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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 18.[1,2] Molecular Geometry of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN}{=}CPh_2)$

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The complex $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN}{=}CPh_2)$ has been fully characterized by a single-crystal X-ray diffraction analysis. This species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 13.668$ (3) Å, $b = 12.015$ (2) Å, $c = 16.824$ (4) Å, $\beta = 101.31$ (2)°, $V = 2709$ (1) Å^3, and $Z = 4$. Diffraction data [Mo Kα radiation, $2\theta(\max) = 45°$] were collected with a Syntex P2$_1$ automated diffractometer, and the structure was refined by full-matrix least-squares methods to $R_F = 4.3\%$ and $R_{wF} = 3.5\%$ using all 3565 independent reflections. The complex contains a triangular cluster of osmium atoms in which Os(1) and Os(3) are each linked to three terminal carbonyl ligands while Os(2) is linked to four. Additionally, Os(1) and Os(3) are bridged by a hydride ligand (not located in the analysis) and by a $>$NHN=CPh$_2$ ligand. Nonbridged osmium–osmium bond lengths are 2.8468 (9) and 2.8421 (8) Å; the dibridged osmium–osmium distance is 2.7863 (8) Å. Osmium–nitrogen distances are 2.119 (7) and 2.121 (8) Å while the Os–N–Os angle is 82.2 (3)°.

Introduction

In the course of our continuing studies on osmium carbonyl hydride derivatives, we have examined crystallographically a number of species containing bridging organonitrogen ligands including $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}{=}NEt_2)$,[3] $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-NHSO}_2(p\text{-tol})]$,[4] and $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N}{=}N(p\text{-tol})]$.[1]

The reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with tosyl azide leads to loss of dinitrogen and formation of the saturated amido species $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-NHSO}_2(p\text{-tol})]$ (see above). In contrast to this, diphenyldiazomethane reacts with $(\mu\text{-H})_2Os_3(CO)_{10}$ to yield the unsaturated species $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN}{=}CPh_2)$, in which the dinitrogen fragment is retained[5a] (see eq 1). The complex can also be synthesized by the dehydrogenation of $Ph_2CHNHNH_2$ with $Os_3(CO)_{10}(L')_2$ (L' = loosely held ligand such as acetonitrile or cyclooctene).[5b] We now report the results of a single-crystal X-ray structural analysis on this complex.

$$(\mu\text{-H})_2Os_3(CO)_{10} + Ph_2C{=}N{=}N \rightarrow (\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN}{=}CPh_2) \quad (1)$$

The μ-NHN=CPh$_2$ ligand has previously been reported only in $Fe_2(CO)_6(\mu\text{-NHN}{=}CPh_2)_2$.[6]

Experimental Section

Collection of X-ray Diffraction Data. A sample consisting of yellow microcrystalline $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN}{=}CPh_2)$ was kindly supplied by Professor J. R. Shapley of the University of Illinois at Urbana—Champaign. The material was recrystallized by allowing a cyclohexane solution to evaporate slowly (about 1 week) at room temperature. Of the several large amber chunks obtained, one was cleaved to give a fragment of approximate dimensions 0.1 × 0.1 × 0.3 mm, which was used for the entire investigation. Mounted on a thin-glass fiber, the crystal was transferred to our Syntex P2$_1$ automated diffractometer. Crystal alignment, orientation matrix, and unit cell parameter determination as well as data collection were carried out as previously described.[7] See Table I for details specific to the current analysis.

An empirical absorption correction (based on a series of ψ scans) was applied to all data; the details of this method have been described previously.[8] The reflections used, their 2θ values, and their $I_{\max}/I_{\min}$ values, respectively, were as follows: $0\bar{4}1$, 13.78°, 1.28; $2\bar{5}1$, 18.37°, 1.20; $2\bar{6}0$, 21.30°, 1.23; $3\bar{7}1$, 25.87°, 1.20; $2\bar{8}1$, 28.23°, 1.23; $1\bar{9}1$, 31.12°, 1.30; $2,\overline{10},3$, 35.98°, 1.24; $1,\overline{11},4$, 39.54°, 1.30.

