

the equatorial plane of the pentagonal bipyramid is occupied by the two carbon atoms of coordinated acetylene and three sulfur atoms, whereas the axial positions are taken up by the terminal oxo group and a sulfur atom from a dtc ligand.²⁴ The same stereochemistry is adopted²⁵ by $\text{MoO}(\text{S}_2\text{CNPr}_2)_2$ - (TCNE), where TCNE is tetracyanoethylene. For DTA and TCNE the latter structure is favored both by the small bite angle of the bidentate ligand and by the π -acceptor character of these ligands.

Summary

X-ray structure determination shows that the deep purple complex $\text{MoO}(\text{S}_2\text{CNMe}_2)_2(\text{PhCONNCOPh})$ contains an O,N-coordinated dibenzoyldiazene ligand with a five-membered chelate ring. The same stereochemistry is observed for other complexes of substituted benzoildiazene ligands,¹⁸⁻²¹ as predicted by Ittel and Ibers.¹⁵

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The initial purple material formed from the reaction of bis(dithiocarbamato)oxomolybdenum(IV) compounds with $(\text{EtO}_2\text{C})_2\text{N}_2$ probably has the same stereochemistry as 1. This leaves unanswered the stereochemistry of the final yellow product with the formula $\text{MoO}(\text{S}_2\text{CNMe}_2)_2$ - $(\text{EtO}_2\text{C}(\text{NCO}_2\text{Et}))$. Attempts to obtain suitable crystals of this yellow product for structure determination have been unsuccessful.

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Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, hydrogen positional parameters (Table VI), and least-squares planes (Table VII) (15 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 20.¹ Crystal Structure and NMR Spectra of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$

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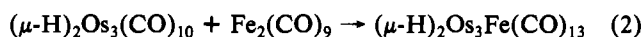
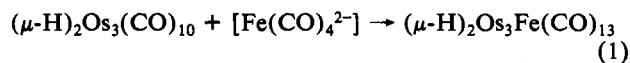
The heteronuclear species $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$, synthesized from $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, has been examined via NMR spectroscopy and a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ [C_{2h} , No. 14] with $a = 8.193$ (2) Å, $b = 14.641$ (3) Å, $c = 16.341$ (5) Å, $\beta = 90.98$ (2)°, $V = 1960.0$ (8) Å³, and $\rho(\text{calcd}) = 3.31$ g cm⁻³ for $Z = 4$ and mol wt 976.75. Diffraction data were collected with a Syntex P2₁ diffractometer, and the structure was refined to $R_F = 3.5\%$ for 1837 reflections with $3^\circ < 2\theta < 40^\circ$ (Mo K α radiation). The molecule contains a tetrahedral heterometallic Os₃Co core. Each osmium atom is linked to three terminal carbonyl ligands, while the cobalt atom is bonded to an η^5 -cyclopentadienyl ring. The structure is completed by an asymmetric bridging carbonyl ligand on the Os(1)-Co edge [Co-C(41) = 1.789 (14) Å, Os(1)-C(41) = 2.208 (13) Å] and bridging hydride ligands across the Os(1)-Os(2) and Os(2)-Os(3) edges. The nonbridged metal-metal distances are normal [Os(1)-Os(3) = 2.778 (1) Å, Os(2)-Co = 2.672 (2) Å, Os(3)-Co = 2.680 (2) Å], while the carbonyl-bridged metal-metal bond is slightly shortened [Os(1)-Co = 2.645 (2) Å] and the hydrido-bridged metal-metal bonds are lengthened [Os(1)-Os(2) = 2.940 (1) Å, Os(2)-Os(3) = 2.870 (1) Å] relative to the normal values for a tetrahedral cluster. The bridging hydride ligands were each located directly in the analysis; their disposition about their tetrahedral edges is discussed in detail.

Introduction

Mixed-metal clusters have previously been prepared from the formally unsaturated hydrido-osmium cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ by procedures that exploit its Lewis acid character.⁴⁻⁷

It has recently been shown⁸ that $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ can also function as an apparent Lewis base. A specific example of the two possibilities is provided by alternative routes to $(\mu\text{-H})_2\text{Os}_3\text{Fe}(\text{CO})_{13}$.

Equation 1 shows $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ acting as a Lewis acid in the route discovered by Geoffroy and Gladfelter,⁹ while eq 2 shows the Lewis base route.⁸



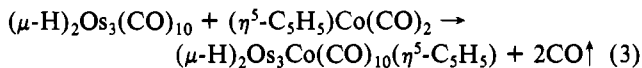
- (1) For recent previous publications in this series see the following: (a) Part 17: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1580. (b) Part 18: Churchill, M. R.; Wasserman, H. J. *Ibid.* **1981**, *20*, 2905. (c) Part 19: Churchill, M. R.; Hollander, F. J. *Ibid.* **1981**, *20*, 4124.
 (2) SUNY at Buffalo.
 (3) The Ohio State University.
 (4) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064.
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Table I. Experimental Data for the X-ray Diffraction Study of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$

(A) Crystal Parameters at 24 °C ^a	
crystal system: monoclinic	
space group: $P2_1/n[C_{2h}^2]$; No. 14	$V = 1960.0 (8) \text{ \AA}^3$
$a = 8.193 (2) \text{ \AA}$	$Z = 4$
$b = 14.641 (3) \text{ \AA}$	mol wt = 976.75
$c = 16.341 (5) \text{ \AA}$	$\rho(\text{calcd}) = 3.31 \text{ g cm}^{-3}$
$\beta = 90.98 (2)^\circ$	$\mu(\text{Mo K}\alpha) = 214.5 \text{ cm}^{-1}$
(B) Measurement of Data	
diffractometer: Syntex P2 ₁	
radiation: Mo K α (λ 0.710 73 \AA)	
monochromator: highly oriented graphite, equatorial mode	
($2\theta_{\text{mono}} = 12.2^\circ$)	
reflctns measd: $\pm h, k, \pm l$	
2θ range: 3–40°	
scan type: $\theta(\text{crystal}) - 2\theta(\text{counter})$	
scan width: $[2\theta(K\alpha_1) - 1.0] - [2\theta(K\alpha_2) + 1.0]^\circ$	
scan speed: 1.5°/min (in 2θ)	
bkgd, meast: stationary crystal and counter at beginning and end of 2θ scan, each for half of the scan time	
reflctns collected: 3990 total, merged to 1837 symmetry-independent reflctns	
standard reflctns: three remeasured after each 97 reflctns (412, 171, 008); no decay was observed over the period of data collection	
^a Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo K α components of 24 reflections with 2θ between 20 and 30°. Reflections used were {521}, {437}, {428}, {363}, {254}, and {171}.	

