Registry No. (triphos)Co(η^3-P_3), 66745-30-0; (triphos)Co(μ-(η^3-P_3))($Cr_2(CO)_{10}$), 69102-14-3; (triphos)Co(μ-(η^3-P_3))Cr$(CO)_5$, 69102-15-4; P_4, 12185-10-3; Cr$(CO)_6$, 13007-92-6; Co$(H_2O)_6(BF_4)_2$, 37041-75-1.

Supplementary Material Available: Listings of structure factor amplitudes for [(triphos)Co(η^3-P_3)] and [(triphos)Co(μ-(η^3-P_3))-{$Cr_2(CO)_{10}$}] (27 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 14.[1,2] X-ray Diffraction Study of $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$, Including the Direct Location of All Four Bridging Hydride Ligands

MELVYN ROWEN CHURCHILL* and FREDERICK J. HOLLANDER

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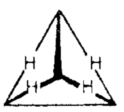
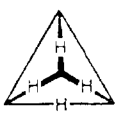
The complex $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$ crystallizes in the monoclinic space group $C2/c$ with a = 8.4605 (16) Å, b = 16.484 (4) Å, c = 15.620 (3) Å, β = 97.73 (2)°, V = 2158.6 (8) Å^3, and ρ(calcd) = 3.43 g cm^{-3} for mol wt 1114.0 and Z = 4. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer using Mo Kα radiation and a θ–2θ scan technique. The structure was solved via Patterson, Fourier, and least-squares refinement techniques; convergence was reached with R_F = 3.5% and R_{wF} = 3.0% for all 1412 independent data (none rejected). The molecule lies on a site of C_2 symmetry, and there is disorder of one CO ligand and the CNMe ligand. The $(\mu\text{-H})_4Os_4$ core approximates to D_{2d} symmetry with the hydrido-bridged Os–Os vectors averaging 2.963 Å (range 2.956 (1)–2.971 (1) Å) and the nonbridged Os–Os bond lengths being 2.822 (1) Å. The hydride ligands occupy the exterior bisecting positions about the appropriate tetrahedral edges. The Os–Os–CO angles and the nature of the disorder in the crystal are discussed in detail.

Introduction

A variety of tetranuclear ruthenium carbonyl complexes derived from $(\mu\text{-H})_4Ru_4(CO)_{12}$ have been examined crystallographically. The species $(\mu\text{-H})_4Ru_4(CO)_{12}$,[3] $(\mu\text{-H})_4Ru_4(CO)_{10}(PPh_3)_2$,[3] and $(\mu\text{-H})_4Ru_4(CO)_{11}[P(OMe)_3]$[4] are based on a $(\mu\text{-H})_4M_4$ core of D_{2d} symmetry (I), whereas the species $(\mu\text{-H})_4Ru_4(CO)_{10}$(diphos)[5] and $(\mu\text{-H})_4Ru_4(CO)_{10}$($\mu$-diphos)[6] have a $(\mu\text{-H})_4M_4$ core of C_s symmetry (II).



I



II

The situation with tetranuclear osmium carbonyl hydrides is rather less well developed although X-ray structural studies of $[NMe_4^+][(\mu\text{-H})_3Os_4(CO)_{12}^-]$,[7] $[(PPh_3)_2N^+]_2[(\mu\text{-H})_2Os_4(CO)_{12}^{2-}]$,[8] and $(\mu\text{-H})_3(\mu\text{-I})Os_4(CO)_{12}$[9] have appeared. However, in none of these studies have the bridging hydride ligands been located directly.

We now report the results of single-crystal X-ray structural analysis of the complex $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$, which was prepared by hydrogenation of $(\mu\text{-H})Os_3(CO)_{10}(CNHMe)$ by Shapley and co-workers.[10] Despite a disorder problem (vide infra) the molecular structure of this new complex has been elucidated, and the hydride ligands have been located directly and their positions optimized by least-squares refinement.

