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Reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$. Crystal Structure of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]\cdot{\sim}0.5CCl_4$, a Complex with a Triply Bridging (μ_3, η^2) Acyl Ligand on the Surface of a Triangulated Rhomboidal Metal Cluster

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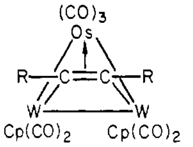
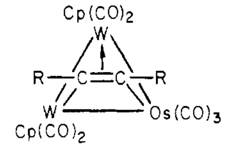
The reaction of $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ and $(\mu\text{-H})_2Os_3(CO)_{10}$ under mild conditions yields three products by parallel pathways: $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$, $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$, and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$. These compounds have been isolated as crystalline solids and have been characterized by spectroscopic (infrared, mass, ^1H and ^{13}C NMR) data. The tetranuclear heterometallic complex $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ has been examined by variable-temperature ^{13}C NMR spectroscopy and by a full three-dimensional X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15] with $a = 33.515$ (5) Å, $b = 11.287$ (2) Å, $c = 16.630$ (3) Å, $\beta = 98.35$ (1)°, $V = 6224$ (2) Å^3 and $\rho(\text{calcd}) = 2.85$ g cm^{-3} for $Z = 8$ and mol wt 1337.8. Diffraction data were collected on a Syntex P2_1 automated four-circle diffractometer, and the structure was refined to $R_F = 6.5\%$ and $R_{wF} = 5.4\%$ for all 4063 reflections with $2\theta = 3.5\text{–}45°$ (Mo Kα radiation). The tetranuclear molecule contains a triangulated rhomboidal arrangement of metal atoms with Os(2) and W at the two bridgehead positions. The dihedral angle between Os(1)–Os(2)–W and Os(3)–Os(2)–W planes is 171.9°, so the tetranuclear metal framework is close to planar. A triply bridging (μ_3, η^2) acyl ligand (defined by C(12)–O(12)) lies above the Os(1)–Os(2)–W plane; the oxygen atom spans the two bridgehead positions [Os(2)–O(12) = 2.115 (10) Å and W–O(12) = 2.150 (10) Å], while the carbon atom spans one bridgehead position and an acute apical position [W–C(12) = 2.162 (16) Å and Os(1)–C(12) = 2.072 (16) Å]. The C(12)–O(12) bond length of 1.372 (20) Å implies significant activation of this bond, relative to a normal C=O linkage. The molecular architecture is completed by an η^5-cyclopentadienyl ligand on the tungsten atom and eleven terminal (or close-to-terminal) carbonyl ligands—four on Os(3), three each on Os(1) and Os(2), and one on W. Metal–metal distances show significant variations—Os(1)–Os(2) = 2.815 (1) Å, Os(2)–Os(3) = 2.839 (1) Å, Os(1)–W = 2.867 (1) Å, Os(2)–W = 2.741 (1) Å, and Os(3)–W = 2.915 (1) Å.

Introduction

The cluster compound $(\mu\text{-H})_2Os_3(CO)_{10}$ undergoes facile insertion reactions with many alkynes (RC≡CR′) to form the alkenyl derivatives $(\mu\text{-H})Os_3(CO)_{10}(CR{=}CHR')$.[2] Stone and co-workers have utilized the isolobal[3] relationship between alkynes and metal alkylidyne complexes ($L_nM{\equiv}CR$) as motivation for examining the interaction of various reactive, low-oxidation-state compounds with alkylidyne compounds.[4] The success of this idea in their hands prompted us to examine it in the specific case of $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$. A preliminary account of this work has been published.[5] We now report full details of this reaction and show that three independent products are formed by parallel pathways. We also describe in full the X-ray structural analysis of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$, the only product derived from a 1:1 combination of the reactants. A second major product $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$ has been shown[6] to crystallize with isomers **1** and **2** in the single crystal. (Interestingly, the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ with $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$, under rather more severe conditions, also provides **1** and **2**.[7]) The crystal structure and solution dynamics of the third product $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$ together with its conversion to $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(CC_6H_4CH_3)_2H$ will be described elsewhere.[8]



1



2

$R = C_6H_4CH_3$; $Cp = \eta^5\text{-}C_5H_5$

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents were rigorously dried before use. 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). The method of Kaesz and co-workers[9] was used to prepare $(\mu\text{-H})_2Os_3(CO)_{10}$; $(\mu\text{-D})_2Os_3(CO)_{10}$ was prepared similarly, except that the compound was purified by crystallization instead of chromatography. $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ was prepared as described in the literature.[10]

Infrared spectra were obtained on a Perkin-Elmer 281B spectrophotometer. Proton NMR spectra were recorded on either a Varian

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Model EM-390 spectrometer (90 MHz) or a Nicolet NT-360 spectrometer (360 MHz). The ^{13}C NMR spectra were recorded on a Nicolet NT-360 spectrophotometer (90 MHz). Cr(acac)$_3$ (ca. 0.02 M) was added as a relaxation reagent. Chemical shifts are given in δ units relative to tetramethylsilane as an internal standard. Mass spectra were recorded by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences at the University of Illinois using either a Varian MAT CH-5 or a Varian MAT-731 mass spectrometer. All m/z values are referenced to ^{192}Os and ^{184}W. Microanalytical data were provided by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

Reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$. A cold (−30 °C) dichloromethane solution of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$ (94 mg, 0.23 mmol) was added to a dichloromethane solution of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ (195 mg, 0.23 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 5 h and then slowly warmed to room temperature and stirred for 10 h. Evaporation of the solvent under vacuum and preparative TLC (pentane–dichloromethane, 3:2) provided dark red $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$ (59 mg, 21%, R_f 0.5), red $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Os(CO)}_7[\text{C}_2(\text{C}_6\text{H}_4\text{CH}_3)_2]$ (40 mg, 33%, R_f 0.3), and dark red $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{10}(\text{CC}_6\text{H}_4\text{CH}_3)_2\text{H}$ (32 mg, 22%, R_f 0.1) isolated as crystalline solids. Recrystallization from pentane–dichloromethane gave analytically pure samples of each compound. A crystal of $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$ suitable for X-ray analysis was grown from pentane–carbon tetrachloride at −10 °C.

