bridging ligand. Thus, in $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$, Rh–ClT = 2.3967 (11) Å and Rh–ClB (average) = 2.4586 Å while Rh–ClT = 2.3929 (17) Å and Rh–ClB = 2.4374 (17) Å in $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE76-05564, to M.R.C.). We also thank the Computer Center of SUNY at Buffalo for providing us with time on their CDC 6400 computer.

Registry No. $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$, 12354-85-7.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **15**, 1843 (1976).

(2) R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, **50**, 53 (1973).

(3) R. Mason, Special Lectures, XXIIIrd IUPAC Congress, Boston, Mass., July 26–30, 1971, Vol. 6, p 31 ff.

(4) There is an ambiguity in the literature concerning which mono-μ-hydrido-bridged species was actually studied. In ref 3 it is correctly identified as the complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SEt)$, whereas in ref 2 it is erroneously identified as the analogous $(\mu\text{-}H)(\mu\text{-}OMe)$ complex.

(5) M. R. Churchill and S. W.-Y. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973).

(6) J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, **91**, 5970 (1969).

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

(8) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18a**, 104 (1965).

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); see Table II on p 3178.

(11) (a) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970); (b) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1976; see Table 2.3.1, pp 149–150.

(12) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973).

(13) *Chem. Soc., Spec. Publ.*, **No. 18**, S15s (1965).

Contribution from the Departments of Chemistry, State University of New York at Buffalo,
Buffalo, New York 14214, and University of Illinois at Chicago Circle, Chicago, Illinois 60680

Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 2.[1] Direct Location of the μ_2-Hydride Ligand and Characterization of the 1,3-Dipolar $>C^-HCH_2P^+Me_2Ph$ Ligand in the $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ Molecule

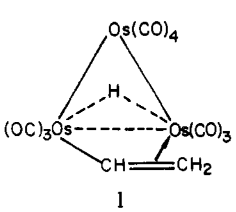
MELVYN ROWEN CHURCHILL*[2] and BARRY G. DeBOER

Received November 4, 1976 AIC607940

The species $HOs_3(CO)_{10}(C^-HCH_2P^+Me_2Ph)$, prepared previously from $HOs_3(CO)_{10}(CH{=}CH_2)$ and PMe_2Ph, has been studied via a single-crystal x-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 11.3389 (18) Å, b = 16.4265 (25) Å, c = 13.8840 (20) Å, β = 100.64 (2)°, V = 2541.5 (7) Å^3, ρ(obsd) = 2.66 (1) g cm^{-3}, and ρ(calcd) = 2.657 g cm^{-3} for mol wt 1016.91 and Z = 4. Diffraction data were collected on a Picker FACS-1 automated diffractometer and the structure was solved via Patterson, Fourier, and least-squares refinement techniques. All atoms other than the methyl hydrogens were located, the final discrepancy indices being R_F = 3.61% and R_{wF} = 3.31% for the 3342 reliable reflections with $2\theta < 45°$ (Mo Kα radiation). The molecule contains a triangular arrangement of osmium atoms. Os(1) and Os(2) are each associated with three carbonyl ligands, while Os(3) is linked to four such ligands. In addition, Os(1) and Os(2) are mutually bridged by a hydride ligand (which was located and refined in the course of the structural analysis) and by a 1,3-dipolar $>C^-HCH_2P^+Me_2Ph$ ligand. Osmium–osmium bond lengths are Os(1)–Os(2) = 2.8002 (6) Å, Os(1)–Os(3) = 2.8688 (6) Å, and Os(2)–Os(3) = 2.8729 (6) Å. Since a single unsupported bridging hydride ligand normally causes an expansion in a metal–metal bond (relative to its value in an analogous nonbridged system), it follows that this effect is counterbalanced by a contrary bond-shortening influence of the bridging $>C^-HCH_2P^+Me_2Ph$ ligand in the present molecule. Osmium–(μ_2-hydride) distances are Os(1)–H = 1.95 (7) Å and Os(2)–H = 1.80 (8) Å; the angle Os(1)–H–Os(2) is 97 (3)°.

Introduction

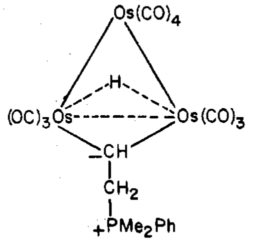
The complex $HOs_3(CO)_{10}(CH{=}CH_2)$ has been characterized[3,4] as having a vinyl group which bridges the edge of an Os_3 triangle in an unsymmetrical σ,π fashion (see I).



I

Shapley and co-workers originally investigated the reaction of I with organophosphines ($:PR_3$) with a view toward determining whether the coordinated double bond could be displaced by a suitable donor ligand. The product of the reaction of I with PMe_2Ph was found to be of the expected stoichiometry, viz., $HOs_3(CO)_{10}(CH{=}CH_2)\cdot PMe_2Ph$, but spectroscopic studies indicated that the incoming phosphine ligand attacked the coordinated double bond rather than its associated osmium atom.

A single-crystal x-ray structural analysis of this product was undertaken in order to obtain unambiguous information on its molecular stereochemistry (believed, correctly, to be as in II). The molecule is also of general relevance to our long-term



II

plan for structurally characterizing transition metal species

Table I. Experimental Data for the X-Ray Diffraction Study of $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

(A) Crystal Parameters at 21.4 ± 0.3 °C[a]

Crystal class: Monoclinic
Space group: $P2_1/n$[b]
$a = 11.3389\ (18)$ Å
$b = 16.4265\ (25)$ Å
$c = 13.8840\ (20)$ Å
$\cos\beta = -0.1847\ (2)$
$\beta = 100.64\ (1)°$
$V = 2541.5\ (7)$ Å^3
$Z = 4$
Mol wt 1016.91
ρ(calcd) = 2.657 g cm^{-3}
ρ(obsd)[c] = 2.66 (1) g cm^{-3}