Table I. Experimental Data for the Diffraction Study on $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$

(A) Crystal Parameters at 25 °C[a]

cryst class: monoclinic	β = 97.73 (2)°
space group: $C2/c$	V = 2158.6 (8) Å^3
a = 8.4605 (16) Å	Z = 4
b = 16.484 (4) Å	mol wt 1114.0
c = 15.620 (3) Å	ρ(calcd) = 3.43 g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα (λ 0.710 730 Å); pyrolytic graphite monochromator
rflctns measd: $\pm h$, $+k$, $\pm l$ (2 forms); 2θ = 4.5–45°
scan type: coupled 2θ(counter)–θ(cryst) at 2.0°/min in 2θ
scan width: $[2\theta(K\alpha_1) - 1.0]° \rightarrow [2\theta(K\alpha_2) + 1.1]°$
bkgd measmt: stationary crystal, stationary counter at each end of scan range; each measured for one-fourth the scan time
rflctns collected: 2816 total, yielding 1412 symmetry-independent data (R_{av} = 2.7% for 1404 averaged pairs of reflections)
abs coeff: μ = 249 cm^{-1}

(C) Data for Absorption Corrections

hkl	2θ, deg	I_{max}/I_{min}[b]
$\pm(3\bar{1}\bar{1})$	14.68	1.23
$\pm(4\underline{0}2)$	20.87	1.22
$\pm(5\bar{1}1)$	25.05	1.21
$\pm(6\underline{02})$	30.60	1.21
$\pm(7\bar{3}\bar{3})$	35.13	1.20

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections of the forms {0,4,10}, {196}, {$22\bar{9}$}, {513}, {$51\bar{5}$}, and {$48\bar{4}$}–all with 2θ between 25 and 30°. [b] Average for the two Friedel-related reflections.

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[1] Part 13: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261.
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[6] Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I., manuscript in preparation.
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0020-1669/80/1319-0306$01.00/0

Table II. Final Positional and Thermal Parameters[a] for $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	0.17063 (5)	0.26784 (3)	0.28800 (2)	3.09 (2)	2.44 (2)	2.44 (2)	0.088 (17)	0.094 (15)	−0.012 (14)
Os(2)	0.03242 (6)	0.38825 (3)	0.15888 (2)	3.82 (3)	2.45 (2)	2.22 (2)	−0.134 (17)	0.440 (15)	0.215 (14)
O(11)	0.1587 (12)	0.1742 (5)	0.4548 (5)	8.6 (6)	4.1 (4)	3.5 (4)	−1.2 (4)	0.3 (4)	1.2 (4)
O(12)	0.4744 (11)	0.3566 (7)	0.3611 (6)	3.1 (4)	7.7 (6)	6.2 (5)	−1.9 (5)	0.4 (4)	−1.1 (5)
O(13)	0.3407 (13)	0.1362 (7)	0.1966 (6)	7.2 (6)	6.9 (6)	6.3 (5)	2.3 (5)	1.3 (5)	−2.3 (5)
O(21)	0.2841 (13)	0.5193 (6)	0.1508 (7)	7.4 (7)	3.7 (5)	10.6 (7)	−3.6 (5)	3.9 (5)	−0.3 (5)
O(22)	0.0699 (14)	0.3098 (7)	−0.0126 (6)	10.2 (8)	7.9 (6)	3.9 (5)	−3.4 (6)	2.4 (5)	−1.1 (5)
O(23)/N	−0.2455 (14)	0.4919 (7)	0.0724 (7)	6.4 (7)	3.9 (5)	4.7 (5)	2.6 (5)	−1.4 (5)	1.6 (4)
C(11)	0.1571 (13)	0.2099 (7)	0.3912 (7)	3.2 (6)	2.5 (5)	3.5 (5)	−0.1 (4)	0.0 (4)	0.3 (4)
C(12)	0.3604 (16)	0.3237 (9)	0.3357 (7)	3.7 (7)	4.7 (7)	4.1 (6)	0.0 (6)	0.9 (5)	0.3 (5)
C(13)	0.2786 (15)	0.1856 (8)	0.2292 (7)	4.3 (6)	4.3 (6)	3.3 (5)	1.1 (6)	0.7 (5)	0.0 (5)
C(21)	0.1901 (16)	0.4717 (8)	0.1507 (7)	5.3 (7)	4.1 (6)	3.8 (6)	−1.1 (6)	1.1 (5)	−0.1 (5)
C(22)	0.0585 (17)	0.3391 (8)	0.0530 (7)	6.7 (8)	4.1 (6)	2.2 (5)	−1.2 (6)	0.9 (5)	−0.5 (5)
C(23)/C	−0.1464 (17)	0.4551 (8)	0.1047 (7)	6.0 (8)	3.5 (6)	3.2 (5)	−0.2 (6)	0.9 (5)	−0.0 (5)
CH3	−0.392 (4)	0.535 (2)	0.0406 (19)	6.8 (7)[b]					
H(11)	0.00000 (0)	0.224 (8)	0.25000 (0)	2.2 (27)[b]					
H(22)	0.00000 (0)	0.444 (6)	0.25000 (0)	0.2 (20)[b]					
H(12)	0.215 (17)	0.348 (9)	0.195 (8)	7.7 (38)[b]					

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. [b] B_{iso} in Å^2.

