

$$(24) \text{ ABS FOM} = \frac{\sum_n \alpha_n - \sum_n \langle \alpha_n^2 \rangle_r^{1/2}}{\langle \alpha_n^2 \rangle_e^{1/2} - \langle \alpha_n^2 \rangle_r^{1/2}}$$

$$\text{RESID} = \frac{\sum_{k_r} |E_h|_{\text{obsd}} - |E_h|_{\text{calcd}}}{\sum_{k_r} |E_h|_{\text{obsd}}}$$

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## A Neutron Diffraction Study of $\text{HFeCo}_3(\text{CO})_9(\text{P}(\text{OCH}_3)_3)_3$ , a Metal Cluster Complex with a Triply Bridging Hydride Ligand

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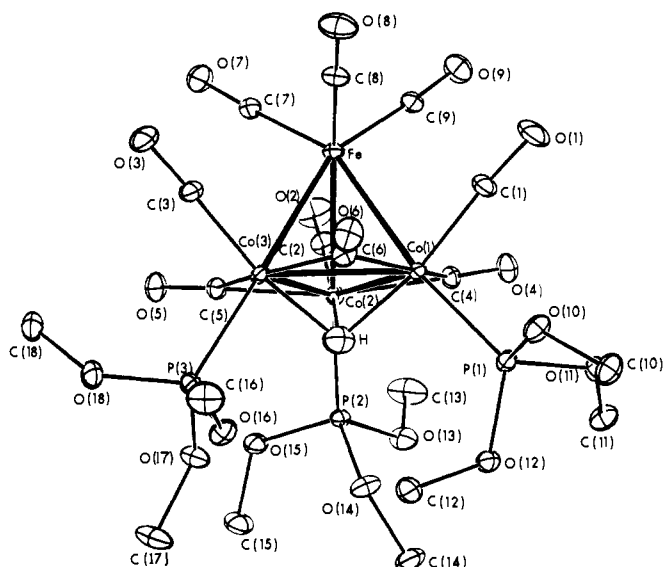
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**Abstract:** We wish to report the first accurate neutron diffraction study of a transition metal structure with a triply bridging hydride ligand, the cluster  $\text{HFeCo}_3(\text{CO})_9(\text{P}(\text{OCH}_3)_3)_3$ . The compound crystallizes in the space group  $P2_1/c$ ,  $Z = 4$ . The cell constants at 90 K are  $a = 15.957(8) \text{ \AA}$ ,  $b = 10.611(5) \text{ \AA}$ ,  $c = 18.383(9) \text{ \AA}$ ,  $\beta = 98.70(2)^\circ$ . The structure was refined, based on the measured intensities of 8229 reflections; the final discrepancy factors for all reflections are  $R_{F^2} = 0.087$ ,  $R_{wF^2} = 0.066$ . The four metal atoms form a tetrahedron with the apical Fe atom additionally bonded to three terminal carbonyl groups. Each Co atom is further bonded to one terminal and two bridging carbonyl ligands, as well as one phosphite group and the hydride ligand. The hydride ligand is located outside the metal cluster,  $0.978(3) \text{ \AA}$  from the  $\text{Co}_3$  face. This result confirms that of an earlier x-ray investigation by Huie, Knobler, and Kaesz.<sup>2</sup> The Co-H distances are  $1.742(3)$ ,  $1.731(3)$ , and  $1.728(3) \text{ \AA}$ , and Co-H-Co angles are  $92.1(1)$ ,  $91.7(1)$ , and  $91.5(1)^\circ$ .

### Introduction

In 1960, Chini and co-workers reported the isolation of  $[\text{FeCo}_3(\text{CO})_{12}]^-$  from the reaction of  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}(\text{CO})_5$  in acetone, and the acidification of that anion to form  $\text{HFeCo}_3(\text{CO})_{12}$ .<sup>3</sup> Subsequent investigations by other workers were aimed at elucidating the structure of this interesting cluster, with the location of the H atom being the focus of these experiments. On the basis of mass spectral evidence and electron-counting arguments, Mays and Simpson<sup>4</sup> in 1968 proposed a structure that placed the H atom inside a tetrahedral "cage" of metal atoms. The arrangement of metal atoms and carbonyl ligands was assumed to be consistent with that of the isoelectronic  $\text{Co}_4(\text{CO})_{12}$ , the x-ray structure of which was reported by Wei and Dahl<sup>5</sup> in 1966. This conclusion was later supported by White and Wright,<sup>6</sup> who, on the basis of inelastic neutron scattering experiments, confirmed the  $C_{3v}$  symmetry of the molecule but rejected a structure which contained the hydrogen on or near the  $\text{Co}_3$  face of the molecule. The model

proposed by these workers indicated a direct Fe...H interaction. Further interest was stimulated by Bor and co-workers in 1975,<sup>7</sup> who reaffirmed the  $C_{3v}$  symmetry of the molecule but favored a structure which placed the hydrogen near the center of the  $\text{Co}_3$  face, in agreement with Chini's original proposal. This conclusion, which was based on IR spectral data, was supported by Mössbauer measurements<sup>8</sup> which indicated no major structural change about the Fe atom upon deprotonation. A particularly useful aspect of this latest report<sup>8</sup> was the preparation of some phosphite-substituted derivatives, which form crystals more suitable for diffraction experiments than the parent compound. In 1975, Huie, Knobler, and Kaesz<sup>2</sup> reported a definitive structure determination of  $\text{HFeCo}_3(\text{CO})_9(\text{P}(\text{OCH}_3)_3)_3$  via x-ray crystallography. These workers clearly identified the H atom as being outside the cluster, capping the  $\text{Co}_3$  face. However, because of the inherent insensitivity of x-ray data to hydrogen positions, we felt that it would be desirable to have a more accurate measure of the  $\mu_3\text{-H}$  linkage in this compound. Accordingly, we undertook the



**Figure 1.** Molecular plot of  $\mu_3$ -HFeCo<sub>3</sub>(CO)<sub>9</sub>(P(OMe)<sub>3</sub>)<sub>3</sub>. Thermal ellipsoids are drawn with 50% probability. The methyl H atoms have been omitted for clarity. The hydride ligand is located 0.978 (3) Å from the Co<sub>3</sub> plane, and the average Co-H distance and Co-H-Co angle are 1.734 (3) Å and 91.8 (1)°, respectively.

neutron diffraction analysis which is reported in the present paper (abbreviations used in this paper are as follows: Me, methyl; Et, ethyl; Ph, phenyl; Cp, cyclopentadienyl).

