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X-ray Structural Study of $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$. An Unusual Example of Two Isomers of a Complex in an Ordered Single Crystal

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The trinuclear heterometallic cluster complex $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$, synthesized from $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4Me$, has been subjected to a full three-dimensional X-ray structural analysis. The complex crystallizes in the polar (noncentrosymmetric) monoclinic space group $P2_1$ (C_2^2; No. 4) with $a = 10.242$ (3) Å, $b = 18.163$ (4) Å, $c = 16.607$ (4) Å, $\beta = 101.22$ (2)°, $V = 3030$ (1) Å^3, and ρ(calcd) = 2.39 g cm^{-3} for $Z = 4$ and mol wt 1090.25. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer using Mo Kα radiation, and the structure was refined to $R_F = 3.7\%$ and $R_{wF} = 3.6\%$ for all 4136 independent reflections with $3.5° < 2\theta < 45.0°$ (*none rejected*). There are two distinct molecules in the crystallographic asymmetric unit, and these have different connectivities; in particular, they are related by a $2\pi/3$ radian rotation of a triply bridging di-*p*-tolylacetylene ligand above the triangular W$_2$Os face. Molecule A (termed the "symmetrical isomer") has an η^2 acetylene–Os linkage in conjunction with two η^1 acetylene–W linkages. Relevant bonding distances (Å) in molecule A include C(18)–C(19) (the "acetylenic" linkage) = 1.463 (28), C(18)–Os = 2.229 (19), C(19)–Os = 2.268 (19), C(18)–W(1) = 2.187 (18), C(19)–W(2) = 2.180 (20), W(1)–W(2) = 3.158 (1), W(1)–Os = 2.857 (1), and W(2)–Os = 2.836 (1). Molecule B (the unsymmetrical isomer) has an η^2 acetylene–W(2) linkage along with η^1 acetylene–Os and η^1 acetylene–W(1) linkages. Bonding distances (Å) in molecule B include C(18)–C(19) = 1.424 (29), C(18)–W(1) = 2.202 (18), C(18)–W(2) = 2.284 (21), C(19)–W(2) = 2.365 (19), C(19)–Os = 2.090 (21), W(1)–W(2) = 3.016 (1), W(1)–Os = 2.987 (1), and W(2)–Os = 2.871 (1). It is suggested that the observed molecular configurations of molecule A and B correspond to the potential minima for the fluxional behavior of the molecule in solution.

Introduction

The so-called "isolobal relationship"[1] between alkynes (RC≡CR′) and metal carbyne complexes ($L_nM{\equiv}CR$) has previously led Stone and co-workers to examine the reactions of low oxidation state compounds with metal carbynes.[2]

Shapley and co-workers[3] have recently studied the reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4Me$ under very mild conditions. The major product of this reaction if $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7(CC_6H_4Me)_2$, the crystal structure of which is reported below. The complex apparently is formed as shown in eq 1.

$$(\mu\text{-}H)_2Os_3(CO)_{10} + 2(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CC_6H_4Me + CO \rightarrow (\mu\text{-}H)_2Os_2(CO)_8 + (\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7(CC_6H_4Me)_2 \quad (1)$$

Experimental Section

An opaque dark red crystal of approximate size 0.18 × 0.20 × 0.35 mm was mounted and aligned on our Syntex P2$_1$ diffractometer, and data were collected as described previously[4] (see Table I). All data were converted to $|F_o|$ values, following correction for absorption and for Lorentz and polarization factors. Any reflection with I(net) < 0 was assigned a value of $|F_o| = 0$. No data were rejected.

During subsequent calculations the analytical forms for neutral atoms were corrected for both the $\Delta f'$ and $i\Delta f''$ terms of anomalous dispersion.[5] The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = [(\sigma(|F_o|))^2 + 0.015|F_o|^2]^{-1}$. All calculations were performed with the SUNY-Buffalo modified Syntex XTL system.

Table I. Experimental Data for the X-ray Diffraction Study of $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$

(A) Crystal Parameters at 24 °C[a]

crystal system: monoclinic

space group: $P2_1$ (C_2^2; No. 4)	$V = 3030.1$ (13) Å^3
$a = 10.242$ (3) Å	$Z = 4$
$b = 18.163$ (4) Å	mol wt = 1090.25
$c = 16.607$ (4) Å	ρ(calcd) = 2.39 g cm^{-3}
$\beta = 101.22$ (2)°	μ(Mo Kα) = 124.9 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.: $h,k,\pm l$
2θ range: 3.5–45.0°
scan width: $[2\theta(K\alpha_1) - 0.9]°$ to $[2\theta(K\alpha_2) + 0.9]°$
scan speed: 3.0°/min (in 2θ)
bkgd measment: stationary crystal and counter at beginning and end of 2θ scan, each for half of the scan time
reflctns collected: 4551 total, merged to 4136 independent reflections
data averaging $R(I)$: 1.69% for 268 pairs
std reflctns: three measured after each 97 reflections (008, 0,10,0, 600); no decay was observed over the period of data collection

[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°.

