
$b = 17.673(2)$ Å	formula $C_{24}H_{14}O_{11}Os_3W$
$c = 15.940(2)$ Å	mol wt: 1232.83
$\beta = 93.00(1)°$	D(calcd) = 2.91 g cm^3
$V = 2809.9(6)$ Å^3	$T = 20$ °C (293 K)

(B) Collection of X-ray Diffraction Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα (λ = 0.710 730 Å)
monochromator: highly orientated (pyrolytic) graphite; equatorial mode with $2\theta(\mu)$ = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction
reflections measured: $+h,+k,+l$ for 2θ = 5.5–45.0°; 3924 total merged to 3679 unique data
scan type: coupled θ(crystal) – 2θ(counter)
scan width: symmetrical, $[1.8 + \Delta(\alpha_1 - \alpha_2)]°$
scan speed: variable, 2.0–10.0° in 2q
standard reflections: three collected after each batch of 97 reflections; no fluctuations were observed
absorption correction: μ(Mo Kα) = 187.0 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) between ψ-scans of close-to-axial reflections

direct methods using the program MULTAN.[7] An "E-map" revealed the positions of the four metal atoms; all remaining non-hydrogen atoms were located from a single difference-Fourier synthesis. Full matrix least-squares refinement led to final convergence with residuals[8] R_F = 5.4% R_{wF} = 3.6% and GOF = 1.18 for 352 variables refined against 3679 data. Residuals for those 3069 reflections with $|F_o| > 3\sigma(|F_o|)$ were R_F = 3.8% and R_{wF} = 3.3%, and for those 2714 reflections with $|F_o| > 6\sigma(|F_o|)$ were R_F = 2.9% and R_{wF} = 3.0%.

Throughout the analysis the calculated structure factors were based upon the analytical expression for the neutral atoms' form factors;[9a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms.[9b] Atomic coordinates are collected in Table 2, and anisotropic thermal parameters are listed in Table S1, which appears in the supplementary material. Hydrogen atoms were included in calculated positions with d(C–H) = 0.95 Å.[10]

Results and Discussion

Synthesis and Characterization of 2 and 3. Pyrolysis of $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (1) in boiling toluene for 30 min provides a new cluster compound 3 in good yield (ca. 80%), but the product is accompanied by a much smaller amount (<10%) of a closely similar species that is now identified as 2 (see Scheme 1). A cleaner preparation of 3 is effected by initial decarbonylation of 1 with the Me_3NO/MeCN reagent, followed by pyrolysis in refluxing toluene for 15 min. Complex 2 is obtained in high yield from the reaction of 3 with carbon monoxide under pressure (5 atm).

The formulations for compounds 2 and 3 are established by mass spectroscopic and analytical data. Furthermore, the ^1H NMR spectrum of 2 is very similar to that of 3: both exhibit signals for the Cp ligand, the tolyl group, and the diastereotopic benzylic hydrogens. The ^{13}C NMR spectra are most definitive, since the acyl carbon resonance of 1 at δ 163 is shifted dramatically downfield to the δ 221 position of the alkylidyne carbon resonances in 2 and 3. A single crystal X-ray diffraction study of 3[2] confirmed its characterization as an oxo–alkylidyne cluster, and analogous information for 2 is provided here.

Table 2. Final Positional Parameters for $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2)

atom	x	y	z
W	0.20811(5)	0.20714(3)	0.65685(3)
Os(1)	–0.04343(5)	0.23893(3)	0.58645(3)
Os(2)	0.18241(5)	0.27223(3)	0.49374(3)
Os(3)	0.36926(6)	0.15220(3)	0.53953(4)
O(1)	0.0665(8)	0.1450(4)	0.6390(5)
O(11)	–0.210(1)	0.1372(7)	0.4661(8)
O(12)	–0.196(1)	0.3813(7)	0.5324(9)
O(13)	–0.211(1)	0.2265(7)	0.7412(8)
O(21)	0.040(1)	0.4120(6)	0.4218(7)
O(22)	0.108(1)	0.1685(6)	0.3441(7)
O(23)	0.433(1)	0.3438(6)	0.4281(7)
O(31)	0.468(2)	0.1395(7)	0.3606(9)
O(32)	0.538(2)	0.0328(8)	0.632(1)
O(33)	0.566(1)	0.2770(7)	0.6013(8)
O(34)	0.136(1)	0.0427(6)	0.4996(7)
C(11)	–0.144(2)	0.1767(9)	0.5111(8)
C(12)	–0.140(2)	0.327(1)	0.550(1)
C(13)	–0.150(2)	0.2333(9)	0.684(1)
C(21)	0.088(1)	0.3585(8)	0.4512(9)
C(22)	0.138(1)	0.2073(8)	0.4002(9)
C(23)	0.341(2)	0.3160(8)	0.4554(9)
C(31)	0.435(2)	0.143(1)	0.428(1)
C(32)	0.475(2)	0.078(1)	0.595(1)
C(33)	0.490(1)	0.2311(9)	0.5759(9)
C(34)	0.222(2)	0.0827(8)	0.5155(9)
C(1)	0.137(1)	0.3064(6)	0.6206(8)
C(2)	0.125(1)	0.3884(7)	0.6539(8)
C(3)	0.260(2)	0.4277(6)	0.6751(9)
C(4)	0.296(2)	0.4435(7)	0.7595(9)
C(5)	0.417(2)	0.4750(7)	0.781(1)
C(6)	0.507(2)	0.4873(8)	0.722(1)
C(7)	0.469(2)	0.4762(9)	0.638(1)
C(8)	0.348(2)	0.4458(7)	0.6150(9)
C(9)	0.647(3)	0.518(1)	0.746(2)
C(51)	0.399(1)	0.1877(7)	0.7545(9)
C(52)	0.299(2)	0.1369(8)	0.7765(9)
C(53)	0.192(2)	0.181(1)	0.802(1)
C(54)	0.223(2)	0.257(1)	0.7919(9)
C(55)	0.351(2)	0.2599(8)	0.766(1)

Crystal Structure of 2. The crystal of 2 contains an ordered racemic arrangement of the two enantiomeric forms of the chiral $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ molecule; there are no abnormally short contacts between the molecular units. The overall molecular geometry and the scheme used for labeling atoms are illustrated in Figure 1, and interatomic distances and angles are collected in Tables 3 and 4.