### Experimental Section

The sample of  $\mu_3$ -hydridononacarbonyl-tris(trimethyl phosphite)-iron tricobalt used in this work was kindly supplied by Professor H. D. Kaesz and Dr. B. T. Huie of the University of California, Los Angeles. Recrystallization by cooling a hexane/CH<sub>2</sub>Cl<sub>2</sub> (6:1) solution of the compound very slowly to ca. -15 °C yielded large, well-formed crystals. A slow rate of cooling was achieved by placing a Schlenk flask containing the solution into a well-insulated Dewar flask filled with ethylene glycol at room temperature, and placing the Dewar into a freezer. The crystal chosen for data collection was a parallelepiped bounded by faces belonging to forms {001}, {100}, {111},  $\{\bar{1}\bar{1}\bar{1}\}$ , {111}, and {111}, with a volume of 32.1 mm<sup>3</sup>. This sample was mounted along the *b*\* axis on a hollow aluminum pin, capped with a thin-walled quartz thimble, and placed in a closed-cycle helium refrigerator.<sup>9</sup> Throughout the experiment the temperature was maintained at 90.0 ± 0.4 K. Neutron diffraction data were collected<sup>10a</sup> on an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor using a germanium-monochromated neutron beam of wavelength 1.1598 (1) Å. The wavelength was calibrated by diffraction from a KBr single crystal (*a* = 6.600 Å) and later checked with an Al<sub>2</sub>O<sub>3</sub> powder sample. To minimize the interference of scattering by the aluminum cryostat walls, a 12-in. long masonite collimator with a 1-in. diameter aperture was placed before the detector.

Cell constants were determined from a least-squares fit to the observed setting angles of 29 reflections with general indices. Data were collected in the  $\omega$  step-scan mode [ $0.004 \leq (\sin \theta/\lambda) \leq 0.330 \text{ \AA}^{-1}$ ] and in the  $\theta/2\theta$  step-scan mode [ $0.330 \leq (\sin \theta/\lambda) \leq 0.684 \text{ \AA}^{-1}$ ]. Two symmetry-related sets of  $\omega$  scan data were collected and merged with a single quadrant of  $\theta/2\theta$  scan data. Throughout data collection, two intense reflections (2 2 10, 7 0 12) were monitored at 50-reflection intervals. Intensities of these standards showed only minor fluctuations throughout the course of the experiment.

Background corrections were made by a method which minimizes the function  $\sigma(I)/I$  where *I* is the integrated intensity and  $\sigma(I)$  its estimated standard deviation based on counting statistics.<sup>10b</sup> Estimated standard deviations for each reflection were calculated from the formula  $\sigma(I) = [I_{\text{net}} + I_{\text{back}} + (0.02I_{\text{net}})^2]^{1/2}$ , where *I*<sub>net</sub> is the net intensity of a reflection and *I*<sub>back</sub> is the background intensity. The observed intensities were corrected for absorption, with the linear absorption coefficient calculated assuming an incoherent scattering cross section for hydrogen of 40 b, and were converted to squared structure factors by the relationship  $F_o^2 = I \sin 2\theta$ . Mass absorption

**Table I.** Crystal Data and Results of Refinement for  $\mu_3$ -HFeCo<sub>3</sub>(CO)<sub>9</sub>(P(OMe)<sub>3</sub>)<sub>3</sub>

Cell constants (at 90 K)	<i>a</i> = 15.957 (8) Å <i>b</i> = 10.611 (5) Å <i>c</i> = 18.383 (9) Å $\beta$ = 98.70 (2)°
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> ; <i>Z</i> = 4
Molecular weight	858.0
Density	$\rho_{\text{calcd}} = 1.852 \text{ g/cm}^3$
Temperature of data collection	90 K
Wavelength of neutrons used	1.1598 (1) Å
2 $\theta$ limit of data collection	105°
Reflections collected	11 851
Unique reflections collected	8229
Linear absorption coefficient	$\mu = 1.544 \text{ cm}^{-1}$
Error of fit parameter	1.345
Isotropic extinction parameter <sup>12</sup>	0.3984
Agreement factors:	
For all data	<i>R</i> ( <i>F</i> <sup>2</sup> ) = 0.087
(8229 reflections)	<i>R</i> ( <i>wF</i> <sup>2</sup> ) = 0.066
For nonnegative data	<i>R</i> ( <i>F</i> ) = 0.070
(7669 reflections)	<i>R</i> ( <i>wF</i> ) = 0.035

coefficients for carbon, oxygen, phosphorus, iron, and cobalt were taken from the "International Tables for X-Ray Crystallography".<sup>10c</sup> A total of 11 851 measurements were merged to yield intensities of 8229 unique reflections for subsequent structure refinement. The agreement factor<sup>11</sup> between equivalent reflections is 0.024.