$(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$: IR ν(CO) (CCl$_4$) 2095 (m), 2063 (vs), 2032 (m), 2021 (s), 2007 (m), 1978 (m), 1939 (vw) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 7.15–7.20 (m, 4 H), 5.43 (s, 5 H), 3.47 (s, 2 H), 2.35 (s, 3 H); mass spectrum (70 eV) m/z 1266 (M$^+$). Anal. Calcd for C$_{25}$H$_{14}$O$_{12}$WOs$_3$: C, 23.82; H, 1.12; W, 14.58; Os, 45.26. Found: C, 24.18; H, 1.21; W, 14.53; Os, 42.64.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Os(CO)}_7[\text{C}_2(\text{C}_6\text{H}_4\text{CH}_3)_2]$: IR ν(CO) (CCl$_4$) 2061 (w), 2046 (vs), 1998 (sh), 1990 (vs), 1977 (vs), 1918 (s), 1830 (w) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 6.9–6.7 (m, 8 H), 5.06 (s, 10 H), 2.23 (s, 6 H); mass spectrum (field desorption) m/z 1092 (M$^+$). Anal. Calcd for C$_{33}$H$_{24}$O$_7$W$_2$Os: C, 36.35; H, 2.22; W, 33.72; Os, 17.44. Found: C, 36.17; H, 2.17; W, 33.20; Os, 16.00.

$(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{10}(\text{CC}_6\text{H}_4\text{CH}_3)_2\text{H}$: IR ν(CO) (C$_6H_{12}$) 2091 (s), 2071 (vs), 2052 (vs), 2025 (m), 2011 (s), 2001 (s), 1996 (m), 1990 (m), 1975 (m), 1703 (m); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 7.11–6.97 (m, 8 H), 5.26 (s, 5 H), 2.34 (s, 3 H), 2.25 (s, 3 H), −21.57 (s, 1 H); mass spectrum (field desorption) m/z 1312 (M$^+$). Anal. Calcd for C$_{31}$H$_{20}$O$_{10}$WOs$_3$: C, 28.49; H, 1.54; W, 14.07; Os, 43.66. Found: C, 28.75; H, 1.68; W, 13.33; Os, 42.77.

Preparation of ^{13}C-Enriched Compounds. W(CO)$_6$ (2.5 g, 7.10 mmol) was added to dry dimethylformamide (100 mL) in a 500-mL glass pressure bottle. A partial vacuum was drawn over the solution, after which the bottle was charged with ^{13}CO (90% ^{13}C, Monsanto Mound) to a pressure of 20 psig. The solution was heated to 140 °C and stirred for 4 days, after which it was cooled to precipitate the ^{13}CO-enriched W(C*O)$_6$. This material was then utilized to prepare first carbon-13-enriched $(\eta^5\text{-C}_5\text{H}_5)(\text{C*O})_2\text{W}{\equiv}\text{C*C}_6\text{H}_4\text{CH}_3$ by the reported procedure[10] and then $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{C*O})_{11}[\text{C*(O)-C*H}_2\text{C}_6\text{H}_4\text{CH}_3]$ by the procedure described above. Integration of the ^{13}C satellite of the benzylic hydrogen resonance in the ^{1}H NMR of $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{C*O})_{11}[\text{C*(O)C*H}_2\text{C}_6\text{H}_4\text{CH}_3]$ showed ca. 30% enrichment. ^{13}CO-enriched $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{C*O})_{11}[\text{C*(O)-CH}_2\text{C}_6\text{H}_4\text{CH}_3]$ was prepared from $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$ and ^{13}CO-enriched $(\mu\text{-H})_2\text{Os}_3(\text{C*O})_{10}$.[2e]

^{1}H NMR Investigation of the Reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ and *$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$*. $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$ (1:1 ratio) were dissolved in CD$_2$Cl$_2$ in an NMR tube. Signals at δ −10.12 [H$_2$Os$_2$(CO)$_8$] and 5.06 [$(\eta^5\text{-C}_5H_5)_2\text{W}_2\text{Os(CO)}_7[\text{C}_2(\text{C}_6\text{H}_4\text{CH}_3)_2]$] were observed to grow in at the same rate in the early stage of the reaction at 10 °C. After 1 h at this temperature a signal at δ 3.47 [$(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)-C}H_2\text{C}_6\text{H}_4\text{CH}_3]$] was apparent. After a 1.5-h reaction time the NMR tube was warmed to 25 °C. Resonances at δ −7.30 [$(\eta^5\text{-C}_5\text{H}_5)\text{-(CO)}_3\text{W}H$] and −21.57 [$(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{10}(\text{CC}_6\text{H}_4\text{CH}_3)_2H$] had grown in to the same extent 1 h later. Upon addition of carbon tetrachloride (ca. 0.1 mL) the two resonances at δ −7.30 and −10.12 disappeared, and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WCl}$[11] and Os$_2(CO)_8Cl_2$[12] were isolated after TLC and identified by IR spectroscopy.

Table I. Experimental Data for the X-ray Diffraction Study of $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]\cdot{\sim}0.5\text{CCl}_4$

(A) Crystal Parameters at 23 °C[a]

cryst syst: monoclinic
space group: $C2/c$ (C_{2h}^6; No. 15)[b]
$a = 33.515$ (5) Å
$b = 11.287$ (2) Å
$c = 16.630$ (3) Å
$\beta = 98.35$ (1)°
$V = 6224$ (2) Å^3
$Z = 8$
mol wt = 1337.8
ρ(calcd) = 2.85 g cm^{-3}
μ(Mo Kα) = 170.6 cm^{-1}

(B) Measurement of Data

diffractometer: Syntex P2$_1$
radiation: Mo Kα ($\bar{\lambda}$ 0.710 73 Å)
monochromator: highly oriented graphite, equatorial mode ($2\theta_{\text{mono}} = 12.2°$)
reflctns measd: $\pm h, +k, +l$ for $2\theta = 3.5$–45.0°
scan type: ω scan over 1.0° at 3.5° min^{-1} (1.0° offset for bkgds)
reflctns collected: 4630 total, merged to 4063 independent reflctns
std reflctns: 3 measd after every 97 reflctns (12,0,0; 240; 006); no decay obsd

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 25 reflections with 2θ between 20 and 30°. [b] The systematic absences were hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ ($h = 2n + 1$). The centrosymmetric space group $C2/c$ was chosen over the noncentrosymmetric space group Cc on the basis of (a) intensity statistics and (b) the successful solution and refinement of the structure under the higher centrosymmetric space group.

