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Crystal structures of [$Fe_3(CO)_9\{P(OR)_3\}_3$] (R = Me or Pr^i)

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The structures of [$Fe_3(CO)_9\{P(OR)_3\}_3$] (R = Me or Pr^i) that were assigned previously on the basis of NMR investigations have been questioned. The crystal structures of these compounds have now been determined and shown to be in complete agreement with the predicted structures. The crystal structure of [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] is the first structure determination of a derivative of [$Fe_3(CO)_{12}$] with pseudo D_3 symmetry and is similar to that commonly found for the ruthenium and osmium analogues.

In 1989, NMR investigations of [$Fe_3(CO)_9\{P(OR)_3\}_3$] were published independently by Aime *et al.*[1] and Mann and co-workers.[2] In both papers, it was concluded that there are two isomers present, **1a** and **1b**, with the probability of semi-bridging carbonyls in **1a**. Aime also suggested a rotation of each $Fe(CO)_3\{P(OR)_3\}$ moiety, giving a structure closer to **1c**, while Mann did not comment on this possibility in the absence of experimental evidence. Both Aime and Mann proposed that the structure of **1a** is similar to that previously reported for [$Ru_3(CO)_9(PMe_3)_3$].[3] In 1993, Johnson and Roberts[4] raised doubt about these structure assignments. They proposed that **1a** has the D_3-icosahedral structure **1c**, in which the $Fe(CO)_3L$ groups are rotated about the C_2 axes of the Fe_3 triangle. This is exactly what happens for [$Ru_3(CO)_9(PMe_3)_3$]. They also concluded that the axial carbonyls lean towards the nearer non-bonded iron atom to acquire some semi-bridging character as is observed in [$Ru_3(CO)_9(PMe_3)_3$]. Mann and co-workers[2] predicted that, as iron has a greater tendency to have bridging carbonyls than does ruthenium, the semi-bridging character of the carbonyls in [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] would be greater than in [$Ru_3(CO)_9(PMe_3)_3$]. Supporting evidence for this was that the ^{13}C NMR chemical shifts of *ca.* δ 230 for these carbonyls are intermediate between that found for a terminal axial ^{13}CO at *ca.* δ 220 and bridging ^{13}CO at *ca.* δ 250 in derivatives of [$Fe_3(CO)_{12}$].[1,2,5] The nature of the disagreement is not clear, but appears to arise from whether or not the axial carbonyls lean towards a second iron atom as indicated in **1a**.

Johnson and Roberts,[4] referring to [$Fe_3(CO)_9\{P(OMe)_3\}_3$], also stated that 'According to Mann and co-workers, isomer **g** is dominant in solution. However, we would emphasise the possibility that **h** cannot be excluded on the basis of the NMR data' (isomer **g** is **1b**, **h** is **1d**).

In this paper, the controversy is resolved by determining the crystal structures of [$Fe_3(CO)_9\{P(OR)_3\}_3$] (R = Me or Pr^i). The NMR data are discussed and show that **1d** can be rejected as an alternative structure by consideration of the published NMR data, contrary to the subsequent claim.[4]

Results and Discussion

[$Fe_3(CO)_9\{P(OPr^i)_3\}_3$]

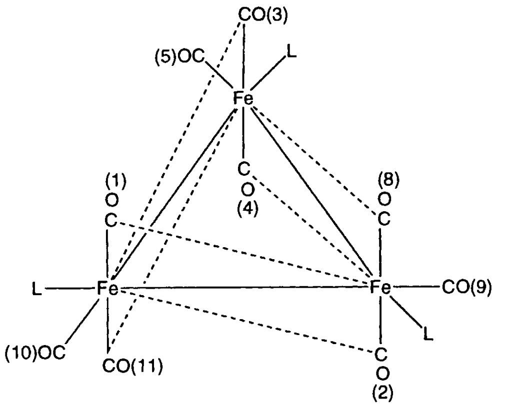
The crystal structure of [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. Examination of the structure shows that each iron has rotated about the pseudo-C_2 axes of the Fe_3 triangle giving what approximates to a D_3 structure. For comparison, the same view of the structure of [$Ru_3(CO)_9(PMe_3)_3$] is shown in Fig. 2. Both Aime *et al.*[1] and Mann and co-workers[2] had predicted that the structure of isomer **1a** would be similar to that of [$Ru_3(CO)_9(PMe_3)_3$].[6] Comparison of the structures of these two compounds shows that this is qualitatively true, see Figs. 1 and 2. The molecules have approximately D_3 symmetry with approximately equal M–M bonds. It was also predicted that the axial carbonyls would be more semi-bridging in [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] than in [$Ru_3(CO)_9(PMe_3)_3$].[2] Comparison of the two crystal structures shows that this is also correct. The pseudo-axial carbonyls of [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] lean towards the nearer non-bonded iron atom with C(1)–Fe(1)–C(3), C(7)–Fe(3)–C(9) and C(4)–Fe(2)–C(6) bond angles of 167.0, 169.0 and 168.9° respectively. The result is that the axial carbonyls on both sides of the Fe_3 ring move towards semi-bridging positions as we predicted.[2] This is accompanied by a reduction in the M–M–C and M–C–O bond angles, and the PMC plane rotates more for [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] than for [$Ru_3(CO)_9(PMe_3)_3$], see Table 2. The effects are more marked for [$Ru_3(CO)_9\{P(OEt)_3\}_3$],[7] which has a structure very similar to [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$].