The Co, Fe, P, O, and C atom positions derived from the x-ray analysis at *T* = 136 K (kindly supplied by Dr. Ben Huie) were used to phase the neutron data. A difference-Fourier synthesis revealed the positions of all the H atoms, and initial refinement was carried out with an automated procedure employing differential synthesis.<sup>10d</sup> Three cycles of full-matrix least-squares refinement on *F*<sub>o</sub><sup>2</sup> were carried out varying all positional and isotropic thermal parameters and the scale factor. At this point, many strong low-angle reflections appeared to have anomalously low *I*<sub>obsd</sub> values, and for this reason an isotropic extinction correction factor<sup>12</sup> was included throughout the remainder of the least-squares refinement. Four cycles varying all positional parameters, anisotropic temperature factors, and scale and extinction factors in three blocks resulted in *R*<sub>*F*<sup>2</sup></sub> = 0.087 and *R*<sub>*wF*<sup>2</sup></sub> = 0.066 for all 8229 reflections.<sup>13</sup> In the final cycle all shifts were less than 25% of their estimated standard deviations. An investigation of the function  $[|F_o^2 - F_c^2|/\sigma(F_o^2)]$  showed no systematic variation with respect to ( $\sin \theta/\lambda$ ) or *F*<sub>o</sub><sup>2</sup>. Based on these criteria the refinement was halted at this point. Crystal data and details of the refinement are reported in Table I.<sup>14a</sup>

### Discussion

The structure of  $\mu_3$ -HFeCo<sub>3</sub>(CO)<sub>9</sub>(P(OMe)<sub>3</sub>)<sub>3</sub> is outlined in Figure 1 and atomic positions and thermal parameters are given in Table II. A listing of the observed and calculated structure factors is available.<sup>14b</sup> The major features are essentially the same as those reported in the earlier x-ray determination.<sup>2,15</sup> The FeCo<sub>3</sub> framework is tetrahedral with the apical Fe atom additionally bonded to three terminal carbonyl ligands. The basal Co<sub>3</sub> group is bonded to three terminal and three bridging carbonyl groups. Each Co atom is also bonded to one phosphite ligand trans to the apical Fe atom. The molecule exhibits approximate *C*<sub>3*v*</sub> symmetry (Figure 2) with the terminal carbonyl groups on the Fe atom staggered with respect to the cobalt terminal carbonyls and eclipsed with respect to the bridging carbonyls. The individual trimethyl phosphite ligands are shown in Figure 3.

Distances and angles are reported in Tables III and IV. The metal-ligand and intraligand distances are quite normal and fall within the range of values reported for other complexes.<sup>16,17</sup> The triply bridging hydride ligand is outside the cluster, 0.978 (3) Å from the Co<sub>3</sub> face, and is equidistant (within error limits) from each Co atom. If the Co-Co bonds are ignored, the coordination geometry about each Co atom is nearly octahedral. Thus the approximate position of the

