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Triosmium Cluster Compounds Containing Isocyanide and Hydride Ligands. Crystal and Molecular Structures of $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$

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The structures of the compounds $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$ have been revealed by X-ray crystallographic techniques. For $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$: $a = 9.064$ (3), $b = 12.225$ (3), $c = 20.364$ (4) Å; $\beta = 98.73$ (3)°; space group $P2_1/c$ [C_{2h}^5], No. 14; $Z = 4$; $d_{\text{calcd}} = 2.79$ g cm^{-3}. This compound contains a triangular cluster of three osmium atoms; Os(1)–Os(2) = 2.930 (1) Å, Os(1)–Os(3) = 2.876 (1) Å, and Os(2)–Os(3) = 3.000 (1) Å. There are ten linear terminal carbonyl groups and one linear terminal isocyanide ligand which occupies an axial coordination site. The hydrogen atoms were not observed crystallographically, but their positions are strongly inferred from considerations of molecular geometry. For $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$: $a = 15.220$ (8), $b = 12.093$ (6), $c = 23.454$ (5) Å; space group *Pbcn* [D_{2h}^{14}], No. 60; $Z = 8$; $d_{\text{calcd}} = 2.79$ g cm^{-3}. The compound is analogous to the parent carbonyl $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ and has two normal and one short osmium–osmium bonds: Os(1)–Os(2) = 2.827 (1) Å, Os(1)–Os(3) = 2.828 (1) Å, Os(2)–Os(3) = 2.691 (1) Å. The isocyanide ligand resides in an equatorial coordination site on osmium Os(2). The hydrogen atoms were not observed but are believed to occupy bridging positions as in the parent carbonyl complex.

Introduction

Recent studies have shown that triosmium carbonyl cluster compounds promote a wide variety of unusual ligand transformations.[1-12] However, even more important is their potential use as catalysts for hydrogenation reactions.[13] We have recently explored the reactivity of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ toward isocyanide molecules.[14] A variety of reactions and products were observed. Initially, $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ reacts with isocyanides to form 1:1 adducts of the type $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}\text{CNR}$ (R = C_6H_5, CH_3, and $t\text{-C}_4\text{H}_9$), I. When heated, these adducts readily lose 1 mol of carbon monoxide to form the compounds $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CNR})$ (R = C_6H_5, CH_3, and $t\text{-C}_4\text{H}_9$), II. Here we present a detailed report on the crystal and molecular structures of the $t\text{-C}_4\text{H}_9$ derivatives of I and II.

Experimental Section

The compounds $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$ were prepared as previously reported.[15] Crystals of each were grown from hexane solutions by cooling to −20 °C. All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer with graphite monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined from 25 randomly selected reflections by using the CAD-4 automatic search, center, index, and least-squares routines. Space groups were determined from the systematic absences observed during data collection.

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Both structures were solved by the heavy-atom method. Anomalous dispersion corrections[16a] were included for the scattering[16b] of all nonhydrogen atoms. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$. Unweighted and weighted residuals were determined by the formulas

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^{\,2}]^{1/2}$$

Crystal data and data collection parameters for both structures are listed in Table I.