It is always subjective to assess when a carbonyl ligand is not terminal, but semi-bridging. We believe that the best evidence for the semi-bridging nature of the axial carbonyls in [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] comes from the chemical shifts of these carbonyls, δ 227.8 and 231.3, which are intermediate between the δ 220 expected for terminal axial carbonyls and δ 250 expected for bridging carbonyls.[1,2,5]

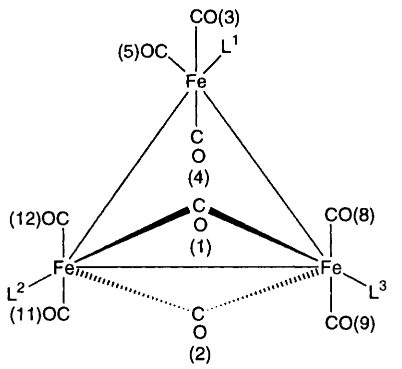
Crabtree and Lavin[8] have suggested that the M–M–C bond angle can be used as a criterion of a carbonyl being semi-bridging. They deduced that semi-bridging carbonyls have an angle of less than 76.5° and recognising the approximations involved, proposed that 75° should be taken as an approximate borderline. They also recognised that M–M–C angles between 75 and 70° could arise from steric factors, so that it is essential to examine steric factors and the direction of the bend of the M–C–O group.

Using Crabtree and Lavin's criterion[8] of the M–M–C angle, only two Fe–Fe–C angles (66.3 and 69.7°) can be taken as being semi-bridging without further evidence. One further Fe–Fe–C angle lies within the possible range at 72.5°, with two more on the margin of this range at 75.5 and 76.6°. The final axial Fe–Fe–C angle is 81.9° and lies in the non-bridging range. A plot of the Fe–Fe–C against Fe–C–O bond angles gives a curve, with no indications of deviation due to steric factors, see Fig. 3. Examination of the FeFeC planes shows that the oxygen atoms lie close to the planes, at distances of 0.026, 0.018, 0.023, 0.017, 0.066 and 0.021 Å and shows no evidence of steric distortions. The oxygen with the 0.066 Å deviation has Fe–Fe–C 69.7°, lying well into the semi-bridging range. It is therefore concluded that three of the six axial carbonyls fulfil Crabtree and Lavin's criteria of being semi-bridging and two further carbonyls are marginally semi-bridging.

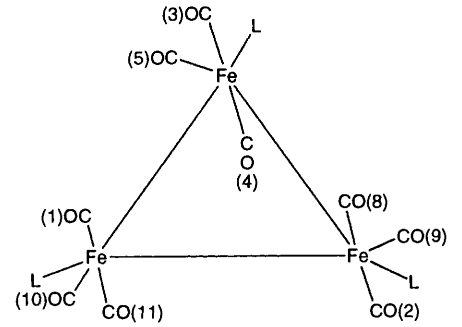
Johnson *et al.*[9] have suggested that the torsion angle between the two triangles formed by the axial carbonyl oxygen atoms



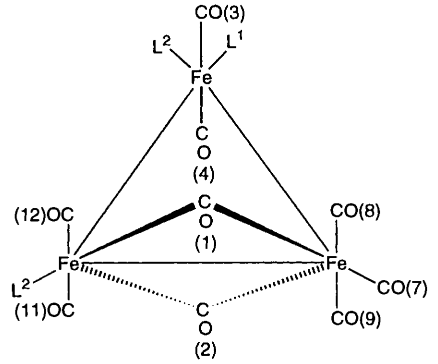
1a



1b



1c



1d

Table 1 Selected bond lengths (Å) and angles (°) in the complex $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$

