4476 *Inorg. Chem.* **1984**, *23*, 4476-4486

C, 40.25; H, 3.75; N, 2.61; Cl, 13.20. Found: C, 40.04; H, 3.58; N, 2.64; Cl, 12.91.

Protonation of $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$. $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$ (108 mg, 0.103 mmol) was dissolved in 5 mL of ether. To this solution was added an ether solution of HCl (5 mL, 1.76 M, 85 equiv). A precipitate formed immediately. Deionized water (10 mL) was added, and the ether was pumped away in vacuo. The mixture was filtered through a layer of Celite, and the Celite was washed twice with water. The filtrate and washes were combined and analyzed for hydrazine by the usual colorimetric method.[19] The result of that determination suggested that 0.100 (5) mmol of hydrazine had been produced.

Acknowledgment. This work was supported by NSF Grant CHE 80-23448 to M.R.C. and NIH Grant GM-31978 to R.R.S. R.R.S. also thanks the Camille and Henry Dreyfus Foundation for seed support in the form of a Teacher-Scholar Grant 1978–1983 and L. Blum for miscellaneous experiments.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table IV-S) and observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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[19] Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006.

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Degenerate Framework Rearrangement in a Capped-Square-Pyramidal Metal–Carbon Cluster and Its Conversion to a Capped-Trigonal-Bipyramidal Cluster. Crystal Structures of $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{10}(\mu_3\text{-}CC_6H_4CH_3)_2H$ and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu_3\text{-}CC_6H_4CH_3)_2H$[1a]

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Received August 25, 1983

The compound $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)H$ (**1**) ($Cp = \eta^5\text{-}C_5H_5$; $Tol = p\text{-}C_6H_4CH_3$) is one of the products (together with 1 equiv of $CpW(CO)_3H$) from the reaction of $H_2Os_3(CO)_{10}$ and $CpW(CO)_2(CTol)$. Variable-temperature ^1H and ^{13}C NMR spectra of $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ show that the compound in solution undergoes a degenerate framework rearrangement that interchanges the two alkylidyne moieties. This can be interpreted as breaking and making hydrogen-bridged metal–metal bonds. In refluxing toluene $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ is converted to $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (**2**) by loss of a carbonyl ligand. The latter has been isolated as a crystalline solid and has been characterized by spectroscopic (infrared, mass, ^1H and ^{13}C NMR) data. Molecular structures of both tetrametallic dialkylidyne complexes have been determined by single-crystal X-ray diffraction studies. Crystals of $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ belong to the monoclinic space group $P2_1/n$ (C_{2h}^5, No. 14) with $a = 10.610$ (4) Å, $b = 16.000$ (3) Å, $c = 19.394$ (6) Å, $\beta = 104.33$ (2)°, $V = 3189$ (2) Å^3, and ρ(calcd) = 2.72 g cm^{-3} for $Z = 4$ and molecular weight 1307. Diffraction data were collected on a Syntex P2$_1$ automated four-circle diffractometer using Mo Kα radiation, and the structure was refined to $R_F = 7.1\%$ and $R_{wF} = 5.1\%$ for all 3001 reflections with $2\theta = 3.0$–$40°$. The four metal atoms adopt a "butterfly" configuration. The dihedral angle between Os(1)–Os(2)–W and Os(3)–Os(2)–W planes is 98.7°. The molecule contains two μ_3-CTol ligands. One occupies a normal position on the outside of the Os(2)–Os(3)–W triangle; the other takes up an unusual position, bridging the "hinge" tungsten atom and the two "wing-tips" of the butterfly. The $WOs_3(\mu_3\text{-}C)_2$ fragment defines a capped square pyramid (base defined by Os(1)–Os(2)–Os(3)–C(11) and principal apex by W). $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ crystallizes in the monoclinic space group $P2_1/n$ (C_{2h}, No. 14) with $a = 19.067$ (3) Å, $b = 16.828$ (3) Å, $c = 19.947$ (3) Å, $\beta = 98.62$ (1)°, $V = 6327$ (2) Å^3, and ρ(calcd) = 2.68 g cm^{-3} for $Z = 8$ and molecular weight 1279. Diffraction data were collected as described above, and the structure was refined to $R_F = 5.4\%$ and $R_{wF} = 5.1\%$ for 6169 reflections with $2\theta = 3.5$–$45°$ and $I > 1.5\sigma(I)$. There are two equivalent molecules (A and B) in the crystallographic asymmetric unit. The tetrametallic cluster adopts a tetrahedral geometry and contains two μ_3-CTol ligands, which are located in almost equivalent environments on opposing sides of the pseudo plane of symmetry. Os(1), a unique osmium atom, and W are bonded to both alkylidyne fragments, and the Os(1)–W vector is almost coincident with the pseudo plane of symmetry. Molecules A and B have similar stereochemistry with the exception of the conformation of the carbonyl ligands surrounding Os(3). A terminal hydride on the tungsten atom was located from a difference-Fourier synthesis only in molecule B.

Introduction

We have previously reported that the reaction of $H_2Os_3(CO)_{10}$ and $CpW(CO)_2(CTol)$ ($Cp = \eta^5\text{-}C_5H_5$; $Tol = p\text{-}C_6H_5CH_3$) yields three products, $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$, $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$, and $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$.[2] The crystal structure of $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$ has been presented elsewhere.[3] The crystal structure and an NMR spectroscopic study of $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ also have been discussed separately.[2b] For the third product, $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ (**1**), variable-temperature ^1H and ^{13}C NMR studies show that it undergoes a degenerate rearrangement of the cluster framework in solution. Furthermore, the capped-square-pyramidal cluster **1** is cleanly converted to a new capped-trigonal-bipyramidal cluster, $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (**2**), by loss of a carbonyl ligand in refluxing toluene. This paper describes these spectroscopic and chemical results together with the X-ray structural analyses of the dialkylidyne

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[1] (a) Part 29 of the series "Structural Studies on Polynuclear Osmium Carbonyl Hydrides". For Part 28, see: Churchill, M. R.; Bueno, C.; Park, J. T.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 1017. (b) University of Illinois. (c) SUNY—Buffalo.

[2] (a) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Bueno, C.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 7385. (b) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579.

[3] Churchill, M. R. Bueno, C.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 640.

0020-1669/84/1323-4476$01.50/0

Table I. Experimental Data for the X-ray Diffraction Studies

	$CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2H$ (1)	$CpWOs_3(CO)_9(\mu_3\text{-CTol})_2H$ (2)
(A) Crystallographic Parameters		
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	10.610 (4)[a]	19.067 (3)[b]
b, Å	16.000 (3)	16.828 (3)
c, Å	19.394 (6)	19.947 (3)
β, deg	104.33 (2)	98.62 (1)
V, Å^3	3189 (2)	6327 (2)
Z	4	8
mol wt	1307	1279
ρ, g cm^{-3}	2.72	2.68
μ(Mo Kα), cm^{-1}	164.8	166.1
temp, °C	22	22
(B) Measurement of Diffraction Data		
diffractometer	Syntex $P2_1$	c
radiation	Mo Kα ($\bar{\lambda}$ = 0.710 30 Å)	c
monochromator	highly oriented graphite, equatorial mode, 2θ(mono) = 12.2°	c
reflcns measd	$h,k,\pm l$	c
2θ range, deg	3.0–40.0	3.5–45.0
scan width, deg	$[2\theta(K\alpha_1) - 0.9] \rightarrow [2\theta(K\alpha_2) + 0.9]$	c
scan speed, deg min^{-1}	1.5 (in 2θ)	3.0 (in 2θ)
bkgd measmt	stationary cryst and counter at beginning and end of 2θ scan, each for $^1/_4$ of scan time	c
reflcns collected	3478 total, merged to 3001 indep reflcns	9271 total, merged and trimmed to 6169 indep data with $I > 1.5\sigma(I)$
standards	3 measd after each batch of 97 reflcns (402, 307, 272); no decay obsd over period of data collecn	3 measd after each 97 reflcns (1,1,13; 11,0,$\bar{3}$; 1,10,$\bar{3}$); 10% linear decay obsd over course of data collecn, corrected for by linear interpolation

[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 values between 20 and 30°. [b] Based on 25 reflections with 2θ = 20–30°. [c] Entry for second column (2) same as for first column (1).

compounds **1** and **2**. A description of **2** formed part of a previous communication.[4]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Solvents were dried before use. The progress of the reactions was monitored by analytical thin-layer chromatography (pre-coated 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 Perkin-Elmer 281B spectrophotometer. Both ^1H NMR (360 MHz) and ^{13}C NMR spectra (90 MHz) were recorded on a Nicolet NT-360 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 Mass Spectroscopy Laboratory of the School of Chemical Sciences at the University of Illinois using either Varian MAT CH-5 or Varian MAT-731 mass spectrometers. All m/z values are referenced to ^{35}Cl, ^{184}W, and ^{192}Os. Microanalytical data were provided by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

$CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2H$ (1). The synthesis and characterization of **1** have been reported previously.[2] Deuterium-labeled $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2D$ was prepared analogously from $D_2Os_3(CO)_{10}$ and $CpW(CO)_2(CTol)$. Carbon-13-enriched $CpWOs_3(^*CO)_{10}(\mu_3\text{-}^*CTol)_2H$ was prepared from ^{13}C-enriched $CpW(^*CO)_2(^*CTol)$ (ca. 30% enrichment) and $H_2Os_3(^*CO)_{10}$ (ca. 50% enrichment) by the same procedure.[2b]

Crystals of **1** suitable for an X-ray analysis were obtained by slow recrystallization from pentane–dichloromethane at −10 °C.

$CpWOs_3(CO)_9(\mu_3\text{-CTol})_2H$ (2). A toluene solution (ca. 50 mL) of **1** (15.0 mg, 0.0115 mmol) was heated to reflux for 1.5 h. Evaporation of the solvent and purification by preparative TLC (pentane:dichloromethane = 3:2, R_f 0.55) provided dark red solid **2** (13.2 mg, 90%): IR (C_6H_{12}) ν(CO) 2072 (s), 2036 (vs), 2031 (vs), 1999 (w), 1991 (m), 1980 (m) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.03–7.11 (m, 8 H), 5.40 (s, 5 H), 3.75 (s, 1 H, $^1J_{WH}$ = 89 Hz), 2.36 (s, 6 H); MS (70 eV) m/z 1284 (M^+). Anal. Calcd for $C_{30}H_{20}O_9WOs_3$: C, 28.18; H, 1.58. Found: C, 28.10; H, 1.56.

Deuterium-labeled $CpWOs_3(CO)_9(\mu_3\text{-CTol})_2D$ and ^{13}C-enriched $CpWOs_3(^*CO)_9(\mu_3\text{-}^*CTol)_2H$ were prepared from $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2D$ and $CpWOs_3(^*CO)_{10}(\mu_3\text{-}^*CTol)_2H$, respectively, by the procedure described above.