Experimental Section

A. Collection of Diffraction Data. A sample of the complex (supplied by Professor J. R. Shapley of the University of Illinois) was recrystallized from hexane. The resulting clear, yellow crystals were columnar in habit. Crystals of a size suitable for X-ray diffraction studies were obtained by cleaving these columns. Preliminary precession photographs indicated that the crystals belonged to the monoclinic system; the systematic absences (hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$) are consistent with the centrosymmetric monoclinic space group $C2/c$ or the noncentrosymmetric space group Cc.

Careful study of the diffraction patterns of several crystals (following transfer to our Syntex P2$_1$ diffractometer) showed that the profiles of θ–2θ scans along the a^* axis were uniformly wider than those along the b^* or c^* axes. In addition, several of the crystals displayed asymmetric peaks attributed to the presence of smaller crystallites attached to the main crystal. The crystal finally selected for data collection was a rectilinear fragment of dimensions 0.073 mm × 0.090 mm × 0.13 mm; this gave sharp symmetric peak scans along the b^* and c^* directions and somewhat broader, but still symmetric, peak scans in the a^* direction. Despite these portents of impending problems (probably disorder) we continued with the structural analysis.

Crystal alignment, determination of accurate cell dimensions and orientation matrix, and data collection were all carried out as described previously.[11] Details specific to the present analysis are given in Table I.

All crystallographic computations were performed by using the Syntex XTL system[12] as implemented and modified by our research group at SUNY at Buffalo.[13] Data were corrected for absorption ($\mu = 249$ cm^{-1}) by an empirical method based on a series of ψ scans of close-to-axial reflections (see Table I and ref 13). All absorption curves were of essentially the same shape, and their maxima and minima matched throughout the 2θ range. Data were next averaged ($R_{av} = 2.7\%$ for equivalent reflections) and converted to unscaled $|F_o|$ values following correction for Lorentz and polarization factors. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$. The assigned esd's, $\sigma_c(|F_o|)$, were based on the larger of (i) $\sigma(I)$ based on counting statistics or (ii) the internal esd, obtained by averaging symmetry-equivalent reflections.

B. Solution of the Structure. The analytical form[14a] of the scattering factors for neutral osmium, oxygen, nitrogen, carbon, and hydrogen was used throughout this analysis; both the real and imaginary components of anomalous dispersion[14b] were included for all nonhydrogen atoms. The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$; the weights used (w) are derived from $\sigma_c(|F_o|)$, modified by an "ignorance factor" of $p = 0.015$.

Data were placed on an approximate absolute scale by means of a Wilson plot, which also provided an overall isotropic thermal parameter of $\bar{B} = 2.86$ Å^2. Intensity statistics (distribution of $|E|$ values etc.) were intermediate between the ideal centric and acentric predictions. It was hoped that the space group would be the noncentrosymmetric Cc since (with $Z = 4$) this would not require any disorder. However, a three-dimensional Patterson map was readily interpreted by assuming the higher centrosymmetric space group $C2/c$, with two osmium atoms in the asymmetric unit and with the molecule positioned on a site of crystallographic C_2 symmetry. Successive cycles of full-matrix least-squares refinement and difference-Fourier syntheses revealed all remaining nonhydrogen atoms (including a feature interpreted as the resultant of disorder of a carbonyl ligand ($-C\equiv O$) and the isocyanide ($-C\equiv N-Me$) ligand; the atoms of this system were treated as C, $^1/_2$(N + O), and $^1/_2$C, respectively). At convergence, the residuals were $R_F = 3.2\%$ and $R_{wF} = 3.1\%$, and GOF = 1.05 for those 1323 reflections with $|F_o| > \sigma(|F_o|)$ (131 variables refined). All atoms other than the $^1/_2$C, corresponding to the methyl carbon, were refined by using anisotropic thermal parameters.

