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# $\mu_3$-$\eta^2$-Acyl and $\mu$-Alkylidene Complexes of a Molybdenum–Triosmium Cluster. Crystal Structure of $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$

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Initial decarbonylation of $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (4; Cp = $\eta^5$-$C_5H_5$, Tol = *p*-$C_6H_4Me$) with $Me_3NO$/MeCN followed by reaction with dihydrogen gives the dihydride complex $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**5**) in a quantitative yield. Thermolysis of **5** induces scission of the acyl C–O to afford the three isomeric hydrido–oxo–alkylidene compounds $CpMoO_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**6a–c**). Complexes **6a,b** are not chromatographically separable, and compound **6c** is produced either by heating a mixture of **6a** and **6b** in toluene (100 °C) or by treating with hydrochloric acid. Compounds **4**, **5**, and **6a–c** have been isolated as crystalline solids and have been characterized by spectroscopic (infrared, mass, $^1H$ and $^{13}C$ NMR) data. The molecular structure of compound **6c** has been determined by a single-crystal X-ray diffraction study. Complex **6c** crystallizes in the orthorhombic space group $Pmn2_1$ with $a = 12.438$ (7) Å, $b = 8.797$ (2) Å, $c = 11.846$ (4) Å, $V = 1296$ (1) Å$^3$, and $D$(calcd) = 2.87 g cm$^{-3}$ for $Z = 2$ and molecular weight 1118.9. Diffraction data were collected on a CAD4 diffractometer, and the structure was refined to $R(F) = 6.0\%$ and $R_w(F) = 7.5\%$ for 1236 data (Mo K$\alpha$ radiation). The molecule is based upon a tetrahedral $MoOs_3$ core. Each osmium atom is coordinated to three terminal CO ligands, and the molybdenum atom is bonded to an $\eta^5$-$C_5H_5$ ligand. The $\mu$-oxo, $\mu$-alkylidene, and $\mu$-hydrido ligands bridge each edge of one of the Os–Os–Mo triangular faces. The $\mu$-oxo and $\mu$-alkylidene groups are disordered out of the crystallographic mirror plane which bisects the $MoOs_3$ core. The $\mu$-hydride ligand is believed to span the elongated Os–Os edge of the tetrahedron. The aryl moiety ($CH_2Tol$) is disposed toward the $\mu$-oxo ligand, which clearly indicates that **6c** is formed from a mixture of **6a** and **6b** by an apparent rotation of the $\mu$-alkylidene carbon.

## Introduction

Acyl ligands have been widely discussed as potential surface intermediates in hydrocarbon chain growth during Fischer–Tropsch reactions.[2] Reduction of the acyl ligands to a hydroxy alkyl species prior to C–O bond scission has been assumed in subsequent deoxygenation processes.[3] However, it has also been noted that the direct C–O bond cleavage of cluster-bound $\mu_3$-$\eta^2$-acyl species may be relevant to the selective production of hydrocarbons on metal surfaces.[4,5] In previous work, the tungsten–triosmium cluster compound $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (1; Cp = $\eta^5$-$C_5H_5$, Tol = *p*-$C_6H_4Me$) has been shown to undergo facile thermal $\mu_3$-$\eta^2$-acyl C–O bond scission, yielding the oxo–alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (**2**) (see Scheme I).[5] This oxo–alkylidyne complex, in turn, undergoes hydrogenation to provide a mixture of two isomers of the hydrido–oxo–alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**3a,b**).[6] We have here extended our studies on the $\mu_3$-$\eta^2$-acyl group to investigate the reactivity of the ligand on a molybdenum–triosmium mixed-metal-cluster framework.

The triply bridging acyl complex $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**4**) is isolated as the major product (60% yield) from a Stone reaction,[7] the reaction of $H_2Os_3(CO)_{10}$ with the molybdenum alkylidyne complex $Cp(CO)_2Mo(CTol)$ under mild conditions (5–20 °C).[8] Initial decarbonylation of compound **4** followed by reaction with dihydrogen gives the dihydride complex $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**5**) in a quantitative yield. The crystal structure and solution dynamics of complex **5** will be described elsewhere.[9] Thermolysis of the dihydride complex **5** induces scission of the acyl C–O bond to afford two isomeric hydrido–oxo–alkylidene complexes $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**6a,b**). The crystal structure of the tungsten analogue **3a** has been determined,[5] but in solution it equilibrates with the second isomer **3b**. The interconversion **3a** ↔ **3b** has been proposed to occur by the $\mu$-hydride migration between edges of osmium–osmium bonds.[6a] This proposal is confirmed by observation of coupling between the $\mu$-alkylidene hydrogen and the $\mu$-hydride in the $^1H$ NMR spectrum of **6b** in the present work. Furthermore, the third *syn* isomer **6c** of the *anti*-alkylidene complexes **6a,b** is formed either by thermolysis of a mixture of **6a** and **6b** or by treatment with hydrochloric acid. This paper describes spectroscopic and chemical results of compounds **5** and **6a–c**, together with the X-ray structural analysis of compound **6c**. This structural characterization clearly indicates that complex **6c** is produced by an apparent rotation of the $\mu$-alkylidene

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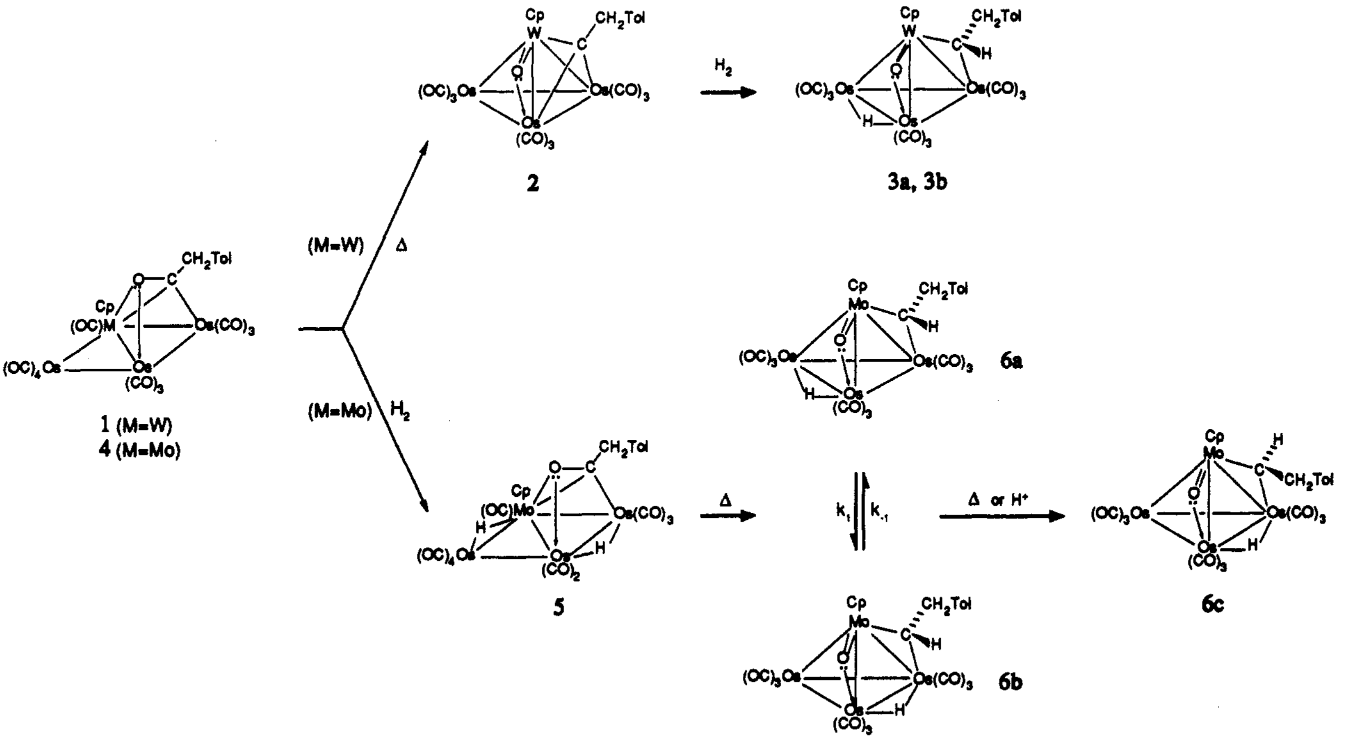
**Scheme I**



carbon in a mixture of **6a** and **6b**. A preliminary account of this work has been published.[8a]