Suitable crystals for an X-ray analysis were obtained from hexane–dichloromethane at room temperature.

$CpWOs_3(CO)_9(\mu_3\text{-CTol})_2Cl$ (3). *tert*-Butyl hypochlorite (0.76 mg, 0.007 mmol) was added to a carbon tetrachloride solution (ca. 30 mL) of **2** (7.4 mg, 0.0058 mmol). The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the crude product was purified by preparative TLC (pentane:dichloromethane = 3:2, R_f 0.40): IR (C_6H_{12}) ν(CO) 2080 (s), 2046 (vs), 2041 (vs), 1999 (m), 1980 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.15–7.33 (m, 8 H), 5.56 (s, 5 H), 2.47 (s, 6 H); MS (field desorption) m/z 1318 (M^+). Anal. Calcd for $C_{30}H_{19}O_9ClWOs_3$: C, 27.44; H, 1.46. Found: C, 27.54; H, 1.40.

^1H NMR Line-Shape Analysis of 1. A complete ^1H NMR line-shape analysis of the tolyl methyl resonances of **1** was carried out over a temperature range of 20–60 °C in $CDCl_3$. The experimental spectra, collected on a Nicolet NT-360 NMR spectrometer, were compared directly on the spectrometer with simulations generated by the Nicolet NTC-1180 computer using the two-site exchange program NTCXCH. Inhomogeneity corrections were estimated from the line width of the tetramethylsilane signal. A small variation of the chemical shift separation, $\delta\omega$, with temperature was allowed for by extrapolation from spectra collected between −40 and +10 °C. The derived data, k (T) (k in s^{-1}, T in °C), were 18 (20), 77 (40), 110 (45), 143 (50), 194 (55), and 278 (60).

X-ray Data Collection and Structure Solution of 1. A small rectangular crystal of opaque black appearance and approximate orthogonal dimensions 0.05 × 0.1 × 0.3 mm was mounted along its needle axis and used for data collection on a Syntex $P2_1$ diffractometer. Crystal alignment and data collection were carried out as described previously[5] (see Table I). All data were corrected for absorption and for Lorentz and polarization factors. Any reflection with I(net) < 0 was assigned a value of $|F_o| = 0$.

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(4) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

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

Table II. Final Positional Parameters for $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2H$

atom	x	y	z	B_{iso}, Å^2
Os1	0.52366 (9)	0.41740 (6)	0.12452 (5)	
Os2	0.36976 (9)	0.40767 (6)	0.22953 (5)	
Os3	0.39171 (9)	0.23240 (6)	0.20010 (5)	
W	0.62400 (9)	0.32812 (6)	0.24903 (5)	
O(1)	0.2937 (17)	0.3719 (10)	−0.0018 (9)	
O(2)	0.7408 (20)	0.4244 (11)	0.0478 (10)	
O(3)	0.4867 (20)	0.6090 (9)	0.1097 (9)	
O(4)	0.1506 (18)	0.3771 (13)	0.3035 (10)	
O(5)	0.1887 (19)	0.5143 (12)	0.1142 (10)	
O(6)	0.4314 (21)	0.5547 (11)	0.3249 (11)	
O(7)	0.2746 (16)	0.1782 (10)	0.0448 (8)	
O(8)	0.1700 (18)	0.1948 (12)	0.2663 (11)	
O(9)	0.5045 (19)	0.0602 (10)	0.2460 (10)	
O(10)	0.6979 (18)	0.5193 (10)	0.2507 (8)	
C(1)	0.3828 (25)	0.3883 (15)	0.0447 (13)	3.6 (5)
C(2)	0.6574 (28)	0.4208 (17)	0.0763 (14)	4.5 (6)
C(3)	0.4950 (23)	0.5364 (17)	0.1143 (12)	3.7 (5)
C(4)	0.2302 (27)	0.3909 (16)	0.2792 (13)	3.9 (6)
C(5)	0.2595 (29)	0.4759 (18)	0.1571 (15)	5.2 (6)
C(6)	0.4395 (27)	0.5019 (18)	0.2898 (14)	4.7 (6)
C(7)	0.3168 (25)	0.1970 (15)	0.1016 (14)	4.0 (6)
C(8)	0.2544 (27)	0.2028 (16)	0.2445 (13)	3.8 (5)
C(9)	0.4665 (22)	0.1239 (16)	0.2287 (11)	3.0 (5)
C(10)	0.6461 (24)	0.4533 (16)	0.2267 (12)	3.8 (5)
C(11)	0.5516 (19)	0.2795 (13)	0.1516 (11)	
C(12)	0.5918 (20)	0.2193 (12)	0.1010 (10)	2.1 (4)
C(13)	0.6498 (24)	0.1429 (15)	0.1278 (12)	4.0 (5)
C(14)	0.6846 (26)	0.0830 (16)	0.0828 (14)	4.8 (6)
C(15)	0.6574 (24)	0.0965 (15)	0.0097 (12)	3.9 (5)
C(16)	0.6031 (24)	0.1753 (15)	−0.0171 (12)	3.8 (5)
C(17)	0.5685 (22)	0.2333 (14)	0.0272 (11)	3.0 (5)
C(18)	0.6810 (28)	0.0285 (18)	−0.0393 (15)	5.7 (7)
C(19)	0.4771 (22)	0.3058 (12)	0.2952 (11)	
C(20)	0.4693 (21)	0.2876 (14)	0.3684 (11)	2.9 (5)
C(21)	0.4788 (23)	0.3492 (14)	0.4190 (12)	3.4 (5)
C(22)	0.4718 (24)	0.3355 (15)	0.4890 (12)	3.9 (5)
C(23)	0.4668 (23)	0.2566 (15)	0.5124 (12)	3.7 (5)
C(24)	0.4591 (25)	0.1917 (16)	0.4655 (13)	4.5 (6)
C(25)	0.4647 (23)	0.2052 (15)	0.3948 (12)	3.6 (5)
C(26)	0.4618 (28)	0.2372 (17)	0.5894 (14)	5.6 (7)
C(27)	0.0104 (27)	0.3573 (18)	0.3369 (14)	5.3 (8)
C(28)	0.7588 (26)	0.2810 (17)	0.3587 (14)	5.1 (8)
C(29)	0.7612 (28)	0.2201 (18)	0.3056 (15)	5.6 (7)
C(30)	0.8199 (29)	0.2590 (19)	0.2586 (15)	6.0 (7)
C(31)	0.8513 (31)	0.3374 (20)	0.2760 (16)	6.8 (8)

All computations were performed with the SUNY—Buffalo modification of the Syntex XTL structure-solving package. The structure was solved by a combination of direct-methods (MULTAN),[6] difference-Fourier, and full-matrix least-squares refinement techniques. Analytical scattering factors for neutral atoms, with corrections for both $\Delta f'$ and $i\Delta f''$ terms, were used throughout the analysis.[7] The function minimized during the least-squares process was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma|(F_o)|^2 + (0.025|F_o|)^2]^{-1}$. All non-hydrogen atoms and the bridging hydride ligand were located directly. Final discrepancy indices[8] were $R_F = 7.1\%$ and $R_{wF} = 5.1\%$ for 261 parameters refined against 3001 reflections. The residuals for those 2336 data with $F_o > 3.0\sigma(F_o)$ were $R_F = 4.5\%$ and $R_{wF} = 4.5\%$. (The substantially lowered discrepancy indices and the 22% reduction in the number of data each indicate a rather weak data set; indeed, few data were observable beyond $2\theta = 40.0°$ with Mo Kα radiation.) A final difference-Fourier map was "clean", and the usual tests for systematic variations of $\sum w(|F_o| - |F_c|)^2$ showed no unusual features. Positional parameters are collected in Table II; anisotropic thermal parameters appear in Table III (supplementary material).

X-ray Data Collection and Structure Solution of 2. The crystal selected for data collection was a rectangular, dark red, opaque crystal with dimensions 0.13 × 0.15 × 0.35 mm. Data were collected and treated as described above. Details are given in Table I. The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$, where the assigned weights are given by $w = [(\sigma(|F_o|))^2 + (p|F_o|^2)]^{-1}$, where $p = 0.020$. All non-hydrogen atoms were successfully located for both molecules. Additionally, a terminal hydride ligand was located from a difference-Fourier synthesis (molecule B only) and was shown to be well-behaved during the least-squares process. The final discrepancy indices[8] were $R_F = 5.4\%$, $R_{wF} = 5.1\%$, and GOF = 1.376 for 388 parameters refined against 6169 reflections that had $I > 1.50\sigma(I)$.

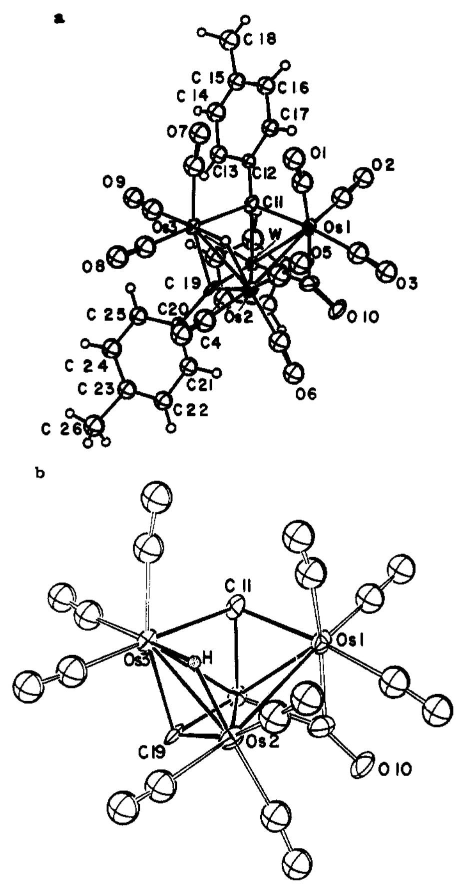


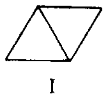
Figure 1. (a) Labeling of atoms in the $CpWOs_3(CO)_{10}(\mu\text{-CTol})_2H$ molecule (ORTEP-II diagram). (b) The $(\mu\text{-H})WOs_3(CO)_{10}(\mu_3\text{-C})_2$ core of molecule **1** (ORTEP-II diagram).

A final difference-Fourier map showed no significant chemical features. The function $\sum w(|F_o| - |F_c|)^2$ showed no dependency on $|F_o|$, $(\sin\theta)/\lambda$, sequence number, identity, or parity class of crystallographic indices; the weighting scheme is thus satisfactory. Positional parameters are collected in Table IV; anisotropic thermal parameters are listed in Table V (supplementary material).