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: Cu foil; used if I(peak) > 10^4 counts/s
Takeoff angle: 3.0°
Detector aperture: 6.3 mm × 6.3 mm
Crystal–detector distance: 330 mm
Crystal orientation: ϕ axis ~ 10.7° from $10\bar{1}$, *not* in $h0l$ plane
Reflections measd: $+h$, $+k$, $\pm l$ except for $h = 0, l \geqslant 0$
Max 2θ: 45°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (0.90 + 0.692 \tan\theta)°$, starting 0.45° below the Mo Kα_1 peak
Background measurement: stationary crystal, stationary counter; 20 s each at beginning and end of 2θ scan
Std reflections: 3 remeasured after every 47 reflections; rms deviations (after application of an anisotropic linear decay correction)[d] were 0.76% for $10\bar{7}$; 0.53% for $06\bar{1}$: 0.67% for 600
Reflections collected: 3343 independent measurements, 2 duplicate or equivalent measurements (averaged into primary data set), and 150 systematic absences

(C) Treatment of Intensity Data

Conversion[d] to $|F_o|$ and $\sigma(|F_o|)$: as in ref 7, using an "ignorance factor" of $p = 0.03$
Absorption coeff: $\mu = 150.9$ cm^{-1}; max and min transmission factors[e] were 0.287 and 0.147, respectively

[a] Unit cell parameters are from a least-squares fit to the setting angles of the Mo Kα_1 peaks (λ 0.709 300 Å) of 12 reflections with $2\theta = 40.4$–49.6°. Maximum and root-mean-square disagreements were 0.038° and 0.014°, respectively. [b] $P2_1/n$ is a nonstandard setting of space group $P2_1/c$ [C_{2h}^5; No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. [c] The density was measured by neutral buoyancy in a mixture of *sym*-tetrabromoethane and carbon tetrachloride. [d] Data reduction and analysis, including decay correction, were performed using the Fortran IV program **RDUS2**, by B. G. DeBoer. Significant decomposition of the crystal did, in fact, occur. The intensities of the three standard reflections dropped steadily during the course of data collection, final values being 83.4% ($10\bar{7}$), 85.1% ($06\bar{1}$), and 80.3% (600) of their initial intensities. [e] Absorption corrections were applied using the program **DRABZ**, by B. G. DeBoer.

Table II. Final Positional Parameters with Esd's[a] for $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

Atom	*x*	*y*	*z*	*B*,[b] Å^2
Os(1)	0.253 65 (3)	0.544 18 (2)	0.195 86 (3)	3.48
Os(2)	0.116 40 (3)	0.401 49 (2)	0.181 38 (3)	3.57
Os(3)	0.079 32 (3)	0.524 51 (2)	0.319 82 (3)	3.82
P	0.551 62 (21)	0.386 27 (15)	0.258 41 (17)	3.60
C(1)	0.305 3 (7)	0.422 1 (6)	0.240 1 (7)	3.7
C(2)	0.395 8 (8)	0.371 3 (6)	0.198 9 (6)	3.9
C(3)	0.642 3 (8)	0.307 2 (5)	0.222 5 (7)	4.0
C(4)	0.631 8 (10)	0.288 2 (7)	0.124 5 (8)	5.6
C(5)	0.702 7 (11)	0.229 5 (7)	0.092 3 (9)	6.5
C(6)	0.786 9 (11)	0.190 9 (7)	0.159 8 (9)	6.4
C(7)	0.800 3 (10)	0.210 7 (7)	0.255 3 (9)	6.6
C(8)	0.730 2 (8)	0.267 2 (6)	0.289 1 (8)	5.3
Me(1)	0.561 3 (9)	0.381 4 (7)	0.390 1 (6)	4.9
Me(2)	0.611 7 (9)	0.482 1 (6)	0.223 5 (9)	5.3
C(11)	0.174 3 (9)	0.643 9 (7)	0.150 7 (8)	5.1
O(11)	0.131 3 (7)	0.704 6 (5)	0.124 3 (6)	7.6
C(12)	0.353 1 (9)	0.549 2 (6)	0.101 8 (7)	4.3
O(12)	0.411 4 (7)	0.556 1 (5)	0.043 0 (5)	7.0
C(13)	0.359 8 (9)	0.588 9 (6)	0.300 5 (7)	4.4
O(13)	0.425 2 (7)	0.617 1 (5)	0.365 4 (6)	7.3
C(21)	−0.051 3 (10)	0.407 6 (6)	0.125 1 (8)	5.2
O(21)	−0.151 0 (7)	0.409 6 (6)	0.090 7 (6)	7.4
C(22)	0.149 5 (9)	0.330 0 (7)	0.083 9 (7)	4.9
O(22)	0.165 7 (7)	0.285 7 (5)	0.023 8 (5)	7.0
C(23)	0.099 9 (8)	0.319 4 (6)	0.274 2 (7)	4.6
O(23)	0.092 6 (7)	0.271 2 (5)	0.330 9 (6)	6.5
C(31)	−0.029 9 (10)	0.568 5 (7)	0.209 0 (8)	5.2
O(31)	−0.097 6 (7)	0.593 8 (5)	0.144 2 (6)	7.2
C(32)	0.205 2 (9)	0.474 9 (6)	0.413 4 (7)	4.4
O(32)	0.278 0 (7)	0.447 1 (5)	0.472 6 (5)	6.1
C(33)	−0.047 0 (9)	0.470 8 (7)	0.366 5 (7)	4.6
O(33)	−0.124 1 (7)	0.438 9 (6)	0.393 8 (6)	7.2
C(34)	0.098 1 (10)	0.623 4 (7)	0.388 2 (8)	5.3
O(34)	0.108 7 (8)	0.683 8 (5)	0.433 1 (6)	7.7
H(Os)	0.125 7 (64)	0.489 4 (48)	0.106 0 (52)	3.1 (17)
H(1)	0.306 3 (70)	0.410 6 (46)	0.316 0 (58)	3.2 (18)
H(2a)	0.388 4	0.385 0	0.131 5	5.9 (17)[c]
H(2b)	0.376 5	0.315 5	0.204 8	5.9
H(4)	0.573 0	0.315 3	0.077 9	5.7 (11)[d]
H(5)	0.693 0	0.216 2	0.024 7	6.4
H(6)	0.835 9	0.150 6	0.137 8	6.3
H(7)	0.859 8	0.183 9	0.301 6	6.5
H(8)	0.740 4	0.279 8	0.356 9	5.4

