no convincing evidence for the existence of metal complexes containing monodentate O-bonded *C*-nitroso ligands.

Acknowledgment. The procedure for obtaining a crystalline sample of this material was developed in large part by Dr. G. P. Khare in this laboratory.

Registry No. $\mathrm{CoCl_2(NODMA)_2}$ (N-bonded isomer), 21452-41-5; $\mathrm{CoCl_2(NODMA)_2}$ (O-bonded isomer), 21512-32-3.

Supplementary Material Available: Table A, a listing of positional parameters of the phenyl hydrogen atoms, Table B, a tabulation of principal amplitudes of thermal motion, and Table C, a listing of observed and calculated structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 8.[1,2] Elucidation of the Geometry and Connectivity of $(\mu\text{-H})\mathrm{Os_3(CO)_9[\overline{CHC({=}O)CH{=}CEtC}({=}CHMe)]}$, a Molecule with a 3-Ethylidene-4-ethyl-1-oxocyclopent-4-en-2-yl Ligand Bridging Three Osmium Atoms

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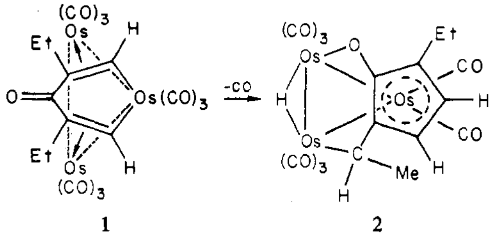
The complex $(\mu\text{-H})\mathrm{Os_3(CO)_9[\overline{CHC({=}O)CH{=}CEtC}({=}CHMe)]}$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* [D_{2h}^{15}; No. 61] with $a = 10.984$ (2) Å, $b = 15.653$ (2) Å, $c = 25.169$ (4) Å, $V = 4327$ (1) Å^3, $Z = 8$, and ρ(calcd) = 2.943 g cm^{-3} for mol wt 958.89. Diffraction data [$3.5° < 2\theta < 45°$] were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved via Patterson, Fourier, and least-squares refinement techniques, the resulting discrepancy indices being $R_F = 3.9\%$ and $R_{wF} = 3.3\%$ for 2607 independent reflections with $|F_o| > 1.0\sigma(|F_o|)$. The molecule contains a triangular arrangement of osmium atoms, each of which is linked to one axial and two equatorial carbonyl ligands. Metal–metal distances are Os(1)–Os(2) = 2.928 (1) Å, Os(1)–Os(3) = 2.880 (1) Å, and Os(2)–Os(3) = 2.965(1)Å. Geometric considerations allow us to assign the μ_2-hydride ligand to the Os(2)–Os(3) bond. The remainder of the molecule consists of a 3-ethylidene-4-ethyl-1-oxocyclopent-4-en-2-yl ligand which is bonded via η^2 linkages to Os(1) and Os(2) and via an η^1 linkage to Os(3).

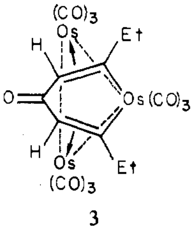
Introduction

It has been shown previously[1,3] that pyrolysis of the symmetrical osmiacyclohexadienone complex **1** proceeds cleanly



1 **2**

under mild conditions (in refluxing cyclohexane for a short period), yielding a complex of stoichiometry "$\mathrm{Os_3(CO)_9(EtC{\equiv}CH)_2}$", which has been identified unambiguously[1] as the hydrido–cyclopentadienyl species **2**. Pyrolysis of the second symmetrical osmiacyclohexadienone complex (**3**) under rather



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more drastic conditions (in refluxing xylene for ${}^1/_2$ h) yields a single product (**4**) of stoichiometry "$\mathrm{Os_3(CO)_{10}(EtC{\equiv}CH)_2}$". The stereochemistry of this species is unknown; however, ^{1}H NMR studies[4] indicate that it contains a dienone

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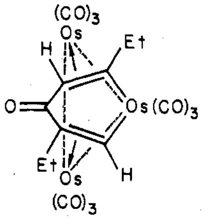
system and a bridging hydride ligand.

Pyrolysis of the asymmetric osmiacyclohexadienone complex (**5**) under intermediate conditions (refluxing cyclohexane for 24 h) produces two products—a species of stoichiometry "$Os_3(CO)_9(EtC{\equiv}CH)_2$" (**6**) (which is clearly an isomer of **2**) and a species of stoichiometry "$Os_3(CO)_{10}(EtC{\equiv}CH)_2$" (**7**) (which is clearly an isomer of **4**).



5

We have now undertaken a single-crystal X-ray diffraction study of complex **4**. Our results, reported below, are of interest, in their own right, to structural chemistry. They are also of relevance to a study of the mechanism of the pyrolysis reaction presently being investigated by Shapley and co-workers.[4]

Experimental Section

(A) Collection of X-ray Diffraction Data. Yellow crystals were supplied by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for the X-ray structural analysis was an irregular trapezoidal prism of height 0.26 mm; dimensions of the base were 0.20 mm × 0.15 mm and dimensions of the "apex" were 0.20 mm × 0.05 mm. It was mounted along its extended direction (b^*) on a thin glass fiber which was then fixed (with beeswax) into an aluminum pin and mounted onto a eucentric goniometer. Preliminary precession and cone-axis photographs indicated *mmm* (D_{2h}) Laue symmetry and revealed the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$. The centrosymmetric orthorhombic space group *Pbca* [D_{2h}^{15}; No. 61] was strongly indicated. The crystal was now transferred to a Syntex $P2_1$ automated diffractometer, was accurately centered, and was aligned in a random orientation (later found to be with [$1\bar{7}3$] about 0.6° from coincidence with the ϕ axis). Crystal alignment, determination of orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[5a] Details appropriate to the current analysis appear in Table I. It should be noted that data were collected via a "wandering ω-scan" method,[5b] because we had some indications of potential overlap of adjacent reflections when testing θ–2θ scans along the c^* axis and the $11l$ row (the c axis is ~25.2 Å in length).