We emphasize here that use of the centrosymmetric space group imposed a crystallographic twofold axis on the (slightly disordered) molecular image and required that the unique isocyanide ligand be involved in disorder with one carbonyl ligand. A model in the noncentrosymmetric space group Cc was a possibility, but this was not pursued for the following reasons: (1) The low residuals and the small and well-behaved thermal parameters of the centric model indicated that most atomic positions would correspond to a model possessing pseudo-twofold symmetry, even in the acentric space group. (2) Given this, the only major difference between the centric and acentric models would be the reallocation of a "half-carbon" atom (3 electrons or ~0.6% of the scattering density of the unit cell), and the least-squares refinement matrix would be close to singular. (3) Although some ordering of the structure is necessary to obviate abnormally short contacts involving the methyl carbon, there is no necessity for this ordering to be cooperative throughout the crystal. (4) The diffracting properties of the crystal are highly suggestive of a disordered system (vide supra).

We therefore continued refinement in the centrosymmetric space group $C2/c$. A difference-Fourier map clearly revealed the positions of all four bridging hydride ligands. With these included, refinement converged [$(\Delta/\sigma)_{max} = 0.01$] with $R_F = 3.5\%$, $R_{wF} = 3.0\%$, and GOF = 0.990 for all 1412 unique data (*none rejected*). The NO:NV ratio was 1412:139 or 10.16:1.

Careful inspection of observed and calculated structure factors provided no evidence for secondary extinction. The function $\sum w(|F_o| - |F_c|)^2$ showed no unusual dependency on $|F_o|$, $(\sin\theta)/\lambda$, or identity or parity of the Miller indices; the weighting scheme is thus satisfactory. The largest peaks on a final difference-Fourier synthesis were of height 0.9 e/Å^3 and were close to the disordered carbonyl and isocyanide ligands. The structure is thus both correct and complete.

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Table **III.** Intramolecular Distances (Å)

	(A) Osmium–Osmium and Osmium–Hydrogen		
Os(1)–Os(1′)	2.970 (1)	Os(1)–H(11)	1.65 (6)
Os(1)–Os(2)	2.956 (1)	Os(1)–H(12)	2.03 (14)
Os(1)–Os(2′)	2.822 (1)	Os(2)–H(12)	1.70 (14)
Os(2)–Os(2′)	2.971 (1)	Os(2)–H(22)	1.75 (5)
	(B) Osmium–Carbon and Osmium···Oxygen		
Os(1)–C(11)	1.891 (11)	Os(1)···O(11)	3.041 (8)
Os(1)–C(12)	1.913 (14)	Os(1)···O(12)	3.043 (10)
Os(1)–C(13)	1.934 (13)	Os(1)···O(13)	3.061 (11)
Os(2)–C(21)	1.932 (14)	Os(2)···O(21)	3.084 (10)
Os(2)–C(22)	1.881 (11)	Os(2)···O(22)	3.029 (10)
Os(2)–C(23)/C	1.968 (13)	Os(2)···O(23)/N	3.069 (11)
	(C) Carbon–Oxygen		
C(11)–O(11)	1.152 (14)	C(21)–O(21)	1.118 (17)
C(12)–O(12)	1.131 (17)	C(22)–O(22)	1.149 (15)
C(13)–O(13)	1.127 (17)	C(23)/C–O(23)/N	1.101 (18)
	(D) Isocyanide Ligand		
C/C(23)–N/O(23)	1.101 (18)	N/O(23)–CH_3	1.457 (35)
	(E) Average Distances[a]		
Os–CO	1.910 [24]	C–O	1.135 [15]
Os···O	3.044 [12]		

[a] Esd's are calculated via the scatter formula $[\sigma(\text{av})] = [\Sigma(d_i - \bar{d})^2/(N-1)]^{1/2}$.

Final positional and thermal parameters are presented in Table II.

Description of the Structure

Intramolecular distances and angles are collected in Tables III and IV. Figure 1 shows the scheme used for labeling atoms, while Figure 2 provides a stereoscopic view of the molecule.

