Ln–N distance favors C over A as being the most important contributor. A similar structure is favored for $(C_5H_5)_3U[\eta^2\text{-}C(Me){=}N(C_6H_{11})]$.[35]

Conclusion

To the extent that CO and isocyanides are similar, these formimidoyl complexes can be viewed as model complexes for the unstable formyl intermediates formed in reductions of CO by metal hydrides.[32,65] The special μ,η^2 nature of the formimidoyl ligands in these complexes precludes assignment of the reaction as a 1,1- or 1,2-metal hydride addition to the C–N bond in $CNCMe_3$. However, the structures demonstrate yet another type of coordination mode for reduced ligands of this type.

The coordination geometry found in these μ,η^2-*N*-alkylformimidoyl complexes demonstrates that multiply bonded oxygen-free organic units can η^2-coordinate to lanthanide metals as well as to yttrium. These complexes provide yet another example of the close parallel between the chemistry of yttrium and that of the late lanthanide elements of similar radial size. Moreover, this similarity was demonstrated in a system which had considerable potential to show differences. Finally, the presence of both staggered and nearly eclipsed arrangements of cyclopentadienyl rings in **4A** and **4B** indicates that minor crystal packing effects can influence the relative orientations of cyclopentadienyl rings in complexes of this type.

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Registry No. 1, 86528-30-5; 2, 86528-32-7; 3, 86528-31-6; 4, 105834-48-8; $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$, 80642-73-5; $[(C_5H_5)_2Y(\mu\text{-}D)(THF)]_2$, 80642-74-6; $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$, 80658-44-2; $[(C_5H_5)_2Er(\mu\text{-}H)(THF)]_2$, 80642-71-3; Me_3CNC, 7188-38-7.

Supplementary Material Available: Tables of thermal parameters for 1 and 4 (2 pages); listings of structure factor amplitudes for 1 and 4 (30 pages). Ordering information is given on any current masthead page.

Synthesis, Crystal Structure, and Stereoisomerism of the Alkylidene Complex $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ and Related Complexes

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The reaction of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (1) with HCl or BCl_3/H_2O at ambient temperatures generates the alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (**3**, isomer **b**) isolated in 65–90% yield. Complex **3b** crystallizes in the triclinic space groups $P\bar{1}$ with a = 9.2724 (32) Å, b = 11.3130 (43) Å, c = 14.0040 (62) Å, α = 69.790 (31)°, β = 77.236 (30)°, γ = 83.700 (20)°, V = 1343.6 (9) Å^3, and Z = 2. Convergence of the structure solution was reached with R_F = 3.7% for all 3526 unique data (R_F = 3.1% for those 3085 data with $|F_o| > 6\sigma(|F_o|)$. The metal atoms adopt the "butterfly" configuration typical of 62-electron clusters, with the chlorine atom bridging the wing-tip osmium atoms (Os(1)–Cl = 2.488 (3) Å, Os(3)–Cl = 2.463 (3) Å; Os(1)–Cl–Os(2) = 98.4 (1)°). Three carbonyl groups are bound to each Os atom, while the Cp ligand is bound to W. The oxygen atom is involved in a $W{=}O{:}\!\rightarrow\!Os$ bridge, with W=O(1) = 1.786(9) Å, Os(3)—O(1) = 2.126 (8) Å, and <W—O(1)—Os(3) = 99.2 (4)°. The μ-alkylidene moiety bridges W and Os(1), with W–C(1) = 2.064 (11) Å, Os(1)–C(1) = 2.196 (11) Å, and <W–C(1)–Os(1) = 85.0 (4)°; the $-CH_2Tol$ substituent is oriented anti to the triply edge-bridged W–Os(1)–Os(3) face. Pyrolysis of **3b** in refluxing toluene generates an isomeric alkylidene complex **3c** isolated in 71% yield and characterized spectroscopically. Treatment of 1 with HBr or HSPh generates analogous alkylidene compounds $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-}CHCH_2Tol)$ (X = Br (4) or SPh (5)); in these cases both stereoisomers are obtained directly. The substitution of a carbonyl ligand in **3b** by ^{13}CO or PPh_2Me is shown to be stereoselective; activation by both the bridging oxo and the bridging chloro ligands is proposed.

Introduction

Treatment of the oxo–alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (1) with hydrogen gas provides the oxo–alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CHCH_2Tol)$ (2).[1,2] The crystal structure of one form of 2 (≡ **2a**) has been determined,[3] but in solution it coexists with a second isomer (≡ **2b**).[2] Pyrolysis of 2 in refluxing xylenes gives yet a third isomer (≡ **2c**).[4] As part of our further study of the reactivity of 1, we have examined its reactions with certain HX reagents (HCl, HBr, and HSPh) and have found that alkylidene complexes $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-}CHCH_2Tol)$ (X = Cl (**3**), Br (**4**), or SPh

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(1) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Ziller, J. W.; Beanan, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1144.

(2) Park, J. T. PhD. Thesis., University of Illinois at Urbana-Champaign, 1983.

(3) Churchill, M. R.; Li, Y. C. *J. Organomet. Chem.* **1985**, *291*, 61.

(4) Chi, Y.; Shapley, J. R., unpublished results.

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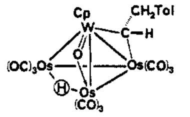
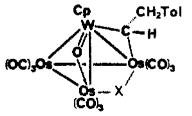
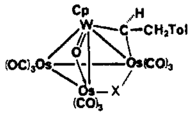
(**5**)) are formed. Furthermore, these complexes show two isomers, represented by analogous forms **b** and **c**. This paper reports the synthesis and spectroscopic characterization of compounds **3**–**5**, the crystal structure of **3b**, and aspects of the reactivity of **3b**.



2a



X = H, **2b**
Cl, **3b**
Br, **4b**
SPh, **5b**



X = H, **2c**
Cl, **3c**
Br, **4c**
SPh, **5c**

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware. Solvents were dried and distilled before use, toluene from molten sodium and dichloromethane from phosphorus pentoxide. The progress of the 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). Deuterium chloride was generated from the hydrolysis of boron trichloride in a dichloromethane solution of deuterium oxide. CpWOs$_3$(CO)$_9$(μ-O)(μ_3-CCH$_2$Tol) (**1**) was prepared by the procedure described previously.[1] Carbon-13 enriched **1** was prepared analogously; note that the alkylidyne carbon as well as the carbonyl carbons are enriched.

Infrared spectra were obtained on a Perkin-Elmer 281B spectrophotometer. Both ^{1}H NMR (360 MHz) and ^{13}C NMR (90.4 MHz) were recorded on a Nicolet NT-360 spectrometer. Mass spectra were recorded by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences at the University of Illinois by using a Varian MAT-731 (field desorption) or VG-ZAB (fast atom bombardment) mass spectrometer. All *m/z* values are referenced to ^{184}W and ^{192}Os. Microanalytical data were provided by the Microanalysis Laboratory of the School of Chemical Sciences at the University of Illinois.

Synthesis of CpWOs$_3$(CO)$_9$(μ-O)(μ-Cl)(μ-CHCH$_2$Tol) (3b) with BCl$_3$. A partial vacuum was drawn over a dichloromethane solution (12 mL) of CpWOs$_3$(CO)$_9$(μ-O)(μ_3-CCH$_2$Tol) (24 mg, 0.02 mmol) in a round-bottom flask, and the flask was charged with boron trichloride (Linde) to a pressure of 1 atm. The solution was then stirred at room temperature for 5 min. The solvent was evaporated in vacuo, the residue was dissolved in dichloromethane, and the solution was washed with distilled water to remove BCl$_3$. Purification by preparative TLC (pentane–dichloromethane, 1:1) followed by crystallization from pentane–dichloromethane provided **3b** (20 mg, 0.016 mmol, 89%) as an orange-red solid. Some starting material (2 mg, 0.0017 mmol) was also recovered. The ^{13}C-enriched complex was prepared from ^{13}C-enriched **1** with BCl$_3$ in a similar manner. Crystals suitable for X-ray diffraction were grown from a layered solution of dichloromethane–hexane at room temperature.