Table I. Experimental Data for the Diffraction Study of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN}{=}CPh_2)$[a]

(A) Crystal Parameters at 25 °C

$a = 13.6677$ (32) Å	mol wt 1047.0
$b = 12.0146$ (20) Å	ρ(calcd) = 2.57 g cm^{-3}
$c = 16.8235$ (43) Å	$Z = 4$
$\beta = 101.312$ (19)°	cryst system: monoclinic
$V = 2708.9$ (10) Å	space group: $P2_1/c$

(B) Measurement of Intensity Data

diffractometer: Syntex P2$_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710\,73$ Å)
monochromator: oriented graphite, equatorial; 2θ (mono) = 12.2°
reflctns measd: $+h,+k,\pm l$
2θ range: 3.5–45.0°
scan type: coupled θ(xtal)–2θ(counter)
scan speed: 2.00°/min in 2θ
scan width: $2\theta[(\text{Mo K}\alpha_1) - 1.00]° \rightarrow 2\theta[(\text{Mo K}\alpha_2) + 1.00]°$
bkgd measurement: stationary crystal–stationary counter at beginning and end of each scan, each for one-quarter total scan time
std reflctns: 10,0,0, $1\bar{7}0$, 1,2,10 measured after every 97 reflctns
reflctns collected: 3565 unique data
μ(calcd) = 149.3 cm^{-1}

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 25 reflections well scattered in reciprocal space with 2θ values between 26 and 33°.

Data reduction programs [including correction for absorption, Lorentz and polarization effects, redundant data averaging, and conversion to approximately scaled $|F_o|$ values (Wilson plot)] were from the SUNY-modified Syntex XTL interactive computational package and were performed on our Nova 1200 computer. All subsequent calculations were performed with the CDC 6600 computer of the Computer Center at SUNY at Buffalo, with use of software which has been described elsewhere.[9]

Analytical scattering factors for neutral atoms were taken from ref 10a; both real and imaginary components for anomalous dispersion were included[10b] for all nonhydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on standard counting statistics modified by an "ignorance" factor of $p = 0.04$.

A set of trial coordinates for three osmium atoms, obtained from a Patterson map, led to $R_F = 12.6\%$. Subsequent ΔF syntheses yielded

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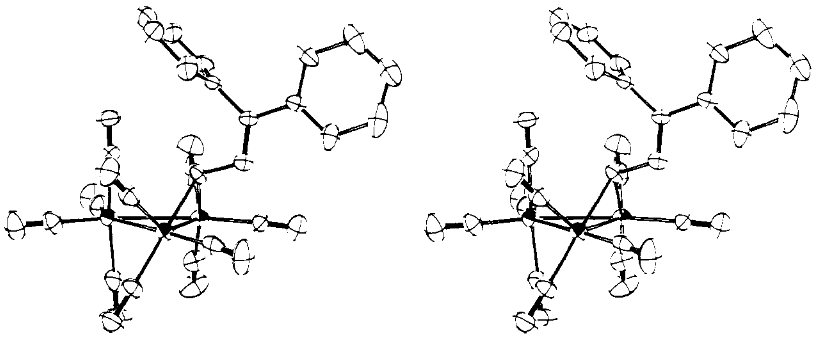

Figure 1. Stereoscopic view of the nonhydrogen atoms in the ($(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN{=}CPh}_2)$) molecule.

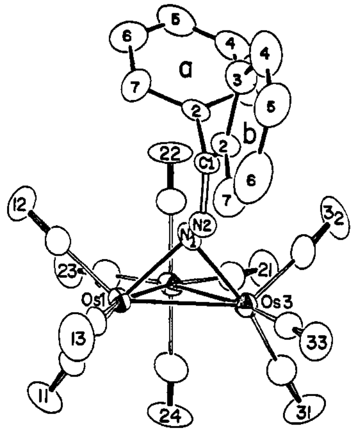

Figure 2. Labeling of nonhydrogen atoms within the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN{=}CPh}_2)$ molecule.

Table II. Final Positional Parameters with Esd's for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN{=}CPh}_2)$[a]

