

Structural Characterization of the Triiron Undecacarbonyl Anion $[\text{HFe}_3(\text{CO})_{11}]^-$ in the $[\text{N}(\text{PPh}_3)_2]^+$ Salt and Locating the Site of the Bridging Hydrogen

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$[\text{N}(\text{PPh}_3)_2](\mu\text{-H})\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})$, $FW=1015.3$, crystallizes in space group $P2_1/c$ with $Z=4$, $a=18.158(13)$, $b=16.512(10)$, $c=15.492(13)$ Å, $\beta=99.62(7)^\circ$, $V=4579.4(60)$ Å³, $D_c=1.47$ g cm⁻³, $F(000)=2064$. The hydrogen atom in the metal cluster was located with low-angle reflection data. The positional and anisotropic thermal parameters of the atoms were refined by the least-squares methods. The final residual R is 0.053 for 2817 reflections ($I > 2\sigma(I)$).

The molecular structure of $[\text{HFe}_3(\text{CO})_{11}]^-$ anion consists of a triangular array of iron atoms with one edge bridged by a carbonyl group and a hydrogen atom. The result is supported by earlier neutron and preliminary X-ray diffraction studies.

The unsubstituted trinuclear iron carbonyl series, e.g. $\text{Fe}_3(\text{CO})_{12}$,¹ $[\text{HFe}_3(\text{CO})_{11}]^-$,^{2,3} and $[\text{Fe}_3(\text{CO})_{11}]^{2-}$,⁴ have been of particular interest due to their unique geometry and fluxional behaviour in solution.⁵ The $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ dianion, for example, possesses an $\text{M}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-CO})$ configuration, with an unsymmetrically triply bridging carbonyl.

Prior to this work only a preliminary X-ray study by Dahl and Blount² on the $[\text{HFe}_3(\text{CO})_{11}]^-$ monoanion has been published with no detailed structural information. The $[\text{HFe}_3(\text{CO})_{11}]^-$ anion was determined as a $[(\text{C}_2\text{H}_5)_3\text{NH}]^+$ salt and found to contain a triangular array of iron atoms with one edge bridged by a CO. The presence of a hydrogen atom was not directly established for $[\text{HFe}_3(\text{CO})_{11}]^-$ by the X-ray work but was inferred both from stereochemical and bonding con-

siderations to bridge the same edge as the only bridging carbonyl.

Teller and Bau tabulate in their review article³ structural parameters of some metal hydride clusters. $[\text{HFe}_3(\text{CO})_{11}]^-$ is also included, but the details of this neutron diffraction study are unpublished. During the course of our studies on mixed-metal cluster syntheses we prepared and characterized the PPN salt of $[\text{HFe}_3(\text{CO})_{11}]^-$. Since no detailed structural information is available of this commonly encountered iron cluster anion, we are reporting our results.

EXPERIMENTAL

The $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ salt was formed as a by-product in a synthesis of $[\text{PPN}][\text{Fe}_3\text{Co}(\text{CO})_{13}]$.⁶ The sources of the hydride are presumably the impurities in the starting materials and solvents.

A dark brown irregularly shaped crystal of size $0.3 \times 0.2 \times 0.4$ 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 MoK α radiation ($\lambda=0.71069$ Å) was used.

The measured lattice constants for the monoclinic unit cell based on 24 centered reflections are $a=18.158(13)$, $b=16.512(10)$, $c=15.492(13)$ Å and $\beta=99.62(7)^\circ$. The unit cell volume of $4579.4(60)$ Å³ and FW of 1015.3 g mol⁻¹ give rise to a calculated density of 1.47 g cm⁻³ based upon $Z=4$. Intensity data were collected in ω -scan

Table 1. Final atomic parameters for $[\text{PPN}]^+[\text{HFe}_3(\text{CO})_{11}]^-$.