The structure was solved with the program MULTAN[6] and difference-Fourier syntheses. Refinement led smoothly to convergence with $R_F = 3.7\%$, $R_{wF} = 3.6\%$, and GOF = 1.449 for 464 parameters refined against all 4136 reflections.[7] ($P2_1$ is a polar space group; refinement with inverted coordinates led to the increased residuals $R_F = 4.0\%$, $R_{wF} = 3.9\%$, and GOF = 1.569. Our initial model therefore defines the correct crystal chirality.) A final difference-Fourier map was "clean" so the structure is complete. Positional parameters are collected in Table II.

Results and Discussion

The crystal consists of discrete molecules of $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7(\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me)$ which are separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. There are two

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

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Table II. Final Positional Parameters for $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$

atom	*x*	*y*	*z*	B_{iso}, Å²	atom	*x*	*y*	*z*	B_{iso}, Å²
		Molecule A					Molecule B		
W(1A)	−0.01455 (7)	−0.25000 (0)	−0.81593 (5)		W(1B)	0.42018 (8)	−0.23494 (7)	−0.42564 (5)	
W(2A)	−0.32588 (7)	−0.24529 (7)	−0.87919 (4)		W(2B)	0.60862 (8)	−0.35218 (6)	−0.46250 (5)	
Os(A)	−0.17501 (8)	−0.12256 (7)	−0.80805 (5)		Os(B)	0.49057 (7)	−0.36779 (6)	−0.32014 (4)	
O(1A)	0.2162 (17)	−0.1455 (10)	−0.7358 (11)		O(1B)	0.1741 (17)	−0.3373 (11)	−0.4942 (13)	
O(2A)	−0.0388 (16)	−0.2555 (12)	−0.6306 (9)		O(2B)	0.3318 (18)	−0.2238 (9)	−0.2597 (11)	
O(3A)	−0.2586 (14)	−0.3476 (9)	−1.0152 (8)		O(3B)	0.4451 (17)	−0.2848 (10)	−0.6215 (9)	
O(4A)	−0.2368 (14)	−0.3727 (9)	−0.7573 (9)		O(4B)	0.3869 (17)	−0.4707 (9)	−0.4914 (11)	
O(5A)	−0.2947 (17)	−0.1546 (12)	−0.6569 (9)		O(5B)	0.5002 (15)	−0.3308 (9)	−0.1421 (9)	
O(6A)	−0.3916 (18)	−0.0080 (10)	−0.8619 (11)		O(6B)	0.2176 (15)	−0.4408 (10)	−0.3448 (13)	
O(7A)	0.0314 (18)	−0.0118 (12)	−0.7221 (12)		O(7B)	0.6148 (20)	−0.5182 (9)	−0.2803 (14)	
C(1A)	0.1225 (27)	−0.1786 (15)	−0.7648 (16)	4.8 (6)	C(1B)	0.2699 (28)	−0.3074 (15)	−0.4705 (16)	4.7 (5)
C(2A)	−0.0374 (19)	−0.2509 (13)	−0.7005 (12)	3.2 (4)	C(2B)	0.3723 (21)	−0.2398 (15)	−0.3205 (13)	4.0 (4)
C(3A)	−0.2767 (21)	−0.3090 (12)	−0.9611 (13)	3.0 (4)	C(3B)	0.4979 (23)	−0.3027 (13)	−0.5596 (15)	3.8 (5)
C(4A)	−0.2543 (21)	−0.3188 (12)	−0.8018 (13)	3.2 (4)	C(4B)	0.4593 (23)	−0.4248 (13)	−0.4722 (14)	3.7 (5)
C(5A)	−0.2470 (25)	−0.1420 (14)	−0.7144 (15)	4.6 (5)	C(5B)	0.4966 (19)	−0.3420 (11)	−0.2112 (12)	2.7 (4)
C(6A)	−0.3009 (24)	−0.0489 (13)	−0.8413 (14)	4.1 (5)	C(6B)	0.3128 (22)	−0.4131 (12)	−0.3379 (13)	3.0 (4)
C(7A)	−0.0417 (26)	−0.0517 (15)	−0.7584 (15)	4.8 (5)	C(7B)	0.5685 (19)	−0.4582 (11)	−0.2970 (11)	2.4 (4)