In a continuation of these studies, $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ was shown⁸ to react with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ to yield the mixed-metal cluster $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ as in eq 3.

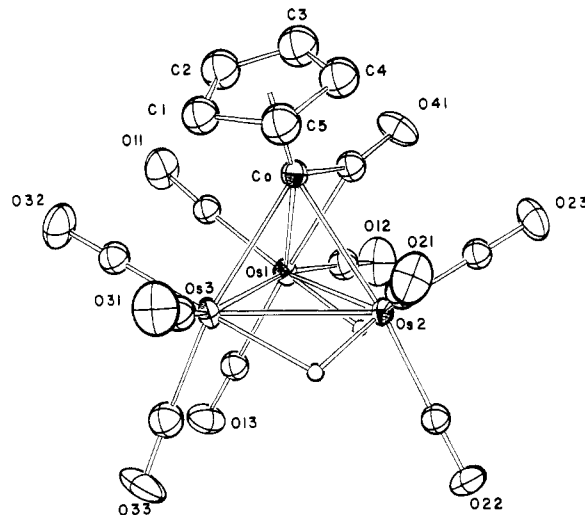


We now report the results of a single-crystal X-ray diffraction study and the NMR spectra (¹H, ¹³C) of this new tetranuclear heteroatomic cluster complex.

Experimental Section

Preparation of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$. Freshly distilled $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (140 mg) was added to a two-neck 50-mL flask and the flask evacuated of air. Approximately 8 mL of toluene was condensed in, followed by the addition of 47 mg of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ under a stream of nitrogen gas. The solution was warmed to 90 °C and stirred until all of the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ had been consumed. After 48 h of reaction time the solvent and unreacted $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ were removed from the reaction mixture. The remaining dark green solid material was dissolved in methylene chloride and chromatographed on preparative silica gel TLC plates. Elution with an 80/20 hexane/benzene solvent mixture yielded one major dark green band, 18 mg of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$. Crystals of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ were obtained by slowly evaporating solvent from a CH_2Cl_2 solution.

Collection of X-ray Diffraction Data for $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$. The complex was obtained in the form of opaque dark (black-green) crystals of maximum dimension ca. 0.5 mm. Smaller fragments were cleaved from these large crystals and were tested for variation in absorbance via a series of ψ scans. The crystal selected for the X-ray diffraction experiment was rather irregular with the approximate dimensions 0.15 × 0.17 × 0.20 mm. The crystal was mounted and aligned on our Syntex P2₁ diffractometer, and intensity data were collected as described previously.¹⁰ Details are given in Table I. The intensities were corrected for absorption by using an empirical method based upon 2-fold interpolation (in 2θ and ϕ) between ψ scans of close-to-axial reflections. The reflections used, their 2θ values, and their maximum-to-minimum intensity ratios for a full 360° scan of ψ were as follows: 24 $\bar{3}$, 16.40°, 1.41:1; 25 $\bar{2}$, 17.80°, 1.44:1; 35 $\bar{2}$, 21.01°, 1.44:1; 37 $\bar{2}$, 25.13°, 1.42:1; 47 $\bar{2}$, 28.45°, 1.43:1; 3, 10, $\bar{3}$,

**Figure 1.** Scheme used for labeling atoms in the $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ molecule (ORTEP-II diagram; 30% probability ellipsoids).

32.76°, 1.41:1; 49 $\bar{7}$, 36.82°, 1.39:1.

Analysis of the standard reflections showed no evidence for crystal decay. All absorption-corrected intensities were therefore converted to (unscaled) $|F_o|$ values following correction for Lorentz and polarization factors. Any reflection with $I_{\text{net}} < 0$ was assigned a value of $|F_o| = 0$.

Solution and Refinement of the Structure. The analytical form^{11a} of the scattering factors for neutral atoms were used throughout the analysis; both $\Delta f'$ and $i\Delta f''$ terms^{11b} were included for all nonhydrogen atoms. The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$, where the assigned weights are given by $w = [(\sigma(|F_o|))^2 + (p|F_o|^2)]^{-1}$, where $p = 0.01$. Data were placed on an approximate scale via a Wilson plot. The structure was solved via a combination of Patterson, difference-Fourier, and least-squares refinement techniques. All nonhydrogen atoms were located; the two bridging hydride ligands were located from a "cut-down" difference-Fourier map, based only on data with $(\sin \theta)/\lambda < 0.30 \text{ \AA}^{-1}$; the cyclopentadienyl ring's hydrogen atoms were included in calculated positions with $d(\text{C-H}) = 0.95 \text{ \AA}$ ¹² and $B(\text{H}_i) = [(B(\text{C}_i) + 1.0) \text{ \AA}^2]$.

The final discrepancy indices¹³ were $R_F = 3.5\%$, $R_{wF} = 2.9\%$, and $\text{GOF} = 1.75$ for 195 parameters refined against all 1837 reflections (none rejected). The residuals for those 1666 data with $|F_o| > 3\sigma(|F_o|)$ were $R_F = 2.9\%$, $R_{wF} = 2.8\%$, and $\text{GOF} = 1.81$.

A final difference-Fourier synthesis showed no significant features. The function $\sum w(|F_o| - |F_c|)^2$ showed no abnormal dependency on $|F_o|$, $(\sin \theta)/\lambda$, sequence number, identity, or parity class of the crystallographic indices; the weighting scheme is thus satisfactory. Positional parameters are collected in Table II; anisotropic thermal parameters are listed in Table III.

Collection of NMR Spectra. Proton NMR spectra were obtained on a Bruker HX-90 spectrometer operating in the FT mode at 90 MHz, and chemical shifts are reported relative to tetramethylsilane, $(\text{CH}_3)_4\text{Si}$ ($\tau = 10.0$). Carbon-13 NMR spectra were obtained on a Bruker WM-300 FT spectrometer operating at 75.5 MHz, and chemical shifts are reported relative to $(\text{CH}_3)_4\text{Si}$ (0.0 ppm). Both ¹H and ¹³C NMR spectra were obtained at temperatures ranging from -80 to +25 °C. Deuterated dichloromethane served as the solvent and source of the lock signal for the ¹H NMR spectra, while the ¹³C NMR spectra were obtained in a mixture of 75% THF of normal isotopic composition and 25% CD₂Cl₂.