Two equivalent forms of data were collected (hkl and $\bar{h}\bar{k}\bar{l}$); these were averaged ($R(I) = 3.43\%$) following the application of an empirical absorption correction to the data (cf. Table I).

(B) Solution of the Structure. All calculations were performed using the Syntex XTL system,[6] consisting of the following: (a) a Data General Nova 1200 computer with 24K of 16-bit word memory and with a parallel floating-point processor for 32- or 64-bit arithmetic, (b) a Diablo moving-head disk unit with 1.2 million 16-bit words, (c) a Versatec electrostatic printer/plotter, and (d) a locally modified version of the XTL interactive (conversational) crystallographic program package.

Following correction for absorption and the merging of symmetry-equivalent reflections (see Table I), all data were corrected for Lorentz and polarization effects and were converted to an (approximate) absolute scale by means of a Wilson plot. For obtaining F_c values, we used the *analytical* scattering factors of Cromer and Mann[7a] for the appropriate *neutral* atoms; real and imaginary components of anomalous dispersion[7b] were applied to all nonhydrogen atoms.

The positions of the three osmium atoms were determined from an unsharpened three-dimensional Patterson map. Full-matrix least-squares refinement of the scale factor along with positional and isotropic thermal parameters led to convergence with $R_F = 13.7\%$; the use of anisotropic thermal parameters for the metal atoms lowered the residuals to $R_F = 12.6\%$ and $R_{wF} = 17.0\%$ and gave a GOF of 5.99. A difference-Fourier synthesis now revealed the positions of all nonhydrogen atoms. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms gave $R_F = 4.6\%$, $R_{wF} = 4.1\%$, and GOF = 1.463. Continued full-matrix least-squares refinement, using anisotropic thermal parameters for all nonhydrogen atoms, led to $R_F = 4.1\%$, $R_{wF} = 3.6\%$, and GOF = 1.323.

Table I. Data for the X-ray Diffraction Study of $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CH=CEtC}(=CHMe)]$

(A) Crystal Data

crystal system: orthorhombic
space group: *Pbca* [D_{2h}^{15}; No. 61]
$a = 10.984$ (2) Å[a]
$b = 15.653$ (2) Å[a]
$c = 25.169$ (4) Å[a]
$V = 4327$ (1) Å^3
temp = 23 °C
$Z = 8$
mol wt = 958.89
ρ(calcd) = 2.943 g cm^{-3}

(B) Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite ($2\theta_m = 12.2°$)
reflections measd: $+h$, $\pm k$, $+l$
max 2θ: 45.0°
min 2θ: 3.5°
scan type: wandering ω scan
scan speed: 1.50°/min
scan range: 0.9° (0.6° offset for bkgd)
reflections collected: 6358 total, 2825 independent
standard reflections: 3 measured every 97 reflections; max devs from the mean were 2.33% for 524, 2.35% for $\bar{2},\bar{2},12$, 3.37% for 1,11,1; there was no significant decay
absorption coeff: $\mu = 176.4$ cm^{-1}
reflections used for empirical absorption correction[b] (hkl, 2θ, I_{max}/I_{min}): $1\bar{5}1$, 13.66°, 2.57; $1\bar{7}3$, 19.30°, 2.56; $0\bar{8}1$, 20.99°, 2.35; $2\bar{8}4$, 23.18°, 2.59; $1\bar{9}4$, 24.77°, 2.53; $0,\overline{10},6$, 28.05°, 2.39; $0,\overline{12},1$, 31.67°, 2.32; $1,\overline{13},2$, 34.71°, 2.25
data averaging: $R(I) = 3.43\%$ for 2693 reflections with two or more contributors
ignorance factor $p = 0.01$

[a] Based upon a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections of the forms {1,11,1}, {1,1,18}, and {724}, all with $2\theta = 27–30°$. [b] For details of the experimental absorption correction, see M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 16, 2655 (1977).

A series of difference-Fourier syntheses were now calculated, being based upon (a) all data, (b) data with $(\sin\theta)/\lambda < 0.4$, and (c) data with $(\sin\theta)/\lambda < 0.3$. Surprisingly, no evidence of the location of the hydride ligand was obtained. We next calculated (d(C–H) = 0.95 Å)[8] the positions of all hydrogen atoms of the cyclic organic ligand (assuming the ethyl group to be perfectly staggered and assuming the hydrogen atoms on C(7) to be staggered relative to the C(3)–C(6) double bond) and input them in fixed positions with $B(H) = [B_{equiv}(C) + 1.0]$ Å^2; continued refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms led to final convergence ($(\Delta/\sigma)_{max} = 0.10$) with $R_F = 3.9\%$, $R_{wF} = 3.3\%$, and GOF = 1.218 for those 2607 reflections with $|F_o| > \sigma(|F_o|)$.

A final difference-Fourier synthesis had peaks of height 1.87 e Å^{-3} down to 0.82 e Å^{-3} in the vicinity of the osmium atoms; all other peaks were less than 0.80 e Å^{-3} in height; there were no indications of the position of the "missing" bridging hydride ligand.