The molecule of 2 has a "butterfly" arrangement of metal atoms with a dihedral angle of 138.4° between the W—Os(2)—Os(1) and W—Os(2)—Os(3) planes. This is the usual arrangement for a species associated with 62 outer valence electrons.[11] Compound 3, with only 60 valence electrons, has the expected closed, tetrahedral arrangement of metal atoms.[2] The osmium–osmium bond lengths in 2 are Os(1)—Os(2) = 2.823(1) and Os(2)—Os(3) = 2.894(1) Å as compared to the average Os—Os bond distance of 2.877(3) Å in $Os_3(CO)_{12}$.[12] The osmium—tungsten distances display the same order in both molecules of 2 and 3, Os(2)—W > Os(1)—W > Os(3)—W, but the average Os—W distance for 2 (2.769 Å) is larger than the average Os—W

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[7] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368.

[8] $R_F = 100(\sum||F_o| - |F_c||/\sum|F_o|)$; $R_{wF} = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

[9] (a) *International Tables for X-ray Crystallography*; Kynoch Process: Birmingham, England, 1974; Vol. 4, pp 99–101. (b) *Ibid.*, pp 149–150.

[10] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[11] Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437.

[12] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

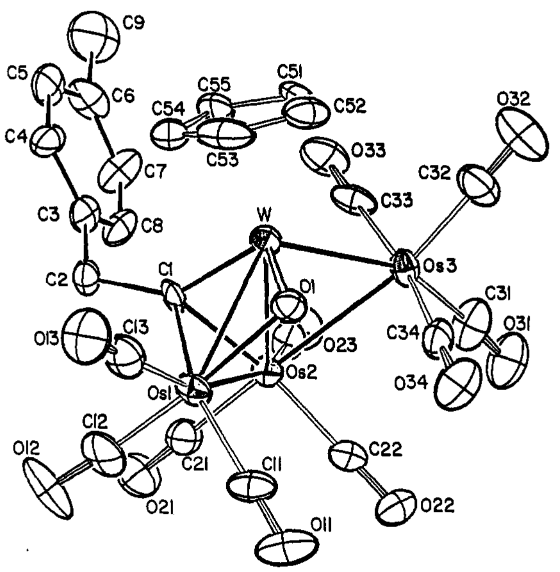

Figure 1. Molecular geometry and atomic labeling scheme for $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3CCH_2Tol)$ (**2**) (ORTEP-II diagram, 30% probability evelopes for all non-hydrogen atoms).

Table 3. Interatomic Distances (Å) and Esd's for $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_3Tol)$ (2)

(A) Metal–Metal Bond Lengths			
Os(1)–Os(2)	2.823(1)	Os(2)–W	2.842(1)
Os(2)–Os(3)	2.894(1)	Os(3)–W	2.710(1)
Os(1)–W	2.755(1)		
(B) Metal–Alkylidyne Bond Lengths			
Os(1)–C(1)	2.20(1)	W–C(1)	1.97(1)
Os(2)–C(1)	2.18(1)		
(C) Metal–Oxygen Bond Lengths			
Os(1)–O(1)	2.14(1)	W–O(1)	1.80(1)
(D) Distances within the μ_3-CCH_2Tol Ligand			
C(1)–C(2)	1.55(2)	C(6)–C(9)	1.54(3)
C(2)–C(3)	1.54(2)	C(6)–C(7)	1.38(3)
C(3)–C(4)	1.40(2)	C(7)–C(8)	1.36(3)
C(4)–C(5)	1.35(2)	C(8)–C(3)	1.37(2)
C(5)–C(6)	1.35(3)		

Table 4. Interatomic Angles (deg), with Esd's for $CpWO_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (2)

