The higher field one with larger coupling to ^{195}Pt is assigned to P^2 trans to oxygen, which exerts a weaker trans influence than the carbon atom. Splitting of this signal due to coupling to ^{19}F also conforms to this assignment. The expected quartet structure is not so certain, but the $^5J(F-P^2)$ value of 1.2 Hz coincides well with 1.1 Hz observed in the ^{19}F spectrum.

The ^{195}Pt NMR spectrum in Figure 5 is composed of double doublets of quartets in accordance with the proposed structure. The coupling constants to ^{31}P and ^{19}F nuclei coincide exactly with those obtained from respective NMR spectra. In the case of **2** and **3**, on the other hand, the expected quartet structure due to coupling to ^{19}F is not observed, but the signal for **2** appears as double doublets and that for **3** as a singlet, both being broad.[22]

Acknowledgment. We are grateful to Mr. J. Gohda for the elemental analysis and also to the Ministry of Education, Japan, for a grant-in-aid (Grant No. 243014).

Registry No. **1**, 67560-32-1; **2**, 76705-35-6; **3**, 67560-33-2; *cis*-[Pt(tfac)$_2$], 67596-99-0; *trans*-[Pt(tfac)$_2$], 76740-70-0.

---

[22] Very recently we have succeeded in preparing several palladium(II) complexes containing the trifluoroacetylacetonate dianion, of which the C,O-chelate structure was confirmed by X-ray analysis of [Pd(tfac-(2−)-*C,O*)PPh$_3$(2,6-Me$_2$-py)]: Kanehisa, N.; Miki, K.; Kasai, N.; Matsumoto, S.; Kawaguchi, S.; Okeya, S. 27th Symposium on Organometallic Chemistry in Japan, Tokyo, 1980; Abstracts, p 73.

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

Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 17.[1] $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$

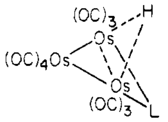
MELVYN ROWEN CHURCHILL* and HARVEY J. WASSERMAN

Received October 1, 1980

A single-crystal X-ray structural analysis has been performed on the complex $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$. This compound crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 9.401 (2) Å, b = 13.463 (4) Å, c = 18.110 (6) Å, β = 99.85 (2)°, V = 2258 (1) Å^3, and Z = 4. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was refined to R_F = 5.4% and R_{wF} = 4.4% for those 2636 reflections with $F_o > \sigma(F_o)$ and $2\theta < 45°$ [Mo Kα radiation]. The molecule consists of a triangular cluster of osmium atoms two of which [Os(1) and Os(3)] are each associated with three terminal carbonyl ligands, while the third [Os(2)] is associated with four. In addition atoms Os(1) and Os(3) are mutually bridged by a hydride ligand (which was located and refined during the course of the analysis) and by a >N=N(p-tol) (p-tol = p-tolyl) ligand. The nonbridged osmium–osmium bond lengths are Os(1)–Os(3) = 2.834 (1) Å and Os(2)–Os(3) = 2.855 (1) Å, while the dibridged Os(2)–Os(3) distance is reduced to 2.823 (1) Å. The osmium–(μ-hydride) distances are equivalent with Os(1)–H = 1.97 (12) Å and Os(3)–H = 2.01 (12) Å. The N(1)–N(2) linkage in the >N=N(p-tol) ligand is 1.238 (18) Å in length—consistent with retention of a formal double bond.

Introduction

For some time we have been interested in the structural chemistry of polynuclear osmium carbonyl hydrides. A particular point of interest has been the geometry of the Os(μ-H)(μ-X)Os bridge in molecules of stoichiometry $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$.[2-7] [Our nomenclature is that X is the bridgehead atom of the uninegatively charged bridging ligand L.] Such molecules have the general core structure I.



I

Table I. Experimental Data for the X-ray Diffraction Study of $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$

(A) Crystal Parameters[a] at 24 °C

crystal system: monoclinic	a = 9.401 (2) Å
space group: $P2_1/n$[b]	b = 13.463 (4) Å
mol wt = 970.6	c = 18.110 (6) Å
ρ(calcd) = 2.86 g/cm^3	β = 99.85 (2)°
Z = 4	V = 2258 (1) Å^3

(B) Intensity Data

radiation: Mo Kα [$\bar{\lambda}$ = 0.710 730 Å]
monochromator: highly oriented graphite
reflctns measd: $+h,+k,\pm l$
2θ range: 3.5–45.0°
scan type: θ(crystal)–2θ(counter)
scan speed: 2.0°/min
scan range: $[2\theta(K\alpha_1) - 0.9]° \rightarrow [2\theta(K\alpha_2) + 0.9]°$
bkgd measmnt: at beginning and end of scan; each for $^1/_3$ of the total scan time
stds: $4\bar{2}2$, 006, and 263 measured every 47 reflections; no significant deviations
reflctns colltd: 3189 total, yielding 2976 independent
abs coeff: 179.0 cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 15 reflections with 2θ = 20–30°. [b] Nonstandard setting of the space group $P2_1/c$ [C_{2h}^5, No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$.