Attempted Interconversion of Reaction Products. A dichloromethane solution of $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$ (5 mg, 0.004 mmol) and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ (5 mg, 0.006 mmol) or $(\eta^5\text{-C}_5\text{H}_5)\text{-(CO)}_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$ (3 mg, 0.007 mmol) was stirred under exactly the same conditions as for the initial reaction. Similarly, the interactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Os(CO)}_7[\text{C}_2(\text{C}_6\text{H}_4\text{CH}_3)_2]$ and $(\eta^5\text{-C}_5\text{H}_5)\text{-(CO)}_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$ were carried out. No indications of interconverting any of the products were observed in monitoring the solutions by analytical TLC and by IR spectroscopy.

X-ray Data Collection and Structure Solution for $(\eta^5\text{-C}_5\text{H}_5)\text{-WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$. An opaque dark red crystal of approximate orthogonal dimensions 0.21 × 0.23 × 0.30 mm was mounted and aligned on our Syntex P2$_1$ diffractometer, and data were collected as described previously.[13] (See Table I.) All data were converted to $|F_o|$ values following correction for absorption and Lorentz and polarization factors. No data were rejected.

All crystallographic calculations were performed on the Syntex XTL system as modified at SUNY—Buffalo. The structure was solved with the use of MULTAN,[14] difference-Fourier syntheses, and full-matrix least-squares refinement. At convergence, discrepancy indices[15] are $R_F = 6.5\%$, $R_{wF} = 5.4\%$, and GOF = 1.19 for 328 parameters refined against 4063 observations. ($R_F = 4.6\%$, $R_{wF} = 5.0\%$ for those 3276 data with $|F_o| > 3\sigma(|F_o|)$.)

The analytical forms for neutral atoms[16a] were corrected for the $\Delta f'$ and $i\Delta f''$ terms.[16b] The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [[\sigma(|F_o|)]^2 + 0.025|F_o|^2]^{-1}$. Hydrogen atoms were placed in calculated positions with $d(\text{C–H}) = 0.95$ Å.[17]

Final positional parameters are given in Table II; hydrogen atom parameters are collected in Table II-S (supplementary material) while anisotropic thermal parameters appear in Table III-S (supplementary material).

Results and Discussion

Synthesis. The reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}{\equiv}\text{CC}_6\text{H}_4\text{CH}_3$ in dichloromethane under mild

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

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Table II. Positional Parameters with Esd's

atom	x	y	z	B_{iso}, Å^2
Os(1)	0.35973 (2)	0.13936 (6)	0.37619 (4)	
Os(2)	0.34163 (2)	0.36820 (6)	0.31402 (4)	
Os(3)	0.31776 (2)	0.42091 (7)	0.14707 (4)	
W	0.34671 (2)	0.18836 (6)	0.20524 (4)	
O(1)	0.4196 (5)	0.1401 (17)	0.5315 (10)	
O(2)	0.3721 (6)	−0.1239 (13)	0.3536 (13)	
O(3)	0.2826 (5)	0.1108 (15)	0.4561 (9)	
O(4)	0.2584 (4)	0.4007 (12)	0.3592 (9)	
O(5)	0.3584 (5)	0.6329 (13)	0.3074 (11)	
O(6)	0.3735 (6)	0.3895 (14)	0.4941 (10)	
O(7)	0.4086 (4)	0.4565 (15)	0.1392 (9)	
O(8)	0.2304 (4)	0.3511 (13)	0.1681 (10)	
O(9)	0.3045 (5)	0.6916 (15)	0.1344 (11)	
O(10)	0.2976 (6)	0.3765 (18)	−0.0354 (10)	
O(11)	0.2631 (4)	0.1309 (11)	0.2596 (8)	
O(12)	0.3926 (3)	0.3025 (9)	0.2670 (7)	
C(1)	0.3959 (6)	0.1417 (18)	0.4755 (14)	
C(2)	0.3676 (6)	−0.0278 (18)	0.3638 (13)	
C(3)	0.3121 (6)	0.1204 (16)	0.4262 (11)	
C(4)	0.2898 (6)	0.3908 (16)	0.3409 (12)	
C(5)	0.3521 (5)	0.5308 (18)	0.3058 (12)	
C(6)	0.3637 (6)	0.3656 (18)	0.4255 (13)	
C(7)	0.3754 (6)	0.4443 (18)	0.1419 (11)	
C(8)	0.2627 (6)	0.3764 (16)	0.1605 (12)	
C(9)	0.3075 (6)	0.5903 (21)	0.1405 (13)	
C(10)	0.3055 (5)	0.3973 (20)	0.0342 (14)	
C(11)	0.2953 (6)	0.1581 (14)	0.2466 (11)	
C(12)	0.3992 (4)	0.1902 (15)	0.2976 (11)	
C(13)	0.4418 (6)	0.1441 (17)	0.2918 (12)	4.0 (4)
C(14)	0.4727 (5)	0.1993 (16)	0.3559 (11)	3.4 (4)
C(15)	0.4962 (5)	0.1311 (16)	0.4148 (11)	3.1 (4)
C(16)	0.5239 (6)	0.1782 (18)	0.4704 (13)	4.6 (4)
C(17)	0.5315 (6)	0.2968 (17)	0.4761 (12)	3.8 (4)
C(18)	0.5092 (6)	0.3693 (17)	0.4204 (12)	4.2 (4)
C(19)	0.4800 (6)	0.3194 (19)	0.3576 (13)	4.6 (4)
C(20)	0.5630 (8)	0.3501 (23)	0.5367 (16)	6.6 (6)
C(21)	0.3349 (6)	−0.0006 (19)	0.1552 (13)	4.8 (5)
C(22)	0.3175 (6)	0.0788 (19)	0.0956 (13)	4.8 (5)
C(23)	0.3479 (7)	0.1439 (19)	0.0650 (14)	5.1 (5)
C(24)	0.3832 (7)	0.1050 (20)	0.1069 (14)	5.2 (5)
C(25)	0.3768 (6)	0.0156 (19)	0.1609 (14)	5.0 (5)
C(26)	0.0134 (17)	0.238 (6)	0.257 (5)	9.0
Cl(1)	−0.0124 (9)	0.1070 (23)	0.2255 (19)	14.6 (13)
Cl(2)	0.0581 (9)	0.248 (3)	0.2478 (17)	14.9 (13)
Cl(3)	−0.0067 (10)	0.271 (4)	0.1520 (24)	18.6 (19)
Cl(4)	0.0036 (11)	0.362 (4)	0.300 (3)	16.9 (19)