## Experimental Section

**General Comments.** All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents were dried before use. Anhydrous trimethylamine *N*-oxide (mp 225–230 °C) was obtained from $Me_3NO{\cdot}2H_2O$ (98%, Aldrich Chemical Ltd.) by sublimation (three times) at 90–100 °C under vacuum. The progress of the reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, silica gel 60 F-254, E. Merck). Preparative thin-layer plates were prepared from silica gel G (Type 60, E. Merck).

Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. $^1H$ NMR (300 MHz), $^2H$ NMR (46 MHz), and $^{13}C$ NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. $Cr(acac)_3$ (ca. 0.02 M) was added to each $^{13}C$ sample as a shiftless relaxation reagent. Mass spectra were recorded by the staff of the Analytical Laboratory at Lucky Ltd. using a JEOL DX-300 mass spectrometer. All $m/z$ values are referenced to $^{98}Mo$ and $^{192}Os$. Microanalytical data were provided by the Analytical Laboratory of Lucky Ltd.

**Reaction of $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (4)[8] with Dihydrogen.** A red dichloromethane (50 mL)–acetonitrile (25 mL) solution of compound 4 (100.2 mg, 0.0854 mmol) was treated with an acetonitrile solution (10 mL) of anhydrous $Me_3NO$ (7.2 mg, 0.096 mmol) in a 500-mL glass pressure bottle, and the reaction mixture was stirred for 20 min. After evaporation of the solvent in vacuo, the residue was dissolved in toluene (100 mL). This solution was degassed by a freeze–pump–thaw cycle, and the bottle was charged with dihydrogen to a pressure of 60 psig. The resulting orange solution was heated at 80 °C for 1 h. After evaporation of the solvent, purification by preparative TLC (petroleum ether–dichloromethane, 3:2) provided $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**5**, 84.4 mg, 0.0736 mmol, 86%, $R_f$ 0.27) as an orange crystalline solid. Recrystallization from pentane–dichloromethane gave an analytically pure sample of compound **5**: $^1H$ NMR ($CDCl_3$, 25 °C) $\delta$ 7.19–7.12 (m, 4 H), 5.33 (s, 5 H), 3.74–3.56 (AB pattern, 2 H, $J = 13.1$ Hz), 2.35 (s, 3 H), −12.2 (s, 1 H), −17.6 (s, 1 H); $^{13}C$ NMR ($CD_2Cl_2$, −10 °C) $\delta$ (carbonyl carbon) Mo–CO 224.9, Os–CO 187.8, 185.9, 181.0 ($^2J_{CC} = 23.4$ Hz), 177.5 ($^2J_{CC} = 34.6$ Hz), 176.5 ($^2J_{CC} = 34.6$ Hz), 175.9 (d, $^2J_{CH} = 11.1$ Hz), 175.3, 169.5 (d, $^2J_{CH} = 7.1$ Hz), 168.2, acyl CO 173.6; IR ($CCl_4$) $\nu$(CO) 2119 (w), 2103 (vw), 2076 (s), 2045 (s), 2033 (sh), 2012 (vs), 2000 (m), 1981 (m), 1946 (w) cm$^{-1}$; MS (70 eV) $m/z$ 1154 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_{11}MoOs_3$: C, 25.13; H, 1.41. Found: C, 25.15; H, 1.43.

**Thermolysis of $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (5).** An orange-red dichloromethane (200 mL)–acetonitrile (10 mL) solution of **5** (128 mg, 0.111 mmol) was treated with an acetonitrile solution (10 mL) of anhydrous $Me_3NO$ (8.97 mg, 0.119 mmol), and the resulting solution was stirred for 20 min. After evaporation of the solvent in vacuo, a toluene solution (200 mL) of the residue was heated at 100 °C for 1 h. Purification by preparative TLC (petroleum ether–dichloromethane, 3:2) and subsequent recrystallization from petroleum ether–dichloromethane afforded two isomers of dark brown $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**6a,b**; 69.6 mg, 0.062 mmol, 56%; $R_f$ 0.3) and brown $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**6c**; 22.6 mg, 0.020 mmol, 18%; $R_f$ 0.5) as crystalline solids.

**6a**: $^1H$ NMR ($CDCl_3$, 25 °C) $\delta$ 7.17–7.27 (m, 4 H), 6.67 (t, 1 H, $J = 7.5$ Hz), 5.90 (s, 5 H), 4.01 (dd, 1 H, $J = 14.4, 6.4$ Hz), 3.52 (dd, 1 H, $J = 14.4, 8.6$ Hz), 2.39 (s, 3 H), −16.6 (s, 1 H); $^1H$ NMR (acetone-$d_6$, 25 °C) $\delta$ 7.33–7.17 (m, 4 H), 6.83 (dd, 1 H, $J = 9.4, 5.4$ Hz), 6.16 (s, 5 H), 4.44 (dd, 1 H, $J = 14.1, 5.4$ Hz), 3.39 (dd, 1 H, $J = 14.1, 9.4$ Hz), 2.32 (s, 3 H), −16.6 (s, 1 H); $^{13}C$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ (carbonyl carbon) Os–CO 185.9, 184.9, 184.3, 182.2, 179.3 (d, $^2J_{CH} = 8.0$ Hz), 177.7, 174.7, 170.2 (d, $^2J_{CH} = 12.0$ Hz), 168.5, 146.3 (d, $^1J_{CH} = 132.5$ Hz, $\mu$-C); MS (70 eV) $m/z$ 1126 (M$^+$). Anal. Calcd for $C_{23}H_{16}O_{10}MoOs_3$: C, 24.69; H, 1.44. Found: C, 24.80; H, 1.56.

**6b**: $^1H$ NMR ($CDCl_3$, 25 °C) $\delta$ 7.14–7.27 (m, 4 H), 5.89 (s, 5 H), 5.70 (t, 1 H, $J = 8.7$ Hz), 3.71 (dd, 1 H, $J = 14.5, 6.4$ Hz), 3.37 (dd, 1 H, $J = 14.5, 8.7$ Hz), 2.38 (s, 3 H), −19.2 (s, 1 H); $^1H$ NMR (acetone-$d_6$, 25 °C) $\delta$ 7.17–7.33 (m, 4 H), 6.15 (s, 5 H), 5.93 (ddd, 1 H, $J = 9.6, 5.8, 2.0$ Hz), 4.02 (dd, 1 H, $J = 14.4, 5.8$ Hz), 3.33 (dd, 1 H, $J = 14.4, 9.6$ Hz), 2.28 (s, 3 H), −19.3 (d, 1 H, $J = 2.0$ Hz); $^{13}C$ NMR ($CD_2Cl_2$, −20 °C) $\delta$ (carbonyl carbon) Os–CO 189.7, 184.3, 183.5, 181.9, 177.3, 173.7, 170.6, 169.5 (d, $^2J_{CH} = 9.6$ Hz), 168.9 (d, $^2J_{CH} = 12.9$ Hz), 135.8 (d, $^1J_{CH} = 134.9$ Hz, $\mu$-C).