We have previously examined the species $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-NHSO}_2(p\text{-tol})]$, which has a saturated (4-coordinate) nitrogen present in the Os(μ-H)(μ-N)Os core,[7] and now

---

[1] Part 16, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})$: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391–2395.

[2] Part 2, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141–1146.

[3] Part 5, $(\mu\text{-H})_2Os_3(CO)_{10}$: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697–2700.

[4] Part 11, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH=NEt}_2)$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848–853.

[5] Part 12, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-Cl})$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–1930.

[6] Part 13, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-Br})$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261–3267.

[7] Part 15, $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-NHSO}_2(p\text{-tol})]$: Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Keister, J. B. *Inorg. Chem.* **1980**, *19*, 1272–1277.

report the results of a structural study on $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$ in which an unsaturated (3-coordinate) nitrogen atom is associated with the $Os(\mu\text{-H})(\mu\text{-N})Os$ core.

This species may be prepared as in eq 1.[8] It is of additional

$$(\mu\text{-H})_2Os_3(CO)_{10} + [(p\text{-tol})N_2^+][BF_4^-] \xrightarrow[\text{(2) dry } NH_3(g)]{\text{(1) }\Delta/CH_2Cl_2\text{ solution}} (\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})] + [NH_4^+][BF_4^-] \quad (1)$$

interest as one of a rather limited number of known complexes with a bridging diazo RN=N group.

Experimental Section

A. Data Collection. Yellow-brown crystals of $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$ were provided by Professor J. R. Shapley of the University of Illinois at Urbana—Champaign. An approximately cube-shaped specimen, 0.17 mm along a side, was cleaved from a larger brick-shaped crystal. This was fit into a 0.2-mm diameter thin-walled glass capillary which was set into a eucentric goniometer head and transferred to a Syntex $P2_1$ automated four-circle diffractometer. Determination of cell parameters, the orientation matrix, and data collection were carried out as described earlier.[9] Details are in Table I. During data collection, the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ were observed, indicating the space group $P2_1/n$ (C_{2h}^5; an alternative setting of $P2_1/c$).

Data were averaged, corrected for Lorentz, polarization, and absorption effects, and reduced to (unscaled) observed structure factor amplitudes.

B. Solution and Refinement of the Structure. All calculations were performed with use of the Syntex XTL Structure Determination System which consists of an in-house Data General NOVA 1200 computer with 24K of 16-bit word memory, a Diablo disk unit of 1.2 million 16-bit words, and a locally modified version of the XTL conversational crystallographic program package.

An approximate scale factor and overall isotropic thermal parameter were obtained from a Wilson plot. A Patterson map yielded the positions of the three osmium atoms. Two cycles of least-squares refinement of positional and anisotropic thermal parameters for the osmium atoms led to $R_F = 12.5\%$ and $R_{wF} = 17.9\%$. A difference-Fourier synthesis now yielded the positions of all remaining nonhydrogen atoms. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all atoms except carbon atoms of the carbonyl groups, for which isotropic temperature factors were used, led to the residuals $R_F = 4.9\%$ and $R_{wF} = 4.9\%$ for those 2378 reflections with $F_o > 3\sigma(F_o)$.

An attempt to find the position of the bridging hydride was now made, via two difference-Fourier syntheses. The first, based upon all data, contained peaks up to 0.98 e A^{-3} in height but none was near the position where the bridging hydride was expected. The second, based upon only those data with $(\sin\theta)/\lambda < 0.30$ Å^{-1}, yielded a peak of height 0.40 e Å^{-3} close to the idealized position for a μ-hydride ligand. This was included in the model with an isotropic thermal parameter fixed at 2.5 Å^2. The four phenyl hydrogen atoms were also included in their idealized positions (d(C–H) = 0.95 Å)[10] with their isotropic thermal parameters set at 7.0 Å^2.

A comparison of observed vs. calculated structure factor amplitudes indicated the necessity of a correction for secondary extinction. All data were corrected by applying an empirical correction of the form shown in eq 2, where the factor K was found, graphically, to have a value of 2.46×10^{-7}.

$$F_o^{\text{cor}} = F_o^{\text{uncor}}(1.0 + kI_o) \quad (2)$$

Continued refinement led to convergence with $R_F = 5.4\%$, $R_{wF} = 4.4\%$, and GOF = 1.512 for those 2636 reflections with $F_o > \sigma(F_o)$. ($R_F = 6.6\%$, $R_{wF} = 4.5\%$ for all 2976 data).