Fe(1)–C(3)	1.767(11)	Fe(2)–C(5)	1.771(1)	O(4)–C(4)	1.145(11)
Fe(1)–C(2)	1.792(11)	Fe(2)–C(6)	1.799(12)	O(5)–C(5)	1.147(11)
Fe(1)–C(1)	1.817(11)	Fe(3)–C(9)	1.804(11)	O(6)–C(6)	1.144(11)
Fe(1)–P(1)	2.192(3)	Fe(3)–C(7)	1.846(12)	O(7)–C(7)	1.137(11)
Fe(1)–Fe(2)	2.702(2)	Fe(3)–P(3)	2.192(3)	O(8)–C(8)	1.155(12)
Fe(1)–Fe(3)	2.709(2)	O(1)–C(1)	1.130(10)	O(9)–C(9)	1.142(11)
Fe(2)–C(4)	1.813(12)	O(2)–C(2)	1.142(11)		
Fe(2)–P(2)	2.181(3)	O(3)–C(3)	1.145(10)		
Fe(2)–Fe(3)	2.685(2)				
Fe(3)–C(8)	1.759(13)				

C(3)–Fe(1)–C(2)	94.9(4)	Fe(2)–Fe(1)–Fe(3)	59.51(5)	P(2)–Fe(2)–Fe(1)	163.67(9)	C(7)–Fe(3)–Fe(1)	96.6(3)
C(3)–Fe(1)–C(1)	167.0(4)	C(5)–Fe(2)–C(6)	95.9(5)	Fe(3)–Fe(2)–Fe(1)	60.38(5)	P(3)–Fe(3)–Fe(1)	105.04(10)
C(2)–Fe(1)–C(1)	97.2(4)	C(5)–Fe(2)–C(4)	94.7(4)	C(8)–Fe(3)–C(9)	93.8(5)	Fe(2)–Fe(3)–Fe(1)	60.11(5)
C(3)–Fe(1)–P(1)	91.0(3)	C(6)–Fe(2)–C(4)	168.9(5)	C(8)–Fe(3)–C(7)	95.9(4)	O(1)–C(1)–Fe(1)	172.6(9)
C(2)–Fe(1)–P(1)	97.2(3)	C(5)–Fe(2)–P(2)	98.2(3)	C(9)–Fe(3)–C(7)	169.0(4)	O(2)–C(2)–Fe(1)	177.5(9)
C(1)–Fe(1)–P(1)	92.2(3)	C(6)–Fe(2)–P(2)	90.4(3)	C(8)–Fe(3)–P(3)	93.7(4)	O(3)–C(3)–Fe(1)	172.1(9)
C(3)–Fe(1)–Fe(2)	75.5(3)	C(4)–Fe(2)–P(2)	91.3(3)	C(9)–Fe(3)–P(3)	91.4(3)	O(4)–C(4)–Fe(2)	172.4(8)
C(2)–Fe(1)–Fe(2)	156.0(3)	C(5)–Fe(2)–Fe(3)	148.4(3)	C(7)–Fe(3)–P(3)	93.0(3)	O(5)–C(5)–Fe(2)	179.7(6)
C(1)–Fe(1)–Fe(2)	91.5(3)	C(6)–Fe(2)–Fe(3)	66.3(3)	C(8)–Fe(3)–Fe(2)	106.8(3)	O(6)–C(6)–Fe(2)	166.1(9)
P(1)–Fe(1)–Fe(2)	104.87(9)	C(4)–Fe(2)–Fe(3)	102.8(3)	C(9)–Fe(3)–Fe(2)	102.5(3)	O(7)–C(7)–Fe(3)	168.3(9)
C(3)–Fe(1)–Fe(3)	96.4(3)	P(2)–Fe(2)–Fe(3)	107.33(9)	C(7)–Fe(3)–Fe(2)	69.7(3)	O(8)–C(8)–Fe(3)	178.7(9)
C(2)–Fe(1)–Fe(3)	100.8(3)	C(5)–Fe(2)–Fe(1)	97.1(3)	P(3)–Fe(3)–Fe(2)	154.12(10)	O(9)–C(9)–Fe(3)	170.3(10)
C(1)–Fe(1)–Fe(3)	76.6(3)	C(6)–Fe(2)–Fe(1)	93.7(3)	C(8)–Fe(3)–Fe(1)	156.7(4)		
P(1)–Fe(1)–Fe(3)	159.88(10)	C(4)–Fe(2)–Fe(1)	81.9(3)	C(9)–Fe(3)–Fe(1)	72.5(3)		