(A) Intermetallic Angles			
Os(1)–W–Os(2)	60.54(2)	Os(1)–Os(2)–W	58.20(2)
Os(1)–O–Os(3)	110.72(2)	Os(1)–Os(2)–Os(3)	103.74(2)
Os(2)–W–Os(3)	62.76(2)	Os(3)–Os(2)–W	56.38(2)
Os(2)–Os(1)–W	61.26(2)	Os(2)–Os(3)–W	60.85(2)
(B) M–M–CO Angles			
W–Os(1)–C(11)	125.8(4)	Os(1)–Os(2)–C(23)	163.6(4)
W–Os(1)–C(12)	136.8(5)	Os(3)–Os(2)–C(21)	168.6(4)
W–Os(1)–C(13)	100.9(5)	Os(3)–Os(2)–C(22)	83.0(4)
Os(2)–Os(1)–C(11)	101.6(4)	Os(3)–Os(2)–C(23)	80.8(4)
Os(2)–Os(1)–C(12)	94.5(5)	W–Os(3)–C(31)	154.9(6)
Os(2)–Os(1)–C(13)	156.9(5)	W–Os(3)–C(32)	105.4(5)
W–Os(2)–C(21)	132.1(4)	W–Os(3)–C(33)	85.2(4)
W–Os(2)–C(22)	118.4(4)	W–Os(3)–C(34)	83.8(4)
W–Os(2)–C(23)	115.0(4)	Os(2)–Os(3)–C(31)	94.2(6)
Os(1)–Os(2)–C(21)	87.6(4)	Os(2)–Os(3)–C(32)	166.2(5)
Os(1)–Os(2)–C(22)	97.0(4)	Os(2)–Os(3)–C(33)	85.9(5)
		Os(2)–Os(3)–C(34)	86.8(4)
(C) Os–C–O and C–Os–C Angles			
Os(1)–C(11)–O(11)	177(1)	C(11)–Os(1)–C(12)	92(1)
Os(1)–C(12)–O(12)	176(1)	C(11)–Os(1)–C(13)	101(1)
Os(1)–C(13)–O(13)	177(2)	C(12)–Os(1)–C(13)	90(1)
Os(2)–C(21)–O(21)	174(1)	C(21)–Os(2)–C(22)	96(1)
Os(2)–C(22)–O(22)	178(1)	C(21)–Os(2)–C(23)	88(1)
Os(2)–C(23)–O(23)	176(1)	C(22)–Os(2)–C(23)	99(1)
Os(3)–C(31)–O(31)	177(2)	C(31)–Os(3)–C(32)	100(1)
Os(3)–C(32)–O(32)	177(2)	C(31)–Os(3)–C(33)	96(1)
Os(3)–C(33)–O(33)	177(1)	C(31)–Os(3)–C(34)	93(1)
Os(3)–C(34)–O(34)	178(1)	C(32)–Os(3)–C(33)	92(1)
		C(32)–Os(3)–C(34)	93(1)
		C(33)–Os(3)–C(34)	169(1)
(D) Angles Involving O(1) or C(1)			
W–O(1)–Os(1)	88(3)	Os(1)–C(1)–C(2)	121(1)
W–Os(1)–O(1)	41(2)	Os(2)–C(1)–C(2)	127(1)
Os(1)–W–O(1)	51(3)	C(1)–W–O(1)	103(4)
Os(2)–W–O(1)	94(3)	C(1)–Os(1)–O(1)	86(4)
Os(3)–W–O(1)	99(3)	Os(1)–W–C(1)	52(4)
Os(2)–Os(1)–O(1)	88(2)	Os(1)–Os(2)–C(1)	50(3)
W–C(1)–Os(1)	83(4)	Os(2)–W–C(1)	50(4)
W–C(1)–Os(2)	86(1)	Os(3)–Os(2)–C(1)	98(3)
W–C(1)–C(2)	140(1)	Os(3)–W–C(1)	110(4)
C(1)–C(2)–C(3)	115(1)		
(E) Angles from "Cent"[a]			
Cent–W–Os(1)	134.8	Cent–W–O(1)	114.4
Cent–W–Os(2)	151.2	Cent–W–C(1)	114.8
Cent–W–Os(3)	114.0		

[a] "Cent" is the centroid of the Cp ring.

distance for **3** (2.711 Å). The oxo ligand, defined by O(1), bridges the W—Os(1) edge with distances that are suggestive of a W—O double bond [cf. W═O = 1.66(1) Å in $W({=}O)({=}CHCMe_3)(PEt_3)Cl_2$[13a] and W═O = 1.70(2) Å in $W({=}O)({=}CHCMe_3)(PMe_3)_2Cl_2]$[13b] and an Os←:O coordinate bond of unit bond order. Both the W═O and Os—O distances are slightly shorter for **2** than for **3**. Table 5 compares interatomic distances and angles in the six compounds shown to contain a bent W═O:→Os system: **2**, **3**,[2] $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$,[14] $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}C{=}CHTol)$,[15] $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)$,[16] $Cp^*WOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_3)$[17] ($Cp^*$ = η^5-C_5Me_5), and $CpWOs_3(CO)_8(PPh_2Me)(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$.[4] The μ_3-alkylidyne ligand caps the W—Os(1)—Os(2) face, with individual metal—carbon distances W—C(1) = 1.97(1) Å. Os(1)—C(1) = 2.20(1) Å, and Os(2)—C(1) = 2.18(1) Å. The pattern of W—(μ_3-alkylidyne) bond lengths being shorter than Os—(μ_3-alkylidyne) bond lengths is normal and occurs also in $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$[18] [W—C = 1.98(2)–2.01(2) Å and Os—C = 2.14(2)–2.25(2) Å] and in $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-}H)$[18b] [W—C = 2.01(2) Å and Os—C = 2.19(2)–2.27(2) Å]; this presumably occurs to compensate for the electron-poor nature of tungsten in all these species. The O(1)···C(1) nonbonded separation in **2** is 2.96 Å, which is nearly 0.2 Å less than the value of 3.15 Å found in **3**.[2] All other distances and angles observed for **2** are in the normally accepted ranges.

Variable-Temperature ^{13}C NMR Studies of 2 and 3. Carbon-13 NMR spectra of ^{13}C-enriched **3***, $CpWOs_3({}^*CO)_9(\mu\text{-}O)(\mu_3\text{-}{}^*CCH_2Tol)$, were obtained over the temperature range −60 to +35 °C in CD_2Cl_2 (see Figure 2). The limiting low-temperature spectrum was obtained at −60 °C and is consistent with the nine nonequivalent carbonyl ligands and an alkylidyne ligand observed in the solid state structure. The resonance at δ 220.8 is assigned to the alkylidyne carbon. As the temperature is raised to 35 °C, one set of three resonances at δ 188.7, 182.5, and

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(15) Churchill, M. R.; Li, Y. J. *J. Organomet. Chem.* **1985**, *294*, 367.

