

Short Communication

Structure of the Disubstituted Triphenyl Phosphine Derivative of $\text{HFeCo}_3(\text{CO})_{12}$

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Mixed metal carbonyl cluster compounds are presently being studied in several laboratories. Their synthesis, characterization and chemical properties are also of industrial interest, since some of them have been shown to act as catalysts or catalyst precursors in reactions like the water gas shift reaction or the hydroformylation.^{1,2}

Iron–cobalt clusters have been studied extensively since the first synthesis of $\text{HFeCo}_3(\text{CO})_{12}$ by Chini *et al.* in 1960.³ The group offers economical systems for catalytical purposes, because it does not involve platinum metal elements. Homogeneous catalysis of the water–gas shift reaction is currently being studied in our laboratory. In the present study the structural characterization of $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ is reported. Ligand substitution has been used to modify the chemical properties of the parent cluster. The catalytical activities of the $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and related clusters will be reported elsewhere.

The location of the hydrogen atom in $\text{HFeCo}_3(\text{CO})_{12}$ has been of particular interest,⁴ since no ^1H NMR signal for the hydrogen has been observed due to the relaxation effects of the quadrupolar cobalt nuclei.⁵ The structure of $\text{HFeCo}_3(\text{CO})_9(\text{P}(\text{OMe})_3)_3$ has been determined in low temperature by x-ray and neutron diffraction.⁶ The hydrogen was shown to be bound to the three cobalt atoms below the Co_3 plane in contrast to the earlier proposal of the location inside the tetrahedral cluster.^{7,8} The ligand substitutions were shown to occur in cobalt atoms, but also substitution to iron is known

in a related cluster.⁹ The structure of $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ gives a possibility to study structural effects of unsymmetrical substitution by two ligands and the influence of ligand substitution to the location of the hydrogen.

Experimental. $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ was prepared by the method of Cooke and Mays⁴ and crystallized from CH_2Cl_2 -hexane mixture. A dark green irregularly shaped crystal of size $0.3 \times 0.3 \times 0.4$ mm was mounted on a glass fiber. After optical alignment of the crystal on a Nicolet R3m diffractometer preliminary unit cell parameters were determined with 10 centered diffraction maxima and with axial photographs. Graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda=0.71069$ Å) was used. The lattice constants for the triclinic unit cell which were refined with

Table 1. Crystal data for $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$.

Formula	$\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$
Molecular mass	1123.3
Space group	$\text{P}\bar{1}$
Unit cell parameters	
a , Å	11.528(2)
b , Å	13.763(2)
c , Å	16.736(3)
α , deg	81.36(1)
β , deg	78.04(1)
γ , deg	65.00(1)
V , Å ³	2348.5(7)
Z	2
$\mu(\text{MoK}\alpha)$, cm^{-1}	16.3
Density, cal kg dm^{-3}	1.59
Range of transmission	0.437–0.534
Radiation used	$\text{MoK}\alpha$
Scan range, deg of 2θ	5–45
hkl range	0, –15, –18 13, –15, –18
Scan mode	$\omega/2\theta$
No. of refl. measured	5879
No. of unique data ^a	4962
R	0.030
R_w ^b	0.034

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^a $I \leq 2\delta(I)$. ^b $\text{Weight} = 1/(\sigma^2|F| + 0.005 F^2)$.