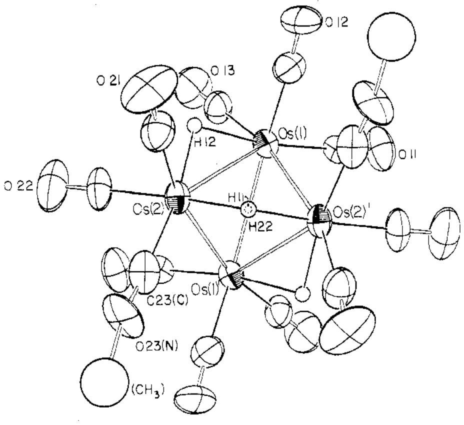


Figure 1. The $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$ molecule, viewed down its twofold axis (passing through H(11) and H(22)). Each carbon atom has the same numerical label as the oxygen atom to which it is attached. The labeling for the isocyanide ligand (C≡N—Me) is given alongside that of the carbonyl ligand (C(23)–O(23)) with which it is disordered (ORTEP-II diagram; 50% probability ellipsoids).

A. The Metal Core of the Molecule. The molecule consists of a central tetrahedral Os_4 core possessing crystallographic C_2 symmetry. There are six Os–Os vectors, four of which are bridged by hydride ligands. (Each osmium atom is additionally coordinated to three terminal ligands—either three carbonyl ligands or two carbonyl ligands and one isocyanide ligand.)

Table **IV.** Intramolecular Angles (deg)

	(A) Os–Os–Os Angles		
Os(1′)–Os(1)–Os(2)	56.87 (1)	Os(1)–Os(2)–Os(1′)	61.82 (1)
Os(1′)–Os(1)–Os(2′)	61.32 (1)	Os(1)–Os(2)–Os(2′)	56.86 (1)
Os(2)–Os(1)–Os(2′)	61.82 (1)	Os(1′)–Os(2)–Os(2′)	61.31 (1)
	(B) Cisoid Os–Os–C Angles		
Os(1′)–Os(1)–C(11)	100.0 (3)	Os(1′)–Os(2)–C(22)	95.9 (4)
Os(1′)–Os(1)–C(13)	107.8 (4)	Os(1′)–Os(2)–C(23)/C	93.3 (4)
Os(2)–Os(1)–C(12)	100.2 (4)	Os(1)–Os(2)–C(21)	108.0 (4)
Os(2)–Os(1)–C(13)	108.4 (4)	Os(1)–Os(2)–C(22)	103.2 (4)
Os(2′)–Os(1)–C(11)	89.7 (3)	Os(2′)–Os(2)–C(21)	106.4 (4)
Os(2′)–Os(1)–C(12)	93.4 (4)	Os(2′)–Os(2)–C(23)/C	100.5 (4)
	(C) Transoid Os–Os–C Angles		
Os(2)–Os(1)–C(11)	149.0 (3)	Os(1′)–Os(2)–C(21)	166.7 (4)
Os(1′)–Os(1)–C(12)	151.1 (4)	Os(2′)–Os(2)–C(22)	154.3 (4)
Os(2′)–Os(1)–C(13)	167.8 (4)	Os(1)–Os(2)–C(23)/C	151.6 (4)
	(D) OC–Os–CO Angles		
C(11)–Os(1)–C(12)	93.1 (5)	C(21)–Os(2)–C(22)	94.8 (6)
C(11)–Os(1)–C(13)	97.9 (5)	C(21)–Os(2)–C(23)/C	94.0 (5)
C(12)–Os(1)–C(13)	95.6 (5)	C(22)–Os(2)–C(23)/C	92.2 (5)
	(E) Cisoid H–Os–CO Angles		
H(11)–Os(1)–C(11)	86.4 (26)	H(12)–Os(2)–C(21)	72.5 (48)
H(11)–Os(1)–C(13)	88.3 (26)	H(12)–Os(2)–C(22)	85.1 (48)
H(12)–Os(1)–C(12)	75.0 (40)	H(22)–Os(2)–C(21)	82.1 (19)
H(12)–Os(1)–C(13)	88.4 (40)	H(22)–Os(2)–C(23)/C	81.9 (19)
	(F) Transoid H–Os–C Angles		
H(11)–Os(1)–C(12)	176.1 (26)	H(12)–Os(2)–C(23)/C	165.9 (48)
H(12)–Os(1)–C(11)	167.1 (40)	H(22)–Os(2)–C(22)	173.1 (19)
	(G) Os–C–O Angles		
Os(1)–C(11)–O(11)	175.9 (10)	Os(2)–C(21)–O(21)	176.0 (12)
Os(1)–C(12)–O(12)	177.5 (12)	Os(2)–C(22)–O(22)	178.0 (12)
Os(1)–C(13)–O(13)	178.1 (11)	Os(2)–C(23)/C–O(23)/N	178.3 (12)
	(H) Angles in Isocyanide Ligand		
Os(2)–C/C(23)–N/O(23)	178.3 (12)	C/C(23)–N/O(23)–CH_3	170.3 (18)
	(I) Os–H–Os Angles		
Os(1)–H(11)–Os(1′)	128.5 (46)	Os(2)–H(22)–Os(2′)	116.2 (32)
Os(1)–H(12)–Os(2)	104.3 (69)		

