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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 6.[1-5] $(\mu\text{-H})Os_3(CO)_8[\overline{C(O-)C(CHMe-)CHCHC}Et]$, a Species with a Trisubstituted η^5-Cyclopentadienyl Ring Derived via Extrusion of Osmium from an Osmiacyclohexadienone System

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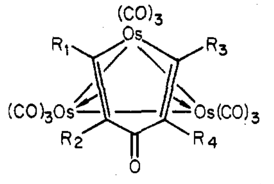
The complex $(\mu\text{-H})Os_3(CO)_8[\overline{C(O-)C(CHMe-)CHCHC}Et]$, synthesized by Shapley and Tachikawa from the pyrolysis of an isomer of the osmiacyclohexadienone complex $Os_3(CO)_9[(EtC_2H)_2CO]$, has been unambiguously identified and characterized via a full three-dimensional single-crystal x-ray structural analysis. The complex crystallizes in the centrosymmetric tetragonal space group $I4_1/a$ [C_{4h}^6; No. 88] with $a = 26.840$ (5) Å, $c = 11.219$ (2) Å, $V = 8082$ (2) Å^3, $Z = 16$, and ρ(calcd) = 3.06 g cm^{-3} for mol wt 930.88. Diffraction data [$5° \leq 2\theta \leq 45°$; Mo Kα radiation] were collected with a Syntex $P2_1$ automated diffractometer, using graphite-monochromatized radiation. The structure was solved via Patterson, difference-Fourier, and least-squares refinement techniques, the resulting discrepancy indices being $R_F = 5.3\%$ and $R_{wF} = 4.5\%$ for 2608 independent reflections. The molecule contains a triangular arrangement of osmium atoms with Os(1)–Os(2) = 2.819 (1) Å, Os(2)–Os(3) = 2.889 (1) Å, and Os(3)–Os(1) = 3.007 (1) Å; this last vector is that associated with a single equatorial μ_2 bridging hydride ligand. Atoms Os(1) and Os(3) are each linked to three terminal carbonyl groups, while Os(2) is associated with two such ligands. In addition, Os(2) is "π bonded" to a trisubstituted cyclopentadienyl ligand [specifically, a $\overline{C(O-)C(CHMe-)CHCHC}Et$ system], which is additionally bridged to Os(1) and Os(3) via C(ring)–O–Os(1) and C(ring)–CHMe–Os(3) linkages. The μ-hydride ligand has clearly been formed by oxidative addition of an aliphatic C–H bond to the triosmium cluster. A further point of interest is that Os(2) formally has a surfeit of bonding electrons while Os(1) and Os(3) each have deficits; the triosmium cluster as a whole is, nevertheless, associated with the normal 48 bonding electrons.

Introduction

We have, for some time, been interested in the structural characteristics of polynuclear osmium carbonyl complexes containing bridging hydride ligands (and related species) and have reported the results of x-ray structural analyses of $Os_3(CO)_{12}$,[1] $(\mu\text{-H})(H)Os_3(CO)_{11}$,[1] $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$,[2] $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$,[3] $(H)Os_3Re(CO)_{15}$,[4] $(\mu\text{-H})_2Os_3(CO)_{10}$,[5] and $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$.[6]

Shapley and co-workers have recently investigated the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with ethylacetylene and found the reaction sequence shown in Scheme I.[7] The species "$Os_3(CO)_{10}(EtC{\equiv}CH)_2$" exists in three separable isomeric forms identified (by analogy with work by Johnson and co-workers[8]) as the metallocyclohexadienone cluster complexes **1a–c**.



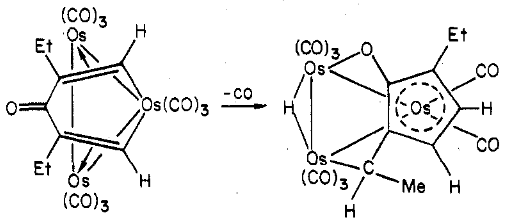
1a, $R_1 = R_3 = H$; $R_2 = R_4 = Et$
b, $R_1 = R_4 = H$; $R_2 = R_3 = Et$
$R_1 = R_4 = Et$; $R_2 = R_3 = H$
c, $R_1 = R_3 = Et$; $R_2 = R_4 = H$

Pyrolysis of isomer **1a** in refluxing hexane for 3 h produced the species examined in the single-crystal x-ray diffraction study described below. Our completed analysis shows the product to have structure **2a**, shown in Scheme II. It is formed from **1a** by a combination of (i) extrusion of the osmium atom from the osmiacyclohexadienone ring to form a contracted five-membered carbocyclic ring with an η^5-cyclopentadienyl→osmium linkage, (ii) loss of a terminal carbonyl ligand, (iii) oxidative addition of an aliphatic C–H bond (previously associated with an ethyl group) to the osmium cluster, and (iv) conversion of a ketonic oxygen into a bridge between the cyclopentadienyl ligand and an osmium atom.