above and below the iron triangle as well as the average deviation of the equatorial ligands from the mean plane can be used as criteria as to whether a compound of the type $[M_3(CO)_{12-n}L_n]$ has an anti-cubeoctahedral or icosahedral ligand arrangement. When this test is applied to $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$, the torsion angle is 74.0° and the average deviation of the equatorial phosphorus and oxygen (of the CO ligands) from the mean plane is 0.8 Å. The torsion angle is larger than any reported by Johnson *et al.*,[9] while the deviation lies within the range found for icosahedral ligand arrangements on C_{2v}-type $[M_3(CO)_{12-n}L_n]$. The cluster $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$ does not fit into the analysis, which raises questions as to its validity.

$[Fe_3(CO)_9\{P(OMe)_3\}_3]$

The claim[4] that the NMR spectra do not distinguish between structures **1b** and **1d** is incorrect. While both structures would give ^{13}CO NMR signals with an intensity ratio of 2:2:2:2:1 and three ^{31}P NMR signals, the number of signals and their intensity, albeit the most easily interpreted are not the only information available from the NMR spectra. Additional information [*e.g.* for L = P(OMe)$_3$] includes (*i*) the ^{31}P–^{13}C coupling constants. The ^{13}CO signals observed for isomer **1b** are δ 252.4, 221.4 [*J*(^{31}P–^{13}C) 30], 215.8 [*J*(^{31}P–^{13}C) 19], 215.6 [*J*(^{31}P–^{13}C) 19 Hz] and 211.3 (intensity 1). These signals are virtually identical to those reported by Aime *et al.*[1] For isomer **1d**, CO(3) and CO(4) would couple approximately equally to L^1 and L^2, giving either a doublet of doublets or a triplet of intensity 2. No such signal is observed, although the signals at δ 215.8 and 215.6 do overlap to give an apparent triplet.[1] The chemical shifts are slightly temperature dependent and at lower temperatures two doublets are resolved. These two doublets are clearly resolved in [Fe$_3$(CO)$_9${P(OPh)$_3$}$_3$].[1] (*ii*) The fluxionality of the carbonyls. After assigning the ^{13}C NMR spectrum, Mann and co-workers[2] stated that 'the merry-go-round mechanism commences at −90 °C, exchanging carbonyls C^1, C^2, C^8, C^9, C^{11} and C^{12}, with an activation energy of 9.8 kcal mol^{-1}' (*ca.* 41 kJ mol^{-1}). This statement requires that the ^{13}CO signals at δ 252.4, 215.8 and 215.6 broaden. This was illustrated for [Fe$_3$(CO)$_9${P(OEt)$_3$}$_3$] (structure **1b**) by Aime *et al.*[1] If this information is used to assign the carbonyl signals in structure **1d**, there is little choice but to assign C^3 and C^4 to the doublet at δ 221.4 (Fig. 3 in ref. 2) and then there are major problems in explaining why one P(OMe)$_3$ ligand on the same iron atom couples with *J*(^{31}P–^{13}C) 30 Hz, while the other has no detectable coupling. Alternatively, the ^{13}CO signals could be reassigned, but it is then necessary to propose an exchange mechanism that exchanges the signals at δ 252.4, 215.8 and 215.6. (*iii*) The interconversion of the isomers **1a** and **1b**, and ligand exchange within **1b**. This was unambiguously demonstrated using ^{31}P magnetisation-transfer measurements (Fig. 5 in ref. 2). Aime *et al.*[1] also reported the variable-temperature ^{31}P NMR spectra of [Fe$_3$(CO)$_9${P(OEt)$_3$}$_3$] (structure **1b**). If the structure of **1b** is reassigned as **1d**, then the fluxionality would require P(OMe)$_3$ to migrate between the iron atoms. At the time the original papers[1,2] and the criticism[4] were published, this was a completely unknown process, however, it has recently been shown to occur in [Ir$_2$Rh$_2$(CO)$_{11}$(PPh$_3$)].[10] The magnetisation-transfer measurements impose a constraint that we cannot fit to the suggestion of the major isomer of [Fe$_3$(CO)$_9${P(OMe)$_3$}$_3$] being **1d**. The ^{31}P NMR spectrum at −33 °C of [Fe$_3$(CO)$_9${P(OMe)$_3$}$_3$] has signals at δ 171.5, 163.6 and 161.8 for the asymmetric isomer and δ 167.5 for the symmetric isomer. No exchange was detected between the signals at δ 171.5 and 161.8, but was detected between the other signals. This was satisfactorily fitted to the isomers being **1a** and **1b** (see Scheme 6, ref. 2).