C(8A)	0.0397 (22)	−0.3194 (12)	−0.9209 (13)	3.6 (4)	C(8B)	0.4665 (23)	−0.1089 (14)	−0.4387 (14)	4.4 (5)
C(9A)	−0.0099 (23)	−0.3733 (14)	−0.8686 (14)	4.2 (5)	C(9B)	0.3579 (25)	−0.1157 (15)	−0.4026 (15)	5.0 (5)
C(10A)	0.0641 (25)	−0.3716 (15)	−0.7922 (15)	5.1 (5)	C(10B)	0.2491 (28)	−0.1504 (15)	−0.4631 (17)	5.6 (6)
C(11A)	0.1750 (24)	−0.3219 (13)	−0.7922 (14)	4.0 (5)	C(11B)	0.3042 (27)	−0.1665 (15)	−0.5363 (16)	5.3 (6)
C(12A)	0.1624 (22)	−0.2904 (12)	−0.8726 (13)	3.6 (5)	C(12B)	0.4415 (29)	−0.1412 (17)	−0.5201 (18)	6.4 (7)
C(13A)	−0.5290 (23)	−0.3033 (13)	−0.8942 (14)	3.9 (5)	C(13B)	0.6756 (22)	−0.4264 (12)	−0.5599 (14)	3.6 (5)
C(14A)	−0.5122 (20)	−0.2623 (11)	−0.8165 (12)	3.0 (4)	C(14B)	0.7161 (24)	−0.4590 (14)	−0.4806 (15)	4.5 (5)
C(15A)	−0.5154 (22)	−0.1872 (12)	−0.8370 (13)	3.3 (4)	C(15B)	0.8176 (21)	−0.4106 (11)	−0.4313 (12)	2.9 (4)
C(16A)	−0.5325 (22)	−0.1854 (12)	−0.9287 (13)	3.4 (4)	C(16B)	0.8327 (20)	−0.3496 (12)	−0.4840 (12)	3.1 (4)
C(17A)	−0.5401 (20)	−0.2572 (12)	−0.9622 (12)	3.4 (4)	C(17B)	0.7489 (21)	−0.3600 (14)	−0.5583 (13)	3.9 (4)
C(18A)	−0.0759 (18)	−0.1638 (10)	−0.9074 (11)		C(18B)	0.6354 (17)	−0.2499 (12)	−0.3809 (11)	
C(19A)	−0.2196 (21)	−0.1645 (10)	−0.9392 (12)		C(19B)	0.6652 (20)	−0.3101 (11)	−0.3254 (11)	
C(20A)	−0.2752 (19)	−0.1184 (12)	−1.0129 (11)	2.6 (4)	C(20B)	0.8000 (18)	−0.3211 (10)	−0.2716 (11)	1.92 (34)
C(21A)	−0.3550 (19)	−0.1519 (10)	−1.0824 (11)	2.5 (4)	C(21B)	0.8113 (19)	−0.3612 (12)	−0.1974 (11)	3.1 (4)
C(22A)	−0.4029 (22)	−0.1097 (13)	−1.1531 (13)	3.8 (4)	C(22B)	0.9371 (19)	−0.3716 (11)	−0.1432 (11)	2.6 (4)
C(23A)	−0.3716 (21)	−0.0368 (12)	−1.1564 (13)	3.3 (4)	C(23B)	1.0496 (20)	−0.3408 (11)	−0.1634 (12)	2.9 (4)
C(24A)	−0.2865 (21)	−0.0035 (12)	−1.0874 (12)	3.3 (4)	C(24B)	1.0424 (20)	−0.3006 (11)	−0.2351 (12)	3.0 (4)
C(25A)	−0.2405 (20)	−0.0437 (11)	−1.0171 (12)	3.0 (4)	C(25B)	0.9173 (20)	−0.2930 (11)	−0.2911 (12)	2.9 (4)
C(26A)	−0.4258 (24)	0.0103 (13)	−1.2332 (14)	4.2 (5)	C(26B)	1.1858 (22)	−0.3512 (13)	−0.1018 (13)	4.0 (5)
C(27A)	0.0165 (18)	−0.1316 (11)	−0.9559 (11)	2.3 (4)	C(27B)	0.7301 (18)	−0.1851 (10)	−0.3877 (10)	1.89 (33)
C(28A)	0.1046 (23)	−0.0734 (13)	−0.9230 (14)	4.0 (5)	C(28B)	0.7723 (19)	−0.1675 (10)	−0.4595 (11)	2.5 (4)
C(29A)	0.1970 (25)	−0.0467 (14)	−0.9709 (15)	4.9 (6)	C(29B)	0.8606 (21)	−0.1066 (12)	−0.4612 (13)	3.5 (4)
C(30A)	0.1935 (24)	−0.0717 (13)	−1.0509 (14)	4.2 (5)	C(30B)	0.9053 (22)	−0.0665 (12)	−0.3907 (13)	3.5 (4)
C(31A)	0.1112 (24)	−0.1265 (14)	−1.0798 (14)	4.6 (5)	C(31B)	0.8634 (23)	−0.0839 (13)	−0.3182 (14)	4.0 (5)
C(32A)	0.0124 (23)	−0.1590 (13)	−1.0368 (14)	3.8 (5)	C(32B)	0.7796 (21)	−0.1445 (11)	−0.3161 (12)	3.2 (4)
C(33A)	0.2904 (30)	−0.0399 (17)	−1.1020 (18)	6.6 (7)	C(33B)	0.9970 (25)	−0.0021 (15)	−0.3955 (15)	4.9 (5)