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^3$) ^a
Fe1	-1975(1)	2859(1)	1849(1)	52(1)
Fe2	-3333(1)	2357(1)	1660(1)	57(1)
Fe3	-2388(1)	1886(1)	3084(1)	62(1)
P1	1664(1)	3007(1)	3160(2)	39(1)
P2	3293(1)	3015(1)	3965(1)	38(1)
N	2538(4)	3055(4)	3301(4)	41(3)
O1	-3063(4)	4015(4)	2329(5)	69(3)
O2	-1870(4)	4150(4)	588(4)	84(3)
O3	-860(5)	1850(6)	1183(7)	129(5)
O4	-1044(5)	3645(5)	3343(5)	113(4)
O5	-3347(5)	704(5)	3749(6)	110(5)
O6	-2820(6)	3216(6)	4163(6)	123(5)
O7	-964(5)	1660(7)	4214(6)	118(5)
O8	-2039(6)	675(5)	1841(5)	114(4)
O9	-4188(6)	3204(6)	210(8)	176(6)
O10	-3750(5)	784(5)	836(7)	130(5)
O11	-4466(5)	2341(6)	2751(7)	135(5)
C1	-2867(6)	3362(7)	2108(6)	57(4)
C2	-1921(5)	3641(6)	1068(6)	54(4)
C3	-1309(6)	2195(7)	1471(7)	71(5)
C4	-1428(6)	3319(7)	2763(7)	71(5)
C5	-2987(7)	1188(8)	3490(9)	87(6)
C6	-2657(7)	2720(7)	3711(8)	79(5)
C7	-1534(7)	1736(8)	3751(7)	79(5)
C8	-2193(7)	1201(7)	2270(7)	83(5)
C9	-3844(7)	2860(7)	777(9)	104(6)
C10	-3543(6)	1374(7)	1198(8)	84(5)
C11	-4008(6)	2362(7)	2340(8)	85(5)
C12	1320(5)	1976(5)	3057(5)	41(3)
C13	618(5)	1771(6)	3200(6)	58(4)
C14	369(6)	968(7)	3080(7)	70(5)
C15	834(7)	397(6)	2834(7)	65(5)
C16	1535(6)	596(6)	2701(6)	62(4)
C17	1775(5)	1371(5)	2809(6)	52(4)
C18	1272(5)	3481(5)	4003(5)	40(3)
C19	1079(5)	4294(6)	3935(6)	52(4)
C20	882(6)	4702(6)	4650(7)	71(5)
C21	852(7)	4300(9)	5397(7)	91(6)
C22	1005(7)	3491(8)	5459(7)	79(5)
C23	1227(5)	3080(6)	4775(6)	53(4)
C24	1309(5)	3521(5)	2142(5)	36(3)
C25	591(5)	3435(6)	1760(7)	63(4)
C26	320(6)	3816(7)	964(7)	75(5)
C27	807(6)	4280(7)	597(6)	69(4)
C28	1515(6)	4383(7)	966(7)	76(5)
C29	1771(5)	4006(6)	1760(6)	60(4)
C30	3599(5)	1996(5)	4168(5)	40(3)
C31	4253(6)	1712(5)	3952(6)	53(4)
C32	4456(6)	916(7)	4051(7)	65(5)
C33	4004(7)	399(6)	4390(8)	88(5)
C34	3343(7)	635(6)	4613(7)	80(5)
C35	3154(5)	1448(6)	4515(7)	66(4)

Table 1. Continued.

C36	3273(5)	3473(5)	5018(6)	42(3)
C37	2942(6)	4209(6)	5060(6)	64(4)
C38	2959(6)	4598(6)	5850(8)	73(5)
C39	3309(6)	4225(7)	6602(7)	74(5)
C40	3648(8)	3520(7)	6579(7)	93(6)
C41	3647(7)	3131(6)	5772(6)	73(5)
C42	3989(4)	3551(5)	3475(5)	40(3)
C43	3910(5)	3624(5)	2585(6)	49(4)
C44	4454(7)	4029(7)	2235(7)	73(5)
C45	5068(7)	4337(8)	2749(10)	95(7)
C46	5141(7)	4252(8)	3619(9)	93(6)
C47	4605(5)	3877(6)	3995(6)	59(4)
H1	-2607(37)	2332(42)	1012(42)	79(29)

^a $U_{eq} = 1/3 \text{ trace } |U|$.

mode with a scan speed of 3 °/min. The intensities of two standard reflections were periodically measured at intervals of every 98 reflections in order to monitor the crystal's alignment and decay. No significant decay was found.

Intensities were measured at ambient temperature between 2 θ limits of 3 and 40° for 4436 reflections. Lorentz and polarization corrections, as well as an empirical absorption correction based on ψ -scan data, were applied to the intensity data; the minimum transmission factor was 86 % from the maximum value, $\mu = 11.0 \text{ cm}^{-1}$. A data reduction gave 2817 independent reflections with $I \geq 2\sigma(I)$. The space group, $P2_1/c$, was deduced from the systematic absences.