$(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$. A thick crystalline plate of dimensions 0.09 mm × 0.29 mm × 0.32 mm was selected and mounted in a thin-walled glass capillary. The crystal faces were identified as 001, 00$\bar{1}$, 011, 0$\bar{1}\bar{1}$, 01$\bar{1}$, 0$\bar{1}$1, 20$\bar{1}$ and $\bar{1}$01. ω-scan peak widths at one-half peak height were in the range 0.1–0.2°. The crystal was mounted with a a^* direction oriented 9.15° from the diffractometer φ axis. From a total of 5332 reflections, 3026 conformed to the relation $F^2 \geq 3.0\sigma(F^2)$ and were used in the structure solution and refinement. The value of the p factor used in calculating $\sigma(F^2)$ was 0.02. Standard reflections monitored periodically showed an approximate 5% decrease during data collection. A linear rescale correction was applied. The linear absorption coefficient is 181.8 cm^{-1}. A correction was applied by using the Gaussian intergration method and a grid of 14 × 10 × 6. The maximum and minimum transmission coefficients were 0.215 and 0.07. The structure was solved by a combination of Patterson and difference Fourier techniques. Full-matrix least-squares refinement with anisotropic thermal parameters for the osmium atoms and isotropic thermal parameters for the remaining atoms converged to the final residuals $R = 0.044$ and $R_w = 0.056$. The hydrogen atoms were not located, and no attempts to include them artifically were made. The largest peaks in the final difference Fourier synthesis were 2.4–2.6 e/Å^3 and were clustered about the metal atoms. The largest value of the shift/error parameter on the final cycle of refinement was 0.03. Although the refinement seemed to converge smoothly, the final values for some of the bond distances (e.g., C(3)–O(3), C(9)–O(9), and Os(3)–C(9)) do appear to be significantly outside the ranges normally found for these groups. The error in an ob-

Table I. Experimental Data for X-ray Diffraction Studies of $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$

	$(\mu\text{-H})(\text{H})\text{Os}_3\text{-}(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$	$(\mu\text{-H})_2\text{Os}_3\text{-}(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$
(A) Crystal Parameters at 23 °C		
space group	$P2_1/c$	*Pbcn*
a, Å	9.064 (3)	15.220 (8)
b, Å	12.225 (2)	12.093 (6)
c, Å	20.364 (4)	23.454 (5)
β, deg	98.73 (3)	
V, Å^3	2230 (2)	4317 (5)
Z	4	8
mol wt	935.86	907.85
ρ_{calcd}, g cm^{-3}	2.79	2.79
(B) Measurement of Intensity Data		
radiation, Å	Mo K$_{\bar{\alpha}}$(0.710 73)	
monochromator	graphite	
detector aperture		
horizontal: $A + B \tan\theta$	$A = 2.6$ mm, $B = 1.2$ min	
vertical	4 mm	
rflctns measd	$+h,+k,\pm l$	$+h,+k,+l$
scan type	moving crystal/stationary counter	
ω-scan width, deg	$0.80 + 0.35 \tan\theta$	
bkgd	one-fourth additional scan at each end of scan	
scan rate max	10.0°/min	
min	1.3°/min	
no. of rflctns measd	5332	3157
data used ($F^2 > 3.0\sigma(F^2)$)	3026	1334
max 2θ, deg	54	45

Table II. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$[a]

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2	atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Os(1)	0.27786 (8)	0.02054 (5)	0.13279 (4)	*a*	C(1)	0.361 (2)	0.000 (1)	0.2234 (10)	5.1 (4)
Os(2)	0.02012 (8)	0.11228 (5)	0.18473 (3)	*a*	C(2)	0.196 (2)	0.065 (1)	0.0423 (10)	4.5 (4)
Os(3)	0.27649 (8)	0.25200 (5)	0.15791 (4)	*a*	C(3)	0.461 (3)	0.007 (2)	0.1083 (11)	6.5 (5)
O(1)	0.423 (2)	−0.0160 (11)	0.2774 (8)	7.1 (4)	C(4)	0.221 (2)	−0.126 (1)	0.1209 (10)	5.2 (4)
O(2)	0.142 (2)	0.0852 (9)	−0.0113 (7)	5.5 (3)	C(5)	−0.141 (2)	0.182 (1)	0.2166 (11)	5.5 (4)
O(3)	0.589 (2)	−0.0048 (13)	0.0917 (10)	9.6 (5)	C(6)	−0.068 (2)	0.143 (1)	0.0945 (9)	4.1 (4)
O(4)	0.190 (2)	−0.2179 (12)	0.1144 (8)	7.8 (4)	C(7)	−0.056 (2)	−0.034 (1)	0.1814 (10)	4.9 (4)
O(5)	−0.240 (2)	0.2262 (12)	0.2344 (9)	8.9 (5)	C(8)	0.117 (2)	0.091 (1)	0.2806 (9)	3.8 (3)
O(6)	−0.129 (2)	0.1656 (9)	0.0429 (7)	5.6 (3)	C(9)	0.435 (3)	0.258 (2)	0.1162 (12)	6.3 (5)
O(7)	−0.105 (2)	−0.1204 (10)	0.1799 (8)	6.6 (3)	C(10)	0.389 (2)	0.244 (1)	0.2465 (10)	5.2 (4)
O(9)	0.543 (2)	0.2649 (11)	0.0862 (9)	8.6 (4)	C(11)	0.244 (3)	0.400 (1)	0.1641 (11)	5.8 (5)
O(10)	0.460 (2)	0.2460 (10)	0.2993 (8)	6.9 (4)	C(21)	0.203 (3)	0.063 (2)	0.4088 (11)	6.0 (5)
O(11)	0.226 (2)	0.4961 (12)	0.1633 (9)	8.2 (4)	C(22)	0.180 (3)	−0.059 (2)	0.4213 (14)	8.2 (6)
N	0.160 (2)	0.080 (1)	0.3368 (8)	4.8 (3)	C(23)	0.363 (4)	0.099 (2)	0.4287 (17)	10.9 (9)
					C(24)	0.087 (3)	0.128 (2)	0.4417 (14)	8.3 (7)