Description of the Structure

The crystal consists of discrete ordered units of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ which are mutually separated by normal van der Waals distances. Figure 1 shows the scheme used for labeling atoms, while Figure 2 provides a stereoscopic

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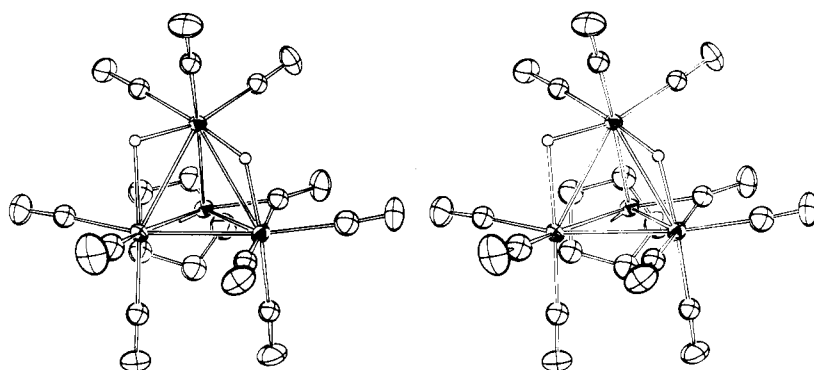
(12) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(13) $R_F = [\sum w(|F_o| - |F_c|) / \sum |F_o|] \times 100 (\%)$; $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100 (\%)$; $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$ (NO = number of observations; NV = number of variables).

Table II. Final Positional and Isotropic Thermal Parameters for $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$

atom	x	y	z	atom	x	y	z
Os(1)	0.23718 (7)	0.34134 (4)	0.56727 (3)	O(21)	0.6971 (13)	0.1802 (7)	0.7908 (6)
Os(2)	0.48066 (6)	0.31895 (4)	0.70005 (3)	O(22)	0.7055 (12)	0.4768 (7)	0.7481 (6)
Os(3)	0.52035 (7)	0.24237 (4)	0.53995 (3)	O(23)	0.2579 (13)	0.3462 (7)	0.8466 (6)
Co	0.29116 (21)	0.18409 (12)	0.64266 (10)	O(31)	0.7832 (13)	0.0971 (8)	0.5660 (7)
O(11)	0.0281 (12)	0.2349 (9)	0.4454 (6)	O(32)	0.3622 (13)	0.1386 (8)	0.3966 (6)
O(12)	-0.0271 (14)	0.4816 (9)	0.6099 (7)	O(33)	0.7289 (14)	0.3634 (8)	0.4325 (7)
O(13)	0.3847 (12)	0.4629 (7)	0.4345 (6)	O(41)	0.0160 (12)	0.2754 (8)	0.7107 (6)

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
C(11)	0.1054 (16)	0.2786 (9)	0.4886 (8)	3.0 (3)	C(2)	0.1826 (20)	0.0624 (12)	0.6010 (10)	5.1 (4)
C(12)	0.0652 (18)	0.4299 (11)	0.5928 (9)	4.1 (3)	C(3)	0.1324 (21)	0.0804 (13)	0.6756 (11)	5.7 (4)
C(13)	0.3336 (16)	0.4167 (9)	0.4836 (8)	3.1 (3)	C(4)	0.2700 (20)	0.0820 (12)	0.7280 (10)	5.3 (4)
C(21)	0.6165 (16)	0.2333 (10)	0.7577 (8)	3.1 (3)	C(5)	0.4070 (20)	0.0650 (11)	0.6817 (10)	5.0 (4)
C(22)	0.6218 (16)	0.4195 (9)	0.7293 (8)	2.8 (3)	H(12)	0.371 (10)	0.388 (6)	0.643 (5)	0.6 (20)
C(23)	0.3401 (16)	0.3373 (9)	0.7915 (8)	2.9 (3)	H(23)	0.637 (11)	0.302 (7)	0.644 (6)	2.0 (25)
C(31)	0.6889 (17)	0.1545 (10)	0.5578 (8)	3.4 (3)	H(1)	0.418	0.031	0.552	5.3
C(32)	0.4186 (17)	0.1779 (10)	0.4500 (9)	3.4 (3)	H(2)	0.111	0.059	0.553	6.2
C(33)	0.6479 (18)	0.3175 (10)	0.4715 (9)	4.1 (3)	H(3)	0.019	0.091	0.692	6.8
C(41)	0.1312 (16)	0.2617 (10)	0.6681 (8)	3.2 (3)	H(4)	0.270	0.094	0.786	6.4
C(1)	0.3532 (19)	0.0481 (11)	0.5986 (9)	4.3 (4)	H(5)	0.520	0.065	0.701	6.0

Figure 2. Stereoscopic view of the $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ molecule (ORTEP-II diagram).

view of the molecule. Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; interatomic angles are listed in Table V, while information on molecular planes and dihedral angles is provided in Table VI.

The molecule is based upon a closed tetrahedral Os_3Co cluster. There are the usual 60 valence electrons associated with a tetrahedral array (three d^8 Os(0) atoms, one d^9 Co(0) atom, one electron from each hydride ligand, two electrons from each carbonyl group, and five electrons from the η^5 -cyclopentadienyl system). Each osmium atom is linked to three terminal carbonyl ligands, and the cobalt atom is bound to the $\eta^5\text{-C}_5\text{H}_5$ ligand; the structure is completed by a rather asymmetric bridging carbonyl group across the Os(1)-Co bond and by bridging hydride ligands (which were located in the course of the structural analysis) across the Os(1)-Os(2) and Os(2)-Os(3) bonds.

The intermetallic distances within the cluster fall into three sets. (Note that the designations "short", "normal", and "long" are used in a local, comparative sense.)

