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# Formation of Tungsten–Triosmium Clusters. Crystal Structure and Reactivity of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$[1]

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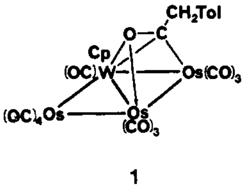
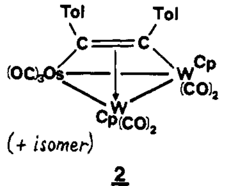
Previous studies have identified three mixed-metal clusters (**1**–**3**) as the major products from the reaction of CpW(CO)$_2$(CTol) (Cp = $\eta^5$-C$_5$H$_5$; Tol = *p*-C$_6$H$_4$CH$_3$) and H$_2$Os$_3$(CO)$_{10}$. A fourth, minor, product has been isolated and identified spectroscopically as CpWOs$_3$(CO)$_{12}$($\mu_3$-CTol)($\mu$-H)$_2$ (**4**). Complex **4** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a$ = 12.531 (3) Å, $b$ = 11.007 (2) Å, $c$ = 21.733 (4) Å, $\beta$ = 105.78 (2)°, $V$ = 2884.6 (11) Å$^3$, and $Z$ = 4. Diffraction data (Mo K$\alpha$, $2\theta$ = 4–45°) were collected on a Syntex P2$_1$ automated diffractometer, and the structure was refined to $R_F$ = 6.2% for 3014 data with $|F_o| > 3.0\sigma(|F_o|)$. The molecule contains a triangular triosmium core (Os(1)–Os(2) = 2.912 (1) Å, Os(2)–Os(3) = 2.875 (1) Å, Os(3)–Os(1) = 2.835 (1) Å) in which the two longer distances are believed to be associated with bridging hydride ligands; in addition, the triosmium system is capped by an asymmetrically triply bridging $\mu_3$-CTol ligand (Os(1)–C(06) = 2.184 (20) Å, Os(2)–C(06) = 2.051 (19) Å, Os(3)–C(06) = 2.025 (20) Å) and Os(1) is linked to a pendant CpW(CO)$_3$ fragment (Os(1)–W = 3.097 (1) Å). In refluxing toluene complex **4** eliminates CpW(CO)$_3$H and reacts with H$_2$ or CO to form H$_3$Os$_3$(CO)$_9$($\mu_3$-CTol) (**5**) or HOs$_3$(CO)$_{10}$($\mu_3$-CTol) (**6**), respectively. The related reaction of **4** with CpW(CO)$_2$(CTol) provides CpWOs$_3$(CO)$_{10}$($\mu_3$-CTol)$_2$H (**3**), which implicates **4** as an intermediate in the previous synthesis of **3**. The reaction of CpW(CO)$_2$(CTol) with D$_2$Os$_3$(CO)$_{10}$ leads to a partially modified product distribution that strongly favors the acyl complex (**1**-$d_2$) at the expense of deuterated **3** + **4**. This is interpreted in terms of linked pathways for forming **1** and **4** but a separate pathway for forming **2**.

## Introduction

In previous work[2,3] we have attempted two different approaches to the systematic assembly of tungsten–triosmium clusters: (1) the oxidative addition of CpW(CO)$_3$H to the labile species Os$_3$(CO)$_{10}$(NCMe)$_2$ and (2) a Stone reaction[4] coupling H$_2$Os$_3$(CO)$_{10}$ with the alkyne analogue CpW(CO)$_3$(CTol) (Cp = $\eta^5$-C$_5$H$_5$; Tol = *p*-C$_6$H$_4$CH$_3$). The former approach has provided two WOs$_3$ products, CpWOs$_3$(CO)$_{12}$($\mu$-H) and CpWOs$_3$(CO)$_{11}$($\mu$-H)$_3$, each with a closed, pseudotetrahedral structure.[2,5] The latter reaction has yielded three mixed-metal products, CpWOs$_3$(CO)$_{11}$[$\mu_3$-$\eta^2$-C(O)CH$_2$Tol] (**1**),[6] Cp$_2$W$_2$Os(CO)$_7$($\mu_3$-$\eta^2$-C$_2$Tol$_2$) (**2**),[7] and CpWOs$_3$(CO)$_{10}$($\mu_3$-CTol)$_2$H (**3**),[8] which display considerable variety in composition and structure. Further investigation of the Stone reaction has revealed a fourth, very minor product, which we now have characterized as CpWOs$_3$(CO)$_{12}$($\mu_3$-CTol)($\mu$-H)$_2$ (**4**). The structure and reactivity of this new compound **4** not only show it to be a probable intermediate in the formation of **3** but also provide a link between the two approaches to WOs$_3$ clusters. We also report a deuterium isotope effect on the formation of **1**, **3**, and **4**, which further illuminates this complex reaction network.



**1**



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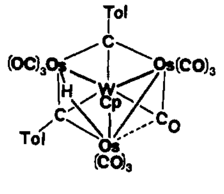

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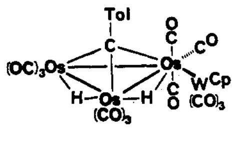

**4**

## Experimental Section

**Reactions and Characterization. Materials and Methods.** 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 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). ($\mu$-H)$_2$Os$_3$(CO)$_{10}$ was prepared by the method of Kaesz and co-workers;[9] ($\mu$-D)$_2$Os$_3$(CO)$_{10}$ was prepared similarly but was purified by recrystallization instead of chromatography.

Infrared spectra were obtained with a Perkin-Elmer 281B spectrophotometer. Both $^1$H NMR (360 MHz) and $^{13}$C NMR (90.6 MHz) spectra 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 using Varian MAT-731 (field desorption) and VG ZAB (fast atom bombardment) mass spectrometers. All $m/z$ values are referenced to $^{184}$W and $^{192}$Os. Microanalysis data were provided by the Microanalysis Laboratory of the School of Chemical Sciences at the University of Illinois.