Results

X-ray Structure of 1. The crystal consists of discrete ordered molecules of $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})H$, which are mutually separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. Figure 1 shows the scheme used for labeling atoms, while Figure 2 provides a stereoscopic view of the molecule. Interatomic distances and angles are collected in Tables VI and VII.

The tetranuclear molecule contains a "butterfly" arrangement of metal atoms (II)—one of the geometric forms, along the isoconnective planar triangulated rhombus (I), typical of a 62-electron tetranuclear array. The dihedral angle between Os(1)-Os(2)-W and Os(3)-Os(2)-W planes is 98.7°. The


I


II

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(6) Germain, G.; Main, P. Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gem. Crystallogr.* **1971**, *A27*, 368.

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

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

Table IV. Positional Parameters (Esd's) for $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
Molecule A									
Os1	0.28062 (4)	0.31254 (5)	0.45733 (4)		C(10)	0.3785 (18)	0.2399 (12)	0.4514 (10)	3.1 (4)
Os2	0.30620 (5)	0.19184 (5)	0.36672 (4)		C(11)	0.4190 (11)	0.1902 (13)	0.5049 (11)	3.8 (5)
Os3	0.25709 (5)	0.34304 (5)	0.31788 (4)		C(12)	0.4744 (13)	0.1401 (15)	0.4871 (12)	5.1 (6)
W	0.40030 (4)	0.32868 (5)	0.39015 (4)		C(13)	0.5146 (13)	0.0948 (15)	0.5351 (12)	4.8 (5)
O(1)	0.2148 (9)	0.1708 (11)	0.5228 (9)	6.5 (4)	C(14)	0.5001 (14)	0.0949 (16)	0.6018 (13)	5.5 (6)
O(2)	0.3548 (9)	0.3849 (11)	0.5891 (9)	6.5 (4)	C(15)	0.4438 (17)	0.1394 (19)	0.6203 (16)	7.9 (8)
O(3)	0.1446 (10)	0.4118 (12)	0.4453 (9)	7.0 (5)	C(16)	0.4009 (13)	0.1885 (16)	0.5721 (13)	5.5 (6)
O(4)	0.3276 (9)	0.0363 (12)	0.4428 (9)	6.8 (5)	C(17)	0.5437 (17)	0.0389 (20)	0.6540 (16)	8.6 (9)
O(5)	0.3855 (12)	0.1446 (14)	0.2538 (11)	9.7 (6)	C(18)	0.3236 (11)	0.4072 (12)	0.3950 (10)	3.3 (4)
O(6)	0.1670 (10)	0.1131 (11)	0.3080 (9)	6.9 (5)	C(19)	0.3203 (12)	0.4939 (14)	0.4056 (11)	4.4 (5)
O(7)	0.1824 (14)	0.5004 (18)	0.2853 (14)	12.4 (8)	C(20)	0.3416 (11)	0.5435 (13)	0.3565 (11)	3.9 (5)
O(8)	0.3114 (13)	0.3220 (15)	0.1864 (13)	11.3 (7)	C(21)	0.3455 (13)	0.6294 (16)	0.3659 (12)	4.9 (5)
O(9)	0.1131 (10)	0.2714 (11)	0.2687 (9)	6.9 (4)	C(22)	0.3311 (12)	0.6613 (14)	0.4269 (12)	4.7 (5)
C(1)	0.2391 (13)	0.2262 (16)	0.4988 (12)	5.1 (6)	C(23)	0.3128 (13)	0.6117 (15)	0.4780 (12)	5.0 (6)
C(2)	0.3249 (12)	0.3571 (14)	0.5421 (12)	4.4 (5)	C(24)	0.3064 (11)	0.5299 (14)	0.4685 (11)	3.9 (5)
C(3)	0.1958 (14)	0.3718 (16)	0.4502 (13)	5.8 (6)	C(25)	0.3362 (14)	0.7533 (17)	0.4366 (13)	6.4 (7)
C(4)	0.3226 (15)	0.0965 (18)	0.4106 (14)	6.4 (7)	C(26)	0.4965 (12)	0.3449 (14)	0.4763 (11)	4.5 (5)
C(5)	0.3535 (16)	0.1601 (18)	0.2968 (15)	7.2 (7)	C(27)	0.5215 (12)	0.3098 (14)	0.4195 (11)	4.3 (5)
C(6)	0.2191 (14)	0.1457 (16)	0.3272 (13)	5.4 (6)	C(28)	0.5153 (11)	0.3637 (13)	0.3668 (10)	3.8 (5)
C(7)	0.2152 (20)	0.4379 (24)	0.2934 (19)	10.0 (10)	C(29)	0.4819 (13)	0.4325 (15)	0.3861 (12)	5.0 (5)
C(8)	0.2902 (17)	0.3361 (20)	0.2384 (17)	8.0 (8)	C(30)	0.4707 (13)	0.4233 (15)	0.4524 (12)	5.3 (6)
C(9)	0.1696 (13)	0.2954 (15)	0.2882 (12)	5.0 (6)					
Molecule B									
Os(1)	0.93180 (4)	0.19120 (5)	0.32903 (4)		C(10)	0.8827 (11)	0.2405 (13)	0.4163 (11)	3.9 (5)
Os(2)	0.80255 (5)	0.26843 (5)	0.33065 (5)		C(11)	0.9151 (11)	0.3009 (13)	0.4668 (10)	3.8 (5)
Os(3)	0.80229 (5)	0.11457 (5)	0.27375 (4)		C(12)	0.8673 (12)	0.3339 (14)	0.5099 (11)	4.3 (5)
W	0.84198 (5)	0.13269 (5)	0.41852 (4)		C(13)	0.8945 (13)	0.3869 (14)	0.4607 (12)	4.7 (5)
O(1)	0.9734 (9)	0.3602 (10)	0.2971 (8)	5.5 (4)	C(14)	0.9628 (13)	0.4103 (15)	0.5719 (12)	5.1 (6)
O(2)	1.0688 (10)	0.1514 (11)	0.4188 (9)	6.9 (5)	C(15)	1.0103 (12)	0.3766 (14)	0.5286 (11)	4.3 (5)
O(3)	0.9791 (9)	0.1304 (10)	0.1995 (8)	5.6 (4)	C(16)	0.9860 (13)	0.3223 (14)	0.4788 (11)	4.7 (5)
O(4)	0.8153 (11)	0.4396 (14)	0.3792 (11)	8.8 (6)	C(17)	0.9950 (15)	0.4679 (17)	0.6293 (14)	6.9 (7)
O(5)	0.6479 (11)	0.2494 (12)	0.3438 (9)	7.7 (5)	C(18)	0.8856 (10)	0.0738 (12)	0.3496 (9)	2.9 (4)
O(6)	0.7854 (10)	0.3413 (12)	0.1905 (10)	7.5 (5)	C(19)	0.9187 (10)	−0.0862 (12)	0.3430 (9)	2.7 (4)
O(7)	0.8429 (9)	−0.0229 (10)	0.1886 (8)	5.6 (4)	C(20)	0.9880 (12)	−0.0140 (14)	0.3275 (11)	4.2 (5)
O(8)	0.6690 (12)	0.0334 (13)	0.3016 (10)	8.6 (6)	C(21)	1.0121 (12)	−0.0949 (14)	0.3176 (11)	4.1 (5)
O(9)	0.7200 (10)	0.1810 (12)	0.1448 (10)	7.4 (5)	C(22)	0.9700 (11)	−0.1604 (13)	0.3266 (10)	3.7 (5)
C(1)	0.9562 (13)	0.2951 (15)	0.3109 (12)	4.7 (5)	C(23)	0.9036 (12)	−0.1511 (14)	0.3427 (11)	4.2 (5)
C(2)	1.0162 (14)	0.1671 (16)	0.3840 (13)	5.8 (6)	C(24)	0.8782 (11)	−0.0741 (13)	0.3517 (10)	3.6 (4)
C(3)	0.9608 (12)	0.1536 (14)	0.2471 (12)	4.6 (5)	C(25)	0.9985 (12)	−0.2457 (15)	0.3166 (12)	5.0 (6)
C(4)	0.8122 (15)	0.3736 (18)	0.3594 (14)	6.3 (7)	C(26)	0.8522 (13)	0.1445 (15)	0.5388 (12)	5.2 (6)
C(5)	0.7092 (15)	0.2633 (17)	0.3390 (13)	6.0 (6)	C(27)	0.9180 (13)	0.1190 (15)	0.5209 (12)	5.1 (6)
C(6)	0.7880 (13)	0.3104 (15)	0.2440 (13)	5.2 (6)	C(28)	0.9085 (13)	0.0430 (14)	0.4918 (12)	4.7 (5)
C(7)	0.8269 (13)	0.0275 (15)	0.2227 (12)	5.0 (6)	C(29)	0.8353 (13)	0.0248 (15)	0.4888 (12)	4.8 (5)
C(8)	0.7206 (15)	0.0655 (16)	0.2916 (13)	5.8 (6)	C(30)	0.8017 (13)	0.0957 (16)	0.5170 (12)	5.2 (6)
C(9)	0.7535 (13)	0.1597 (15)	0.1955 (13)	5.2 (6)	H	0.741 (9)	0.126 (11)	0.409 (9)	

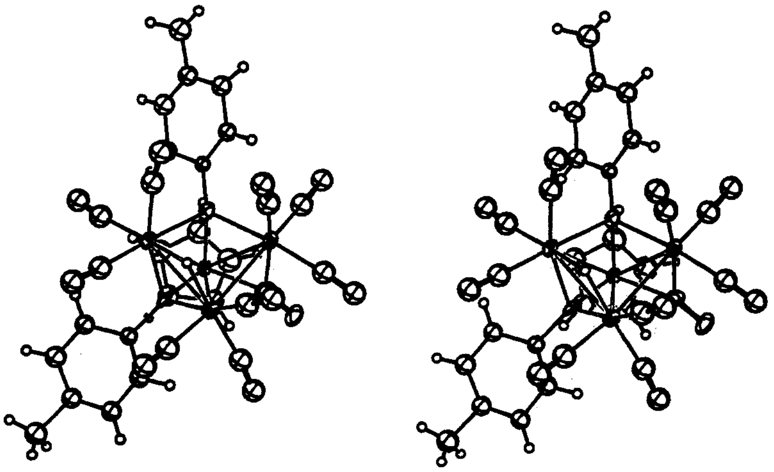

Figure 2. Stereoscopic view of the $CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H$ molecule.

molecular core is illustrated in Figure 1b.

The molecule consists of three $Os(CO)_3$ units and an CpW fragment along with four bridging ligands (two μ_3-CTol ligands, one μ-hydride ligand, and a μ-CO ligand). The five metal–metal bond distances vary considerably (and are discussed below), while the nonbonding "wing-tip" to "wing-tip" distance is given by Os(1)···Os(3) = 3.726 (1) Å.