conditions affords a chromatographically separable mixture of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$, $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$, and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$. With excess $(\mu\text{-}H)_2Os_3(CO)_{10}$ (ca. 3 equiv) or addition of a solution of $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ slowly to a solution of $(\mu\text{-}H)_2Os_3(CO)_{10}$ the relative yield of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ increases, whereas the relative yields of $[(\eta^5\text{-}C_5H_5)W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$ and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$ increase with excess $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ (ca. 5 equiv) or by adding a solution of $(\mu\text{-}H)_2Os_3(CO)_{10}$ to a solution of $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ slowly. Attempted interconversion of products by reaction with starting materials was unsuccessful.

Monitoring the reaction by ^1H NMR reveals that $(\eta^5\text{-}C_5H_2)_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$ is formed rapidly followed by slower formation of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}][C(O)CH_2C_6H_4CH_3]$ and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$. Three signals in the hydride region, at δ −7.30, −10.12, and −21.57, grow in as the reaction proceeds (see Figure 1). Upon addition of carbon tetrachloride the two signals at δ −7.30 and −10.12 disappear. Subsequent isolation of $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$[11] and $Os_2(CO)_8Cl_2$[12] implies that the former resonance is due to $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and the latter signal is due to $H_2Os_2(CO)_8$. The resonance at δ −21.57 is due to the formation of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$. Significantly, the appearance of $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$ and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$ is paralleled by the appearance of equivalent amounts of $H_2Os_2(CO)_8$ and $(\eta^5\text{-}C_5H_5)W(CO)_3H$, respectively.

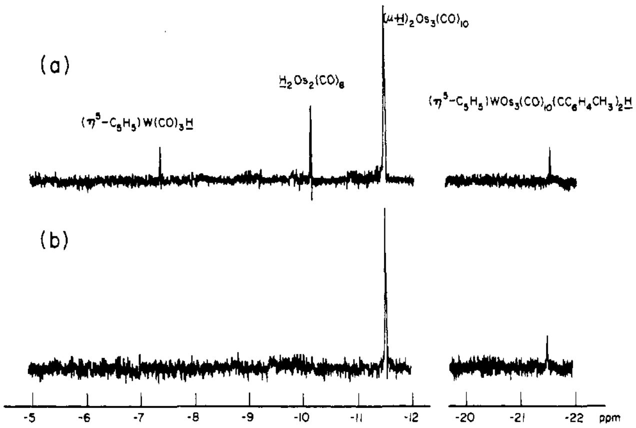

Figure 1. (a) ^1H NMR spectrum (90 MHz, hydride region) of the reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$. (b) ^1H NMR spectrum of the reaction mixture after addition of CCl_4.

The origin of the benzylic hydrogens in $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ and the hydride in $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H$ was confirmed by reaction of $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ with $(\mu\text{-}D)_2Os_3(CO)_{10}$.

The overall stoichiometry for the formation of the three products is shown in eq 1–3.

$$(\mu\text{-}H)_2Os_3(CO)_{10} + (\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3 \rightarrow (\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3] \quad (1)$$

$$(\mu\text{-}H)_2Os_3(CO)_{10} + 2(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3 + CO \rightarrow H_2Os_2(CO)_8 + (\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2] \quad (2)$$

$$(\mu\text{-}H)_2Os_3(CO)_{10} + 2(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3 \rightarrow CO + (\eta^5\text{-}C_5H_5)W(CO)_3H + (\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(CC_6H_4CH_3)_2H \quad (3)$$

We have observed that $(\mu\text{-}H)Os_3(CO)_{11}H$[18] does not react with $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$, which indicates that the coordinatively unsaturated nature of $(\mu\text{-}H)_2Os_3(CO)_{10}$ is a necessary feature. Each of reactions 1–3 is very likely initiated by a 1:1 adduct of $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$. The complex may not have the same structure in each case, however. Only $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ remains a 1:1 combination of the starting materials. The transfer of both hydrogen atoms from $(\mu\text{-}H)_2Os_3(CO)_{10}$ to a single carbon atom in $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4CH_3$ contrasts with the pattern of usually transferring just one hydrogen atom in reactions with alkynes.[2] The acyl carbon atom in $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ was found to be enriched with carbon-13 when the compound was prepared from either $(\mu\text{-}H)_2Os_3(C^*O)_{10}$ or $(\eta^5\text{-}C_5H_5)(C^*O)_2W{\equiv}C^*C_6H_4CH_3$. This result reveals extensive carbonyl scrambling between the tungsten and osmium centers in the 1:1 adduct. Furthermore, it suggests that the benzyl group is formed first, after which migration onto carbon monoxide to form the acyl moiety occurs.