Mixture of **6a** and **6b**: IR ($C_6H_{12}$) $\nu$(CO) 2087 (s), 2061 (vs), 2053 (s), 2033 (sh), 2028 (vs), 2012 (m), 2003 (m), 1987 (s), 1963 (w), 1955 (w), 1930 (w) cm$^{-1}$.

**6c**: $^1H$ NMR ($CDCl_3$, 25 °C) $\delta$ 7.14–7.23 (m, 4 H), 6.59 (dd, 1 H, $J = 11.4$ 5.9 Hz), 5.38 (s, 5 H), 4.74 (dd, 1 H, $J = 12.2, 5.9$ Hz), 2.52 (t, 1 H, $J = 11.7$ Hz), 2.40 (s, 3 H), −18.6 (s, 1 H); $^1H$ NMR (acetone-$d_6$, 25 °C) $\delta$ 7.21–7.27 (m, 4 H), 7.04 (ddd, 1 H, $J = 10.8, 6.2, 1.5$ Hz), 5.59 (s, 5 H), 4.62 (dd, 1 H, $J = 12.9, 6.2$ Hz), 2.79 (dd, 1 H, $J = 12.9, 10.8$ Hz), 2.37 (s, 3 H), −18.4 (d, 1

**Table I. Crystal Data for $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (6c)**

| | | | |
|---|---|---|---|
| formula | $C_{23}H_{16}O_{10}MoOs_3$ | *V*, Å³ | 1296 (1) |
| fw | 1118.92 | *Z* | 2 |
| cryst syst | orthorhombic | ρ(calcd), g cm⁻³ | 2.87 |
| space group | *Pmn*2₁ | temp, °C | 20 ± 1 |
| *a*, Å | 12.438 (7) | λ(Mo Kα), Å | 0.709 26 |
| *b*, Å | 8.797 (2) | μ, cm⁻¹ | 152.0 |
| *c*, Å | 11.846 (4) | | |

H, $J = 1.5$ Hz); $^{13}$C NMR ($CDCl_3$, −10 °C) δ (carbonyl carbon) Os–CO 189.0, 185.2, 185.1, 182.4, 176.1, 175.2, 170.2, 169.7 (d, $^2J_{CH} = 13.1$ Hz), 168.3 (d, $^2J_{CH} = 9.8$ Hz), 140.5 (d, $^1J_{CH} = 140.6$ Hz, μ-C); IR ($C_6H_{12}$) ν(CO) 2086 (s), 2060 (vs), 2028 (vs), 2012 (s), 2000 (m), 1990 (w), 1955 (w), 1941 (m) cm⁻¹; MS (70 eV) *m/z* 1126 ($M^+$). Anal. Calcd for $C_{23}H_{16}O_{10}MoOs_3$: C, 24.69; H, 1.44. Found: C, 24.85; H, 1.66.

**Thermolysis of a Mixture of 6a and 6b.** A toluene solution (30 mL) of a mixture of **6a** and **6b** (10 mg, 0.0089 mmol) was heated at 100 °C for 13 h. After evaporation of the solvent, purification by preparative TLC (petroleum ether–dichloromethane, 3:2) provided compound **6c** (7.0 mg, 0.0062 mmol, 70%) and unreacted starting compounds **6a,b** (2.5 mg, 0.0022 mmol, 24%). A single crystal of **6c** suitable for an X-ray analysis was grown from chloroform–methanol at −15 °C.

**Reaction of a Mixture of 6a and 6b with Aqueous HCl.** A mixture of **6a** and **6b** (10 mg, 0.0089 mmol) was dissolved in acetone (40 mL), and 6 N aqueous hydrochloric acid (10 μL, 0.06 mmol) was added. The reaction mixture was heated at 45 °C for 4 h. The solution was neutralized and dried with anhydrous potassium carbonate. The anhydrous salt was filtered, and the solvent was evaporated. Dark brown crystals of **6c** (7.2 mg, 0.0064 mmol, 72%) and unreacted starting compound **6a,b** (2.3 mg, 0.0021 mmol, 24%) were isolated after purification by preparative TLC (petroleum ether–dichloromethane, 3:2).

**Preparation of $^{13}$C-Enriched Compounds.** The $^{13}$C-enriched $CpMoOs_3(^*CO)_{11}[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ (**4**) was prepared from the reaction of $^{13}$CO-enriched $H_2Os_3(^*CO)_{10}$ (ca. 50% enrichment) with $Cp(CO)_2Mo(CTol)$ by the reported procedure.[8b] This complex was then utilized to prepare $CpMoOs_3(^*CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ (**5**) and $CpMoOs_3(^*CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}^*CHCH_2Tol)$ (**6a–c**) by procedures similar to those described above.

**X-ray Data Collection and Structure Solution of 6c.** A dark brown crystal of approximate dimensions 0.3 × 0.3 × 0.5 mm was mounted and aligned on an Enraf-Nonius CAD4 diffractometer. Details of the relevant crystallographic data are given in Table I. The positions of 25 strong reflections within $7 \le \theta \le 10°$ were located using a "blind" search procedure. These positions were carefully centered and were used in the subsequent autoindexing procedure. The dimensions and symmetry of the resulting cell were confirmed by examining the axial photograph along each axis. All data (5129 reflections) within the hemisphere of $2\theta \le 50$ ($k \ge 0$) were measured using a $2\theta$–ω scan procedure ($\Delta\omega = 1.2 + 0.35 \tan\theta$). As a general check on the electronic and crystal stability, the intensities of three reference reflections were remeasured every 2 h. These were not observed to vary significantly throughout the data collection period. The intensity data were corrected for the absorption effect using the empirical ψ-scan data and were averaged together in *mmm* Laue symmetry, yielding 1352 unique reflections with the internal consistency factor $R_I \equiv \sum|I - \langle I \rangle|/\sum I = 5.4\%$. As the observed systematic absences ($h + l = 2n + 1$ for *h*0*l*) did not differentiate *a* and *c* axes (*Pmn*2₁ vs *P*2₁*nm*), the correct assignment of the space group required separate trials of the structural solution with each setting. Direct methods were used to locate the metal cluster.[10] The structure factor calculations with the metal cluster allowed identification of *Pmn*2₁ as the correct space group (*R* = 15% vs 30%). The remaining atoms were located from differnce electron density maps. The crystallographic mirror plane bisects the metal cluster framework and also the cyclopentadienyl ring. The oxo and alkylidene ligands were disordered out of the mirror plane. The mirror plane nearly bisects the tolyl group of the alkylidene ligand, and its electron density overlaps with that of its symmetry mate. For this group, carbon atoms were located at the nominal maxima of the electron density and in the refinement were treated as ordered. No attempt has been made to locate hydrogen atoms. The metal atoms and the carbonyl and cyclopentadienyl ligands were refined anisotropically, while the disordered oxo and alkylidene ligands were isotropically refined. The full-matrix least-squares refinement cycles employing unit weights on 1236 reflections ($F \ge \sigma_F$) smoothly converged to $R \equiv \sum||F_o| - |F_c||/\sum|F_o| = 6.0\%$ and $R_w \equiv [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 7.5\%$. For all 1352 reflections, the residual was *R* = 6.7%. All the crystallographic calculation was done with the MolEN package.[11] The final positional and thermal parameters are listed in Table II.