There are two μ_3-CTol ligands, in substantially different locations. The first, centered on atom C(19), is "normal" and is bonded to the outer face of the Os(2)–Os(3)–W triangle. The osmium–alkylidyne distances (Os(2)–C(19) = 2.203 (21) Å and Os(3)–C(19) = 2.185 (21) Å) are equivalent but are longer than the W–C(19) distance of 2.012 (24) Å. There are some irregularities in the angular geometry about C(19),

Table VI. Interatomic Distances (Å) and Esd's for $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})_2H$

(A) Metal–Metal Distances			
W–Os(1)	2.781 (1)	Os(1)–Os(2)	2.913 (1)
W–Os(2)	2.921 (1)	Os(2)–Os(3)	2.883 (1)
W–Os(3)	2.857 (1)	Os(1)···Os(3)	3.726 (1)
(B) Metal–Carbonyl and Metal–Bridging (μ) Carbonyl Distances			
Os(1)–C(1)	1.923 (25)	Os(1)···O(1)	3.087 (17)
–C(2)	1.882 (30)	···O(2)	3.038 (21)
–C(3)	1.962 (27)	···O(3)	3.094 (15)
Os(2)–C(4)	1.974 (28)	Os(2)···O(4)	3.059 (20)
–C(5)	1.929 (29)	···O(5)	3.079 (19)
–C(6)	1.939 (28)	···O(6)	3.045 (19)
Os(3)–C(7)	1.963 (27)	Os(3)···O(7)	3.085 (16)
–C(8)	1.926 (28)	···O(8)	3.043 (20)
–C(9)	1.932 (25)	···O(9)	3.048 (17)
W–C(10)	2.075 (26)	W···O(10)	3.156 (16)
Os(1)–C(10)	2.160 (24)	Os(1)···O(10)	3.135 (16)
(C) Possible Metal···Carbon (Semibridging Carbonyl) Distances			
Os(1)···C(5)	3.163 (31)	Os(2)···C(10)	3.035 (26)
(D) Metal–Carbon (Alkylidyne) Distances			
Os(1)–C(11)	2.270 (21)	Os(2)–C(19)	2.203 (21)
Os(3)–C(11)	2.263 (21)	Os(3)–C(19)	2.185 (21)
W–C(11)	2.012 (21)	W–C(19)	2.012 (24)
(E) Tungsten–Carbon (Cyclopentadienyl) Distances			
W–C(27)	2.316 (28)	W–C(30)	2.321 (32)
–C(28)	2.374 (27)	–C(31)	2.342 (34)
–C(29)	2.349 (29)	–Cp	2.016
(F) Carbon–Oxygen Distances			
C(1)–O(1)	1.165 (30)	C(6)–O(6)	1.106 (34)
C(2)–O(2)	1.156 (36)	C(7)–O(7)	1.122 (31)
C(3)–O(3)	1.134 (31)	C(8)–O(8)	1.119 (35)
C(4)–O(4)	1.087 (35)	C(9)–O(9)	1.117 (30)
C(5)–O(5)	1.151 (35)	C(10)–O(10)	1.229 (30)
(G) Distances within the μ_3-CTol Ligands			
C(11)–C(12)	1.508 (29)	C(19)–C(20)	1.473 (30)
C(12)–C(13)	1.410 (31)	C(20)–C(21)	1.376 (31)
C(13)–C(14)	1.405 (35)	C(21)–C(22)	1.395 (32)
C(14)–C(15)	1.392 (34)	C(22)–C(23)	1.347 (34)
C(15)–C(16)	1.429 (34)	C(23)–C(24)	1.370 (34)
C(15)–C(18)	1.508 (37)	C(23)–C(26)	1.539 (36)
C(16)–C(17)	1.375 (33)	C(24)–C(25)	1.404 (34)
C(17)–C(12)	1.410 (28)	C(25)–C(20)	1.419 (32)

with M–C(19)–M angles (M = metal atom) in the range 82.1 (7)–87.6 (8)° and M–C(19)–C(20) angles of 124.0 (15)–134.3 (16)°.

The second μ_3-CTol ligand, centered on atom C(11), spans the tungsten bridgehead (or "hinge") position and the two "wing-tip" osmium atoms, Os(1) and Os(3). As might be expected, this second μ_3-CTol ligand is far more distorted than the first. The osmium–alkylidyne distances (Os(1)–C(11) = 2.270 (21) Å and Os(3)–C(11) = 2.263 (21) Å) are equivalent but are "stretched" by about 0.07 Å relative to those in the first μ_3-CTol ligand; interestingly, the W–C(11) distance is again short (W–C(11) = 2.012 (21) Å) and is identical with that in the first ligand. Irregularities around C(11) in this ligand are more pronounced than those around C(19) in the first, with M–C(11)–M angles of 80.7 (7)–110.6 (9)° and M–C(11)–C(12) angles of 114.8 (14)–138.9 (15)°. (It is rather surprising that the "wing-tip" to "wing-tip" Os(1)–C(11)–Os(3) angle of 110.6 (9)° is that close to a regular tetrahedral angle!)

The observed W–C(alkylidyne) bond distances are approximately 0.1 Å shorter than the shortest W–C single bonds reported by Cotton et al.[9] and presumably have some multiple-bond character. The Os–C(alkylidyne) bond distances all seem slightly longer than a normal Os–C single bond (cf. values of 2.159 (15)–2.188 (16) Å for the Os–C(alkylidene) linkages in $Os_3(CO)_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$).[10]

The bridging carbonyl ligand, C(10)–O(10), spans the Os(1)–W linkage with W–C(10) = 2.075 (26) Å and Os(1)–C(10) = 2.160 (24) Å; in addition there is some interaction with a *third* metal atom, with Os(2)···C(10) = 3.035 (26) Å. The ligand may perhaps be referred to as a semi triply bridging carbonyl group.[11] (The "α values" for the Os(1)–C(10)···Os(2) and W–C(10)···Os(2) systems are 0.41 and 0.46, respectively. This is toward the weak-interaction end of the semibridging regime ($0.1 < \alpha < 0.6$) suggested by Curtis et al.[12]) Bridging carbonyl groups between third-row transition-metal atoms are rather rare, and only a few cases have been studied by X-ray crystallography. For example, $Os_3(CO)_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$[13] and $Os_3(CO)_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$[10] have been shown to have symmetrical bridging carbonyl groups and a very unsymmetrical μ-CO group is found in $Os_3(CO)_{10}(PhC_2Ph)$.[14] Two instances involving larger osmium clusters are the anions $[HOs_4(CO)_{12}(\mu\text{-CO})]^-$[15] and $[Os_5C(CO)_{13}(\mu\text{-CO})]^{2-}$.[16]

The bridging hydride ligand, which spans the Os(2)–Os(3) bond, was located from a difference-Fourier map but was not well-behaved during the least-squares refinement process. Evidence to support its postulated position is as follows.

(i) The Os(2)–Os(3) bond length of 2.883 (1) Å is longer than expected if it were bridged only by the μ_3-alkylidyne ligand.

(ii) The adjacent and coplanar Os–Os–CO angles, Os(2)–Os(3)–C(7) = 116.1 (8)° and Os(3)–Os(2)–C(5) = 118.1 (9)°, are typical of those found in such equatorially bridged hydrido species as $(H)(\mu\text{-H})Os_3(CO)_{11}$[17] and $(H)(\mu\text{-H})Os_3(CO)_{10}(PPh_3)$.[18]

(iii) The proposed μ-hydride site occupies a "hole" in the coordination surface of the cluster and is trans to two carbonyl ligands; the systems H–Os(3)–C(9)–O(9) and H–Os(2)–C(6)–O(6) are each close to linear. This orientation is reflected in strong ^{13}C–^1H coupling observable in the ^{13}C NMR spectrum of **1** (vide infra).

The overall ligand distribution leads to each metal atom having a unique environment and molecular symmetry of only C_1. Consequently, there are significant variations in metal–metal distances within the tetranuclear core.

The bond length Os(1)–W = 2.781 (1) Å is the shortest intermetallic distance in the molecule. It is some 0.13–0.14 Å shorter than the average Os–W distance of 2.919 (13) Å in $CpWOs_3(CO)_{12}H$[19] and the nonbridged Os–W distance of 2.915 (1) Å within the $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$[2b] molecule. The shortness of this bond probably results from the presence of two ligands (the bridging carbonyl, C(10)–O(10), and the μ_3-alkylidyne ligand, centered on C(11)), each of which acts as a bond-contacting bridging ligand.

The W–Os(3) bond length of 2.857 (1) Å reveals a similar, but less drastic, shortening, due now to the effects of two μ_3-alkylidyne ligands. Apparently, the μ_3-CTol ligand causes

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Table VII. Selected Interatomic Angles (deg) and Esd's for $CpWOs_3(CO)_{10}(\mu_3\text{-CTol})H$