**Reaction of H$_2$Os$_3$(CO)$_{10}$ with CpW(CO)$_2$(CTol).** Dichloromethane (500 mL) was transferred by cannula to a reaction flask containing a mixture of H$_2$Os$_3$(CO)$_{10}$ (1.5 g, 1.76 mmol) and CpW(CO)$_2$(CTol) (0.92 g, 2.25 mmol). The reaction mixture was stirred at 0 °C for 18 h under an argon atmosphere. Evaporation of the solvent on a rotary evaporator and preparative TLC (3:2 pentane–dichloromethane) of the residue provided yellow-orange **4** (106 mg, 0.204 mmol, 4.8%), dark red **1** (570 mg, 0.452 mmol, 25.7%), red **2** (259 mg, 0.238 mmol, 13.5%), and dark red **3** (214 mg, 0.164 mmol, 9.3%). The compounds are listed in the order of their $R_f$ values and were isolated as crystalline solids from dichloromethane–methanol (**4** and **2**), carbon tetrachloride–pentane (**1**), or dichloromethane–pentane (**3**). A crystal of **4** suitable for X-ray analysis was grown from a layered solution of dichloromethane and methanol at room temperature. The $^{13}$C-enriched complexes **1**–**4** were prepared from the reaction of CpW(CO)$_2$(CTol) and $^{13}$C-enriched H$_2$Os$_3$(CO)$_{10}$. The reaction with D$_2$Os$_3$(CO)$_{10}$ was carried out analo-

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gously; comparative yields are shown in Table V. Characterization data for **1–3** have been reported in previous papers.[6,8] $CpWOs_3(CO)_{12}(CTol)H_2$ (**4**): Anal. Calcd for $WOs_3C_{25}H_{14}O_{12}$: C, 23.82; H, 1.11. Found: C, 23.84; H, 1.05. FAB mass spectrum: *m/z* 1266 ($M^+$). IR ($C_6H_{12}$, $\nu$(CO)): 2098 (m), 2075 (vs), 2067 (s), 2052 (m), 2024 (vs), 2010 (vs), 1944 (m), 1986 (s), 1921 (m), 1909 (s) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.44–7.05 (4 H, m), 5.45 (5 H, s), 2.37 (3 H, s), −17.50 (1 H, d, $J_{H-H}$ = 1.4 Hz), −19.78 (1 H, d, $J_{H-H}$ = 1.4 Hz). $^{13}C$ NMR ($CD_2Cl_2$): M–*C*O, $\delta$ 222.3 ($^1J_{C-W}$ = 146 Hz), 216.5 ($^1J_{C-W}$ = 159 Hz), 215.9 ($^1J_{C-W}$ = 158 Hz), 189.8 ($^2J_{C-C}$ = 30 Hz), 183.7 ($^2J_{C-C}$ = 30 Hz), 176.1 ($J_{C-H}$ = 9.2 Hz), 174.0, 171.5 ($J_{C-H}$ = 11.2 Hz), 169.0, 168.8 ($J_{C-H}$ = 11.8 Hz), 167.1, 164.7 ($J_{C-H}$ = 11.5 Hz); $\mu_3$-*C*Tol, $\delta$ 190.4.

**Reaction of 4 with Hydrogen.** A toluene solution of **4** (22.6 mg, 0.018 mmol) was heated to reflux under 1 atm of hydrogen for 15 min. Evaporation of the solvent and purification by preparative TLC (8:1 pentane–dichloromethane) provided yellow $H_3Os_3(CO)_9(\mu_3\text{-CTol})$ (15.8 mg, 0.017 mmol, 94%) as a crystalline solid from dichloromethane–methanol. The major coproduct in this reaction was $CpW(CO)_3H$, which was identified by $^1H$ NMR of the reaction mixture and isolated as $CpW(CO)_3Cl$ (3.9 mg, 0.011 mmol, 59%) by addition of carbon tetrachloride before workup. $H_3Os_3(CO)_9(\mu_3\text{-CTol})$ (**5**): Anal. Calcd for $Os_3C_{17}H_{10}O_9$: C, 21.98; H, 1.09. Found: C, 21.87; H, 1.09. FD mass spectrum: *m/z* 934 ($M^+$). IR ($C_6H_{12}$), $\nu$(CO)): 2078 (s), 2018 (vs, br) $cm^{-1}$. $^1H$ NMR ($C_6D_6$): $\delta$ 7.74–6.88 (4 H, m), 2.06 (3 H, s), −18.83 (3 H, s).

**Reaction of 4 with Carbon Monoxide.** A toluene solution of **4** (16.1 mg, 0.013 mmol) was heated to reflux under 1 atm of carbon monoxide for 15 min. Evaporation of the solvent and purification by preparative TLC (8:1 pentane–dichloromethane) provided orange-red $HOs_3(CO)_{10}(\mu_3\text{-CTol})$ (10.6 mg, 0.011 mmol, 87%) as a crystalline solid from acetone. The major coproduct in this reaction was $CpW(CO)_3H$, which was identified by $^1H$ NMR of the reaction mixture and isolated as $CpW(CO)_3Cl$ (2.2 mg, 0.006 mmol, 47%) by addition of carbon tetrachloride before workup. $HOs(CO)_{10}(\mu_3\text{-CTol})$ (**6**): Anal. Calcd for $Os_3C_{18}H_8O_{10}$: C, 22.64; H, 0.84; Os, 59.76. Found: C, 22.76; H, 0.89; Os, 59.5. FD mass spectrum: *m/z* 960 ($M^+$). IR ($C_6H_{12}$), $\nu$(CO)): 2123 (m), 2057 (vs), 2020 (vs), 1995 (s), 1987 (m) $cm^{-1}$. $^1H$ NMR ($C_6D_6$): $\delta$ 7.77–6.70 (4 H, m), 1.85 (3 H, s), −16.27 (1 H, s).

**Reaction of 4 with $CpW(CO)_2(CTol)$ at Room Temperature.** A dichloromethane solution of **4** (26.3 mg, 0.021 mmol) and $CpW(CO)_2(CTol)$ (14.8 mg, 0.036 mmol) was stirred at room temperature for 40 h. Evaporation of the solvent and purification by preparative TLC (1:1 pentane–dichloromethane) provided **4** (2 mg, 0.0016 mmol, 8%), **3** (7.1 mg, 0.0054 mmol, 26%), **5** (4.2 mg, 0.0046 mmol, 22%), and **6** (4.2 mg, 0.0046 mmol, 22%). A trace amount of $CpWOs_3(CO)_9(\mu_3\text{-CTol})_2H$ (**7**) was also observed on the TLC plate.

**Reaction of 4 with $CpW(CO)_2(CTol)$ in Refluxing Benzene.** A benzene solution of **4** (34.5 mg, 0.027 mmol) and $CpW(CO)_2(CTol)$ (18.5 mg, 0.045 mmol) was heated to reflux for 25 min. After evaporation of the solvent, the crude product was separated by preparative TLC (2:1 pentane–dichloromethane), providing orange **7** (18.4 mg, 0.0144 mmol, 53%) as the only mixed-metal cluster compound. Compounds **5** (3.5 mg, 0.0038 mmol, 13%) and **6** (3.5 mg, 0.0038 mmol, 13%) were also isolated as the major side products in this reaction.