**Table II. Final Positional Parameters for $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (6c)**

| atom | *x* | *y* | *z* | *B*, Å² |
|---|---|---|---|---|
| Os(1) | 0.1203 (1) | 0.0671 (2) | 0.648 | 4.54 (3) |
| Os(2)[a] | 0.000 | 0.2430 (3) | 0.8007 (2) | 3.19 (3) |
| Mo[a] | 0.000 | 0.3297 (6) | 0.5870 (5) | 3.9 (1) |
| O(1)[a] | 0.129 (4) | 0.240 (5) | 0.535 (4) | 3.4 (9)[b] |
| O(11) | 0.131 (2) | −0.156 (4) | 0.848 (3) | 5.8 (7) |
| O(12) | 0.235 (3) | −0.143 (4) | 0.489 (3) | 8.6 (9) |
| O(13) | 0.328 (3) | 0.214 (5) | 0.737 (5) | 14 (2) |
| O(21)[a] | 0.000 | 0.051 (6) | 1.022 (4) | 7 (1) |
| O(22) | 0.180 (3) | 0.448 (4) | 0.879 (3) | 6.5 (8) |
| C(2)[a] | −0.092 (6) | 0.208 (8) | 0.488 (7) | 4 (1)[b] |
| C(3)[a] | −0.051 (7) | 0.120 (9) | 0.373 (7) | 5 (2)[b] |
| C(4)[a] | 0.000 | 0.25 (1) | 0.287 (8) | 7 (2)[b] |
| C(5) | 0.099 (5) | 0.316 (7) | 0.256 (5) | 9 (2)[b] |
| C(6) | 0.095 (4) | 0.435 (6) | 0.172 (5) | 7 (1)[b] |
| C(7)[a] | 0.000 | 0.494 (8) | 0.135 (8) | 7 (2)[b] |
| C(8)[a] | 0.000 | 0.628 (9) | 0.056 (7) | 7 (2)[b] |
| C(11) | 0.123 (2) | −0.063 (5) | 0.775 (3) | 3.8 (8) |
| C(12) | 0.193 (4) | −0.065 (5) | 0.544 (4) | 5 (1) |
| C(13) | 0.245 (3) | 0.167 (5) | 0.700 (7) | 13 (2) |
| C(21)[a] | 0.000 | 0.137 (8) | 0.936 (6) | 5 (1) |
| C(22) | 0.109 (3) | 0.368 (5) | 0.846 (5) | 6 (1) |
| C(51)[a] | 0.000 | 0.578 (6) | 0.669 (8) | 9 (3) |
| C(52) | 0.052 (3) | 0.545 (6) | 0.484 (4) | 6 (1) |
| C(53) | 0.096 (3) | 0.565 (5) | 0.600 (5) | 7 (2) |

[a] Atoms were refined with half-occupancy. [b] Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

## Results and Discussion

**Characterization of 5 and Scission of the $\mu_3$-$\eta_2$-Acyl Group.** The direct thermal activation of a cluster-bound acyl C–O bond has been previously observed in the triply bridging tungsten–triosmium acyl complex $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**1**)[12] to produce the oxo–alkylidyne complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (**2**),[5] as shown in Scheme I. The reactivity of the analogous molybdenum–triosmium acyl complex $CpMoOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**4**) has been examined regarding the acyl C–O bond activation by employing the analogous procedure for **1**. Initial decarbonylation of **4** with $Me_3NO$/MeCN followed by thermolysis results in extensive decomposition of the starting compound **4**, and many bands (more than eight) in low yields are observed on a preparative TLC plate. However, initial decarbonylation of **4** and subsequent reaction with dihydrogen proceeds smoothly and affords the dihydride complex $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**5**) in a quantitative yield. The molecular structure of compound **5** has been deter-

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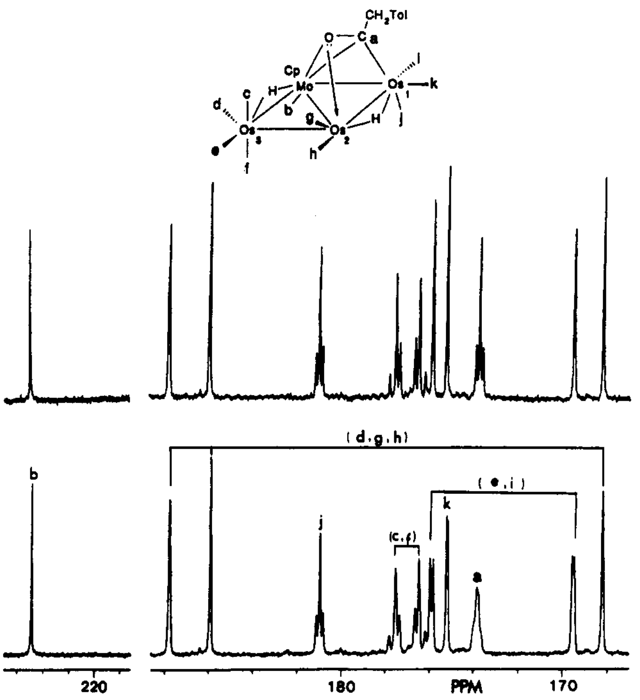

**Figure 1.** $^{13}$C NMR spectra (75 MHz) of $CpMoOs_3(CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**5**) in $CD_2Cl_2$ at −10 °C: (upper) $^1$H decoupled; (lower) $^1$H coupled.

mined by a single-crystal X-ray diffraction study, which formed part of our previous communication.[8a] The limiting low-temperature $^{13}$C NMR spectrum of $^{13}$C-enriched **5**, $CpMoOs_3(^*CO)_{10}(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}^*C(O)CH_2Tol]$ (see Figure 1) was obtained at −10 °C in $CD_2Cl_2$ and is consistent with the molecular structure observed in the solid state. Note that the acyl carbon in $^{13}$C-enriched **5** is also enriched by carbon-13, which indicates that it is derived from $^{13}$CO. The spectrum shows 11 carbonyl resonances at $\delta$ 224.9, 187.8, 185.9, 181.0, 177.5, 176.5, 175.9, 175.3, 173.6, 169.5, and 168.2 (each of intensity 1). The most downfield signal at $\delta$ 224.9 is assigned to the carbonyl group b on the molybdenum atom on the basis of its chemical shift and temperature behavior.[9] The resonances at $\delta$ 177.5 and 176.5 exhibit an AB pattern of $^{13}$C satellites ($^2J_{CC}$ = 34.6 Hz), characteristic of inequivalent trans axial carbonyls c and f.[12b,13] The signal at $\delta$ 181.0 shows $^{13}$C satellites ($^2J_{CC}$ = 23.4 Hz) and is assigned to the carbonyl ligand j trans to the acyl carbon a. The latter resonance is broad at $\delta$ 173.6, presumably due to coupling to both carbonyl carbon j and hydrides: the resonance shows resolved $^{13}$C satellites ($^2J_{CC}$ = 23.4 Hz) in the $^{13}C\{^1H\}$ NMR spectrum and remains sharp at higher temperatures. The carbonyl groups e and i, trans to the bridging hydrogens, are doublets at $\delta$ 175.9 ($^2J_{CH}$ = 11.1 Hz) and 169.5 ($^2H_{CH}$ = 7.1 Hz), respectively. These couplings were also verified by obtaining the $^1$H-coupled spectrum as shown in Figure 1. The resonances due to the two hydrides appear at $\delta$ −12.2 and −17.6 as singlets in the $^1$H NMR spectrum.