Synthesis of CpWOs$_3$(CO)$_9$(μ-O)(μ-Cl)(μ-CHCH$_2$Tol) (3b) with HCl. In a 200-mL pressure bottle capped with a neoprene stopcock, a toluene solution (10 mL) of **1** (7 mg, 0.0058 mmol) was stirred under 1 atm of a mixture of HCl and N$_2$ (about 1:5) for 1 h at room temperature; the solution color changed to orange. Evaporation of the volatiles, purification by preparative TLC, and subsequent crystallization provided **3b** (4.8 mg, 0.0039 mmol, 67%).

3b: FD mass spectrum, *m/z* 1246 (M$^+$); IR (C$_6$H$_{12}$) ν(CO) 2090 (s), 2064 (vs), 2030 (vs), 2008 (s), 1997 (s), 1987 (s), 1970 (vw), 1956 (w), 1942 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 18 °C) δ 7.30 (d) + 7.22 (d) (4 H, ^3J = 7 Hz, C$_6H_4$CH$_3$), 6.33 (1 H, dd, ^3J = 5.5 and 9.0 Hz, μ-C*H*CH$_2$Tol), 6.13 (5 H, s, C$_5$H$_5$), 4.49 (1 H, dd, ^2J = 14.3 Hz, ^3J = 5.5 Hz, μ-CHCH_2Tol), 4.01 (1 H, dd, ^2J = 14.3, ^3J = 9.0 Hz, μ-CHCH$_2$Tol), 2.38 (3 H, s, C$_6$H$_4$CH_3); ^{13}C NMR (CD$_2$Cl$_2$, 18 °C) Os–CO, δ 189.5, 186.7, 186.3, 183.3, 182.1, 175.7, 175.1, 174.4, 173.1; ^{13}C NMR (CD$_2$Cl$_2$, 18 °C) δ 135.8 ($^1J_{\text{C-H}}$ = 130 Hz, $^1J_{\text{C-W}}$ = 100 Hz, μ-*C*HCH$_2$Tol). Anal. Calcd for WOs$_3$C$_{23}$H$_{15}$O$_{10}$Cl: C, 22.54; H, 1.22; Cl, 2.86. Found: C, 22.33; H, 1.19; Cl, 3.12.

Synthesis of CpWOs$_3$(CO)$_9$(μ-O)(μ-Cl)(μ-CDCH$_2$Tol) (3b-*d*) with BCl$_3$/D$_2$O. To a dichloromethane (30 mL) solution of **1** (30 mg, 0.0249 mmol) in a 50-mL reaction flask was added 0.25 mL of D$_2$O. After a partial vacuum was drawn, the flask was then charged to 1 atm with BCl$_3$. After the solution was stirred for 5 min at room temperature, the volatiles were evaporated in vacuo, and the residue was handled as described above, giving deuterium-labeled CpWOs$_3$(CO)$_9$(μ-O)(μ-Cl)(μ-CDCH$_2$Tol) (19 mg, 0.0153 mmol, 61%) as well as some unreacted starting material. The deuterium atom enrichment, as estimated by ^{1}H NMR integration, was about 90%.

Synthesis of CpWOs$_3$(CO)$_9$(μ-Cl)(μ-CHCH$_2$Tol) (3c). A toluene solution (25 mL) containing **3b** (68 mg, 0.055 mmol) was heated under reflux for 1 h. After evaporation of the solvent, the mixture was purified by preparative TLC (pentane–dichloromethane, 1:1) to provide **3c** (48 mg, 0.039 mmol, 71%) as an orange-red viscous oil, which could not be crystallized. ^{13}CO enriched **3c** and **3c**-*d* were prepared analogously; in the latter case there was no loss or scrambling of the label (by ^{1}H NMR).

3c: FD mass spectrum, *m/z* 1246 (M$^+$), 1208 (M$^+$ – CO); IR (C$_6$H$_{12}$) ν(CO), 2090 (s), 2064 (vs), 2030 (vs), 2008 (s), 1997 (s), 1987 (s), 1970 (vw), 1956 (w), 1942 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 18 °C) δ 7.49 (d) + 7.34 (d) (4 H, ^3J = 7 Hz, C$_6H_4$CH$_3$), 6.81 (1 H, dd, ^3J = 11.3 and 5.7 Hz, μ-C*H*CH$_2$Tol), 5.63 (5 H, s, C$_5$H$_5$), 5.22 (μ-CHCH_2Tol, 1 H, dd, ^2J = 12.9, ^3J = 5.7 Hz), 3.87 (1 H, tr, $J \approx$ 12 Hz, μ-CHCH_2Tol), 2.48 (3 H, s, C$_6$H$_4$CH_3); ^{13}C NMR (CDCl$_3$, 18 °C) Os–CO, δ 189.0, 187.1, 185.0, 183.6, 183.3, 175.0, 174.9, 173.4, 172.6; ^{13}C NMR (CDCl$_3$, 18 °C) δ 133.5 ($^1J_{\text{C-H}}$ = 140 Hz, $^1J_{\text{C-W}}$ = 100 Hz, μ-*C*HCH$_2$Tol). Anal. Calcd. for WOs$_3$C$_{23}$H$_{15}$O$_{10}$Cl: C, 22.54; H, 1.22. Found: C, 23.14; H, 1.58

Synthesis of CpWOs$_3$(CO)$_9$(μ-O)(μ-Br)(μ-CHCH$_2$Tol) (4b and 4c). A toluene solution (15 mL) of **1** (20.8 mg, 0.017 mmol) was stirred under 1 atm of HBr gas for 1.5 h, until the color changed to orange. Orange **4b** (4.7 mg, 0.0037 mmol, 21%) and the corresponding **4c** (2.4 mg, 0.0019 mmol, 11%) were obtained following purification of the reaction mixture residues by preparative TLC. The analytically pure solid of **4b** was crystallized from dichloromethane–pentane at room temperature. All attempts to crystallize **4c** failed.

4b: FD mass spectrum, *m/z* 1290 (M$^+$); IR (C$_6$H$_{12}$) ν(CO), 2090 (s), 2064 (vs), 2030 (vs), 2005 (s), 1987 (s), 1970 (vw), 1956 (w), 1942 (w) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 18 °C) δ 7.30 (d) + 7.21 (d) (4 H, ^3J = 7 Hz, C$_6H_4$CH$_3$), 6.53 (1 H, tr, $J \approx$ 8 Hz, μ-C*H*CH$_2$Tol), 6.05 (5 H, s, C$_5$H$_5$), 4.47 (1 H, dd, ^3J = 6.8, $^2J_{\text{H-H}}$ = 14.8 Hz, μ-CHCH_2Tol), 4.13 (1 H, dd, ^3J = 8.4, ^2J = 14.8 Hz, μ-CHCH_2Tol), 2.37 (3 H, s, C$_6$H$_4$CH_3). Anal. Calcd. for WOs$_3$C$_{23}$H$_{15}$O$_{10}$Br: C, 21.48; H, 1.18. Found: C, 21.58; H, 1.24.