**Collection of X-ray Diffraction Data for $CpWOs_3(CO)_{12}(\mu_3\text{-CTol})(\mu\text{-H})_2$ (4).** A well-formed yellow-orange crystal of approximate dimensions 0.13 × 0.14 × 0.21 $mm^3$ was selected for data collection. It was glued onto a thin glass fiber that was fixed (with beeswax) into an aluminum pin mounted in a eucentric goniometer on a Syntex P2$_1$ automated four-circle diffractometer. Crystal alignment, determination of unit cell parameters (along with orientation matrix), and data collection were carried out as described previously.[10] Intensity data were collected via a $\theta$(crystal)–2$\theta$(counter) scan. Details appear in Table I.

All data were corrected for the effects of absorption and for Lorentz and polarization factors. Data were placed on an approximately absolute scale by means of a Wilson plot.

**Solution and Refinement of the Structure of 4.** The analytical scattering factors for the neutral atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[11] The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = [\sigma(|F_o|)]^2 + (0.03|F_o|)^2$.

The systematic absences (*h*0*l* for *h* + *l* = 2*n* + 1 and 0*k*0 for *k* = 2*n* + 1) are consistent only with the centrosymmetric monoclinic space group $P2_1/n$ (a nonstandard setting of $P2_1/c$ with equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$).

**Table I.** Experimental Data for the X-ray Diffraction Study of $CpWOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-H})_2$

(A) Crystallographic Parameters

cryst syst: monoclinic
space group: $P2_1/n$
$a$ = 12.5313 (33) Å
$b$ = 11.0065 (20) Å
$c$ = 21.7331 (44) Å
$\beta$ = 105.780 (20)°
$V$ = 2884.6 (11) Å$^3$
$Z$ = 4
formula: $C_{25}H_{14}O_{12}Os_3W$
mol wt: 1260.84
$D$(calcd) = 2.90 g $cm^{-3}$
temp: 23 °C (296 K)

(B) Data Collection

diffractometer: Syntex P2$_1$
radiation: Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented graphite, equatorial geom, $2\theta_m$ = 12.2°, assumed 50% perfect
reflecns measd: $-h,+k,\pm l$ for $2\theta$ = 4.0–45.0°
scan type: couple $\theta$(cryst)–2$\theta$(counter)
scan width: symmetrical [2.0 + $\Delta$(K$\alpha_1$ − K$\alpha_2$)]°
scan speed: 2.0° $min^{-1}$ (in 2$\theta$)
bkgd: stationary cryst, stationary counter at beginning and end of 2$\theta$ scan; each for half of total scan time
stds: 3 check reflecns remeasd after each 97 reflecns; decay was corrected
reflecns collected: 3997 total, merged to 3794 indep reflecns (file name WOSF)
abs coeff: $\mu$(Mo K$\alpha$) = 182.2 $cm^{-1}$; empirical cor applied

**Table II.** Atomic Coordinates for $CpWOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-H})_2$

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| W | 0.98694 (8) | 0.75412 (8) | 0.35138 (5) | |
| Os(1) | 0.79243 (7) | 0.67847 (8) | 0.40567 (4) | |
| Os(2) | 0.64060 (8) | 0.88409 (8) | 0.38526 (5) | |
| Os(3) | 0.67093 (8) | 0.72949 (8) | 0.49529 (4) | |
| O(11) | 0.6907 (15) | 0.5760 (17) | 0.2699 (10) | 5.49 (42) |
| O(12) | 0.9642 (13) | 0.7611 (14) | 0.5293 (8) | 4.04 (34) |
| O(13) | 0.8406 (15) | 0.4180 (18) | 0.4485 (9) | 5.67 (43) |
| O(21) | 0.5578 (16) | 0.8695 (18) | 0.2410 (10) | 6.23 (47) |
| O(22) | 0.4183 (15) | 0.9807 (17) | 0.3917 (9) | 5.52 (42) |
| O(23) | 0.7501 (18) | 1.1322 (22) | 0.3937 (11) | 7.48 (56) |
| O(31) | 0.6684 (15) | 0.4670 (19) | 0.5370 (10) | 5.91 (45) |
| O(32) | 0.8204 (19) | 0.8200 (22) | 0.6268 (12) | 7.93 (58) |
| O(33) | 0.4522 (18) | 0.7861 (20) | 0.5207 (11) | 7.07 (52) |
| O(41) | 1.0511 (13) | 0.6300 (15) | 0.2381 (8) | 4.53 (37) |
| O(42) | 1.0422 (14) | 0.4867 (17) | 0.4005 (9) | 5.17 (40) |
| O(43) | 0.7894 (15) | 0.8048 (17) | 0.2311 (10) | 5.65 (43) |
| C(11) | 0.7261 (21) | 0.6155 (24) | 0.3198 (14) | 4.54 (57) |
| C(12) | 0.8939 (18) | 0.7341 (21) | 0.4835 (11) | 3.36 (47) |
| C(13) | 0.8260 (21) | 0.5189 (26) | 0.4348 (13) | 4.53 (57) |
| C(21) | 0.5949 (19) | 0.8780 (21) | 0.2949 (12) | 3.53 (48) |
| C(22) | 0.5030 (22) | 0.9428 (25) | 0.3882 (13) | 4.75 (59) |
| C(23) | 0.7059 (20) | 1.0397 (23) | 0.3882 (12) | 3.77 (50) |
| C(31) | 0.6656 (21) | 0.5703 (25) | 0.5229 (13) | 4.52 (56) |
| C(32) | 0.7657 (22) | 0.7884 (25) | 0.5730 (14) | 4.91 (60) |
| C(33) | 0.5382 (22) | 0.7624 (24) | 0.5129 (13) | 4.49 (56) |
| C(41) | 1.0276 (18) | 0.6730 (21) | 0.2800 (11) | 3.22 (45) |
| C(42) | 1.0109 (19) | 0.5853 (22) | 0.3842 (12) | 3.69 (50) |
| C(43) | 0.8590 (19) | 0.7788 (22) | 0.2780 (12) | 3.61 (49) |
| C(01) | 1.0223 (22) | 0.9176 (25) | 0.4225 (14) | 4.95 (60) |
| C(02) | 1.1115 (21) | 0.8438 (24) | 0.4410 (13) | 4.35 (55) |
| C(03) | 1.1638 (23) | 0.8348 (26) | 0.3915 (14) | 5.31 (64) |
| C(04) | 1.0955 (25) | 0.9182 (29) | 0.3448 (16) | 6.24 (72) |
| C(05) | 1.0093 (25) | 0.9634 (29) | 0.3620 (16) | 6.20 (73) |
| C(06) | 0.6170 (15) | 0.7030 (18) | 0.3996 (9) | 2.03 (37) |
| C(07) | 0.5231 (15) | 0.6131 (17) | 0.3650 (9) | 1.96 (37) |
| C(08) | 0.5348 (18) | 0.4870 (20) | 0.3712 (11) | 3.23 (46) |
| C(09) | 0.4450 (18) | 0.4112 (21) | 0.3422 (11) | 3.40 (48) |
| C(010) | 0.3398 (18) | 0.4573 (21) | 0.3094 (11) | 3.30 (46) |
| C(011) | 0.3328 (20) | 0.5816 (23) | 0.3037 (12) | 4.11 (53) |
| C(012) | 0.4237 (18) | 0.6595 (22) | 0.3321 (12) | 3.60 (48) |
| C(M) | 0.2434 (25) | 0.3760 (29) | 0.2784 (15) | 6.31 (73) |