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are derived from the inverse of the least-squares matrix from the last cycle of refinement. [b] For anisotropic thermal parameters of the non-hydrogen atoms, see Table III. [c] This is the esd for the thermal parameters of H(2a) and H(2b), which were treated as a single group. [d] This is the esd for the thermal parameters of atoms H(4)–H(8), which were treated as a single group. They were initially assigned the thermal parameter of their individual attached carbon atoms. During the course of refinement all were given equal shifts.

containing bridging hydride ligands; it is pertinent to our current series of studies on polynuclear osmium carbonyl hydrides (see ref 1 and references contained therein); and it is closely related to $HRu_3(CO)_{10}(C^-{=}N^+Me_2)$, a species with which we also have recently been concerned.[5]

A preliminary account of this structural analysis has appeared previously in conjunction with related spectroscopic and synthetic studies.[6]

Experimental Section

A. Data Collection. A crystalline sample of $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ was provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystals are approximately rectangular plates (between {010} faces) and are elongated along $[10\bar{1}]$. The crystal selected for the structural analysis was of approximate dimensions 0.30 mm × 0.13 mm × 0.10 mm. (Indices of its faces were determined and the dimensions of the crystal were measured accurately for future use in the absorption correction routine—vide infra.) The crystal was mounted with its elongated $[10\bar{1}]$ direction collinear with the thin glass fiber to which it was glued. Preliminary precession photographs ($h0l$, $h1l$, and $hk\bar{h}$ levels) and cone-axis photographs (up b and [101]) yielded approximate cell dimensions, indicated C_{2h} ($2/m$) Laue symmetry, and revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the space group is thus $P2_1/n$.

The crystal was transferred to a Picker FACS-1 automated diffractometer, was accurately centered, and was aligned with $[10\bar{1}]$ offset by approximately 10.7° from the instrumental ϕ axis. Refinement of unit cell parameters, determination of the orientation matrix, and data collection were carried out as described in a previous publication;[7] details of the current study are given in Table I.

With the completion of data collection, the crystal was reoriented such that $[10\bar{1}]$ was precisely coincident with the ϕ axis. The intensity of the axial $40\bar{4}$ reflection was measured (at $\chi = 90°$) by θ–2θ scans at 10° intervals from $\phi = 0°$ to $\phi = 360°$. The intensity of this reflection was found to vary by 61.8% [variation (%) = 100(maximum − minimum)/average] indicating that an absorption correction was

Table III. Final Anisotropic Thermal Parameters[a,b] for $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle$[c]
Os(1)	3.546 (19)	3.164 (18)	3.880 (18)	0.246 (13)	1.063 (13)	0.155 (13)	0.196, 0.204, 0.229
Os(2)	3.238 (18)	3.578 (19)	3.816 (18)	−0.034 (13)	0.474 (13)	−0.178 (13)	0.201, 0.211, 0.224
Os(3)	3.759 (19)	3.929 (20)	3.978 (19)	0.514 (15)	1.235 (14)	0.123 (14)	0.197, 0.220, 0.241
P	3.56 (11)	3.41 (11)	3.87 (10)	0.14 (9)	0.74 (9)	0.01 (9)	0.205, 0.214, 0.221
C(1)	2.5 (4)	3.7 (4)	4.6 (5)	0.1 (3)	0.2 (3)	−0.0 (4)	0.18, 0.22, 0.25
C(2)	4.4 (5)	3.3 (4)	3.9 (4)	−0.3 (4)	0.9 (4)	−0.0 (3)	0.20, 0.22, 0.24
C(3)	3.8 (4)	2.9 (4)	5.4 (5)	0.3 (4)	1.6 (4)	0.6 (4)	0.19, 0.21, 0.27
C(4)	5.9 (6)	5.6 (6)	5.5 (6)	1.5 (5)	1.3 (5)	0.4 (5)	0.23, 0.26, 0.30
C(5)	7.9 (7)	5.8 (6)	6.3 (6)	0.8 (6)	3.0 (6)	−1.1 (5)	0.22, 0.29, 0.33
C(6)	6.4 (7)	5.5 (6)	7.6 (7)	1.4 (5)	1.8 (6)	−1.6 (6)	0.21, 0.30, 0.33
C(7)	5.5 (6)	5.2 (6)	8.5 (8)	2.4 (5)	−0.3 (6)	−0.2 (6)	0.19, 0.30, 0.36
C(8)	4.9 (5)	5.2 (6)	5.5 (5)	1.8 (5)	0.2 (4)	0.6 (4)	0.20, 0.27, 0.30
Me(1)	5.1 (5)	6.1 (6)	3.5 (4)	0.4 (4)	0.7 (4)	−0.7 (4)	0.20, 0.25, 0.29
Me(2)	4.2 (5)	3.7 (5)	8.5 (6)	−0.6 (4)	1.7 (5)	0.3 (5)	0.20, 0.24, 0.33
C(11)	4.9 (5)	4.5 (6)	6.3 (6)	1.3 (5)	1.8 (4)	0.8 (5)	0.21, 0.25, 0.30
O(11)	7.4 (5)	5.1 (4)	10.4 (6)	2.1 (4)	1.8 (4)	2.3 (4)	0.21, 0.32, 0.38
C(12)	4.6 (5)	4.9 (5)	3.5 (4)	1.2 (4)	1.1 (4)	0.6 (4)	0.20, 0.21, 0.28
O(12)	7.3 (5)	9.4 (6)	5.0 (4)	2.9 (4)	3.2 (4)	2.9 (4)	0.20, 0.26, 0.40
C(13)	4.2 (5)	4.3 (5)	5.0 (5)	−0.2 (4)	1.2 (4)	−0.9 (4)	0.21, 0.23, 0.27
O(13)	6.1 (4)	8.1 (5)	7.9 (5)	−2.1 (4)	1.2 (4)	−2.6 (4)	0.23, 0.30, 0.37
C(21)	4.3 (5)	5.1 (6)	6.5 (6)	1.3 (5)	1.2 (5)	−0.1 (5)	0.20, 0.28, 0.29
O(21)	4.2 (4)	9.2 (6)	8.2 (5)	0.3 (4)	−0.2 (3)	1.4 (4)	0.22, 0.31, 0.36
C(22)	5.7 (5)	4.9 (5)	3.8 (5)	0.1 (5)	0.3 (4)	0.1 (4)	0.22, 0.25, 0.27
O(22)	8.7 (5)	6.5 (5)	5.5 (4)	1.0 (4)	0.6 (4)	−1.8 (4)	0.23, 0.30, 0.35
C(23)	4.1 (5)	4.2 (5)	5.6 (5)	−0.3 (4)	0.7 (4)	−0.0 (4)	0.22, 0.24, 0.27
O(23)	6.8 (4)	5.5 (4)	7.1 (4)	−0.6 (3)	1.0 (3)	2.2 (4)	0.22, 0.29, 0.34
C(31)	5.6 (6)	4.8 (5)	5.4 (5)	1.0 (5)	1.5 (5)	1.0 (4)	0.22, 0.25, 0.29
O(31)	5.7 (4)	8.4 (6)	7.3 (4)	2.7 (4)	0.7 (4)	1.9 (4)	0.22, 0.31, 0.36
C(32)	5.2 (5)	4.8 (5)	3.3 (4)	−0.3 (4)	1.2 (4)	−0.1 (4)	0.20, 0.24, 0.26
O(32)	6.1 (4)	7.5 (5)	4.6 (3)	1.3 (4)	0.9 (3)	0.6 (3)	0.24, 0.26, 0.32
C(33)	3.4 (4)	5.8 (6)	4.6 (5)	−0.5 (4)	0.6 (4)	−0.3 (4)	0.20, 0.24, 0.27
O(33)	5.1 (4)	10.1 (6)	6.6 (4)	−2.0 (4)	2.0 (3)	−0.1 (4)	0.22, 0.29, 0.37
C(34)	6.0 (6)	4.1 (5)	5.9 (6)	0.3 (5)	1.1 (5)	0.0 (5)	0.23, 0.27, 0.28
O(34)	9.2 (5)	4.9 (4)	8.7 (5)	0.2 (4)	1.1 (4)	−0.9 (4)	0.24, 0.33, 0.35