There was no evidence of secondary extinction. The average value of $\sum w(|F_o| - |F_c|)^2$ showed no significant variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme is therefore acceptable. The final data to parameter ratio was 2607:280 or approximately 9.3:1.

Final positional and thermal parameters are listed in Tables II and III.

Results and Discussion

The crystal consists of discrete monomeric molecular units of $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CH=CEtC}(=CHMe)]$ (which corresponds to "$Os_3(CO)_{10}(EtC{\equiv}CH)_2$") separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. Selected views of the molecule are illustrated in Figures 1 and 2, which also indicate the scheme used for labeling atoms and the relative orientations of the atomic vibration ellipsoids. Figure 3 shows a stereo-

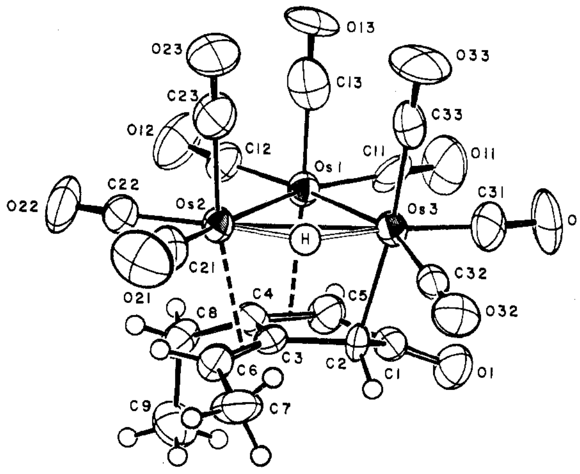


Figure 1. General view of the molecule (ORTEP-II diagram; 50% ellipsoids). The hydride ligand is shown in its deduced position; it was not located directly.

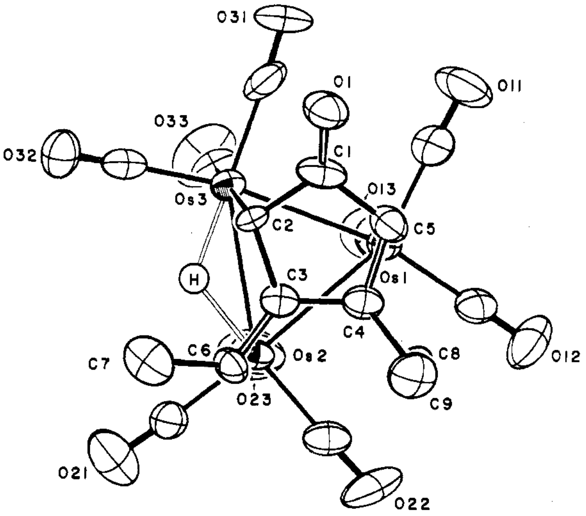


Figure 2. The molecule projected onto the triosmium plane.

Table II. Final Atomic Positions (with Esd's) for $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CH=CEtC}(=CHMe)]$

atom	*x*	*y*	*z*	*B*, Å^2
Os(1)	0.05622 (4)	0.21109 (3)	0.06724 (2)	
Os(2)	0.02434 (4)	0.05810 (3)	0.13270 (2)	
Os(3)	−0.02903 (4)	0.23100 (3)	0.17476 (2)	
C(11)	0.0531 (14)	0.3291 (11)	0.0504 (5)	
O(11)	0.0540 (12)	0.4003 (8)	0.0398 (5)	
C(12)	0.1063 (11)	0.1693 (9)	−0.0012 (6)	
O(12)	0.1281 (9)	0.1443 (8)	−0.0421 (4)	
C(13)	−0.1128 (16)	0.1988 (10)	0.0486 (6)	
O(13)	−0.2093 (8)	0.1934 (7)	0.0357 (4)	
C(21)	−0.0001 (11)	−0.0358 (10)	0.1777 (6)	
O(21)	−0.0231 (10)	−0.0911 (8)	0.2063 (5)	
C(22)	0.0863 (11)	−0.0111 (9)	0.0765 (6)	
O(22)	0.1204 (9)	−0.0508 (8)	0.0412 (5)	
C(23)	−0.1375 (13)	0.0432 (10)	0.1045 (7)	
O(23)	−0.2331 (9)	0.0316 (8)	0.0927 (5)	
C(31)	−0.0236 (13)	0.3537 (11)	0.1689 (6)	
O(31)	−0.0286 (11)	0.4247 (7)	0.1667 (5)	
C(32)	−0.0421 (9)	0.2286 (8)	0.2502 (6)	
O(32)	−0.0484 (7)	0.2248 (7)	0.2959 (4)	
C(33)	−0.2009 (14)	0.2315 (9)	0.1600 (6)	
O(33)	−0.3022 (9)	0.2307 (9)	0.1523 (5)	
O(1)	0.2434 (8)	0.3621 (6)	0.1646 (4)	
C(1)	0.2192 (10)	0.2901 (9)	0.1516 (6)	
C(2)	0.1681 (10)	0.2194 (7)	0.1838 (4)	
C(3)	0.2042 (9)	0.1400 (8)	0.1550 (5)	
C(4)	0.2453 (10)	0.1613 (8)	0.1025 (5)	
C(5)	0.2421 (12)	0.2523 (9)	0.0984 (5)	
C(6)	0.2117 (11)	0.0589 (8)	0.1784 (5)	
C(7)	0.2079 (11)	0.0452 (10)	0.2369 (6)	
C(8)	0.3298 (10)	0.1103 (9)	0.0689 (5)	
C(9)	0.4594 (12)	0.1142 (10)	0.0890 (6)	
H(2)	0.2035	0.2207	0.2189	3.23
H(5)	0.2523	0.2858	0.0658	4.35
H(6)	0.2210	0.0087	0.1555	3.91
H(7A)	0.2134	−0.0150	0.2464	5.35
H(7B)	0.2722	0.0740	0.2548	5.35
H(7C)	0.1316	0.0652	0.2516	5.35
H(8A)	0.3026	0.0506	0.0693	4.16
H(8B)	0.3263	0.1286	0.0327	4.16
H(9A)	0.5138	0.0806	0.0680	5.49
H(9B)	0.4645	0.0942	0.1251	5.49
H(9C)	0.4881	0.1722	0.0885	5.49