(a) "Normal" Metal-Metal Bond Distances. The Os(1)-Os(3) bond length of 2.778 (1) Å and the distances Os(2)-Co = 2.672 (2) Å and Os(3)-Co = 2.680 (2) Å are considered to be normal, since there are no bridging ligands present on these tetrahedral edges that might interfere with the metal-metal bond order. Although the Os(1)-Os(3) bond length of 2.778 (1) Å is 0.099 Å shorter than the mean value of 2.877 (3) Å in the triangular species $\text{Os}_3(\text{CO})_{12}$,¹⁴ it is close to the unbridged osmium-osmium distances in neutral tetrahedral cluster complexes: viz., 2.822 (1) Å in $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{11}(\text{CNMe})$,¹⁵ 2.784 (2)-2.799 (2) Å in $(\mu\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}$ -

$(\eta^5\text{-C}_5\text{H}_5)$,¹⁶ and 2.825 (2)-2.827 (2) Å in $(\mu\text{-H})_3\text{Os}_3\text{W}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$.¹⁷ The observed osmium-cobalt distances are fairly similar to those found⁷ in $(\mu\text{-H})_3\text{Os}_3\text{Co}(\text{CO})_{12}$ (Os-Co = 2.690 (1)-2.698 (1) Å).

(b) "Long" Osmium-Osmium Bond Lengths. The Os(1)-Os(2) and Os(2)-Os(3) distances are 2.940 (1) and 2.870 (1) Å, respectively. (The difference in these must be attributed to their different environment—vide infra.) They are lengthened appreciably relative to the nonbridged Os(1)-Os(3) distance of 2.778 (1) Å. This is entirely consistent with their being bridged by μ -hydride ligands^{18,19} (as shown directly by the diffraction study) and is a result of the Os(μ -H)Os system being held together by an electron-deficient two-electron, three-center bond.

Hydride-bridged Os-Os distances in other tetranuclear osmium carbonyl clusters have similar values: 2.941 (2) Å in $(\mu\text{-H})_3\text{OsW}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$,¹⁷ 2.932 (2) Å in $(\mu\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$,¹⁶ 2.956 (1)-2.971 (1) Å in $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{11}(\text{CNMe})$,¹⁵ and 2.893 (1)-2.909 (1) Å in $(\mu\text{-H})_3\text{Os}_3\text{Co}(\text{CO})_{13}$.⁷ It is worth noting that the three μ -hydride ligands in this last complex, $(\mu\text{-H})_3\text{Os}_3\text{Co}(\text{CO})_{13}$, again span the Os-Os vectors, rather than the Os-Co vectors. Presumably M-H-M bridges involving two third-row metal atoms are energetically favored over M-H-M' bridges involving a first-row and a third-row transition metal.

(c) A Rather "Short" Osmium-Cobalt Bond. The Os(1)-Co bond length of 2.645 (2) Å, the shortest osmium-cobalt dis-

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Table IV. Selected Interatomic Distances (Å) for the $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ Molecule

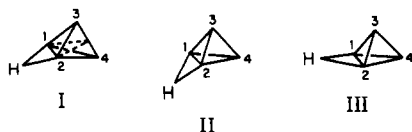
(A) Metal–Metal Distances			
Os(1)–Os(2)	2.940 (1)	Os(2)–Os(3)	2.870 (1)
Os(1)–Os(3)	2.778 (1)	Os(2)–Co	2.672 (2)
Os(1)–Co	2.645 (2)	Os(3)–Co	2.680 (2)
(B) Metal–Carbonyl Distances			
Os(1)–C(11)	1.902 (13)	Os(1)–O(11)	3.036 (11)
Os(1)–C(12)	1.965 (15)	Os(1)–O(12)	3.073 (12)
Os(1)–C(13)	1.935 (13)	Os(1)–O(13)	3.070 (10)
Os(2)–C(21)	1.914 (13)	Os(2)–O(21)	3.062 (10)
Os(2)–C(22)	1.927 (13)	Os(2)–O(22)	3.049 (10)
Os(2)–C(23)	1.922 (13)	Os(2)–O(23)	3.062 (10)
Os(3)–C(31)	1.906 (14)	Os(3)–O(31)	3.051 (11)
Os(3)–C(32)	1.924 (14)	Os(3)–O(32)	3.061 (11)
Os(3)–C(33)	1.895 (15)	Os(3)–O(33)	3.041 (11)
(C) Metal–Hydride Distances			
Os(1)–H(12)	1.78 (8)	Os(2)–H(23)	1.61 (10)
Os(2)–H(12)	1.63 (9)	Os(3)–H(23)	2.12 (10)
(D) Distances Involving the $\eta^5\text{-C}_5\text{H}_5$ Ligand			
Co–C(1)	2.181 (16)	C(1)–C(2)	1.414 (23)
Co–C(2)	2.100 (17)	C(2)–C(3)	1.321 (24)
Co–C(3)	2.077 (18)	C(3)–C(4)	1.403 (24)
Co–C(4)	2.053 (17)	C(4)–C(5)	1.387 (23)
Co–C(5)	2.080 (17)	C(5)–C(1)	1.443 (22)
Co–Cp ^a	1.732		
(E) Carbon–Oxygen Distances			
C(11)–O(11)	1.138 (17)	C(23)–O(23)	1.140 (16)
C(12)–O(12)	1.110 (19)	C(31)–O(31)	1.147 (18)
C(13)–O(13)	1.136 (17)	C(32)–O(32)	1.137 (18)
C(21)–O(21)	1.149 (17)	C(33)–O(33)	1.147 (19)
C(22)–O(22)	1.122 (17)		
(F) Bridging Carbonyl Distances			
Co–C(41)	1.789 (14)	Co–O(41)	2.862 (10)
Os(1)–C(41)	2.208 (13)	C(41)–O(41)	1.199 (16)

^a Cp is the centroid of the $\eta^5\text{-C}_5\text{H}_5$ system.

tance in the molecule, is contracted by 0.031 Å from the mean "normal" Os–Co distance of 2.676 [6] Å. This presumably is a result of the asymmetrically bridging carbonyl group associated with this tetrahedral edge [Co–C(41) = 1.789 (14) Å, Os(1)–C(41) = 2.208 (13) Å, C(41)–O(41) = 1.199 (16) Å, $\angle\text{Co–C(41)–O(41)} = 145.9^\circ$ (11)°, $\angle\text{Os(1)–C(41)–O(41)} = 131.9$ (10)°].