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Table 5. Dimensions of the W(μ-O)Os Moiety in WOs$_3$ Clusters

complex	W—O (Å)	Os—O (Å)	W—Os (Å)	W—O—Os (deg)	ref
CpWOs$_3$(CO)$_{10}$(μ-O)(μ_3-CCH$_2$Tol) (**2**)	1.80(8)	2.137(8)	2.755(1)	88.4(3)	this work
CpWOs$_3$(CO)$_9$(μ-O)(μ_3-CCH$_2$Tol) (**3**)	1.812(7)	2.169(8)	2.663(1)	83.5(3)	2
CpWOs$_3$(CO)$_8$(PPh$_2$Me)(μ-O)(μ_3-CCH$_2$Tol)	1.810(8)	2.156(7)	2.641(1)	83.0(3)	4a
CpWOs$_3$(CO)$_9$(μ-H)(μ-O)(μ_3-CHCH$_2$Tol) (**4a**)	1.74(2)	2.17(2)	2.916(1)	96.0(7)	14
CpWOs$_3$(CO)$_9$(μ-H)(μ-O)(μ-C=CHTol) (**5**)	1.79(2)	2.13(2)	2.868(2)	93.6(9)	15
CPWOs$_3$(CO)$_8$(μ-H)(μ-O)(μ_3-η^2-C$_2$H$_2$)	1.761(8)	2.200(8)	2.885(1)	92.8(4)	16
Cp*WOs$_3$(CO)$_9$(μ-O)(μ_3-CCH$_3$)	1.84(1)	2.17(1)	2.653(1)		17

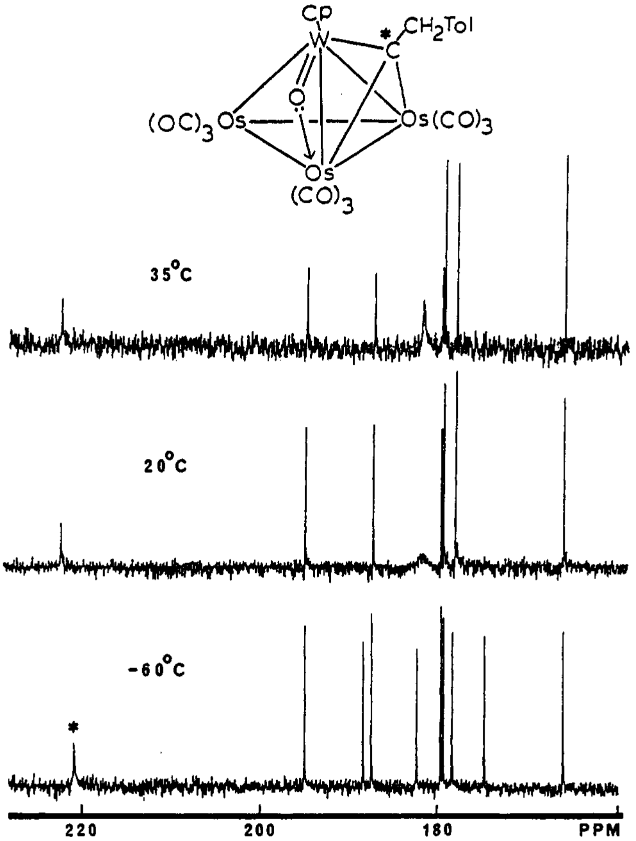

Figure 2. Variable-temperature ^{13}C NMR spectra (CD$_2$Cl$_2$) of **3***.

175.0 broadens and coalesces to a single resonance. Another set of three at δ 195.2, 187.7, and 179.9 starts to broaden, while the third set at δ 179.6, 178.6, and 166.2 remains sharp. This indicates that each osmium center has a different energy barrier for localized 3-fold exchange of carbonyl ligands. By comparison with the ^{13}C NMR spectrum of CpWOs$_3$(CO)$_8$(PPh$_2$Me)(μ-O)(μ_3-CCH$_2$Tol),[4] the structure of which has the phosphorus ligand replacing a carbonyl at the oxo–osmium center, the set of three carbonyls (at δ 179.6, 178.6, and 166.2) with the highest barrier and lowest average chemical shift in the spectrum of **3** can be assigned to the ligands attached to the oxo–osmium(1) center.

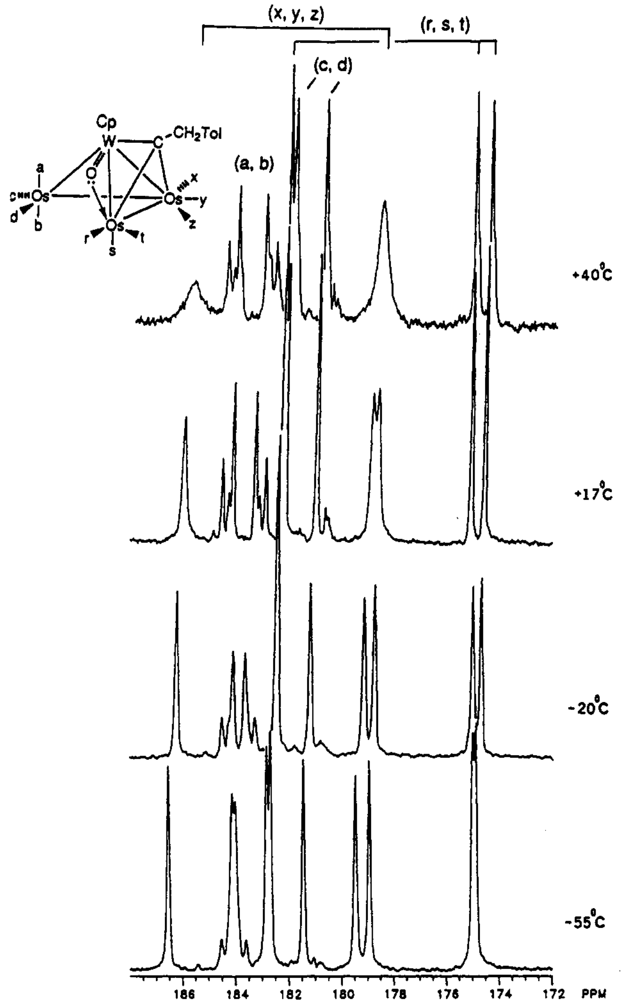

Figure 3. Variable-temperature ^{13}C NMR spectra (carbonyl region, toluene-d_8) of **2***.