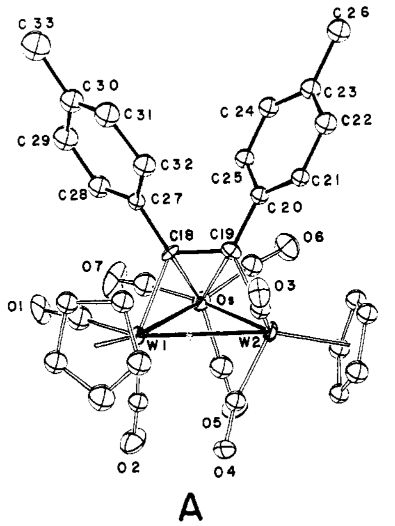


Figure 1. Labeling of atoms in molecule A, the symmetrical isomer of $(\eta\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$.

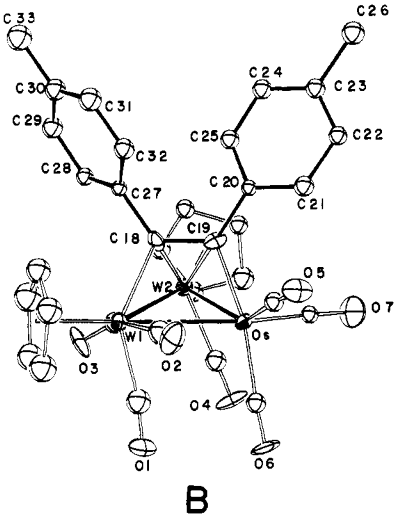


Figure 2. Labeling of atoms in molecule B, the unsymmetrical isomer of $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$. The di-*p*-tolylacetylene ligand is shown in the same orientation as in Figure 1. Note that C(3)–O(3) is bonded primarily to W(2).

molecules in the crystallographic asymmetric unit, and these are two isomers interrelated principally by rotation of the μ_3-(di-*p*-tolylacetylene) ligand above the triangular W_2Os plane. Molecule A (hereafter termed the "symmetrical" isomer) is shown in Figure 1, while molecule B (the "unsymmerical" isomer) is pictured in Figures 2 and 3. Detailed views of the μ^3-acetylene to metal interactions are illustrated in Figures 4 and 5. Interatomic distances and angles are collected in Tables III and IV.

Table III. Interatomic Distances (Å) and Esd's for $(\eta^5\text{-}C_5H_5)_2W_2Os(CO)_7[\mu_3\text{-}MeC_6H_4C{\equiv}CC_6H_4Me]$

	molecule A ("sym")	molecule B (unsym)
(A) Metal-Metal Distances		
Os-W(1)	2.857 (1)	2.987 (1)
Os-W(2)	2.836 (1)	2.871 (1)
W(1)-W(2)	3.158 (1)	3.016 (1)
(B) Metal-Carbonyl Distances		
W(1)-C(1)	1.977 (27)	2.052 (28)
W(1)-C(2)	1.976 (20)	1.906 (22)
W(2)-C(3)	1.927 (21)	1.996 (24)
W(2)-C(4)	1.899 (22)	2.002 (24)
Os-C(5)	1.880 (25)	1.857 (19)
Os-C(6)	1.865 (25)	1.967 (23)
Os-C(7)	1.939 (27)	1.833 (20)
(C) Metal-(Bridging Acetylene) Ligand Distances		
W(1)-C(18)	2.187 (18)	2.202 (18)
W(1)-C(19)	3.056 (20)	3.050 (20)
W(2)-C(18)	3.071 (19)	2.284 (21)
W(2)-C(19)	2.180 (20)	2.365 (19)
Os-C(18)	2.229 (19)	2.896 (21)
Os-C(19)	2.268 (19)	2.090 (21)
Os(A)· · ·Pi(A)[a]	2.126	
W(2B)· · ·Pi(B)[a]		2.213
(D) Metal-η^5-C_5H_5 Ligand Distances		
W(1)-Cp(1)[b]	1.999	1.988
W(1)-C(8)	2.305 (22)	2.356 (25)
W(1)-C(9)	2.409 (25)	2.311 (27)
W(1)-C(10)	2.358 (28)	2.322 (29)
W(1)-C(11)	2.309 (24)	2.342 (27)
W(1)-C(12)	2.318 (22)	2.354 (30)
W(2)-Cp(2)[b]	2.028	1.996
W(2)-C(13)	2.302 (24)	2.309 (23)
W(2)-C(14)	2.366 (21)	2.279 (25)
W(2)-C(15)	2.429 (22)	2.354 (21)
W(2)-C(16)	2.380 (22)	2.390 (21)
W(2)-C(17)	2.363 (21)	2.346 (22)
(E) Distances within the η^5-C_5H_5 Ligands		
C(8)-C(9)	1.465 (33)	1.368 (35)
C(9)-C(10)	1.346 (33)	1.487 (38)
C(10)-C(11)	1.450 (36)	1.467 (39)
C(11)-C(12)	1.436 (32)	1.454 (41)
C(12)-C(8)	1.452 (32)	1.449 (37)
C(13)-C(14)	1.472 (30)	1.429 (33)
C(14)-C(15)	1.405 (30)	1.481 (33)
C(15)-C(16)	1.499 (30)	1.438 (29)
C(16)-C(17)	1.415 (31)	1.372 (29)
C(17)-C(13)	1.392 (31)	1.418 (33)
(F) Carbon-Oxygen Distances		
C(1)-O(1)	1.155 (33)	1.123 (34)
C(2)-O(2)	1.166 (25)	1.198 (28)
C(3)-O(3)	1.181 (26)	1.113 (28)
C(4)-O(4)	1.219 (27)	1.120 (29)
C(5)-O(5)	1.175 (30)	1.159 (24)
C(6)-O(6)	1.186 (31)	1.083 (28)
C(7)-O(7)	1.128 (33)	1.200 (27)
(G) Distances within the $CH_3C_6H_4C{\equiv}CC_6H_4CH_3$ Ligand		
C(18)-C(19)	1.463 (28)	1.424 (29)
C(19)-C(20)	1.501 (28)	1.505 (27)
C(20)-C(21)	1.414 (27)	1.417 (26)
C(21)-C(22)	1.408 (29)	1.434 (27)
C(22)-C(23)	1.367 (32)	1.380 (28)
C(23)-C(24)	1.432 (30)	1.387 (28)
C(23)-C(26)	1.546 (32)	1.572 (30)
C(24)-C(25)	1.379 (29)	1.436 (29)
C(25)-C(20)	1.408 (30)	1.400 (28)
C(18)-C(27)	1.477 (26)	1.543 (27)
C(27)-C(28)	1.428 (30)	1.383 (25)
C(28)-C(29)	1.435 (35)	1.432 (29)
C(29)-C(30)	1.398 (34)	1.379 (30)
C(30)-C(31)	1.332 (35)	1.392 (31)
C(30)-C(33)	1.538 (39)	1.512 (35)
C(31)-C(32)	1.470 (34)	1.398 (32)
C(32)-C(27)	1.425 (28)	1.408 (27)
(H) Possible Metal-"Semibridging" Carbonyl Distances		
W(1)· · ·C(3)		2.791 (24)
W(1)· · ·C(4)	2.805 (22)	
Os· · ·C(1)	3.160 (28)	
Os· · ·C(2)	3.103 (22)	2.621 (26)
Os· · ·C(4)		2.689 (23)