Table 2. Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$, \AA^2).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Co(1)	-382(1)	3139(1)	2787(1)	34(1)
Co(2)	137(1)	1475(1)	2088(1)	32(1)
Co(3)	-377(1)	3238(1)	1284(1)	35(1)
Fe	1791(1)	2337(1)	1819(1)	41(1)
P(1)	-2189(1)	3955(1)	3674(1)	37(1)
P(2)	-1148(1)	590(1)	2181(1)	34(1)
O(1)	1299(3)	3418(3)	3710(2)	88(2)
O(2)	-770(3)	5245(2)	1931(1)	64(1)
O(3)	1235(3)	3841(2)	-91(2)	75(1)
O(4)	-2670(3)	4403(2)	494(2)	75(1)
O(5)	549(3)	1363(2)	308(1)	58(1)
O(6)	2490(2)	-447(2)	2156(2)	80(1)
O(7)	438(3)	1110(2)	3814(1)	60(1)
O(8)	3570(3)	1174(3)	2995(2)	98(2)
O(9)	2575(3)	4148(2)	1448(2)	76(1)
O(10)	3546(3)	1117(2)	437(2)	81(2)
C(1)	680(3)	3296(3)	3315(2)	53(2)
C(2)	-628(3)	4356(3)	2014(2)	42(1)
C(3)	662(3)	3582(3)	466(2)	49(2)
C(4)	-1828(3)	3928(3)	832(2)	48(2)
C(5)	233(3)	1757(2)	922(2)	40(1)
C(6)	1594(3)	334(3)	2100(2)	47(2)
C(7)	130(3)	1638(3)	3228(2)	43(1)
C(8)	2862(4)	1619(3)	2540(2)	60(2)
C(9)	2266(3)	3444(3)	1606(2)	52(2)
C(10)	2859(3)	1591(3)	970(2)	54(2)
C(11)	-2577(3)	5362(3)	3821(2)	42(1)
C(12)	-1609(4)	5687(3)	3863(2)	61(2)
C(13)	-1906(5)	6738(4)	4018(3)	73(2)
C(14)	-3142(4)	7470(3)	4115(3)	75(2)
C(15)	-4121(4)	7177(3)	4059(3)	76(2)
C(16)	-3842(4)	6124(3)	3921(2)	57(2)
C(17)	-2150(3)	3336(3)	4723(2)	41(1)
C(18)	-2078(4)	3847(3)	5354(2)	64(2)
C(19)	-2006(5)	3336(4)	6131(2)	80(2)
C(20)	-2023(4)	2345(3)	6290(2)	70(2)
C(21)	-2072(4)	1832(3)	5681(2)	63(2)
C(22)	-2129(4)	2315(3)	4895(2)	52(2)
C(23)	-3694(3)	4057(2)	3405(2)	42(1)
C(24)	-4529(4)	3643(3)	3894(2)	60(2)
C(25)	-5648(4)	3762(4)	3645(3)	76(2)
C(26)	-5977(4)	4314(4)	2929(3)	83(2)
C(27)	-5180(4)	4744(4)	2439(3)	76(2)
C(28)	-4027(4)	4606(3)	2668(2)	56(2)
C(29)	-2052(3)	458(2)	3194(2)	37(1)
C(30)	-3393(3)	906(3)	3381(2)	48(2)
C(31)	-3996(4)	763(3)	4168(3)	62(2)
C(32)	-3309(5)	163(4)	4756(2)	68(2)
C(33)	-1980(5)	-309(4)	4586(2)	65(2)
C(34)	-1353(4)	-153(3)	3806(2)	52(2)
C(35)	-295(3)	-810(2)	1904(2)	38(1)
C(36)	744(3)	-1095(3)	1271(2)	49(2)

C(37)	1371(4)	-2135(3)	1047(2)	63(2)
C(38)	966(4)	-2901(3)	1437(3)	67(2)
C(39)	-68(4)	-2639(3)	2059(3)	69(2)
C(40)	-709(4)	-1598(3)	2296(2)	55(2)
C(41)	-2372(3)	1167(2)	1512(2)	36(1)
C(42)	-3208(3)	2249(3)	1547(2)	46(2)
C(43)	-4156(3)	2720(3)	1062(2)	52(2)
C(44)	-4285(4)	2119(3)	522(2)	58(2)
C(45)	-3465(4)	1064(3)	480(2)	61(2)
C(46)	-2517(4)	576(3)	967(2)	50(2)
C(47)	6592(7)	7733(7)	1742(4)	155(5)
Cl(1)	5794(2)	8983(2)	2104(2)	166(1)
Cl(2)	5531(3)	7236(2)	1537(2)	191(2)
H	-1039(29)	2761(24)	2117(18)	49(9)

^a Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalised U_{ij} tensor.

24 centered reflections in the 2θ range $20-22^\circ$ are $a=11.528(2)$ \AA , $b=13.763(2)$ \AA , $c=16.736(3)$ \AA , $\alpha=81.36(1)$, $\beta=78.04(1)$ and $\gamma=65.00(1)^\circ$. The unit cell volume is $2348.5(7)$ \AA^3 .