The iron, phosphorus and nitrogen atoms were located by direct methods of the SHELXTL program package.⁷ The other nonhydrogen atoms were found in successive Fourier syntheses. The asymmetric unit contains one [HFe₃(CO)₁₁]⁻ anion and one [PPN]⁺ cation. Isotropic and anisotropic refinements were made for the nonhydrogen atoms. The scattering factors for neutral atoms were taken from International Tables.⁸ The phenyl hydrogens were placed in idealized positions with isotropic temperature factors. The final anisotropic refinement converged to an $R = 0.056$.

In order to locate the hydrogen atom in the metal cluster, a difference Fourier map was calculated. Three peaks were found in the edges of the Fe₃ triangle. The hydrogen atom peak was assigned by the method of La Placa and Ibers.⁹ A series of difference Fourier maps based on low angle reflection data were calculated with $\sin \theta/\lambda$ limits (0.30, 0.25, 0.20 Å⁻¹). One of the peaks enhanced relative to the others, and was assigned to the hydrogen atom. The positional parameters

and the isotropic temperature factor of the hydrogen were refined with the low angle data ($\sin \theta/\lambda < 0.30 \text{ Å}^{-1}$) keeping the rest of the structure fixed. Finally the hydrogen parameters were fixed and all the other atoms were refined with all the reflection data. The final agreement factor is $R = 0.053$ (701 parameters refined). The refinement was based on F_o with unit weights. The final atomic parameters are given in Table 1. Interatomic distances and bond angles are listed in Table 2. The listings of the structure factors and anisotropic thermal parameters are available from the authors upon request.

DISCUSSION

The unit cell contains four [PPN]⁺ and [HFe₃(CO)₁₁]⁻ ions. In the [PPN]⁺ ion there is a slight structural distortion in the orientation of the phenyl rings (Fig. 1). The P-N bond lengths are equal (1.568(7) and 1.573(6) Å). The bonding angle P-N-P seems to be sensitive to the nature of the anion. A bond angle of 147.2(5)° was observed in the present structure, while smaller angles of 140.0(2)° and 139.7(6)° are found in the [PPN]⁺ salts of [CoRu₃(CO)₁₃]⁻⁶ and [HRu₃(CO)₁₁]⁻,¹⁰ respectively. All the other dimensions of the cation are similar to those found in other cluster complexes containing the [PPN]⁺ ion.¹⁰

The structure of the [HFe₃(CO)₁₁]⁻ anion (Fig. 2) consists of a triangular array of iron atoms containing an Fe(CO)₄ group which is symmetrically linked to two iron atoms in the Fe₂(CO)₆(μ -CO)(μ -H) fragment by Fe-Fe

Table 2. Selected interatomic distances (Å) and bond angles (°) for [PPN]⁺[HFe₃(CO)₁₁]⁻.