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å². They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] See footnote *a* to Table II. [c] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see figures.

mandatory. These "ϕ-scan" data were used to check on the validity of the absorption correction prior to its being applied to the primary data set. The variation was thereby reduced to 3.8%, indicating a most satisfactory absorption correction.

B. Solution and Refinement of the Structure. Programs used during the course of the structure solution were FORDAP (Fourier synthesis, by A. Zalkin), LSHF (full-matrix least-squares refinement, by B. G. DeBoer), STAN1 (calculation of distances and angles with esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid plotting program, by C. K. Johnson). All calculations were performed on an IBM 370/158 computer at the University of Illinois at Chicago Circle.

Analytical scattering factors for neutral atoms were taken from the compilation of Cromer and Mann;[8a] $\Delta f'$ and $\Delta f''$ values for all nonhydrogen atoms were taken from the listing of Cromer and Liberman.[8b] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \{\sigma|F_o|\}^{-2}$. Discrepancy indices are defined as in (1) and (2).

$$R_F = \left[\frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}\right] \times 100\ (\%) \qquad (1)$$

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

The positions of the three independent osmium atoms were determined from a Patterson synthesis. Refinement of the scale factor and positional and anisotropic thermal parameters of the three osmium atoms led to $R_F = 16.1\%$ and $R_{wF} = 22.1\%$. A difference-Fourier map now revealed the positions of the remaining 31 nonhydrogen atoms.

Two cycles of full-matrix least-squares refinement of positional and anisotropic thermal parameters for all 34 atoms (307 parameters in all) led to a reduction in the discrepancy indices to $R_F = 3.97\%$ and $R_{wF} = 3.72\%$. Careful comparison of observed and calculated structure factor amplitudes indicated that a correction for secondary extinction was necessary; also data with $(\sin\theta)/\lambda \leq 0.077$ Å^{-1} were corrected for *K*-edge absorption by the Nb β filter.[7] Continued refinement led to convergence with $R_F = 3.79\%$ and $R_{wF} = 3.60\%$. A difference-Fourier map had, as its strongest feature, a peak of height 0.94 e Å^{-3} at the position where a μ_2-bridging hydride ligand was to be expected. There were also clear indications of the hydrogen atoms on the $(CHCH_2PC_6H_5)$ portion of the bridging ligand; positions of the methyl hydrogen were not, however, unequivocally revealed. A difference-Fourier map based only on those data with $(\sin\theta)/\lambda < 0.30$ Å^{-1} showed similar features, the highest peak, of height 0.40 e Å^{-3}, again occurring at the position expected for a μ_2-bridging hydride ligand.

All but the methyl hydrogens were now included in the model. The bridging hydride ligand and the hydrogen atom associated with C(1) were refined independently with isotropic thermal parameters; the other hydrogen atoms were positioned with idealized geometry (d(C–H) = 0.95 Å)[9] and were assigned the equivalent isotropic thermal parameters of their associated carbon atoms. During subsequent cycles of refinement these hydrogen atoms had their positional shifts coupled to those of their carbon atoms; thermal parameters for H(2a) and H(2b) were coupled and refined as a single variable; thermal parameters for H(4)–H(8) were likewise coupled and refined as a single variable.