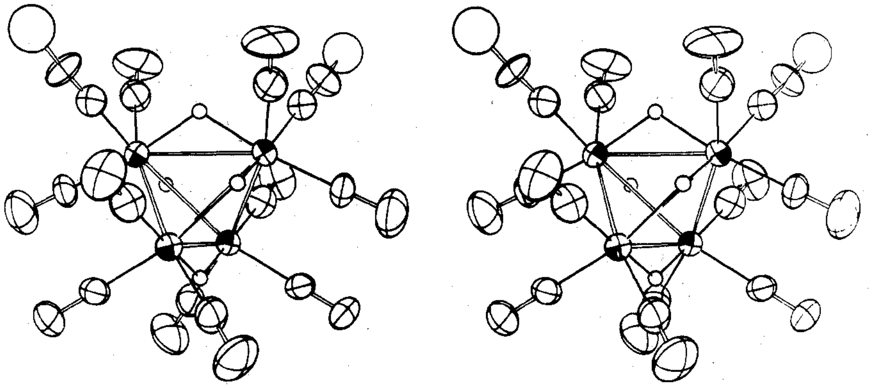


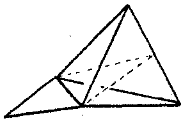
Figure 2. A stereoscopic view of the disordered $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$ molecule. The crystallographic twofold axis lies vertically in the plane of the paper.

The nonbridged osmium–osmium distances (Os(1)–Os(2′) = Os(1′)–Os(2) = 2.822 (1) Å) are significantly shorter than the average Os–Os bond length of 2.877 (3) Å in the trinuclear species $Os_3(CO)_{12}$[15] but are comparable to the nonbridged Os–Os distances in the neutral tetranuclear species $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ (Os–Os = 2.825 (2) and 2.827 (2) Å)[16] and $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$ (2.784 (2) and 2.799 (2) Å).[17] The shortening of metal–metal distances in tetrahedral (relative to triangular) clusters appears to be general.

The hydrido-bridged osmium–osmium distances are Os(1)–Os(1′) = 2.970 (1) Å, Os(2)–Os(2′) = 2.971 (1) Å, and Os(1)–Os(2) = Os(1′)–Os(2′) = 2.956 (1) Å. The average value of 2.963 Å represents an increase of ~0.14 Å over the nonbridged osmium–osmium distances in this molecule and may be compared to values of 2.941 (2) Å for the Os(H)Os distance in $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$[16] and 2.932 (2) Å in $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$.[17]

Similar differences between M(H)M and M–M distances have been observed in a variety of other molecules.[18]

B. The Hydride Ligands. Since the hydride ligands were both located and refined in the present structural determination, some comments can be made on their positions. The four hydride ligands consist of a pair (H(11) and H(22)) which are constrained individually to lie on the crystallographic twofold axis and a symmetry-related pair (H(12) and H(12′)) which are in the general position. Atoms H(11) and H(22) thus are symmetrically disposed about their bridged osmium–osmium vectors (Os(1)–H(11) = Os(1′)–H(11) = 1.65 (6) Å, Os(1)–H(11)–Os(1′) = 128.5 (46)°; Os(2)–H(22) = Os(2′)–H(22) = 1.75 (5) Å, Os(2)–H(22)–Os(2′) = 116.2 (32)°). The Os–H–Os planes *bisect* the exterior angle between the two triosmium planes that meet at the bridged Os–Os vector (as shown schematically in III).[19]



III

The remaining hydride ligands (H(12) and the symmetry-related H(12′)) are not subjected to any positional restraints. The relevant bond distances are Os(1)–H(12) = 2.03 (14) Å and Os(2)–H(12) = 1.70 (14) Å; the large esd's make it impossible to confirm the apparent asymmetry. The Os(1)–H(12)–Os(2) plane is also close (within experimental error) to the exterior bisecting position relative to the Os(1)–Os(2)–Os(2′) and Os(1)–Os(2)–Os(1′) planes which meet at the Os(1)–Os(2) bond. Relevant interplanar angles are 156.55 and 130.94°, as compared to the bisecting angle of 143.75°.