4c: FD mass spectrum, *m/z* 1290 (M$^+$), 1262 (M$^+$ – CO); IR (C$_6$H$_{12}$) ν(CO), 2090 (s), 2064 (vs), 2030 (vs), 2005 (s), 1987 (s), 1970 (vw), 1956 (w), 1942 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$, 18 °C) δ 7.47 (d) + 7.32 (d) (4 H, J = 7 Hz, C$_6H_4$CH$_3$), 5.56 (5 H, s, C$_5$H$_5$), 6.77 (1 H, dd, ^3J = 5.6 and 11.3 Hz, μ-C*H*CH$_2$Tol), 5.13 (1 H, dd, ^3J = 5.6, ^2J = 12.9 Hz, μ-CHCH_2Tol), 3.96 (1 H, tr, $J \approx$ 12 Hz, μ-CHCH_2Tol), 2.45 (3 H, s, C$_6$H$_4$CH_3).

Synthesis of CpWOs$_3$(CO)$_9$(μ-O)(μ-SPh)(μ-CHCH$_2$Tol) (5b and 5c). A toluene solution (18 mL) of **1** (44.0 mg, 0.0365 mmol) and excess thiophenol (Aldrich, 30 μL, 0.29 mmol) was heated under reflux. Over a period of 15 min, the color of solution slowly turned from red-brown to red-orange. After evaporation of the solvent and excess thiophenol in vacuo, the mixture was separated by preparative TLC (pentane–dichloromethane, 4:3), providing orange-red **5b** (28.2 mg, 0.0214 mmol, 59%) and **5c** (10.5 mg, 0.0078 mmol, 22%). The crystalline solids of **5b** and **5c** were obtained from dichloromethane–pentane and dichloromethane–methanol, respectively. The ^{13}CO-enriched samples were prepared in a similar manner.

5b: FD mass spectrum *m/z* 1320 (M$^+$); IR (C$_6$H$_{12}$) ν(CO), 2081 (s), 2056 (vs), 2026 (vs), 2006 (s), 2000 (m), 1985 (s), 1963 (vw), 1955 (m), 1948 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 18 °C) δ 7.31 (d) + 7.00 (d) (4 H, J = 7 Hz, C$_6H_4$CH$_3$), 7.00 (m) + 6.70 (d) (5 H, J = 7 Hz, SC$_6H_5$), 6.04 (5 H, s, C$_5H_5$), 5.62 (1 H, tr, $J \approx$ 7 Hz, μ-C*H*CH$_2$Tol), 4.24 (1 H, dd, ^2J = 14.8, ^3J = 6.9 Hz, μ-CHCH_2Tol), 3.98 (1 H, dd, ^2J = 14.8, ^3J = 7.9 Hz, μ-CHCH_2Tol), 2.34 (3 H, s, C$_6$H$_4$CH_3); ^{13}C NMR (CDCl$_3$, 18 °C) Os–CO, δ 186.6, 186.1, 186.0, 181.2, 179.6, 179.3, 176.3, 173.1, 172.5; ^{13}C NMR (CDCl$_3$, 18 °C) δ 133.8 ($^1J_{\text{C-H}}$ = 127 Hz, $^1J_{\text{C-W}}$ = 96 Hz, μ-*C*HCH$_2$Tol). Anal.

Calcd. for $WOs_3C_{29}H_{20}O_{10}S$: C, 26.49; H, 1.53. Found: C, 26.52; H, 1.54.

5c: FD mass spectrum, *m/z* 1320 (M^+), 1292 ($M^+ - CO$); IR (C_6H_{12} ν(CO), 2081 (s), 2057 (vs), 2026 (vs), 2008 (s), 1999 (m), 1990 (s), 1968 (vw), 1957 (m), 1940 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 18 °C) δ 7.34 (d) + 7.15 (d) (4 H, J = 7 Hz, $C_6H_4CH_3$), 7.34–7.15 (5 H, m, SC_6H_5), 6.63 (1 H, dd, ^3J = 11.6 and 5.8 Hz, μ-$CHCH_2$Tol), 5.57 (5 H, s, C_5H_5), 4.65 (1 H, dd, ^2J = 12.8, $^3J_{H-H}$ = 5.8 Hz, μ-$CHCH_2$Tol), 3.65 (1 H, tr, $J \approx 12$ Hz, μ-$CHCH_2$Tol), 2.45 (3 H, s, $C_6H_4CH_3$); ^{13}C NMR ($CDCl_3$, 18 °C) Os–CO, δ 187.8, 185.6 (2C), 182.7, 180.3, 179.2, 175.7, 173.5, 173.2; ^{13}C NMR ($CDCl_3$, 18 °C) δ 133.3 ($^1J_{C-H}$ = 138 Hz, $^1J_{C-W}$ = 103 Hz, μ-$CHCH_2$Tol). Anal. Calcd. for $WOs_3C_{29}H_{20}O_{10}S$: C, 26.49; H, 1.53. Found: C, 26.13; H, 1.54.

Reaction of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (3b) with PPh_2Me. A toluene solution (15 mL) of **3b** (37 mg, 0.03 mmol) and a large excess of PPh_2Me (65 μL, 0.32 mmol) was heated under reflux for 5 min. After evaporation of the solvent, the mixture was separated by preparative TLC (pentane–dichloromethane, 4:3) to provide $CpWOs_3(CO)_8(PPh_2Me)(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (30.5 mg, 0.022 mmol, 71%) as an orange-red viscous oil. A crystalline solid was obtained from dichloromethane–pentane at room temperature. The ^{13}CO-enriched sample was prepared analogously.

FAB mass spectrum: *m/z* 1418 (M^+). IR (C_6H_{12}): ν(CO), 2064 (s), 2030 (vs), 2000 (m), 1983 (vs), 1966 (s), 1941 (w), 1931 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 18 °C): δ 7.54 (10 H, s, br, $2PC_6H_5$), 7.30 (d) + 7.22 (d) (4 H, J = 7 Hz, $C_6H_4CH_3$), 6.04 (5 H, s, C_5H_5), 5.95 (1 H, tr, $J \approx 7$ Hz, μ-$CHCH_2$Tol), 4.38 (1 H, dd, ^2J = 15.0, ^3J = 6.7 Hz, μ-$CHCH_2$Tol), 4.19 (1 H, dd, ^2J = 15.0, ^3J = 8.1 Hz, μ-$CHCH_2$Tol), 2.39 (3 H, s, $C_6H_4CH_3$), 2.09 (3 H, d, $^2J_{P-H}$ = 9.4 Hz, PCH_3). ^{13}C NMR ($CDCl_3$, 18 °C): Os–CO, δ 189.5, 187.3, 184.1, 183.7, 182.9, 179.8, 174.9; ^{13}C NMR ($CDCl_3$, 18 °C) δ 131.8 ($^1J_{C-W}$ = 94 Hz, $^1J_{C-H}$ = 128 Hz, μ-$CHCH_2$Tol). Anal. Calcd. for $WOs_3C_{35}H_{28}O_9PCl$: C, 29.73; H, 2.00; Cl, 2.51. Found: C, 29.47; H, 1.89; Cl, 3.06.

Collection of X-ray Diffraction Data for $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (3b). A dard red crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was sealed in a glass capillary under saturated dichloromethane vapor at low temperature. It was aligned accurately on the Syntex $P2_1$ automated diffractometer at SUNY—Buffalo. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of the intensity data were carried out by the previously described techniques of this laboratory[5]; details appear in Table I. The diffraction symmetry is $\bar{1}$ and there are no systematic absences. The crystal belongs to the triclinic system; with $Z = 2$, it was assigned the centrosymmetric space group $P\bar{1}$ (C^{12}; No. 2). Successful solution of the structure under this space group proves it to be the correct choice.