Scheme I

$$(\mu\text{-H})_2Os_3(CO)_{10} + EtC{\equiv}CH \rightarrow \text{“}Os_3(CO)_{10}(EtC{\equiv}CH)_2\text{”} \xrightarrow{\Delta} \text{“}Os_3(CO)_9(EtC{\equiv}CH)_2\text{”}$$

Scheme II



1a **2a**

A preliminary account of this work has appeared previously.[9]

Experimental Section

A. Data Collection. Yellow crystals of **2a** were kindly supplied by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for the x-ray structural analysis was of approximately square cross section (0.2 mm in thickness) and 0.25 mm in length. It was mounted in a 0.2-mm diameter Lindemann glass capillary, which was then flushed with nitrogen, flame-sealed, and inserted into a brass pin with beeswax on a eucentric goniometer.

Preliminary precession and cone-axis photographs indicated that the unit cell was of the body-centered tetragonal variety, with $4/m$ Laue symmetry. The systematic absences hkl for $h + k + l = 2n + 1$, $hk0$ for $h = 2n + 1$ ($hk0$ also for $k = 2n + 1$), and $00l$ for $l \neq 4n$ allow the space group to be uniquely defined as $I4_1/a$ [C_{4h}^6; No. 88].[10]

The crystal was transferred to and centered on a Syntex $P2_1$ automated diffractometer under the control of a Data General Nova 1200 computer. Determination of the crystal quality (via a series of θ–2θ and ω scans over reflections along the principal axes), orientation matrix, and unit-cell parameters was carried out as described in detail previously.[11] The unit-cell parameters are based upon the automatic centering of 25 strong reflections, well dispersed in reciprocal space, with $30° \leq 2\theta \leq 32.5°$.

Intensity data for one octant of reciprocal space were collected using graphite-monochromatized Mo Kα radiation, the monochromator

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Table I. Data for the X-Ray Diffraction Study of $HOs_3(CO)_8$[C(O–)C(CHMe–)CHCHCEt]

(A) Crystal Data

Crystal system: tetragonal
Space group: $I4_1/a$ [C_{4h}^6; No. 88]
$a = 26.8398$ (46) Å
$c = 11.2194$ (19) Å
$V = 8082.2$ (24) Å^3
Temp 23 °C
$Z = 16$
Mol wt 930.880
ρ(calcd) = 3.060 g cm^{-3}

(B) Intensity Data

Radiation: Mo Kα [$\bar{\lambda}$ 0.710 730 Å]
Monochromator: highly oriented graphite
Reflections measd: $+h$, $+k$, $+l$
Max 2θ: 45°
Min 2θ: 5°
Scan type: θ–2θ
Scan speed: 2.0°/min
Scan range: symmetrical, $[1.4 + \Delta(\alpha_2 - \alpha_1)]^\circ$
Reflections collected: 2821 total, 2624 independent
Max dev from mean for standard reflections: 1.51% for 600, 1.68% for 060, 1.73% for 004
Absorption coeff: $\mu = 188.86$ cm^{-1}

being in a parallel (equatorial) position and assumed to be 50% perfect in the reflecting direction. Details of data collection are collected in Table I. Diffraction data were reduced to net intensities (I) and their esd's ($\sigma(I)$) as shown in eq 1 and 2. Here CT is the count

$$I = \mathrm{CT} - \tau(\mathrm{B1} + \mathrm{B2}) \tag{1}$$

$$\sigma(I) = [\mathrm{CT} + \tau^2(\mathrm{B1} + \mathrm{B2})]^{1/2} \tag{2}$$

associated with the θ–2θ scan, B1 and B2 are initial and final backgrounds, and τ is the ratio of time taken for the main scan relative to total time for background measurement (=1 in the present case).

All data were corrected for the effects of absorption [μ(Mo Kα) = 188.9 cm^{-1}] by the following empirical method, using the program TAPER. Several relatively intense and close-to-axial reflections, distributed evenly over the range of 2θ values used in data collection, were measured at 36 positions around the diffraction vector (from $\psi = 0°$ to $\psi = 350°$, $\Delta\psi = 10°$). Each reflection was used to define a normalized absorption curve vs. ϕ, corrected for ω and χ. The curves bracketing the primary data reflection under consideration were interpolated both in 2θ and in ϕ to derive the absorption correction (specifically, a "pseudotransmission factor") for the intensity of the reflection under consideration. Reflections used for the absorption curves, their 2θ values, and their maximum intensity:minimum intensity ratios were as follows: 541, 10.36°, 1.95:1; 961, 16.83°, 1.84:1; 11,9,2, 22.86°, 1.82:1; 15,9,2, 27.73°, 1.75:1; 16,12,0, 30.64°, 1.62:1; 16,16,0, 34.79°, 1.54:1; 23,11,2, 40.09°, 1.55:1.