atom	*x*	*y*	*z*
Os(1)	0.30164 (3)	−0.02715 (4)	−0.14142 (2)
Os(2)	0.09299 (3)	−0.05900 (4)	−0.19718 (3)
Os(3)	0.23538 (3)	−0.16545 (4)	−0.27406 (3)
C(11)	0.2834 (8)	−0.0728 (10)	−0.0370 (7)
O(11)	0.2702 (7)	−0.1000 (8)	0.0249 (5)
C(12)	0.2932 (8)	0.1261 (10)	−0.1174 (7)
O(12)	0.2900 (7)	0.2198 (7)	−0.1054 (6)
C(13)	0.4436 (10)	−0.0328 (9)	−0.1149 (6)
O(13)	0.5297 (6)	−0.0360 (9)	−0.0925 (6)
C(21)	−0.0232 (9)	−0.1159 (11)	−0.2697 (8)
O(21)	−0.0931 (6)	−0.1419 (9)	−0.3127 (6)
C(22)	0.0963 (8)	0.0726 (10)	−0.2651 (8)
O(22)	0.0930 (7)	0.1487 (7)	−0.3023 (6)
C(23)	0.0387 (9)	0.0271 (11)	−0.1232 (8)
O(23)	0.0034 (7)	0.0807 (10)	−0.0779 (6)
C(24)	0.1060 (8)	−0.1923 (12)	−0.1299 (8)
O(24)	0.1136 (7)	−0.2690 (9)	−0.0894 (6)
C(31)	0.1789 (9)	−0.3057 (11)	−0.2604 (8)
O(31)	0.1485 (7)	−0.3940 (7)	−0.2540 (7)
C(32)	0.1489 (10)	−0.1472 (11)	−0.3579 (8)
O(32)	0.0964 (8)	−0.1309 (10)	−0.4376 (5)
C(33)	0.3482 (8)	−0.2292 (9)	−0.3080 (7)
O(33)	0.4158 (6)	−0.2715 (8)	−0.3269 (5)
N(1)	0.2988 (5)	−0.0037 (7)	−0.2668 (4)
N(2)	0.3918 (6)	0.0014 (7)	−0.2942 (5)
C(1)	0.4015 (7)	0.0828 (8)	−0.3422 (6)
C(2a)	0.3242 (7)	0.1708 (8)	−0.3674 (6)
C(3a)	0.2467 (9)	0.1567 (10)	−0.4312 (7)
C(4a)	0.1780 (10)	0.2400 (14)	−0.4533 (8)
C(5a)	0.1841 (10)	0.3347 (13)	−0.4118 (9)
C(6a)	0.2593 (11)	0.3506 (11)	−0.3496 (10)
C(7a)	0.3304 (9)	0.2681 (10)	−0.3241 (8)
C(2b)	0.4948 (7)	0.0865 (9)	−0.3744 (6)
C(3b)	0.5047 (10)	0.1590 (10)	−0.4349 (7)
C(4b)	0.5905 (12)	0.1588 (13)	−0.4697 (9)
C(5b)	0.6658 (11)	0.0880 (13)	−0.4424 (10)
C(6b)	0.6576 (9)	0.0163 (13)	−0.3805 (11)
C(7b)	0.5712 (9)	0.0125 (11)	−0.3470 (8)
H(N1)	0.2709	0.0609	−0.2949
H(3a)	0.2405	0.0894	−0.4618
H(4a)	0.1255	0.2297	−0.4983
H(5a)	0.1334	0.3928	−0.4267
H(6a)	0.2646	0.4193	−0.3209
H(7a)	0.3825	0.2795	−0.2784
H(3b)	0.4528	0.2110	−0.4534
H(4b)	0.5951	0.2087	−0.5126
H(5b)	0.7245	0.0870	−0.4648
H(6b)	0.7114	−0.0322	−0.3603
H(7b)	0.5653	−0.0398	−0.3060
H(br)	0.300	−0.102	−0.219

[a] Hydrogen atoms are in their idealized calculated positions, and each was included with an isotropic thermal parameter equal to 1.0 plus the equivalent *B* value of the carbon atom to which it was attached.

all remaining nonhydrogen atoms. Full-matrix least-squares refinement, using anisotropic thermal parameters for all atoms, led to R_F = 4.6%, R_{wF} = 3.9%, and GOF = 1.29. Difference-Fourier syntheses were now performed in an effort to locate the bridging hydride ligand. None, including one which used only those data with $(\sin \theta)/\lambda < 0.3$, showed any indication of the position of the hydride ligand. All other hydrogen atoms were placed in idealized positions with $d(\text{C–H}) = 0.95$ Å.[11] Refinement continued and convergence was reached with R_F = 4.3%, R_{wF} = 3.5%, and GOF = 1.21. No correction was necessary for secondary extinction. In the final refinement all 3565 data were refined against 343 parameters; NO/NV = 10.4. The two largest peaks in the last difference-Fourier calculations had heights of ~1.0 e Å^{-3} and were located within 1 Å of Os(2). The analysis is thus complete.

Final positional and thermal parameters are collected in Tables II and III. Note that Table II lists the coordinates of an atom labeled H(br). This is the position *calculated* for the bridging hydride ligand on the basis of the following geometrical constraints. (1) The hydride bisects the angle and lies in the plane formed by the vectors C(12)→Os(1) and C(32)→Os(3). (2) Individual Os–H(br) bond lengths are approximately 1.85 Å.[12] The hydride coordinates were used in preparing the figures only; they were not used in any structure factor calculations.

Description of the Structure

The crystal consists of discrete molecular units of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN{=}CPh}_2)$. There are no unusually short intermolecular contacts. Table IV gives a listing of interatomic distances, and Table V shows the interatomic angles.

The geometry of the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN{=}CPh}_2)$ molecule can be seen as a stereoview in Figure 1, while Figure 2 depicts the atomic labeling scheme. The complex contains a triangular array of osmium atoms in which there are two nonbridged metal–metal vectors, Os(2)–Os(1) and Os(2)–Os(3), of length 2.8468 (9) and 2.8421 (8) Å, respectively. The average nonbridged distance is 2.844 [3] Å and is sig-

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(12) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314–319.
(13) Part 1: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878–884.