**Table II.** Positional<sup>a</sup> and Thermal<sup>a,b</sup> Parameters for  $\mu_3\text{-HFeCo}_3(\text{CO})_9(\text{P}(\text{OMe})_3)_3$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co(1)	34 873 (13)	7180 (21)	23 654 (11)	56 (7)	195 (18)	39 (6)	-14 (10)	-1 (5)	11 (9)
Co(2)	19 393 (13)	11 595 (21)	23 080 (12)	71 (8)	196 (20)	41 (6)	29 (11)	-2 (6)	-8 (9)
Co(3)	24 895 (13)	-10 007 (21)	25 760 (12)	65 (8)	139 (19)	60 (6)	0 (10)	10 (5)	-2 (9)
Fe	28 318 (4)	7105 (3)	35 559 (3)	87 (2)	193 (5)	38 (1)	1 (3)	7 (1)	-10 (2)
H	25 469 (11)	1035 (17)	18 942 (9)	201 (7)	397 (17)	110 (5)	4 (9)	19 (5)	-7 (8)
P(1)	40 783 (7)	5843 (10)	13 719 (6)	73 (4)	211 (10)	54 (3)	-7 (5)	17 (3)	4 (5)
P(2)	10 517 (7)	17 022 (10)	13 435 (6)	67 (4)	199 (10)	53 (3)	-5 (5)	4 (3)	8 (4)
P(3)	21 573 (7)	-23 260 (10)	16 802 (6)	87 (4)	166 (10)	53 (3)	-4 (5)	7 (3)	-16 (4)
O(1)	48 994 (7)	17 834 (11)	33 598 (6)	118 (4)	548 (11)	109 (3)	-91 (6)	2 (3)	-79 (5)
O(2)	10 946 (8)	28 216 (12)	32 140 (6)	268 (5)	545 (12)	123 (3)	218 (7)	29 (4)	-79 (5)
O(3)	25 451 (8)	-27 080 (11)	38 136 (6)	299 (6)	418 (12)	107 (3)	-29 (7)	14 (4)	116 (5)
O(4)	29 812 (7)	33 766 (10)	20 998 (6)	150 (4)	175 (9)	161 (3)	-17 (5)	8 (3)	21 (4)
O(5)	7196 (6)	-6527 (10)	27 787 (6)	96 (4)	347 (10)	125 (3)	-4 (5)	47 (3)	29 (5)
O(6)	42 945 (6)	-17 154 (10)	28 112 (6)	110 (4)	272 (9)	123 (3)	57 (5)	8 (3)	38 (4)
O(7)	15 358 (6)	2919 (11)	45 123 (6)	166 (4)	534 (11)	109 (3)	-19 (6)	68 (3)	19 (5)
O(8)	41 567 (7)	-5639 (11)	45 869 (6)	168 (4)	465 (11)	105 (3)	110 (6)	-23 (3)	17 (5)
O(9)	32 296 (8)	33 103 (11)	40 589 (6)	267 (5)	269 (10)	118 (3)	-70 (6)	46 (3)	-57 (5)
O(10)	50 825 (6)	6942 (10)	14 233 (6)	81 (4)	369 (10)	94 (3)	-11 (5)	23 (3)	4 (4)
O(11)	38 254 (6)	15 638 (10)	7166 (5)	112 (4)	285 (9)	69 (9)	-26 (5)	2 (3)	37 (4)
O(12)	38 169 (7)	-7091 (10)	9688 (6)	157 (4)	250 (9)	81 (3)	-59 (5)	49 (3)	-35 (4)
O(13)	724 (6)	13 834 (9)	13 486 (6)	76 (3)	242 (9)	88 (3)	-12 (5)	16 (3)	-2 (4)
O(14)	10 201 (6)	31 972 (10)	13 041 (6)	118 (3)	196 (9)	93 (3)	-2 (5)	-17 (3)	19 (4)
O(15)	11 045 (6)	12 406 (10)	5195 (5)	91 (4)	354 (9)	57 (3)	-19 (5)	9 (2)	-9 (4)
O(16)	29 086 (6)	-32 885 (10)	16 348 (6)	141 (4)	250 (9)	87 (3)	42 (5)	-2 (3)	-47 (4)
O(17)	19 276 (7)	-16 965 (10)	8904 (6)	186 (4)	254 (9)	70 (3)	-23 (5)	-21 (3)	5 (4)
O(18)	13 280 (7)	-31 884 (11)	16 618 (6)	152 (4)	375 (10)	114 (3)	-121 (5)	38 (3)	-61 (5)
C(1)	43 298 (5)	13 690 (8)	29 818 (5)	100 (3)	282 (8)	66 (3)	-30 (4)	4 (2)	-29 (4)
C(2)	14 573 (6)	21 558 (9)	28 802 (5)	144 (4)	286 (8)	76 (2)	81 (5)	17 (3)	-29 (4)
C(3)	25 188 (6)	-20 128 (9)	33 343 (5)	143 (3)	246 (8)	74 (2)	-8 (4)	11 (2)	38 (4)
C(4)	28 635 (5)	23 070 (8)	21 797 (5)	114 (3)	157 (7)	78 (2)	-4 (4)	5 (2)	9 (3)
C(5)	13 671 (5)	-3509 (8)	26 099 (5)	77 (3)	272 (8)	68 (2)	1 (4)	19 (2)	5 (4)
C(6)	37 302 (5)	-10 282 (8)	26 417 (5)	93 (3)	210 (7)	68 (2)	34 (4)	5 (2)	5 (3)
C(7)	20 275 (5)	4440 (8)	41 236 (4)	110 (3)	303 (8)	59 (2)	-5 (4)	26 (2)	2 (4)
C(8)	36 547 (5)	-733 (8)	41 680 (5)	109 (3)	289 (8)	65 (2)	26 (4)	7 (2)	-8 (4)
C(9)	30 788 (6)	22 984 (8)	38 599 (5)	143 (3)	246 (8)	61 (2)	-11 (4)	21 (2)	-21 (4)
C(10)	56 784 (6)	1219 (9)	19 971 (5)	86 (4)	335 (10)	121 (3)	30 (5)	11 (3)	2 (5)
C(11)	41 700 (6)	28 114 (9)	7524 (5)	222 (5)	272 (10)	118 (3)	-45 (6)	34 (3)	32 (5)
C(12)	58 768 (7)	39 190 (10)	46 996 (5)	262 (5)	361 (11)	103 (3)	76 (7)	87 (3)	82 (5)
C(13)	97 495 (6)	1431 (9)	11 555 (5)	130 (4)	290 (10)	96 (3)	-70 (5)	2 (3)	2 (5)
C(14)	3995 (6)	38 602 (9)	7903 (5)	125 (4)	265 (10)	105 (3)	28 (5)	-10 (3)	42 (5)
C(15)	19 009 (6)	13 029 (9)	2453 (5)	109 (4)	426 (10)	84 (3)	-29 (6)	33 (3)	-12 (5)
C(16)	70 824 (6)	8448 (10)	39 650 (5)	221 (5)	335 (11)	107 (3)	-77 (6)	17 (3)	65 (5)
C(17)	86 714 (6)	28 258 (10)	47 089 (5)	189 (5)	393 (11)	84 (3)	-43 (6)	-42 (3)	38 (5)
C(18)	87 917 (8)	10 778 (11)	27 055 (6)	322 (6)	536 (13)	141 (4)	262 (8)	100 (4)	59 (6)
H(1)	58 544 (21)	7791 (31)	24 205 (16)	740 (21)	1341 (43)	321 (12)	453 (25)	-275 (13)	-293 (20)
H(2)	37 793 (17)	49 096 (39)	32 179 (16)	365 (15)	2883 (72)	318 (12)	-753 (28)	118 (11)	-225 (24)
H(3)	45 635 (18)	43 318 (33)	27 855 (23)	369 (15)	1528 (49)	896 (24)	293 (22)	-254 (15)	-933 (30)
H(4)	37 368 (22)	33 925 (24)	4138 (18)	861 (24)	567 (30)	447 (14)	-88 (21)	-307 (15)	199 (17)
H(5)	42 475 (20)	31 922 (24)	12 976 (13)	776 (21)	744 (30)	208 (9)	-254 (20)	19 (11)	-64 (14)
H(6)	47 677 (22)	28 162 (27)	5773 (24)	675 (21)	775 (35)	1089 (28)	-365 (23)	653 (22)	-213 (25)
H(7)	61 012 (23)	30 004 (27)	48 299 (17)	1018 (27)	925 (36)	437 (14)	498 (26)	448 (16)	440 (19)
H(8)	60 815 (22)	4487 (29)	1366 (13)	967 (25)	1310 (43)	144 (9)	397 (27)	157 (12)	93 (16)
H(9)	52 019 (17)	39 000 (33)	46 210 (16)	354 (14)	1893 (52)	354 (12)	-10 (23)	171 (11)	348 (21)
H(10)	91 353 (15)	851 (24)	13 255 (15)	343 (13)	979 (32)	395 (22)	-322 (17)	208 (10)	-218 (16)
H(11)	96 872 (15)	-21 (21)	5693 (11)	423 (13)	739 (27)	139 (7)	-143 (15)	21 (8)	-92 (12)
H(12)	98 488 (17)	44 234 (21)	35 692 (15)	475 (14)	448 (24)	372 (11)	52 (16)	-175 (11)	-75 (14)
H(13)	97 785 (13)	37 536 (24)	9472 (13)	200 (10)	994 (31)	305 (10)	155 (15)	62 (8)	168 (15)
H(14)	105 826 (16)	48 316 (20)	8132 (14)	453 (14)	343 (23)	354 (11)	-12 (14)	-118 (10)	98 (13)
H(15)	103 965 (14)	35 103 (22)	2358 (11)	372 (12)	963 (31)	123 (7)	164 (16)	-14 (8)	34 (12)
H(16)	17 621 (15)	37 292 (31)	46 592 (12)	314 (12)	2054 (50)	132 (8)	171 (21)	65 (8)	43 (16)
H(17)	22 315 (14)	21 608 (23)	4071 (15)	292 (12)	778 (30)	412 (12)	-225 (16)	150 (10)	-136 (16)
H(18)	22 971 (15)	5174 (25)	4481 (15)	272 (12)	940 (33)	428 (13)	153 (17)	146 (10)	134 (17)
H(19)	64 872 (16)	3585 (26)	38610 (15)	428 (15)	1074 (36)	343 (11)	-417 (19)	-46 (10)	249 (16)
H(20)	71 324 (17)	13 529 (23)	44 813 (12)	598 (17)	781 (29)	150 (8)	-105 (18)	98 (9)	9 (13)
H(21)	75 965 (17)	1724 (23)	39 879 (14)	523 (16)	636 (28)	319 (11)	186 (18)	94 (10)	168 (14)
H(22)	86 519 (18)	18 259 (23)	47 537 (14)	575 (17)	579 (27)	328 (11)	-68 (18)	-180 (11)	170 (15)
H(23)	85 069 (19)	17 586 (30)	2001 (13)	645 (19)	1560 (45)	132 (8)	-297 (24)	-25 (10)	59 (16)
H(24)	92 974 (15)	31 171 (30)	46 450 (16)	233 (12)	1544 (44)	395 (13)	-177 (19)	-71 (10)	333 (19)
H(25)	82 393 (21)	5142 (28)	25 187 (17)	648 (20)	1116 (41)	425 (14)	-67 (24)	177 (14)	-357 (20)
H(26)	89 305 (19)	16 918 (26)	22 688 (14)	712 (20)	1036 (35)	233 (9)	304 (21)	239 (11)	191 (16)
H(27)	93 187 (20)	4739 (30)	28 611 (15)	750 (21)	1499 (45)	286 (11)	822 (27)	157 (13)	100 (19)