All curves were mutually consistent—i.e., maxima and minima were at constant ϕ values from one curve to the next. The profiles, in general, become smoother with increasing 2θ.

Data were averaged according to $4/m$ symmetry, yielding a unique data set of 2624 reflections. Intensities were now corrected for Lorentz and polarization factors, and (unscaled) $\sigma_c(F)$ values, based solely on counting statistics, were generated by finite differences—see eq 3.

$$\sigma_c(F_o) = [|F^2| + \sigma(F^2)]^{1/2} - [|F^2|]^{1/2} \tag{3}$$

B. Solution and Refinement of the Structure. All calculations were performed using the Syntex XTL structure determination system, consisting of the following components: an in-house Data General Nova 1200 computer with 24K of 16-bit words, a Diablo disk unit of 1.2 million 16-bit words, and a locally modified version of the XTL conversational crystallographic program package.[12]

The analytical scattering factors of Cromer and Waber[13a] for neutral osmium, oxygen, carbon, and hydrogen were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[13b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights are those shown in eq 4. Here, p is the

$$w = [\{\sigma_c(F_o)\}^2 + \{p|F_o|\}^2]^{-1} \tag{4}$$

"ignorance factor"; it was initially set at a value of 0.035 but was changed, during the final stages of the analysis, to 0.025.

Discrepancy indices used below are defined in eq 5 and 6.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100\ (\%) \tag{5}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \tag{6}$$

The positions of the osmium atoms were found (with considerable difficulty) from a combination of unsharpened and sharpened three-dimensional Patterson syntheses. Full-matrix least-squares refinement of the scale factor along with positional and anisotropic thermal parameters for the three osmium atoms led to convergence with $R_F = 13.0\%$. A difference-Fourier synthesis at this stage revealed the positions of all remaining nonhydrogen atoms. Continued refinement, with anisotropic thermal parameters for all nonhydrogen atoms, and using only those 2260 reflections with $F_o > 2\sigma(F_o)$, led to $R_F = 4.4\%$, $R_{wF} = 5.0\%$, and a goodness of fit of 1.04. (The goodness of fit (GOF) is defined in eq 7. Here, NO is the number

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \tag{7}$$

of observations and NV is the number of variables.)

We now attempted to ascertain the locations of all hydrogen atoms. A difference-Fourier synthesis based upon all data provided no useful information, all major features being close to the positions of the osmium atoms. A difference-Fourier synthesis based upon only those reflections with $(\sin\theta)/\lambda < 0.30$ Å^{-1} had, as its highest feature, a peak of height 0.49 e/Å^3 at (0.097, 0.348, −0.066), a position consistent with being a hydride ligand bridging atoms Os(1) and Os(2). This map also revealed the positions of hydrogen atoms of the organic ligand, with peak heights ranging from 0.34 e/Å^3 down to 0.18 e/Å^3.

Refinement was continued with the bridging hydride ligand (H(br)) included in its observed position and with all other hydrogen atoms included in idealized calculated positions (based upon a staggered conformation, where applicable). Convergence (i.e., $(\Delta/\sigma)_{\max} < 0.05$) was reached with $R_F = 5.3\%$, $R_{wF} = 4.5\%$, and GOF = 1.090 for those 2608 reflections with $F_o > 0.1\sigma(F_o)$ and $F_o > 0.1$.[14]

The hydride ligand was now removed from the model, and refinement to convergence was carried out once more, resulting in $R_F = 5.4\%$, $R_{wF} = 4.7\%$, and GOF = 1.126. The incorporation of the hydride ligand thus clearly represents a statistically significant improvement, even though we cannot claim that it is *accurately* located. [Attempted refinement of its positional and thermal parameters led to no appreciable positional movement but gave an esd of ~0.15 Å, leading to our terminating this venture; the thermal parameter likewise was stable, reducing to a value of ~1.3 Å^2.]

Final positional parameters are listed in Table II; anisotropic thermal parameters are collected in Table III. A list of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

The crystal consists of discrete molecular units of (μ-H)$Os_3(CO)_8$[C(O–)C(CHMe–)CHCHCEt] separated by normal van der Waals distances; there are no abnormally short contacts. A general view of the molecule and the system used for numbering atoms are illustrated in Figure 1. Figure 2 shows the molecule projected onto the plane of the three osmium atoms. Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; bond angles, with esd's, are listed in Table V.