Table III. Anisotropic Thermal Parameters ($Å^2$)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	3.345 (20)	4.358 (22)	2.967 (20)	−0.363 (15)	0.336 (14)	−0.111 (16)
Os(2)	4.017 (21)	3.846 (22)	3.420 (21)	−0.427 (16)	0.127 (15)	−0.180 (16)
Os(3)	3.274 (20)	4.796 (24)	3.854 (22)	−0.332 (16)	0.370 (15)	0.714 (17)
C(11)	4.47 (55)	5.81 (64)	3.89 (59)	−0.59 (48)	0.26 (45)	0.05 (51)
O(11)	7.40 (53)	10.15 (64)	4.19 (44)	0.15 (46)	1.51 (38)	1.89 (45)
C(12)	5.89 (64)	5.42 (70)	4.03 (58)	−0.93 (53)	1.46 (48)	−0.50 (52)
O(12)	10.38 (70)	4.77 (48)	8.11 (60)	0.21 (45)	2.34 (49)	−2.24 (44)
C(13)	7.83 (79)	4.66 (58)	2.25 (47)	−0.91 (55)	1.13 (49)	−0.62 (43)
O(13)	3.53 (40)	11.91 (78)	8.70 (64)	0.22 (44)	−0.03 (41)	−2.57 (53)
C(21)	4.59 (64)	6.62 (72)	5.79 (73)	0.24 (55)	0.41 (55)	−0.23 (59)
O(21)	4.84 (46)	10.19 (69)	7.95 (59)	−1.05 (44)	−1.70 (43)	−2.10 (50)
C(22)	4.65 (59)	5.41 (66)	5.85 (70)	1.38 (51)	1.00 (50)	0.74 (58)
O(22)	7.64 (56)	6.78 (54)	10.89 (72)	2.17 (44)	3.49 (51)	5.78 (54)
C(23)	4.62 (60)	7.54 (80)	5.47 (70)	−0.39 (56)	1.48 (53)	−0.02 (62)
O(23)	6.87 (54)	11.77 (77)	5.85 (53)	0.28 (52)	1.32 (43)	−1.72 (53)
C(24)	3.50 (54)	8.19 (84)	6.43 (75)	−0.88 (55)	1.32 (51)	1.27 (68)
O(24)	8.37 (63)	9.79 (72)	9.15 (70)	−1.02 (53)	0.82 (51)	6.00 (61)
C(31)	5.25 (60)	4.22 (57)	4.70 (60)	0.94 (58)	1.03 (48)	0.20 (46)
O(31)	5.98 (47)	7.68 (56)	7.08 (53)	1.55 (42)	1.02 (40)	−1.34 (44)
C(32)	5.42 (64)	5.78 (72)	6.32 (74)	−0.79 (57)	−0.19 (53)	−0.15 (60)
O(32)	8.03 (60)	4.04 (45)	13.64 (87)	−2.16 (43)	−0.76 (55)	1.29 (51)
C(33)	6.31 (70)	6.16 (72)	5.38 (73)	−0.07 (57)	1.02 (59)	−2.07 (58)
O(33)	9.59 (67)	13.56 (87)	4.10 (48)	1.39 (61)	−2.16 (46)	−2.01 (53)
N(1)	3.38 (38)	5.43 (46)	2.52 (36)	−0.64 (32)	0.66 (29)	0.13 (32)
N(2)	4.36 (43)	4.18 (44)	3.96 (43)	−0.11 (34)	0.63 (35)	0.36 (36)
C(1)	3.77 (47)	3.25 (46)	3.04 (46)	−0.05 (38)	0.26 (37)	0.71 (40)
C(2a)	4.12 (50)	4.40 (55)	2.86 (46)	−0.44 (42)	0.73 (40)	1.10 (42)
C(3a)	6.08 (65)	6.42 (69)	3.13 (52)	0.78 (56)	0.28 (49)	0.02 (50)
C(4a)	6.91 (80)	9.30 (100)	4.50 (69)	2.39 (76)	0.48 (57)	2.03 (72)
C(5a)	6.44 (82)	9.31 (107)	5.70 (82)	1.39 (75)	1.87 (68)	1.76 (76)
C(6a)	7.28 (82)	4.62 (67)	9.36 (101)	1.24 (62)	2.35 (77)	0.23 (66)
C(7a)	5.12 (61)	5.29 (67)	6.40 (73)	0.07 (54)	0.86 (52)	−1.11 (58)
C(2b)	4.28 (54)	4.16 (52)	3.48 (50)	−0.61 (44)	0.70 (41)	−0.67 (44)
C(3b)	7.55 (76)	5.72 (68)	5.15 (65)	−0.72 (56)	3.13 (59)	0.34 (56)
C(4b)	8.64 (97)	8.88 (103)	6.45 (84)	−2.50 (85)	4.20 (77)	−1.42 (73)
C(5b)	7.47 (94)	7.46 (94)	9.37 (109)	−2.28 (77)	5.31 (86)	−2.36 (84)
C(6b)	4.05 (65)	8.41 (95)	11.26 (117)	0.54 (64)	2.03 (71)	−2.55 (90)
C(7b)	4.55 (61)	6.03 (68)	7.00 (76)	−0.24 (54)	1.20 (54)	−0.22 (59)

nificantly longer than the doubly bridged Os(1)–Os(3) distance of 2.7863 (8) Å.