[a] Pi(A) and Pi(B) are the centroids of the acetylenic bonds [C(18)≡C(19)] for molecule A and B, respectively. [b] Cp(1) is the centroid of the C(8)→C(12) cyclopentadienyl system; Cp(2) is the centroid of the C(13)→C(17) cyclopentadienyl ring.

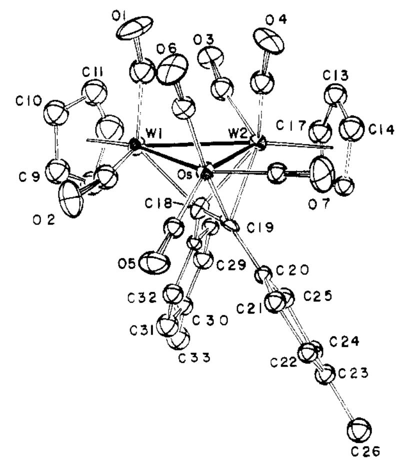


Figure 3. Another view of molecule B, showing the bending of the semibridging carbonyl ligands C(2)–O(2), C(3)–O(3), and C(4)–O(4). (N.B.: This diagram corresponds to the opposite handedness to that determined for the crystal studied.)

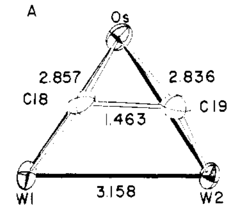


Figure 4. Bond lengths for the $W_2Os[\mu_3\text{-}C(18)\text{-}C(19)]$ portion of the symmetrical molecule A.

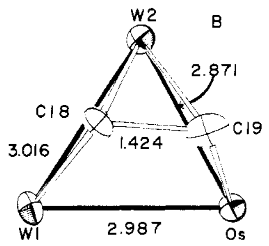


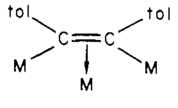
Figure 5. Bond lengths for the $W_2Os[\mu_3\text{-}C(18)\text{-}C(19)]$ portion of the unsymmetrical molecule B.