The molecule contains a central $Os_3(CO)_8$ core which possesses approximate C_s symmetry. Atoms Os(1) and Os(3) are each linked to three terminal carbonyl ligands, while Os(2) is associated with two such ligands. The extrusion of the osmium atom from the metallocyclohexadienone complex **1a** (quod vide) has produced a complicated trisubstituted η^5-cyclopentadienyl system which is "π bonded" to Os(2) and which is bridged across to the other osmium atoms via the systems C(1)–O(1)–Os(1) and C(2)–C(6)–Os(3). Internal angles at O(1) and C(6) which are fairly close to 90° [viz., C(1)–O(1)–Os(1) = 100.1 (8)° and C(2)–C(6)–Os(3) = 96.7

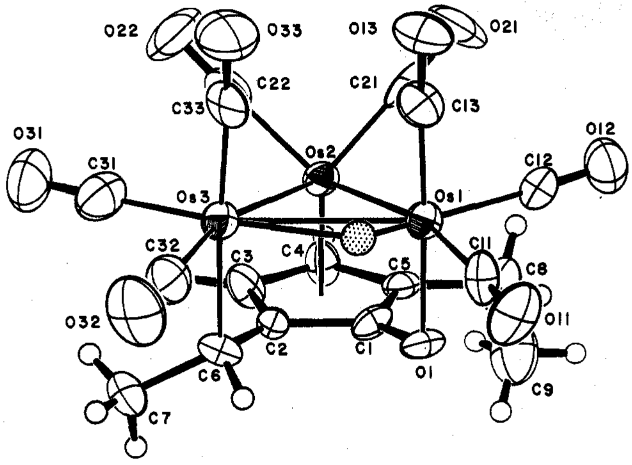

Figure 1. General view of the $(\mu\text{-H})Os_3(CO)_8[\overline{C(O\text{–})C(CHMe\text{–})CHCHC}Et]$ molecule, indicating the numbering scheme (ORTEP diagram; 50% probability ellipsoids for nonhydrogen atoms and artificially reduced hydrogen atoms). H(br), which is stippled, is shown in the position indicated by a difference-Fourier synthesis based upon low-angle data.

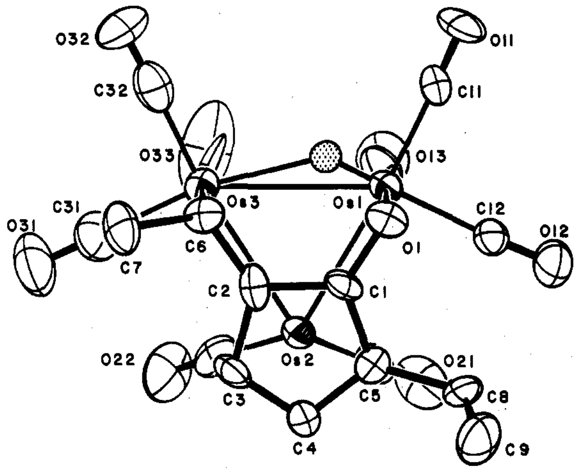

Figure 2. The molecule projected onto its triosmium plane.

(10)°], along with the gross similarity in the Os(1)–Os(3) and O(1)···C(6) distances, result in the η^5-cyclopentadienyl system being displaced by only 8.7° from being parallel with the triosmium plane (see Table VI). The center of the molecule has a superficial resemblence to a trigonal-prismatic fragment (see Figure 1).

The Os(1)–O(1) and Os(3)–C(6) bonds appear to be normal single bonds. Observed bond lengths of 2.138 (9) and 2.194 (14) Å (respectively) are within experimental error of those predicted from addition of appropriate covalent radii (viz., Os–O(calcd) = 2.099 Å and Os–C(calcd) = 2.211 Å, based upon Pauling's covalent radii[15] of 0.66 Å for O and 0.772 Å for C(sp^3), and r(Os) = 1.439 Å, based upon the average Os–Os distance of 2.877 (3) Å in $Os_3(CO)_{12}$[1]).

The nonbridged osmium–osmium distances within the present molecule are Os(1)–Os(2) = 2.819 (1) Å and Os(3)–Os(2) = 2.889 (1) Å; while these are each fairly close to the "baseline" value of 2.877 (3) Å (average) in $Os_3(CO)_{12}$,[1] they are, nevertheless, significantly different one from the other, with the Os(1)–Os(2) value being "atypical". This anomaly presumably results from some combination of the following: (i) geometric constraints caused by the C(1)–O(1) bond being shorter than the C(2)–C(6) bond (i.e., 1.303 (16) Å vs. 1.488 (22) Å) in addition to the O(1)–Os(1) vector being 0.056 (17) Å shorter than the Os(3)–C(6) vector (vide supra); (ii) the electronegativity of oxygen [O(1)] being higher than that of carbon [C(6)]. Appropriate Allred–Rochow electronegativities are as follows: 3.50 for oxygen, 2.50 for carbon, and 1.52 for osmium.[16]

Table II. Final Positional Parameters, with Esd's,[a] for $HOs_3(CO)_8[\overline{C(O\text{-})C(CHMe\text{–})CHCHC}Et]$