atom	β(1,1)	β(2,2)	β(3,3)	β(1,2)	β(1,3)	β(2,3)
Os(1)	0.00994 (9)	0.00570 (4)	0.00232 (2)	0.0005 (1)	0.00067 (7)	−0.00040 (5)
Os(2)	0.00841 (8)	0.00652 (4)	0.00170 (2)	−0.0008 (1)	−0.00017 (6)	−0.00024 (5)
Os(3)	0.01043 (9)	0.00559 (4)	0.00242 (2)	−0.0028 (1)	−0.00034 (7)	−0.00017 (5)

[a] Anisotropic thermal parameters are given in the lower half of the table. The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)\cdot h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.

Table III. Bond Distances (Å) with Errors for $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$

Os(1)–Os(2)	2.930 (1)	C(2)–O(2)	1.151 (13)
Os(1)–Os(3)	2.876 (1)	C(3)–O(3)	1.268 (15)
Os(2)–Os(3)	3.000 (1)	C(4)–O(4)	1.155 (12)
Os(1)–C(1)	1.902 (13)	C(5)–O(5)	1.148 (14)
Os(1)–C(2)	1.958 (12)	C(6)–O(6)	1.145 (12)
Os(1)–C(3)	1.811 (15)	C(7)–O(7)	1.141 (12)
Os(1)–C(4)	1.875 (11)	C(8)–N	1.161 (13)
Os(2)–C(5)	1.893 (13)	C(9)–O(9)	1.232 (16)
Os(2)–C(6)	1.926 (11)	C(10)–O(10)	1.169 (14)
Os(2)–C(7)	1.919 (10)	C(11)–O(11)	1.190 (12)
Os(2)–C(8)	2.032 (11)	N–C(21)	1.473 (16)
Os(3)–C(9)	1.775 (15)	C(21)–C(22)	1.526 (16)
Os(3)–C(10)	1.934 (13)	C(21)–C(23)	1.509 (22)
Os(3)–C(11)	1.836 (11)	C(21)–C(24)	1.550 (19)
C(1)–O(1)	1.171 (19)		

Table IV. Bond Angles (deg) with Errors for $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$