The μ -hydride ligands were located directly from a difference-Fourier synthesis, and their positions were optimized by least-squares refinement (vide supra). Atom H(12) bridges Os(1) and Os(2), with Os(1)–H(12) = 1.78 (8) Å, Os(2)–H(12) = 1.63 (9) Å, and $\angle\text{Os(1)–H(12)–Os(2)} = 119.2$ (50)°; H(23) bridges Os(2) and Os(3), with Os(2)–H(23) = 1.61 (10) Å, Os(3)–H(23) = 2.12 (10) Å, and $\angle\text{Os(2)–H(23)–Os(3)} = 99.6$ (47)°. While the hydride ligands are located with rather poor precision (as expected, with $Z(\text{H}) = 1$ vs. $Z(\text{Os}) = 76$), one may easily observe their effects on the ligand distribution about the tetrahedral metal cluster.

We have previously commented¹⁷ that bridging hydride ligands in tetrahedral clusters can occur at various angles about the bridged metal–metal vector. Obvious symmetrical possibilities include (a) the case where an $\text{M}_1\text{–H–M}_2$ plane bisects the exterior angle between the $\text{M}_1\text{–M}_3\text{–M}_2$ and $\text{M}_1\text{–M}_4\text{–M}_2$ tetrahedral faces meeting at $\text{M}_1\text{–M}_2$ (see I) and (b) cases



where the $\text{M}_1\text{–H–M}_2$ plane is coplanar with one of the two triangular faces meeting at the $\text{M}_1\text{–M}_2$ edge—either with $\text{M}_1\text{–M}_3\text{–M}_2$ (as in II) or with $\text{M}_1\text{–M}_4\text{–M}_2$ (as in III). A

continuum of less symmetrical locations between these extremes is, in principle, possible. (Note that II and III will be equivalent only when M_3 and M_4 are identical metal atoms in the same ligand environment.)

Figure 3 shows portions of the molecule projected, in turn, onto each of the four triangular faces of the tetrahedral cluster. Atom H(12) lies only 0.23 (8) Å above (relative to Figure 3A) the Os(1)–Os(2)–Co plane, whereas it is 0.70 (9) Å above (relative to Figure 3B) the Os(1)–Os(2)–Os(3) plane. The appropriate dihedral angles²⁰ are $[\text{Os(1)–Os(2)–Co}]/[\text{Os(1)–H(12)–Os(2)}] = 16^\circ$ and $[\text{Os(1)–Os(2)–Os(3)}]/[\text{Os(1)–H(12)–Os(2)}] = 55^\circ$. The near coplanarity of H(12) with the Os(1)–Os(2)–Co plane would appear to be associated with the expanded equatorial Os–Os–Co angles in Figure 3A [$\text{Os(1)–Os(2)–C(22)} = 119.6$ (4)° and $\text{Os(2)–Os(1)–C(13)} = 107.7$ (4)°] as compared to those in Figure 3B [$\text{Os(2)–Os(1)–C(12)} = 113.4$ (4)° and $\text{Os(1)–Os(2)–C(23)} = 98.6$ (4)°]. However, this correlation is not carried over to the second bridging hydride ligand.

Atom H(23) lies 0.66 (10) Å above the Os(1)–Os(2)–Os(3) plane (Figure 3B) and 0.64 (10) Å above the Os(2)–Os(3)–Co plane (Figure 3C); the relevant dihedral angles are equivalent,²⁰ with $[\text{Os(1)–Os(2)–Os(3)}]/[\text{Os(2)–H(23)–Os(3)}] = 34^\circ$ and $[\text{Os(2)–Os(3)–Co}]/[\text{Os(2)–H(23)–Os(3)}] = 33^\circ$. This corresponds closely to the external bisecting geometry shown in structure I above. Related expanded M–M–C angles here are $\text{Os(2)–Os(3)–C(33)} = 112.5$ (4)° and $\text{Os(3)–Os(2)–C(22)} = 116.6$ (4)° (Figure 3C) and $\text{Os(2)–Os(3)–C(31)} = 102.6$ (4)° and $\text{Os(3)–Os(2)–C(21)} = 96.8$ (4)° (Figure 3B).

Other points of interest include the following.

(1) The OC–M–CO angles are all close to 90°—those within the $\text{Os}(\text{CO})_3$ fragments range from 91.8 (6) to 95.1 (6)°, while the cis angles involving the bridging carbonyl groups are $\text{C(41)–Os(1)–C(11)} = 91.3$ (5)° and $\text{C(41)–Os(1)–C(12)} = 84.1$ (6)°.

(2) There are carbonyl ligands trans to each end of the bridging hydrides—appropriate angles are $\angle\text{H(12)–Os(1)–C(11)} = 173.5$ (28)°, $\angle\text{H(12)–Os(2)–C(21)} = 174.8$ (30)°, $\angle\text{H(23)–Os(2)–C(23)} = 163.6$ (35)°, and $\angle\text{H(23)–Os(3)–C(32)} = 174.9$ (27)°.

(3) The bridging carbonyl group is asymmetric, with Co–C(41) = 1.789 (14) Å and Os(1)–C(41) = 2.208 (13) Å. The asymmetry probably results from a combination of two effects: (a) the different covalent radii of cobalt and osmium ($r(\text{Os}) = 1.389$ Å and $r(\text{Co}) = 1.287$ Å, based upon internal non-bridged metal–metal distances within the present molecule) and (b) a component from some "semibridging" nature of this carbonyl group. In keeping with this, the Co–C(41)–O(41) angle of 145.9 (11)° is 14.0° larger than the Os(1)–C(41)–O(41) angle of 131.9 (10)°. The effects of this bridging carbonyl ligand on peripheral ligands can clearly be seen in Figure 3D; the angle C(13)–Os(1)–C(41) is 176.5 (5)°.

(4) The molecule is quite unsymmetrical, with the three $\text{Os}(\text{CO})_3$ groups in different environments—Os(1) interacts with a $\mu\text{-CO}$ and a $\mu\text{-H}$ ligand, Os(2) interacts with two $\mu\text{-H}$ ligands, and Os(3) interacts with a single $\mu\text{-H}$ ligand.

(5) Osmium–carbonyl distances are self-consistent and are in the normal range with Os–CO = 1.895 (15)–1.965 (15) Å, Os–O = 3.036 (11)–3.073 (12) Å, and C–O = 1.110 (19)–1.149 (17) Å.