Atom	x	y	z
Os(1)	0.09105 (2)	0.33667 (2)	−0.16013 (6)
Os(2)	0.19298 (2)	0.31135 (2)	−0.16608 (6)
Os(3)	0.15278 (2)	0.33900 (2)	0.06350 (6)
C(11)	0.0282 (6)	0.3698 (7)	−0.1492 (15)
O(11)	−0.0084 (4)	0.3909 (5)	−0.1392 (12)
C(12)	0.0785 (6)	0.3164 (6)	−0.3221 (16)
O(12)	0.0691 (5)	0.3028 (5)	−0.4138 (13)
C(13)	0.0669 (6)	0.2731 (7)	−0.1107 (17)
O(13)	0.0525 (5)	0.2346 (5)	−0.0882 (14)
C(21)	0.1711 (6)	0.2575 (7)	−0.2627 (16)
O(21)	0.1578 (5)	0.2252 (4)	−0.3214 (14)
C(22)	0.2215 (7)	0.2627 (7)	−0.0641 (17)
O(22)	0.2386 (6)	0.2326 (5)	−0.0054 (13)
C(31)	0.2113 (8)	0.3256 (7)	0.1557 (19)
O(31)	0.2455 (6)	0.3171 (6)	0.2115 (15)
C(32)	0.1237 (7)	0.3742 (7)	0.1931 (20)
O(32)	0.1066 (6)	0.3934 (6)	0.2737 (14)
C(33)	0.1247 (9)	0.2752 (7)	0.1012 (15)
O(33)	0.1066 (9)	0.2379 (6)	0.1348 (16)
C(1)	0.1719 (5)	0.3912 (5)	−0.2169 (14)
C(2)	0.2028 (6)	0.3926 (5)	−0.1099 (14)
C(3)	0.2503 (5)	0.3707 (6)	−0.1460 (15)
C(4)	0.2484 (5)	0.3560 (6)	−0.2658 (14)
C(5)	0.1998 (5)	0.3685 (5)	−0.3106 (13)
C(6)	0.1850 (6)	0.4100 (5)	0.0048 (14)
C(7)	0.2254 (6)	0.4349 (6)	0.0838 (17)
C(8)	0.1832 (6)	0.3663 (7)	−0.4411 (15)
C(9)	0.2126 (7)	0.4028 (9)	−0.5162 (18)
O(1)	0.1251 (4)	0.4043 (3)	−0.2193 (10)

Atom	x	y	z	B(iso), Å^2
H(br)[b]	0.0974	0.3477	−0.0658	2.0
H(3)	0.2791	0.3665	−0.0938	3.5
H(4)	0.2745	0.3399	−0.3115	3.5
H(6)	0.1618	0.4376	0.0065	2.5
H(7A)	0.2112	0.4462	0.1576	4.0
H(7B)	0.2392	0.4634	0.0438	4.0
H(7C)	0.2513	0.4121	0.1005	4.0
H(8A)	0.1881	0.3329	−0.4722	4.0
H(8B)	0.1480	0.3732	−0.4470	4.0
H(9A)	0.2024	0.4022	−0.5976	5.5
H(9B)	0.2072	0.4363	−0.4865	5.5
H(9C)	0.2472	0.3960	−0.5118	5.5

[a] Esd's, shown in parentheses, are right adjusted to the least significant digit of the preceding number. They are derived from the inverse of the final least-squares matrix. [b] The position of H(br) is taken from a difference-Fourier synthesis. All other hydrogen atoms are in idealized positions.

The hydride ligand, while not located accurately, lies close to the triosmium plane (deviation 0.13 Å—see Table VI) and bridges the Os(1)–Os(3) vector. The accompanying equatorially bridged metal–metal distance, Os(1)–Os(3) = 3.007 (1) Å, is appreciably longer than the non-hydrido-bridged osmium–osmium distances of 2.819 (1) and 2.889 (1) Å in the present molecule. Similar results have been found by us previously in such equatorially mono-μ_2-hydrido-bridged species as $(\mu\text{-H})(H)Os_3(CO)_{11}$ (Os–(H)–Os = 2.9886 (9) Å),[1] $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$ (Os–(H)–Os = 3.0185 (6) Å),[3] and $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ (Os–(H)–Os = 3.058 (3)–3.083 (3) Å).[6] Such results are, of course, consistent with our suggestion[17] that the bent M–H–M system may be considered (to a first approximation) to contain a closed two-electron, three-center bond.