All data were corrected for the effects of absorption and for Lorentz and polarization effects, were converted to unscaled $|F_o|$ values, and were placed on an approximately absolute scale by means of a Wilson plot. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. No datum was rejected.

Solution and Refinement of the Structure. The structure was solved by using G. M. Sheldrick's SHELX 76 programs on the CDC Cyber 173 computer at SUNY—Buffalo. The positions of the metal atoms were obtained by using the multisolution tangent formula with hand-selected starting phases. A single difference-Fourier synthesis revealed the positions of all remaining non-hydrogen atoms. All subsequent calculations were performed with our locally modified version of the Syntex XTL interactive crystallographic program package. The function minimized during full-matrix least-squares refinement was $\sum w(|F_o|-|F_c|)^2$, where $1/w = [\sigma(|F_o|)]^2 + [0.015|F_o|]^2$. Hydrogen atoms were included in calculated positions on the basis of the appropriate idealized geometry, with d(C–H) = 0.95 Å. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence[6] with $R_F = 3.7\%$, $R_{wF} = 4.0\%$, and GOF = 1.78 for 343 varibles refined against all 3526 unique data, none rejected. Residuals for those 3283 reflections with $|F_o| > 3\sigma(|F_o|)$ were $R_F = 3.4\%$, $R_{wF} = 4.0\%$ and for those 3085 reflections with $|F_o| > 6\sigma(|F_o|)$, $R_F = 3.1\%$, $R_{wF} = 3.8\%$.

Table I. Experimental Data for the X-ray Diffraction Study of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$

(A) Unit Cell Data

a = 9.2724 (32) Å	crystal system: triclinic
b = 11.3130 (43) Å	space group: $P\bar{1}$ (C_i^1; No. 2)
c = 14.0040 (62) Å	Z = 2
α = 69.790 (31)°	formula: $C_{23}H_{15}O_{10}ClOs_3W$
β = 77.236 (30)°	mol wt 1241.27
γ = 83.700 (29)°	D(calcd) = 3.07 g cm^{-3}
V = 1343.6 (9) $Å^3$	T = 21 °C (274 K)

(B) Collection of X-ray Diffraction Data

diffractometer	Syntex $P2_1$
radiation	Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator	highly oriented (pyrolytic) graphite; equatorial mode with $2\theta(m)$ = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction
reflctns measd	$+h$, $\pm k$, $\pm l$ for 2θ = 4.5–45.0°; 3786 total, merged to 3526 symmetry-independent data (file name WOSB-190)
scan type	coupled θ(crystal)–2θ(counter)
scan width	$[2\theta(K\alpha_1) - 0.9]° \rightarrow [2\theta(K\alpha_2) + 0.9]°$
scan speed	4.0 deg min^{-1} (in 2θ)
std reflctns	three collected after each batch of 97 reflections; no significant fluctuations observed
abs correctn	μ(Mo Kα) = 196.5 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) between ψ scans of close-to-axial reflections

Calculated structure factors were based upon the analytical expression for the neutral atoms' form factors; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms.[7] An extinction correction was applied. Analysis of the function $\sum w(|F_o| - |F_c|)^2$ showed no unusual trends as a function of Miller indices, $|F_o|$, $(\sin\theta)/\lambda$, or sequence number. A final difference-Fourier synthesis was featureless. Final positional parameters are collected in Table II.

Results and Discussion

Synthesis and Identification of the Alkylidene Complexes. Treatment of the oxo–alkylidyne compound **1** with gaseous HCl at ambient temperature produces an oxo–chloro–alkylidene compound $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (**3b**) isolated in 65–70% yield. The same compound is generated in somewhat higher isolated yield (ca. 90%) from the reaction of **1** with gaseous BCl_3 and then hydrolysis with water. Pyrolysis of **3b** in refluxing toluene provides a second chloro–alkylidene compound, **3c**. The solution IR spectra in the region of ν(CO) absorptions are identical for both **3c** and **3b**, within the accuracy of the measurement.

The analogous reaction of **1** with HBr, however, provides both isomers of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Br)(\mu\text{-}CHCH_2Tol)$ (**4b** and **4c**) directly. Again, the IR ν(CO) spectra of **4b** and **4c** are indistinguishable as well as being very close to those of **3b** and **3c**. It is noteworthy that even though the respective sets of isomers have identical IR ν(CO) spectra, they are easily separated by thin-layer chromatography. This procedure appears to give reasonably pure compounds, but neither **3c** or **4c** could be induced to crystallize.

Finally, the reaction of **1** with thiophenol (at 110 °C) also gives two isomers of the phenylthio derivative $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}SPh)(\mu\text{-}CHCH_2Tol)$ (**5b** and **5c**). The IR

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

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

(7) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

Table II. Final Parameters for $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$

atom	x	y	z	B, Å^2
W	0.06839 (4)	0.15272 (4)	0.30250 (3)	
Os(1)	0.33001 (4)	0.27109 (4)	0.29911 (3)	
Os(2)	0.25451 (5)	0.23700 (5)	0.12284 (3)	
Os(3)	0.30382 (5)	−0.02490 (5)	0.24181 (4)	
Cl	0.42595 (31)	0.04844 (29)	0.34943 (23)	
O(1)	0.10897 (78)	−0.01275 (74)	0.35191 (57)	
O(11)	0.2092 (12)	0.5391 (10)	0.24474 (81)	
O(12)	0.4869 (10)	0.2757 (10)	0.46846 (83)	
O(13)	0.6020 (10)	0.3685 (11)	0.12829 (79)	
O(21)	0.1469 (12)	0.5112 (11)	0.04414 (87)	
O(22)	0.5435 (11)	0.2643 (13)	−0.03550 (80)	
O(23)	0.0791 (13)	0.1745 (13)	−0.01040 (82)	
O(31)	0.3545 (12)	−0.3031 (10)	0.36812 (86)	
O(32)	0.1431 (12)	−0.1039 (12)	0.11050 (82)	
O(33)	0.5929 (11)	−0.0158 (11)	0.09098 (82)	
C(11)	0.2519 (14)	0.4379 (13)	0.26477 (92)	
C(12)	0.4215 (12)	0.2801 (10)	0.40497 (93)	
C(13)	0.4998 (14)	0.3226 (13)	0.1890 (10)	
C(21)	0.1949 (15)	0.4087 (16)	0.0720 (10)	
C(22)	0.4391 (17)	0.2548 (15)	0.0247 (10)	
C(23)	0.1520 (15)	0.2002 (13)	0.0387 (10)	
C(31)	0.3359 (13)	−0.1999 (16)	0.3228 (11)	
C(32)	0.2032 (14)	−0.0694 (15)	0.1596 (11)	
C(33)	0.4826 (16)	−0.0145 (13)	0.1453 (10)	
C(1)	0.1258 (11)	0.2096 (11)	0.41376 (84)	
C(2)	0.0436 (12)	0.3008 (12)	0.47007 (92)	
C(3)	0.1189 (11)	0.3238 (11)	0.54690 (82)	
C(4)	0.1946 (13)	0.4333 (11)	0.52103 (91)	
C(5)	0.2653 (14)	0.4511 (11)	0.59258 (92)	
C(6)	0.2605 (12)	0.3653 (12)	0.68841 (94)	
C(7)	0.1815 (17)	0.2559 (13)	0.7161 (10)	
C(8)	0.1100 (15)	0.2383 (13)	0.6451 (11)	
C(9)	0.3324 (16)	0.3884 (14)	0.7688 (11)	
C(51)	−0.1834 (12)	0.0975 (13)	0.3376 (11)	
C(52)	−0.1386 (12)	0.1452 (14)	0.2300 (10)	
C(53)	−0.1129 (13)	0.2741 (14)	0.2059 (10)	
C(54)	−0.1313 (13)	0.3013 (14)	0.2969 (13)	
C(55)	−0.1779 (13)	0.1915 (17)	0.3796 (11)	
H(1)	0.1139	0.1512	0.4823	6.0
H(2A)	−0.0502	0.2673	0.5063	6.0
H(2B)	0.0301	0.3798	0.4187	6.0
H(4)	0.1981	0.4958	0.4546	6.0
H(5)	0.3202	0.4834	0.6272	6.0
H(7)	0.1768	0.1942	0.7829	6.0
H(8)	0.0537	0.1653	0.6648	6.0
H(9A)	0.3171	0.3190	0.8316	6.0
H(9B)	0.2893	0.4630	0.7815	6.0
H(9C)	0.4355	0.3983	0.7422	6.0
H(51)	−0.2130	0.0138	0.3763	6.0
H(52)	−0.1276	0.1002	0.1825	6.0
H(53)	−0.0871	0.3328	0.1378	6.0
H(54)	−0.1152	0.3799	0.3025	6.0
H(55)	−0.2014	0.1829	0.4511	6.0