The timing of the various transformations involved in the reactions of 1:2 stoichiometry (eq 2, 3) remains obscure. The coupling of two alkylidyne groups into an alkyne ligand as shown in (2) has been observed also by Stone in related re-

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[18] (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975**, *88*, C21; **1976**, *114*, 313. (b) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (c) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304.

Table III. Interatomic Distances (Å) and Esd's for $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$

(A) Metal–Metal Distances			
Os(1)–Os(2)	2.815 (1)	Os(2)–Os(3)	2.839 (1)
Os(1)–W	2.867 (1)	Os(3)–W	2.915 (1)
Os(2)–W	2.741 (1)		
(B) Metal–(μ_3-η^2-Acyl) Distances			
Os(1)–C(12)	2.072 (16)	W–C(12)	2.162 (16)
Os(2)–O(12)	2.115 (10)	W–O(12)	2.150 (10)
Os(2)···C(12)	2.827 (16)	W–midpt[a]	2.044
Os(1)···O(12)	2.913 (11)	Os(1)···midpt	2.433
		Os(2)···midpt	2.400
(C) Distances within the $\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3$ Ligand			
O(12)–C(12)	1.372 (20)	C(16)–C(17)	1.363 (28)
C(12)–C(13)	1.536 (25)	C(17)–C(20)	1.477 (32)
C(13)–C(14)	1.508 (27)	C(17)–C(18)	1.373 (28)
C(14)–C(15)	1.396 (25)	C(18)–C(19)	1.439 (29)
C(15)–C(16)	1.323 (27)	C(19)–C(14)	1.377 (28)
(D) Metal–Carbonyl Distances			
Os(1)–C(1)	1.902 (22)	Os(1)···O(1)	3.032 (17)
–C(2)	1.920 (20)	···O(2)	3.032 (15)
–C(3)	1.915 (20)	···O(3)	3.090 (16)
Os(2)–C(4)	1.874 (21)	Os(2)···O(4)	3.014 (14)
–C(5)	1.877 (20)	···O(5)	3.045 (15)
–C(6)	1.894 (21)	···O(6)	3.039 (17)
Os(3)–C(7)	1.962 (22)	Os(3)···O(7)	3.092 (15)
–C(8)	1.958 (21)	···O(8)	3.101 (14)
–C(9)	1.942 (23)	···O(9)	3.091 (17)
–C(10)	1.881 (23)	···O(10)	3.054 (17)
W–C(11)	1.977 (19)	W···O(11)	3.136 (12)
(E) Possible Metal–"Semibridging" Carbonyl Distances			
Os(1)···C(6)	2.680 (21)	Os(1)···C(11)	2.829 (19)
(F) Carbon–Oxygen (Carbonyl) Distances			
C(1)–O(1)	1.133 (27)	C(7)–O(7)	1.129 (26)
C(2)–O(2)	1.113 (25)	C(8)–O(8)	1.144 (25)
C(3)–O(3)	1.175 (25)	C(9)–O(9)	1.152 (29)
C(4)–O(4)	1.140 (25)	C(10)–O(10)	1.174 (29)
C(5)–O(5)	1.172 (25)	C(11)–O(11)	1.172 (22)
C(6)–O(6)	1.172 (25)		
(G) Metal–η^5-C_5H_5 Ligand Distances			
W–C(21)	2.303 (21)	W–C(24)	2.374 (23)
–C(22)	2.300 (22)	–C(25)	2.362 (22)
–C(23)	2.391 (22)	W–Cp[b]	2.026

[a] "midpt" is the midpoint of the aoyl group [C(12)=O(12)] bond. [b] Cp is the centroid of the C(21) → C(25) cyclopentadienyl system.

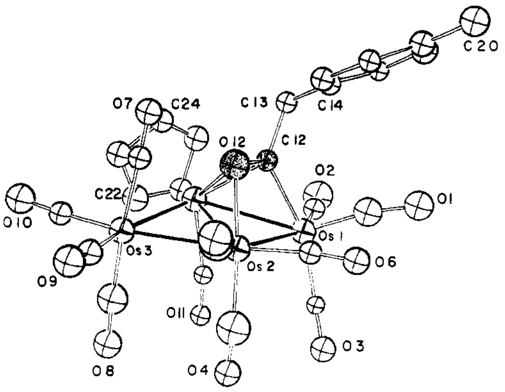

Figure 2. Geometry of the $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$ molecule. The μ_3-η^2-acyl fragment is stippled for clarity.

Table IV. Selected Interatomic Angles (deg) and Esd's for $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$