A final difference-Fourier synthesis showed peaks of height 1.01–1.49 e Å^{-3} around the osmium atoms. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme is therefore correct. The final NO:NV ratio was 2636:242 or approximately 10.9:1.

Table II. Final Positional Parameters, with Esd's for $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$

atom	x	y	z	B_{iso}, Å^2
Os1	0.43763 (6)	0.28015 (5)	0.13691 (4)	
Os2	0.21661 (7)	0.26353 (5)	0.00978 (4)	
Os3	0.15882 (7)	0.21939 (5)	0.15598 (4)	
H(Os)	0.358 (13)	0.162 (9)	0.179 (7)	2.5
N1	0.2742 (11)	0.3490 (8)	0.1775 (7)	
N2	0.2662 (13)	0.4320 (10)	0.2059 (8)	
C(1)	0.127 (2)	0.4562 (13)	0.2286 (10)	
C(2)	0.027 (2)	0.5121 (14)	0.1822 (11)	
C(3)	−0.101 (2)	0.5358 (14)	0.2019 (12)	
C(4)	−0.137 (2)	0.5049 (15)	0.2691 (12)	
C(5)	−0.038 (2)	0.4483 (14)	0.3172 (11)	
C(6)	0.099 (2)	0.4255 (13)	0.2980 (11)	
C(7)	−0.281 (2)	0.529 (2)	0.2907 (14)	
C11	0.520 (2)	0.3945 (13)	0.1002 (10)	3.9 (4)
O11	0.5708 (14)	0.4637 (10)	0.0785 (8)	
C12	0.555 (2)	0.1940 (13)	0.0868 (10)	4.2 (4)
O12	0.6162 (15)	0.1473 (10)	0.0507 (9)	
C13	0.566 (2)	0.2771 (12)	0.2294 (10)	3.6 (3)
O13	0.647 (2)	0.2826 (10)	0.2840 (8)	
C21	0.337 (2)	0.2903 (14)	−0.0624 (11)	5.1 (4)
O21	0.4035 (15)	0.3057 (11)	−0.1081 (8)	
C22	0.263 (2)	0.125 (2)	0.0109 (11)	5.2 (4)
O22	0.292 (2)	0.0428 (10)	0.0072 (8)	
C23	0.026 (3)	0.239 (2)	−0.0424 (14)	7.0 (5)
O23	−0.084 (2)	0.2305 (14)	−0.0823 (11)	
C24	0.188 (2)	0.4014 (14)	0.0256 (10)	4.0 (4)
O24	0.1739 (14)	0.4864 (10)	0.0303 (8)	
C31	0.090 (2)	0.0882 (14)	0.1237 (11)	4.6 (4)
O31	0.049 (2)	0.0128 (10)	0.1045 (10)	
C32	0.160 (2)	0.1851 (14)	0.2600 (11)	4.5 (4)
O32	0.1592 (15)	0.1659 (10)	0.3202 (8)	
C33	−0.034 (2)	0.2725 (13)	0.1356 (10)	4.4 (4)
O33	−0.1467 (14)	0.3016 (12)	0.1196 (11)	
H(2)	0.0475	0.5343	0.1354	7.0
H(3)	−0.1678	0.5748	0.1688	7.0
H(5)	−0.0617	0.4246	0.3630	7.0
H(6)	0.1705	0.3902	0.3318	7.0
H(7A)	−0.2855	0.5019	0.3384	7.0
H(7B)	−0.3561	0.5023	0.2545	7.0
H(7C)	−0.2916	0.5995	0.2925	7.0

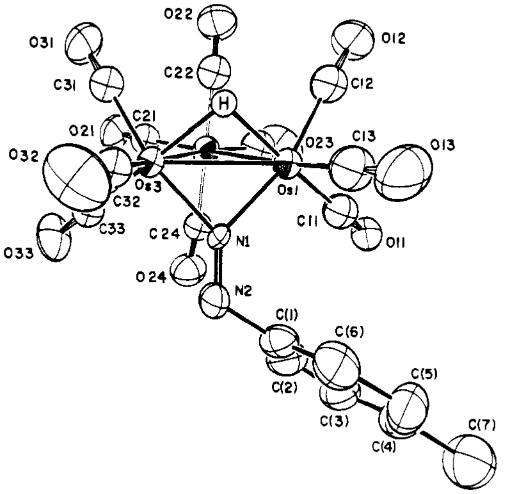


Figure 1. Overall geometry and atomic labeling scheme for the $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$ molecule.

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

Results

The crystal is composed of discrete molecular units of $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$, which are mutually separated by normal van der Waals distances. The geometry of the $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$ molecule and the system

---

[8] Samkoff, D. E.; Shapley, J. R., to be submitted for publication.