Os(2)–Os(1)–Os(3)	62.22 (1)	C(6)–Os(2)–C(8)	176.2 (4)
Os(1)–Os(2)–Os(3)	58.01 (1)	C(7)–Os(2)–C(8)	90.9 (4)
Os(2)–Os(3)–Os(1)	59.77 (1)	Os(1)–Os(3)–C(9)	86.1 (4)
Os(2)–Os(1)–C(1)	85.6 (4)	Os(1)–Os(3)–C(10)	95.7 (3)
Os(2)–Os(1)–C(2)	91.3 (3)	Os(1)–Os(3)–C(11)	170.0 (4)
Os(2)–Os(1)–C(3)	161.6 (4)	Os(2)–Os(3)–C(9)	144.6 (4)
Os(2)–Os(1)–C(4)	101.1 (4)	Os(2)–Os(3)–C(10)	96.5 (3)
Os(3)–Os(1)–C(1)	88.3 (3)	Os(2)–Os(3)–C(11)	114.4 (4)
Os(3)–Os(1)–C(2)	83.3 (3)	C(9)–Os(3)–C(10)	95.7 (6)
Os(3)–Os(1)–C(3)	99.8 (4)	C(9)–Os(3)–C(11)	97.9 (5)
Os(3)–Os(1)–C(4)	163.1 (4)	C(10)–Os(3)–C(11)	93.1 (5)
C(1)–Os(1)–C(2)	171.5 (4)	Os(1)–C(1)–O(1)	174.7 (10)
C(1)–Os(1)–C(3)	90.5 (6)	Os(1)–C(2)–O(2)	175.7 (9)
C(1)–Os(1)–C(4)	93.4 (5)	Os(1)–C(3)–O(3)	178.9 (11)
C(2)–Os(1)–C(3)	90.0 (6)	Os(1)–C(4)–O(4)	177.8 (11)
C(2)–Os(1)–C(4)	95.0 (5)	Os(2)–C(5)–O(5)	178.1 (12)
C(3)–Os(1)–C(4)	97.0 (5)	Os(2)–C(6)–O(6)	174.5 (9)
Os(1)–Os(2)–C(5)	175.7 (3)	Os(2)–C(7)–O(7)	178.2 (10)
Os(1)–Os(2)–C(6)	88.2 (3)	Os(2)–C(8)–N	174.1 (10)
Os(1)–Os(2)–C(7)	86.2 (3)	Os(3)–C(9)–O(9)	178.3 (12)
Os(1)–Os(2)–C(8)	92.6 (3)	Os(3)–C(10)–O(10)	175.4 (9)
Os(3)–Os(2)–C(5)	117.8 (3)	Os(3)–C(11)–O(11)	175.1 (1)
Os(3)–Os(2)–C(6)	86.5 (3)	C(8)–N–C(21)	175.6 (13)
Os(3)–Os(2)–C(7)	144.2 (3)	N–C(21)–C(22)	106.2 (10)
Os(3)–Os(2)–C(8)	90.8 (3)	N–C(21)–C(23)	108.9 (13)
C(5)–Os(2)–C(6)	90.5 (5)	N–C(21)–C(24)	105.3 (11)
C(5)–Os(2)–C(7)	98.0 (5)	C(22)–C(21)–C(23)	113.0 (13)
C(5)–Os(2)–C(8)	88.4 (5)	C(22)–C(21)–C(24)	107.9 (12)
C(6)–Os(2)–C(7)	92.9 (4)	C(23)–C(21)–C(24)	114.8 (12)

servation of unit weight was 3.12. Final atomic coordinates and thermal parameters are listed in Table II. Bond distances and angles with errors from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV. Tables of structure factors and intermolecular contacts are available (see supplementary material).