scopic view of the molecule. Interatomic distances and angles are compiled in Tables IV and V; important least-squares planes (and deviations of atoms therefrom) are listed in Table VI.

As can very clearly be seen from the figures, the molecule is chiral; however, the *crystal* is composed of an ordered racemic mixture of the two enantiomeric forms by virtue of the crystallographic glide planes and inversion centers in space group *Pbca*.

The molecule is based upon a central $Os_3(CO)_9$ core, which itself is a linked triangular array of $Os(CO)_3$ groups; the overall $Os_3(CO)_9$ core resembles an $Os_3(CO)_{12}$ molecule[10,11] from which three mutually adjacent axial carbonyl ligands have been removed.

The organic portion of the molecule is a 3-ethylidene-4-ethyl-1-oxocyclopent-4-en-2-yl ligand which bridges all three osmium atoms. There is an η^1 linkage (or σ bond) between C(2) and Os(3) [Os(3)–C(2) = 2.185 (11) Å], an η^2 linkage (or ethylenic "π bond") from Os(1) to the C(4)=C(5) linkage [Os(1)–C(4) = 2.390 (12) Å and Os(1)–C(5) = 2.281 (13) Å], and a second η^2 linkage from Os(2) to the exocyclic olefinic linkage C(3)=C(6) [Os(2)–C(3) = 2.421 (11) Å and Os(2)–C(6) = 2.357 (12) Å]. The triosmium plane and the

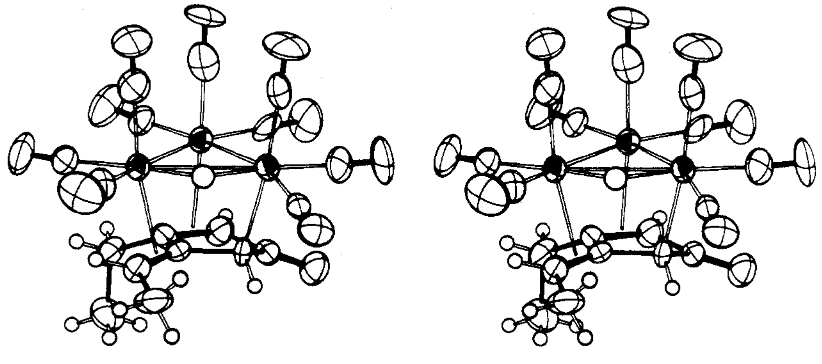


Figure 3. Stereoscopic view of the molecule.

Table III. Final Anisotropic Thermal Parameters (with Esd's) for $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CH=CEtC}(=CHMe)]$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2.978 (22)	2.185 (24)	2.598 (23)	0.034 (19)	−0.146 (17)	−0.058 (19)
Os(2)	2.490 (21)	1.833 (25)	3.413 (25)	−0.240 (18)	−0.081 (19)	−0.102 (20)
Os(3)	2.422 (22)	2.297 (25)	2.828 (24)	0.282 (18)	0.114 (17)	−0.241 (19)
C(11)	6.5 (9)	3.8 (8)	2.3 (6)	−0.2 (7)	−2.1 (5)	−0.9 (6)
O(11)	12.3 (10)	3.1 (6)	6.4 (7)	1.1 (6)	−2.4 (6)	1.3 (6)
C(12)	3.5 (6)	2.5 (7)	4.3 (8)	−0.8 (5)	−0.1 (5)	−0.4 (6)
O(12)	7.0 (6)	7.0 (8)	4.2 (6)	−1.7 (6)	1.5 (5)	−2.4 (5)
C(13)	7.1 (10)	4.2 (9)	3.2 (7)	1.3 (8)	0.6 (6)	0.8 (6)
O(13)	2.2 (4)	6.9 (7)	7.9 (7)	1.0 (5)	−2.2 (4)	0.0 (6)
C(21)	3.2 (6)	3.2 (7)	3.9 (7)	0.0 (5)	0.8 (5)	−0.0 (6)
O(21)	6.5 (6)	6.1 (7)	7.9 (8)	−0.3 (6)	0.3 (5)	2.9 (6)
C(22)	3.1 (6)	2.7 (7)	5.2 (8)	−0.2 (5)	−0.5 (5)	−0.7 (7)
O(22)	5.3 (6)	5.1 (6)	8.0 (8)	−0.6 (5)	1.2 (5)	−4.2 (6)
C(23)	4.2 (8)	3.4 (8)	7.6 (10)	−0.9 (6)	−0.4 (7)	−0.5 (7)
O(23)	3.1 (5)	5.7 (7)	11.9 (9)	−1.4 (5)	−1.7 (5)	−1.3 (7)
C(31)	5.2 (8)	4.6 (10)	3.5 (7)	1.2 (7)	0.8 (6)	−1.6 (7)
O(31)	9.3 (8)	1.9 (5)	8.2 (8)	1.7 (5)	0.6 (6)	−0.3 (5)
C(32)	1.6 (5)	2.1 (6)	5.1 (8)	−0.2 (5)	0.0 (5)	−0.5 (6)
O(32)	3.5 (4)	5.5 (6)	3.8 (5)	0.2 (4)	0.6 (4)	0.2 (5)
C(33)	4.5 (8)	3.7 (8)	4.4 (8)	1.1 (6)	0.8 (6)	−1.3 (6)
O(33)	1.9 (4)	11.4 (11)	9.0 (8)	1.4 (5)	−0.6 (4)	−2.0 (7)
O(1)	5.0 (5)	2.9 (5)	4.6 (5)	−0.6 (4)	−0.3 (4)	0.0 (4)
C(1)	1.9 (5)	1.9 (6)	6.0 (8)	−0.6 (5)	−0.5 (5)	−0.3 (6)
C(2)	3.1 (5)	1.7 (5)	2.1 (5)	0.2 (4)	0.3 (4)	−0.7 (5)
C(3)	1.9 (5)	2.3 (6)	3.2 (6)	−0.4 (5)	−0.5 (4)	−0.3 (5)
C(4)	2.5 (6)	2.6 (7)	3.8 (7)	0.5 (5)	−0.3 (5)	−0.0 (6)
C(5)	4.1 (6)	2.6 (6)	3.2 (6)	−0.4 (5)	−0.4 (5)	0.4 (6)
C(6)	4.4 (7)	2.4 (6)	2.3 (6)	−0.1 (5)	−0.7 (5)	0.5 (5)
C(7)	4.3 (7)	4.9 (9)	5.0 (9)	−0.5 (6)	−2.2 (6)	0.7 (7)
C(8)	2.9 (6)	4.0 (8)	3.4 (7)	−0.9 (5)	0.4 (5)	−1.1 (6)
C(9)	3.2 (6)	4.9 (9)	6.3 (9)	0.3 (6)	0.9 (6)	−0.1 (7)