[9] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

[10] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

Table III. Anisotropic Thermal Parameters[a] (Å^2) for (μ-H)Os$_3$(CO)$_{10}$[μ-N=N(p-tol)]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os1	2.39 (3)	3.05 (3)	3.65 (3)	0.09 (2)	0.62 (2)	−0.11 (3)
Os2	3.25 (3)	4.28 (4)	3.78 (4)	−0.06 (3)	0.34 (2)	−0.67 (3)
Os3	2.81 (3)	3.07 (3)	4.81 (4)	−0.26 (2)	1.29 (3)	−0.49 (3)
N1	1.9 (6)	1.9 (6)	5.1 (8)	0.3 (4)	1.7 (5)	−0.2 (5)
N2	2.5 (6)	3.3 (7)	5.3 (8)	−0.0 (5)	0.8 (5)	−0.3 (6)
C(1)	3.0 (8)	4.0 (8)	3.7 (9)	0.3 (7)	−0.1 (7)	−1.2 (7)
C(2)	6.3 (12)	4.6 (10)	5.1 (11)	0.6 (9)	1.5 (9)	−0.7 (8)
C(3)	4.5 (10)	4.8 (10)	6.2 (13)	0.9 (8)	1.3 (9)	−1.2 (9)
C(4)	3.9 (9)	4.9 (10)	6.0 (12)	0.6 (8)	1.7 (9)	−1.5 (9)
C(5)	6.0 (11)	4.8 (10)	5.2 (12)	0.9 (9)	3.2 (9)	0.8 (8)
C(6)	5.3 (11)	3.9 (9)	5.2 (11)	0.3 (8)	1.0 (9)	0.7 (8)
C(7)	4.4 (11)	8.1 (14)	9.1 (16)	0.7 (9)	2.7 (10)	−1.6 (12)
O11	5.8 (8)	5.7 (7)	7.8 (9)	−1.3 (6)	1.6 (6)	3.1 (7)
O12	5.8 (8)	6.7 (8)	9.5 (11)	0.2 (6)	3.8 (7)	−2.3 (7)
O13	8.8 (10)	7.2 (9)	5.1 (8)	−1.2 (7)	−0.8 (7)	0.0 (7)
O21	6.6 (8)	8.4 (9)	7.0 (9)	−0.7 (7)	3.5 (7)	−1.4 (7)
O22	8.5 (10)	5.1 (7)	8.1 (10)	−0.3 (7)	3.2 (8)	−2.1 (7)
O23	7.3 (10)	11.8 (13)	12.0 (14)	−1.8 (9)	−5.3 (10)	0.3 (11)
O24	7.1 (8)	5.1 (7)	6.5 (9)	1.0 (6)	1.6 (7)	0.5 (6)
O31	7.3 (9)	3.9 (7)	13.8 (13)	−2.9 (6)	4.1 (9)	−3.7 (8)
O32	7.4 (8)	6.1 (7)	4.6 (7)	1.1 (6)	2.6 (6)	0.5 (6)
O33	2.3 (6)	9.0 (10)	15.7 (15)	0.4 (6)	−0.1 (7)	−2.6 (10)

[a] The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

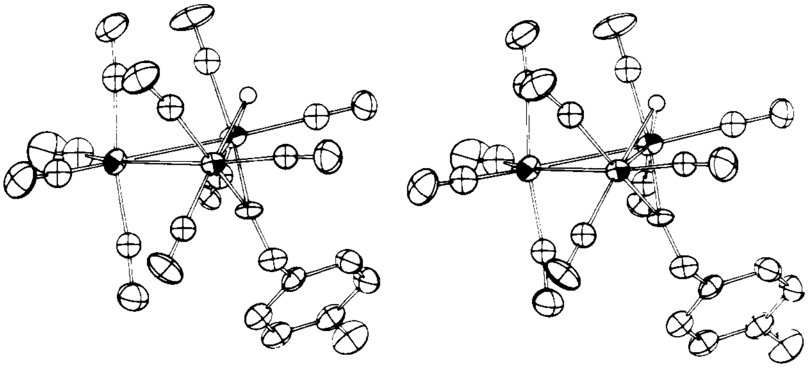


Figure 2. Stereoscopic view of the (μ-H)Os$_3$(CO)$_{10}$[μ-N=N(p-tol)] molecule.