<sup>a</sup> All positional and thermal parameters have been multiplied by a factor of  $10^5$ . <sup>b</sup> The form of the anisotropic Debye-Waller factor is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

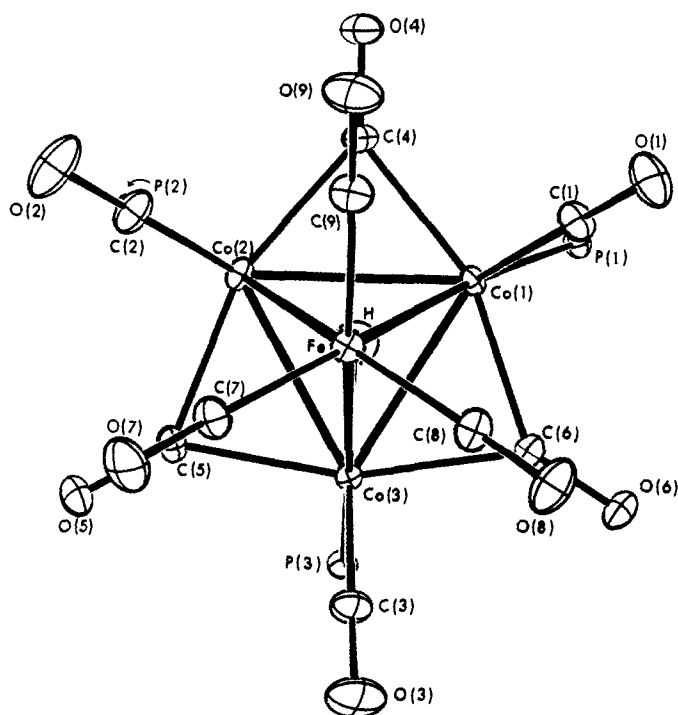


Figure 2. A plot of the  $\mu_3$ -HFeCo<sub>3</sub>(CO)<sub>9</sub>(P(OCH<sub>3</sub>)<sub>3</sub>)<sub>3</sub> molecule viewed from above the Fe atom, illustrating the approximate C<sub>3v</sub> symmetry of the molecule. The methoxy groups have been removed for clarity.

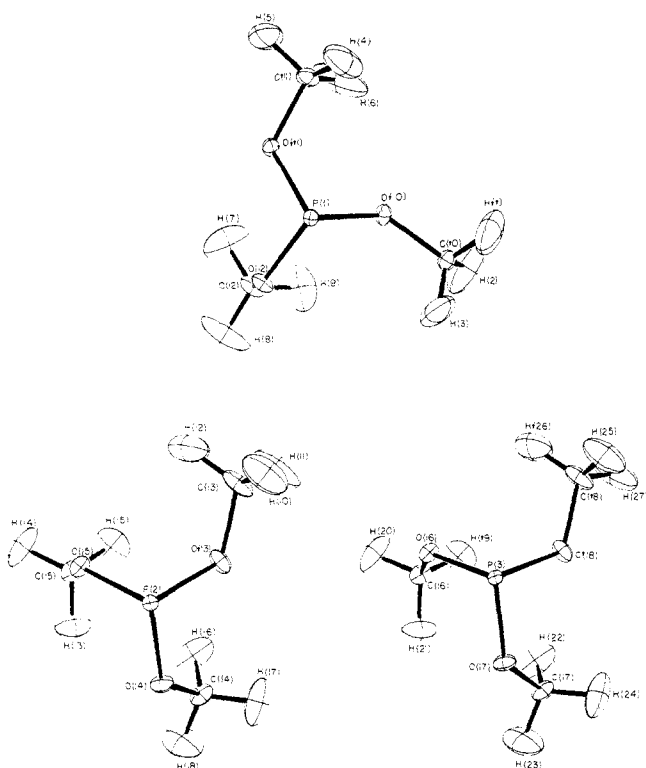


Figure 3. Plots of the individual trimethyl phosphite ligands, viewed approximately along the Co-P directions.

hydride ligand could be inferred by the presence of one vacancy, common to all three octahedra, trans to the terminal carbonyls on each Co atom. The average Co-H distance [1.734 (3) Å] falls within the bridging hydride distance limits reported for other first-row transition metal complexes.<sup>18</sup> This value is close to the average Ni-H bond distance in H<sub>3</sub>Ni<sub>4</sub>Cp<sub>4</sub> [1.691 (8) Å], a cluster which contains three triply bridging H