[a] The anisotropic thermal parameter enters the equation for F_c in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Table IV. Interatomic Distances and Esd's for $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CH=CEtC}(=CHMe)]$

(a) Osmium–Osmium Distances			
Os(1)–Os(2)	2.928 (1)	Os(2)–Os(3)	2.965 (1)
Os(1)–Os(3)	2.880 (1)		
(b) Osmium–Organic Ligand Distances			
Os(1)–C(4)	2.390 (12)	Os(2)–C(3)	2.421 (11)
Os(1)–C(5)	2.281 (13)	Os(2)–C(6)	2.357 (12)
Os(3)–C(2)	2.185 (11)		
(c) Osmium–Carbonyl Distances			
Os(1)–C(11)	1.896 (17)	Os(2)–C(21)	1.876 (15)
Os(1)–C(12)	1.923 (15)	Os(2)–C(22)	1.907 (14)
Os(1)–C(13)	1.925 (17)	Os(2)–C(23)	1.928 (15)
Os(3)–C(31)	1.928 (18)	Os(3)–C(33)	1.924 (15)
Os(3)–C(32)	1.904 (15)		
(d) Carbonyl Distances			
C(11)–O(11)	1.146 (21)	C(21)–O(21)	1.154 (19)
C(12)–O(12)	1.127 (19)	C(22)–O(22)	1.148 (18)
C(13)–O(13)	1.111 (19)	C(23)–O(23)	1.106 (18)
C(31)–O(31)	1.113 (21)	C(33)–O(33)	1.130 (18)
C(32)–O(32)	1.155 (18)		
(e) Distances in the Organic Ligand			
C(1)–O(1)	1.204 (17)	C(5)–C(1)	1.483 (19)
C(1)–C(2)	1.481 (17)	C(3)–C(6)	1.402 (18)
C(2)–C(3)	1.492 (17)	C(6)–C(7)	1.490 (19)
C(3)–C(4)	1.435 (18)	C(4)–C(8)	1.487 (18)
C(4)–C(5)	1.429 (19)	C(8)–C(9)	1.512 (18)

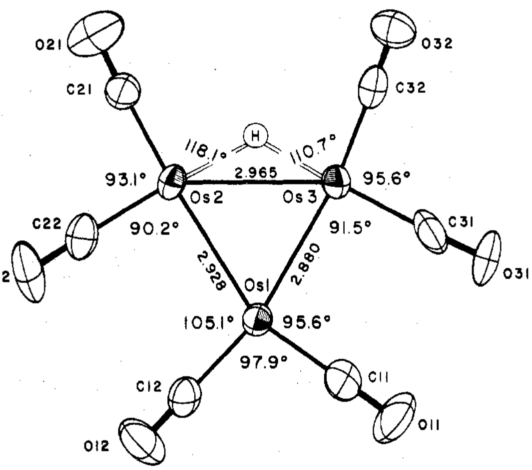


Figure 4. Distances and angles within the equatorial plane of the molecule.

diene system (as defined by atoms C(2)–C(3)–C(4)–C(5)–C(6)—cf. Table VI) deviate by only 3.49° from being strictly parallel. The center of the molecule has a superficial resemblance to a trigonal prism (see, especially, Figure 1). A similar feature was observed in the structure of $(\mu\text{-H})Os_3(CO)_8[\overline{C(O-)C(CHMe-)CHCHCEt}]$[1] In each case, the "trigonal-prismatic" appearance of the central framework results simply from three osmium atoms forming three separate linkages to a complex planar parallel organic system.