As indicated previously from structural studies on $(\mu\text{-H})(H)Os_3(CO)_{11}$ [1] and $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$,[3] the equatorial carbonyl ligands adjacent to the μ-hydride ligand

Table III. Anisotropic Thermal Parameters, with Esd's,[a] for HOs$_3$(CO)$_8$[C(O–)C(CHMe–)CHCHCEt]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	1.83 (3)	2.48 (3)	2.50 (3)	0.07 (2)	−0.04 (2)	−0.00 (2)
Os(2)	1.95 (3)	2.09 (3)	2.58 (3)	0.28 (2)	−0.09 (2)	−0.00 (2)
Os(3)	3.03 (3)	2.53 (3)	2.26 (3)	0.12 (2)	−0.18 (2)	0.02 (2)
C(11)	2.6 (8)	5.0 (9)	2.8 (8)	0.1 (7)	−0.9 (6)	−0.3 (7)
O(11)	2.8 (5)	6.6 (8)	5.2 (7)	2.5 (5)	0.2 (5)	0.5 (6)
C(12)	2.7 (7)	3.2 (8)	2.6 (9)	0.4 (6)	−0.1 (6)	0.5 (7)
O(12)	4.8 (6)	5.3 (7)	4.0 (7)	0.8 (5)	−1.1 (6)	−1.3 (6)
C(13)	2.1 (7)	3.7 (9)	5.0 (10)	−1.3 (6)	−0.4 (7)	0.4 (8)
O(13)	6.1 (7)	3.0 (6)	6.8 (9)	−1.5 (6)	−0.5 (6)	−0.0 (6)
C(21)	2.7 (7)	4.0 (9)	3.1 (9)	0.6 (6)	−0.0 (6)	2.7 (7)
O(21)	5.0 (7)	2.9 (6)	8.7 (10)	−0.3 (5)	−1.5 (6)	−3.0 (6)
C(22)	4.4 (9)	3.3 (8)	3.2 (9)	−0.2 (7)	0.1 (8)	−1.4 (7)
O(22)	9.7 (10)	4.6 (7)	4.4 (7)	2.7 (7)	−1.2 (7)	1.5 (6)
C(31)	5.4 (11)	4.1 (9)	4.9 (11)	1.1 (8)	−0.7 (9)	0.4 (8)
O(31)	6.9 (9)	6.9 (8)	6.9 (10)	2.3 (7)	−3.7 (8)	−0.9 (7)
C(32)	3.3 (8)	4.2 (9)	5.1 (11)	−1.0 (7)	−1.2 (8)	0.5 (8)
O(32)	6.6 (8)	8.1 (9)	4.2 (8)	0.9 (7)	1.0 (7)	−2.6 (7)
C(33)	10.9 (15)	3.8 (9)	0.8 (7)	−1.6 (10)	−1.3 (8)	−0.1 (7)
O(33)	18.9 (19)	4.7 (8)	7.1 (11)	−4.4 (10)	−4.4 (11)	2.5 (8)
C(1)	1.8 (6)	2.2 (6)	3.1 (8)	0.8 (5)	0.1 (6)	0.6 (6)
C(2)	3.1 (7)	1.8 (6)	2.9 (8)	−0.7 (5)	−1.3 (6)	0.5 (6)
C(3)	1.4 (6)	3.4 (7)	4.1 (10)	0.2 (6)	−0.6 (6)	−1.2 (7)
C(4)	2.3 (7)	3.7 (8)	2.7 (8)	0.2 (6)	−0.4 (6)	−0.5 (6)
C(5)	3.0 (7)	1.4 (6)	2.2 (7)	−0.1 (5)	0.1 (6)	0.3 (5)
C(6)	2.8 (7)	1.9 (6)	3.2 (8)	−0.4 (5)	0.3 (6)	−0.5 (6)
C(7)	4.2 (8)	3.5 (8)	4.7 (10)	−0.6 (7)	−1.9 (8)	−0.8 (7)
C(8)	3.2 (8)	5.4 (9)	1.9 (8)	1.1 (7)	0.8 (6)	0.4 (7)
C(9)	5.3 (10)	8.0 (13)	3.1 (10)	−1.2 (10)	0.2 (8)	0.9 (9)
O(1)	2.7 (5)	1.5 (4)	3.6 (6)	0.3 (4)	0.1 (4)	0.5 (4)

[a] The anisotropic temperature factors (units Å^2) enter the equation for the calculated structure factor in the form $\exp\{-0.25[(B_{11}h^2 + B_{22}k^2 + 2B_{12}hk)a^{*2} + B_{33}l^2c^{*2} + 2(B_{13}hl + B_{23}kl)a^*c^*]\}$.