The Symmetrical Molecule (A). Although each of the molecules belongs to point group C_1, molecule A is referred to as the symmetrical isomer because the acetylenic ligand (formed by dimerization of $\equiv CC_6H_4Me$ fragments) bridges the two tungsten atoms and has a η^2-linkage to the osmium atom. In this molecule the W(1)–W(2) bond is 3.158 (1) Å in length while the osmium–tungsten distances are fairly similar to each other with Os–W(1) = 2.857 (1) Å and Os–W(2) = 2.836 (1) Å. Each of these bond lengths is affected

Table IV. Selected Interatomic Angles (Deg) and Esd's

	molecule A	molecule B
(A) Intermetallic Angles		
W(1)–Os–W(2)	67.39 (3)	61.93 (3)
Os–W(1)–W(2)	55.99 (3)	57.15 (3)
W(1)–W(2)–Os	56.62 (3)	60.92 (3)
(B) M–M–CO and M–M–Cp Angles		
Os–W(1)–C(1)	79.4 (8)	76.9 (8)
Os–W(1)–C(2)	77.6 (6)	60.0 (7)
Os–W(1)–Cp(1)	166.8	166.7
W(2)–W(1)–C(1)	135.4 (8)	86.4 (8)
W(2)–W(1)–C(2)	91.2 (6)	116.2 (7)
W(2)–W(1)–Cp(1)	118.1	134.8
Os–W(2)–C(3)	124.8 (6)	116.5 (7)
Os–W(2)–C(4)	99.4 (7)	64.1 (7)
Os–W(2)–Cp(2)	116.5	134.9
W(1)–W(2)–C(3)	80.4 (6)	63.9 (7)
W(1)–W(2)–C(4)	61.6 (7)	88.4 (7)
W(1)–W(2)–Cp(2)	164.8	161.0
W(1)–Os–C(5)	102.0 (8)	109.0 (6)
W(2)–Os–C(5)	85.8 (8)	146.9 (6)
W(1)–Os–C(6)	159.8 (8)	98.0 (6)
W(2)–Os–C(6)	98.7 (8)	116.3 (6)
W(1)–Os–C(7)	101.2 (8)	153.2 (6)
W(2)–Os–C(7)	168.5 (8)	91.5 (6)
(C) Metal–Carbon–Oxygen Angles		
W(1)–C(1)–O(1)	169.5 (23)	168.4 (24)
W(1)–C(2)–O(2)	173.0 (19)	162.3 (20)
W(2)–C(3)–O(3)	173.8 (18)	167.3 (21)
W(2)–C(4)–O(4)	165.2 (18)	165.0 (21)
Os–C(5)–O(5)	178.5 (22)	175.6 (18)
Os–C(6)–O(6)	172.5 (21)	176.2 (20)
Os–C(7)–O(7)	172.8 (24)	177.2 (18)
(D) M–C–M, M–M–C, and M–C–C Angles Involving the C(18)–C(19) System		
W(1)–C(18)–Os	80.6 (6)	
C(18)–W(1)–Os	50.3 (5)	
W(1)–Os–C(18)	49.1 (5)	
W(2)–C(19)–Os	79.2 (6)	80.0 (7)
C(19)–W(2)–Os	51.8 (5)	45.8 (5)
W(2)–Os–C(19)	49.0 (5)	54.2 (6)
W(1)–C(18)–C(19)	112.2 (13)	112.8 (14)
C(19)–C(18)–W(2)		75.3 (11)
W(2)–C(19)–C(18)	113.4 (13)	69.1 (11)
W(1)–C(18)–W(2)		84.5 (7)
C(18)–W(2)–W(1)		46.6 (5)
W(2)–W(1)–C(18)	67.3 (5)	48.9 (5)
C(19)–W(2)–W(1)	66.9 (5)	67.8 (5)
C(18)–C(19)–Os	69.6 (11)	109.6 (14)
C(19)–C(18)–Os	72.5 (10)	
C(18)–Os–C(19)	37.9 (7)	
C(18)–W(2)–C(19)		35.6 (7)
(E) Other Angles at the "Acetylenic" Carbon Atoms		
C(18)–C(19)–C(20)	119.0 (17)	122.9 (17)
C(19)–C(18)–C(27)	120.9 (16)	125.0 (17)
W(1)–C(18)–C(27)	122.2 (13)	118.9 (13)
Os–C(18)–C(27)	134.7 (13)	
Os–C(19)–C(20)	124.7 (14)	127.1 (14)
W(2)–C(19)–C(20)	127.2 (14)	123.6 (13)
W(2)–C(18)–C(27)		125.6 (13)
(F) Other Angles within the $MeC_6H_4C{\equiv}CC_6H_4Me$ Ligand		
C(19)–C(20)–C(21)	119.5 (17)	119.6 (16)
C(20)–C(21)–C(22)	119.9 (18)	121.6 (18)
C(21)–C(22)–C(23)	120.9 (20)	119.0 (18)
C(22)–C(23)–C(26)	121.3 (20)	118.1 (17)
C(26)–C(23)–C(24)	119.5 (19)	120.9 (18)
C(22)–C(23)–C(24)	119.2 (20)	121.0 (18)
C(23)–C(24)–C(25)	120.6 (19)	119.9 (18)
C(24)–C(25)–C(20)	120.2 (19)	120.9 (18)
C(25)–C(20)–C(21)	119.0 (18)	117.4 (17)
C(25)–C(20)–C(19)	121.2 (18)	122.9 (17)
C(18)–C(27)–C(28)	120.5 (17)	123.0 (16)
C(27)–C(28)–C(29)	118.3 (20)	119.9 (18)
C(28)–C(29)–C(30)	121.3 (23)	119.9 (19)
C(29)–C(30)–C(33)	120.1 (22)	118.2 (20)
C(33)–C(30)–C(31)	120.9 (23)	121.4 (20)
C(29)–C(30)–C(31)	118.8 (23)	120.4 (20)
C(30)–C(31)–C(32)	124.9 (23)	119.7 (21)
C(31)–C(32)–C(27)	114.8 (20)	120.8 (19)
C(32)–C(27)–C(28)	121.3 (18)	119.1 (17)
C(32)–C(27)–C(18)	118.1 (17)	117.8 (16)
(G) Angles within the η^5-Cyclopentadienyl Ligands		
C(8)–C(9)–C(10)	110.3 (21)	108.0 (22)
C(9)–C(10)–C(11)	108.2 (22)	106.6 (23)
C(10)–C(11)–C(12)	108.7 (21)	107.3 (24)
C(11)–C(12)–C(8)	106.3 (19)	106.8 (24)
C(12)–C(8)–C(9)	106.2 (19)	111.2 (23)
C(13)–C(14)–C(15)	106.6 (18)	108.0 (20)
C(14)–C(15)–C(16)	105.1 (18)	105.5 (18)
C(15)–C(16)–C(17)	111.4 (19)	108.7 (18)
C(16)–C(17)–C(13)	104.3 (19)	111.7 (20)
C(17)–C(13)–C(14)	112.6 (19)	106.1 (20)