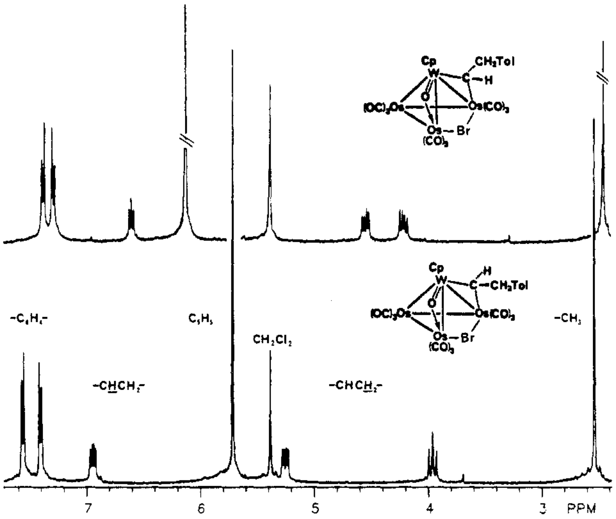

Figure 1. ^1H NMR spectra of **4b** (upper) and **4c** (lower) in $CDCl_2$ at 18 °C.

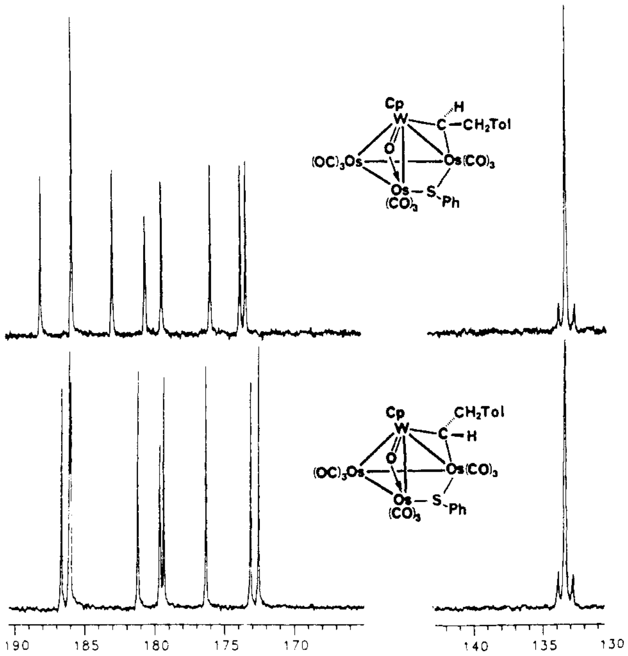

Figure 2. ^{13}C NMR spectra of **5b** (lower) and **5c** (upper) in $CDCl_3$ at 18 °C.

ν(CO) spectra of **5b** and **5c** are not quite identical but are nevertheless very close as well as very similar to those of compounds **3** and **4**. In this case both isomers have been isolated as crystalline solids.

The field-desorption mass spectra of compounds **3**–**5** in all cases show multiplets corresponding to the molecular ion. Interestingly, in all cases the spectra for the **c** isomers show ion multiplets corresponding to $(M - CO)^+$ as well.

The most characteristic spectroscopic aspect of compounds **3**–**5** is their respective ^1H NMR spectra, which fully establish them as alkylidene complexes and also provide a clear distinction between the **b** and **c** isomers. Figure 1 shows a typical pair of spectra. In addition to Tol and Cp signals, the spectrum of each isomer exhibits three separate resonances with 1:1:1 relative intensities (AMX pattern) corresponding to the CH and CH_2 hydrogens of the μ-alkylidene moiety. These resonances can be assigned on the basis of their H–H coupling constants, the lowest field resonance due to the α-hydrogen showing vicinal couplings to the two benzylic β-hydrogens at higher field. Furthermore, the lowest field signal shows satellites when the alkylidene α-carbon is enriched by ^{13}C and greatly diminishes when the sample is deuterium substituted, i.e., in **3b**-*d* and **3c**-*d*.

The ^{13}C NMR spectra obtained for ^{13}C-enriched **3b**,**c** and **5b**,**c** show nine signals in the region expected for carbonyls attached to osmium and one alkylidene carbon resonance with tungsten satellites. The spectra for **5b** and **5c** are displayed in Figure 2, in order to illustrate that the patterns are very similar but nevertheless unique for each isomer.

Crystal Structure of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ (3b). The crystal contains an ordered racemic arrangement of discrete molecules of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ which are mutually separated by normal van der Waals' distances; there are no unusually short intermolecular contacts. The overall molecular geometry and the scheme used for labeling atoms are illustrated in Figure 3; a stereoscopic view of the molecule appears at Figure 4. Interatomic distances and angles are

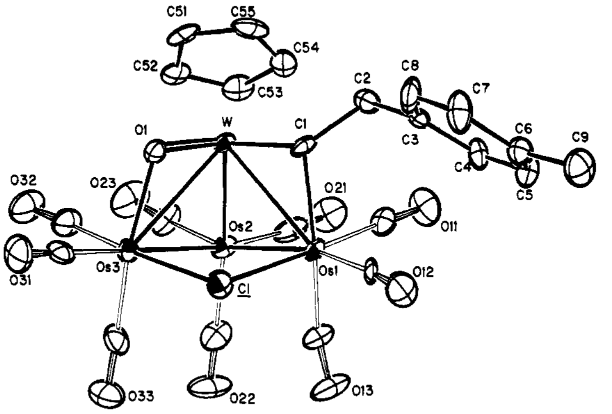

Figure 3. ORTEP-II diagram showing the labeling of non-hydrogen atoms and the molecular geometry for $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$, **3b**. Note that the molecule would have approximate C_s symmetry save for the inequivalence of the bridging oxo and alkylidene ligands.