Upon thermolysis of **5**, scission of the acyl C–O bond is now induced and subsequent reduction of the resulting alkylidyne moiety to the alkylidene group by a hydride ligand produces hydrido–oxo–alkylidene complexes $CpMoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**6a,b**). A possible intermediate for the conversion **5** → **6a,b** is assumed to be the dihydridomolybdenum analogue of compound **2**, which could not be isolated in this study. Previous work has demonstrated cleavage of formyl or acyl ligands by nucleophilic attack at carbon,[4a] by electrophilic attack at oxygen,[4b] or by direct thermolysis.[5] Facile reductive cleavage by a variety of hydride reagents has also been reported by several groups.[3] However, the present reductive cleavage in **5** is unique in that the internal hydride ligands assist the C–O bond scission. This may result from the fact that the two hydride ligands in **5** withdraw electron density from the cluster framework and increase the oxidation states and oxophilicity of metal centers. The positions of carbonyl region infrared absorption bands of compound **5** are shifted to higher frequency than those of compound **4**, reflecting the electronic effect due to the hydride ligands.[8]

**Characterization of Compounds 6a,b.** The tungsten oxo–alkylidyne compound **2** has been shown to react readily with molecular hydrogen to yield an equilibrium mixture of two isomeric hydrido–oxo–alkylidene clusters $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ (**3a,b**).[5,6] The crystal structure of one isomer, **3a**, has been previously determined, but in solution it coexists with a second isomer, **3b**. Shapley et al. have proposed that **3a,b** are interconverted in solution by hydride migration between edges of osmium–osmium bonds (see structures **6a,b** in Scheme I): they in fact isolated and structurally characterized the chlorotungsten derivative of **6b** $CpWOs_3(CO)_9(\mu\text{-}Cl)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ from the reaction of **2** with HCl.[14]

Complexes **6a,b** are not chromatographically separable but crystallize from petroleum ether–dichloromethane as pure **6a**. Compounds **6a,b** show essentially the same spectroscopic data as those of **3a,b** and therefore are isomorphous with **3a,b**, respectively. Both $^1$H and $^{13}$C NMR data for **6a,b** are shown in Figure 2. These data clearly indicate that the species exists as two isomers in solution. The $^1$H NMR spectrum of each isomer in $CDCl_3$ exhibits a hydride resonance as a singlet ($\delta$ −16.6 for **6a** and −19.2 for **6b**) and three separate resonances of AMX pattern with 1:1:1 relative intensities corresponding to the $\mu$-alkylidene CH hydrogen ($\delta$ 6.67 for **6a** and 5.70 for **6b**) and the two diasterotopic benzylic $CH_2$ hydrogens ($\delta$ 4.01, 3.52 for **6a** and 3.71, 3.37 for **6b**). These resonances can be assigned on the basis of a deuterium-labeling study and decoupling experiment. Interestingly, when the $^1$H NMR spectrum of **6a,b** is obtained in acetone-$d_6$, coupling between the $\mu$-alkylidene hydrogen and the $\mu$-hydride in **6b** is observed: the dd pattern of the $\mu$-alkylidene hydrogen resonance in $CDCl_3$ is further split into a doublet of the dd pattern, eight peaks at $\delta$ 5.93 with $^3J_{HH}$ = 2.0 Hz, and the singlet of the $\mu$-hydride resonance is split into a doublet at $\delta$ −19.3 with $^3J_{HH}$ = 2.0 Hz (see inserts in Figure 2). This observation supports the fact that the hydride and the alkylidene ligands in **6b** bridge the adjacent metal–metal bonds. The $^{13}$C NMR spectrum for $^{13}$C-enriched **6a,b**, $CpMoOs_3(^*CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}^*CHCH_2Tol)$, shows nine signals of carbonyls bonded to osmium atoms and one $\mu$-alkylidene carbon resonance ($\delta$ 146.3 ($^1J_{CH}$ = 132.5 Hz) for **6a** and 135.8 ($^1J_{CH}$ = 134.9 Hz) for **6b**), respectively. Of the nine carbonyl resonances, two signals are doublets at $\delta$ 179.3 ($^2J_{CH}$ = 8.0 Hz) and 170.2 ($^2J_{CH}$ = 12.0 Hz) for **6a** and at $\delta$ 169.5 ($^2J_{CH}$ = 9.6 Hz) and 168.9 ($^2J_{CH}$ = 12.9 Hz) for **6b**, due to coupling to each $\mu$-hydride ligand.

The hydride migration rate between **6a** and **6b** was studied at 23 °C by $^1$H NMR spectroscopy. Crystals of **6a** were dissolved in acetone-$d_6$ in an NMR tube, and signals due to **6b** were observed to grow in as a function of time (see Figure 3). Relative concentrations of the two

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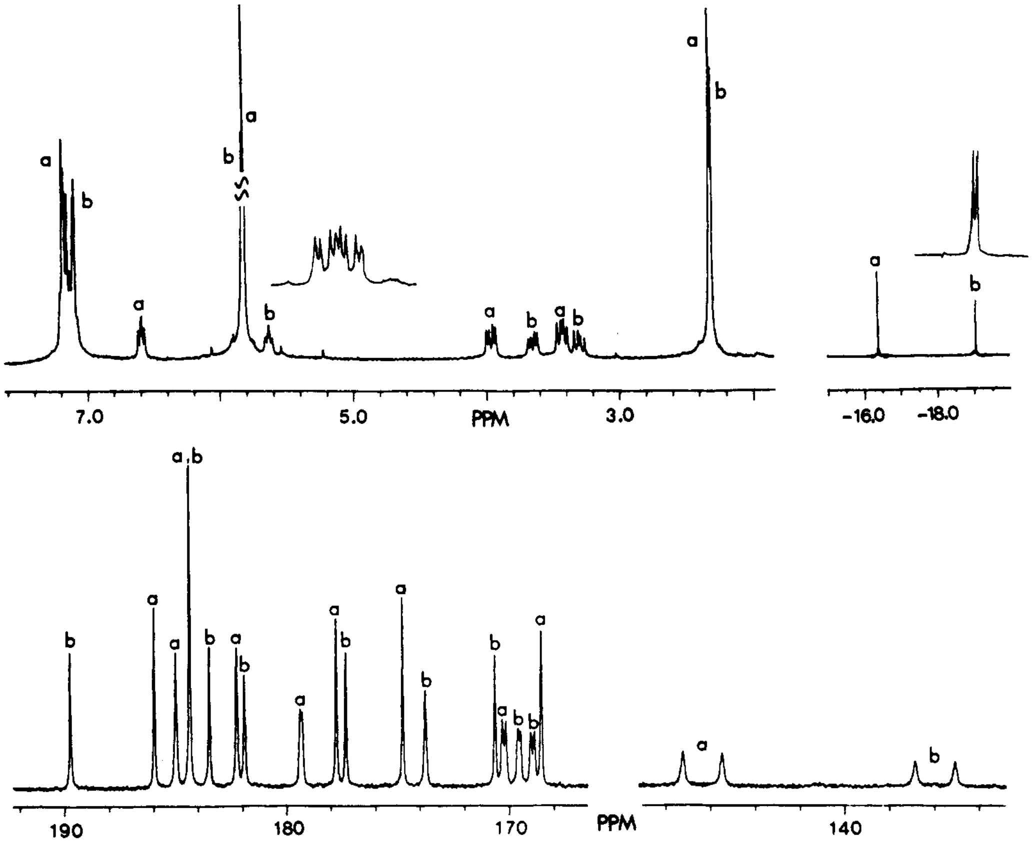

**Figure 2.** $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, upper) and $^{13}C$ NMR (75 MHz, $CD_2Cl_2$, -20 °C, lower) spectra of a mixture of **6a** and **6b**. Inserts are resonances due to $\mu$-C*H* and $\mu$-*H* or **6b** in acetone-$d_6$.