The ^{13}C NMR spectrum of **2*** at room temperature displays resonances for ten osmium carbonyl ligands (see Figure 3). A strong coupling ($^2J_{CC}$ = 35.4 Hz) is observed for the carbonyl signals at δ 183.7 and 182.7 which therefore appear as an AB pattern overlapping a noncoupled doublet. This pattern is characteristic of inequivalent trans carbonyl ligands in a typical Os(CO)$_4$ unit;[19] it was observed also for **1**.[3] The remaining signals are assigned in groups on the basis of their line broadening behavior as the temperature is raised above room temperature. By 70 °C (not shown) three resonances (δ 185.5, 178.4, and 178.0 at 17 °C) have coalesced completely and two resonances (δ 181.6 and 180.3) are beginning to broaden along with the trans diaxial pair. The remaining three resonances (δ 182.0, 174.7, and 173.7) are assigned to the carbonyls on the oxo–osmium(1) center which again appear to have the highest barrier to localized carbonyl exchange.

In addition the chemical shifts of the carbonyl resonances show a notable temperature dependence. With decreasing temperature the AB pattern becomes progressively compressed; at −80 °C (not shown) only a single resonance is seen. Merging and crossing of various resonances in the rest of the spectrum also is evident. These changes cannot be due to a dynamic process since no line broadening is observed at −20 °C and below. Such large temperature dependent chemical shifts are unusual for osmium carbonyl clusters (cf. Figure 2) and are probably due in this case to temperature dependent rotomeric equilibria involving the CH$_2$Tol substituent, possibly correlated with flexing of the "butterfly" framework.[11]

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[19] Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* 1977, *128*, C9.

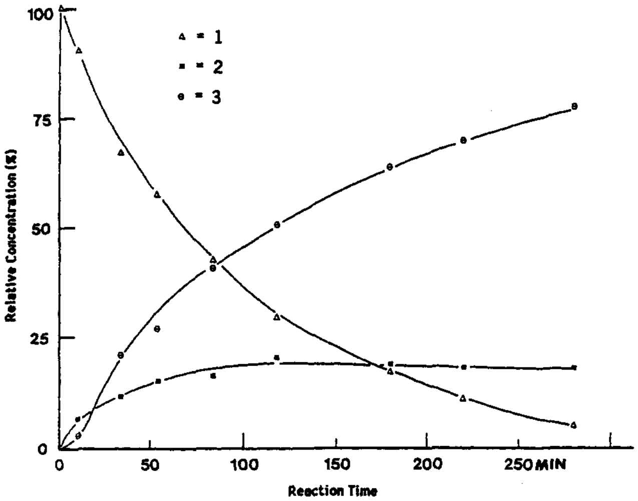
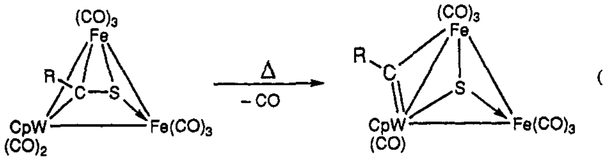


Figure 4. Relative intensities of the cyclopentadienyl ^1H NMR signals observed during the pyrolysis of 1 at 105 °C in toluene-d_8.

Kinetic Studies of C–O Bond Scission in 1. Monitoring the pyrolysis of 1 in toluene-d_8 at 105 °C by ^1H NMR spectroscopy reveals that the signals due to 2 are formed rapidly in the beginning, but as the reaction proceeds, the signals due to 3 become dominant (see Figure 4). Photolysis of 1 in toluene-d_8 at room temperature (low-pressure Hg lamp) also provides both complexes 2 and 3.

The disappearance of complex 1 provides a linear plot of $\log(I_0/I_t)$ vs time for over 3 half-lives; the first-order rate constant calculated from the slope is $k_1 = 1.65(8) \times 10^{-4}\ s^{-1}$. Direct pyrolysis of 2 at 105 °C showed first-order behavior over 1 half-life, with $k_2 = 5.3(1) \times 10^{-4}\ s^{-1}$, but the rate gradually slowed with time. This is consistent with CO inhibition, since the carbon monoxide released in the reaction is enclosed in the sealed NMR tube. Reversible formation of 2 from 3 is also consistent with the observed concentrations of 2 and 3 with time in the pyrolysis of 1, as shown in Figure 4, since attempts to fit these data to expressions appropriate for two sequential (irreversible) first-order reactions[20] did not provide a well defined rate constant for the second step. Equilibration of 2 and 3 under 1 atm of CO in toluene at 105 °C, followed by quenching to room temperature, provided a value of the ratio [2]:[3] = 0.29.