Table III. Interatomic Distances (Å) and Esd's for $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$

(A) Metal–Metal Distances			
Os(1)–Os(2)	2.866 (1)	Os(2)–W	2.646 (1)
Os(2)–Os(3)	2.897 (1)	Os(3)–W	2.987 (1)
Os(1)–W	2.881 (1)	Os(1)···Os(3)	3.747 (1)
(B) Metal–(Bridging Ligand) Distances			
Os(1)–Cl	2.488 (3)	W–O(1)	1.786 (9)
Os(3)–Cl	2.463 (3)	W–C(1)	2.064 (11)
Os(3)–O(1)	2.126 (8)	Os(1)–C(1)	2.196 (11)
(C) Distances within the μ-$CHCH_2Tol$ Ligand			
C(1)–C(2)	2.546 (18)	C(6)–C(9)	1.535 (19)
C(2)–C(3)	1.509 (16)	C(6)–C(7)	1.400 (20)
C(3)–C(4)	1.389 (17)	C(7)–C(8)	1.388 (20)
C(4)–C(5)	1.390 (18)	C(8)–C(3)	1.372 (18)
C(5)–C(6)	1.352 (17)		
(D) Os–CO and C–O Bond Lengths			
Os(1)–C(11)	1.882 (15)	C(11)–O(11)	1.129 (19)
Os(1)–C(12)	1.899 (12)	C(12)–O(12)	1.167 (16)
Os(1)–C(13)	1.924 (13)	C(13)–O(13)	1.156 (16)
Os(2)–C(21)	1.889 (18)	C(21)–O(21)	1.161 (22)
Os(2)–C(22)	1.925 (15)	C(22)–O(22)	1.122 (18)
Os(2)–C(23)	1.840 (14)	C(23)–O(23)	1.183 (19)
Os(3)–C(31)	1.940 (17)	C(31)–O(31)	1.135 (21)
Os(3)–C(32)	1.851 (15)	C(32)–O(32)	1.157 (19)
Os(3)–C(33)	1.879 (15)	C(33)–O(33)	1.134 (18)
(E) Tungsten–Carbon (Cp) Distances			
W–C(51)	2.384 (12)	W–C(54)	2.356 (15)
W–C(52)	2.383 (12)	W–C(55)	2.365 (14)
W–C(53)	2.400 (13)		

Table IV. Interatomic Angles (Deg) and Esd's for $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$

(A) Intermetallic Angles			
Os(1)–W–Os(2)	62.29 (2)	Os(1–)Os(2)–W	62.87 (2)
Os(1)–W–Os(3)	79.34 (2)	Os(1–)Os(2)–Os(3)	81.10 (2)
Os(2)–W–Os(3)	61.54 (2)	Os(3)–Os(2)–W	65.03 (2)
Os(2)–Os(1)–W	54.84 (2)	Os(2)–Os(3)–W	53.42 (2)
(B) M–M–CO Angles			
W–Os(1)–C(11)	97.25 (41)	Os(1)–Os(2)–C(23)	162.16 (44)
W–Os(1)–C(12)	133.20 (35)	Os(3)–Os(2)–C(21)	167.64 (47)
W–Os(1)–C(13)	129.07 (41)	Os(3)–Os(2)–C(22)	96.57 (46)
Os(2)–Os(1)–C(11)	92.37 (41)	Os(3)–Os(2)–C(23)	94.06 (44)
Os(2)–Os(1)–C(12)	167.47 (35)	W–Os(3)–C(31)	126.04 (45)
Os(2)–Os(1)–C(13)	74.70 (41)	W–Os(3)–C(32)	96.28 (47)
W–Os(2)–C(21)	102.85 (47)	W–Os(3)–C(33)	167.42 (45)
W–Os(2)–C(22)	157.89 (46)	Os(2)–Os(3)–C(31)	179.41 (45)
W–Os(2)–C(23)	99.48 (44)	Os(2)–Os(3)–C(32)	88.45 (47)
Os(1)–Os(2)–C(21)	91.24 (47)	Os(2)–Os(3)–C(33)	85.24 (45)
Os(1)–Os(2)–C(22)	103.86 (46)		
(C) Os–C–O and C–Os–C Angles			
Os(1)–C(11)–O(11)	177.7 (12)	C(11)–Os(1)–C(12)	95.5 (5)
Os(1)–C(12)–O(12)	173.2 (11)	C(11)–Os(1)–C(13)	90.7 (6)
Os(1)–C(13)–O(13)	169.6 (12)	C(12)–Os(1)–C(13)	95.5 (5)
Os(2)–C(21)–O(21)	174.6 (14)	C(21)–Os(2)–C(22)	94.7 (7)
Os(2)–C(22)–O(22)	177.0 (14)	C(21)–Os(2)–C(23)	90.3 (7)
Os(2)–C(23)–O(23)	176.0 (13)	C(22)–Os(2)–C(23)	93.7 (6)
Os(3)–C(31)–O(31)	178.3 (14)	C(31)–Os(3)–C(32)	91.9 (7)
Os(3)–C(32)–O(32)	176.3 (14)	C(31)–Os(3)–C(33)	95.2 (6)
Os(3)–C(33)–O(33)	175.6 (13)	C(32)–Os(3)–C(33)	91.8 (7)
(D) Angles Involving the Bridging Ligands			
W–O(1)–Os(3)	99.2 (4)	W–Os(1)–C(1)	44.6 (3)
W–Os(3)–O(1)	36.2 (2)	Os(1)–W–C(1)	49.4 (3)
Os(3)–W–O(1)	44.7 (3)	Os(2)–W–C(1)	111.0 (3)
Os(2)–W–O(1)	105.7 (3)	Os(1)–Cl–Os(3)	98.4 (1)
Os(1)–W–O(1)	105.2 (3)	Cl–Os(3)–O(1)	84.1 (2)
Os(2)–Os(3)–O(1)	89.3 (2)	Cl–Os(1)–C(1)	88.9 (3)
W–C(1)–Os(1)	85.0 (4)	W–Os(1)–Cl	81.6 (1)
W–C(1)–C(2)	130.1 (8)	W–Os(3)–Cl	79.8 (1)
Os(1)–C(1)–C(2)	118.5 (8)	Os(2)–Os(1)–Cl	88.2 (1)
Os(2)–Os(1)–C(1)	99.8 (3)	Os(2)–Os(3)–Cl	88.0 (1)
(E) Angles from "Cent"[a]			
Cent–W–Os(1)	138.5 (–)	Cent–W–O(1)	115.1 (–)
Cent–W–Os(2)	112.7 (–)	Cent–W–C(1)	111.4 (–)
Cent–W–Os(3)	137.5 (–)		
(F) Angles within the μ-$CHCH_2Tol$ Ligand			
C(1)–C(2)–C(3)	116.4 (10)	C(5)–C(6)–C(7)	118.9 (12)
C(2)–C(3)–C(4)	120.9 (11)	C(9)–C(6)–C(7)	119.5 (12)
C(3)–C(4)–C(5)	119.8 (11)	C(6)–C(7)–C(8)	119.4 (13)
C(4)–C(5)–C(6)	121.8 (12)	C(7)–C(8)–C(3)	121.5 (13)
C(5)–C(6)–C(9)	121.5 (12)	C(8)–C(3)–C(2)	120.5 (11)
		C(8)–C(3)–C(4)	118.6 (11)
(G) Angles within the Cp Ring			
C(51)–C(52)–C(53)	106.0 (12)	C(54)–C(55)–C(51)	107.6 (13)
C(52)–C(53)–C(54)	109.3 (13)	C(55)–C(51)–C(52)	109.5 (13)
C(53)–C(54)–C(55)	107.6 (13)		

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

collected in Tables III and IV.