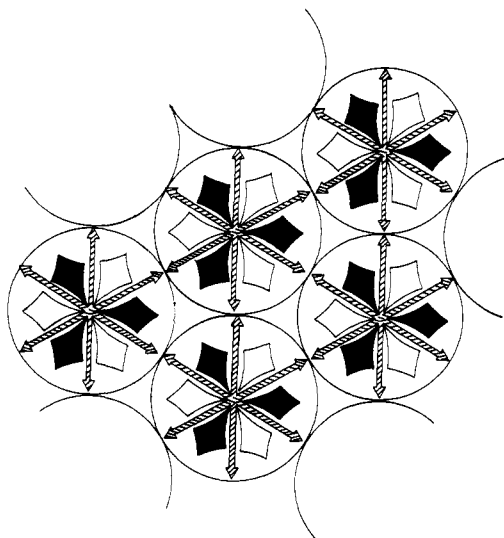
Table III. Bond Distances (Å) in HFeCo<sub>3</sub>(CO)<sub>9</sub>(P(OMe)<sub>3</sub>)<sub>3</sub><sup>a</sup>

A. Distances Involving Fe, H, Co(1), Co(2), and Co(3)			
Co(1)-H	1.742 (3)	Co(1)-Co(2)	2.501 (2)
Co(2)-H	1.731 (3)	Co(1)-Co(3)	2.489 (3)
Co(3)-H	1.728 (3)	Co(2)-Co(3)	2.477 (3)
Average	1.734 (4)	Average	2.489 (7)
Co(1)-Fe	2.563 (2)	Co(1)-C(1)	1.763 (2)
Co(2)-Fe	2.556 (2)	Co(2)-C(2)	1.749 (2)
Co(3)-Fe	2.558 (2)	Co(3)-C(3)	1.755 (2)
Average	2.559 (2)	Average	1.756 (4)
Co(1)-C(4)	1.962 (2)	Co(1)-P(1)	2.182 (2)
Co(1)-C(6)	1.945 (2)	Co(2)-P(2)	2.174 (2)
Co(2)-C(4)	1.954 (2)	Co(3)-P(3)	2.170 (2)
Co(2)-C(5)	1.965 (2)	Average	2.175 (3)
Co(3)-C(5)	1.929 (2)		
Co(3)-C(6)	1.965 (2)	Fe-C(7)	1.794 (1)
Average	1.953 (6)	Fe-C(8)	1.799 (1)
		Fe-C(9)	1.800 (1)
		Average	1.798 (2)
B. Distances within the Carbonyl Ligands			
C(1)-O(1)	1.145 (1)	C(4)-O(4)	1.163 (1)
C(2)-O(2)	1.148 (1)	C(5)-O(5)	1.167 (1)
C(3)-O(3)	1.145 (1)	C(6)-O(6)	1.164 (1)
Average	1.146 (1)	Average	1.165 (1)
C(7)-O(7)	1.149 (1)		
C(8)-O(8)	1.149 (1)		
C(9)-O(9)	1.148 (1)		
Average	1.149 (1)		
C. Distances within the Phosphite Ligands			
P(1)-O(10)	1.595 (3)	C(10)-H(1)	1.052 (3)
P(1)-O(11)	1.596 (2)	C(10)-H(2)	1.034 (3)
P(1)-O(12)	1.586 (2)	C(10)-H(3)	1.026 (3)
P(2)-O(13)	1.600 (2)	C(11)-H(4)	1.056 (3)
P(2)-O(14)	1.589 (2)	C(11)-H(5)	1.070 (3)
P(2)-O(15)	1.606 (2)	C(11)-H(6)	1.052 (4)
P(3)-O(16)	1.587 (2)	C(12)-H(7)	1.054 (3)
P(3)-O(17)	1.590 (2)	C(12)-H(8)	1.060 (3)
P(3)-O(18)	1.605 (2)	C(12)-H(9)	1.065 (3)
Average	1.594 (2)	C(13)-H(10)	1.074 (3)
		C(13)-H(11)	1.078 (2)
		C(13)-H(12)	1.074 (3)
		C(14)-H(13)	1.079 (2)
		C(14)-H(14)	1.071 (2)
		C(14)-H(15)	1.084 (2)
O(10)-C(10)	1.440 (2)	C(15)-H(16)	1.067 (3)
O(11)-C(11)	1.431 (2)	C(15)-H(17)	1.072 (3)
O(12)-C(12)	1.444 (2)	C(15)-H(18)	1.078 (3)
O(13)-C(13)	1.438 (2)	C(16)-H(19)	1.072 (3)
O(14)-C(14)	1.444 (2)	C(16)-H(20)	1.084 (2)
O(15)-C(15)	1.437 (2)	C(16)-H(21)	1.083 (3)
O(16)-C(16)	1.438 (2)	C(17)-H(22)	1.065 (3)
O(17)-C(17)	1.438 (2)	C(17)-H(23)	1.072 (3)
O(18)-C(18)	1.436 (2)	C(17)-H(24)	1.069 (3)
Average	1.438 (1)	C(18)-H(25)	1.078 (4)
		C(18)-H(26)	1.082 (3)
		C(18)-H(27)	1.062 (3)
		Average	1.067 (3)

<sup>a</sup> Standard deviations of mean values are calculated as  $\sigma(\bar{x}) = [\sum(x_i - \bar{x})^2/n(n-1)]^{1/2}$ . The resulting deviations are to be regarded as rough estimates of uncertainty, in cases where  $n = 3$ .

atoms.<sup>19</sup> The average Co-H-Co angle in HFeCo<sub>3</sub>(CO)<sub>9</sub>(P(OMe)<sub>3</sub>)<sub>3</sub> [91.8 (1)°] also compares well with those found in hydride bridges of various types: M(μ<sub>2</sub>-H)<sub>4</sub>M [85.0 (3)° in H<sub>8</sub>Re<sub>2</sub>(PEt<sub>2</sub>Ph)<sub>4</sub>],<sup>20</sup> M(μ<sub>2</sub>-H)<sub>3</sub>M [89.6° in H<sub>3</sub>Ir<sub>2</sub>(C<sub>5</sub>-Me<sub>5</sub>)<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>],<sup>21</sup> and (μ<sub>3</sub>-H)<sub>3</sub>M<sub>4</sub> [93.9 (3)° in H<sub>3</sub>Ni<sub>4</sub>Cp<sub>4</sub>].<sup>19</sup> It is, however, significantly different from the M-H-M angles in M(μ<sub>2</sub>-H)M-type linkages [125.0 (2) and 125.9 (4)° in