The four heavy atoms were located by direct methods (MULTAN); a series of difference-Fourier maps led to the location of all non-hydrogen atoms and allowed the distinction between W ($Z$ = 74) and Os ($Z$ = 76) atoms on the basis of their chemical environment. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic only for atoms in the $WOs_3$ core) resulted in convergence with[12] $R_F$ = 8.6%,

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**Table III.** Interatomic Distances (in Å) for $CpWOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$

| | | | |
|---|---|---|---|
| (A) Metal–Metal Bond Lengths | | | |
| W–Os(1) | 3.097 (1) | Os(2)–Os(3) | 2.875 (1) |
| Os(1)–Os(2) | 2.912 (1) | Os(3)–Os(1) | 2.835 (1) |
| (B) Metal–Carbon (Carbonyl) Distances | | | |
| Os(1)–C(11) | 1.935 (28) | Os(3)–C(31) | 1.859 (29) |
| Os(1)–C(12) | 1.919 (24) | Os(3)–C(32) | 1.896 (29) |
| Os(1)–C(13) | 1.875 (28) | Os(3)–C(33) | 1.841 (28) |
| Os(2)–C(21) | 1.891 (25) | W–C(41) | 1.972 (23) |
| Os(2)–C(22) | 1.859 (29) | W–C(42) | 1.984 (25) |
| Os(2)–C(23) | 1.891 (25) | W–C(43) | 1.948 (25) |
| (C) Metal–Carbyne Distances | | | |
| Os(1)–C(06) | 2.184 (20) | Os(3)–C(06) | 2.025 (20) |
| Os(2)–C(06) | 2.051 (19) | | |
| (D) Tungsten–Carbon (Cyclopentadienyl) Distances | | | |
| W–C(01) | 2.34 (3) | W–C(04) | 2.29 (3) |
| W–C(02) | 2.36 (3) | W–C(05) | 2.32 (3) |
| W–C(03) | 2.33 (3) | | |
| (E) Carbon–Oxygen Distances | | | |
| C(11)–O(11) | 1.14 (4) | C(31)–O(31) | 1.18 (4) |
| C(12)–O(12) | 1.17 (3) | C(32)–O(32) | 1.23 (4) |
| C(13)–O(13) | 1.15 (4) | C(33)–O(33) | 1.17 (4) |
| C(21)–O(21) | 1.14 (3) | C(41)–O(41) | 1.13 (3) |
| C(22)–O(22) | 1.16 (4) | C(42)–O(42) | 1.18 (3) |
| C(23)–O(23) | 1.15 (4) | C(43)–O(43) | 1.18 (3) |
| (F) Distances within the $\mu_3\text{-}CC_6H_4CH_3$ Ligand | | | |
| C(06)–C(07) | 1.57 (3) | C(010)–C(011) | 1.37 (3) |
| C(07)–C(08) | 1.40 (3) | C(011)–C(012) | 1.43 (4) |
| C(08)–C(09) | 1.41 (3) | C(012)–C(07) | 1.36 (3) |
| C(09)–C(010) | 1.41 (3) | C(M)–C(010) | 1.51 (4) |
| (G) Distances within the Cyclopentadienyl Ligand | | | |
| C(01)–C(02) | 1.35 (4) | C(04)–C(05) | 1.33 (5) |
| C(02)–C(03) | 1.41 (4) | C(05)–C(01) | 1.38 (4) |
| C(03)–C(04) | 1.46 (4) | | |