Table IV. Interatomic Distances (Å), with Esd's, for (μ-H)Os$_3$(CO)$_{10}$[μ-N=N(p-tol)]

(A) Osmium-Osmium Distances			
Os(1)-Os(2)	2.834 (1)	Os(1)-Os(3)	2.823 (1)
Os(2)-Os(3)	2.855 (1)		
(B) Osmium-Bridging Ligand Distances			
Os(1)-N(1)	2.036 (11)	Os(1)-H(Os)	1.97 (12)
Os(3)-N(1)	2.056 (11)	Os(3)-H(Os)	2.01 (12)
(C) Osmium-Carbonyl Distances			
Os(1)-C(11)	1.895 (17)	Os(2)-C(23)	1.906 (25)
Os(1)-C(12)	1.928 (18)	Os(2)-C(24)	1.905 (18)
Os(1)-C(13)	1.891 (18)	Os(3)-C(31)	1.936 (19)
Os(2)-C(21)	1.906 (20)	Os(3)-C(32)	1.938 (20)
Os(2)-C(22)	1.914 (21)	Os(3)-C(33)	1.922 (19)
(D) Carbon-Oxygen Distances			
C(11)-O(11)	1.145 (22)	C(23)-O(23)	1.166 (31)
C(12)-O(12)	1.135 (23)	C(24)-O(24)	1.157 (23)
C(13)-O(13)	1.142 (23)	C(31)-O(31)	1.121 (24)
C(21)-O(21)	1.137 (25)	C(32)-O(32)	1.121 (24)
C(22)-O(22)	1.146 (25)	C(33)-O(33)	1.122 (23)
(E) Distances within the N=N(p-tol) Ligand			
N(1)-N(2)	1.238 (18)	C(4)-C(5)	1.389 (28)
N(2)-C(1)	1.470 (21)	C(5)-C(6)	1.431 (29)
C(1)-C(2)	1.378 (27)	C(6)-C(1)	1.389 (26)
C(2)-C(3)	1.347 (29)	C(4)-C(7)	1.507 (28)
C(3)-C(4)	1.381 (30)		

used for numbering the atoms is shown in Figure 1; Figure 2 presents a stereoscopic view of the molecule. Interatomic distances and their estimated standard deviations (esd's) are shown in Table IV, bond angles (with esd's) are given in Table V, and important intramolecular planes are listed in Table VI.

The molecule is based upon a triangular arrangement of osmium atoms, one of which [Os(2)] is associated with four terminal carbonyl ligands, while the other two osmium atoms [Os(1) and Os(3)] are each linked to three terminal carbonyl ligands and are mutually bridged both by a hydride and by a >N=N(p-tol) ligand. The (μ-H)Os$_3$(CO)$_{10}$ portion of the molecule has approximate (but not exact) $C_s(m)$ symmetry; however, as is clearly shown in Figure 1, this symmetry does not extend to include the bridging >N=N(p-tol) ligand.

Within the triosmium system, the doubly bridged Os(1)-Os(3) bond length is 2.823 (1) Å, i.e., 0.022 Å *shorter* than the average nonbridged distance of 2.845 [14] Å[11] [Os(1)-Os(2) = 2.834 (1) Å and Os(2)-Os(3) = 2.855 (1) Å].

The μ-hydride ligand, which was located and refined (vide supra), bridges the Os(1)-Os(3) system in a symmetrical manner with Os(1)-H = 1.97 (12) Å, Os(3)-H = 2.01 (12) Å, and ∠Os(1)-H-Os(3) = 90 (5)°. These osmium-(bridging hydride) distances are consistent with the more precise values for such systems as determined via neutron diffraction studies, viz., 1.840 (3)-1.852 (3) Å in (μ-H)$_2$Os$_3$(CO)$_{10}$,[12] 1.754 (8)-1.883 (9) Å in (μ-H)$_2$Os$_3$(CO)$_{10}$(μ-CH$_2$),[13] and 1.813

---

[11] Within the text, esd's of average values are given in square brackets; these are calculated with the use of the "scatter formula" $[\sigma] = [\sum_N (d_i - \bar{d})^2/(N-1)]^{1/2}$

Table V. Interatomic Angles (Deg) with Esd's for $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$