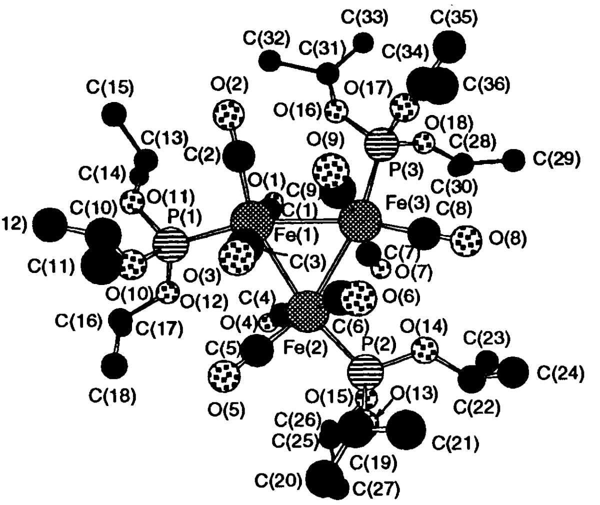


Fig. 1 Crystal structure of the major isomer of [Fe$_3$(CO)$_9${P(OPr^i)$_3$}$_3$]. The projection is such that the iron triangle is in the plane of the paper

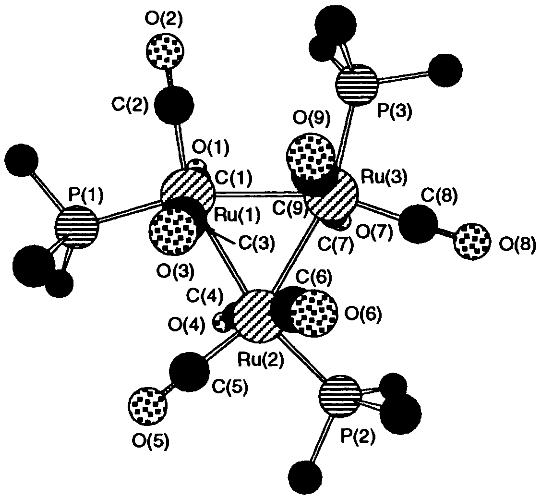


Fig. 2 Crystal structure of [Ru$_3$(CO)$_9$(PMe$_3$)$_3$];[6] in order to compare with the crystal structure in Fig. 1, the mirror image is shown

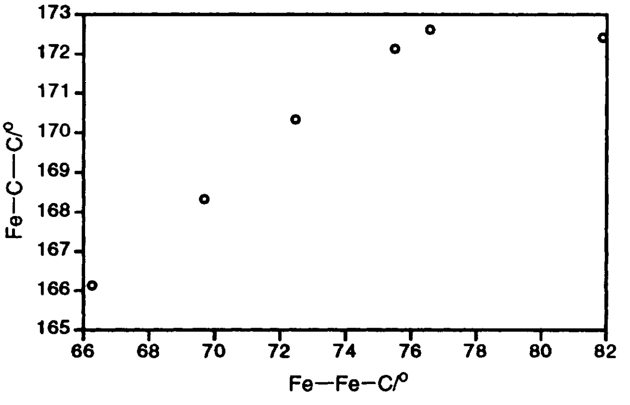


Fig. 3 Plot of Fe–Fe–C against Fe–C–O bond angles for [Fe$_3$(CO)$_9${P(OPr^i)$_3$}$_3$]

Table 2 Selected data from the crystal structures of [Fe$_3$(CO)$_9${P(OPr^i)$_3$}$_3$], [Ru$_3$(CO)$_9$(PMe$_3$)$_3$] and [Ru$_3$(CO)$_9${P(OEt)$_3$}$_3$][7]