Continued refinement (now, of 318 parameters) led to final convergence with $R_F = 3.614\%$ and $R_{wF} = 3.378\%$ for all 3343 reflections and $R_F = 3.609\%$ and $R_{wF} = 3.312\%$ for the 3342 reflections with $|\Delta F| < 10\sigma$. [The "bad" reflection is the weak low-angle 011, for which $\Delta/\sigma = -12.39$.]

The "goodness-of-fit", defined by (3), had a value of 1.114, where

$$\text{GOF} = \left[\Sigma w(|F_o| - |F_c|)^2/(m - n)\right]^{1/2} \qquad (3)$$

m, the number of observations, was 3342, and n, the number of

Table IV. Intramolecular Distances (Å) with Esd's[a] for $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

(A) Osmium–Osmium Distances			
Os(1)–Os(2)	2.8002 (6)	Os(2)–Os(3)	2.8729 (6)
Os(1)–Os(3)	2.8688 (6)		
(B) Osmium– (Bridging Ligand) Distances			
Os(1)–H(Os)	1.95 (7)	Os(1)–C(1)	2.148 (9)
Os(2)–H(Os)	1.80 (8)	Os(2)–C(1)	2.173 (8)
(C) Osmium–Carbonyl Distances			
Os(1)–C(11)	1.917 (11)	Os(2)–C(21)	1.920 (11)
Os(1)–C(12)	1.878 (10)	Os(2)–C(22)	1.882 (11)
Os(1)–C(13)	1.858 (10)	Os(2)–C(23)	1.899 (11)
Os(3)–C(31)	1.929 (11)	Os(3)–C(32)	1.925 (11)
Os(3)–C(33)	1.896 (11)	Os(3)–C(34)	1.874 (12)
(D) Carbon–Oxygen Distances			
C(11)–O(11)	1.140 (11)	C(21)–O(21)	1.144 (11)
C(12)–O(12)	1.147 (11)	C(22)–O(22)	1.147 (11)
C(13)–O(13)	1.154 (11)	C(23)–O(23)	1.130 (11)
C(31)–O(31)	1.147 (11)	C(32)–O(32)	1.147 (11)
C(33)–O(33)	1.142 (11)	C(34)–O(34)	1.166 (12)
(E) Distances in $CHCH_2PMe_2Ph$ Ligand			
C(1)–C(2)	1.514 (12)	C(3)–C(4)	1.380 (13)
C(1)–H(1)	1.07 (8)	C(4)–C(5)	1.382 (14)
C(2)–P	1.823 (9)	C(5)–C(6)	1.364 (14)
P–Me(1)	1.813 (9)	C(6)–C(7)	1.347 (15)
P–Me(2)	1.816 (10)	C(7)–C(8)	1.360 (14)
P–C(3)	1.784 (9)	C(8)–C(3)	1.393 (12)

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are calculated from the full positional correlation matrix from the last cycle of refinement using the program STAN1. Errors in unit cell parameters are included. No allowance has been made for possible systematic errors on these distances resulting from thermal motion of the molecule.

variables, was 318. This function showed no appreciable dependence either upon $|F_o|$ or upon $(\sin\theta)/\lambda$; the weighting scheme was deemed acceptable.

A final difference-Fourier synthesis, based upon all data, had a maximum peak height of 0.78 e $Å^{-3}$ and maximum trough depth of −1.18 e $Å^{-3}$; these features were both close to osmium atom positions. The structure is thus both correct and complete.

The final value for the secondary extinction parameter (c) was 2.64 (19) × 10^{-6} mm^{-1} e^{-2}. $F_{c,cor}$, the corrected calculated structure factor, is given by eq 4, β being defined by eq 5.[10,11]

$$F_{c,cor} = F_{c,uncor}(1 + c\beta F_{c,uncor}^{\ 2})^{-1/4} \tag{4}$$

$$\beta = \left(\frac{1 + \cos^4 2\theta}{\sin 2\theta(1 + \cos^2 2\theta)}\right)\left(\frac{-d\ ln\ T}{d\mu}\right) \tag{5}$$

We note here that the final value for R_{wF} based on the 3342 data with $|\Delta F| < 10\sigma$ is 3.312%, while the corresponding value with H(Os) omitted from the refinement is 3.356%. The R-factor ratio for the model with the bridging hydride ligand included, relative to that omitting this ligand, is 1.014. This represents an improvement valid far beyond the 99.5% confidence level. The tabulated value for $\mathcal{R}(b = 4, n - m = 3000, \alpha = 0.005)$ is 1.0025.[12] The inclusion of the bridging hydride ligand is, then, both chemically and statistically valid.

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

Results and Discussion

Interatomic distances and their estimated standard deviations (esd's) are shown in Table IV; interatomic angles are listed in Table V. Important least-squares planes are collected in Table VI.

The crystal consists of discrete ordered units of $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ which are mutually separated by normal van der Waals distances. [Shortest intermolecular contacts of each pertinent type are as follows: hydrogen···oxygen, H(4)···O(12) $[2_1]$ = 2.724 (13) Å; hydrogen···carbon, H(7)···Me(2) $[2_1]$ = 3.355 (11) Å; oxygen···oxygen, O(22)···O(34) $[2_1]$ = 3.022 (12) Å; oxygen···carbon, O(33)···C(34) $[\bar{1}]$ = 3.156 (13) Å.]

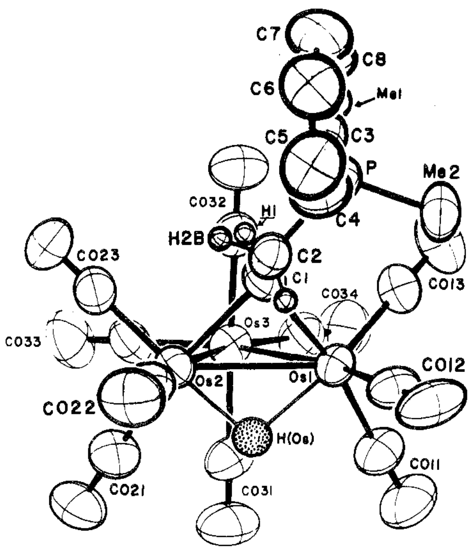


Figure 1. Labeling of atoms in the $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ molecule (ORTEP diagram).