(6) The η^5 -cyclopentadienyl ligand is displaced from its possible symmetrical apical position by the bridging carbonyl group—the resulting Co–C distances vary from 2.053 (17) to 2.181 (16) Å. The pentaatomic carbocyclic ring is planar

(20) We estimate an error of about 5° on these dihedral angles. This estimate is based on the derived esd of about 5° for M–H–M angles (see Table VG).

Table V. Selected Interatomic Angles (Deg) for $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$

(A) Intermetallic Angles			
Os(2)-Os(1)-Os(3)	60.17 (2)	Os(1)-Os(3)-Os(2)	62.72 (2)
Os(2)-Os(1)-Co	56.86 (4)	Os(1)-Os(3)-Co	57.94 (4)
Os(3)-Os(1)-Co	59.16 (4)	Os(2)-Os(3)-Co	57.44 (4)
Os(1)-Os(2)-Os(3)	57.11 (2)	Os(1)-Co-Os(2)	67.15 (4)
Os(1)-Os(2)-Co	55.99 (4)	Os(1)-Co-Os(3)	62.90 (4)
Os(3)-Os(2)-Co	57.70 (4)	Os(2)-Co-Os(3)	64.87 (4)
(B) M-M-CO Angles			
Os(2)-Os(1)-C(11)	144.6 (4)	Os(1)-Os(3)-C(31)	158.8 (4)
Os(3)-Os(1)-C(11)	96.1 (4)	Os(2)-Os(3)-C(31)	102.6 (4)
Co-Os(1)-C(11)	89.0 (4)	Co-Os(3)-C(31)	101.7 (4)
Os(2)-Os(1)-C(12)	113.4 (4)	Os(1)-Os(3)-C(32)	91.5 (4)
Os(3)-Os(1)-C(12)	169.2 (4)	Os(2)-Os(3)-C(32)	146.4 (4)
Co-Os(1)-C(12)	126.2 (4)	Co-Os(3)-C(32)	91.3 (4)
Os(2)-Os(1)-C(13)	107.7 (4)	Os(1)-Os(3)-C(33)	105.2 (4)
Os(3)-Os(1)-C(13)	80.3 (4)	Os(2)-Os(3)-C(33)	112.5 (4)
Co-Os(1)-C(13)	139.3 (4)	Co-Os(3)-C(33)	162.5 (5)
Os(1)-Os(2)-C(21)	144.8 (4)	Os(1)-Co-C(41)	55.8 (4)
Os(3)-Os(2)-C(21)	96.8 (4)	Os(2)-Co-C(41)	82.7 (4)
Co-Os(2)-C(21)	91.0 (4)	Os(3)-Co-C(41)	117.9 (4)
Os(1)-Os(2)-C(22)	119.6 (4)	Os(1)-Co-Cp	154.6
Os(3)-Os(2)-C(22)	116.6 (4)	Os(2)-Co-Cp	137.9
Co-Os(2)-C(22)	173.8 (4)	Os(3)-Co-Cp	118.3
Os(1)-Os(2)-C(23)	98.6 (4)		
Os(3)-Os(2)-C(23)	147.4 (4)		
Co-Os(2)-C(23)	91.3 (4)		
(C) Carbon-Metal-Carbon Angles			
C(12)-Os(1)-C(11)	93.5 (6)	C(32)-Os(3)-C(31)	95.1 (6)
C(13)-Os(1)-C(11)	91.8 (6)	C(33)-Os(3)-C(31)	94.4 (6)
C(13)-Os(1)-C(12)	94.4 (6)	C(33)-Os(3)-C(32)	94.0 (6)
C(22)-Os(2)-C(21)	92.1 (6)	C(41)-Co-Cp	121.0
C(23)-Os(2)-C(21)	93.4 (6)	C(41)-Os(1)-C(13)	176.6 (5)
C(23)-Os(2)-C(22)	93.7 (5)	C(41)-Os(1)-C(11)	91.3 (5)
		C(41)-Os(1)-C(12)	84.1 (6)
(D) Metal-Carbon-Oxygen Angles			
Os(1)-C(11)-O(11)	174.4 (12)	Os(3)-C(31)-O(31)	175.2 (12)
Os(1)-C(12)-O(12)	176.6 (13)	Os(3)-C(32)-O(32)	178.2 (12)
Os(1)-C(13)-O(13)	177.3 (12)	Os(3)-C(33)-O(33)	177.5 (13)
Os(2)-C(21)-O(21)	178.3 (12)	Co-C(41)-O(41)	145.9 (11)
Os(2)-C(22)-O(22)	178.2 (12)	Os(1)⋯C(41)-O(41)	131.9 (10)
Os(2)-C(23)-O(23)	178.4 (12)		
(E) Metal-Metal-Hydride Angles			
Os(3)-Os(1)-H(12)	78.8 (28)	Os(1)-Os(2)-H(23)	97.7 (35)
Co-Os(1)-H(12)	84.9 (28)	Co-Os(2)-H(23)	98.6 (35)
Os(3)-Os(2)-H(12)	78.1 (30)	Os(1)-Os(3)-H(23)	91.3 (26)
Co-Os(2)-H(12)	86.9 (30)	Co-Os(3)-H(23)	86.6 (26)
(F) Carbon-Metal-Hydride Angles			
H(12)-Os(1)-C(11)	173.5 (28)	H(23)-Os(2)-C(21)	73.5 (35)
-C(12)	92.0 (28)	-C(22)	77.3 (35)
-C(13)	91.2 (28)	-C(23)	163.6 (35)
H(12)-Os(2)-C(21)	174.8 (30)	H(23)-Os(3)-C(31)	80.8 (27)
-C(22)	89.5 (30)	-C(32)	174.9 (27)
-C(23)	91.4 (30)	-C(33)	89.3 (27)
		H(12)-Os(1)⋯C(41)	85.8 (28)
(G) Metal-Hydride-Metal Angles			
Os(1)-H(12)-Os(2)	119.2 (50)	Os(2)-H(23)-Os(3)	99.6 (47)
(H) Carbon-Carbon-Carbon Angles			
C(5)-C(1)-C(2)	103.6 (13)	C(3)-C(4)-C(5)	108.3 (15)
C(1)-C(2)-C(3)	112.3 (15)	C(4)-C(5)-C(1)	107.8 (14)
C(2)-C(3)-C(4)	107.8 (16)		
(I) Hydride-Metal-Hydride Angle			
H(12)-Os(2)-H(23)	102.0 (46)		
(J) Metal-Carbonyl-Metal Angle			
Co-C(41)-Os(1)	82.1 (5)		

within the limits of experimental error.