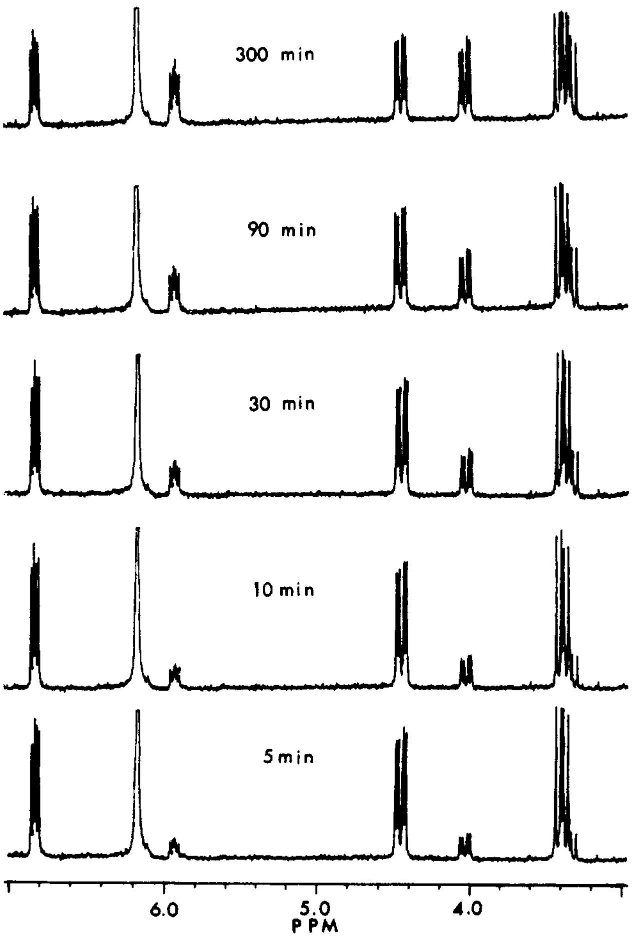

**Figure 3.** $^1H$ NMR spectra (300 MHz, acetone-$d_6$, 23 °C) for the isomerization of **6a** to **6b** as a function of time.

isomers were measured by integration of the peaks at $\delta$ 6.83 for **6a** and at $\delta$ 5.93 for **6b** in the $^1H$ NMR spectrum. The two isomers are in equilibrium, and analysis according to reversible first-order kinetics gives excellent fits of experimental data: $K_{eq} = [\mathbf{6b}]/[\mathbf{6a}] = 0.981 \pm 0.003$, $k_{obs} = (1.00 \pm 0.07) \times 10^{-2}\ s^{-1}$, $k_1 = (4.95 \pm 0.02) \times 10^{-3}\ s^{-1}$, and $k_{-1} = (5.05 \pm 0.02) \times 10^{-3}\ s^{-1}$.

**Synthesis and Characterization of 6c.** The third isomer of hydrido–oxo–alkylidene complex **6c** is produced either by thermolysis of a mixture of **6a** and **6b** or by treatment with hydrochloric acid. Maximum yields of 70% and 72% are obtained together with the recovered starting material by thermolysis at 100 °C for 13 h and by reaction with HCl at 45 °C for 4 h, respectively. Either a longer reaction time and higher temperatures or use of other acids such as $CH_3CO_2H$, $HBF_4$, and $H_2SO_4$ results in extensive decomposition and lower yields of **6c**. The $^1H$ and $^{13}C$ NMR spectra of **6c** establish it as a hydrido–alkylidene complex and also provide clear spectroscopic distinction of **6c** from the **6a,b** isomers. The $^1H$ NMR spectrum in $CDCl_3$ exhibits a $\mu$-hydride resonance ($\delta$ -18.6) and three resonances of AMX pattern due to the alkylidene CH ($\delta$ 6.59) and benzylic $CH_2$ ($\delta$ 4.74 and 2.52) hydrogens of the $\mu$-alkylidene moiety. The $^1H$ NMR spectrum of **6c** in acetone-$d_6$ also shows coupling ($^3J_{HH}$ = 1.5 Hz) of the $\mu$-alkylidene hydrogen and the $\mu$-hydride, which is consistent with the location of the hydride ligand in the solid state. The $^{13}C$ NMR spectrum of $^{13}C$-enriched **6c**, $CpMoOs_3(^*CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}^*CHCH_2Tol)$, was obtained at -10 °C in $CDCl_3$. This spectrum shows an alkylidene carbon resonances at $\delta$ 140.5 ($^1J_{CH}$ = 140.6 Hz) and nine carbonyl resonances at $\delta$ 189.0, 185.2, 185.1, 182.4, 176.1, 175.2, 170.2, 169.7, and 168.3. The two carbonyl groups trans to the bridging hydride appear as doublets at $\delta$ 169.7 ($^2J_{CH}$ = 13.1 Hz) and 168.3 ($^2J_{CH}$ = 9.8 Hz). Increasing the

NMR sample temperature from −10 to 100 °C in toluene-$d_8$ causes three carbonyl resonances at δ 189.0, 185.1, and 182.4 to broaden to the same extent and to coalesce to a broad single peak, while the other six carbonyls remain sharp. Thus, the three signals are assigned to the three carbonyl ligands on the unique Os(2) atom, which undergoes localized 3-fold carbonyl exchange.

The actual structure of **6c** has been determined by a single-crustal X-ray diffraction study (vide infra): this analysis shows the $CH_2Tol$ group on the alkylidene carbon to be oriented syn with respect to the $MoOs_2$ face associated with the three edge-bridging ligands. This clearly indicates that **6c** is formed from anti isomers **6a,b** by an apparent rotation of the μ-alkylidene carbon. Shapley and co-workers have found that pyrolysis of the chlorotungsten derivative of **6b** $CpWOs_3(CO)_9(\mu\text{-Cl})(\mu\text{-O})(\mu\text{-CHCH}_2Tol)$ provided the second chloro–alkylidene isomer; they were not successful at inducing crystallization of this second isomer and assumed its structure to be the corresponding syn configuration. The thermal conversion anti → syn isomer, however, is clearly shown in the present molybdenum–triosmium clusters. A detailed mechanism concerning the apparent thermal rotation of the μ-alkylidene carbon remains speculative at the moment. The μ-alkylidene carbon rotation has been proposed to occur either by bridge–terminal alkylidene movement[15] or by oxidative addition of the alkylidene carbonyl–hydrogen bond to form a hydrido–alkylidyne species followed by reformation of the C–H bond from the opposite side.[14] The third probable mechanism in the present complex is a "windshield wiper" movement of the μ-oxo ligand on a $MoOs_2$ face: while remaining bonded to the molybdenum atom, the oxo ligand of an anti isomer swings to bridge the other Mo–Os edge of the triangular face with concomitant rearrangement of a hydride, giving a syn isomer.