(A) Intermetallic Angles			
W–Os(1)–Os(2)	57.67 (2)	W–Os(3)–Os(2)	56.88 (2)
Os(1)–Os(2)–W	62.11 (2)	Os(3)–Os(2)–W	62.96 (2)
Os(2)–W–Os(1)	60.22 (2)	Os(2)–W–Os(3)	60.16 (2)
Os(1)–Os(2)–Os(3)	124.51 (3)	Os(1)–W–Os(3)	119.88 (3)
(B) M–M–CO and M–M–Cp Angles			
W–Os(1)–C(1)	147.7 (6)	Os(2)–Os(3)–C(7)	86.1 (6)
–C(2)	95.0 (6)	–C(8)	88.3 (6)
–C(3)	115.8 (6)	–C(9)	106.5 (6)
Os(2)–Os(1)–C(1)	112.5 (6)	–C(10)	159.4 (7)
–C(2)	152.6 (6)	W–Os(3)–C(7)	81.6 (6)
–C(3)	96.5 (6)	–C(8)	90.3 (6)
Os(1)–Os(2)–C(4)	101.3 (6)	–C(9)	162.3 (6)
–C(5)	153.1 (6)	–C(10)	102.6 (7)
–C(6)	66.0 (6)	Os(1)–W–C(11)	68.7 (5)
W–Os(2)–C(4)	114.0 (6)	Os(2)–W–C(11)	75.9 (5)
–C(5)	130.2 (6)	Os(3)–W–C(11)	90.4 (5)
–C(6)	125.6 (6)	Os(1)–W–Cp	125.1
Os(3)–Os(2)–C(4)	93.7 (6)	Os(2)–W–Cp	174.0
–C(5)	75.7 (6)	Os(3)–W–Cp	114.9
–C(6)	167.2 (6)		
(C) Metal–Carbon–Oxygen Angles			
Os(1)–C(1)–O(1)	174.9 (19)	Os(3)–C(7)–O(7)	179.2 (18)
Os(1)–C(2)–O(2)	177.3 (19)	Os(3)–C(8)–O(8)	179.6 (17)
Os(1)–C(3)–O(3)	178.7 (17)	Os(3)–C(9)–O(9)	174.3 (19)
Os(2)–C(4)–O(4)	177.2 (17)	Os(3)–C(10)–O(10)	176.6 (20)
Os(2)–C(5)–O(5)	174.4 (17)	W–C(11)–O(11)	169.3 (15)
Os(2)–C(6)–O(6)	164.5 (18)		
(D) M–C–M, M–O–M, M–M–C, M–M–O, and M–C–O Angles Involving the O(12)–C(12) System			
W–C(12)–Os(1)	85.2 (6)	W–O(12)–Os(2)	80.0 (4)
W–Os(1)–C(12)	48.7 (5)	W–Os(2)–O(12)	50.6 (3)
Os(1)–W–C(12)	46.1 (4)	Os(2)–W–O(12)	49.4 (3)
Os(2)–Os(1)–C(12)	68.7 (5)	Os(1)–Os(2)–O(12)	70.8 (3)
Os(1)–C(12)–O(12)	114.0 (11)	Os(2)–O(12)–C(12)	106.4 (9)
W–C(12)–O(12)	71.0 (8)	W–O(12)–C(12)	71.9 (8)
Os(3)–Os(2)–O(12)	80.8 (3)	Os(3)–W–O(12)	78.4 (3)
C(12)–W–O(12)	37.1 (5)	Os(3)–W–C(12)	115.1 (4)
(E) Other Angles at the "Acyl" Carbon Atom			
C(13)–C(12)–W	128.4 (12)	C(13)–C(12)–Os(1)	129.1 (12)
(F) Other Angles within the $\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3$ Ligand			
O(12)–C(12)–C(13)	113.1 (14)	C(16)–C(17)–C(18)	117.4 (18)
C(12)–C(13)–C(14)	111.4 (15)	C(16)–C(17)–C(20)	123.7 (19)
C(13)–C(14)–C(15)	121.8 (16)	C(20)–C(17)–C(18)	118.9 (19)
C(13)–C(14)–C(19)	121.5 (17)	C(17)–C(18)–C(19)	120.2 (18)
C(14)–C(15)–C(16)	122.4 (17)	C(18)–C(19)–C(14)	120.0 (18)
C(15)–C(16)–C(17)	123.2 (19)	C(19)–C(14)–C(15)	116.7 (17)

actions,[7] but the W≡C bond scission evident in (3) has not appeared previously in this chemistry. Nevertheless, in both reactions it seems that the elimination of relatively stable metal hydride compounds ($\text{H}_2\text{Os}_2(\text{CO})_8$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{H}$, respectively) facilitates extensive reorganization of metal–metal bonds under unusually mild conditions.[19]

Structure of $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$. The crystal consists of isolated molecules of $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]$ in general positions along with CCl_4 molecules of solvation, which are severely disordered about the crystallographic twofold axis.[20] The idealized stoichiometry is thus $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{11}[\text{C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3]\cdot 0.5\text{CCl}_4$. The essential atomic numbering is presented in Figure 2. A stereoscopic view of the molecule is given in Figure 3. Interatomic distances and angles are listed in Tables III and IV.

The tetranuclear molecule contains an almost planar triangulated rhomboidal arrangement of metal atoms, with atoms Os(2) and W at the bridgehead positions. (The angle between Os(1)–Os(2)–W and Os(3)–Os(2)–W planes is 171.9°—see Figure 4.) The observed geometry is entirely consistent with that expected for a tetranuclear complex with 62 outer valence

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[19] For facile reductive elimination involving HRe(CO)_5, see: Churchill, M. R.; Hollander, F. J.; Lashewycz, R. A.; Pearson, G. A.; Shapley, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 2430.

[20] We experienced substantial difficulty in satisfactorily refining atoms of the solvent molecule. However, the remainder of the structure is well-behaved.

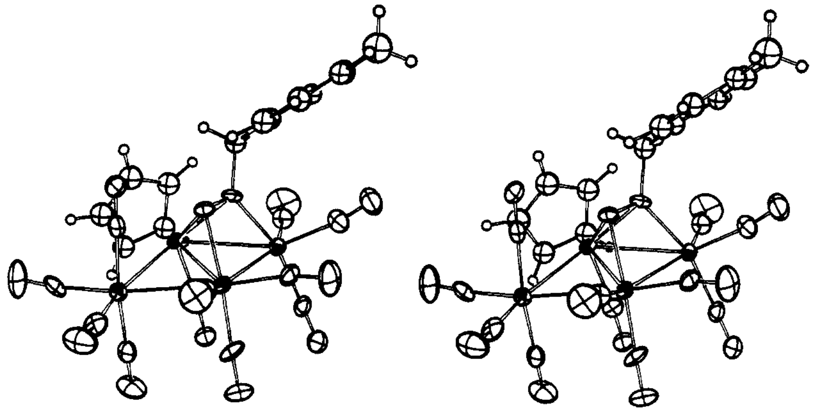


Figure 3. Stereoscopic view of the $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ molecule, showing the thermal vibration ellipsoids (ORTEP-II diagram).