(A) Osmium-Osmium-Osmium Angles			
Os(3)-Os(1)-Os(2)	60.62 (2)	Os(2)-Os(3)-Os(1)	59.88 (2)
Os(1)-Os(2)-Os(3)	59.50 (2)		
(B) Angles Involving the Bridging Ligands			
Os(1)-N(1)-Os(3)	87.2 (5)	Os(1)-H(Os)-Os(3)	90 (5)
N(1)-Os(1)-Os(3)	46.7 (3)	H(Os)-Os(1)-Os(3)	45 (4)
N(1)-Os(3)-Os(1)	46.1 (3)	H(Os)-Os(3)-Os(1)	44 (4)
N(1)-Os(1)-C(11)	97.9 (6)	H(Os)-Os(1)-C(12)	89 (4)
N(1)-Os(1)-C(12)	165.9 (6)	H(Os)-Os(1)-C(11)	177 (4)
N(1)-Os(1)-C(13)	95.6 (6)	H(Os)-Os(1)-C(13)	82 (4)
N(1)-Os(1)-Os(2)	80.5 (3)	H(Os)-Os(1)-Os(2)	89 (4)
N(1)-Os(3)-Os(2)	79.7 (3)	H(Os)-Os(3)-Os(2)	88 (4)
N(1)-Os(3)-C(31)	165.6 (7)	H(Os)-Os(3)-C(33)	178 (4)
N(1)-Os(3)-C(32)	95.9 (7)	H(Os)-Os(3)-C(32)	82 (4)
N(1)-Os(3)-C(33)	99.8 (6)	H(Os)-Os(3)-C(31)	88 (4)
N(1)-Os(1)-H(Os)	82 (4)	N(1)-Os(3)-H(Os)	81 (4)
(C) Osmium-Osmium-Carbonyl Angles			
Os(2)-Os(1)-C(11)	93.8 (5)	Os(1)-Os(3)-C(31)	119.7 (6)
Os(2)-Os(1)-C(12)	88.2 (5)	Os(1)-Os(3)-C(32)	109.8 (6)
Os(2)-Os(1)-C(13)	170.6 (5)	Os(1)-Os(3)-C(33)	137.1 (5)
Os(3)-Os(1)-C(11)	136.3 (5)	Os(2)-Os(3)-C(31)	90.0 (6)
Os(3)-Os(1)-C(12)	120.0 (5)	Os(2)-Os(3)-C(32)	168.8 (6)
Os(3)-Os(1)-C(13)	110.6 (5)	Os(2)-Os(3)-C(33)	93.8 (5)
Os(1)-Os(2)-C(21)	95.9 (6)	Os(3)-Os(2)-C(21)	154.9 (6)
Os(1)-Os(2)-C(22)	86.2 (6)	Os(3)-Os(2)-C(22)	82.3 (6)
Os(1)-Os(2)-C(23)	155.9 (7)	Os(3)-Os(2)-C(23)	96.4 (7)
Os(1)-Os(2)-C(24)	84.5 (5)	Os(3)-Os(2)-C(24)	90.5 (5)
(D) Carbonyl-Osmium-Carbonyl Angles			
C(11)-Os(1)-C(12)	91.3 (8)	C(31)-Os(3)-C(32)	91.3 (8)
C(11)-Os(1)-C(13)	95.2 (8)	C(31)-Os(3)-C(33)	91.6 (8)
C(12)-Os(1)-C(13)	94.3 (8)	C(32)-Os(3)-C(33)	97.1 (8)
C(21)-Os(2)-C(22)	91.7 (9)	C(22)-Os(2)-C(23)	91.5 (9)
C(21)-Os(2)-C(23)	108.2 (9)	C(22)-Os(2)-C(24)	170.3 (8)
C(21)-Os(2)-C(24)	92.1 (8)	C(23)-Os(2)-C(24)	95.9 (8)
(E) Osmium-Carbon-Oxygen Angles			
Os(1)-C(11)-O(11)	179 (2)	Os(2)-C(23)-O(23)	170 (2)
Os(1)-C(12)-O(12)	172 (2)	Os(2)-C(24)-O(24)	174 (2)
Os(1)-C(13)-O(13)	174 (2)	Os(3)-C(31)-O(31)	178 (2)
Os(2)-C(21)-O(21)	176 (2)	Os(3)-C(32)-O(32)	179 (2)
Os(2)-C(22)-O(22)	175 (2)	Os(3)-C(33)-O(33)	176 (2)
(F) Angles within the N=N(*p*-tol) Ligand			
N(1)-N(2)-C(1)	116 (1)	N(1)-C(1)-C(2)	119 (1)
C(1)-C(2)-C(3)	121 (2)	C(4)-C(5)-C(6)	120 (2)
C(2)-C(3)-C(4)	121 (2)	C(5)-C(6)-C(1)	118 (2)
C(3)-C(4)-C(5)	119 (2)	C(6)-C(1)-C(2)	121 (2)

(4)–1.887 (4) Å in $(\mu\text{-H})Os_3(CO)_{10}(\sigma,\pi\text{-CH=CH}_2)$.[14]

The Os(1)–H–Os(3) bridge makes an angle of 121.45° with the triosmium plane and an angle of 132.81° with the Os(1)–N(1)–Os(3) bridge.