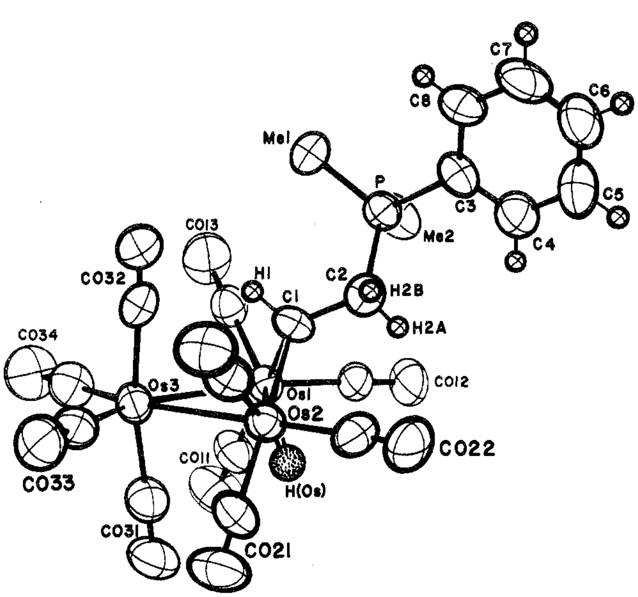


Figure 2. The $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ molecule, showing the staggered conformation of the $CHCH_2PMe_2Ph$ ligand.

The numbering scheme and the atomic thermal vibration ellipsoids for the $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ molecule are shown in Figures 1 and 2.

The $HOs_3(CO)_{10}$ portion of the molecule has approximate C_s (m) symmetry; however, as clearly shown in Figure 1, this symmetry does not continue into the bridging $>CHCH_2PMe_2Ph$ ligand.

The $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ molecule is based upon a triangular arrangement of osmium atoms, one of which [Os(3)] is associated with four terminal carbonyl ligands and two of which [Os(1) and Os(2)] are each linked to three terminal carbonyl ligands and are mutually bridged both by a hydride and by a $CHCH_2PMe_2Ph$ ligand.

The triosmium cluster defines an isosceles triangle in which the doubly bridged Os(1)–Os(2) vector is 2.8002 (6) Å—i.e., slightly, but significantly, shorter than the nonbridged bonds [Os(1)–Os(3) = 2.8688 (6) Å and Os(2)–Os(3) = 2.8729 (6) Å].

We note here that a *single unsupported* bridging hydride ligand is always observed to cause a metal–metal vector to be

Table V. Interatomic Angles (deg) with Esd's for $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

(A) Os–Os–Os Angles			
Os(3)–Os(1)–Os(2)	60.88 (1)	Os(2)–Os(3)–Os(1)	58.38 (1)
Os(1)–Os(2)–Os(3)	60.74 (1)		
(B) Angles Involving the Bridging Ligands			
Os(1)–H(Os)–Os(2)	97 (3)	Os(1)–C(1)–Os(2)	80.8 (3)
Os(1)–Os(2)–H(Os)	44 (2)	Os(1)–Os(2)–C(1)	49.2 (2)
Os(2)–Os(1)–H(Os)	40 (2)	Os(2)–Os(1)–C(1)	50.0 (2)
C(1)–Os(1)–H)Os)	83 (2)	C(1)–Os(2)–H(Os)	86 (2)
Os(3)–Os(1)–H(Os)	80 (2)	Os(3)–Os(1)–C(1)	84.5 (2)
Os(3)–Os(2)–H(Os)	82 (2)	Os(3)–Os(2)–C(1)	84.0 (2)
C(13)–Os(1)–H(Os)	169 (2)	C(11)–Os(1)–C(1)	168.0 (4)
C(23)–Os(2)–H(Os)	172 (3)	C(21)–Os(2)–C(1)	168.0 (4)
(C) Osmium–Osmium–Carbonyl Angles			
Os(2)–Os(1)–C(11)	118.1 (3)	Os(1)–Os(2)–C(21)	118.8 (3)
Os(2)–Os(1)–C(12)	112.6 (3)	Os(1)–Os(2)–C(22)	113.1 (3)
Os(2)–Os(1)–C(13)	131.2 (3)	Os(1)–Os(2)–C(23)	132.0 (3)
Os(3)–Os(1)–C(11)	87.6 (3)	Os(3)–Os(2)–C(21)	88.8 (3)
Os(3)–Os(1)–C(12)	172.2 (3)	Os(3)–Os(2)–C(22)	173.6 (3)
Os(3)–Os(1)–C(13)	89.7 (3)	Os(3)–Os(2)–C(23)	90.0 (3)
Os(1)–Os(3)–C(31)	83.8 (3)	Os(2)–Os(3)–C(31)	83.2 (3)
Os(1)–Os(3)–C(32)	86.9 (3)	Os(2)–Os(3)–C(32)	88.4 (3)
Os(1)–Os(3)–C(33)	154.9 (3)	Os(2)–Os(3)–C(33)	96.6 (3)
Os(1)–Os(3)–C(34)	100.4 (3)	Os(2)–Os(3)–C(34)	158.7 (3)
(D) Carbonyl–Osmium–Carbonyl Angles			
C(11)–Os(1)–C(12)	92.4 (4)	C(21)–Os(2)–C(22)	93.1 (4)
C(11)–Os(1)–C(13)	96.6 (4)	C(21)–Os(2)–C(22)	95.7 (4)
C(12)–Os(1)–C(13)	98.1 (4)	C(22)–Os(2)–C(23)	95.9 (4)
C(31)–Os(3)–C(32)	169.8 (4)	C(32)–Os(3)–C(33)	94.9 (4)
C(31)–Os(3)–C(33)	91.9 (4)	C(32)–Os(3)–C(34)	91.4 (4)
C(31)–Os(3)–C(34)	94.3 (5)	C(33)–Os(3)–C(34)	104.6 (5)
(E) Osmium–Carbon–Oxygen Angles			
Os(1)–C(11)–O(11)	177.4 (13)	Os(2)–C(21)–O(21)	178.5 (8)
Os(1)–C(12)–O(12)	176.5 (10)	Os(2)–C(22)–O(22)	177.7 (14)
Os(1)–C(13)–O(13)	179.5 (6)	Os(2)–C(23)–O(23)	178.3 (7)
Os(3)–C(31)–O(31)	178.0 (16)	Os(3)–C(33)–O(33)	179.2 (6)
Os(3)–C(32)–O(32)	176.8 (10)	Os(3)–C(34)–O(34)	178.0 (18)
(F) Angles in $CHCH_2PMe_2Ph$ Ligand			
Os(1)–C(1)–C(2)	125.0 (7)	C(2)–P–C(3)	109.6 (4)
Os(2)–C(1)–C(2)	117.5 (6)	C(2)–P–Me(1)	108.9 (4)
Os(1)–C(1)–H(1)	114 (4)	C(2)–P–Me(2)	112.1 (5)
Os(2)–C(1)–H(1)	100 (4)	C(3)–P–Me(1)	108.6 (5)
C(2)–C(1)–H(1)	113 (4)	C(3)–P–Me(2)	107.0 (5)
C(1)–C(2)–P	115.0 (6)	Me(1)–P–Me(2)	110.6 (5)
C(4)–C(3)–P	119.4 (8)	C(8)–C(3)–P	122.5 (8)
C(8)–C(3)–C(4)	118.0 (9)	C(5)–C(6)–C(7)	120.1 (11)
C(3)–C(4)–C(5)	121.8 (10)	C(6)–C(7)–C(8)	122.5 (11)
C(4)–C(5)–C(6)	118.5 (11)	C(7)–C(8)–C(3)	119.0 (10)