$(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$. A crystalline plate with dimensions 0.034 mm × 0.302 mm × 0.167 mm was mounted in a thin-walled glass capillary. The faces were identified as 001, 00$\bar{1}$, 110, $\bar{1}\bar{1}$0, 1$\bar{2}$0 and $\bar{1}$20. ω-scan peak half-widths were in the range 0.15–0.25°. The crystal was mounted with the normal to the 110 face oriented 16.6° from the diffractometer φ axis. Of 3157 reflections which were collected, 1334 conformed to the relation $F^2 \geq 3.0\sigma(F^2)$. Only the latter were used in the structure solution and refinement. Standard reflections monitored every 55 min showed a 7% decrease during the course of data collection. A linear rescale correction was applied. The linear absorption coefficient is 187.8 cm^{-1}. An absorption correction was applied by using the Gaussian integration method and a grid of 14 × 10 × 6. The maximum and minimum transmission coefficients were 0.532 and 0.080, respectively. The structure was solved by a combination of Patterson and difference Fourier techniques. Least-squares refinement with anisotropic thermal parameters for the osmium atoms and isotropic thermal parameters for all remaining atoms converged to the final residuals $R = 0.040$ and $R_w = 0.039$. The *tert*-butyl group was disordered between two conformations with one rotated approximately 60° from the other. In refinement both conformations were given equivalent weights. Hydrogen atoms were not located, and no attempts to include them artificially were made. The largest value of the shift/error parameter on the final cycle was 0.30 for a methyl group. The largest value for a nonmethyl group was 0.11. The error in an observation of unit weight was 1.89. The largest peaks in the final difference Fourier synthesis were 1.2–1.4 e/Å^3 and were in the vicinity of the osmium atoms. Final atomic coordinates are listed in Table V. Bond distances and angles are listed in Tables VI and VII. Structure factors and intermolecular contacts are available (see supplementary material).

Results and Discussion

$(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$. The molecular structure of $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ is shown in Figure 1. No unusually short intermolecular contacts were observed. The shortest contact is between carbonyl oxygen atoms, O(4)···O(5) = 3.12 (1) Å. The molecule consists of a triangular cluster of osmium atoms with distances Os(1)–Os(2) = 2.930 (1) Å, Os(2)–Os(3) = 3.000 (1) Å, and Os(1)–Os(3) = 2.876 (1) Å. Ten linear carbonyl groups are arranged such that Os(1) has four while the remaining osmium atoms have three each. ^{1}H NMR spectra show that the compound has one bridging and one terminal hydride ligand.[14] Although these ligands were not located crystallographically, the seemingly empty

Table V. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\mu\text{-H})_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$[a]

atom	x/a	y/b	z/c	B	atom	x/a	y/b	z/c	B
Os(1)	0.05557 (7)	0.17707 (8)	0.14740 (5)	*a*	C(3)	−0.027 (2)	0.072 (2)	0.117 (1)	5.3 (7)
Os(2)	0.17359 (7)	0.08944 (9)	0.06610 (6)	*a*	C(4)	0.143 (2)	0.288 (2)	0.160 (1)	6.4 (8)
Os(3)	0.06123 (7)	0.24845 (9)	0.03267 (5)	*a*	C(5)	0.242 (2)	0.047 (2)	0.003 (1)	7.4 (9)
O(1)	0.116 (1)	0.032 (2)	0.2459 (9)	7.1 (5)	C(6)	0.145 (2)	−0.053 (2)	0.090 (1)	5.0 (7)
O(2)	−0.086 (1)	0.324 (2)	0.1985 (9)	7.8 (6)	C(7)	0.268 (2)	0.095 (2)	0.119 (1)	4.2 (6)
O(3)	−0.076 (1)	0.010 (2)	0.0976 (9)	7.1 (5)	C(8)	−0.062 (2)	0.244 (2)	0.024 (1)	5.4 (6)
O(4)	0.198 (1)	0.358 (1)	0.1689 (9)	7.2 (5)	C(9)	0.050 (2)	0.396 (2)	0.052 (1)	5.5 (7)
O(5)	0.284 (1)	0.022 (2)	−0.0359 (10)	8.7 (6)	C(10)	0.091 (2)	0.273 (2)	−0.052 (1)	4.3 (6)
O(6)	0.126 (1)	−0.143 (2)	0.1060 (9)	7.2 (5)	C(11)	0.135 (2)	0.304 (2)	−0.158 (1)	7.6 (9)
O(7)	0.325 (1)	0.113 (1)	0.1504 (9)	7.0 (5)	C(12)	0.106 (4)	0.206 (6)	−0.194 (3)	9.1 (21)
O(8)	−0.136 (1)	0.237 (2)	0.0209 (9)	7.2 (5)	C(13)	0.080 (3)	0.407 (5)	−0.180 (3)	6.2 (14)
O(9)	0.048 (1)	0.490 (2)	0.0612 (9)	6.8 (5)	C(14)	0.233 (5)	0.324 (6)	−0.155 (3)	10.1 (21)
N	0.112 (1)	0.285 (2)	−0.097 (1)	6.2 (6)	C(121)	0.049 (5)	0.271 (6)	−0.193 (3)	10.8 (22)
C(1)	0.093 (2)	0.089 (2)	0.208 (1)	5.1 (6)	C(131)	0.188 (5)	0.414 (6)	−0.162 (3)	10.7 (22)
C(2)	−0.035 (2)	0.264 (2)	0.179 (1)	5.7 (7)	C(141)	0.198 (5)	0.203 (6)	−0.172 (3)	10.2 (22)

atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Os(1)	0.00469 (5)	0.00649 (7)	0.00175 (3)	−0.0001 (1)	0.00035 (8)	0.00080 (9)
Os(2)	0.00455 (5)	0.00641 (7)	0.00207 (3)	0.0014 (1)	0.00008 (8)	0.00015 (10)
Os(3)	0.00473 (5)	0.00675 (7)	0.00174 (3)	0.0014 (1)	−0.00004 (8)	0.00056 (9)

[a] Anisotropic thermal parameters are given in the lower part of the table. The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)\cdot h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.

Table VI. Bond Distances (Å) with Errors for $(\mu\text{-H})_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$

Os(1)–Os(2)	2.826 (1)	C(3)–O(3)	1.16 (3)
Os(1)–Os(3)	2.827 (1)	C(4)–O(4)	1.20 (2)
Os(2)–Os(3)	2.690 (1)	C(5)–O(5)	1.15 (3)
Os(1)–C(1)	1.87 (2)	C(6)–O(6)	1.18 (2)
Os(1)–C(2)	1.88 (2)	C(7)–O(7)	1.14 (2)
Os(1)–C(3)	1.92 (2)	C(8)–O(8)	1.13 (2)
Os(1)–C(4)	1.92 (2)	C(9)–O(9)	1.16 (2)
Os(2)–C(5)	1.89 (3)	C(10)–N	1.12 (2)
Os(2)–C(6)	1.87 (2)	N–C(11)	1.49 (3)
Os(2)–C(7)	1.91 (2)	C(11)–C(12)	1.52 (7)
Os(3)–C(8)	1.88 (2)	C(11)–C(13)	1.58 (6)
Os(3)–C(9)	1.85 (2)	C(11)–C(14)	1.51 (7)
Os(3)–C(10)	2.05 (2)	C(11)–C(121)	1.60 (7)
C(1)–O(1)	1.18 (2)	C(11)–C(131)	1.55 (7)
C(2)–O(2)	1.16 (3)	C(11)–C(141)	1.58 (7)

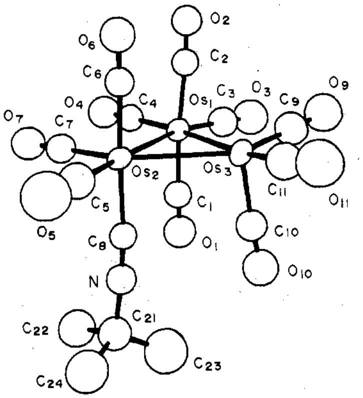

Figure 1. ORTEP diagram of $(\mu\text{-H})(H)Os_3(CO)_{10}(CN\text{-}t\text{-}C_4H_9)$ showing 50% probability elliposids.