The arrangement of carbonyl ligands in the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=CPh}_2)$ molecule (i.e., four associated with Os(2), three each associated with Os(1) and Os(3)) provides approximate (but not exact) $C_s(m)$ symmetry to the basic $Os_3(CO)_{10}$ framework, as is found in all other $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$ molecules. However, as is suggested by Figure 2, this approximate C_s symmetry extends outward to include the $>NHN=CPh_2$ ligand, a feature not usually found in this type of complex except in systems with smaller nonintrusive bridging ligands, i.e., L = H,[12] Cl,[14] Br,[15] or OMe.[2] Perfect mirror symmetry within the bridging ligand is disrupted by slight rotations about the C(1)–C(2a) and C(1)–C(2b) bonds. Thus, the dihedral angle between the plane defined by atoms N(2), C(1), C(2a), and C(2b) and that defined by the atoms of phenyl ring "b" is 8.98° (see Table VI for a listing of important molecular planes and dihedral angles).

The $>NHN=CPh_2$ ligand bridges the Os(1)–Os(3) bond in a symmetrical manner with Os(1)–N(1) = 2.119 (7) Å and Os(3)–N(1) = 2.121 (8) Å (average 2.120 [1] Å). The bridging Os(1)–N(1)–Os(3) angle is 82.2(3)°, and the plane defined by these atoms makes an angle of 106.86° with the triosmium plane.

The position of the bridging hydride ligand was not obtained directly in this structural study. However its location has been estimated (vide supra), and Figure 3 shows the resulting geometry.

Table IV. Interatomic Distances (Å) and Esd's for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=CPh}_2)$

(A) Osmium-Osmium Distances			
Os(1)–Os(2)	2.8468 (9)	Os(1)–Os(3)	2.7863 (8)
Os(2)–Os(3)	2.8421 (8)		
(B) Osmium-Carbonyl Distances			
Os(1)–C(11)	1.902 (11)	Os(2)–C(23)	1.878 (13)
Os(1)–C(12)	1.894 (12)	Os(2)–C(24)	1.949 (14)
Os(1)–C(13)	1.904 (13)	Os(3)–C(31)	1.888 (13)
Os(2)–C(21)	1.928 (12)	Os(3)–C(32)	1.893 (13)
Os(2)–C(22)	1.956 (13)	Os(3)–C(33)	1.901 (11)
(C) Osmium-Bridging Nitrogen Distances			
Os(1)–N(1)	2.119 (7)	Os(3)–N(1)	2.121 (8)
Os(1)···N(2)	3.078 (8)	Os(3)···N(2)	2.996 (8)
(D) Carbon-Oxygen Distances			
C(11)–O(11)	1.138 (12)	C(23)–O(23)	1.171 (14)
C(12)–O(12)	1.146 (13)	C(24)–O(24)	1.138 (14)
C(13)–O(13)	1.163 (13)	C(31)–O(31)	1.150 (13)
C(21)–O(21)	1.123 (12)	C(32)–O(32)	1.157 (14)
C(22)–O(22)	1.105 (13)	C(33)–O(33)	1.153 (12)
(E) Distances within the μ-NHN=CPh_2 Ligand			
N(1)–N(2)	1.436 (11)	C(6a)–C(7a)	1.394 (17)
N(2)–C(1)	1.293 (12)	C(7a)–C(2a)	1.372 (15)
C(1)–C(2a)	1.495 (13)	C(2b)–C(3b)	1.366 (15)
C(1)–C(2b)	1.479 (14)	C(3b)–C(4b)	1.409 (17)
C(2a)–C(3a)	1.368 (14)	C(4b)–C(5b)	1.345 (20)
C(3a)–C(4a)	1.372 (16)	C(5b)–C(6b)	1.372 (21)
C(4a)–C(5a)	1.328 (19)	C(6b)–C(7b)	1.405 (17)
C(5a)–C(6a)	1.330 (19)	C(7b)–C(2b)	1.379 (15)

Within the organonitrogen ligand, the N(1)–N(2) distance is 1.436 (11) Å while the N(2)–C(1) bond length is 1.293 (12) Å, confirming the formulation as N—N=C. Additionally, the $N(sp^3)$–$N(sp^2)$–C angle is 116.1 (8)°, and the N–C–Ph

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(14) Part 12: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–1930.