Mechanistic Features of the Acyl C—O bond Scission. An unsaturated cluster is needed in order to cleave the acyl C—O linkage and to generate strong interactions with the newly formed fragments. In both the thermolysis and photolysis of 1 the reaction is apparently initiated by W—CO dissociation. This is consistent with previous reports of alkyne C≡C bond cleavage in W/Os mixed metal clusters,[21] wherein elimination of a carbonyl ligand from a tungsten center has been demonstrated as the key process. Apparently, the W—CO bond is significantly weaker in comparison with the strong W═O and W—C bonds generated.[22] Furthermore, Stone and co-workers have shown that CO dissociation from tungsten also induces the cleavage of a thioacyl ligand on a WFe_2 framework (see eq 1).[23] Related C—O



(1)

bond scission reactions have also been observed in the acyl complex $Os_3(CO)_{10}(\mu\text{-}H)[\mu\text{-}C(O)CH_2W(CO)_3Cp]$[17] and in the tungsten bis(cyclopentanone) complex $W(C_5H_8O[\eta^2\text{-}O{=}C])_2Cl_2(PMePh_2)_2$.[24]

The exact pathway for converting 1 to 2 is not established, but some ideas concerning the mechanism are presented in Scheme 3. The sequence of steps involves (a) elimination of a carbonyl ligand from tungsten and (b) scission of the acyl C–O bond to form a bridging oxo ligand and bridging alkylidyne ligand. If the oxo is doubly bridging and the alkylidyne triply bridging (**A**) as in 2, then breaking the Os(1)–Os(2) interaction and forming the Os(1)–Os(3) bond is required. However, if the initial scission leads to a triply bridging oxo ligand and a doubly bridging alkylidyne ligand (**B**), then conversion of the alkylidyne to triply bridging and the oxo to doubly bridging gives 2 without requiring any Os–Os bond reorganization. The latter possibility is supported by the WFe_2(thioacyl) case[23] shown in eq 1 and by some rearrangements observed for a trimethyl phosphite derivative of 2.[4]

The transformation from 2 to 3 is a reversible butterfly to tetrahedral cluster rearrangement.[11,25] In a related $PtOs_3$ system, a butterfly form is generated upon reaction of the tetrahedral form with either CO or H_2.[25a] In the present case, CO causes the opening of the tetrahedral framework of 2, but H_2 reacts differently to form the alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHCH_2\text{-}Tol)$, which again has a closed structure (*vide infra*).

Reactivity of 3 with Dihydrogen. The tungsten oxo–alkylidyne compound 3 reacts readily with molecular hydrogen in refluxing toluene to afford an equilibrium mixture of isomeric hydrido–oxo–alkylidene clusters $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**4a,b**) (see Scheme 2). The mixture of complexes **4a,b** is not chromatographically separable but crystallizes from methanol–dichloromethane as pure **4a**. The crystal structure of **4a** has been reported.[14] The key stereochemical feature is that the CH_2Tol substituent is oriented away (*anti*) from the μ-oxo group that is associated with the same WOs_2 face as the bridging alkylidene group.

The ^1H NMR spectrum of each isomer in CD_2Cl_2 exhibits a hydride resonance (δ −16.93 for **4a** and −18.87 for **4b**) and three separate resonances of the AMX pattern with 1:1:1 relative intensities corresponding to the μ-alkylidene CH hydrogen (δ 5.80 for **4a** and 4.95 for **4b**) and the two diastereotopic benzylic CH_2 hydrogens (δ 4.06, 3.60 for **4a** and 3.71, 3.44 for **4b**). These resonances can be assigned on the basis of a deuterium-labeling study and a decoupling experiment. The ^{13}C NMR spectrum for ^{13}C-enriched **4a*,b*** $CpWOs_3(^*CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}^*CHCH_2Tol)$ shows nine signals of carbonyls bonded to osmium atoms and one μ-alkylidene carbon resonance [δ 131.6 ($^1J_{CH}$ = 132.6

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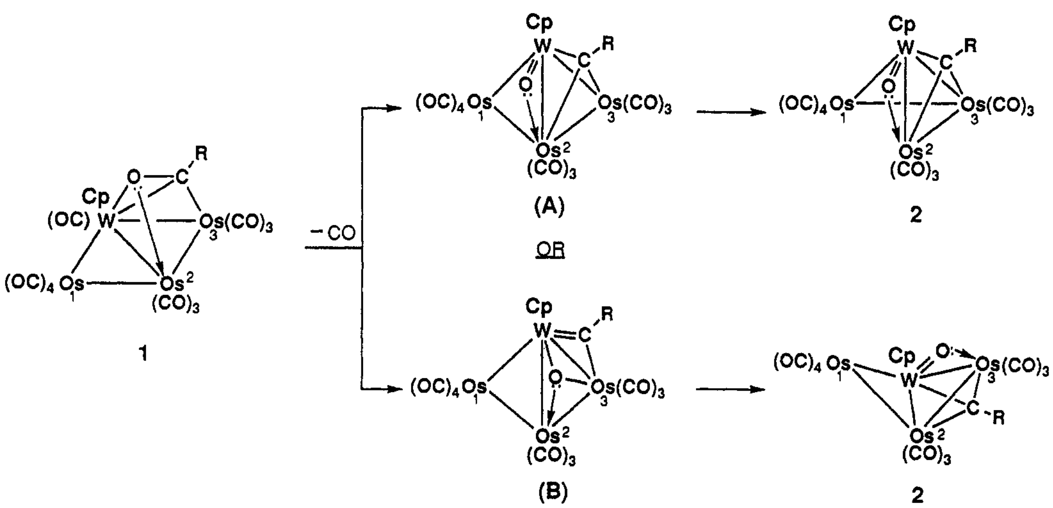
Scheme 3



Hz) for **4a** and 124.7 ($^1J_{CH}$ = 131.5 Hz) for **4b**], respectively. Two carbonyl resonances appear as doublets at δ 178.4 ($^2J_{CH}$ = 4.7 Hz) and 170.7 ($^2J_{CH}$ = 11.1 Hz) for **4a** and at δ 170.2 ($^2J_{CH}$ = 10.9 Hz) and 169.2 ($^2J_{CH}$ = 7.1 Hz) for **4b**, due to coupling to each μ-hydride ligand.