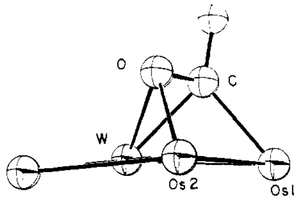


Figure 4. $WOs_3(C(O)C)$ core of the molecule, showing the 171.9° angle between the two triangular planes of the metal cluster.

electrons.[21] Thus, we normally expect a tetrahedral cluster shape (**3**) with 60 electrons, a triangulated rhomboidal (**4**) or

3

4

5

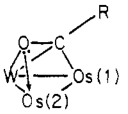
6

7

8

"butterfly" (**5**) arrangement with 62 electrons, and a "spiked triangular"[22,23] (**6** or **7**) or "square" (**8**)[24] arrangement with 64 electrons. Interestingly, while there are several examples of the "butterfly" geometry, there is a very limited number of structures embracing the 62-electron triangulated rhomboidal geometry: The archetypal examples are $[Re_4(CO)_{16}{}^{2-}]$[25] and $HOs_3Re(CO)_{15}$.[26] Related complexes containing bridging ligands such as $\mu\text{-PPh}_2$, $\mu_3\text{-PPh}$, $\mu\text{-}\eta^2\text{-C}{\equiv}\text{CR}$, $\mu_3\text{-}\eta^2\text{-C}{\equiv}\text{CR}$, etc. frequently take up atypical geometries. Thus, we have shown[27] that the 64-electron species $FeRu_3(CO)_{13}(\mu\text{-PPh}_2)_2$ has the triangulated rhomboidal geometry; Carty and coworkers have very recently shown[28] that the 64-electron complexes $Ru_4(CO)_{13}(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-C}{\equiv}\text{C-}t\text{-Bu})$ and $Ru_4(CO)_8(\mu\text{-PPh}_2)_2(\mu\text{-}\eta^2\text{-C}{\equiv}\text{C-}t\text{-Bu})(\mu_3\text{-}\eta^2\text{-C}{\equiv}\text{C-}t\text{-Bu})(Ph_2PC{\equiv}\text{C-}t\text{-Bu})$ also have a close-to-planar triangulated rhomboidal geometry.[29]

The present molecule has a triply bridging acyl group, C(12)–O(12), associated with the triangular Os(1)–Os(2)–W system. The mode of bonding may formally be represented as a linear combination of **9** and **10**. In either case the



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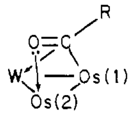

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$\mu_3\text{-}\eta^2$-acyl ligand acts as a net five-electron donor to the cluster. Relevant distances involving the acyl group include Os(1)–C(12) = 2.072 (16) Å, W–C(12) = 2.162 (16) Å, W–O(12) = 2.150 (10) Å, and Os(2)–O(12) = 2.115 (10) Å. The C(12)–O(12) distance of 1.372 (20) Å suggests significant activation of this linkage; this is far closer to the accepted C—O single-bond distance of 1.43 Å than to the unperturbed C═O distance of 1.215 ± 0.005 Å found in aldehydes and ketones.[30] For comparison, we note that a C–O distance of 1.32 (2) Å is found for the $\mu_3\text{-}\eta^2$-acyl ligand in the trinuclear $[Fe_3(CO)_9(MeCO)^-]$ anion.[31] The observed C(12)–C(13) distance of 1.536 (25) Å confirms that C(13) is a saturated carbon atom. The $\mu_3\text{-}\eta^2$-acyl ligands found both in the present $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]$ molecule and in $[Fe_3(CO)_9(MeCO)^-]$ represent possible models for chemisorbed acyl fragments on metal surfaces.

An interesting feature of the structure is that the bridgehead Os(2)–W bond length of 2.741 (1) Å is far shorter than the Os(1)–W and Os(3)–W bond lengths of 2.867 (1) and 2.915 (1) Å; this is presumably a result of this linkage being bridged by O(12). (A similar feature is observed in the $[Fe_3(CO)_9(MeCO)^-]$ anion, where the oxygen-bridged Fe–Fe bond length of 2.478 (5) Å is shorter than the other two linkages of 2.541 (6) and 2.592 (5) Å.)

Other points of interest include the following:

(1) There are indications of two rather weak semibridging carbonyl interactions. The system Os(2)–[C(6)–O(6)]···Os(1), with Os(2)–C(6) = 1.894 (21) Å, ∠Os(2)–C(6)–O(6) = 164.5 (18)°, and Os(1)···C(6) = 2.680 (21) Å (α = 0.415),[32,33] acts so as to shift electron density from the electron-rich Os(2) to

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(21) Counting all metal atoms as in a formal oxidation state of zero, we have three d^8 Os(0) atoms, one d^6 W(0) atom, two electrons from each of eleven terminal CO ligands, five electrons from the $\eta^5\text{-}C_5H_5$ ligand, and five electrons from the $\mu_3\text{-}\eta^2$-acyl ligand—62 electrons in all.

(22) **6** and **7** can be termed "equatorially metalloligated" and "axially metalloligated" clusters, respectively (cf. ref 23). We know of no simpler, more elegant nomenclature for these systems.

(23) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1981**, *20*, 4124.

(24) The "square" arrangement need be neither square nor planar. It merely requires a cyclic connectivity.

(25) (a) Bau, R.; Fontal, B.; Kaesz, H. D.; Churchill, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 6374. (b) Churchill, M. R.; Bau, R. *Inorg. Chem.* **1968**, *7*, 2606.

(26) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1977**, *16*, 2493.

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(28) Carty, A. J.; MacLaughlin, S. A.; Wagner, J. V.; Taylor, N. J. *Organometallics* **1982**, *1*, 1013.

(29) Correlations of electron count with nonplanarity and with metal–metal bond length are dealt with in ref 27 and 28 and will not be further discussed here.

(30) *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*, S20s–S21s.

(31) Wong, W. K.; Wilkinson, G.; Galas, A. M.; Hursthouse, M. B.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1981**, 2496.