Figure 4 shows the osmium–osmium distances and the interligand angles within the equatorial $Os_3(CO)_6$ system and allows us to determine the location of the recalcitrant bridging hydride ligand based upon the following observations.

(1) The Os(2)–Os(3) distance of 2.965 (1) Å is longer than the other two metal–metal distances (viz., Os(1)–Os(2) = 2.928 (1) Å and Os(1)–Os(3) = 2.880 (1) Å). For comparison we note that the average Os–Os distance in $Os_3(CO)_{12}$[10] is 2.877 ± 0.003 Å and that unsupported mono-μ_2-hydrido-bridged Os(H)Os distances are 2.9886 (9) Å in $(\mu\text{-H})(H)Os_3(CO)_{11}$,[10] 3.0185 (6) Å in $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$,[11]

Table V. Angles (in deg, with Esd's) within the $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CHCEtC}(=CHMe)]$ Molecule

Osmium-Osmium-Osmium Angles			
Os(2)-Os(1)-Os(3)	61.38 (2)	Os(1)-Os(3)-Os(2)	60.10 (2)
Os(1)-Os(2)-Os(3)	58.52 (2)		
(b) Osmium-Osmium-Carbonyl Angles			
Os(2)-Os(1)-C(11)	157.0 (5)	Os(1)-Os(2)-C(21)	176.6 (4)
Os(2)-Os(1)-C(12)	105.1 (4)	Os(1)-Os(2)-C(22)	90.2 (4)
Os(2)-Os(1)-C(13)	86.6 (5)	Os(1)-Os(2)-C(23)	90.2 (5)
Os(3)-Os(1)-C(11)	95.6 (5)	Os(3)-Os(2)-C(21)	118.1 (4)
Os(3)-Os(1)-C(12)	166.2 (4)	Os(3)-Os(2)-C(22)	148.6 (4)
Os(3)-Os(1)-C(13)	85.8 (5)	Os(3)-Os(2)-C(23)	93.4 (5)
Os(1)-Os(3)-C(31)	91.5 (5)	Os(2)-Os(3)-C(31)	151.2 (5)
Os(1)-Os(3)-C(32)	163.5 (4)	Os(2)-Os(3)-C(32)	110.7 (4)
Os(1)-Os(3)-C(33)	98.0 (4)	Os(2)-Os(3)-C(33)	97.4 (4)
(c) Carbonyl-Osmium-Carbonyl Angles			
C(11)-Os(1)-C(12)	97.9 (6)	C(21)-Os(2)-C(22)	93.1 (6)
C(11)-Os(1)-C(13)	91.5 (7)	C(21)-Os(2)-C(23)	89.7 (6)
C(12)-Os(1)-C(13)	91.3 (6)	C(22)-Os(2)-C(23)	89.3 (6)
C(31)-Os(3)-C(32)	95.6 (6)	C(32)-Os(3)-C(33)	96.8 (6)
C(31)-Os(3)-C(33)	90.7 (6)		
(d) Osmium-Carbon-Oxygen Angles			
Os(1)-C(11)-O(11)	178.3 (14)	Os(2)-C(21)-O(21)	175.2 (12)
Os(1)-C(12)-O(12)	175.7 (13)	Os(2)-C(22)-O(22)	177.0 (12)
Os(1)-C(13)-O(13)	176.9 (14)	Os(2)-C(23)-O(23)	173.6 (14)
Os(3)-C(31)-O(31)	175.1 (14)	Os(3)-C(33)-O(33)	178.5 (13)
Os(3)-C(32)-O(32)	178.0 (11)		
(e) Angles between the Os_3 Framework and the Organic Ligand			
C(4)-Os(1)-C(5)	35.5 (4)	C(3)-Os(2)-C(6)	34.1 (4)
Os(1)-C(4)-C(8)	120.4 (8)	Os(2)-C(3)-C(2)	109.7 (7)
Os(1)-C(5)-C(1)	105.8 (8)	Os(2)-C(3)-C(4)	99.6 (8)
Os(2)-Os(1)-C(4)	68.2 (3)	Os(2)-C(6)-C(7)	117.2 (9)
Os(2)-Os(1)-C(5)	98.3 (3)	Os(1)-Os(2)-C(3)	66.4 (3)
Os(3)-Os(1)-C(5)	86.4 (3)	Os(1)-Os(2)-C(6)	99.5 (3)
Os(3)-Os(1)-C(4)	88.2 (3)	Os(3)-Os(2)-C(6)	89.6 (3)
		Os(3)-Os(2)-C(3)	66.1 (3)
Os(1)-Os(3)-C(2)	75.6 (3)		
Os(2)-Os(3)-C(2)	76.4 (3)		
Os(3)-C(2)-C(1)	104.9 (8)		
Os(3)-C(2)-C(3)	106.4 (7)		
(f) Angles within the Organic Ligand			
C(1)-C(2)-C(3)	104.8 (10)	C(2)-C(3)-C(6)	124.5 (10)
C(2)-C(3)-C(4)	109.7 (10)	C(4)-C(3)-C(6)	125.3 (11)
C(3)-C(4)-C(5)	106.8 (11)	C(3)-C(6)-C(7)	122.9 (11)
C(4)-C(5)-C(1)	109.7 (11)	C(3)-C(4)-C(8)	126.5 (11)
C(5)-C(1)-C(2)	105.1 (10)	C(5)-C(4)-C(8)	120.6 (11)
C(5)-C(1)-O(1)	125.5 (12)	C(4)-C(8)-C(9)	112.1 (11)
C(2)-C(1)-O(1)	129.4 (12)		

3.059 (3)–3.084 (2) Å for $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$,[7,12] and 3.007 (1) Å in $(\mu\text{-H})Os_3(CO)_8[\overline{C(O-)C(CHMe-)CHCHCEt}]$.[1,3] The Os(2)–Os(3) bond is thus indicated as the most likely to be associated with a μ_2-bridging-hydride ligand.