NMR Spectra

Proton and carbon-13 NMR spectra of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ are consistent with the X-ray structure determination. Under conditions of slow exchange (ca. -70°C)

the ^1H NMR spectrum indicates that two nonequivalent bridging hydrogens are present and the ^{13}C NMR spectrum indicates that this compound contains ten distinct carbonyl groups.

(a) ^1H NMR Spectra. At -80°C the ^1H NMR spectrum of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ consists of a sharp signal of

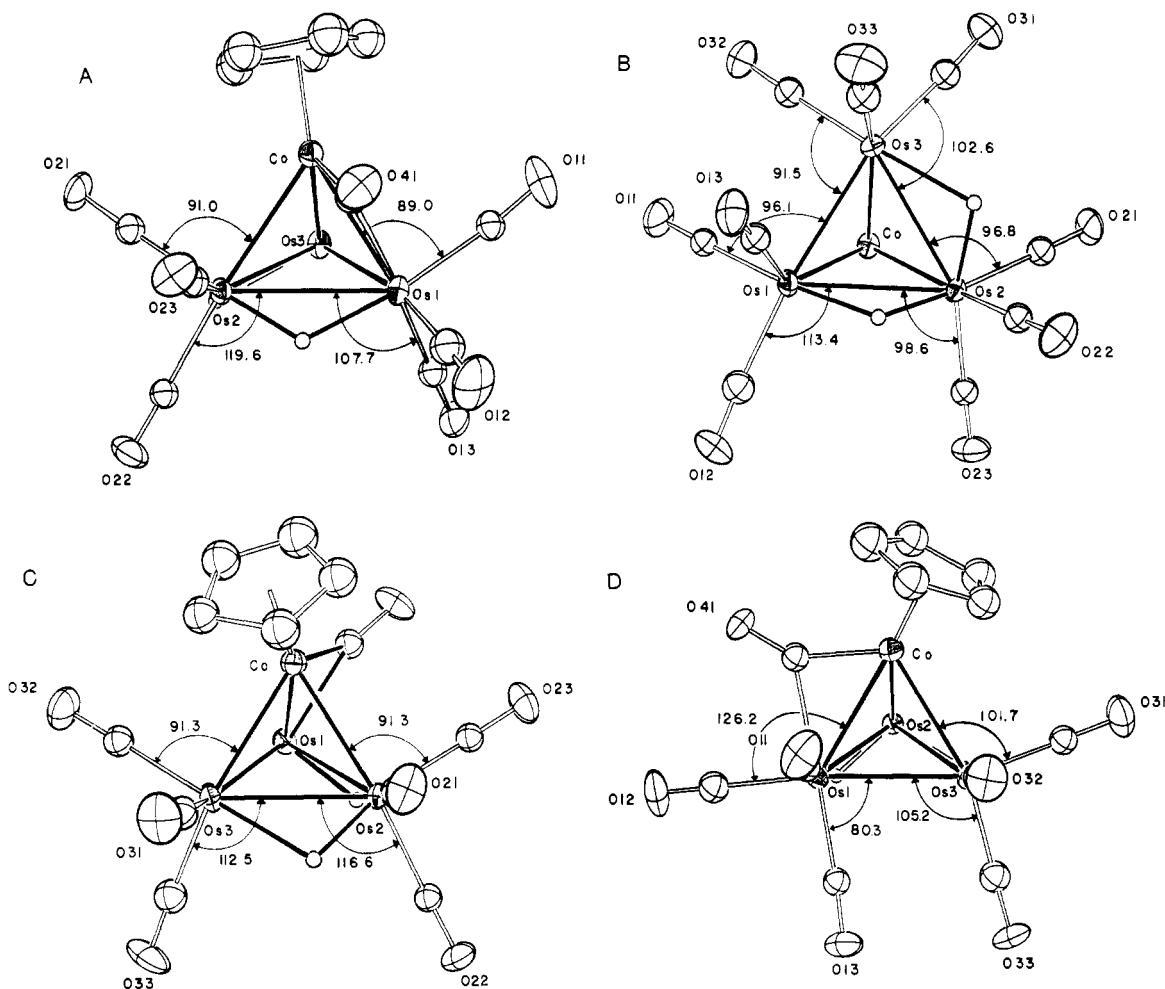


Figure 3. Projections of the molecule onto each of the four faces of the Os_3Co tetrahedral core, showing the equatorial angles. (A) Projection onto the $\text{Os}(1)\text{-Os}(2)\text{-Co}$ plane; the terminal carbonyl groups on $\text{Os}(3)$ are omitted for clarity. (B) Projection onto the $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$ plane; the $\eta^5\text{-C}_5\text{H}_5$ and $\mu\text{-CO}$ ligands are omitted. (C) Projection onto the $\text{Os}(2)\text{-Os}(3)\text{-Co}$ face; the terminal carbonyl ligands on $\text{Os}(1)$ are omitted. (D) Projection onto the $\text{Os}(1)\text{-Os}(3)\text{-Co}$ face; the terminal carbonyl ligands on $\text{Os}(2)$ are omitted.

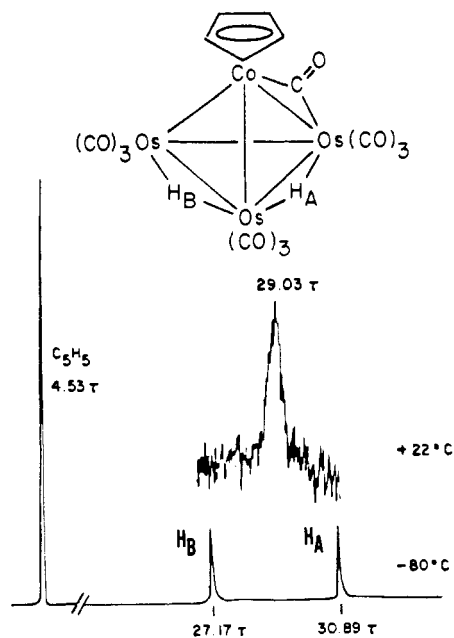


Figure 4. Proton NMR spectra (90 MHz) of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ at $+22$ and -80°C .

relative area 5 (τ 4.53), assigned to $\eta^5\text{-C}_5\text{H}_5$, and two sharp singlets at high field (τ 27.17 and 30.89), each of relative area 1, assigned to the bridging hydrogens H_B and H_A (Figure 4).