coordination site on atom Os(3) undoubtedly signifies the location of the terminal hydride ligand. Bridging hydride ligands are known to produce significant lengthening effects on metal–metal bonds,[17] thus we predict that the bridging hydride ligand straddles the Os(2)–Os(3) bond since this bond is substantially longer than the other two. The linear isocyanide ligand, C(8)–N–C(21) = 175.6 (13)°, is in an axial coordination site perpendicular to the Os_3 triangle on the opposite side of the triangle from the terminal hydride ligand. As observed in several other isocyanide metal carbonyl compounds,[18-24] the metal–carbon bond to the isocyanide ligand at 2.032 (11) Å is significantly longer than the corresponding distance to the carbonyl ligands, $Os\text{–}C(CO)_{av}$ = 1.88 (5) Å. Overall the molecule is very similar to the compounds $(\mu\text{-H})(H)Os_3(CO)_{11}$[24] and $(\mu\text{-H})(H)Os_3(CO)_{10}P(C_6H_5)_3$[25] which have been analyzed by Churchill, except that in the latter compound the triphenylphosphine ligand was found to occupy an equatorial coordination site.

Table VII. Bond Angles (deg) with Errors for $(\mu\text{-H})_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$

Os(2)–Os(1)–Os(3)	56.83 (3)	C(8)–Os(3)–C(10)	96.8 (8)
Os(1)–Os(2)–Os(3)	61.61 (3)	C(9)–Os(3)–C(10)	96.6 (8)
Os(2)–Os(3)–Os(1)	61.56 (3)	Os(1)–C(1)–O(1)	179 (2)
Os(2)–Os(1)–C(1)	96.0 (6)	Os(1)–C(2)–O(2)	175 (2)
Os(2)–Os(1)–C(2)	159.8 (7)	Os(1)–C(3)–O(3)	178 (2)
Os(2)–Os(1)–C(3)	85.3 (6)	Os(1)–C(4)–O(4)	179 (2)
Os(2)–Os(1)–C(4)	85.6 (7)	Os(2)–C(5)–O(5)	179 (2)
Os(3)–Os(1)–C(1)	152.9 (6)	Os(2)–C(6)–O(6)	179 (2)
Os(3)–Os(1)–C(2)	103.0 (7)	Os(2)–C(7)–O(7)	171 (2)
Os(3)–Os(1)–C(3)	82.6 (7)	Os(3)–C(8)–O(8)	177 (2)
Os(3)–Os(1)–C(4)	84.8 (7)	Os(3)–C(9)–O(9)	175 (2)
C(1)–Os(1)–C(2)	104.1 (9)	Os(3)–C(10)–N	175 (2)
C(1)–Os(1)–C(3)	95.8 (9)	C(10)–N–C(11)	176 (2)
C(1)–Os(1)–C(4)	94.1 (9)	N–C(11)–C(12)	110 (3)
C(2)–Os(1)–C(3)	92.2 (8)	N–C(11)–C(13)	106 (3)
C(2)–Os(1)–C(4)	93.3 (9)	N–C(11)–C(14)	104 (3)
C(3)–Os(1)–C(4)	167.1 (10)	N–C(11)–C(121)	106 (3)
Os(1)–Os(2)–C(5)	170.1 (8)	N–C(11)–C(131)	108 (3)
Os(1)–Os(2)–C(6)	89.7 (6)	N–C(11)–C(141)	103 (3)
Os(1)–Os(2)–C(7)	91.4 (6)	C(12)–C(11)–C(13)	106 (3)
Os(3)–Os(2)–C(5)	108.5 (7)	C(12)–C(11)–C(14)	116 (4)
Os(3)–Os(2)–C(6)	127.0 (6)	C(13)–C(11)–C(14)	114 (3)
Os(3)–Os(2)–C(7)	130.3 (6)	C(121)–C(11)–C(131)	127 (4)
C(5)–Os(2)–C(6)	96.7 (9)	C(121)–C(11)–C(141)	101 (3)
C(5)–Os(2)–C(7)	96.1 (9)	C(131)–C(11)–C(141)	109 (3)
C(6)–Os(2)–C(7)	90.4 (8)	C(12)–C(11)–C(121)[a]	45 (3)
Os(1)–Os(3)–C(8)	93.6 (6)	C(12)–C(11)–C(131)[a]	141 (4)
Os(1)–Os(3)–C(9)	93.5 (7)	C(12)–C(11)–C(141)[a]	57 (3)
Os(1)–Os(3)–C(10)	165.8 (5)	C(13)–C(11)–C(121)[a]	66 (3)
Os(2)–Os(3)–C(8)	129.8 (6)	C(13)–C(11)–C(131)[a]	65 (3)
Os(2)–Os(3)–C(9)	132.7 (6)	C(13)–C(11)–C(141)[a]	149 (3)
Os(2)–Os(3)–C(10)	104.2 (5)	C(14)–C(11)–C(121)[a]	150 (4)
C(8)–Os(3)–C(9)	88.0 (9)	C(14)–C(11)–C(131)[a]	50 (3)
		C(14)–C(11)–C(141)[a]	63 (3)