(15) Part 13: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261–3267.

Table V. Intermolecular Angles (Deg) with Esd's for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=CPh}_2)$

A. Os-Os-Os Angles

Os(1)-Os(2)-Os(3)	58.65 (2)	Os(3)-Os(1)-Os(2)	60.59 (2)
Os(2)-Os(3)-Os(1)	60.76 (2)		

B. Os-Os-C Angles

Os(2)-Os(1)-C(11)	87.8 (3)	Os(1)-Os(3)-C(31)	120.8 (4)
Os(2)-Os(1)-C(12)	95.8 (3)	Os(1)-Os(3)-C(32)	134.6 (4)
Os(2)-Os(1)-C(13)	168.72 (3)	Os(1)-Os(3)-C(33)	108.9 (3)
Os(3)-Os(1)-C(11)	119.1 (3)	Os(2)-Os(3)-C(31)	90.8 (4)
Os(3)-Os(1)-C(12)	136.6 (4)	Os(2)-Os(3)-C(32)	89.9 (4)
Os(3)-Os(1)-C(13)	108.8 (3)	Os(2)-Os(3)-C(33)	169.4 (4)
Os(1)-Os(2)-C(21)	154.6 (4)	Os(3)-Os(2)-C(21)	96.0 (4)
Os(1)-Os(2)-C(22)	87.0 (3)	Os(3)-Os(2)-C(22)	90.1 (3)
Os(1)-Os(2)-C(23)	102.0 (4)	Os(3)-Os(2)-C(23)	160.6 (4)
Os(1)-Os(2)-C(24)	87.0 (3)	Os(3)-Os(2)-C(24)	84.4 (4)

C. C-Os-C Angles

C(11)-Os(1)-C(12)	93.3 (5)	C(31)-Os(3)-C(32)	91.0 (6)
C(11)-Os(1)-C(13)	94.9 (4)	C(31)-Os(3)-C(33)	92.9 (5)
C(12)-Os(1)-C(13)	94.9 (5)	C(32)-Os(3)-C(33)	100.0 (5)
C(21)-Os(2)-C(22)	91.6 (5)	C(22)-Os(2)-C(23)	89.9 (5)
C(21)-Os(2)-C(23)	103.4 (5)	C(22)-Os(2)-C(24)	173.4 (5)
C(21)-Os(2)-C(24)	92.7 (5)	C(23)-Os(2)-C(24)	94.1 (6)

D. Os-C-O Angles

Os(1)-C(11)-O(11)	178.5 (8)	Os(2)-C(23)-O(23)	179.0 (8)
Os(1)-C(12)-O(12)	177.2 (14)	Os(2)-C(24)-O(24)	178.9 (9)
Os(1)-C(13)-O(13)	174.7 (11)	Os(3)-C(31)-O(31)	176.2 (16)
Os(2)-C(21)-O(21)	175.4 (14)	Os(3)-C(32)-O(32)	177.0 (17)
Os(2)-C(22)-O(22)	175.9 (12)	Os(3)-C(33)-O(33)	177.3 (14)

E. Os-Os-Bridge and Os-Bridge-Os Angles

Os(1)-Os(3)-N(1)	48.9 (2)	Os(3)-Os(1)-N(1)	49.0 (2)
Os(2)-Os(3)-N(1)	82.5 (2)	Os(2)-Os(1)-N(1)	82.4 (2)
Os(1)-N(1)-Os(3)	82.2 (3)		

F. N-C-Os-Bridge Angles

N(1)-Os(1)-C(11)	167.5 (4)	N(1)-Os(3)-C(31)	169.6 (5)
N(1)-Os(1)-C(12)	95.3 (4)	N(1)-Os(3)-C(32)	97.0 (4)
N(1)-Os(1)-C(13)	93.3 (4)	N(1)-Os(3)-C(33)	92.3 (4)

G. Internal C-C-C Angles of the $\mu\text{-NHN=CPh}_2$ Ligand

C(7a)-C(2a)-C(3a)	118.9 (11)	C(7b)-C(2b)-C(3b)	118.7 (11)
C(2a)-C(3a)-C(4a)	120.2 (12)	C(2b)-C(3b)-C(4b)	121.4 (13)
C(3a)-C(4a)-C(5a)	121.1 (13)	C(3b)-C(4b)-C(5b)	120.1 (14)
C(4a)-C(5a)-C(6a)	119.7 (14)	C(4b)-C(5b)-C(6b)	119.0 (12)
C(5a)-C(6a)-C(7a)	121.6 (13)	C(5b)-C(6b)-C(7b)	121.6 (14)
C(6a)-C(7a)-C(2a)	118.4 (12)	C(6b)-C(7b)-C(2b)	119.0 (13)