(A) Intermetallic Angles							
W-Os(1)-Os(2)	61.69 (3)	Os(3)-Os(2)-W	58.97 (3)	W-Os(3)-Os(2)	61.19 (3)	Os(3)-W-Os(2)	59.84 (3)
Os(1)-Os(2)-W	56.93 (3)	Os(1)-Os(2)-Os(3)	80.03 (4)	Os(1)-W-Os(2)	61.38 (3)	Os(1)-W-Os(3)	82.74 (4)
(B) M-M-CO, M-M-(μ-CO), and M-M-Cp[a] Angles							
W-Os(1)-C(1)	129.0 (7)	Os(3)-Os(2)-C(5)	118.1 (9)	Os(2)-Os(1)-C(1)	95.3 (7)	Os(2)-Os(3)-C(9)	149.8 (7)
-C(2)	105.8 (9)	-C(6)	147.0 (8)	-C(2)	165.9 (9)	Os(1)-W-C(10)	50.3 (7)
-C(3)	127.7 (7)	W-Os(3)-C(7)	125.9 (8)	-C(3)	91.4 (7)	Os(2)-W-C(10)	72.6 (7)
Os(1)-Os(2)-C(4)	165.1 (8)	-C(8)	132.0 (8)	W-Os(2)-C(4)	131.1 (8)	Os(3)-W-C(10)	125.5 (7)
-C(5)	78.7 (9)	-C(9)	97.3 (7)	-C(5)	135.6 (9)	Os(1)-W-Cp	137.6
-C(6)	100.6 (8)	W-Os(1)-C(10)	47.6 (7)	-C(6)	93.4 (8)	Os(2)-W-Cp	154.0
Os(3)-Os(2)-C(4)	94.1 (8)	Os(2)-Os(1)-C(10)	71.8 (7)	Os(2)-Os(3)-C(7)	116.1 (8)	Os(3)-W-Cp	129.1
				-C(8)	92.5 (8)		
(C) Metal-(μ_3-C)-Metal Angles							
Os(1)-C(11)-W	80.7 (7)	Os(1)-C(11)-Os(3)	110.6 (9)	Os(3)-C(19)-W	85.7 (8)	Os(2)-C(19)-Os(3)	82.1 (7)
Os(3)-C(11)-W	83.6 (8)	Os(2)-C(19)-W	87.6 (8)				
(D) Metal-(μ-C)-Metal Angles							
Os(1)-C(10)-W	82.1 (9)						
(E) Metal-Carbon-Oxygen Angles							
Os(1)-C(1)-O(1)	176.9 (21)	Os(2)-C(4)-O(4)	175.1 (24)	Os(3)-C(7)-O(7)	178.6 (23)	W-C(10)-O(10)	144.5 (19)
-C(2)-O(2)	178.4 (24)	-C(5)-O(5)	176.7 (25)	-C(8)-O(8)	175.8 (24)	Os(1)-C(10)-O(10)	133.5 (19)
-C(3)-O(3)	175.6 (22)	-C(6)-O(6)	178.5 (25)	-C(9)-O(9)	176.8 (21)		
(F) M···C(semibridging carbonyl)-M Angles							
Os(2)···C(10)-Os(1)	65.7 (6)	Os(1)···C(5)-Os(2)	64.6 (8)	Os(2)···C(10)-W	66.7 (7)		
(G) M-(μ_3-C)-C Angles							
Os(1)-C(11)-C(12)	120.8 (14)	W-C(11)-C(12)	138.9 (15)	Os(3)-C(19)-C(20)	124.0 (15)	W-C(19)-C(20)	134.3 (16)
Os(3)-C(11)-C(12)	114.8 (14)	Os(2)-C(19)-C(20)	124.0 (15)				
(H) Other Angles within the (μ_3-CTol) Ligands							
C(11)-C(12)-C(13)	118.8 (19)	C(18)-C(15)-C(16)	121.4 (22)	C(19)-C(20)-C(21)	122.3 (20)	C(26)-C(23)-C(24)	118.7 (22)
C(12)-C(13)-C(14)	121.4 (22)	C(15)-C(16)-C(17)	120.8 (22)	C(20)-C(21)-C(22)	124.7 (22)	C(23)-C(24)-C(25)	121.5 (23)
C(13)-C(14)-C(15)	120.4 (24)	C(16)-C(17)-C(12)	121.4 (21)	C(21)-C(22)-C(23)	119.5 (22)	C(24)-C(25)-C(20)	120.5 (22)
C(14)-C(15)-C(18)	120.4 (23)	C(17)-C(12)-C(11)	123.5 (18)	C(22)-C(23)-C(26)	122.0 (22)	C(25)-C(20)-C(19)	123.1 (20)
C(14)-C(15)-C(16)	118.2 (22)	C(17)-C(12)-C(13)	117.6 (19)	C(22)-C(23)-C(24)	119.1 (23)	C(25)-C(20)-C(21)	114.3 (20)
(I) Carbon (Carbonyl)-Metal-Carbon (Carbonyl) Angles							
C(1)-Os(1)-C(2)	98.0 (11)	C(1)-Os(1)-C(10)	166.7 (10)	C(4)-Os(2)-C(5)	92.3 (12)	C(7)-Os(3)-C(8)	101.3 (10)
C(1)-Os(1)-C(3)	95.0 (10)	C(2)-Os(1)-C(10)	95.2 (11)	C(4)-Os(2)-C(6)	91.8 (11)	C(7)-Os(3)-C(9)	93.4 (10)
C(2)-Os(1)-C(3)	92.2 (11)	C(3)-Os(1)-C(10)	82.7 (10)	C(5)-Os(2)-C(6)	94.0 (12)	C(8)-Os(3)-C(9)	87.3 (11)
(J) Carbon (Carbonyl)-Metal-Carbon (Alkylidyne) Angles							
C(1)-Os(1)-C(11)	89.0 (9)	C(4)-Os(2)-C(19)	87.7 (10)	C(8)-Os(3)-C(11)	174.0 (10)	C(8)-Os(3)-C(19)	87.5 (10)
C(2)-Os(1)-C(11)	94.1 (10)	C(5)-Os(2)-C(19)	166.7 (10)	C(9)-Os(3)-C(11)	97.0 (9)	C(9)-Os(3)-C(19)	100.7 (9)
C(3)-Os(1)-C(11)	172.0 (9)	C(6)-Os(2)-C(19)	99.3 (10)	C(10)-W-C(11)	102.3 (9)	C(10)-W-C(19)	113.8 (9)
C(10)-Os(1)-C(11)	91.8 (9)	C(7)-Os(3)-C(11)	81.7 (9)	C(7)-Os(3)-C(19)	163.8 (10)		

[a] Cp is the centroid of the η^5-C_5H_5 ligand.

a less dramatic shortening of a spanned metal–metal bond than does a μ-CO ligand.

The observed Os(2)–Os(3) bond length of 2.883 (1) Å is only 0.006 Å longer than the nonbridged Os–Os distance of 2.877 (3) Å in the archetypal species $Os_3(CO)_{12}$.[17] It would seem that the normal bond-lengthening effect of a single, unsupported, equatorial hydride ligand[20] is precisely counterbalanced by the contrasting effect of the associated μ_3-alkylidyne ligand centered on C(19).

The W–Os(2) bond length of 2.921 (1) Å appears to be a normal W–Os single-bond distance (vide supra), despite being in association with the μ_3-alkylidyne ligand centered on C(19). Finally, we note that the nonbridged Os(1)–Os(2) bond length of 2.913 (1) Å is slightly longer than a normal Os–Os distance, perhaps to compensate for surrounding perturbations on metal–metal bond lengths.

Solution Dynamics of 1. The molecular dynamics of **1** have been examined by variable-temperature ^1H and ^{13}C NMR spectroscopy. The limiting low-temperature ^{13}C NMR spectrum (−50 °C, Figure 3) shows 2 alkylidyne carbon signals

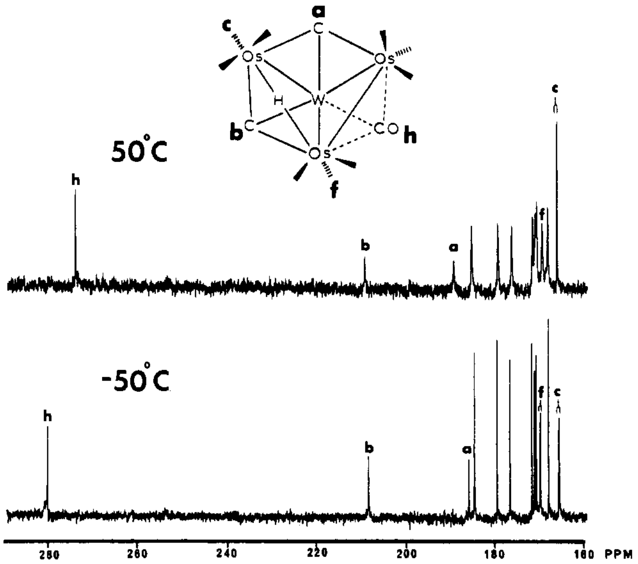

Figure 3. ^{13}C (^1H coupled) NMR spectra (90 MHz) of $CpWOs_3(^*CO)_{10}(\mu_3\text{-}^*CTol)_2H$ in $CDCl_3$.

at δ 186.5 (C_a, $^1J_{WC}$ = 106 Hz) and δ 209.0 (C_b, $^1J_{WC}$ = 108 Hz) and 10 carbonyl carbon resonances. The two resonances

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(20) (a) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36. (b) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843 (see, especially, the discussion on pp 1848–1852).

(21) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319.

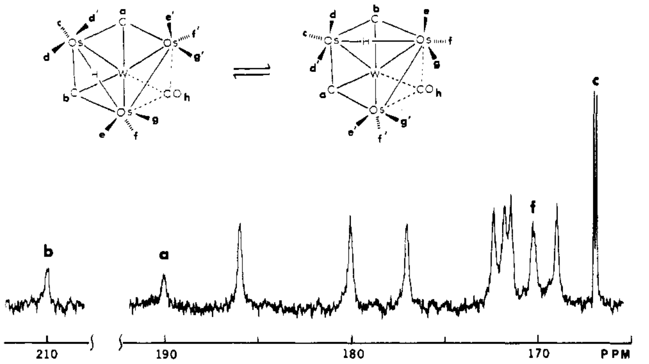


Figure 4. Partial ^{13}C NMR spectrum of $CpWOs_3(^*CO)_{10}(\mu_3\text{-}^*CTol)_2H$ at 50 °C.

assigned to the alkylidyne carbon atoms are absent when **1** is prepared from $CpW(CO)_2(CTol)$ and ^{13}C-enriched $H_2Os_3(^*CO)_{10}$. On the basis of the chemical shift of the alkylidyne carbon atoms (vide infra) in the symmetrical dialkylidyne cluster $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (**2**), the more downfield resonance is presumably due to C_b, the alkylidyne carbon atom on the *closed* WOs_2 face. The carbonyl groups c and f, trans to bridging hydrogen, are doublets at δ 166.3 ($^2J_{CH}$ = 12.3 Hz) and δ 170.5 ($^2J_{CH}$ = 11.8 Hz), respectively. These couplings were verified by obtaining the ^1H-decoupled spectrum. The surprisingly low-field resonance at 281.0 ppm ($^1J_{WC}$ = 108 Hz) is assigned to the semi triply bridging carbonyl (h) on the WOs_2 face. This carbonyl presumably corresponds to the IR band at 1703 cm^{-1} observed for **1** in cyclohexane solution.

Increasing the NMR sample temperature from −50 to +50 °C causes eight carbonyl resonances and both alkylidyne carbon resonance to broaden to the same extent (see Figure 3 and 4), while the carbonyls c and h remain sharp (NB: hydride coupling to carbonyl c is retained throughout). The complete coalescence of the two alkylidyne carbon resonances cannot be observed by ^{13}C NMR, due to the conversion of **1** to **2** above 70 °C. The variable-temperature ^1H NMR spectra of **1** show two distinct methyl resonances, arising from the tolyl moieties, which broaden above room temperature and coalesce at 50 °C (360 MHz) to a single peak.

On the basis of the above observations, we propose that, in solution, compound **1** undergoes a degenerate framework rearrangement that interchanges the two possible enantiomeric forms (see Figure 4). Thus, while remaining bonded to the unique osmium atom bearing both alkylidyne ligands, the hydride exchanges reversibly between sites bridging to one or other of the two remaining osmium atoms. The signals for the carbonyl ligands c and h are predicted not to show NMR line broadening, whereas the signals for the alkylidyne carbon atoms and the remaining carbonyls, which exchange in a pairwise manner a → b, d → d′, e → e′, f → f′, and g → g′, should show line broadening. At 50 °C the extent of line broadening is the same for both alkylidyne and carbonyl carbon signals, which indicates that only one process is taking place. A complete ^1H NMR line-shape analysis was carried out for the methyl resonances of **1** over the temperature range 20–60 °C (see Experimental Section). This analysis gave $\Delta G^{\ddagger}$ = 15.7 ± 0.3 kcal/mol for the enantiometer-interchange process.