Fe1-C1	1.922(11)	Fe2-C10	1.790(11)
Fe1-C2	1.783(10)	Fe2-C11	1.744(13)
Fe1-C3	1.801(12)	Fe3-C5	1.770(14)
Fe1-C4	1.761(10)	Fe3-C6	1.798(13)
Fe2-C1	1.938(11)	Fe3-C7	1.732(12)
Fe2-C9	1.731(12)	Fe3-C8	1.774(12)
Fe1-Fe2	2.572(2)	Fe1-H1	1.80(7)
Fe1-Fe3	2.699(2)	Fe2-H1	1.79(7)
Fe2-Fe3	2.674(2)		
C1-O1	1.202(13)	C7-O7	1.163(15)
C2-O2	1.137(12)	C8-O8	1.155(14)
C3-O3	1.145(16)	C9-O9	1.141(16)
C4-O4	1.172(13)	C10-O10	1.155(14)
C5-O5	1.147(15)	C11-O11	1.129(16)
C6-O6	1.149(16)		
P1-N	1.568(7)	P1-C24	1.812(8)
P2-N	1.573(6)	P2-C30	1.783(8)
P1-C12	1.811(9)	P2-C36	1.804(9)
P1-C18	1.772(9)	P2-C42	1.810(9)
Fe1-Fe2-Fe3	61.9(1)	Fe2-Fe3-Fe1	57.2(1)
Fe3-Fe1-Fe2	60.9(1)		
Fe1-H1-Fe2	92(3)	Fe1-C1-Fe2	83.5(4)
Fe1-Fe2-H1	45(2)	Fe3-Fe1-H1	90(2)
Fe2-Fe1-H1	44(2)	Fe3-Fe2-H1	91(2)
Fe2-Fe1-C1	48.5(3)		
Fe1-Fe2-C1	48.0(3)	Fe1-Fe3-C6	93.5(4)
Fe3-Fe1-C1	76.4(3)	Fe2-Fe3-C6	91.6(4)
Fe3-Fe2-C1	76.8(3)	Fe1-Fe3-C7	100.4(4)
Fe2-Fe1-C2	108.4(3)	Fe2-Fe3-C7	157.1(4)
Fe3-Fe1-C2	164.8(3)	Fe1-Fe3-C8	76.3(4)
Fe2-Fe1-C3	116.8(4)	Fe2-Fe3-C8	77.0(4)
Fe3-Fe1-C3	98.6(4)	Fe1-Fe2-C9	108.2(4)
Fe2-Fe1-C4	129.2(4)	Fe3-Fe2-C9	167.6(4)
Fe3-Fe1-C4	82.7(4)	Fe1-Fe2-C10	118.3(4)
Fe1-Fe3-C5	154.1(4)	Fe3-Fe2-C10	97.5(4)
Fe2-Fe3-C5	97.8(4)	Fe1-Fe2-C11	133.4(4)
		Fe3-Fe2-C11	85.5(4)
Fe1-C1-O1	138.3(8)	Fe2-C10-O10	171.7(10)
Fe1-C2-O2	177.9(9)	Fe2-C11-O11	176.7(10)
Fe1-C3-O3	172.1(11)	Fe3-C5-O5	176.3(11)
Fe1-C4-O4	176.6(11)	Fe3-C6-O6	175.1(11)
Fe2-C1-O1	137.5(8)	Fe3-C7-O7	177.6(12)
Fe2-C9-O9	178.3(13)	Fe3-C8-O8	169.8(10)
C1-Fe1-C2	88.4(5)	C9-Fe2-C10	94.0(5)
C1-Fe1-C3	165.1(5)	C9-Fe2-C11	97.9(6)
C1-Fe1-C4	91.5(5)	C10-Fe2-C11	97.0(6)
C1-Fe2-C9	91.0(5)	C5-Fe3-C6	93.9(6)

Table 2. Continued.

C1-Fe2-C10	166.2(5)	C5-Fe3-C7	103.7(6)
C1-Fe2-C11	95.1(5)	C5-Fe3-C8	92.5(6)
C2-Fe1-C3	96.0(5)	C6-Fe3-C7	94.8(6)
C2-Fe1-C4	98.4(5)	C6-Fe3-C8	167.6(5)
C3-Fe1-C4	101.8(5)	C7-Fe3-C8	93.9(6)
P1-N-P2	147.2(5)		

bonds. The two unbridged edges Fe1-Fe3 and Fe2-Fe3 are essentially equivalent 2.699(2) and 2.674(2) Å, while the third, bridged Fe1-Fe2 bond is considerably shorter, 2.572(2) Å. In the terminal carbonyl ligands the small variations in the Fe-C bond lengths, 1.731(12)-1.801(12) Å, and in the C-O bond lengths, 1.129(16)-

1.172(13) Å, are similar to the variations observed in related structures.¹⁰

The bridging carbonyl ligand is symmetrically coordinated to two iron atoms Fe1 and Fe2 with almost identical Fe1-C1 and Fe2-C1 distances of 1.922(11) and 1.938(11) Å. The C1-O1 bond length of 1.202(13) Å and Fe1-C1-Fe2 bond angle of 83.5(4)° are within the normal ranges for doubly bridged carbonyl ligands.⁴ The bridging hydrogen atom lies above the plane of the iron triangle. The iron-hydrogen bond distances are essentially equal [1.80(7) and 1.79(7) Å]. The symmetric coordination of the bridging CO and hydrogen gives the [HFe₃(CO)₁₁]⁻ ion an approximate C_s point group symmetry.