	[Fe$_3$(CO)$_9${P(OPr^i)$_3$}$_3$]	[Ru$_3$(CO)$_9$(PMe$_3$)$_3$]	[Ru$_3$(CO)$_9${P(OEt)$_3$}$_3$]
M–M/Å	2.702, 2.709, 2.685	2.860, 2.854, 2.862	2.863, 2.852, 2.852
Axial C–M–C/°	167.0, 168.9, 169.0 (average = 168.3)	172.9, 171.4, 171.6 (average = 172.0)	169.0, 168.6, 170.0 (average = 169.2)
Angle between M$_3$ and CMP triangles/°	18.9, 24.9, 29.4 (average = 24.3)	11.7, 12.7, 17.0 (average = 13.8)	17.1, 17.5, 14.8 (average = 16.5)
Axial C–M–M/°	76.6, 75.5, 66.3, 81.9, 69.7, 72.5 (average = 73.7)	78.1, 84.7, 80.1, 80.1, 76.1, 82.8 (average = 80.3)	76.6, 74.1, 73.0, 75.6, 78.5, 74.0 (average = 75.3)
Axial O–C–M/°	172.6, 172.1, 166.1, 172.4, 168.3, 170.3 (average = 170.3)	172.3, 173.2, 172.9, 171.9, 171.5, 173.1 (average = 172.5)	169.9, 166.1, 167.2, 166.9, 169.4, 165.1 (average = 167.4)

Table 3 Selected bond lengths (Å) and angles (°) in the complex [$Fe_3(CO)_9\{P(OMe)_3\}_3$]

Fe(1)–C(1)	1.766(9)	Fe(2)–C(6)	1.780(12)	O(5)–C(5)	1.156(11)
Fe(1)–C(2)	1.814(10)	Fe(2)–C(5)	1.785(11)	O(6)–C(6)	1.155(12)
Fe(1)–C(4)	1.952(8)	Fe(3)–C(7)	1.798(10)	O(7)–C(7)	1.127(10)
Fe(1)–C(3)	2.067(9)	Fe(3)–C(8)	1.803(9)	O(8)–C(8)	1.135(9)
Fe(1)–P(1)	2.159(3)	Fe(3)–P(3)	2.172(2)	O(9)–C(9)	1.163(11)
Fe(1)–Fe(2)	2.556(2)	O(1)–C(1)	1.145(10)		
Fe(1)–Fe(3)	2.705(2)	O(2)–C(2)	1.111(10)		
Fe(2)–C(3)	1.923(9)	O(3)–C(3)	1.168(9)		
Fe(2)–C(4)	2.064(9)	O(4)–C(4)	1.152(9)		
Fe(2)–P(2)	2.165(3)				
Fe(2)–Fe(3)	2.705(2)				
Fe(3)–C(9)	1.788(10)				