(2) A survey of Os–Os–CO angles in the equatorial plane shows that the angles bordering the Os(2)–Os(3) bond [i.e., Os(3)–Os(2)–C(21) = 118.1 (4)° and Os(2)–Os(3)–C(32) = 110.7 (4)°] are significantly greater than angles bordering the Os(1)–Os(2) bond [Os(2)–Os(1)–C(12) = 105.1 (4)° and Os(1)–Os(2)–C(22) = 90.2 (4)°] or the Os(1)–Os(3) bond [Os(3)–Os(1)–C(11) = 95.6 (5)° and Os(1)–Os(3)–C(31) = 91.5 (5)°]. Again, the Os(2)–Os(3) bond is strongly indicated as the likely site for the μ_2-bridging site. Our illustrations have all been drawn accordingly (see Figures 1–4).

Table VI. Least-Squares Planes[a] and Deviations of Atoms Therefrom

atom	dev, Å	atom	dev, Å
Plane I	$-0.9448X + -0.0803Y + -0.3177Z = -1.3866$		
Os(1)[b]	0.0000 (5)		
Os(2)[b]	0.0000 (5)		
Os(3)[b]	0.0000 (5)		
C(11)	0.018 (15)	O(11)	0.005 (13)
C(12)	0.080 (13)	O(12)	0.212 (10)
C(13)	1.919 (17)	O(13)	3.029 (9)
C(21)	0.012 (12)	O(21)	0.091 (11)
C(22)	−0.107 (13)	O(22)	−0.128 (10)
C(23)	1.923 (15)	O(23)	3.024 (10)
C(31)	−0.164 (15)	O(31)	−0.184 (12)
C(32)	−0.464 (11)	O(32)	−0.759 (8)
C(33)	1.901 (15)	O(33)	3.015 (10)
C(2)	−2.104 (11)	C(4)	−2.182 (12)
C(3)	−2.147 (11)	C(5)	−2.230 (13)
C(6)	−2.310 (12)		
Plane II	$-0.9287X + -0.1314Y + -0.3467Z = -3.7783$		
C(2)[b]	0.008 (11)	O(1)	−0.886 (9)
C(3)[b]	0.055 (11)	C(1)	−0.377 (11)
C(4)[b]	0.049 (12)	C(7)	−0.502 (13)
C(5)[b]	−0.070 (13)	C(8)	−0.415 (12)
C(6)[b]	−0.058 (12)	C(9)	−1.920 (13)
Os(1)	2.1839 (5)		
Os(2)	2.2525 (5)		
Os(3)	2.0742 (5)		

[a] Orthonormal coordinates $(X, Y, Z) = (ax, by, cz)$. The angle between normals to planes I and II is 3.49°. [b] Atoms used in calculating the planes.

Bond distances within the 3-ethylidene-4-ethyl-1-oxocyclopentenyl system are in accord with our illustrations of the structure. The coordinated ethylenic linkages, C(3)=C(6) and C(4)=C(5), are 1.402 (18) and 1.429 (19) Å in length; the bond linking these two systems, which is formally a C(sp^2)–C(sp^2) single bond, is C(3)–C(4) = 1.435 (18) Å. There are five C(sp^2)–C(sp^3) single bonds and the bond lengths determined are in good agreement with each other: C(1)–C(2) = 1.481 (17) Å, C(1)–C(5) = 1.483 (19) Å, C(2)–C(3) = 1.492 (17) Å, C(4)–C(8) = 1.487 (18) Å, and C(6)–C(7) = 1.490 (19) Å. The C(8)–C(9) bond length of 1.512 (18) Å is reasonable for a C(sp^3)–C(sp^3) single bond, while the C(1)=O(1) distance of 1.204 (17) Å is in the range expected for a ketonic linkage. The system defined by atoms C(2)–C(3)–C(4)–C(5) and C(6) is approximately planar (the root-mean-square deviation from planarity is 0.058 Å), but atoms C(1) and O(1) of the cyclopentenyl system are displaced from this plane (by −0.377 (11) Å and −0.886 (9) Å) in a direction away from the triosmium plane.

Osmium–carbonyl distances range from 1.876 (15) to 1.928 (15) Å, averaging 1.912 ± 0.018 Å; while the axial osmium–carbonyl linkages are among the longest [Os(1)–C(13) = 1.925 (17) Å, Os(2)–C(23) = 1.928 (15) Å, Os(3)–C(33) = 1.924 (15) Å; average = 1.926 ± 0.002 Å], there is a wide range of equatorial osmium–carbonyl distances (1.876 (15)–1.928 (15) Å; average = 1.906 ± 0.019 Å) and no statistically valid separation of axial and equatorial distances is possible. In contrast to this, we note that in $Os_3(CO)_{12}$ the average Os–CO (axial) distance of 1.946 ± 0.006 Å *is* significantly longer than the average Os–CO (equatorial) bond length of 1.912 ± 0.007 Å. It should be noted also that the average equatorial Os–CO distances for $Os_3(CO)_{12}$ and the present structure are in good agreement, but the average axial Os–CO distances [1.946 ± 0.006 Å vs. 1.926 ± 0.002 Å] show significant variation, thereby reflecting the higher π-acceptor capability of three carbonyl ligands vis-à-vis two ethylenic linkages and a metal–alkyl σ bond.