Since each terminal ligand in the present structure is cisoid to at least one hydrido-bridged Os–Os vector, it is difficult to detail the steric effect of the hydride ligands on the angular arrangement of the carbonyl (or isocyanide) ligands. However, several general observations can be made.

(i) The average Os–Os–CO bond angle cisoid to nonbridged Os–Os bonds is 93.1 [25]°[20] (range 89.7 (3) → 95.9 (4)°) and resembles that observed within the equatorial plane of triangular (triosmium) clusters.[15]

(ii) The average of Os–Os–CO bond angle cisoid to hydrido-bridged Os–Os vectors is 104.3 [37]°. Furthermore, these angles may be subdivided into two categories: (a) those in which the carbonyl ligand is cisoid to only one bridging hydride ligand (the average Os–Os–CO angle here is 107.6 [9]° (range 106.4 (4) → 108.4 (4)°)) and (b) those in which the carbonyl ligand is cisoid to *two* bridging hydride ligands (here the competing effect of the two hydride ligands results in a smaller increase in the Os–Os–CO angles, the average value being 101.0 [15]° (range 100.0 (3) → 103.2 (4)°)).

(iii) Of the angles *cisoid* to a hydrido-bridged Os–Os vector, none is greater than 108.4 (4)°, while analogous angles cis-coplanar to equatorial bridging hydride ligands in *triangular* osmium clusters are typically greater (~111 → 118°). This observation is consistent with the observed (refined) positions of the hydride ligands in the present structure—i.e., that they lie in the external-bisecting position (III), rather than coplanar with any of the triangular faces which define the tetrahedral array. This observation should be useful in speculating successfully on the positions of hydride ligands in structural studies of clusters where they cannot (or *have* not) been located directly by crystallographic techniques.

C. The Terminal Ligands. The (ordered) carbonyl ligands appear all to be normal, the average C–O bond length being 1.135 [15] Å. The metal–carbon distances average 1.910 [24] Å, with those which are trans to a bridging hydride ligand being slightly shorter [Os–CO = 1.895 [16] Å] than those which are not [Os–CO = 1.933 [2] Å]. The difference is barely significant in terms of the associated esd's, but it is consistent with the idea that a OC–M–system will compete more effectively for π-electron density than will a bridging hydride ligand.

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(15) Part 1: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(16) Part 9: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161.

(17) Part 10: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 843.

(18) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36.

(19) The rotational orientation of bridging hydride ligands in tetrahedral clusters is discussed in detail in ref 16 and 17.

(20) Values in square brackets are esd' on average values, calculated via the "scatter formula" (see footnote to Table III).

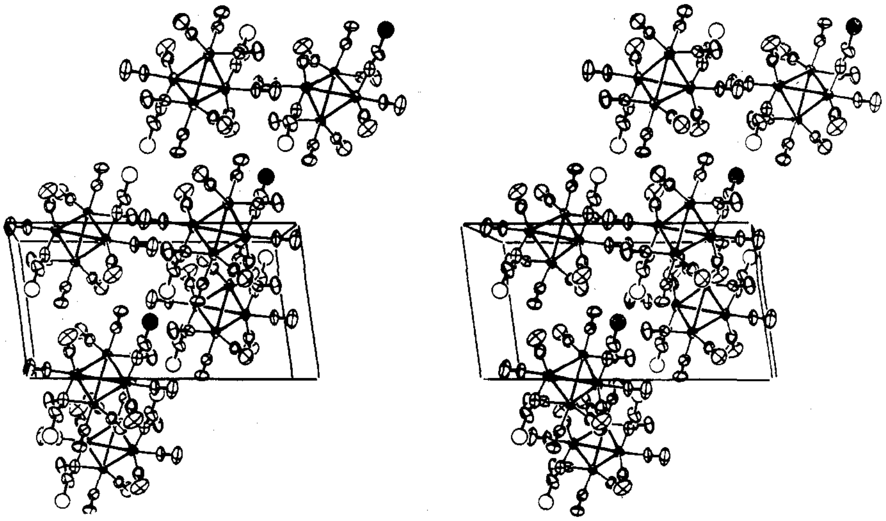

Figure 3. Stereoscopic view of the packing within the crystal, as viewed down the *b* axis (*c* is horizontal and *a* close to vertical). The methyl carbons of the isocyanide ligands corresponding to an ordered row (or "chain") in the [201] direction have been stippled (see text). Hydrogen atoms have been omitted for clarity.