This molecule has the four atoms of the WOs_3 core arranged in a "butterfly" pattern; atoms W and Os(2) occupy the "hinge" positions with W–Os(2) = 2.646 (1) Å. Other metal–metal bond lengths are W–Os(1) = 2.881 (1) Å, W–Os(3) = 2.987 (1) Å, Os(2)–Os(1) = 2.886 (1) Å, and Os(2)–Os(3) = 2.897 (1) Å. Thus, the osmium–osmium bond lengths are self-consistent and similar to those in the parent carbonyl (Os–Os(av) = 2.877 (3) Å in $Os_3(CO)_{12}$),[8] while there is a range of ~0.34 Å in the tungsten–osmium distances. The "wing-tip" atoms Os(1) and Os(3) are 3.747 (1) Å apart and are symmetrically bridged by the μ-chloro ligand (Os(1)–Cl = 2.488 (3) Å, Os(3)–Cl = 2.463 (3) Å, <Os(1)–Cl–Os(3) = 98.4 (1)°). The butterfly has a slightly obtuse angle between its wings, as evidenced by the angle Os(1)–midpt–Os(3) = 92.67 (1)° (midpt = midpoint of the W-Os(2) bond) and the dihedral angle of 87.31° or 92.69°[9] between the two planes defined by W–Os(2)–Os(1) and W–Os(2)–Os(3). Each of the four metal atoms is in a different chemical environment, and the cluster as a whole is chiral; in addition, atom C(1) behaves as an isolated chiral center. The cluster as a whole has the 62 outer valence electrons expected for a butterfly, 5M–M, arrangement.

The W(μ-O)Os system is characterized by the short tungsten–oxygen bond length of W–O(1) = 1.786 (9) Å and the comparatively long osmium–oxygen bond length of

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

[9] The usual method of calculating interplanar angles gives possible answers of ϕ° and 180–ϕ°; it is not always possible to determine instantly which of these represents the angle of interest.

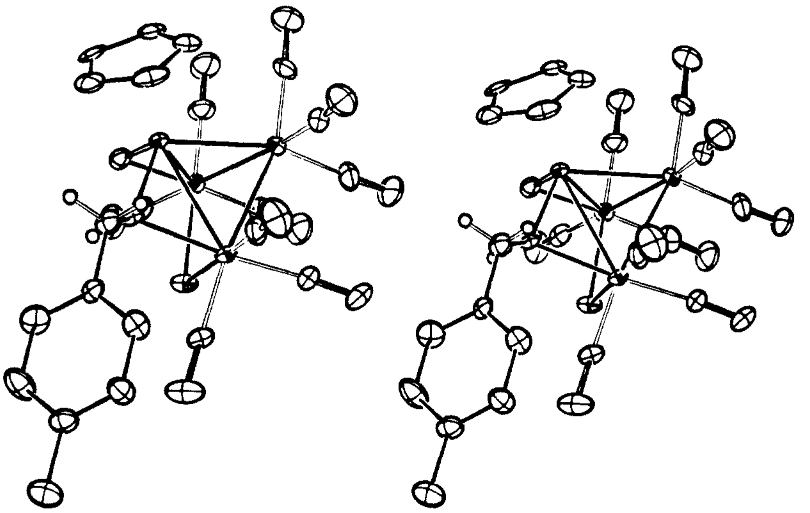


Figure 4. Stereoscopic view of the **3b** molecule projected onto the W-Os(1)-Os(2) plane; Os(3) lies below. The hydrogen atoms on C(1) and C(2) of the μ-–CHCH$_2$Tol group are included to emphasize the chiral center at C(1).

Table V. Dimensions in W(μ-O)Os Systems of WOs$_3$ Clusters

complex	d(W=O), Å	d(Os—O), Å	d(W—Os), Å	∠W—O—Os, deg
CpWOs$_3$(CO)$_9$(μ-O)[μ_3-CCH$_2$Tol]	1.812 (7)	2.169 (8)	2.663 (1)	83.5 (3)
CpWOs$_3$(CO)$_9$(μ-O)(μ-Cl)[μ-CHCH$_2$Tol]	1.786 (9)	2.126 (8)	2.987 (1)	99.2 (4)
CpWOs$_3$(CO)$_9$(μ-O)(μ-H)[μ-CHCH$_2$Tol]	1.737 (17)	2.167 (16)	2.916 (1)	96.0 (7)
CpWOs$_3$(CO)$_9$(μ-O)(μ-H)[μ-C=CHTol]	1.791 (23)	2.131 (21)	2.868 (2)	93.6 (9)
CpWOs$_3$(CO)$_8$(μ-O)(μ-H)[μ_3-η^2-C$_2$H$_2$]	1.761 (8)	2.200 (8)	2.885 (1)	92.8 (4)

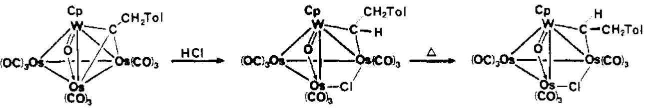
Os(3)-O(1) = 2.126 (8) Å; the angle W-O(1)-Os(3) is 99.2 (4)°. These data are compatible with the presence of a W=O:→Os system (in which the neutral μ-O ligand is a four-electron donor) as has been found previously in such related species as CpWOs$_3$(CO)$_9$(μ-O)(μ_3-CCH$_2$Tol),[1,10] CpWOs$_3$(CO)$_9$(μ-O)(μ-H)(μ-CHCH$_2$Tol) (**2a**),[2] CpWOs$_3$(CO)$_9$(μ-O)(μ-H)(μ-C=CHTol),[11] and CpWOs$_3$(CO)$_8$(μ-O)(μ-H)(μ_3-η^2-C$_2$H$_2$).[12] Parameters for the W(μ-O)Os portions of these five species are compared in Table V.

The μ-alkylidene ligand bridges the W-Os(1) bond, with W-C(1) = 2.064 (11) Å, Os(1)-C(1) = 2.196 (11) Å, and <W-C(1)-Os(1) = 85.0 (4)°. This pattern of W—C < Os—C bond length also occurs in the closely related μ-alkylidene species **2a**[2] (W—C = 2.068 (26) Å and Os—C = 2.281 (26) Å) as well as the μ-vinylidene species CpWOs$_3$(CO)$_9$(μ-O)(μ-H)(μ-C=CHTol)[11] (W—C = 2.082 (40) Å and Os—C = 2.148 (39) Å). The configuration of C(1) is such that the C(1)-C(2) vector is oriented toward the face defined by W, Os(1), and Os(2) (see Figure 4). This configuration positions the CH$_2$Tol moiety anti to the WOs$_2$ face that is edge-bridged by the oxo group and the μ-alkylidene ligand, as well as the chloro ligand; an analogous configuration is displayed in the hydrido–alkylidene species **2a**.[2] The specific conformation adopted by the μ-alkylidene ligand (<C(3)-C(2)-C(1)-W = 178.9°) places the bulky CpW and Tol moieties in a trans relationship.

Other distances within the molecule are both internally consistent and within the normally accepted ranges (viz., Os-CO = 1.840 (14)-1.940 (17) Å, C-O = 1.122 (18)-1.183 (19) Å, W-C(Cp) = 2.356 (15)-2.400 (13) Å, C-C(aliphatic) = 1.509 (16)-1.535 (19) Å, and C-C(benzenoid) = 1.352 (17)-1.400 (20) Å).

Structural and Chemical Relationships between Isomers b and c. The structure of **3b** shows the –CH$_2$Tol substituent on the alkylidene carbon to be oriented anti with respect to the WOs$_2$ face associated with the three edge-bridging groups. Since the spectroscopic properties of **3c** are very similar, its structure is assumed to be the corresponding syn configuration, with the -CH$_2$Tol substituent oriented toward this triply edge-bridged face. Analogous anti/syn diastereomers are assigned to represent the structures of the other **b**/**c** pairs of compounds as well.