C(1)–Fe(1)–C(2)	95.5(4)	C(3)–Fe(1)–Fe(3)	85.2(3)	C(6)–Fe(2)–Fe(3)	89.0(4)	C(8)–Fe(3)–Fe(2)	90.9(2)
C(1)–Fe(1)–C(4)	88.4(4)	P(1)–Fe(1)–Fe(3)	178.87(10)	C(5)–Fe(2)–Fe(3)	83.9(3)	P(3)–Fe(3)–Fe(2)	162.52(9)
C(2)–Fe(1)–C(4)	174.1(4)	Fe(2)–Fe(1)–Fe(3)	61.81(4)	C(3)–Fe(2)–Fe(3)	88.0(3)	Fe(1)–Fe(3)–Fe(2)	56.40(4)
C(1)–Fe(1)–C(3)	172.9(4)	C(6)–Fe(2)–C(5)	94.0(5)	C(4)–Fe(2)–Fe(3)	83.2(2)	O(1)–C(1)–Fe(1)	176.8(8)
C(2)–Fe(1)–C(3)	82.7(3)	C(6)–Fe(2)–C(3)	87.8(5)	P(2)–Fe(2)–Fe(3)	175.29(11)	O(2)–C(2)–Fe(1)	176.5(8)
C(4)–Fe(1)–C(3)	92.9(3)	C(5)–Fe(2)–C(3)	171.7(4)	Fe(1)–Fe(2)–Fe(3)	61.79(4)	O(3)–C(3)–Fe(2)	143.8(8)
C(1)–Fe(1)–P(1)	93.1(3)	C(6)–Fe(2)–C(4)	172.0(4)	C(9)–Fe(3)–C(7)	96.1(4)	O(3)–C(3)–Fe(1)	136.5(7)
C(2)–Fe(1)–P(1)	89.9(3)	C(5)–Fe(2)–C(4)	83.2(4)	C(9)–Fe(3)–C(8)	172.1(4)	Fe(2)–C(3)–Fe(1)	79.6(3)
C(4)–Fe(1)–P(1)	94.4(3)	C(3)–Fe(2)–C(4)	93.9(4)	C(7)–Fe(3)–C(8)	91.2(4)	O(4)–C(4)–Fe(1)	143.9(8)
C(3)–Fe(1)–P(1)	93.8(3)	C(6)–Fe(2)–P(2)	95.6(4)	C(9)–Fe(3)–P(3)	90.2(3)	O(4)–C(4)–Fe(2)	137.1(7)
C(1)–Fe(1)–Fe(2)	129.7(3)	C(5)–Fe(2)–P(2)	96.4(3)	C(7)–Fe(3)–P(3)	100.1(3)	Fe(1)–C(4)–Fe(2)	79.0(3)
C(2)–Fe(1)–Fe(2)	121.8(3)	C(3)–Fe(2)–P(2)	91.4(3)	C(8)–Fe(3)–P(3)	91.6(3)	O(5)–C(5)–Fe(2)	178.4(9)
C(4)–Fe(1)–Fe(2)	52.4(3)	C(4)–Fe(2)–P(2)	92.2(2)	C(9)–Fe(3)–Fe(1)	85.9(3)	O(6)–C(6)–Fe(2)	177.5(11)
C(3)–Fe(1)–Fe(2)	47.7(2)	C(6)–Fe(2)–Fe(1)	128.6(4)	C(7)–Fe(3)–Fe(1)	153.3(3)	O(7)–C(7)–Fe(3)	179.2(10)
P(1)–Fe(1)–Fe(2)	117.14(9)	C(5)–Fe(2)–Fe(1)	120.9(3)	C(8)–Fe(3)–Fe(1)	86.1(3)	O(8)–C(8)–Fe(3)	176.1(7)
C(1)–Fe(1)–Fe(3)	88.0(3)	C(3)–Fe(2)–Fe(1)	52.7(3)	P(3)–Fe(3)–Fe(1)	106.52(8)	O(9)–C(9)–Fe(3)	174.5(8)
C(2)–Fe(1)–Fe(3)	90.4(3)	C(4)–Fe(2)–Fe(1)	48.6(2)	C(9)–Fe(3)–Fe(2)	85.2(3)		
C(4)–Fe(1)–Fe(3)	85.3(3)	P(2)–Fe(2)–Fe(1)	114.32(11)	C(7)–Fe(3)–Fe(2)	97.1(3)		

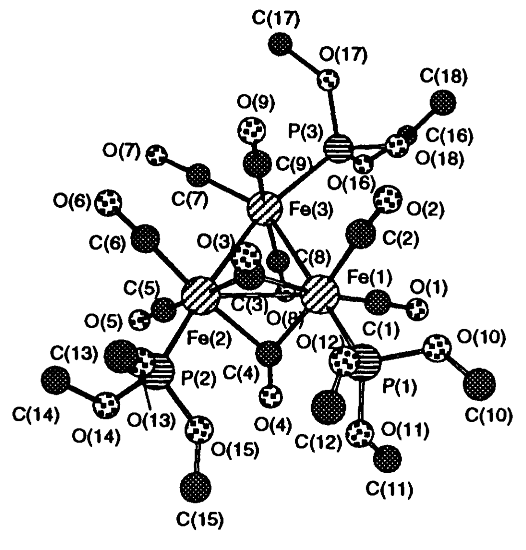


Fig. 4 Crystal structure of [$Fe_3(CO)_9\{P(OMe)_3\}_3$]

Thus, the NMR spectra are completely consistent with [$Fe_3(CO)_9\{P(OMe)_3\}_3$] possessing the structure **1b** and inconsistent with structure **1d**. However, in view of the criticism of the assignment as **1b**, we have determined the X-ray crystal structure, see Fig. 4. Selected bond lengths and bond angles are given in Table 3.