The Os(1)–N(1)–Os(3) bridge makes an angle of 105.74° with the triosmium plane; this bridge has ∠Os(1)–N(1)–Os(3) = 87.2 (5)° and is symmetrical within the limits of experimental error [Os(1)–N(1) = 2.036 (11) Å, Os(3)–N(1) = 2.056 (11) Å, and Os–N(average) = 2.046 [14] Å]. These bridging Os–N(sp^2) distances in $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$ are thus more than 0.1 Å *shorter* than the bridging Os–N(sp^3) distances found in $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-NHSO}_2(p\text{-tol})]$ [Os–N = 2.145 (7) and 2.162 (7) Å; average = 2.154 [12] Å].[7] This change is, however, associated with variation in the bridging Os–N–Os angle (87.2 (5) and 81.6 (2)°, respectively) rather than with any substantial change in the dibridged Os–Os bond length (2.823 (1) and 2.814 (1) Å, respectively). Indeed, the Os–Os distance associated with the shorter Os–N(sp^2) bonds in $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$ is marginally *longer* than that associated with the longer Os–N(sp^3) bonds in $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-NHSO}_2(\pi\text{-tol})]$. This perhaps is due to a decreased degree of strain at nitrogen in the Os–N(sp^2)–Os vs. the Os–N(sp^3)–Os system.

Table VI.

Selected Planes and Deviations (Å) of Atoms Therefrom[a]

Plane I:[b] $0.2771X - 0.9543Y - 0.1116Z = -2.8494$			
Os(1)*[b]	0.000	O(13)	0.095 (4)
Os(2)*	0.000	C(21)	0.176 (19)
Os(3)*	0.000	O(21)	0.282 (15)
H(Os)[b]	1.20 (12)	C(22)	1.897 (21)
N(1)	−1.425 (11)	O(22)	3.041 (14)
N(2)	−2.594 (3)	C(23)	−0.026 (23)
C(11)	−1.149 (17)	O(23)	−0.097 (18)
O(11)	−1.845 (13)	C(24)	−1.892 (18)
C(12)	1.555 (18)	O(24)	−3.034 (14)
O(12)	2.417 (14)	C(31)	1.599 (19)
C(13)	0.110 (16)	O(31)	2.514 (13)
C(32)	0.147 (18)	C(33)	−1.126 (18)
O(32)	0.220 (14)	O(33)	−1.748 (16)
Plane II: $-0.2170X + 0.3287Y - 0.9192Z = -1.8066$			
Os(1)*	0.000	C(12)	0.167 (18)
Os(3)*	0.000	O(12)	0.403 (15)
N(1)*	0.000	C(31)	0.068 (14)
H(Os)	−1.02 (12)	O(31)	0.120 (17)
Os(2)	2.3769 (7)		
Plane III: $0.0189X - 0.4361Y - 0.8997Z = -3.7731$			
Os(1)*	0.000	C(11)	−0.065 (17)
Os(3)*	0.000	O(11)	−0.114 (14)
H(Os)*	0.000	C(33)	−0.018 (18)
N(1)	−1.087 (13)	O(33)	−0.050 (19)
Os(2)	2.1067 (7)		
Plane IV: $-0.3257X - 0.8404Y - 0.4332Z = -7.1016$			
C(1)	0.013 (17)	C(4)	0.000 (20)
C(2)	0.001 (20)	C(5)	0.014 (19)
C(3)	−0.009 (19)	C(6)	−0.021 (18)

Dihedral Angles, Deg

plane I–plane II	105.74 (74.26)
plane I–plane III	121.45 (58.55)
plane II–plane III	132.81 (47.19)
plane I–plane IV	139.47 (40.53)

[a] Equations of planes are expressed in orthonormal coordinates.
[b] All atoms marked with an asterisk were given unit weight in the corresponding plane, all others given zero weight.

Within the μ-N=N(*p*-tol) ligand, the N(1)–N(2) bond length is 1.238 (18) Å, consistent with its assignment as a N=N double bond and comparable to that found in $[PhN{=}NMn(CO)_4]_2$ (N=N = 1.233 (2) Å).[15] The atom N(2) is linked to the *p*-tolyl group via N(2)–C(1) = 1.470 (21) Å, with ∠N(1)–N(2)–C(1) = 116 (1)°. The aromatic ring of the *p*-tolyl group makes an angle of 139.47° with the triosmium plane. The orientation of the *p*-tolyl group destroys the potential C_s symmetry of the molecule since it lies essentially under Os(1).

All distances and angles within the $Os_3(CO)_{10}$ framework are both self-consistent and normal. Thus, Os–CO distances lie in the range 1.891 (18)–1.938 (20) Å, C–O distances are 1.121 (24)–1.166 (31) Å, and Os–C–O angles vary from 170 (2) to 179 (2)°.

Os(μ-H)(μ-X)Os Bridges in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$ Molecules

Information on these species is presented in Table VII. Most of the results are from diffraction studies in our own laboratories,[1,2,4-7] but the values used for $(\mu\text{-H})_2Os_3(CO)_{10}$ are from the neutron diffraction study by Broach and Williams,[13]

---

(12) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314–319.
(13) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319–323.
(14) Orpen, A. G.; Rivera, A. V.; Bryan, E. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc., Chem. Commun.* **1978**, 723–724.
(15) Churchill, M. R.; Lin, K.-K. G. *Inorg. Chem.* **1975**, *14*, 1133–1138.