**Table IV.** Interatomic Angles (deg) for $CpWOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$

| | | | |
|---|---|---|---|
| (A) Intermetallic Angles | | | |
| W–Os(1)–Os(2) | 106.40 (4) | Os(3)–Os(2)–Os(1) | 58.68 (3) |
| W–Os(1)–Os(3) | 146.48 (4) | Os(1)–Os(3)–Os(2) | 61.32 (3) |
| Os(2)–Os(1)–Os(3) | 60.00 (3) | | |
| (B) M–M–CO Angles | | | |
| W–Os(1)–C(11) | 84.6 (8) | Os(1)–Os(2)–C(23) | 116.1 (8) |
| W–Os(1)–C(12) | 81.3 (7) | Os(3)–Os(2)–C(21) | 141.0 (7) |
| W–Os(1)–C(13) | 104.7 (8) | Os(3)–Os(2)–C(22) | 95.2 (9) |
| Os(2)–Os(1)–C(11) | 92.3 (8) | Os(3)–Os(2)–C(23) | 123.3 (8) |
| Os(2)–Os(1)–C(12) | 97.8 (7) | Os(1)–Os(3)–C(31) | 96.2 (9) |
| Os(2)–Os(1)–C(13) | 148.9 (8) | Os(1)–Os(3)–C(32) | 110.9 (9) |
| Os(3)–Os(1)–C(11) | 123.9 (8) | Os(1)–Os(3)–C(33) | 150.0 (8) |
| Os(3)–Os(1)–C(12) | 71.5 (7) | Os(2)–Os(3)–C(31) | 144.9 (9) |
| Os(3)–Os(1)–C(13) | 93.8 (8) | Os(2)–Os(3)–C(32) | 116.6 (9) |
| Os(1)–Os(2)–C(21) | 97.6 (7) | Os(2)–Os(3)–C(33) | 97.7 (8) |
| Os(1)–Os(2)–C(22) | 147.0 (9) | | |
| (C) M–C–O Angles | | | |
| Os(1)–C(11)–O(11) | 177.5 (24) | Os(3)–C(31)–O(31) | 174.1 (24) |
| Os(1)–C(12)–O(12) | 173.1 (20) | Os(3)–C(32)–O(32) | 173.2 (25) |
| Os(1)–C(13)–O(13) | 174.7 (24) | Os(3)–C(33)–O(33) | 176.2 (24) |
| Os(2)–C(21)–O(21) | 173.2 (22) | W–C(41)–O(41) | 177.8 (21) |
| Os(2)–C(22)–O(22) | 178.2 (24) | W–C(42)–O(42) | 168.1 (21) |
| Os(2)–C(23)–O(23) | 175.7 (23) | W–C(43)–O(43) | 171.5 (21) |
| (D) OC–M–CO Angles | | | |
| C(11)–Os(1)–C(12) | 164.5 (11) | C(31)–Os(3)–C(32) | 96.0 (12) |
| C(12)–Os(1)–C(13) | 88.1 (11) | C(32)–Os(3)–C(33) | 97.5 (12) |
| C(13)–Os(1)–C(11) | 89.3 (12) | C(33)–Os(3)–C(31) | 90.3 (12) |
| C(21)–Os(2)–C(22) | 91.5 (11) | C(41)–W–C(42) | 79.2 (10) |
| C(22)–Os(2)–C(23) | 94.6 (12) | C(42)–W–C(43) | 115.8 (10) |
| C(23)–Os(2)–C(21) | 94.2 (11) | C(43)–W–C(41) | 75.6 (10) |
| (E) Angles Involving C(06), the Carbyne Carbon | | | |
| Os(1)–C(06)–Os(2) | 86.8 (7) | C(13)–Os(1)–C(06) | 105.4 (10) |
| Os(2)–C(06)–Os(3) | 89.7 (8) | C(21)–Os(2)–C(06) | 96.2 (9) |
| Os(3)–C(06)–Os(1) | 84.6 (7) | C(22)–Os(2)–C(06) | 99.1 (10) |
| Os(1)–C(06)–C(07) | 124.3 (13) | C(23)–Os(2)–C(06) | 162.5 (9) |
| Os(2)–C(06)–C(07) | 131.5 (14) | C(31)–Os(3)–C(06) | 99.4 (10) |
| Os(3)–C(06)–C(07) | 125.6 (13) | C(32)–Os(3)–C(06) | 156.6 (10) |
| C(11)–Os(1)–C(06) | 80.0 (10) | C(33)–Os(3)–C(06) | 100.0 (10) |
| C(12)–Os(1)–C(06) | 115.4 (9) | | |
| (F) C–C–C Angles within the Cp Ring | | | |
| C(01)–C(02)–C(03) | 109.6 (25) | C(04)–C(05)–C(01) | 103.7 (28) |
| C(02)–C(03)–C(04) | 100.4 (25) | C(05)–C(01)–C(02) | 112.1 (26) |
| C(03)–C(04)–C(05) | 114.0 (29) | | |
| (G) Angles within the $\mu_3\text{-}CC_6H_4CH_3$ Ligand | | | |
| C(06)–C(07)–C(08) | 122.4 (18) | C(011)–C(012)–C(07) | 120.8 (22) |
| C(07)–C(08)–C(09) | 119.8 (20) | C(012)–C(07)–C(08) | 118.8 (20) |
| C(08)–C(09)–C(010) | 122.5 (21) | C(012)–C(07)–C(06) | 118.5 (18) |
| C(09)–C(010)–C(011) | 115.6 (22) | C(M)–C(010)–C(09) | 122.5 (22) |
| C(010)–C(011)–C(012) | 122.4 (23) | C(M)–C(010)–C(011) | 121.8 (23) |

$R_{wF}$ = 7.1%, and GOF = 1.30 for 191 variables refined against all 3794 reflections; $R_F$ = 6.2% and $R_{wF}$ = 6.6% for those 3014 reflections with $|F_o| > 3\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features.

Final parameters are collected in Table II.

It should be noted that a correction was made for the effects of secondary extinction, with use of the approximate Zachariasen formula, $|F_{o,corr}| = |F_{o,uncorr}|(1.0 + gI_o)$. The value $1.51 \times 10^{-7}$ was determined for $g$.

## Results and Discussion

**Isolation of 4.** The reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $CpW(CO)_2(CTol)$ in dichloromethane under mild conditions affords a chromatographically separable mixture of tungsten–osmium clusters. In previous reports, structural and spectroscopic characterization were reported for the three major products (**1**–**3**).[3,6-8] When the reaction scale was increased multifold, in order to provide more material for subsequent investigations, a new, minor product was observed as the leading band on the TLC plate. This fourth product (**4**) was separated and shown to have the same formula as **1**, that is, a 1:1 combination of the starting materials. Spectroscopic and reactivity data (vide infra) suggested a structure for this new compound, but in order to place our deductions on a sound footing, we proceeded to establish the crystal structure of **4**.

**Description of the X-ray Crystallographically Determined Molecular Structure of 4.** The monoclinic crystal contains an ordered array of discrete molecular units of $CpWOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$, which are separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. No crystallographic symmetry is imposed upon the molecule; indeed, the complex is chiral and the centrosymmetric crystal contains an ordered racemic mixture of the two enantiomeric forms. Figure 1 shows the labeling of atoms in the molecule. Important interatomic distances and angles are collected in Tables III and IV.

The metallic core of the $CpWOS_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$ molecule is associated *as a whole* with 64 valence electrons. The metal atom core takes up the expected "equatorially metallo-ligated triangular" geometry, previously observed in such 64-electron species as $(\mu\text{-}H)Os_3Re(CO)_{15}(NCMe)$.[13] The $(\eta^5\text{-}C_5H_5)W(CO)_3$ portion of the structure has the usual geometry for such a species (cf. the structure of $CpW(CO)_3Cl$[14]) and is linked to the triosmium fragment with a rather long single bond (W–Os(1) = 3.097 (1) Å).