H. Other Angles with the $\mu\text{-NHN=CPh}_2$ Ligand

Os(1)-N(1)-C(1)	135.3 (4)	N(2)-C(1)-C(2a)	124.0 (9)
Os(3)-N(1)-C(1)	131.6 (4)	N(2)-C(1)-C(2b)	116.9 (9)
N(1)-N(2)-C(1)	116.1 (8)		

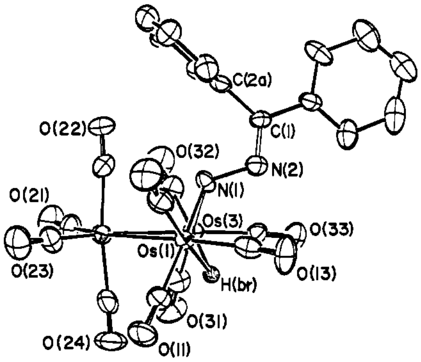

Figure 3. View of the $(\mu\text{-H})Os_3(\mu\text{-NHN=CPh}_2)$ molecule, showing H(br) in its calculated position.

angles are 124.0 (9)° [N(2)-C(1)-C(2a)] and 116.9 (9)° [N(2)-C(1)-C(2b)]. The N(2)-C(1)-C(2a)-C(2b) system is planar, with a root-mean-square displacement of 0.006 Å. All other distances and angles within the ligand are normal.

Osmium-carbonyl and carbon-oxygen bond lengths are all within their expeected ranges. The longest Os-C distances occur in the mutually trans (axial) carbonyl ligands on Os(2) [Os(2)-C(22) = 1.956 (13) Å and Os(2)-C(24) = 1.949 (14) Å].

All Os-C-O systems are close to linear, with angles ranging from 174.7 (11) to 179.0 (8)°.

Table VI. Important Least-Squares Planes and Dihedral Angles within the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=CPh}_2)$ Molecule[a]

plane	*A*	*B*	*C*	*D*
I	0.10018	0.78204	−0.61512	1.6386
II	0.90950	−0.40092	0.10991	4.0472
III	0.69326	0.38886	−0.60678	8.3790
IV	0.29009	0.67464	0.67876	−1.1725
V	0.27793	0.55764	0.78127	−2.0264

atoms	dist	atoms	dist
	I: Triosmium Plane		
Os(1)*[b]	0.0000	C(21)	0.066 (13)
Os(2)*	0.0000	O(21)	0.176 (10)
Os(3)*	0.0000	C(23)	−0.040 (13)
N(1)	1.529 (8)	O(23)	−0.060 (10)
C(13)	−0.136 (11)	C(33)	−0.089 (11)
O(13)	−0.283 (10)	O(33)	−0.196 (9)
	II: Os(1)-N(1)-Os(3) Plane		
Os(1)*	0.0000	C(11)	−0.132 (11)
Os(3)*	0.0000	O(11)	−0.237 (9)
N(1)*	0.0000	C(31)	−0.041 (13)
Os(2)	−2.3734 (4)	O(31)	−0.002 (10)
	III: Phenyl Ring "a"		
C(2a)*	−0.007 (10)	C(5a)*	−0.008 (15)
C(3a)*	−0.002 (12)	C(6a)*	0.013 (15)
C(4a)*	0.002 (15)	C(7a)*	−0.013 (12)
	IV: Phenyl Ring "b"		
C(2b)*	0.002 (10)	C(6b)*	0.016 (16)
C(3b)*	0.009 (13)	C(7b)*	−0.015 (13)
C(4b)*	−0.008 (15)		
C(5b)*	−0.005 (16)		
	V: N(2)-C(1)-C(2a)-C(2b) Plane		
N(2)*	−0.002 (8)	C(2a)*	−0.002 (10)
C(1)*	0.005 (10)	C(2b)*	−0.002 (1)

planes	angles, deg	planes	angles, deg
I-II	106.86	III-IV	87.04
I-III	41.69	III-V	93.73
I-IV	82.00	IV-V	8.98
I-V	90.98		

[a] Equations of planes: $AX + BY + CZ = D$ [in orthonormal (Å) coordinates]. [b] Atoms marked with an asterisk were used in calculating the plane; all other received zero weight.

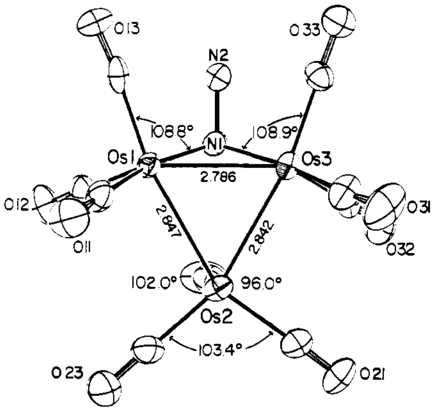

Figure 4. Portion of the molecule projected onto the triosmium plane. Note that C(24)-O(24), an axial carbonyl ligand on Os(2), has been deleted for clarity along with the CPh_2 system.