Table IV. Interatomic Distances (Å) and Esd's for HOs$_3$(CO)$_8$[C(O–)C(CHMe–)CHCHCEt]

(a) Osmium–Osmium and Osmium–Hydride Distances			
Os(1)–Os(2)	2.819 (1)	Os(1)–H(br)	1.11[a]
Os(1)–Os(3)	3.007 (1)	Os(3)–H(br)	2.09[a]
Os(2)–Os(3)	2.889 (1)		
(b) Osmium–Organic Ligand Distances			
Os(1)–O(1)	2.138 (9)	Os(2)–C(4)	2.213 (15)
Os(2)–C(1)	2.289 (14)	Os(2)–C(5)	2.241 (14)
Os(2)–C(2)	2.286 (14)	Os(3)–C(6)	2.194 (14)
Os(2)–C(3)	2.227 (15)		
(c) Osmium–Carbonyl Distances			
Os(1)–C(11)	1.910 (17)	Os(2)–C(22)	1.897 (18)
Os(1)–C(12)	1.926 (18)	Os(3)–C(31)	1.916 (21)
Os(1)–C(13)	1.908 (18)	Os(3)–C(32)	1.902 (21)
Os(2)–C(21)	1.901 (18)	Os(3)–C(33)	1.918 (20)
(d) Carbonyl Bond Lengths			
C(11)–O(11)	1.142 (21)	C(22)–O(22)	1.138 (23)
C(12)–O(12)	1.121 (23)	C(31)–O(31)	1.134 (27)
C(13)–O(13)	1.131 (22)	C(32)–O(32)	1.137 (26)
C(21)–O(21)	1.144 (22)	C(33)–O(33)	1.174 (27)
(e) Distances in the Organic Ligand			
C(1)–C(2)	1.459 (22)	C(1)–O(1)	1.303 (16)
C(2)–C(3)	1.463 (21)	C(2)–C(6)	1.448 (22)
C(3)–C(4)	1.403 (23)	C(6)–C(7)	1.551 (23)
C(4)–C(5)	1.438 (21)	C(5)–C(8)	1.531 (22)
C(5)–C(1)	1.428 (21)	C(8)–C(9)	1.514 (27)

[a] The position of H(br) is taken from a difference-Fourier synthesis.

are repelled. Thus Os(3)–Os(1)–C(11) = 115.0 (6)° and Os(1)–Os(3)–C(32) = 115.0 (5)°. For comparison, we note that the other two metal–metal–(equatorial carbonyl) angles are some 20° less obtuse—viz., Os(2)–Os(1)–C(12) = 94.5 (5)° and Os(2)–Os(3)–C(31) = 97.3 (6)°; the equatorial interligand angles are C(11)–Os(1)–C(12) = 92.2 (7)° and C(31)–Os(3)–C(32) = 91.0 (9)°. Further analysis of the propagation of angular distortions in the equatorial plane caused by H(br) is obviated by the presence of only semiaxial carbonyl ligands at Os(2).

Other points of interest in the molecular structure are as follows.

(1) There are no discernible differences between equatorial, axial, or "semiaxial" Os–CO bond lengths. The total range of the eight such distances is from Os(2)–C(22) = 1.897 (18) Å to Os(1)–C(12) = 1.926 (18) Å, the average value being 1.910 ± 0.010 Å. Carbon–oxygen distances within the carbonyl ligands are, similarly, in mutual agreement, the range being from 1.121 (23) Å for C(12)–O(12) up to 1.174 (27) Å for C(33)–O(33), with an average value of 1.140 ± 0.015 Å.

(2) Formal electron counting shows that Os(2) has a surfeit of electron density (nominally 19 outer valence electrons—8 from the d^8 Os(0) atom, 5 from the η^5-cyclopentadienyl ligand, 4 from the two carbonyl ligands, and 2 from the two osmium–osmium bonds), while Os(1) and Os(3) each have a deficit (17.5 electrons each). The cluster as a whole is associated with the normal 48 bonding electrons expected for a triangular, trinuclear cluster. We suggest that this apparent uneven distribution of charge be borne in mind by those attempting to predict the connectivity and molecular geometry of complex osmium clusters and of related species.

(3) The η^5-cyclopentadienyl ring is planar within the limits of experimental error (the root-mean-square deviation from planarity being 0.005 Å—see Table VI). The π-bonded osmium atom Os(2) lies −1.8887 (6) Å from the plane. The bridging substituents O(1) and C(6) are displaced from the carbocyclic plane by −0.095 (9) and −0.098 (14) Å, respectively, while the third substituent C(8) is displaced in the opposite direction (i.e., away from Os(2)) by +0.192 (18) Å. Clearly, the displacement of substituents on an η^5-cyclopentadienyl system can be affected dramatically by other steric and/or electronic effects within the molecule. Carbon–carbon distances within the carbocyclic ring range from C(3)–C(4)

Table V. Angles (in Deg, with Esd's) within the $\mathrm{HOs_3(CO)_8}[\overline{\mathrm{C(O-)C(CHMe-)CHCHC}}\mathrm{Et}]$ Molecule