Bond lengths within the triosmium fragment are inequivalent, increasing as Os(3)–Os(1) = 2.835 (1) Å, Os(2)–Os(3) = 2.875

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(12) $R_F = 100\sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

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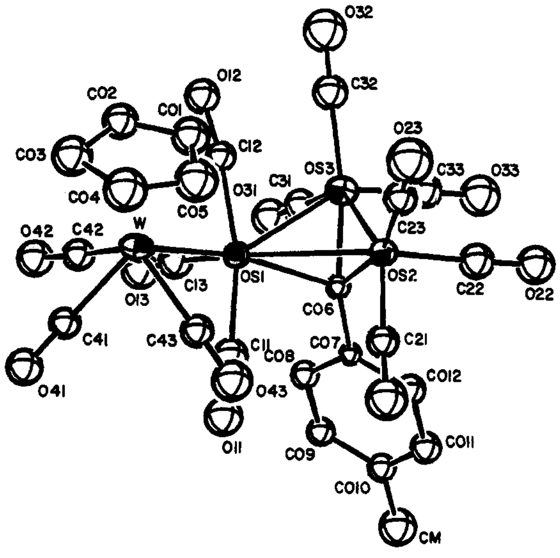

**Figure 1.** Labeling of atoms in the $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$ molecule.

(1) Å, and Os(1)–Os(2) = 2.912 (1) Å. The shortest of these is assigned to the non-hydrido-bridged Os–Os bond, while the other two are believed to be bridged by hydride ligands; the first bridges Os(2) and Os(3), trans to C(21)–O(21) and C(31)–O(31), and the second bridges Os(1) and Os(2), trans to C(13)–O(13) and C(22)–O(22). The hydrogen atom positions were included in the refinement, but the estimated standard deviations were sufficiently large as to render them chemically uninformative. A stereoview of the molecule appears as Figure 2.

The $\mu_3$-Tol ligand is present in an asymmetric capping mode, previously referred to as "semi triply bridging", with short bonds to Os(2) and Os(3) (Os(2)–C(06) = 2.051 (19) Å and Os(3)–C(06) = 2.025 (20) Å) and a rather longer bond to Os(1) (Os(1)–C(06) = 2.184 (20) Å). Similar situations are observed in $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$,[15] $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$,[16] $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CCH_2CHMe_2)$,[17] and $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$.[18] The present case is, however, the closest to the symmetrical $\mu_3$-bridging structure.

All other distances and angles observed for **4** are in the normally accepted ranges.

**NMR Spectroscopic Characterization of 4.** The $^1H$ NMR spectrum of **4** indicates that it contains two nonequivalent bridging hydride ligands (at $\delta$ −17.50 and −19.78); a small mutual H–H coupling of 1.4 Hz is observed. The $^{13}C$ NMR spectrum (see Figure 3) shows three downfield resonances for the carbonyls on the $CpW(CO)_3$ unit, identified by the $^{183}W$ satellites, and another nine resonances to higher field for the carbonyls attached to the osmium atoms. A large coupling ($^2J_{C-C}$ = 30 Hz) is observed between the resonances at $\delta$ 189.8 and 183.7, identifying these signals as due to the trans axial carbonyls on Os(1). In addition, the four resonances at $\delta$ 176.1, 171.5, 168.8, and 164.7 show relatively large couplings to hydrogen ($^2J_{C-H}$ = ca. 10 Hz), which is consistent with the solid-state structure in that four carbonyls are trans to the two bridging hydrides.

**Reactivity of 4 (See Scheme I).** Compound **4** reacts with hydrogen and carbon monoxide in refluxing toluene to form $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CTol)$ (**5**) and $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CTol)$ (**6**), respectively. These compounds are formulated on the basis of analytical and spectroscopic data in comparison with their phenyl analogues.[16] The formation of $CpW(CO)_3H$ in these reactions suggests that the reductive elimination of $CpW(CO)_3H$ from **4** produces the unsaturated species $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}CTol)$ (A) as an intermediate. The reductive elimination of a metal hydride has been observed before, viz. $HRe(CO)_5$ from triosmium centers,[13b] and its inverse—oxidative addition—is assuredly involved in the reaction of $CpW(CO)_3H$ and $Os_3(CO)_{10}(NCMe)_2$ to give $CpWOs_3(CO)_{12}H$.[2] In the present case intermediate A can react further with hydrogen or carbon monoxide to give the saturated products **5** or **6**. Keister and co-workers have studied the reactivity of closely related intermediates, especially $HRu_3(CO)_9(COMe)$, toward hydrogen or carbon monoxide and have proposed that oxidative addition/reductive elimination passes through a species with at least one terminal hydride.[20] We suggest that **4** provides a model for this species, i.e., that oxidative addition of hydrogen to A first gives $H(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}CTol)$, which then rearranges to **5**.

**Scheme I**

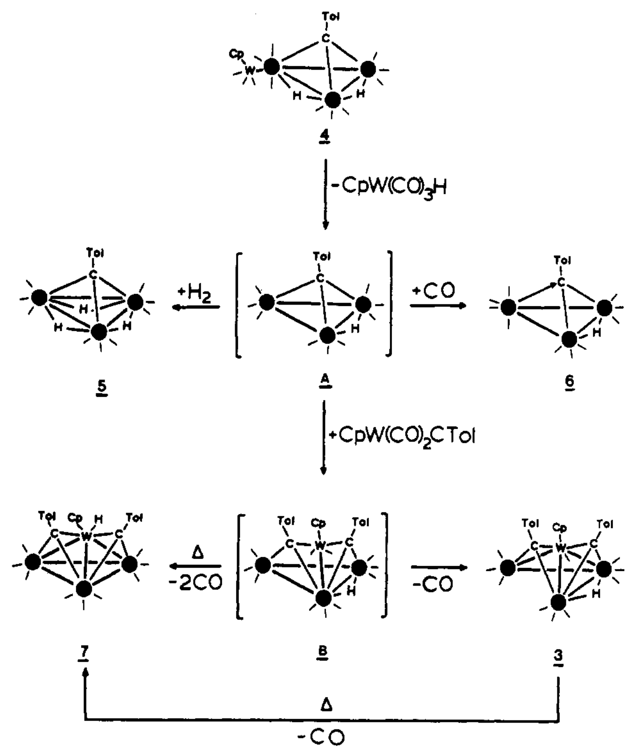

**Table V.** Product Distributions in the Reactions of $Cp(CO)_2W(CTol)$ with $H_2Os_3(CO)_{10}$ or $D_2Os_3(CO)_{10}$

| product | yield, %[a] $H_2Os_3(CO)_{10}$ | yield, %[a] $D_2Os_3(CO)_{10}$ |
|---|---|---|
| **1** | 21–26 | 42–49 |
| **2** | 14–15 | 13–16 |
| **3** | 9.2–11 | 2.4–3.7 |
| **4** | 2.6–4.8 | ~0 |

[a] The yields were calculated on the basis of the consumption of $H_2Os_3(CO)_{10}$ or $D_2Os_3(CO)_{10}$; 1.3 equiv of $Cp(CO)_2W(CTol)$ was utilized in each case.