The acid-induced isomerization reaction was examined by a deuterium-labeling study. When the deuterated acid (DCl, acetone-$d_6$, 56 °C, 14 h) was used, the hydrogen at δ 6.59 (100%) on the μ-alkylidene carbon and the hydride ligand at δ −18.6 (37%) was labeled as deuterium in the $^2H$ NMR spectrum. The result implies that the deuterium exchange may occur independently for the two sites and a likely pathway for the formation of **6c** by the acid involves protonation of an alkylidene carbon–metal bond to form a cationic alkyl species followed by rotation around a carbon–metal single bond and subsequent deprotonation.

**Crystal Structure of $CpMoOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2Tol)$ (6c).** The crystal contains a disordered arrangement of discrete $CpMoOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2Tol)$ molecules, which are mutually separated by normal van der Waals distances; there are no unusually close intermolecular contacts. The overall molecular geometry and the atomic labeling scheme are illustrated in Figure 4. Interatomic distances and angles are listed in Tables III and IV.

The metal core is associated with 60 outer valence electrons, as expected for a cluster with a tetrahedral arrangement.[16] The hydrido, oxo, and alkylidene ligands bridge each edge of the Os(1)–Mo–Os(1)′ triangular face. The μ-oxo and μ-alkylidene groups, however, are disordered out of the crystallographic mirror plane which includes the Mo and Os(2) atoms and bisects the Os(1) and Os(1)′ bond, each occupying the opposite side of the plane with half-occupancy. As carbon atoms of the tolyl group,

**Table III. Interatomic Distances (Å) and Esd's for $CpMoOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2Tol)$ (6c)**

| | | | |
|---|---|---|---|
| (A) Metal–Metal Distances | | | |
| Os(1)–Os(1)′ | 2.992 (3) | Os(1)–Mo | 2.845 (5) |
| Os(1)–Os(2) | 2.812 (3) | Os(2)–Mo | 2.643 (6) |
| (B) Metal–Alkylidene Distances | | | |
| Os(1)–C(2) | 2.29 (8) | Mo–C(2) | 1.96 (8) |
| (C) Metal–Oxygen Distances | | | |
| Os(1)–O(1) | 2.03 (5) | Mo–O(1) | 1.89 (5) |
| (D) Distances within the μ-$CHCH_2$Tol Ligand | | | |
| C(2)–C(3) | 1.6 (1) | C(5)–C(6) | 1.44 (8) |
| C(3)–C(4) | 1.7 (1) | C(6)–C(7) | 1.37 (6) |
| C(4)–C(5) | 1.40 (8) | C(7)–C(8) | 1.5 (1) |
| (E) Metal–Carbon (Carbonyl) Distances | | | |
| Os(1)–C(11) | 1.89 (4) | Os(2)–C(21) | 1.85 (7) |
| Os(1)–C(12) | 1.92 (4) | Os(2)–C(22) | 1.83 (4) |
| Os(1)–C(13) | 1.89 (5) | | |
| (F) Carbon–Oxygen (Carbonyl) Distances | | | |
| C(11)–O(11) | 1.20 (5) | C(21)–O(21) | 1.27 (9) |
| C(12)–O(12) | 1.08 (6) | C(22)–O(22) | 1.19 (5) |
| C(13)–O(13) | 1.20 (6) | | |
| (G) Metal–Carbon (Cp) Distances | | | |
| Mo–C(51) | 2.39 (6) | Mo–C(53) | 2.40 (5) |
| Mo–C(52) | 2.34 (4) | | |
| (H) Distances within the Cp Ligand | | | |
| C(51)–C(53) | 1.45 (7) | C(52)–C(53) | 1.49 (8) |
| C(52)–C(52) | 1.30 (6) | | |

**Table IV. Interatomic Angles (deg) and Esd's for $CpMoOs_3(CO)_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2Tol)$ (6c)**

| | | | |
|---|---|---|---|
| (A) Intermetallic Angles | | | |
| Os(1)–Mo–Os(2) | 61.5 (1) | Os(1)–Os(2)–Os(1)′ | 64.27 (7) |
| Os(1)–Mo–Os(1)′ | 63.4 (1) | Os(1)–Os(1)–Mo | 58.28 (7) |
| Os(2)–Os(1)–Mo | 55.7 (1) | Os(1)–Os(1)′–Os(2) | 57.86 (5) |
| Os(1)–Os(2)–Mo | 62.8 (1) | | |
| (B) M–M–CO Angles | | | |
| Mo–Os(1)–C(11) | 135 (1) | Os(1)′–Os(1)–C(12) | 118 (1) |
| Mo–Os(1)–C(12) | 125 (1) | Os(1)′–Os(1)–C(13) | 145 (2) |
| Mo–Os(1)–C(13) | 98 (1) | Mo–Os(2)–C(21) | 166 (2) |
| Os(2)–Os(1)–C(11) | 80 (1) | Mo–Os(2)–C(22) | 96 (2) |
| Os(2)–Os(1)–C(12) | 175 (1) | Os(1)–Os(2)–C(21) | 106 (2) |
| Os(2)–Os(1)–C(13) | 88 (2) | Os(1)–Os(2)–C(22) | 97 (1) |
| Os(1)′–Os(1)–C(11) | 91.1 (9) | Os(1)–Os(2)–C(22)′ | 156 (2) |
| (C) Os–C–O and C–Os–C Angles | | | |
| Os(1)–C(11)–O(11) | 173 (3) | C(11)–Os(1)–C(12) | 97 (2) |
| Os(1)–C(12)–O(12) | 178 (3) | C(11)–Os(1)–C(13) | 90 (2) |
| Os(1)–C(13)–O(13) | 172 (4) | C(12)–Os(1)–C(13) | 96 (2) |
| Os(2)–C(21)–O(21) | 174 (6) | C(21)–Os(2)–C(22) | 93 (2) |
| Os(2)–C(22)–O(22) | 178 (4) | C(22)–Os(2)–C(22)′ | 96 (2) |
| (D) Angles Involving O(1) or C(2) | | | |
| Mo–O(1)–Os(1) | 93 (2) | Os(1)′–C(2)–C(3) | 119 (5) |
| Mo–Os(1)–O(1) | 42 (1) | Mo–C(2)–C(3) | 125 (5) |
| Os(1)–Mo–O(1) | 45 (1) | C(2)–Mo–O(1) | 94 (3) |
| Os(2)–Mo–O(1) | 101 (1) | Os(1)–Mo–C(2) | 91 (2) |
| Os(1)′–Mo–O(1) | 101 (1) | Os(2)–Mo–C(2) | 115 (2) |
| Os(1)′–Os(1)–O(1) | 93 (1) | Os(1)–Os(1)′–C(2) | 81 (2) |
| Os(2)–Os(1)–O(1) | 92 (1) | Os(1)′–Mo–C(2) | 53 (2) |
| Mo–C(2)–Os(1)′ | 84 (3) | | |
| (E) Angles within the μ-$CHCH_2$Tol Ligand | | | |
| C(2)–C(3)–C(4) | 107 (6) | C(6)–C(7)–C(6)′ | 120 (7) |
| C(4)–C(5)–C(6) | 116 (6) | C(6)–C(7)–C(8) | 120 (4) |
| C(5)–C(6)–C(7) | 122 (5) | | |
| (F) Angles within the Cp Ligand | | | |
| C(51)–C(53)–C(52) | 103 (4) | C(53)–C(51)–C(53)′ | 111 (7) |
| C(52)–C(52)′–C(53) | 111 (4) | | |