The hydride migration interconverting **4a** and **4b** was studied at 20 °C by ^{1}H NMR spectroscopy. Crystals of **4a** were dissolved in CD_2Cl_2 in an NMR tube and signals due to **4b** were observed to grow in as a function of time. Relative concentrations of the two isomers were measured by integration of the peaks at δ 5.80 for **4a** and at δ 4.95 for **4b** in the ^{1}H NMR spectra. The analysis according to reversible first-order kinetics gives excellent fits of experimental data: K_{eq} = [**4b**]/[**4a**] = 0.67(5), k_{obs} = 1.49(2) × 10^{-4}, k_3 = 6.0(4) × 10^{-5} s^{-1} and k_{-3} = 8.9(6) × 10^{-5} s^{-1}. The equilibration of the molybdenum–triosmium analogues of **4a** and **4b** has been shown to occur by hydride migration between edges of osmium–osmium bonds at significantly faster rates [K_{eq} = 0.981(3), k_3 = 4.95(2) × 10^{-3} s^{-1}, and k_{-3} = 5.05(2) × 10^{-3} s^{-1}].[26]

The third isomer **4c** of the hydrido–oxo–alkylidene complex is produced either by thermolysis of a mixture of **4a** and **4b** or by treatment with hydrochloric acid. Complex **4c** shows spectroscopic data essentially identical to those reported for the molybdenum analogue.[26] Therefore they are presumably isostructural and the CH_2Tol group in **4c** is oriented *syn* to the WOs_2 triangular face that is associated with the three edge-bridging groups. The ^{1}H and ^{13}C NMR spectra of **4c** establish it as a hydrido–alkylidene complex and also provide clear spectroscopic distinction of **4c** from the **4a,b** isomers. The ^{13}C NMR spectrum (CD_2Cl_2, 20 °C) of **4c***, $CpWOs_3(^*CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-}^*CHCH_2Tol)$, reveals a μ-alkylidene carbon resonance at δ 129.6 ($^1J_{CH}$ = 101.7 Hz, $^1J_{CH}$ = 141.5 Hz) and nine carbonyl resonances at δ 192.1, 185.3, 184.4, 181.2, 175.4, 174.1, 171.6 ($^2J_{CH}$ = 12.0 Hz), 170.2, and 168.2 ($^2J_{CH}$ = 7.9 Hz). The three broad resonances at δ 192.1, 184.4, and 181.2 are due to localized 3-fold exchange at the nonbridged $Os(CO)_3$ center. Increasing the temperature to 100 °C in toluene-d_8 causes the three resonances to coalesce to a broad singlet while the other six carbonyl resonances remain sharp. This temperature behavior is also consistent with those observed in the $MoOs_3$ analogue of **4c**[26] and in the dioxo cluster $CpWOs_3(CO)_9(\mu\text{-O})_2(\mu\text{-H})$.[25b]

For the molybdenum analogues the acid-induced isomerization of *anti* to *syn* isomers was proposed to occur by protonation of an alkylidene carbon–metal bond, forming a cationic alkyl species, followed by rotation around the carbon–metal single bond and subsequent deprotonation.[26] An analogous mechanism is feasible for these tungsten compounds as well.

Two likely pathways for the thermal isomerization of **4a,b** to **4c** involve (1) bridge–terminal alkylidene movement[27] and (2) oxidative addition of the alkylidene C–H bond to form a dihydrido–alkylidyne species followed by reformation of the alkylidene C–H bond from the opposite side.[28] The selectively deuterated complex $CpWOs_3(CO)_9(\mu\text{-O})(\mu\text{-X})(\mu\text{-CDCH}_2Tol)$ (**4a,b**, X = H (20%), D (80%) by ^{1}H NMR) was prepared from the reaction of **3** and D_2. The presence of some hydrogen at the hydride site arises from H–D exchange during chromatographic workup on silica gel, but no hydrogen was observed at the alkylidene α-position by ^{1}H NMR (<1%). Upon pyrolysis of the partially deuterated compound in the solid state at 180 °C, isomer **4c** obtained possessed considerably less deuterium content at the alkylidene α-carbon than recovered **4a,b**. This result strongly argues against the bridge–terminal pathway, in which no scrambling of the hydride and alkylidene α-H is expected. However, if fast intramolecular hydride scrambling is assumed in the dihydrido–alkylidyne intermediate, the latter pathway is supported. Rotation of an alkylidene ligand via intramolecular hydrogen migration from an alkylidene to an alkylidyne ligand has been reported in the heterometallic trinuclear cluster $(Cp)(MeCp)Fe_2Mn(CO)_5(\mu\text{-CHCH}_3)(\mu_3\text{-COCH}_3)$.[28c]

Characterization and Reactivity of 5. Thermolysis of compound **1** in refluxing toluene for a prolonged period (2.5 h) results in its conversion to $CpWOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-C=CHTol})$ (**5**) in 36% yield. Monitoring this reaction by analytical TLC and IR reveals that it proceeds stepwise to yield first complex **3**, which then undergoes

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further reaction to give complex **5**. The intermediacy of **3** was further confirmed by preparation of **5** from pure **3** in a higher (52%) yield. The ^1H NMR spectrum of **5** in CD_2Cl_2 shows a downfield resonance at δ 8.20 and a hydride resonance at δ 17.78, indicating that a benzylic hydrogen has undergone oxidative addition to a metal center to afford hydrido–vinylidene complex **5**. The crystal structure of **5** has been described[15] and is depicted in Scheme 2. The μ_2-bonding mode observed in **5** is rather unusual, since other such cluster compounds have their vinylidene ligands coordinated to three (μ_3) and four (μ_4) metal atoms.[29] The ^{13}C NMR spectrum of **5*** in toluene-d_8 exhibits nine carbonyl resonances at δ 187.6, 186.5, 185.0, 181.3, 179.7 ($^2J_{CH}$ = 6.1 Hz), 178.7, 174.8, 168.6 ($^2J_{CH}$ = 11.5 Hz), and 168.0. The spectrum does not show any appreciable change over the temperature range 20–100 °C.