Conversion of 1 to 2. Compound **1** is transformed upon pyrolysis to the new cluster **2** by loss of a carbonyl ligand as shown in eq 1.

$$\underset{\mathbf{1}}{CpWOs_3(CO)_{10}(\mu_3\text{-}CTol)_2H} \xrightarrow[-CO]{\Delta} \underset{\mathbf{2}}{CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H} \quad (1)$$

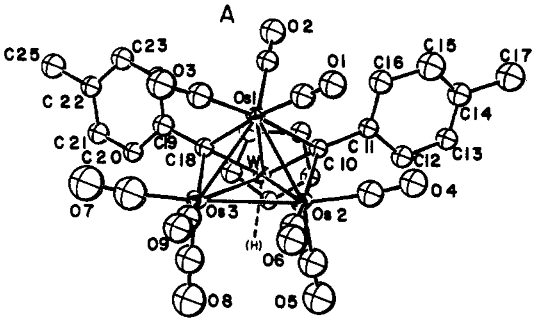


Figure 5. Labeling diagram for molecule A of $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (ORTEP-II diagram).

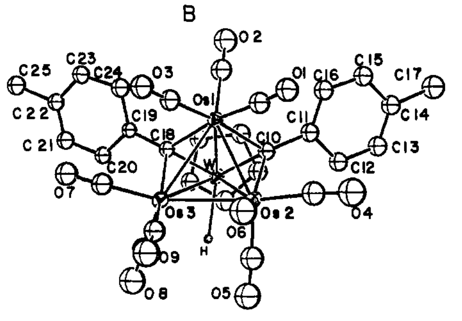


Figure 6. Labeling diagram for molecule B of $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$ (ORTEP-II diagram).

The ^1H NMR spectrum of **2** shows a single methyl resonance for the two tolyl groups and a hydride signal at the unusually low-field position of δ 3.75 with ^{183}W satellites ($^1J_{WH}$ = 89 Hz). This hydride signal is absent in the ^1H NMR spectrum of $CpWOs_3(CO)_9(\mu_3\text{-}CTol)D$ (**2**-*d*). The unusual chemical shift for a cluster hydride suggested the possibility that the hydrogen atom bridges between an alkylidyne carbon atom and the tungsten atom; however, no coupling between the alkylidyne carbons and the hydride is observed in either the ^1H or the ^{13}C NMR spectrum of the sample ^{13}C enriched at the alkylidyne carbon. This then requires that the hydride ligand in **2** is terminally bound to the tungsten atom. Consistent with this proposal, compound **2** reacts with carbon tetrachloride, in the presence of *t*-BuOCl at room temperature, to produce the chloro derivative, $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2Cl$ (**3**). The hydride signal found at δ 3.75 for **2** is absent in the ^1H NMR spectrum of **3**. The IR spectra of **2** and **3** are similar, but the absorptions for **3** are shifted to slightly higher energy. Also, a weak band at 1999 cm^{-1} in the spectrum of **2** may be obscured by the strong band that occurs at 1999 cm^{-1} in the spectrum of **3**. No bands could be assigned to the W–H or W–D stretching mode in IR spectra (both solution and KBr pellet) of **2** or **2**-*d*.

X-ray Structure of 2. The crystal consists of discrete ordered units of $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$, which are mutually separated by normal van der Waals distances. There are two equivalent molecules in the crystallographic asymmetric unit. Figure 5 shows the scheme used for labeling atoms in both molecules and is an illustration of molecule A, while Figure 6 is an equivalent view for molecule B. Interatomic distances and their estimated standard deviation (esd's) are collected in Table VIII, while interatomic angles are listed in Table IX.

Each molecule contains two μ_3-CTol ligands, which are located in almost equivalent environments on opposing sides of the pseudo plane of symmetry. Os(1), a unique osmium atom, and W are bonded to both alkylidyne fragments, and the Os(1)–W vector is almost coincident with the pseudo plane of symmetry. The W–H distance in molecule B is 1.92 (18) Å, and the hydride ligand is more than 3.0 Å from the other metal atoms. Indeed, the terminal hydride ligand occupies

Table VIII. Interatomic Distances (Å) and Esd's for $CpWOs_3(CO)_9(\mu_3\text{-CTol})_2H$

	molecule A	molecule B		molecule A	molecule B
(A) Metal–Metal and Tungsten–Hydride Distances					
W–Os(1)	2.827 (1)	2.831 (1)	Os(1)–Os(3)	2.798 (1)	2.857 (1)
W–Os(2)	2.914 (1)	2.910 (1)	Os(2)–Os(3)	2.833 (1)	2.827 (1)
W–Os(3)	2.900 (1)	2.891 (1)	W–H		1.92 (18)
Os(1)–Os(2)	2.810 (1)	2.791 (1)			
(B) Metal–Carbon (Carbonyl) Distances					
Os(1)–C(1)	1.902 (26)	1.858 (25)	Os(2)–C(6)	1.895 (26)	1.849 (25)
–C(2)	1.926 (24)	1.851 (27)	Os(3)–C(7)	1.819 (40)	1.883 (25)
–C(3)	1.887 (27)	1.910 (24)	–C(8)	1.796 (33)	1.843 (28)
Os(2)–C(4)	1.831 (30)	1.861 (31)	–C(9)	1.866 (26)	1.856 (25)
–C(5)	1.850 (31)	1.814 (28)			
(C) Metal–(μ_3-C) Distances					
Os(1)–C(10)	2.249 (20)	2.254 (21)	Os(1)–C(18)	2.249 (20)	2.224 (20)
Os(2)–C(10)	2.169 (19)	2.166 (21)	Os(3)–C(18)	2.135 (20)	2.136 (19)
W–C(10)	2.013 (20)	1.977 (22)	W–C(18)	1.985 (21)	1.978 (19)
(D) Tungsten–Carbon (Cyclopentadienyl) Distances					
W–C(26)	2.334 (23)	2.384 (24)	W–C(29)	2.349 (25)	2.308 (24)
–C(27)	2.319 (23)	2.330 (24)	–C(30)	2.319 (25)	2.349 (24)
–C(28)	2.382 (21)	2.337 (24)	–Cp[a]	2.011	2.014
(E) Carbon–Oxygen Distances					
C(1)–O(1)	1.174 (32)	1.188 (30)	C(6)–O(6)	1.150 (33)	1.181 (32)
C(2)–O(2)	1.123 (30)	1.162 (33)	C(7)–O(7)	1.222 (50)	1.156 (30)
C(3)–O(3)	1.179 (34)	1.130 (29)	C(8)–O(8)	1.192 (42)	1.167 (36)
C(4)–O(4)	1.196 (35)	1.178 (38)	C(9)–O(9)	1.162 (32)	1.168 (32)
C(5)–O(5)	1.154 (38)	1.210 (35)	C(10)–O(10)	1.174 (32)	1.188 (30)
(F) Os···O Distances					
Os(1)···O(1)	3.075 (18)	3.045 (17)	Os(2)···O(6)	3.041 (19)	3.024 (20)
···O(2)	3.046 (18)	3.013 (19)	Os(3)···O(7)	3.031 (29)	3.038 (17)
···O(3)	3.065 (20)	3.040 (17)	···O(8)	2.982 (26)	3.010 (22)
Os(2)···O(4)	3.022 (19)	3.037 (23)	···O(9)	3.025 (19)	3.020 (19)
···O(5)	3.002 (23)	3.016 (21)			
(G) Distances within the μ_3-CTol Ligands					
C(10)–C(11)	1.479 (29)	1.498 (30)	C(18)–C(19)	1.475 (32)	1.501 (28)
C(11)–C(12)	1.437 (33)	1.458 (31)	C(19)–C(20)	1.393 (32)	1.408 (30)
C(12)–C(13)	1.379 (34)	1.389 (32)	C(20)–C(21)	1.458 (34)	1.460 (32)
C(13)–C(14)	1.380 (34)	1.347 (35)	C(21)–C(22)	1.394 (33)	1.391 (31)
C(14)–C(17)	1.552 (42)	1.555 (38)	C(22)–C(25)	1.562 (38)	1.559 (33)
C(14)–C(15)	1.401 (42)	1.457 (34)	C(22)–C(23)	1.402 (34)	1.360 (31)
C(15)–C(16)	1.429 (41)	1.378 (33)	C(23)–C(24)	1.393 (34)	1.402 (32)
C(16)–C(11)	1.434 (32)	1.386 (32)	C(24)–C(19)	1.453 (31)	1.405 (29)

[a] Cp is the centroid of the η^5-C_5H_5 ligand.

a normal coordination site around W since no atom or ligand approaches closely to it. During final refinement the net shift of this hydride ligand was only *0.084* Å with a fixed isotropic thermal parameter set at 4.5 Å^2. After close scrutiny of distances, angles, and the stereochemistries of molecule A and molecule B, a terminal hydride ligand is proposed to occupy almost exactly the same position in molecule A. It should be noted that the hydride ligand in molecule B is also close to being coincident with the pseudo plane of symmetry.

The idealized, symmetric form of **2** would have two carbonyls on Os(2) eclipsed with the mirror-related carbonyls on Os(3). The real molecules A and B (see Figures 5 and 6) have responded to the nonbonded interactions between these vicinal carbonyls by twisting the $Os(CO)_3$ moieties in opposite directions around the Os(2)–Os(3) bond axis: in A, Os(2)–C-O(6) is turned *away* from Os(1) and Os(3)–CO(7) is turned *toward* Os(1), whereas in B, the sense of twist is reversed. It is likely that this distortion toward staggered carbonyl conformations is responsible for the variation in observed M–M and M–C(alkylidyne) distances.