Intensity data were collected in the $\omega/2\theta$ -scan mode with a scan speed of $3^\circ/\text{min}$. The intensities of two standard reflections were periodically measured at intervals of 98 reflections. No significant decay was found. Lorentz, polarization and empirical absorption correction based on ψ -scan data were applied to the intensity data; the minimum transmission factor was 82 % from the maximum value. The details of the data collection are given in Table 1.

The structure was solved by direct methods of the SHELXTL program package.¹⁰ Space group $P\bar{1}$ was found to give a plausible structure. Iron, cobalt and phosphorus atoms were first located

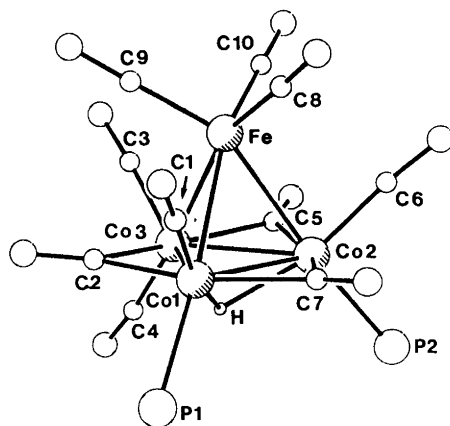


Fig. 1. Atom numbering scheme for $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$.

Table 3. Selected interatomic distances (Å) and bond angles (°) for $\text{HFeCo}_3(\text{CO})_{10}[\text{PPh}_3]_2$.

Co(1)–Co(2)	2.515(1)	Co(1)–Fe	2.577(1)
Co(1)–Co(3)	2.498(1)	Co(2)–Fe	2.577(1)
Co(2)–Co(3)	2.487(1)	Co(3)–Fe	2.562(1)
Co(1)–H	1.72(4)	Co(2)–H	1.72(3)
Co(2)–H	1.63(3)		
Co(1)–C(7)	1.962(3)	Co(2)–C(7)	1.952(4)
Co(1)–C(2)	1.913(3)	Co(3)–C(2)	1.997(4)
Co(2)–C(5)	1.921(3)	Co(3)–C(5)	1.999(3)
Co(1)–C(1)	1.748(5)	Co(2)–C(6)	1.750(3)
Co(3)–C(3)	1.771(4)	Co(3)–C(4)	1.799(4)
Fe–C(8)	1.784(4)	Fe–C(9)	1.792(4)
Fe–C(10)	1.798(3)		
Co(1)–P(1)	2.246(1)	Co(2)–P(2)	2.253(1)
P(1)–C(11)	1.837(4)	P(2)–C(29)	1.825(3)
P(1)–C(17)	1.833(3)	P(2)–C(35)	1.836(3)
P(1)–C(23)	1.836	P(2)–C(41)	1.821(3)
C(1)–O(1)	1.141(6)	C(2)–O(2)	1.155(4)
C(3)–O(3)	1.129(4)	C(4)–O(4)	1.127(4)
C(5)–O(5)	1.152(4)	C(6)–O(6)	1.141(4)
C(7)–O(7)	1.153(4)	C(8)–O(8)	1.147(5)
C(9)–O(9)	1.144(6)	C(10)–O(10)	1.137(4)
Co(1)–Co(2)–Co(3)	59.9	Co(1)–Co(3)–Co(2)	60.6
Co(2)–Co(1)–Co(3)	59.5		
Co(1)–Fe–Co(2)	48.4	Co(1)–Fe–Co(3)	58.2
Co(2)–Fe–Co(3)	57.9		
Co(1)–H–Co(2)	94(2)	Co(1)–H–Co(3)	96(2)
Co(2)–H–Co(3)	96(2)		
C(8)–Fe–C(9)	95.7(2)	C(8)–Fe–C(10)	94.7(2)
C(9)–Fe–C(10)	96.3(2)		
Co(1)–C(2)–Co(3)	79.4(1)	Co(1)–C(7)–Co(2)	80.0(1)
Co(2)–C(5)–Co(3)	78.7(1)		
Co(1)–Co(2)–P(2)	126.7	Co(3)–Co(2)–P(2)	120.0
Co(2)–Co(1)–P(1)	125.4	Co(3)–Co(1)–P(1)	122.5
Fe–Co(1)–P(1)	173.6	Fe–Co(2)–P(2)	172.3