Table VII. Dimensions within $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$ Molecules

μ-L	bridgehead atom (X)	Os-X, Å	Os-X-Os, deg	Os-Os, Å		Δ,[a] Å
				bridged	nonbridged	
μ-H[12]	H	1.845 [3]	94.3 [18]	2.683 (1)	2.815 [1]	−0.132
μ-N=N(*p*-tol)	N(sp^2)	2.046 [14]	87.2 (5)	2.823 (1)	2.845 [14]	−0.022
μ-OMe[1]	O	2.103 [13]	83.9 (2)	2.812 (1)	2.818 [6]	−0.006
μ-$NHSO_2$(*p*-tol)[7]	N(sp^3)	2.154 [12]	81.6 (2)	2.814 (1)	2.853 [8]	−0.039
μ-CHCH=NEt_2[4]	C	2.155 [7]	80.6 (9)	2.785 (2)	2.868 [3]	−0.083
μ-$CHCH_2PMe_2Ph$[2]	C	2.161 [18]	80.8 (3)	2.800 (1)	2.871 [3]	−0.071
μ-SEt[16]	S	2.40 [1]	73.1 (3)	2.863 (2)	2.849 [10]	+0.014
μ-S(1)–CH_2–S(2)-μ[17]	S(2)	2.409 [8]		2.867 (1)	2.863 [13]	+0.004
	S(1)	2.415 [6]		2.871 (1)	2.875 [0]	−0.004
μ-Cl[5]	Cl	2.456 [3]	70.8 (1)	2.846 (1)	2.833 [5]	+0.013
μ-Br[6] (mol "B")	Br(B)	2.583 [3]	67.65 (5)	2.876 (1)	2.836 [3]	+0.040
μ-Br[6] (mol "A")	Br(A)	2.587 [6]	66.87 (5)	2.851 (1)	2.843 [1]	+0.008

[a] Δ = (bridged Os–Os distance) − (nonbridged Os–Os distance).

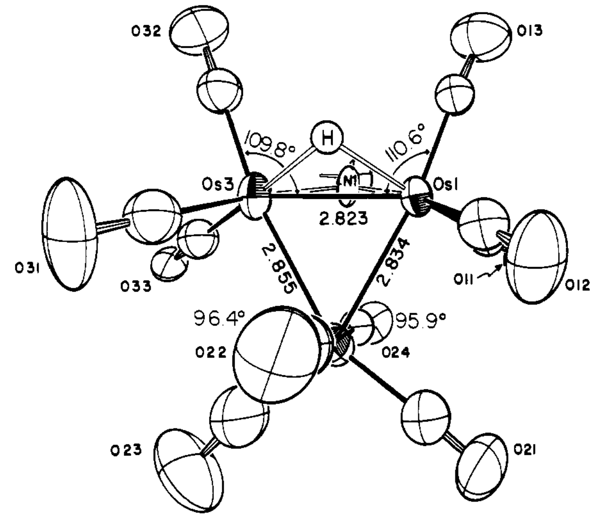


Figure 3. Important distances and angles within the equatorial (triosmium) plane.

and parameters for Os(μ-H)(μ-S)Os bridges are from the studies of Mason et al. on $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SEt})$[16] and of Adams et al. on $[(\mu\text{-H})Os_3(CO)_{10}]_2(\mu\text{-SCH}_2\text{S-}\mu)$.[17]

The following qualitative trends are listed in probable order of importance.

(1) The Os–X–Os angle decreases regularly with increasing Os–X distance. (This means that the μ-hydride ligand is acting so as to restrict any drastic increases in the dibridged Os–Os bond length.)

(2) The dibridged Os–Os bond length increases with increasing size of X (as judged either by Os–X distance or by covalent radius of X). This effect is far smaller that the first listed correlation.

(3) Changes in the nonbridged Os–Os distances are significant. Excluding the species $(\mu\text{-H})_2Os_3(CO)_{10}$, the nonbridged Os–Os distances tend to increase slightly with decreasing electronegativity of the bridgehead atom. However, the correlation is not absolute and the range of distances is rather small.

(4) The parameter Δ is negative for small bridgehead atoms [H and atoms of the first-row main-group elements (C, N, O)] and 0 or positive for larger bridgehead atoms (S, Cl, Br). Further studies on $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$ complexes having larger bridgehead atoms (X) and multiatom bridges are currently under way.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE79-24560, to M.R.C.).

Registry No. $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$, 76756-17-7.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

---

(16) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *144*, 297–307.

(17) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 1306–1307.