The corresponding M–C(alkylidyne) bond distances are similar for molecules A and B, and within each molecule the pseudo-mirror-related Os–C(alkylidyne) and W–C(alkylidyne) distances are essentially equivalent. The Os(1)–C(alkylidyne) bond distances are approximately 0.07–0.10 longer than the Os(2)–C(10) and Os(3)–C(18) bond distances. The latter are comparable with that we consider to be a normal Os–C (σ) single-bond distance of 2.15–2.17 Å.[4,10] As in the case of compound, **1**, the W–C(alkylidyne) bond distances are short, ca. 2.0 Å, which is approximately 0.1 Å shorter than the shortest W–C single bond reported by Cotton et al.[9]

If each alkylidyne ligand formed three normal M–C single bonds, donating one electron to each metal atom, the resulting formal valence electron counts would be 17 electrons for W, 19 electrons for Os(1), and 18 electrons for each Os(2) and Os(3). However, the long Os(1)–C(alkylidyne) distances and short W–C(alkylidyne) distances suggest that the alkylidyne ligands help to shift charge from electron-rich Os(1) to electron-poor W, much in the same way that semibridging carbonyl ligands act.[11] The alkylidyne carbon atoms have a variable bond order and therefore a variable electron donation to their individual metal atoms. If the C(alkylidyne)–M electron donations are redefined to be C(10)–W and C(18)–W = 1.5 electrons, C(10)–Os(1) and C(18)–Os(1) = 0.5 electron, and C(10)–Os(2) and C(18)–Os(3) = 1 electron, then each metal atom contains exactly 18 valence electrons. Alternatively, the same formal situation is achieved by considering the Os(1)–W interaction as a coordinate covalent Os→W donor bond.

The W–Os(1) bond distance is the shortest heterometallic bond observed in both molecule A and molecule B of **2**. This shortening is due directly to the bond contracting of the two

Table IX. Selected Interatomic Angles (deg) and Esd's for $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$

	molecule A	molecule B		molecule A	molecule B
(A) Intermetallic Angles					
Os(2)-Os(1)-Os(3)	60.69 (3)	60.06 (3)	Os(1)-Os(3)-Os(2)	59.86 (3)	58.81 (3)
Os(2)-Os(1)-W	62.25 (3)	62.34 (3)	Os(1)-Os(3)-W	59.46 (3)	59.00 (3)
Os(3)-Os(1)-W	62.08 (3)	61.11 (3)	Os(2)-Os(3)-W	61.07 (3)	61.16 (3)
Os(1)-Os(2)-Os(3)	59.45 (3)	61.13 (3)	Os(1)-W-Os(2)	58.58 (3)	58.16 (3)
Os(1)-Os(2)-W	59.17 (3)	59.50 (3)	Os(1)-W-Os(3)	58.46 (3)	59.89 (3)
Os(3)-Os(2)-W	60.61 (3)	60.52 (3)	Os(2)-W-Os(3)	58.32 (3)	58.32 (3)
(B) M-M-CO and M-M-Cp Angles					
Os(2)-Os(1)-C(1)	81.4 (8)	79.1 (7)	W-Os(2)-C(4)	123.9 (9)	123.8 (9)
-C(2)	138.7 (7)	141.8 (8)	-C(5)	89.5 (10)	94.4 (9)
-C(3)	124.3 (8)	122.2 (7)	-C(6)	150.6 (8)	106.8 (8)
Os(3)-Os(1)-C(1)	123.9 (8)	125.2 (7)	Os(1)-Os(3)-C(7)	115.2 (12)	106.8 (8)
-C(2)	141.8 (7)	138.9 (8)	-C(8)	147.2 (10)	146.5 (8)
-C(3)	79.6 (8)	82.2 (7)	-C(9)	103.9 (8)	115.8 (8)
W-Os(1)-C(1)	134.2 (8)	130.0 (7)	Os(2)-Os(3)-C(7)	171.8 (12)	160.8 (8)
-C(2)	95.7 (7)	96.0 (8)	-C(8)	95.9 (10)	106.4 (8)
-C(3)	131.1 (8)	134.8 (7)	-C(9)	87.6 (8)	86.2 (8)
Os(1)-Os(2)-C(4)	111.1 (9)	113.6 (9)	W-Os(3)-C(7)	123.3 (12)	125.0 (8)
-C(5)	147.7 (10)	149.2 (9)	-C(8)	90.3 (10)	87.5 (8)
-C(6)	109.8 (8)	100.1 (8)	-C(9)	148.5 (8)	145.2 (8)
Os(3)-Os(2)-C(4)	167.1 (9)	171.5 (9)	Os(1)-W-Cp	131.8	131.8
-C(5)	100.0 (10)	92.9 (9)	Os(2)-W-Cp	150.4	151.1
-C(6)	90.1 (8)	89.1 (8)	Os(3)-W-Cp	150.5	149.5
(C) Metal-(μ_3-C)-Metal Angles					
Os(1)-C(10)-Os(2)	78.9 (7)	78.3 (7)	Os(1)-C(18)-Os(3)	79.3 (7)	81.8 (7)
Os(1)-C(10)-W	82.9 (7)	83.7 (8)	Os(1)-C(18)-W	83.5 (7)	84.5 (7)
Os(2)-C(10)-W	88.3 (8)	89.1 (8)	Os(3)-C(18)-W	89.4 (8)	89.2 (8)
(D) Metal-Carbon-Oxygen Angles					
Os(1)-C(1)-O(1)	177.3 (22)	176.9 (21)	Os(2)-C(6)-O(6)	173.9 (23)	173.0 (22)
-C(2)-O(2)	174.8 (21)	179.4 (23)	Os(3)-C(7)-O(7)	170.5 (33)	176.0 (22)
-C(3)-O(3)	177.1 (23)	178.4 (21)	-C(8)-O(8)	172.3 (29)	178.5 (24)
Os(2)-C(4)-O(4)	173.2 (24)	176.7 (25)	-C(9)-O(9)	172.3 (29)	178.5 (24)
-C(5)-O(5)	175.8 (27)	171.5 (24)			
(E) M-(μ_3-C)-C Angles					
Os(1)-C(10)-C(11)	128.1 (14)	126.4 (15)	Os(1)-C(18)-C(19)	126.4 (15)	126.7 (13)
Os(2)-C(10)-C(11)	123.6 (14)	123.7 (15)	Os(3)-C(18)-C(19)	124.7 (15)	120.2 (13)
W-C(10)-C(11)	136.4 (15)	136.9 (16)	W-C(18)-C(19)	135.5 (16)	137.4 (14)
(F) Other Angles within the μ_3-CTol Ligands					
C(10)-C(11)-C(12)	118.5 (19)	115.3 (19)	C(18)-C(19)-C(20)	117.9 (20)	121.5 (18)
C(11)-C(12)-C(13)	120.0 (22)	118.6 (20)	C(19)-C(20)-C(21)	121.2 (20)	116.2 (19)
C(12)-C(13)-C(14)	120.2 (23)	123.7 (23)	C(20)-C(21)-C(22)	118.8 (21)	121.4 (20)
C(13)-C(14)-C(17)	118.2 (24)	124.8 (23)	C(21)-C(22)-C(25)	118.3 (21)	119.5 (19)
C(13)-C(14)-C(15)	121.4 (25)	117.3 (21)	C(21)-C(22)-C(23)	120.6 (22)	121.0 (20)
C(17)-C(14)-C(15)	120.2 (25)	117.9 (21)	C(25)-C(22)-C(23)	121.1 (21)	119.5 (20)
C(14)-C(15)-C(16)	121.1 (27)	120.9 (21)	C(22)-C(23)-C(24)	121.0 (22)	119.2 (20)
C(15)-C(16)-C(11)	116.5 (23)	120.7 (22)	C(23)-C(24)-C(19)	120.5 (21)	122.0 (19)
C(16)-C(11)-C(10)	120.8 (20)	125.8 (20)	C(24)-C(19)-C(18)	123.6 (20)	118.4 (17)
C(16)-C(11)-C(12)	120.6 (21)	118.7 (20)	C(24)-C(19)-C(20)	117.8 (20)	120.1 (18)
(G) C(carbonyl)-M-C(carbonyl) Angles					
C(1)-Os(1)-C(2)	94.1 (10)	95.8 (11)	C(5)-Os(2)-C(6)	93.7 (12)	95.3 (12)
C(1)-Os(1)-C(3)	91.7 (11)	91.9 (10)	C(7)-Os(3)-C(8)	91.1 (13)	92.4 (11)
C(2)-Os(1)-C(3)	96.8 (11)	95.6 (11)	C(7)-Os(3)-C(9)	87.5 (14)	89.9 (11)
C(4)-Os(2)-C(5)	92.3 (13)	94.0 (12)	C(8)-Os(3)-C(9)	96.2 (13)	90.8 (12)
C(4)-Os(2)-C(6)	85.2 (12)	85.4 (12)			
(H) C(carbonyl)-M-C(alkylidyne) and C(alkylidyne)-M-C(alkylidyne) Angles					
C(1)-Os(1)-C(10)	90.6 (9)	87.0 (9)	C(4)-Os(2)-C(10)	84.9 (10)	86.4 (11)
C(2)-Os(1)-C(10)	90.0 (9)	92.8 (10)	C(5)-Os(2)-C(10)	111.7 (11)	120.2 (10)
C(3)-Os(1)-C(10)	172.7 (10)	171.7 (9)	C(6)-Os(2)-C(10)	153.1 (10)	144.0 (10)
C(1)-Os(1)-C(18)	172.3 (9)	171.2 (9)	C(7)-Os(3)-C(18)	86.5 (13)	85.1 (9)
C(2)-Os(1)-C(18)	93.5 (9)	91.7 (10)	C(8)-Os(3)-C(18)	114.9 (12)	106.3 (10)
C(3)-Os(1)-C(18)	87.9 (10)	92.1 (9)	C(9)-Os(3)-C(18)	148.5 (9)	162.3 (9)
C(10)-Os(1)-C(18)	89.0 (7)	87.9 (7)	C(10)-W-C(18)	104.1 (8)	103.6 (8)
(I) Angles Involving the Terminal Hydride Ligand on the Tungsten Atom[a]					
Os(1)-W-H		131 (5)	C(10)-W-H		116 (5)
Os(2)-W-H		79 (5)	C(18)-W-H		115 (5)
Os(3)-W-H		78 (5)	Cp-W-H		97

[a] The terminal hydride was located directly *only* in molecule B.

bridging alkylidyne ligands associated with this bond. It should be pointed out, however, that these bond distances are approximately 0.05 Å longer than in a similar environment W–Os bond found in **1** (W–Os(2) = 2.781 (1) Å). This lengthening may be due to the "weaker" Os(1)–C(alkylidyne) bonds observed in **2** as compared with the Os(2)–C(alkylidyne)