Comparison of the results from the present structure determination with earlier determinations on two related triangular iron clusters with a structural formula of Fe₃(CO)₁₀(μ-H)(μ-Y), where Y = CNMe₂¹¹ or COMe,¹² reveals almost isosceles triangles of iron atoms. The two unbridged Fe-Fe bonds are longer than the bridged Fe-Fe bond in the [Fe₃(CO)₁₀(μ-H)(μ-CO)]⁻ monoanion [2.687(2), 2.572(2) Å], in Fe₃(CO)₁₀(μ-H)(μ-COMe) [2.667(2), 2.596(2) Å] and in Fe₃(CO)₁₀(μ-H)(μ-C=NMe₂) [2.696(2),

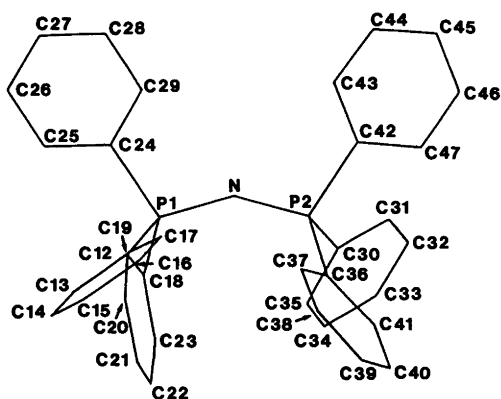


Fig. 1. The numbering scheme of the [PPN]⁺ cation. Hydrogen atoms have been omitted for clarity.

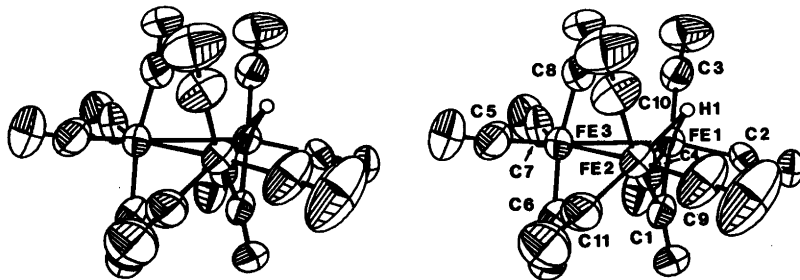


Fig. 2. Stereoscopic view of the structure of the [HFe₃(CO)₁₁]⁻ anion. The thermal ellipsoids enclose 50% electron probability.

Table 3. Comparison of bridged metal-metal and metal-hydrogen distances and metal-hydrogen-metal bond angles in hydrogen bridged triangulo-tri-iron complexes.

Molecule	Fe-Fe (Å) ^a	Fe-H (Å) ^a	Fe-H-Fe (°) ^a	Type ^b	Ref.
[Et ₃ NH] ⁺ [HFe ₃ (CO) ₁₁] ⁻	2.577(3)	—	—	X	2
[N(PPh ₃) ₂] ⁺ [HFe ₃ (CO) ₁₁] ⁻	2.589(2)	1.693(4)	99.7(2)	N	3
[N(PPh ₃) ₂] ⁺ [HFe ₃ (CO) ₁₁] ⁻	2.572(2)	1.80(7)	92(3)	X	c
HFe ₃ (CO) ₁₀ (C=NMe ₃)	2.565(2)	1.61(9)	106(5)	X	11
HFe ₃ (CO) ₁₀ (COMe)	2.596(2)	—	—	X	12
HFe ₃ (CO) ₉ (SPR ⁺)	2.678(2)	1.80(13)	96(6)	X	13
HFe ₃ (CO) ₉ (N=CHMe)	2.588(1)	1.65(6)	103(3)	X	14
HFe ₃ (CO) ₉ (NH=CMe)	2.754(1)	1.71(3)	107(2)	X	14
H ₂ Fe ₃ (CO) ₈ (PMe ₂) ₂	2.645(1)	1.57(5)	116(3)	X	15
H ₃ Fe ₃ (CO) ₉ (CMe)	2.618	—	104	X	16

^a Whenever appropriate, averages are reported. ^b N=neutron, X=X-ray. ^c Present paper.

2.565(2) Å]. This shortening is ascribed mainly to double bridging since a single bridging hydride ligand normally causes a lengthening of the distance between metal atoms.¹⁷ Ligands such as μ -CO, μ -COMe and μ -CNMe₂ have a similar bond-shortening effect which more than counterbalances the lengthening effect of the μ -hydride.

Although the bridged Fe-Fe bonds in the hydrogen bridged triangulo-tri-iron complexes listed in Table 3 are single bonds on the basis of the 18-electron rule, the bond lengths range from 2.565 to 2.754 Å. The longest Fe-Fe distance of 2.754 Å observed in HFe(CO)₉(NH=CMe)¹⁴ is attributed mainly to the steric requirements of the bridging iminyl group. A rather large variation in the observed Fe-H distances and Fe-H-Fe bond angles reflects the low accuracy of the metal-hydrogen bond length determinations by X-ray methods.

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