by the acetylenic ligand—the Os–W(1) bond is bridged by C(18), and Os–W(2) bond is bridged by C(19), and the W(1)–W(2) bond is bridged by the two atom system C(18)–C(19). The normal unperturbed Os–Os distance in a triangular arrangement is 2.877 [3] Å (from $Os_3(CO)_{12}$),[8] but we have no good estimate for a W–W distance in such a system. [The W–W bond length in $(\eta^5\text{-}C_5H_5)(CO)_3WW(CO)_3(\eta^5\text{-}C_5H_5)$, a *dinuclear* species, is 3.222 (1) Å.[9–13]] The W–CO distances in this isomer range from 1.899 (22) Å through 1.977 (27) Å and are, on average, longer than the Os–CO distances (range 1.865 (25)–1.939 (27) Å). In molecule A each metal atom is associated formally with 18 outer-valence electrons. The d^8 Os(0) atom receives two electrons from each of three terminal carbonyl groups, two electrons from the η^2-acetylenic ligand, and one electron from each tungsten atom; the d^6 W(0) atoms each receive five electrons from the $\eta^5\text{-}C_5H_5$ ring, two electrons from each of their two carbonyl groups, one electron from an η^1-acetylenic linkage, one electron from the other tungsten atom, and one electron from the osmium atom. As expected for a "saturated" triangular species, there are a total of 48 electrons associated with the cluster as a whole. The (terminal) W(1)–C(18) and W(2)–C(19) distances are equivalent [2.187 (18) and 2.180 (20) Å, respectively] and are slightly shorter than the Os–(η^2-acetylenic) distances [Os–C(18) = 2.229 (19), Os–C(19) = 2.268 (19) Å]. The C(18)–C(19) bond length of 1.463 (28) Å, coupled with the cis-bent geometry of the di-*p*-tolylacetylene" fragment, suggests that it is better regarded as a coordinated dimetalloolefin (**1**).



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

(9) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

(10) The W–W distance in $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$ is 2.991 (1) Å: Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D.; Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 7383.

(11) Os–W distances have been measured in *tetra*nuclear clusters. In $(\mu\text{-}H)_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$,[12] the Os–W distance is 2.880 (3) Å; in $(\mu\text{-}H)Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$[13] the non-hydrido-bridged Os–W distances are 2.909 (2), 2.915 (2), and 2.934 (2) Å. However, M–M distances in tetranuclear clusters are usually about 0.05–0.10 Å shorter than those in triangular clusters.

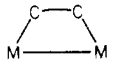
(12) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161.

(13) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, 18, 843.

The M–C–O bond angles in molecule A range from 165.2 (18) through 178.5 (22)°. The most distorted system [W(2)–C(4)–O(4) = 165.2 (18)°] is associated with a rather short contact with W(1) W(1)···C(4) = 2.805 (22) Å vis-à-vis W(2)–C(4) = 1.899 (22) Å). This W(2)–[C(4)–O(4)]···W(1) system *could* be viewed as containing a weakly "semibridging" carbonyl group;[14–16] even so, it clearly arises from steric crowding, rather than being required for electronic reorganization (cf. molecule B, below). The W(1)–C(1)–O(1) angle is 169.5 (23)°, while W(1)–C(2)–O(2) = 173.0 (19) Å; there are intramolecular contacts of Os···C(1) = 3.160 (28) Å and Os···C(2) = 3.103 (22) Å. These yield α values[15] of 0.598 and 0.570—i.e., they are of little significance energetically.