[a] Angles between methyl groups of the two rotational conformations.

$(\mu\text{-H})_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$. The molecular structure of $(\mu\text{-H})_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$ is shown in Figure 2. A triangular cluster of three osmium atoms contains one linear terminal isocyanide and nine linear terminal carbonyl ligands. Overall, the molecule has a 46-electron configuration which is two electrons less than the 48-electron configuration which

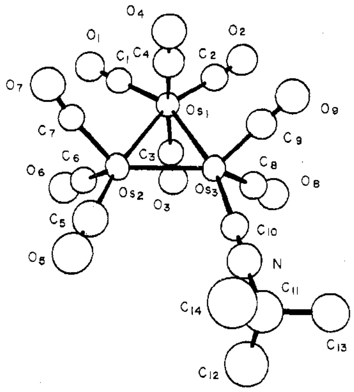

Figure 2. ORTEP diagram of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$ showing 50% probability ellipsoids. Only one of the disordered rotational conformations of the *tert*-butyl group is shown.

characterizes the closed-shell arrangement.[26] It is, thus, very similar to the parent molecule $(\mu\text{-H})_2\text{Os}(\text{CO})_{10}$. The osmium–osmium bond distances, Os(1)–Os(2) = 2.826 (1) Å, Os(1)–Os(3) = 2.827 (1) Å, and Os(2)–Os(3) = 2.690 (1) Å, are all marginally longer than the corresponding distances 2.817 (1), 2.812 (1), 2.681 (1) Å,[27] and 2.813 (1), 2.804 (1), and 2.670 (1) Å[28] that have been reported in two independent X-ray structure analyses of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. As with the parent carbonyl compound, the isocyanide derivative also contains one significantly short osmium–osmium bond. These short bonds are believed to be a manifestation of the electron unsaturation in the compounds.[29] The linear isocyanide ligand (C(10)–N–C(11) = 176 (2)°) occupies an equatorial coordination site on atom Os(3). We do not believe that this configuration has any special importance because in solution the compound exists as a mixture of two isomers, and in the other isomer the isocyanide ligand occupies one of the equivalent *pseudoaxial* sites located on Os(2) and Os(3).[15]

The osmium–carbon(isocyanide) bond distance Os(3)–C(10) = 2.05 (2) Å and is again significantly longer than the osmium–carbon(carbonyl) bond distances which averaged to 1.89 (2) Å in this molecule. The *tert*-butyl group was found to contain a twofold rotational disorder with one conformation, assumed to have an equivalent occupancy, rotated approximately 60° from the one shown in Figure 2. The hydrogen atoms were not located crystallographically and are therefore omitted from the figures. However, neutron studies have recently unambiguously shown that the two hydride ligands bridge the short osmium–osmium bond in the parent carbonyl complex.[29,30] We anticipate a similar arrangement in this isocyanide derivative.

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Registry No. $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$, 69942-19-4; $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$, 70084-45-6.

Supplementary Material Available: Tables of intermolecular contacts and structure factor amplitudes for both structures (33 pages). Ordering information is given on any current masthead page.

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