**Figure 4.** Diagrammatic representation of the emergence of orbitals at the [111] face of a face-centered cubic metal (from Bond, ref 36). Filled arrows,  $e_g$  orbitals emerging at an angle of  $36.3^\circ$  to the plane of the paper; open arrows,  $t_{2g}$  orbitals emerging at  $30^\circ$  to the plane of paper; hatched arrows,  $t_{2g}$  orbitals in plane of paper.

the  $Ru_6$  octahedron.<sup>25</sup> For  $HFeCo_3(CO)_9(P(OMe)_3)_3$ , the most relevant comparison is with  $Co_4(CO)_{12}$ .<sup>5,26</sup> Both molecules contain bridging carbonyl groups in the basal  $Co_3$  plane: in  $Co_4(CO)_{12}$  the basal fragment is  $Co_3(CO)_3(\mu_2-CO)_3$ , and in  $HFeCo_3(CO)_9(P(OMe)_3)_3$  it is  $Co_3(P(OMe)_3)_3(\mu_2-CO)_3(\mu_3-H)$ . The Co-Co distances in the basal planes of the two molecules are virtually indistinguishable [ $2.485(13)$  Å in  $Co_4(CO)_{12}$  and  $2.489(3)$  Å in  $HFeCo_3(CO)_9(P(OMe)_3)_3$ ], even though one of them contains a triply bridging H atom and the other does not. This reinforces our previous conclusion,<sup>27</sup> that metal-metal bonds bridged by a H atom are not necessarily longer than unbridged M-M bonds *when other bridging groups are present* (the  $\mu_2-CO$  groups in this case). The structure of  $H_2Ru_6(CO)_{18}$  is consistent with this statement since it does not contain any bridging carbonyl groups.<sup>25</sup>

Agreement between the x-ray<sup>15</sup> and neutron diffraction results for  $HFeCo_3(CO)_9(P(OMe)_3)_3$  is excellent. Both experiments were performed at low temperatures, and consequently both structures are characterized by relatively high resolution and favorable data-to-parameter ratios: 6057 reflections and 392 variables in the x-ray case; 8229 reflections and 641 variables in the neutron case. The most important difference between the two structure determinations is the apparent displacement in the H atom position determined by x rays, toward the  $Co_3$  face. This shift is a consequence of the presence of bonding electron density, and also may be enhanced by series termination errors in the vicinity of the Co atoms. In the case of  $HFeCo_3(CO)_9(P(OMe)_3)_3$ , the Co-H distances determined by x rays [ $1.46(11)$ ,  $1.68(11)$ ,  $1.74(11)$  Å] are an average of  $0.11$  Å shorter than the distances determined by neutrons [ $1.742(3)$ ,  $1.731(3)$ ,  $1.728(3)$  Å], and the displacements of the H atom from the  $Co_3$  plane are  $0.75$  and  $0.978(3)$  Å in the x-ray and neutron cases, respectively.

The geometry of the  $P(OMe)_3$  group is much better defined than that found in our earlier neutron diffraction study of a trimethyl phosphite complex,  $HW_2(CO)_8(NO)(P(OMe)_3)$ .<sup>17</sup> The latter structure determination, based on data collected at room temperature, was complicated by high thermal motion of the methoxy groups. Indeed, an earlier attempt of ours to refine the structure of  $HFeCo_3(CO)_9(P(OMe)_3)_3$  using room temperature neutron data was unsuccessful partly because of this problem.<sup>28</sup> It was mainly to overcome these difficulties that we decided to collect the present data set for  $HFeCo_3-$

$(CO)_9(P(OMe)_3)_3$  at a low temperature. The resulting analysis shows no indication of packing disorder or high thermal motion in the phosphite groups.

This structure determination affords perhaps the most precise comparison yet possible between bridging and terminal C-O bond lengths. Although these differences are small, they are consistently reproducible. Terminal C-O distances follow: on Fe,  $1.145(1)$ ,  $1.148(1)$ ,  $1.145(1)$  Å; on Co,  $1.149(1)$ ,  $1.149(1)$ ,  $1.148(1)$  Å. Bridging distances are  $1.163(1)$ ,  $1.167(1)$ ,  $1.164(1)$  Å (on Co). The difference between the two sets of numbers is significant at the 99% confidence level and can be attributed to the increased  $\pi$ -back-bonding from metal atoms to a bridging carbonyl group relative to a terminal group. Another manifestation of this phenomenon is the well-known lowering of CO stretching frequencies from terminal carbonyl groups ( $1900-2125$   $cm^{-1}$ ) to bridging carbonyls ( $1700-1850$   $cm^{-1}$ ).<sup>29</sup>

Because of the unambiguous location of the triply bridging hydride ligand in this structure, we are in a position to comment on some of the earlier spectral investigations of  $HMCo_3(CO)_{12}$  ( $M = Fe, Ru$ ). The mass spectral data<sup>4</sup> which led to the misassignment of the hydride position showed that the strongest peaks in the spectra are due to  $HMCo_3(CO)_n^+$  ions ( $n = 1-12$ ). This stepwise loss of CO implicated a strongly bonded  $HMCo_3$  group. Electron-counting rationale indicated that the hydride ligand should be bonded to the Fe (Ru) atom, but no terminal M-H stretching vibration was seen in the IR spectra of the clusters. The H atom was therefore placed in the metal cage. It turns out that this mass spectrum is consistent with the structure described here, for it is seen that the loss of hydrogen from the cluster requires its removal from three metal atoms, while the carbonyl groups need break only one (terminal) or two (bridging) bonds. Additionally, it has already been noted that although  $HCo_3^+$  ions were detected,  $HFe^+$  ions were not.<sup>7</sup>