The Unsymmetrical Molecule (B). The acetylenic ligand in this molecule now spans the Os–W(1) linkage and is linked via an η^2-metal linkage to W(2). The Os–W(1) bond length is 2.987 (1) Å, i.e., some 0.116 Å longer than the C(19)-bridged Os–W(2) length of 2.871 (1) Å. The C(18)-bridged W(1)–W(2) bond is now 3.016 (1) Å in length—a value 0.142 Å shorter than the acetylene-bridged W(1)–W(2) bond in molecule A. Thus it appears that a

system of this type is associated with a M–M bond length some 0.12–0.14 Å shorter than is found in a system such as



In molecule B, the normal methods of electron counting (vide supra) lead to a 17-electron count for Os, an 18-electron count for W(1), and a 19-electron count for W(2). This gives rise to a number of geometric irregularities.

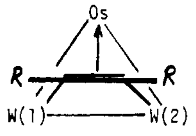
First, the metal–carbon distances involving the C(18)–C(19) system are no longer as regular as in molecule A. In molecule B the terminal Os–C(19) linkage of 2.090 (21) Å is significantly shorter than the other terminal linkage [W(1)–C(18) = 2.202 (18) Å], and the two W(2)–(η^3-acetylenic) linkages also appear to be inequivalent with W(2)–C(18) = 2.284 (21) Å and W(2)–C(19) = 2.365 (19) Å (difference = 0.081 ± 0.028 Å).

Second, there are a number of clear "semibridging" carbonyl interactions which help to redistribute electronic charge. The system W(2)–[C(4)–O(4)]···Os (∠W(2)–C(4)–O(4) = 165.0 (21)°, W(2)–C(4) = 2.002 (24) Å, Os···C(4) = 2.689 (23) Å, α = 0.343) shifts electronic charge from the electron-rich W(2) to the electron-poor Os atom. The system W(2)–[C(3)–O(3)]···W(1) (∠W(2)–C(3)–O(3) = 167.3 (21)°, W(2)–C(3) = 1.996 (24) Å, W(1)···C(3) = 2.791 (24) Å, α = 0.398) shifts electronic charge from electron-rich W(2) to neutral W(1). The system W(1)–[C(2)–O(2)]···Os (∠W(1)–C(2)–O(2) = 162.3 (20)°, W(1)–C(2) = 1.906 (22) Å, Os···C(2) = 2.621 (26) Å, α = 0.375°) shifts electronic charge from neutral W(1) to electron-poor Os. The overall effect is shift of charge from W(2) to Os via the two possible routes around the triangular cluster (i.e., direct W(2) → Os and indirect W(2) → W(1) → Os).

General Considerations

All other bond lengths and angles in the molecule are normal—e.g., W–C(η^5-C_5H_5) distances are compatible with those found in (η^5-C_5H_5)W(CO)$_3$Cl.[17]

The two isomers in the crystal describe the possible rotomers of μ^3-acetylenic bonding to a M_2M' system. Structure **2**



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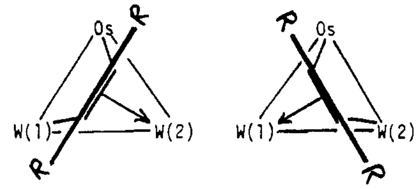

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corresponds to the symmetrical molecule A while structures **3** and **4** correspond to molecule B. (Actually **3** and **4** are mirror images of one another and simply depend upon the chirality of the crystal selected for the structural analysis; 50% of the crystals will contain **2** and **3** while the rest will contain **2** and **4**.)

The structures of molecules A and B therefore provide evidence that the observed fluxional behavior of the complex[3] is caused by rotation of a μ_3-acetylenic moiety on the triangular W_2Os face. The crystal structure provides the geometry for the potential minima in this process. Note that only minor movements of the carbonyl and cyclopentadienyl ligands are required.[18]

Acknowledgment. This work was supported by the National Science Foundation. We thank Professor J. R. Shapley for providing the crystals.

Registry No. *sym*-(η^5-C_5H_5)$_2$W$_2$Os(CO)$_7$[μ_3-MeC$_6$H$_4$C≡CC$_6$H$_4$Me], 79991-95-0; *unsym*-(η^5-C_5H_5)$_2$W$_2$Os(CO)$_7$[μ_3-MeC$_6$H$_4$C≡CC$_6$H$_4$Me], 80028-15-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, and least-squares planes (28 pages). Ordering information is given on any current masthead page.

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(14) "Semibridging" carbonyls have been the subject of a recent review article: Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

(15) The "α-value" for this system is 0.48. This falls toward the end of the semibridging regime (0.1 < α < 0.6) suggested by Curtis et al.[16]

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

(17) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197 and references contained therein.

(18) Preliminary results of an independent study of this structure have recently appeared and are consistent with our reported structure. See: Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101–1103.