Compound **4** reacts with $CpW(CO)_2(CTol)$ to give **3** in dichloromethane at room temperature, but the same reaction in refluxing benzene provides $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (**7**). These results are consistent with the reactivity of **3**, which is transformed into **7** by loss of a carbonyl ligand upon pyrolysis.[8] The isolation of both **5** and **6** as coproducts in these reactions is consistent with the involvement of the unsaturated species A; the two hydrogen

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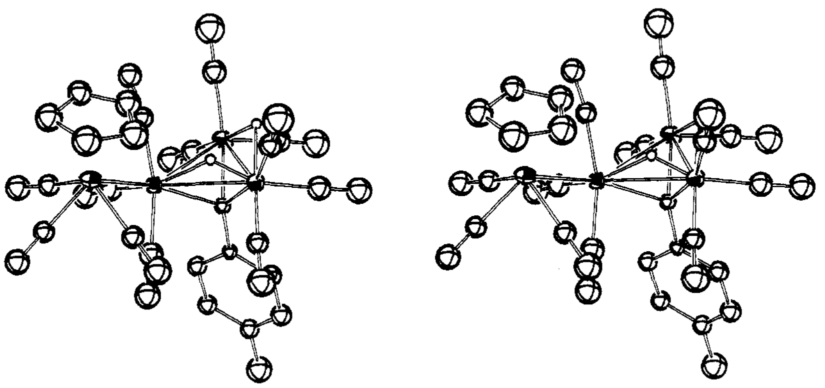

**Figure 2.** Stereoscopic view of the $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{12}(\mu_3\text{-}CC_6H_4CH_3)(\mu\text{-}H)_2$ molecule. The *probable* locations of the bridging hydride ligands are shown.

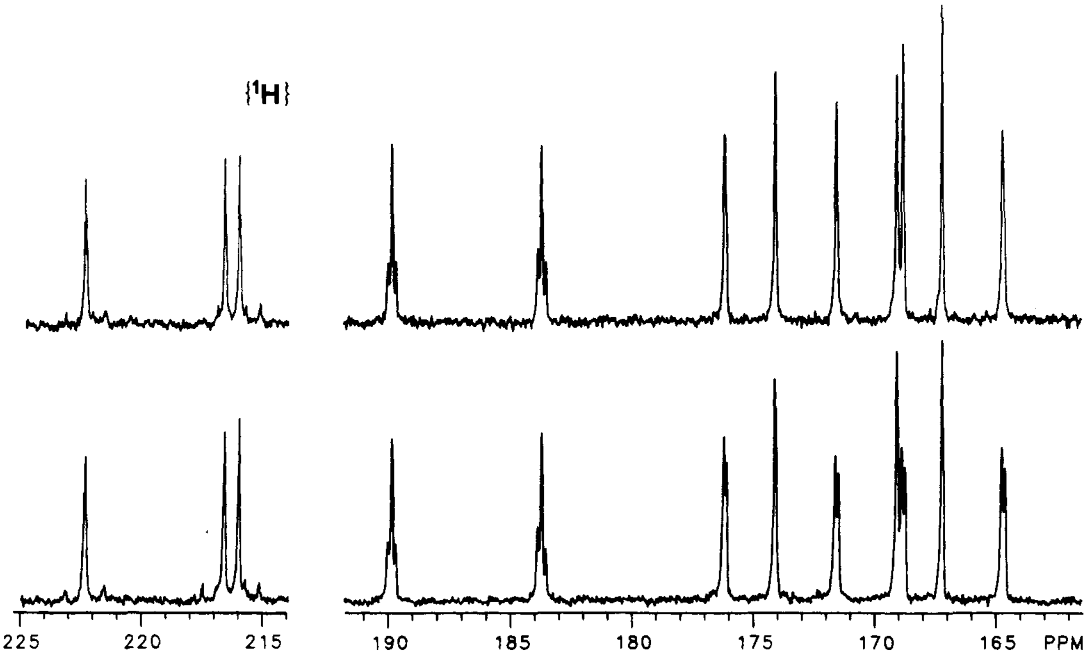

**Figure 3.** $^{13}C$ NMR (90.56 MHz, $CD_2Cl_2$, 25 °C) spectra of compound **4** in the metal carbonyl region: (above) $^1H$ decoupled; (below) nondecoupled.

atoms needed for **5** presumably come from $CpW(CO)_3H$. Keister[21] has shown that the intermediate $HRu_3(CO)_9(COMe)$ reacts with alkynes to give the coupled products $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}MeOCC(R)CR)$. The formation of **3** can be rationalized in similar terms, viewing the carbyne $CpW(CO)_2(CTol)$ as an alkyne analogue.[4] Thus, coordination of the carbyne to A followed by coupling would produce $HOs_3(CO)_9(\mu_3\text{-}\eta^3\text{-}TolC\text{-}\{CpW(CO)_2\}\text{-}CTol)$ (B). Loss of carbon monoxide from B and modest rearrangement would give **3** or at higher temperatures proceed to **7**.

**Deuterium Isotope Effect.** The distribution of mixed-metal products from the reaction of $CpW(CO)_2(CTol)$ with $H_2Os_3(CO)_{10}$ or with $D_2Os_3(CO)_{10}$ is displayed in Table V. The observation of a twofold increase in the yield of **1** and a concomitant decrease in the yields of **3** + **4** strongly suggests that the formation of **1** and **4** involves a common intermediate that partitions in two ways. The formation of **2**, however, apparently proceeds via an independent reaction channel. Since **2** is accompanied by an equal amount of $H_2Os_2(CO)_8$,[6] initial partitioning into $H_2Os_2(CO)_7$ and $CpW(CO)_2(\mu\text{-}CTol)Os(CO)_3$ is suggested; the latter species could then couple with a second molecule of $CpW(CO)_2(CTol)$ to give **2**. Studies by Stone and co-workers[22] have provided strong evidence for an analogous unsaturated bimetallic species in the formation of the coupled product $Cp_2W_2Fe(CO)_6(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$.

The common intermediate involved in the formation of **1** and **4** may simply be a 1:1 adduct of the starting materials closely related to other adducts between $H_2Os_3(CO)_{10}$ and simple donors.[23] The point of departure then resides in whether further reaction occurs at the tungsten center or at the carbon center of the coordinated tungsten–carbon triple bond. The structures of **1** and **4** suggest that hydrogen migration to the carbon would initiate the formation of **1** whereas CO migration to the tungsten would lead to **4**. Both modes of reaction are in fact known for reactions of $H_2Os_3(CO)_{10}$ with alkynes.[24] However, the competition between these two reactions will be affected by substituting deuterium for hydrogen, since the inverse isotope effect (either kinetic or equilibrium) will favor C–D vs. Os–D–Os bonds relatively more than C–H vs. Os–H–Os bonds.[25] Thus, relatively more deuterated **1** and relatively less deuterated **3** and **4** are produced.