lengthened relative to its normal unbridged value;[5a] thus the μ_2-hydrido-bridged osmium–osmium vector in $(\mu_2\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$ is 2.9886 (9) Å—as compared to nonbridged Os–Os bond lengths of 2.8574 (7) and 2.9097 (7) Å in that molecule and 2.8737 (5)–2.8824 (5) Å in $Os_3(CO)_{12}$.[1] Clearly then, the bond-lengthening effect of the μ_2-hydrido ligand in $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$ is more than counterbalanced by a contrary bond-shortening influence of the $CHCH_2PMe_2Ph$ ligand. [A similar situation has been observed previously in the $HRu_3(CO)_{10}(C{=}NMe_2)$ molecule.[5a]]

The μ_2-hydride ligand in the present molecule was located with reasonable precision and its isotropic thermal parameter was well behaved during the least-squares refinement procedure. In keeping with this, its final value of 3.1 (17) $Å^2$ is completely consistent with the "equivalent isotropic thermal parameters" of nearby atoms—viz., 3.48 $Å^2$ for Os(1), 3.57 $Å^2$ for Os(2), and 3.7 $Å^2$ for C(1).

The angle Os(1)–H(Os)–Os(2) is 97 (3)° and individual osmium–hydrogen distances are Os(1)–H(Os) = 1.95 (7) Å and Os(2)–H(Os) = 1.80 (8) Å. The average osmium–hydrogen distance is 1.88 ± 0.11 Å, a value which may be compared to a predicted terminal Os–H distance of 1.74 Å (based upon $r(\text{Os}) = 1.44$ Å from the nonbridged osmium–osmium bonds in the present molecule and upon $r(\text{H}) = 0.30$ Å[13]). It is worth observing here that one cannot be certain that the Os(1)–H(Os)–Os(2) bridge is really symmetrical; indeed, the slight asymmetry of the Os(1)–C(1)–Os(2) bridge [Os(1)–C(1) = 2.148 (9) Å; Os(2)–C(2) = 2.173 (8) Å; $\Delta = 0.025 \pm 0.012$ Å] is in a direction opposed to the observed order of Os–H(Os) distances; the differences are, however, all on the borderline of statistical significance.

The μ_2-hydride ligand, H(Os), is displaced outward by approximately 1.25 Å from the midpoint of the Os(1)–Os(2) bond. The Os(1)–H(Os)–Os(2) bridge makes an angle of 110.25° with the Os_3 plane and an angle of 140.78° with the plane of the other bridging ligand (as defined by Os(1)–C(1)–Os(2)).

There are five different environments for carbonyl ligands. The longest osmium–carbonyl bond lengths are, as expected, for the mutually trans carbonyl ligands on Os(3), i.e., Os(3)–C(31) = 1.929 (11) Å and Os(3)–C(32) = 1.925 (11) Å. The other rather long duo of osmium–carbonyl vectors