The vinylidene complex **5** reacts with H_2 (1 atm) for a prolonged period (15 h) to produce a mixture of alkylidene complexes **4a,b** in 66% yield. When the hydrogenation of **5** is carried out under 1 atm of deuterium gas, deuterium incorporation is found in the resulting alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}D)(\mu\text{-}O)(\mu\text{-}CDCH_2Tol)$ only at the hydride position and the α- but *not* the β-position of the alkylidene ligand. This result can be understood if the hydride ligand in **5** first migrates back to the vinylidene β-carbon to form an alkylidyne group in an intermediate, which then undergoes hydrogenation at the metal centers to produce hydride ligands and subsequent hydride migration to form the alkylidene moiety. Note that the formula of the intermediate, a dihydrido–alkylidyne complex, is the same as that postulated above for the **4a,b** to **4c** isomerization. However, the fact that **4a,b** is formed from **5** and not **4c** implies that there are two different intermediates of this kind.

Related chemistry has shown that the hydrido–vinylidene anion $[Fe_3(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CCH_2)]^-$ reacts reversibly with CO to form the alkylidyne anion $[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)]^-$ [30] and that deuteration of $Os_3(CO)_9(\mu\text{-}H)_2(C{=}CH_2)$ in refluxing *n*-heptane scrambles all the ligand hydrogens, producing significant quantities of tri- and tetradeuterated derivatives of $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$.[31] A direct H_2 addition to the vinylidene C=C bond, as is believed to occur in the nucleophilic addition to the vinylidene group of $[CpFe(C{=}CH_2)(CO)(PPh_3)]^+$, to generate Fischer carbene complexes,[32] has been ruled out in this case by the deuteration results.

Thermolysis of **5** in refluxing xylene induces loss of a carbonyl ligand to yield the alkyne complex $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}CHCTol)$ (**6**). This alkyne complex is also formed together with complex **4c** upon prolonged pyrolysis of **4a,b** (see Experimental Section), indicating that at least two other processes, i.e. dehydrogenation and decarbonylation, can occur under the reaction conditions for the alkylidene isomerization.

Structural characterization **6** has been achieved by spectroscopic data. The IR spectrum (ν(CO) region) of **6** is essentially identical with that of structurally characterized $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)$ prepared independently by decarbonylation of $CpWOs_3(CO)_{10}(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2H_2)$ with $Me_3NO/MeCN$.[16] The ^1H NMR spectrum of **6** shows an alkyne hydrogen resonance at δ 10.63 and a hydride resonance at δ −10.29 which are comparable with the respective acetylene and hydride resonances at δ +10.62 and −9.70 for $CpWOs_3(CO)_8(\mu\text{-}H)(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)$.[16] The ^{13}C NMR spectrum of **6** is consistent with the reported structure[16] in that the presence of a single resonance at δ 176.4 with $^2J_{CH}$ (=9.8 Hz) coupling indicates that only one carbonyl ligand on the H-bridged $Os(CO)_3$ center is trans to the bridging hydride. Furthermore, the resonance for the alkyne CH carbon is at δ 140.9 ($^1J_{CH}$ = 168 Hz) with tungsten satellites ($^1J_{CW}$ = 110 Hz). When **6*** was prepared from vinylidene α-carbon labeled **5***, $CpWOs_3({}^*CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}{}^*C{=}CHTol)$, the ^1H NMR spectrum of **6*** showed a set of distinct ^{13}C satellites for the alkyne *CH, indicating that a hydrogen migration rather than an aryl migration had occurred.

The likely pathways for the formation of **6** would involve (1) formation of a μ_3-vinylidene after elimination of a CO ligand followed by a direct 1,2-hydrogen migration, (2) formation of a dihydrido acetylide complex and subsequent hydride transfer to the α-carbon after CO loss, or (3) formation of a μ-vinyl complex by hydride ligand transfer to the α-carbon followed by hydrogen transfer from the β-carbon after CO loss. Although these possibilities might be differentiable by selective deuterium labeling, the severe conditions necessary for the formation of **6** discouraged us from attempting such experiments. To our knowledge this is the first example of the transformation of a μ_2-vinylidene ligand to a μ_3-η^2-alkyne ligand, but it is related conceptually to the conversion of $Fe_3(CO)_9(\mu\text{-}H)(CH_3C{=}NH)$ to $Fe_3(CO)_9(\mu\text{-}H)(CH_3CH{=}N)$,[33] the conversion of $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}AsMe_2)(HCCH)$ to $Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}AsMe_2)(C{=}CH_2)$,[34] and the conversion of $RuCo_2(CO)_9(HCCR)$ to $RuCo_2(CO)_9(C{=}CHR)$ (R = H, Ph).[35]

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Supplementary Material Available: A table of anisotropic thermal parameters for the crystal structure determination of $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (1 page). Ordering information is given on any current masthead page.

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