The anti configuration of **3b** places the hydrogen atom on the bridging alkylidene carbon in the position where this carbon was bonded to an osmium atom in **1**, i.e., an Os-C bond has been transformed into an H-C bond with retention of configuration at the carbon center (see eq 1). The formation of CpWOs$_3$(μ-O)(μ-Cl)(μ-CDCH$_2$Tol) in the reaction of **1** with BCl$_3$/D$_2$O shows that the hydrogen is actually delivered to this carbon. Protonolysis of the Os-C bond followed by chloride coordination is the probable reaction pathway for forming **3b** directly from HCl, but the reaction with BCl$_3$ is likely more complex, since the reaction time is shorter and the yield is higher.[13] The formation of both **4b** and **4c** in the reaction of **1** with HBr may imply acid catalysis of the **4b** to **4c** rearrangement; this point is being investigated further. Interpreting the formation of both **5b** and **5c** in the reaction of **1** with HSPh is likewise complicated by the possibility that the temperature required by the reaction (110 °C) is in itself sufficient to cause rearrangement.



1 isomer-b isomer-c

The thermal rearrangement **3b** → **3c** has been observed directly, but we cannot yet fully define the mechanism.

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[10] Churchill, M. R.; Ziller, J. W.; Beanan, L. R. *J. Organomet. Chem.* **1985**, *287*, 235.

[11] Churchill, M. R.; Li, Y. J. *J. Organomet. Chem.* **1985**, *294*, 367.

[12] Churchill, M. R.; Bueno, C.; Park, J. T.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 1017.

[13] Ongoing studies of this reaction have shown that the initial product with BCl$_3$ in the absence of deliberate hydrolysis is a BCl$_3$ adduct of **3b**. Chi, Y.; Wilson, S. R.; Shapley, J. R., in preparation.

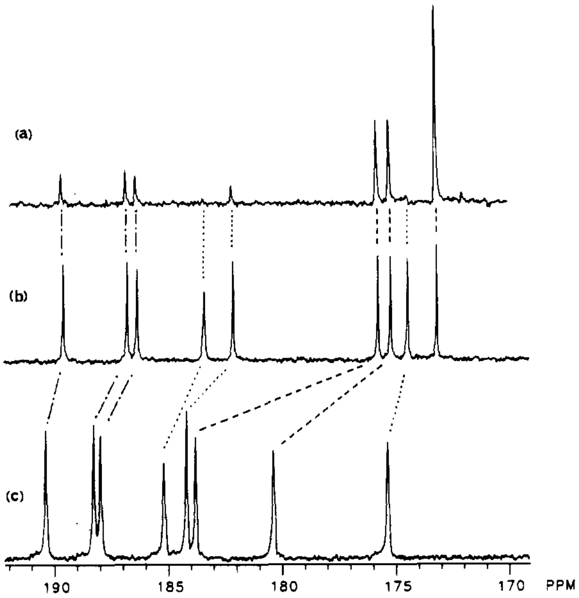

Figure 5. ^{13}C NMR spectra of (a) **3b** after brief treatment with ^{13}CO at 105 °C (see text), (b) **3b** prepared from ^{13}C-enriched precursors, and (c) enriched **3b** + PPh_2Me, i.e., $CpWOs_3(CO)_8(PPhMe_2)(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$.

Limiting features are (1) that a deuterium atom attached to the α-carbon of the alkylidene ligand is *not* scrambled with the hydrogen atoms on the β-carbon and (2) that a carbon monoxide atmosphere completely inhibits the rearrangement. The two most obvious pathways are (1) conversion to a terminal alkylidene bonded to the tungsten center, followed by rotation about the W=C bond and rebridging,[14] or (2) oxidative addition to form a hydrido–alkylidyne species, in which hydride mobility allows reformation of the C(α)–H bond from the opposite side.[15] The observed CO inhibition is consistent with the latter pathway, but, of course, does not confirm it.

Stereoselective Carbonyl Substitution in Compound 3b. Brief (5 min) treatment of **3b** with excess PPh_2Me in refluxing toluene provides the monosubstitution product $CpWOs_3(CO)_8(PPh_2Me)(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}CHCH_2Tol)$ in high yield. The ^{13}C NMR of this compound (Figure 5c) shows evidence for only one set of eight carbonyl signals, that is, only one stereoisomer is formed. By comparing the spectrum of the phosphine derivative with that of **3b** (Figure 5b), a correlation can be developed in which two sets of three resonances are shifted only 1–2 ppm to lower field upon substitution, whereas the remaining set loses one resonance and has the other two shifted 6–8 ppm to lower field. The former sets are assigned to the unsubstituted $Os(CO)_3$ centers and the latter set to the osmium center undergoing substitution; the differential effect of substitution is similar to that seen for $H_2Os_3(CO_9L$ (L = CO, PPh_2Et)[16] and in related triosmium derivatives.[17]

Further evidence in support of selective substitution in **3b** comes from study of its exchange with ^{13}CO. Samples of **3b** in toluene-d_8 were exposed to 1 atm of ^{13}CO (99%) at 105 °C for 10 min, after which the solvent was evaporated and the residue was redissolved in CD_2Cl_2. The ^{13}C NMR spectrum of this sample is shown in Figure 5a, where by comparison with the spectrum of the completely enriched **3b**, it can be seen that selective ^{13}CO enrichment does occur. The CO resonances can be grouped into three sets by virtue of their relative intensities, corresponding to the three $Os(CO)_3$ units. The resonances of highest relative intensity, at δ 173.1, 175.1, and 175.7, can be assigned to the CO's on the osmium atom undergoing exchange, and this is clearly the same center which is substituted by the phosphine ligand.

The specific site of substitution in **3b** cannot be determined unequivocally from our spectroscopic data. However, the Os—O=W system in **3b** can be considered analogous to the Ru—O=C(R) system studied by Kaesz and co-workers.[18] They found that substitution reactions in the acyl complexes $Ru_3(\mu\text{-}X, \mu\text{-}O{=}CR)(CO)_{10}$ (R = Me, X = H; R = Et, X = Cl, Br, I) occur on the ruthenium atom to which the acyl oxygen is bonded; the substitution is site specific for PPh_3 and $P(OMe)_3$ and at least highly selective for ^{13}CO. Furthermore, the site for phosphorus ligand coordination was specifically cis to both bridging groups, yet the bridging halide compounds reacted much more quickly and completely than the bridging hydride compound. These results can be rationalized by Brown's cis-labilization effect,[19] which predicts that substitution will occur preferentially at the site cis to labilizing π-donor ligands. In terms of our system, since there is just one carbonyl (C(31)–O(31), Figure 2) in **3b** that is cis to both the bridging oxo and the bridging chloro ligands, it is likely that this is the preferred site for substitution. In comparison, the corresponding hydride complex **2b** does not undergo observable substitution with PPh_2Me under conditions even more severe than those necessary for complete substitution in **3b**.[4]

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a listing of observed and caluculated structure factors (17 pages). Ordering information is given on any current masthead page.

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[14] For recent examples involving bridge–terminal alkylidene movement, see: (a) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 889. (b) Dyke, A. K.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Comm.* **1981**, 861. (c) Kroswagn, R.; Alt, R.; Septh, D.; Zeigler, M. L. *Angew. Chem.* **1981**, *93*, 1073. (d) Casey, C. P.; Fagan, P. J.; Miles W. H. *J. Am. Chem.* Soc. **1982**, *104*, 1134. Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464. (f) Holmgren, J. R.; Shapley, J. R. *Organometallics* **1985**, *4*, 793.

[15] In both mechanisms microscopic reversibility demands that the rearrangement proceed in both directions, but the equilibrium apparently favors **3c** strongly.

[16] Brown, S. C.; Evans, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1049.

[17] Bryan, E. G.; Alison, F.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1978**, 196.

[18] (a) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4640. (b) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646.

[19] Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366 and references therein.