Finally, we note that carbon–oxygen distances within the carbonyl ligands range from 1.106 (18) to 1.155 (18) Å, averaging 1.132 ± 0.019 Å, and that the Os–C–O systems are all close to linear (173.6 (14)–178.5 (13)°).

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Registry No. $(\mu\text{-H})Os_3(CO)_9[\overline{CHC(=O)CH=CEtC}(=CH\text{-}Me)]$, 68297-91-6.

Supplementary Material Available: Data processing formulas and a listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 9.[1,2] The Molecular Geometry of $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ Including Some Comments on the Positions of μ-Hydride Ligands in Tetranuclear Metal Clusters

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The heteronuclear species $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ has been examined via a single-crystal X-ray diffraction study. This complex crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ [C_2^2; No. 4] with a = 8.385 (2) Å, b = 14.682 (4) Å, c = 8.872 (2) Å, β = 104.60 (2)°, V = 1057.0 (4) Å^3, and ρ(calcd) = 3.553 g cm^{-3} for Z = 2 and mol wt 1130.68. Diffraction data were collected with a Syntex $P2_1$ diffractometer and the structure was refined to $R_F = 5.4\%$ for 1454 reflections with $3° < 2\theta < 45°$ (Mo Kα radiation). The molecule contains a tetrahedral heterometallic core in which the tungsten atom is coordinated to two carbonyl ligands and an η^5-cyclopentadienyl ring, while each osmium atom is bonded to three terminal carbonyl ligands. There is evidence that the two carbonyl ligands primarily associated with W(4) act in a "semibridging" capacity and donate electron density to the otherwise electron-poor atom Os(2). There are three normal metal–metal distances [Os(1)–Os(2) = 2.825 (2) Å, Os(2)–Os(3) = 2.827 (2) Å, Os(2)–W(4) = 2.880 (3) Å] and three long (hydride-bridged) metal–metal vectors [Os(1)–Os(3) = 2.941 (2) Å, Os(1)–W(4) = 3.073 (2) Å, Os(3)–W(4) = 3.082 (3) Å]. Careful consideration of metal–metal–ligand angles leads to the conclusion that the three hydride ligands occupy mutually cisoid sites and that the three M–H–M systems lie essentially perpendicular to the Os(1)–Os(3)–W(4) face of the tetrahedron. This arrangement is consistent with ease of interchange of hydride ligands between nonequivalent sites, as indicated previously by ^{1}H NMR spectroscopy.

Introduction

The heteronuclear metal carbonyl hydride $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ can be prepared either by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with a threefold excess of $HW(CO)_3(\eta^5\text{-}C_5H_5)$ or by the action of H_2 on $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$.[3] A single-crystal X-ray diffraction study of this species was taken in order to determine (i) the overall connectivity of metal atoms and ligands in this cluster complex and (ii) the location of the hydride ligands. (^{1}H NMR studies showed only a broad singlet at τ 30.50 (intensity 3) along with the $\eta^5\text{-}C_5H_5$ resonance at τ 4.25 (intensity 5).[3] The hydride ligands cannot be equivalent and are thus involved in some dynamic process in solution.)

Experimental Section

A small sample of the complex was provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The complex forms clear orange tabular crystals. Only one of the crystals provided appeared to be suitable for diffraction work; this was rather large but was trimmed to yield a rather irregular fragment of approximate dimensions 0.36 × 0.33 × 0.30 mm, which was mounted on a glass fiber with quick-setting transparent epoxy resin. Preliminary precession photographs provided approximate cell dimensions and indicated monoclinic ($2/m$) diffraction symmetry.

The crystal was transferred to our Syntex $P2_1$ automated diffractometer. Crystal alignment, determination of the orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[4] Details specific to the present analysis are given in Table I. Two complete asymmetric sets of data were collected, one with indices $-h$, $+k$, $\pm l$ and a second with indices $+h$, $+k$, $\pm l$. The latter set was later discarded (vide infra).

All crystallographic computations were performed using the Syntex XTL system[5] which consists of (i) a Data General Nova 1200 computer with 24K of 16-bit word memory and a parallel floating-point processor for 32- or 64-bit arithmetic, (ii) a Diablo moving-head disk unit with 1.2 million 16-bit words, (iii) a Versetec electrostatic printer/plotter, and (iv) the XTL conversational crystallographic program package as modified by our research group at SUNY at Buffalo.

Data were corrected for absorption (μ = 232.5 cm^{-1}) by an empirical method based upon ψ scans of reflections near χ = 90°.[6] The reflections used for the absorption curves (their 2θ values and maximum:minimum intensity ratios) were as follows: $\bar{1}4\bar{1}$ (13.52°, 3.47:1), $\bar{2}5\bar{1}$ (18.47°, 3.32:1), $\bar{1}7\bar{1}$ (20.97°, 3.17:1), $\bar{2}8\bar{2}$ (27.24°, 2.91:1), $\bar{2},10,\bar{2}$ (32.10°, 2.85:1), $\bar{2},12,\bar{2}$ (37.27°, 2.72:1). The shapes of the curves and the positions (in ϕ) of maxima and minima were self-consistent for all of these reflections; there was the usual broadening of the intensity profile with increasing 2θ.

Analysis of the check reflections showed a gradual linear decrease in intensity of approximately 6% over the period of data collection.

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