(32) The "α value" for these systems falls near the weak-interaction end of the semibridging regime (0.1 < α < 0.6) suggested by Curtis et al.[33]

(33) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

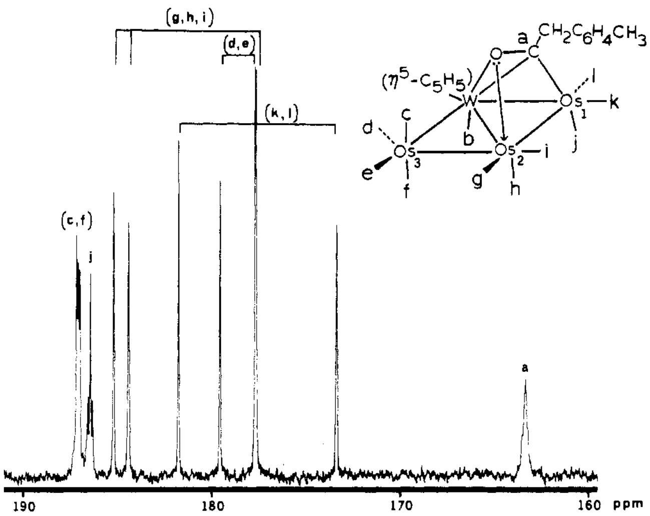

Figure 5. Partial ^{13}C NMR spectrum (90 MHz) of (η^5-C_5H_5)-$WOs_3(C^*O)_{11}[C^*(O)CH_2C_6H_4CH_3]$ in CD_2Cl_2 at −30 °C.

the electron-poor Os(1). Similarly, the system W–[C(11)–O(11)]···Os(1), with W–C(11) = 1.977 (19) Å, ∠W-C-(11)–O(11) = 169.3 (15)°, and Os(1)···C(11) = 2.829 (19) Å (α = 0.431),[32,33] donates electron density from the electron-rich W also to the electron-poor Os(1).

(2) The mutually trans Os(3)–CO (axial) bond distances (Os(3)–C(7) = 1.962 (22) Å and Os(3)–C(8) = 1.958 (21) Å) are slightly longer than the remaining Os–CO distances in the molecule, which otherwise range from 1.874 (21) to 1.942 (23) Å. This is consistent with values for $Os_3(CO)_{12}$ (Os–CO (axial) = 1.946 (6) Å vs. Os–CO (equatorial) = 1.912 (7) Å)[34] and is a result of competition for $d_\pi \rightarrow \pi^*$(CO) back-donation of electron density between the mutually trans ligands.

(3) The molecule has C_1 symmetry; each metal atom is in a different coordination environment.

(4) All cis OC–Os–CO angles are close to 90° (the precise range is 90.3 (9)–95.6 (9)°).

(5) All other distances and angles in the molecule are within normal accepted ranges.

^{13}C NMR Spectra for (η^5-C_5H_5)$WOs_3(CO)_{11}[C(O)$-$CH_2C_6H_4CH_3]$. The limiting low-temperature spectrum (−30 °C, CD_2Cl_2) of (η^5-C_5H_5)$WOs_3(C^*O)_{11}[C^*(O)CH_2$-$C_6H_4CH_3]$ shows 12 carbonyl resonances at δ 224.3, 187.2, 187.0, 186.4, 185.2, 184.4, 181.7, 179.5, 177.7, 177.6, 173.4, and 163.3. The most downfield signal is assigned to the carbonyl group on tungsten, on the basis of its chemical shift and ^{183}W satellites ($^1J_{CW}$ = 155.4 Hz). The remaining signals (see Figure 5) can be assigned in groups on the basis of their behavior with increasing sample temperature and by consideration of carbon–carbon coupling. Increasing the temperature from −30 to 0 °C causes the three resonances at δ 186.4, 181.7, and 173.4 to broaden. Of these three only the signal at δ 186.4 shows ^{13}C satellites ($^2J_{CC}$ = 22.0 Hz) in the limiting spectrum; it therefore is assigned to the carbonyl ligand j trans to the acyl carbon (a). The latter signal is at δ 163.3. The line broadening then is due to localized threefold exchange at the Os(1) center. The signals at δ 187.2 and 187.0 show a superimposed AB pattern of ^{13}C satellites ($^2J_{CC}$ = 34.7 Hz) (which becomes clearer at higher temperatures), characteristic of inequivalent trans axial carbonyls (c and f).[35] At higher temperatures (ca. 50 °C, $CDCl_3$) another set of three resonances (δ 187.0, 179.5, and 177.7) starts to broaden, while the signal at δ 187.2 remains sharp. This change is due to localized threefold exchange at the $(CO)_4Os(3)$ center, as previously observed for the analogous center in $HOs_3(CO)_{10}(COCH_3)$.[36] The resonances at δ 179.5 and 177.7 are therefore assigned to the two equatorial carbonyls d and e on Os(3). The remaining resonances at δ 186.4, 181.7, and 173.4, which remains sharp at 50 °C, are assigned to the three carbonyls g, h, and i on the Os(2) center. It is apparent that the activation barriers for localized carbonyl exchange increase as Os(1) < Os(3) < Os(2).

In the ^{13}C NMR spectrum of (η^5-C_5H_5)$WOs_3(C^*O)_{11}$-$[C^*(O)C^*H_2C_6H_4CH_3]$ (from $W(C^*O)_6$) the acyl carbon resonance at δ 163.3 shows ^{13}C satellites ($^1J_{CC}$ = 58.2 Hz) due to coupling to the benzylic carbon. The signal for the latter at δ 61.2 also shows triplet splitting ($^1J_{CH}$ = 127.2 Hz) in the proton-coupled spectrum.

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Registry No. (η^5-C_5H_5)$WOs_3(CO)_{11}[C(O)CH_2C_6H_4CH_3]\cdot 0.5CCl_4$, 85335-19-9; ($\eta^5$-$C_5H_5$)$_2W_2Os(CO)_7[C_2(C_6H_4CH_3)_2]$, 80028-15-5; ($\mu$-H)$_2Os_3(CO)_{10}$, 41766-80-7; ($\eta^5$-$C_5H_5$)$(CO)_2W{\equiv}CC_6H_4CH_3$, 60260-15-3.

Supplementary Material Available: Tables of hydrogen atom positions, anisotropic thermal parameters, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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