	(a) Angles within the Os_3 Framework		
Os(2)–Os(1)–Os(3)	59.36 (2)	Os(1)–Os(3)–Os(2)	57.08 (2)
Os(1)–Os(2)–Os(3)	63.56 (2)		
	(b) Other Angles within the $HOs_3(CO)_8$ Cluster		
Os(1)–H(br)–Os(3)	137.8	C(11)–Os(1)–C(12)	92.2 (7)
C(11)–Os(1)–H(br)	87.2	C(12)–Os(1)–C(13)	87.9 (7)
C(12)–Os(1)–H(br)	178.4	C(13)–Os(1)–C(11)	95.6 (7)
C(13)–Os(1)–H(br)	90.8	C(21)–Os(2)–C(22)	86.8 (8)
C(31)–Os(3)–H(br)	168.3	C(31)–Os(3)–C(32)	91.0 (9)
C(32)–Os(3)–H(br)	100.6	C(32)–Os(3)–C(33)	96.6 (9)
C(33)–Os(3)–H(br)	88.5	C(33)–Os(3)–C(31)	92.0 (9)
	(c) Angles between the $HOs_3(CO)_8$ Cluster and the Organic Ligand		
Os(1)–O(1)–C(1)	100.1 (8)	C(4)–Os(2)–C(5)	37.6 (5)
C(1)–Os(2)–C(2)	37.2 (5)	C(5)–Os(2)–C(1)	36.7 (5)
C(2)–Os(2)–C(3)	37.8 (6)	Os(3)–C(6)–C(2)	96.7 (10)
C(3)–Os(2)–C(4)	36.8 (6)	O(1)–Os(1)–H(br)	90.2
		C(6)–Os(3)–H(br)	88.6
	(d) Angles within the Organic Ligand		
C(1)–C(2)–C(3)	104.9 (12)	C(5)–C(1)–C(2)	108.6 (12)
C(2)–C(3)–C(4)	110.3 (13)	C(1)–C(2)–C(6)	123.6 (13)
C(3)–C(4)–C(5)	107.6 (13)	C(2)–C(6)–C(7)	114.7 (13)
C(4)–C(5)–C(1)	108.6 (12)	C(6)–C(2)–C(3)	131.4 (14)
C(4)–C(5)–C(8)	126.1 (13)	C(5)–C(1)–O(1)	127.2 (13)
C(5)–C(8)–C(9)	110.8 (14)	O(1)–C(1)–C(2)	123.9 (13)
C(8)–C(5)–C(1)	124.6 (13)		
	(e) Angles within the Carbonyl Groups		
Os(1)–C(11)–O(11)	177.1 (15)	Os(2)–C(22)–O(22)	178.2 (16)
Os(1)–C(12)–O(12)	175.8 (15)	Os(3)–C(31)–O(31)	178.8 (18)
Os(1)–C(13)–O(13)	176.0 (16)	Os(3)–C(32)–O(32)	176.9 (18)
Os(2)–C(21)–O(21)	179.6 (15)	Os(3)–C(33)–O(33)	173.7 (19)

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

Atom	Dev, Å	Atom	Dev, Å
Plane I:	$0.3382X + 0.9008Y - 0.2724Z = 11.6755$		
C(1)	0.005 (14)	C(6)	−0.098 (14)
C(2)	−0.007 (14)	C(7)	0.629 (17)
C(3)	0.006 (15)	C(8)	0.192 (18)
C(4)	−0.002 (16)	C(9)	1.570 (23)
C(5)	−0.002 (13)	O(1)	−0.095 (9)
Os(2)	−1.8887 (6)		
Plane II:	$0.2331X + 0.9561Y - 0.1778Z = 9.5281$		
Os(1)	0.0000 (6)		
Os(2)	0.0000 (6)		
Os(3)	0.0000 (6)		
H(br)	0.13		
C(13)	−1.882 (18)	O(13)	−3.004 (12)
C(33)	−1.888 (19)	O(33)	−3.024 (16)
C(11)	0.436 (18)	O(11)	0.728 (13)
C(32)	0.463 (19)	O(32)	0.688 (16)
C(12)	−0.274 (16)	O(12)	−0.500 (13)
C(31)	−0.162 (19)	O(31)	−0.276 (15)
C(21)	−1.327 (18)	O(21)	−2.121 (12)
C(22)	−1.274 (18)	O(22)	−2.055 (14)
O(1)	2.067 (9)		
C(6)	2.140 (14)		

[a] Angle between normals to planes I and II is 8.71°.

= 1.403 (23) Å to C(2)–C(3) = 1.463 (21) Å, averaging 1.438 Å; internal angles range from C(1)–C(2)–C(3) = 104.9 (12)° to C(2)–C(3)–C(4) = 110.3 (13)°, averaging 108.0°. The ring thus has D_{5h} symmetry within the limits of experimental error. Osmium–carbon(cyclopentadienyl) distances are fairly symmetric, ranging from Os(2)–C(4) = 2.213 (15) Å to Os(2)–C(1) = 2.289 (14) Å and Os(2)–C(2) = 2.286 (14) Å.

(4) The bridging hydride ligand is clearly derived from the oxidative addition of an aliphatic C–H bond (that involving initially atom C(6), the α-carbon atom of an ethyl group) to the triosmium cluster.

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Supplementary Material Available: A listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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