Table V. Intramolecular Contacts <3.25 Å

atom 1···atom 2	symop[a]	dist, Å
$CH_3\cdots CH_3$	3 −1 1 0	2.372 (46)
O(12)···H(12)	2 1 0 0	2.89 (14)
O(13)···O(13)	2 1 0 0	2.972 (15)
O(13)···O(23)/N	5 0 −1 0	3.094 (15)
O(11)···O(21)	6 0 −1 0	3.113 (13)
O(11)···O(11)	7 0 0 1	3.168 (13)
O(13)···O(22)	7 0 0 0	3.196 (14)
O(11)···CH_3	6 −1 −1 0	3.227 (35)
(CH_3···O(23)/N)	3 −1 1 0	3.354 (34)

[a] The symop (symmetry operator) for the second atom is expressed as a number designating the symmetry operation followed by three numbers designating the number of unit cell translations, on the *a*, *b*, and *c* axes, respectively, which must be added following the symmetry operation. Symops: (1) x, y, x; (2) $-x, y, \frac{1}{2} - z$; (3) $-x, -y, -z$; (4) $x, -y, \frac{1}{2} + z$; (5) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (6) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (7) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (8) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

"Interatomic distances" within the disordered isocyanide/carbonyl system [Os(2)–C(23)/C = 1.968 (13) Å; C(23)/C–O(23)/N = 1.101 (18) Å; O(23)/N–CH_3 = 1.457 (35) Å] are reasonable, even though they are distorted by the overlap of the two ligand images. Upon the basis of the Os(2)–C(23)/C distance of 1.968 (13) Å and the average Os–CO distance of 1.910 [24] Å, one might estimate the correct Os–CNMe distance at ~2.03 ± 0.03 Å. This may be compared to observed values (in *polyhedral* osmium carbonyl clusters) of 2.00 (4) Å in $Os_6(CO)_{18}(CNC_6H_4Me)$[21] and 1.98 (2) and 1.89 (3) Å in $Os_6(CO)_{16}[CN(t\text{-}Bu)]_2$.[22]

D. Packing in the Crystal. Table V lists intermolecular contacts within the unit cell. There is only one abnormally short "contact"—of 2.37 (5) Å between methyl groups of isocyanide ligands in neighboring molecules. This short contact (as can clearly be seen in Figure 3) is across a crystallographic inversion center. As there exists a crystallographic twofold axis through the molecule, a similar contact must occur on the other side of the molecule and so forth, in a chain. These infinite chains extend along the [201] direction in the real cell. The crystal structure may be visualized as numbers of these infinite chains stacked side by side.

Now the intermolecular distances and relationships are such that it is necessary for there to be a cooperative ordering of the molecules such that *within a given "chain"* the isocyanide ligands of the $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$ molecule *all point in the same direction.* This removes the anomalously short Me···Me contact of 2.37 (5) Å and substitutes for it a CNMe···OC contact of 3.35 (3) Å. Such a cooperative chain is shown in Figure 3.

Note that a structure in which all chains pointed in the same direction (e.g., to the upper right in Figure 3) would not belong to the centrosymmetric space group *C*2/*c* but would be describable in the polar, acentric *Cc*. However, inspection of Table V reveals that there are no other strong interactions involving the disordered isocyanide/carbonyl system. Thus, while there must be very strong cooperative influence within the rows (it being essentially impossible to reverse except at a grain boundary), there is no reason to expect cooperative behavior between adjacent chains. The successful solution of the structure with low residuals, plus the evident problem of peak shape of reflections along the *a** (as opposed to *b** and *c**) direction, confirms the prediction that no strong interchain cooperative behavior is present and that the crystal contents define an averaged structure conforming to the centrosymmetric space group *C*2/*c*.

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Registry No. $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$, 72332-24-2.

Supplementary Material Available: Listings of crystallographic data processing formulas and observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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