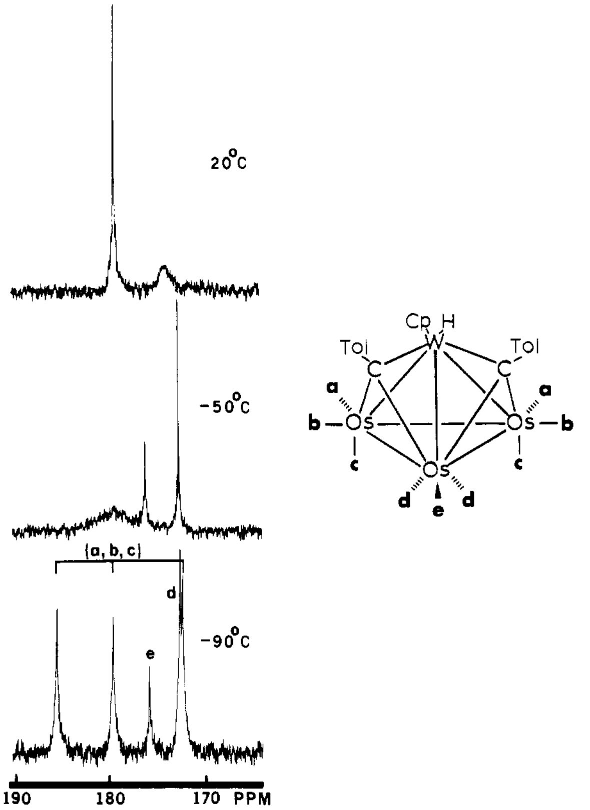


Figure 7. Variable-temperature ^{13}C NMR spectra (90 MHz, carbonyl region) of $CpWOs_3(*CO)_9(\mu_3\text{-}*CTol)_2H$ in CD_2Cl_2.

bonds in **1**, since W-C(alkylidyne) bond lengths appear to be equivalent for the two structural analyses. The W-Os(2) bond distances are similar for both molecules A and B and are close in length to the pseudo mirror related W-Os(3) bond distances. However, the Os(1)-Os(2) and Os(1)-Os(3) bond distances display a pattern that reflects the twisted configuration around the Os(2)-Os(3) bond (vide supra). Thus, a carbonyl twisted *away* from Os(1) is associated with a longer bond whereas a carbonyl twisted *toward* Os(1) appears with a shorter bond (molecule A, Os(1)-Os(2) = 2.810 (1) Å (long), Os(1)-Os(3) = 2.798 (1) Å (short); molecule B, Os(1)-Os(2) = 2.791 (1) Å (short), Os(1)-Os(3) = 2.857 (1) Å (long)). Molecule B is more strongly twisted than molecule A, and the difference between the long and short bonds is correspondingly greater. Finally, the Os(2)-Os(3) bond is unique and has self-consistent distances for the two molecules.

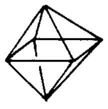
^{13}C NMR of 2. The limiting low-temperature ^{13}C NMR spectrum of **2**, $CpWOs_3(*CO)_9(\mu_3\text{-}*CTol)_2H$ (see Figure 7), was obtained at -95 °C in CD_2Cl_2 and is consistent with the X-ray structure determination. This spectrum shows six sets of resonances with relative intensities of 2:2:2:1:2:2 at δ 268.1, 185.5, 179.6, 175.7, 172.6, and 172.3. The most downfield signal at 268.1 with an intensity of 2 is assigned to the two alkylidyne carbon atoms, based on its chemical shift and ^{183}W satellites ($^1J_{WC}$ = 106 Hz).

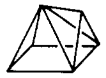
Increasing the temperature from -95 to -50 °C causes the three resonances at δ 185.5, 179.6, and 172.3 to broaden and coalesce (see Figure 7). These are assigned to the six carbonyls (a, b, and c pairs) on the Os(2) and Os(3) centers. Finally, in the temperature range of -50 to +20 °C, the remaining resonances at δ 175.7 (e) and 172.6 (d) with an intensity ratio of 1:2 show similar line broadening and coalescence. The temperature dependence of this spectrum may be understood in terms of carbonyl scrambling involving localized threefold exchange at each osmium center. It is apparent that the activation barriers for localized carbonyl exchange are in the order of Os(2) = Os(3) < Os(1). This order of energy barriers for the carbonyl-scrambling process contrasts with that proposed for isostructural $Os_6(CO)_{18}$, i.e., that an 8-coordinate $Os(CO)_3$ center undergoes exchange at a lower temperature than a 7-coordinate $Os(CO)_3$ center.[22] However, in the case of **2** the 7-coordinate centers may actually be more distorted, as evidenced by the conformational changes seen in comparing the solid-state structures of molecules A and B, and therefore may be able to undergo a threefold rotation more easily than the nominally 8-coordinate but sterically less encumbered $Os(CO)_3$ center.

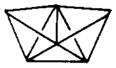
Discussion

Compounds **1** and **2** are, to our knowledge, the first tetrametallic dialkylidyne complexes known. Stone[23] has shown how the isolobal analogy of $CpW(CO)_2(CTol)$ with an alkyne leads to a widely useful synthesis of heteronuclear trimetallic alkylidyne complexes. In addition, the homonuclear trimetallic dialkylidyne complexes $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$,[24a] $(\eta^5\text{-}C_5Me_5)_3Rh_3(\mu_3\text{-}CH)_2$,[24b] $(\eta^5\text{-}C_5Me_5)_3Co_3(\mu_3\text{-}CMe)_2$,[24c] and $Cp_3M_3(CR)_3$ (M = Co, Rh, Ir)[25] have been reported. The last species are formed by splitting the corresponding alkyne, and in related work we have shown that an alkyne complex isomer of **1**, i.e., $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol)_2H$, also rearranges to **2** after CO loss.[4]

Such polymetallic alkylidyne complexes may be considered as metal-carbon clusters, i.e., incorporating both metal and carbon atoms into a polyhedral skeleton, analogous to metal-boron clusters. Compound **1** formally contains seven skeletal electron pairs for the six skeletal atoms, and therefore an octahedral (closo) structure (see III) is predicted by the Wade-Mingos rules.[26] Compound **1**, however, actually adopts a capped square pyramid (nido) structure (see IV), where one alkylidyne carbon atom caps a triangular face of the square pyramid defined by the remaining WOs_3C skeletal atoms. It is noteworthy that $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)H$[4] also adopts structure IV (with an Os_2C_2 square base and a W cap) instead of structure III. An analogous capped-square-pyramid structure is observed for $H_2Os_6(CO)_{18}$,[27] which also contains seven skeletal electron pairs. In contrast, other isoelectronic six-atom species such as $HOs_6(CO)_{18}^-$[28] and $Os_6(CO)_{18}^{2-}$[29] have the expected closo-octahedral structure. Compound **2** has only six skeletal electron pairs for six skeletal atoms. The only previous example of this situation is $Os_6(CO)_{18}$,[30] and both


III


IV


V

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compounds adopt the same geometry, i.e., a capped trigonal bipyramid (see V). Thus, the rearrangement of the WOs_3C_2 framework in the conversion of **1** into **2** is related formally to the rearrangement in the Os_6 framework for the overall two-electron change of $H_2Os_6(CO)_{18}$ into $Os_6(CO)_{18}$.

As detailed herein, evidence has been obtained for a degenerate framework rearrangement in **1**, which involves metal–metal bond cleavage in concert with hydridge migration and leads to interconversion of the two possible enantiomers. This process can also be viewed as a rearrangement that interchanges the capping atom with a basal atom in the WOs_3C_2 capped-square-pyramidal skeleton. The participation of a cluster framework in fluxional processes is a relatively rare phenomenon;[31] however, certain instances have been reported recently. For example, the layered compounds $[Pt_3(CO)_6]_n^{2-}$ (n = 2–4)[32] show intramolecular rotation of the Pt_3 triangles about the stacking axis, $[Rh_9P(CO)_{21}]^{2-}$ [33] apparently undergoes a $C_{4v} \leftrightarrow D_{3h}$ polyhedral rearrangement, and $H_2FeRuOs_2(CO)_{13}$[34] exhibits metal atom framework movement coupled with hydrogen migration.

An especially interesting aspect of **2** is the presence of a terminal hydride ligand associated with the tungsten atom. This ligand was located directly from the crystallographic analysis for molecule B. Although there have been several metal carbonyl cluster compounds with terminal hydride ligands in the literature,[17,18,35] only in one other case, $(H)(\mu\text{-}H)Os_3(CO)_{10}(PPh_3)$,[18] was a terminal hydride ligand successfully located directly by X-ray methods. The ^1H NMR chemical shifts of terminal hydride ligands are generally found at lower field than those of corresponding bridging hydride ligands,[36] but the exceptionally low-field position (*downfield* of $SiMe_4$) of the hydride signal for **2** is unique for a cluster compound. Several mononuclear tungsten(VI) hydride compounds display signals in this low-field region.[37] Given the electronegativity difference between tungsten and osmium, it is not unreasonable to assign the pair of electrons in a normal W–Os σ bond totally to the osmium atom, as for a W–C or W–H σ bond. In this way the tungsten atom in **2** is viewed as bonded to six anionic ligands ($C_5H_5^-$, H^-, 2 C^-, 2 Os^-) and a neutral donor osmium center (Os(1)), i.e., its formal oxidation state is VI. Although this analysis is clearly just a formalism, its message is consistent with the structural evidence for **2**, i.e., that the tungsten center is significantly more electron poor than the osmium centers are.

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Supplementary Material Available: Tables of calculated hydrogen atom positions for **1** (Table II-B), anisotropic thermal parameters for **1** and **2** (Tables III and V), and observed and calculated structure factors for **1** and **2** (50 pages). Ordering information is given on any current masthead page.

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Structural Investigations on Solid Tetraphosphorus Hexaoxide

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Single crystals of P_4O_6 have been grown from the melt. By X-ray diffraction at –5 ± 1 °C the space group ($P2_1/m$), the unit cell (a = 642.2 (1) pm, b = 787.7 (2) pm, c = 678.6 (3) pm, β = 106.1 (1)°, $V = 329.8 \times 10^6$ pm^3, d_{calcd} = 2.215 g cm^{-3}, Z = 2, M_r = 219.89), and the crystal and molecular structure have been determined. As compared to those in gaseous P_4O_6, the bonding angles remain almost unchanged, while—obviously because of crystal forces—the molecule as a whole is expanded; $\bar{d}$(P–O) = 165.3 pm (solid) and 163.8 pm (gas). With respect to the globular shape of P_4O_6, the molecular packing is unexpected: rods extending along [100] are formed by aligning P_4O_6 molecules with protrusions of one unit fitting into the hollows of the next. Between the liquid and solid states, no plastically crystalline phase was detected. At –45 ± 4 °C a structural phase transition of probably higher order to a triclinic low-temperature modification occurs.

Introduction

The phosphorus oxides P_4O_{6+n} (n = 0–4) and their derivatives seem ideally suited for comparative studies on chemical bonding within the cage molecules[1] as well as on the packing of the similarly shaped units in the crystalline state.[2] These studies have been hampered by incomplete or insufficient reliable structural information. The problems with crystal structure determinations on this type of compound arise from a strong tendency to disorder[1a] or from formation of solid solutions ($P_4O_{7.9}$[3] = $0.1P_4O_7 + 0.9P_4O_8$). Recently the

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