and subsequent Fourier syntheses revealed all other nonhydrogen atoms including a CCl_2 fragment in the asymmetric unit, which comes from CH_2Cl_2 solvent molecules trapped in the crystal. After an isotropic refinement of the nonhydrogenic atoms a difference Fourier map was calculated revealing hydrogen atoms in the phenyl ring and a hydrogen atom bound to the three cobalt atoms. Isotropic refinement of the hydrogens converged to $R=0.030$ and $R_w=0.034$. The final atomic coordinates and equivalent temperature factors are given in Table 2. Selected bond lengths and angles are listed in Table 3. Anisotropic temperature factors and

parameters for the CH_2Cl_2 and phenyl hydrogen atoms are available from the authors on request.

Results and discussion. The unit cell contains two $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ molecules and two CH_2Cl_2 solvent molecules in centrosymmetric positions. The FeCo_3 frame is tetrahedral containing three cobalt atoms bound to an apical iron atom (Fig. 1). Triphenyl phosphine ligands are coordinated to cobalt atoms axially with respect to the Co_3 plane. Seven of the ten carbonyls are terminal, three of them bridge the cobalt atoms. The hydrogen atom forms a triple bridge under the Co_3 -plane. Ligand substitution lengthens the Co1–Co2 distance to 2.515(1) Å while the

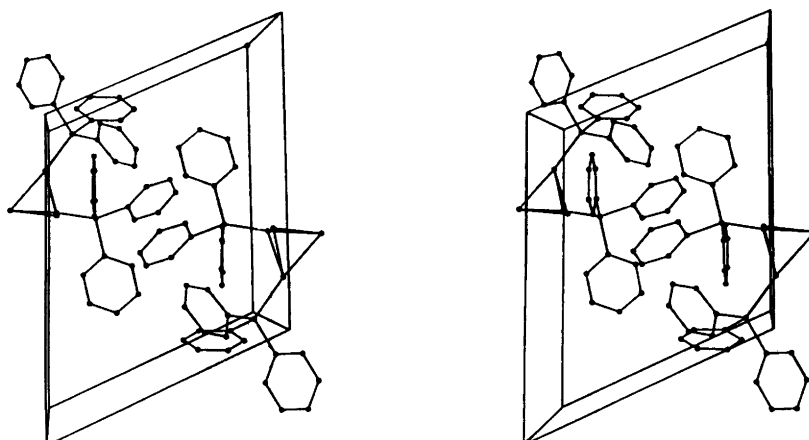


Fig. 2. Stereoview of the unit cell. Hydrogens, carbonyls and solvent molecules have been omitted for clarity. *a*-Axis is horizontal and *b* axis vertical.

Table 4. Average bond lengths of some FeCo₃ clusters (Å).

Compound	Co-Co	Co-Fe	Co-P	Co-H	Ref.
HFeCo ₃ (CO) ₉ (P(OMe) ₃) ₃	2.489	2.559	2.175	1.734	5
HFeCo ₃ (CO) ₉ (PMe ₂ Ph) ₃ ^a	2.480	2.565	^b	^b	6
FeCo ₃ (CO) ₁₂ ⁻	2.37	241	—	—	11
HFeCo ₃ (CO) ₁₀ (PPh ₃) ₂	2.500	2.572	2.250	1.69	This work
FeCo ₃ (CO) ₁₂ AuPPh ₃	2.52	2.56	—	—	12

^a Iron monosubstituted, ^b Not reported.

Co1-Co3 and Co2-Co3 distances are 2.498(1) and 2.487(1) Å. Asymmetric ligand substitution pulls the bridging carbonyls C2-O2 and C5-O5 towards the substitution centers Co1 and Co2 and pushes the hydrogen towards the unsubstituted Co3 (Table 2). Fig. 2 shows molecular packing in the unit cell. The solvent molecules are omitted for clarity. The optimum packing is achieved by the eclipsed orientation of the PPh₃ groups of the neighbouring molecules.

Geometries of related FeCo₃ clusters are shown in Table 4. Ligand substitution does not change the cluster geometry considerably, even if the hydrogen is replaced by an AuPPh₃ group. Deprotonation of the cluster contracts it markedly.

The present study confirms the current views of hydrogen bridging and carbonyl bridging in the FeCo₃ clusters.⁶

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