Table VII. Carbon-13 NMR Data (75.5 MHz) for $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ at -75°C

δ	assignment (see Figure 5)
237.4	1
183.3	10
181.1	4
178.7	7
178.2 (d; $J(^1\text{H}\text{-}^{13}\text{C}) = 10$ Hz)	9
177.9	3
172.3	8
170.3 (d; $J(^1\text{H}\text{-}^{13}\text{C}) = 10$ Hz)	6
169.9 (d; $J(^1\text{H}\text{-}^{13}\text{C}) = 10$ Hz)	5
167.9 (d; $J(^1\text{H}\text{-}^{13}\text{C}) = 10$ Hz)	2

The assignments of these hydrogens are based upon the fact that in related compounds, bridging hydrogens cis to a carbonyl bridge have chemical shifts larger than τ 30 (e.g., $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$, τ 30.7;⁸ $\text{HCoOs}_3(\text{CO})_{13}$, τ 30.3²¹) while hydrogens that bridge osmium atoms and are not cis to a bridge carbonyl have chemical shifts less than τ 30 (e.g., $\text{H}_3\text{CoOs}_3(\text{CO})_{12}$, τ 29.1;⁷ $(\mu\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$, τ 28.8⁵). As the temperature of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ is raised, the signals due to H_A and H_B merge into a single signal at τ 29.03 (τ 29.03 av) while the signal due to $(\eta^5\text{-C}_5\text{H}_5)$ is temperature independent.

(21) Kennedy, S., unpublished work.

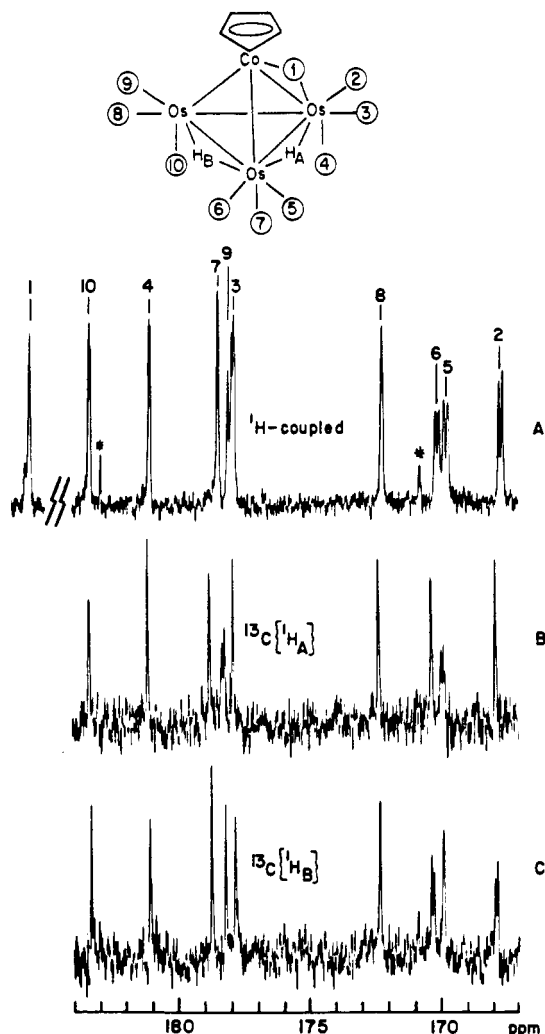


Figure 5. Carbon-13 NMR spectra (75.5 MHz) of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ at -75°C : (A) ^1H -coupled spectrum; (B) ^1H -decoupled spectrum at the resonance frequency of H_A ; (C) ^1H -decoupled spectrum at the resonance frequency of H_B . Peaks denoted by an asterisk are due to $\text{Os}_3(\text{CO})_{12}$ impurity.

(b) ^{13}C NMR Spectra. The room-temperature ^{13}C NMR spectrum of $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$ contains several very broad signals which indicate that ligand exchange (H and CO) is occurring at a rate comparable to the ^{13}C NMR time

scale. However, at about -70°C exchange is sufficiently slow for ten distinct carbonyl signals to be observed (Figure 5, Table VII). The low-field signal at 237.4 ppm is assigned to the edge-bridging carbonyl, 1, while the nine remaining signals at 183.3–167.9 ppm indicate the presence of nine terminal carbonyl groups. Assignments of these terminal carbonyls are based upon the examination of the ^1H -coupled and selectively ^1H -decoupled ^{13}C NMR spectra shown in Figure 5.

The ^1H -coupled spectrum (Figure 5A) displays the expected patterns of nine signals, four of which are split into doublets with a coupling constant of approximately 10 Hz. These signals are attributed to the four carbonyls that are in positions trans to the bridging hydrogens. Careful inspection reveals that two of the doublets display further splitting on the order of 2–3 Hz. These signals, therefore, must be the number 5 and 6 carbonyls, which are each adjacent to both bridge hydrogens. Selective irradiation at the frequency of each of the bridging hydrogens allows the assignment of the number 2, 5, 6, and 9 carbonyls.

Assignment of the remaining five carbonyls cis to the bridging hydrogens is achieved in an analogous manner. In general, axial carbonyls in this type of cluster appear at lower field in ^{13}C NMR spectra. Therefore, the three lowest field terminal resonances were assumed to be the axial carbonyls (4, 7, and 10). The specific assignments shown were made on the basis of intensities in the coupled and decoupled spectra. The attenuation of the signals labeled as 4 and 10 in spectra 5B and 5C, respectively, allows these assignments to be made. The remaining carbonyls (numbers 3 and 8) were assigned in the same manner.

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Registry No. $(\mu\text{-H})_2\text{Os}_3\text{Co}(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)$, 79840-19-0; $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, 12078-25-0; $\text{H}_2\text{Os}_3(\text{CO})_{10}$, 41766-80-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Table III), and least-squares planes (Table VI) (14 pages). Ordering information is given on any current masthead page.