It can never be assumed that the solid-state structure is identical to that found in solution, but the crystal structure clearly shows that the structure of [$Fe_3(CO)_9\{P(OMe)_3\}_3$] is identical to that previously predicted for the major isomer **1b** on the basis of the NMR spectra. Only two isomers of [$Fe_3(CO)_9\{P(OMe)_3\}_3$] are detected in the ^{13}C and ^{31}P NMR spectra. The minor isomer has very similar NMR properties to **1a**, L = $P(OPr^i)_3$. The major isomer has NMR properties that are perfectly consistent with structure **1b** and with the structure determined by X-ray crystallography.

The structure **1b** has previously been observed in the crystal structure of [$Fe_3(CO)_9(PMe_2Ph)_3$],[11] while there are no examples of monodentate ligands giving isomer **1d**, even for ruthenium or osmium analogues, where there are many more structures reported. As is usual in [$Fe_3(CO)_{12}$] derivatives, the structure has two bridging carbonyls, which are bonded asymmetrically, with Fe(1)–C(4) 1.952(8), Fe(1)–C(3) 2.067(9), Fe(2)–C(3) 1.923(9) and Fe(2)–C(4), 2.064(9) Å. In general, the structure is very similar to that reported previously for [$Fe_3(CO)_9(PMe_2Ph)_3$],[11] with the exception of slightly shorter Fe–P bond lengths, as would be expected for a phosphite, rather than a phosphine ligand.

A crystal structure never proves a solution structure, but in this case, the solution structures were predicted independently by two research groups using NMR spectroscopy and then identical structures were determined subsequently using X-ray crystallography. The structure **1d** for the major isomer when L = $P(OMe)_3$, and the minor isomer when L = $P(OPr^i)_3$, can be eliminated on the basis of published NMR data. In conclusion, the structures of [$Fe_3(CO)_9\{P(OMe)_3\}_3$] and [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] are as originally proposed by Aime *et al.*[1] and by Mann and co-workers[2] based on NMR data.

Experimental

The compounds [$Fe_3(CO)_9\{P(OMe)_3\}_3$] and [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$] were synthesised as previously described for [$Fe_3(CO)_9\{P(OMe)_3\}_3$], from [$Fe_3(CO)_{12}$] and the appropriate phosphite using [$Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$] as catalyst.[12] In the case of [$Fe_3(CO)_9\{P(OPr^i)_3\}_3$], the yield increased from the previously reported 2%[13] to 20%.

Crystallography

[$Fe_3(CO)_9\{P(OMe)_3\}_3$]. Crystal data for $C_{18}H_{27}Fe_3O_{18}P_3$, *M* = 791.86, crystallises from methanol containing 10% hexane, as black oblong crystals, crystal dimensions 0.66 × 0.44 × 0.25 mm, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$ C^5_{2h}, no. 14), $a = 9.382(4)$, $b = 17.974(4)$, $c = 18.950(4)$ Å, $\beta = 99.57(2)°$, $U = 3151(2)$ Å^3, $Z = 4$, $D_c = 1.669$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\ 73$ Å), μ(Mo-Kα) = 1.588 mm^{-1}, $F(000) = 1608$.

Three-dimensional, room-temperature data were collected in the range $3.5 < 2\theta < 50°$ on a Siemens P4 diffractometer by the omega-scan method. Of the 7111 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 3329 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0731$ ($wR_2 = 0.2209$, for all 5553 data, 379 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.608 and 0.560 e Å^{-3}.

A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1156P)^2 + 3.2846P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93,[14] as implemented on the Viglen 486dx computer.

$[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$. Crystal data for $C_{36}H_{63}Fe_3O_{18}P_3$, $m = 1044.32$, crystallises from acetonitrile as black oblong crystals, crystal dimensions 0.71 × 0.35 × 0.34 mm, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$ C^5_{2h}, no.14), $a = 9.827(6)$, $b = 40.956(13)$, $c = 13.431(4)$ Å, $\beta = 107.14(4)°$, $U = 5166(4)$ Å^3, $Z = 4$, $D_c = 1.343$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\ 73$ Å), μ(Mo-Kα) = 0.986 mm^{-1}, $F(000) = 2180$.

Three-dimensional, room-temperature data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the omega-scan method. Of the 8436 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 4056 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least squares on F^2. Two methyls C(35) and C(36) were found to be disordered (1 : 1) between two sites. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0742$ ($wR_2 = 0.1769$, for all 6761 data, 546 parameters, mean and maximum δ/σ 0.000, 0.080), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.406 and 0.981 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 13.3672P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93,[14] as implemented on the Viglen 486dx computer.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/45.

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