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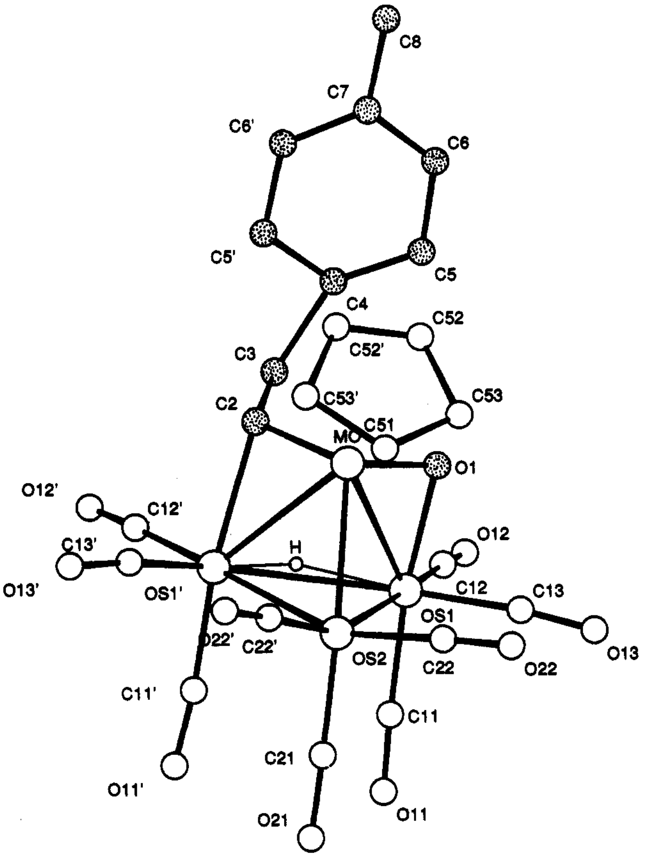

**Figure 4.** Molecular geometry and atomic labeling scheme for CpMoOs$_3$(CO)$_9$($\mu$-H)($\mu$-O)($\mu$-CHCH$_2$Tol) (**6c**). The $\mu$-oxo and $\mu$-CHCH$_2$Tol ligands are stippled for clarity.

C(4)–C(8), are located nearly on the mirror plane and their electron densities are overlapped with their own symmetry equivalents, they were treated as ordered in the refinement. Each of the four metal atoms is in a different stereochemical environment, and the cluster as a whole is chiral. The crystal, therefore, contains a disordered racemic mixture of the two enantiomeric molecules.

The metal-metal bond distances are Os(1)–Os(1)′ = 2.992 (3) Å, Os(1)–Os(2) = 2.812 (3) Å, Mo–Os(1) = 2.845 (5) Å, and Mo–Os(2) = 2.643 (6) Å. The relatively short Mo–Os(2) distance of 2.643 (6) Å is believed to be due to the formally electron-poor nature of Mo and Os(2) (17e each), which could be compensated for by increased bond order in the Mo–Os(2) linkages.[17] The longest of the metal–metal bonds, Os(1)–Os(1)′ = 2.992 (3) Å, is believed to be associated with a single, unsupported $\mu$-hydride ligand.[18] The presence of this bridging hydride ligand is further confirmed by the enlargement of the M–M–CO angles coplanar with and adjacent to the M–H–M linkage, ∠Os(1)′–Os(1)–C(12) = 118 (1)°. The $\mu$-hydride occupies a position trans to both C(13)–O(13) on Os(1) and C(13)′–O(13)′ on Os(1)′. We note here that the following Os–Os distances have been observed in tetranuclear clusters which are associated with a single, unsupported $\mu$-hydride ligand: 2.938 (1) Å and 2.909 (1) Å in CpMoOs$_3$(CO)$_{11}$($\mu$-H)$_3$,[19] 2.941 (2) Å in CpWOs$_3$(CO)$_{11}$($\mu$-H)$_3$,[20] 2.932 (2) Å in CoWOs$_3$(CO)$_{12}$($\mu$-H),[21] 2.951 (1) Å in CpWOs$_3$(CO)$_9$($\mu$-H)($\mu$-O)($\mu$-CHCH$_2$Tol) (**3a**),[5b] and 2.930 (2) Å in CpWOs$_3$(CO)$_9$($\mu$-H)($\mu$-O)($\mu$-C=CHTol).[22]

The $\mu$-oxo ligand (defined as O(1)) spans the Mo–Os(1) edge such that Mo–O(1) = 1.89 (5) Å, Os(1)–O(1) = 2.03 (5) Å, and ∠Mo–O(1)–Os(1) = 93 (2)°. The presence of W=O:→Os (W=O(av) = 1.78 Å and Os—O(av) = 2.16 Å) has been found previously in ($\mu$-oxo)tungsten complexes such as CpWOs$_3$(CO)$_9$($\mu$-O)($\mu_3$-CCH$_2$Tol) (**2**),[5] CpWOs$_3$(CO)$_9$($\mu$-H)($\mu$-O)($\mu$-CHCH$_2$Tol) (**3a**),[6] CpWOs$_3$(CO)$_9$($\mu$-H)($\mu$-O)($\mu$-C=CHTol),[22] CpWOs$_3$(CO)$_8$($\mu$-H)($\mu$-O)($\mu_3$-$\eta^2$-C$_2$H$_2$),[17] CpWOS$_3$(CO)$_9$($\mu$-Cl)($\mu$-O)($\mu$-CHCH$_2$Tol),[14] and CpWOs$_3$(CO)$_8$(PPh$_2$Me)($\mu$-O)($\mu_3$-CCH$_2$Tol).[23] The typical terminal oxo M=O distances (ca. 1.70 Å) are known to be similar in molybdenum and tungsten oxo complexes.[24] The oxo ligand in **6c**, therefore, bridges the molybdenum–osmium edge more or less symmetrically.

The $\mu$-alkylidene ligand bridges the Mo–Os(1)′ edge, with Mo–C(2) = 1.96 (8) Å, Os(1)′–C(2) = 2.29 (8) Å, and ∠Mo–C(2)–Os(1)′ = 84 (3)°. It was formed from the $\mu_3$-$\eta^2$-acyl precursor by cleavage of the acyl C–O bond and in conjunction with hydrogenation of C(2) by a hydride ligand. The configuration of C(2) is such that the C(2)–C(3) vector is oriented toward the $\mu$-oxo ligand and the triangular Mo–Os(1)–Os(1)′ face. This configuration positions the CH$_2$Tol group syn to the Mo–Os(1)–Os(1)′ triangular face which is associated with the three edge-bridging groups. The syn configuration adopted by the $\mu$-alkylidene ligand places the bulky Cp and CH$_2$Tol moieties apart and avoids their steric congestion.

All other features of the molecular geometry are within the expected range. Individual Os–CO distances range from 1.83 (4) through 1.92 (4) Å, C–O bond lengths range from 1.08 (6) through 1.27 (9) Å, and ∠Os–C–O angles are in the range 172 (4)–178 (4)°. Molybdenum–carbon (Cp) distances vary from 2.34 (4) through 2.40 (5) Å, and carbon–carbon (Cp) distances are in the range 1.30 (6)–1.49 (8) Å.

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**Supplementary Material Available:** A table of anisotropic thermal parameters and a stereoscopic view of **6c** (2 pages). Ordering information is given on any current masthead page.

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