Previously, we[6] reported evidence suggesting that both hydrogen atoms were transferred to the alkylidyne carbon, forming an alkyl, prior to coupling with CO to give acyl complex **1**. This was taken to cast doubt upon the intervention of a ketene intermediate

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generated by coupling of CO with an alkylidene moiety. The isotope effect on the (**1**):(**3** + **4**) yield ratio is also consistent with, although it does not require, the intervention of an alkyl species. Jeffery et al.[26] have demonstrated the stepwise conversion of an alkylidyne ligand to a bridging acyl ligand via an unsymmetrically bridging alkyl at a Re–W bimetallic center, and the alkylidyne–alkyl–acyl sequence was proposed for a related heterotrinuclear system as well.[27] Recently, we[28] have shown that the sequence can be taken a step further to regenerate an alkylidyne ligand—but containing one more methylene group—by thermal cleavage of the acyl ligand in **1**.

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**Registry No.** **1**, 93454-10-5; **2**, 80028-15-5; **3**, 85335-18-8; **4**, 104439-75-0; **5**, 104439-76-1; **6**, 104463-65-2; **7**, 86885-48-5; $H_2Os_3(CO)_{10}$, 41766-80-7; $CpW(CO)_2(CTol)$, 60260-15-3; $CpW(CO)_3H$, 12128-26-6; $D_2$, 7782-39-0.

**Supplementary Material Available:** Tables of hydrogen atom positions and anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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# Trialkoxynitridomolybdenum Compounds: $(RO)_3Mo\equiv N$. Preparation, Structures (R = *t*-Bu and *i*-Pr), and Comparisons with a Tungsten Analogue (R = *t*-Bu)†

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The compound $(t\text{-}BuO)_3Mo\equiv N$ is formed in the reaction between $Cl_3Mo\equiv N$ and LiO-*t*-Bu (3 equiv) in THF and is obtained as a white crystalline compound by either sublimation (85 °C, $5 \times 10^{-3}$ torr) or recrystallization from toluene. In the solid state the compound forms a linear polymer $[(t\text{-}BuO)_3Mo\equiv N]$ involving alternating short, 1.66 (1) Å, and long, 2.86 (2) Å, Mo–N bonds, corresponding formally to triple and weak dative bonds, respectively. In benzene solution, a cryoscopic molecular weight determination indicates the monomeric species is present. The solubilities of the compounds $[(t\text{-}BuO)_3M\equiv N]$ where M = Mo and W differ quite markedly, with the molybdenum compound being appreciably more soluble in aromatic solvents. It is suggested that this results from different $M\equiv N$—M bonding along the infinite chain with the tungsten compound having a more basic or nucleophilic nitrogen atom. This suggestion finds support from MO calculations employing the Fenske–Hall method. The $W\equiv N$ distance is significantly longer (1.740 (15) Å) and the W–N distance shorter (2.661 (15) Å). Furthermore, the molybdenum and tungsten compounds differ in their reactivity toward alcohols, yielding, respectively, $(RO)_3Mo\equiv N$ and $W(OR)_6$ (R = *i*-Pr, *neo*-Pe, Et) and ammonia. These results are compared with other nitrido compounds of molybdenum and tungsten. Crystal data for $(t\text{-}BuO)_3Mo\equiv N$ (**1**): at −90 °C, $a$ = 10.125 (3) Å, $b$ = 10.125 (3) Å, $c$ = 9.087 (2) Å, $\gamma$ = 120.00°, $Z$ = 2, $d_{calcd}$ = 1.356 g cm$^{-3}$, and the space group is $P6_3cm$; at −160 °C, $a$ = 10.060 (4) Å, $b$ = 10.060 (4) Å, $c$ = 9.035 (3) Å, $\gamma$ = 120.00°, $Z$ = 2, $d_{calcd}$ = 1.381 g cm$^{-3}$, and the space group is $P6_3$. Crystal data for $(i\text{-}PrO)_3M\equiv N$: space group $P6_3cm$, $a$ = 9.877 (3) Å, $b$ = 9.877 (3) Å, $c$ = 8.223 (2) Å, $\gamma$ = 120.00°, $Z$ = 2, and $d_{calcd}$ = 1.373 g cm$^{-3}$.

## Introduction

The reaction between $(t\text{-}BuO)_3W\equiv W(O\text{-}t\text{-}Bu)_3$ and nitriles in hydrocarbon solvents proceeds[1] according to eq 1. The ni-

$$W_2(O\text{-}t\text{-}Bu)_6 + RC\equiv N \xrightarrow{25\ ^{\circ}C} (t\text{-}BuO)_3W\equiv N + (t\text{-}BuO)_3W\equiv CR \qquad (1)$$

R = alkyl or aryl

tridotungsten compound is readily separated from the alkylidyne derivative because the nitride is sparingly soluble in hydrocarbon solvents.

Rather interestingly, alkane- and arenenitriles do not show any reactivity toward $Mo_2(O\text{-t-}Bu)_6$, though dimethylcyanamide forms a 1:1 adduct, $Mo_2(O\text{-}t\text{-}Bu)_6(NCNMe_2)$.[2,3] We report here simple syntheses of the $(RO)_3Mo\equiv N$ compounds together with characterization data and a comparison with a tungsten analogue, $(t\text{-}BuO)_3W\equiv N$.[4]

## Results and Discussion

**Synthesis.** The compound $(t\text{-}BuO)_3Mo\equiv N$ is formed by the reactions shown in eq 2.

$$MoCl_4(L)_2 + Y\text{-}N_3 \xrightarrow[\text{solvent = L}]{25\ ^{\circ}C} MoCl_3(N) + YCl + N_2 + 2L \qquad (2i)$$

Y = Na or $Me_3Si$; L = THF or $CH_3CN$

$$MoCl_3(N) + 3LiO\text{-}t\text{-}Bu \xrightarrow[\text{THF/toluene}]{25\ ^{\circ}C} (t\text{-}BuO)_3MoN + 3LiCl \qquad (2ii)$$

The synthesis takes advantage of the established routes to $MoCl_3(N)$[5,6] followed by a metathetic reaction involving LiO-*t*-Bu.

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