Table VI. Selected Least-Squares Planes[a] and Deviations (Å) of Atoms Therefrom

Atom	Dev	Atom	Dev
(A) Os(1)–Os(2)–Os(3) Plane $0.57401X - 0.43072Y + 0.69642Z = -0.6263$			
Os(1)*	0.000	C(12)	−0.144 (10)
Os(2)*	0.000	O(12)	−0.286 (8)
Os(3)*	0.000	C(22)	−0.062 (10)
C(1)	+1.556 (9)	O(22)	−0.125 (8)
H(Os)	−1.17 (7)	C(33)	−0.068 (10)
C(2)	+2.172 (9)	O(33)	−0.124 (8)
P	+3.559 (2)	C(34)	−0.028 (11)
H(1)	+2.25 (8)	O(34)	−0.026 (9)
C(13)	+1.214 (10)	C(11)	−1.585 (11)
O(13)	+1.962 (9)	O(11)	−2.506 (8)
C(23)	+1.219 (10)	C(21)	−1.586 (11)
O(23)	+1.968 (8)	O(21)	−2.526 (9)
C(32)	+1.922 (10)	C(31)	−1.913 (11)
O(32)	+3.068 (8)	O(31)	−3.052 (8)
(B) Os(1)–Os(2)–H(Os) Plane $0.7741X - 0.4655Y - 0.4290Z = -3.470$			
Os(1)*	0.000	C(13)	−0.230 (10)
Os(2)*	0.000	O(13)	−0.381 (9)
H(Os)*	0.000	C(23)	−0.245 (10)
C(1)	+1.040 (9)	O(23)	−0.385 (8)
Os(3)	−2.3514 (4)		
(C) Os(1)–Os(2)–C(1) Plane $-0.3934X + 0.1790Y + 0.9018Z = 3.076$			
Os(1)*	0.0000	C(11)	+0.046 (11)
Os(2)*	0.0000	O(11)	+0.065 (8)
C(1)*	0.0000	C(21)	+0.017 (11)
H(Os)	−0.79 (7)	O(21)	+0.009 (9)
Os(3)	+2.3702 (4)		
(D) Dihedral Angles, Deg			
Plane A–Plane B	110.25 ± 3.2		
Plane A–Plane C	108.97 ± 0.31		
Plane B–Plane C	140.78 ± 3.2		

[a] Equations of planes are expressed in the orthonormal (Å) coordinate system given by $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$. Atoms marked by an asterisk were assigned unit weight; all others were given zero weight.

involves the carbonyl ligands trans to the $CHCH_2PMe_2Ph$ ligand—Os(1)–C(11) = 1.917 (11) Å and Os(2)–C(21) = 1.920 (11) Å. All other osmium–carbonyl bond lengths lie in the range 1.858 (10)–1.899 (11) Å.

The $CHCH_2PMe_2Ph$ ligand is in a symmetrical or close to symmetrical bridging mode (vide supra) and is best regarded as a 1,3-dipolar species (see III). The two Os–C(1) distances

$$\rangle\overset{-}{C}H-CH_2-\overset{+}{P}Me_2Ph$$

III

are Os(1)–C(1) = 2.148 (9) Å and Os(2)–C(1) = 2.173 (8) Å. The average Os–C(1) distance of 2.161 ± 0.017 Å may be compared to the predicted Os–C(sp^3) single-bond distance of 2.21 Å (based on r(Os) = 1.44 Å, vide supra, and r(C(sp^3)) = 0.77 Å). Any discrepancy between observed and idealized osmium–carbon distances is probably due to the deviation of atom C(1) from a regular tetrahedral environment. [Appropriate angles are as follows: Os(1)–C(1)–Os(2) = 80.8 (3)°, Os(1)–C(1)–C(2) = 125.0 (7)°, Os(2)–C(1)–C(2) = 117.5 (6)°, Os(1)–C(1)–H(1) = 114 (4)°, Os(2)–C(1)–H(1) = 100 (4)°, and C(2)–C(1)–H(1) = 113 (4)°.]

The phosphorus atom within the phosphonium moiety has a fairly regular tetrahedral stereochemistry with individual C–P–C angles ranging from C(3)–P–Me(2) = 107.0 (5) to C(2)–P–Me(2) = 112.1 (5)°. Phosphorus–carbon distances break down into two classes based upon the hybridization state of the carbon atom involved; thus, the phosphorus–phenyl distance (P–C(3) = 1.784 (9) Å) is approximately 0.04 Å shorter than the other three phosphorus–carbon distances (P–C(2) = 1.823 (9) Å, P–Me(1) = 1.813 (9) Å, and P–Me(2) = 1.816 (10) Å).

Finally, we note that the phenyl group has the expected C_{2v} symmetry—the root-mean-square deviation from planarity is only 0.009 Å, carbon–carbon bond distances range from 1.347 (15) to 1.393 (12) Å (average 1.371 Å), and internal C–C–C bond angles range from 118.0 (9) to 122.5 (11)°, with the smallest angle being, as expected,[14] at the P-bonded carbon atom (C(8)–C(3)–C(4) = 118.0 (9)°).

Acknowledgment. We thank Professor J. R. Shapley for providing us with crystals of $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$. This work was generously supported by the National Science Foundation through Grant No. CHE76-05564 (to M.R.C.).

Registry No. $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$, 61966-88-9.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 1: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
(2) State University of New York at Buffalo.
(3) J. R. Shapley, S. I. Richter, M. Tachikawa, and J. B. Keister, *J. Organomet. Chem.*, **94**, C43 (1975); J. B. Keister and J. R. Shapley, *ibid.*, **85**, C29 (1975).
(4) A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1614 (1975). **Note Added in Proof.** The crystal structure of the related species $HOs_3(CO)_{10}(CH{=}CHEt)$ has now been reported: J. J. Guy, B. E. Reichert, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **32b**, 3319 (1976).
(5) (a) M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **15**, 1843 (1976); (b) M. R. Churchill, B. G. DeBoer, F. J. Rotella, E. W. Abel, and R. J. Rowley, *J. Am. Chem. Soc.*, **97**, 7158 (1975).
(6) M. R. Churchill, B. G. DeBoer, J. R. Shapley, and J. B. Keister, *J. Am. Chem. Soc.*, **98**, 2357 (1976).
(7) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
(8) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1975: (a) Table 2.2B pp 99–101; (b) Table 2.3.1, pp 149–150.
(9) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(10) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); **23**, 558 (1967); see also A. C. Larson, in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 251 ff.
(11) $d \ln T/d\mu = \bar{t}$, the intensity-weighted average path length (in mm) of x rays through the crystal.
(12) See ref 8, Table 4.2, pp 288–292.
(13) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960; Table 7-4, p 226.
(14) A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31b**, 221, 1630 (1975).