Recently there has been an increased interest in metal clusters from the point of view of catalysis, partly because of the potential use of clusters as models for heterogeneous catalytic systems.<sup>30</sup> It is thought that a thorough understanding of the bonding of various substrates (ligands) to clusters can serve to illuminate the detailed processes occurring on metal surfaces during catalysis. It has occurred to us that the structures of covalent metal hydride cluster complexes might serve as good models for hydrogen chemisorbed onto metal surfaces. Cobalt metal crystallizes in both cubic and hexagonal close-packed forms.<sup>31</sup> The [111] face of the face-centered cubic form<sup>32</sup> and the [001] face of the hexagonal close-packed form<sup>33</sup> both consist of triangular arrays of Co atoms. The distance between Co atoms on these faces is  $2.507$  Å, which compares favorably with the  $2.489(7)$  Å average value in the present structure. Indeed, the Ni-Ni distance in  $H_3Ni_4Cp_4$  [ $2.469(6)$  Å]<sup>19</sup> is also very close to that in metallic nickel [ $2.492$  Å].<sup>34</sup> It is widely believed that when hydrogen is chemisorbed onto a metallic surface the H-H bond is broken and the hydrogen becomes bound in the monatomic form. Kinetic studies of hydrogenation reactions catalyzed by cobalt indicate that  $H_2$  is adsorbed by a dissociative mechanism.<sup>35</sup> One can envisage, for the H/Co system, a model in which H atoms are chemisorbed on adjacent triangular units of the metallic surface, or on alternate triangles. These models would give rise to non-bonding H...H separations of  $1.447$  and  $2.507$  Å, respectively. By analogy with the structure of  $HFeCo_3(CO)_9(P(OMe)_3)_3$ , one could postulate these adsorbed H atoms to be situated about  $0.95-1.00$  Å from the metallic surface, and about equidistant ( $\sim 1.70-1.75$  Å) from three Co atoms. In an analysis of the orbitals on the surface of a face-centered cubic metal, Bond<sup>36</sup> has pointed out that there are no orbitals normal to the [111] face. Rather, free metal orbitals are all directed at points situated above the centers of the  $M_3$  triangles (Figure

4). In this model, Bond postulates an alternating pattern of triangles, some with three  $e_g$  orbitals emerging at an angle of  $36.3^\circ$  to the surface of the metal, and others with three  $t_{2g}$  orbitals emerging at an angle of  $30^\circ$  to the surface.<sup>36</sup> Interestingly enough, in  $\text{HFeCo}_3(\text{CO})_9(\text{P}(\text{OMe})_3)_3$  the Co-H bonds are inclined at a mean angle of  $34.3^\circ$  to the plane of the Co atoms.

We now turn to a discussion of whether in fact there is sufficient room within a tetrahedral metal cluster to accommodate a H atom. In  $\text{HFeCo}_3(\text{CO})_9(\text{P}(\text{OMe})_3)_3$  the centroid of the tetrahedron can be calculated to be 1.546 Å from the corners, a value which confirms the estimate given earlier by Mays and Simpson for  $\text{HFeCo}_3(\text{CO})_{12}$  (1.5–1.6 Å).<sup>4</sup> From a number of recent neutron diffraction analyses, we now know that bridging M-H distances involving first-row transition metals (Cr, Co, Ni) lie in the range 1.69–1.74 Å.<sup>19a,37</sup> It thus seems unlikely that the  $\text{FeCo}_3$  tetrahedron (or the  $\text{Fe}_4$  or  $\text{Co}_4$  tetrahedra, for that matter) would be able to accommodate a H atom in its center without appreciable "swelling". By contrast, in the case of octahedral metal clusters there is ample room in the cage for a H atom, as shown by powder neutron diffraction studies on  $\text{HNb}_6\text{I}_{11}$ <sup>38</sup> and more recent single-crystal neutron work on  $[\text{HNi}_{12}(\text{CO})_{21}]^{3-}$  and  $[\text{H}_2\text{Ni}_{12}(\text{CO})_{21}]^{2-}$ .<sup>39</sup> The situation thus parallels that of transition metal carbide complexes, which contain many examples of C atoms in octahedral metal clusters but not in tetrahedral clusters.<sup>40</sup> It is hoped that as additional accurate neutron diffraction measurements of bridging M-H distances become available, it will be possible to predict which  $\text{M}_4$  tetrahedra (if any) might comfortably accommodate H atoms in their centers.

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**Supplementary Material Available:** Listings of the observed and calculated squared structure factor amplitudes for the neutron analysis (8 pages). Ordering information is given on any current masthead page.

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$$R = \sum |F_o^2 - \bar{F}_o^2| / \sum \bar{F}_o^2.$$
- (12) An extinction parameter,  $g$ , as defined by Zachariasen [*Acta Crystallogr.*, **23**, 558 (1967)] was included in the final cycles of refinement. Here 
$$E_{hkl} = \left[ 1 + \frac{27}{V} \frac{|F_c|^2 g}{\sin^2 2\theta} \right]^{-1/4}$$
 where  $E_{hkl}$  is the extinction correction which divides  $F_o$  for reflection  $hkl$ ;  $F_c$  is the calculated structure factor;  $T$  is the average beam path length in the crystal for reflection  $hkl$ , appropriately modified for absorption;  $V = (V_c^2/\lambda^3)$ , where  $V_c$  is the volume of the unit cell;  $\lambda$  is the wavelength of neutrons employed; and  $2\theta$  is the Bragg diffraction angle.
- (13)  $R$  factors reported in the text have the following form:  $R_F = \sum |F_o - |F_c|| / \sum F_o$ ;  $R_{wF} = \{ \sum w |F_o - |F_c||^2 / \sum w F_o^2 \}^{1/2}$ ;  $R_{F2} = \sum |F_o^2 - |F_c|^2| / \sum |F_o^2|$ ;  $R_{wF2} = \{ \sum w |F_o^2 - |F_c|^2|^2 / \sum w F_o^4 \}^{1/2}$ .
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