Discussion

Comparison with Related $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-L})$ Molecules. Figure 4 shows a portion of the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=}$

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 bridged	Os-Os, Å nonbridged	Δ,[a] Å
μ-H[12]	H	1.845 [3]	94.3 [18]	2.683 (1)	2.815 [1]	−0.132
μ-N=N(*p*-tol)[1]	N(sp^2)	2.046 [14]	87.2 (5)	2.823 (1)	2.845 [14]	−0.022
μ-OMe[2]	O	2.103 [13]	83.9 (2)	2.812 (1)	2.818 [6]	−0.006
μ-NHN=CPh_2[b]	N(sp^3)	2.120 [1]	82.2 (3)	2.786 (1)	2.844 [3]	−0.058
μ-$NHSO_2$(*p*-tol)[4]	N(sp^3)	2.154 [12]	81.6 (2)	2.814 (1)	2.853 [8]	−0.039
μ-CHCH=NEt_2[3]	C	2.155 [7]	80.6 (9)	2.785 (2)	2.868 [3]	−0.083
μ-$CHCH_2PMe_2Ph$[16]	C	2.161 [18]	80.8 (3)	2.800 (1)	2.871 [3]	−0.071
μ-SEt[17]	S	2.40 [1]	73.1 (3)	2.863 (2)	2.849 [10]	+0.014
μ-S(1)CH_2S(2)-μ[18]	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[14]	Cl	2.456 [3]	70.8 (1)	2.846 (1)	2.833 [5]	+0.013
μ-Br[15] molecule B	Br(B)	2.583 [3]	67.65 (5)	2.876 (1)	2.836 [3]	+0.040
molecule 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. [b] This work.

CPh_2) molecule projected onto the triosmium plane. The dibridged Os–Os bond length of 2.786 (1) Å represents a decrease of 0.091 Å over the "normal" Os–Os length of 2.877 [4] Å found in $Os_3(CO)_{12}$. The parameter Δ (defined in Table VII) is −0.058. These results are quite consistent with information available for other Os(μ-H)(μ-L)Os systems,[1–4,12,14–18] where the ligand, L, contains a relatively small bridgehead atom, X. Data for X = H, N, O, C, S, Cl, and Br are shown in Table VII, where it is seen that the doubly bridged Os–Os bond length is shortened relative to a nonbridged bond for small X atoms.

Comparison with Other Triangular Species with Os(μ-H)(μ-N)Os Bridges. The Os–N(sp^3)–Os angle of 82.2 (3)° found for the present molecule is very similar to the value of 81.6 (2)° found for $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}NHSO_2(p\text{-tol})]$.[4] Each of these angles is substantially more acute that the Os–N(sp^2)–Os angle observed in the complex $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-N=N}(p\text{-tol})]$. In keeping with this, the average Os–N(sp^2) distance of 2.046 [14] Å is substantially shorter than the average Os–N(sp^3) bond lengths of 2.120 [1] Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=}CPh_2)$ and 2.154 [12] Å in $(\mu\text{-H})Os_3(CO)_{10}[\mu\text{-}NHSO_2[p\text{-tol})]$. This shortening may reflect the decreased radius of sp^2- vs. sp^3-hybridized nitrogen or it may suggest some partial double-bond character in the Os–N(sp^2) linkages.

It is not clear why the dibridged Os–Os distance of 2.786 (1) Å in the present (μ-NHN=CPh_2) derivative is significantly shorter than that of 2.814 (1) Å in the closely related [μ-$NHSO_2$(*p*-tol)] derivative, especially when we note that the *unsaturated* [μ-N=N(*p*-tol)] derivative has a dibridged Os–Os distance of 2.823 (1) Å. Despite this anomaly, the prevailing trend in Table VII is that the Os–X distance increases with increasing covalent radius of X and the Os–X–Os angle decreases with increasing covalent radius of X.

It seems likely that a detailed understanding of these systems will have to take into account such secondary features as the asymmetry in equatorial angles about Os(2). The C(23)–Os(2)–Os(1) angle of 102.0 (4)° is some 6.0° larger than the "equivalent" C(21)–Os(2)–Os(3) angle of 96.0 (4)°. The corresponding angles in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})$ [106.9 (5)° and 94.7 (5)°] and even in $(\mu\text{-H})_2Os_3(CO)_{10}$ [107.80 (4)° and 97.75 (4)° by neutron diffraction;[12] 106.6 (5)° and 98.4 (5)° by X-ray diffraction[19]] are even more asymmetric.

Further studies on related systems are currently under way in an effort to resolve these difficulties.

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Registry No. $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHN=}CPh_2)$, 77924-84-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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