

The crystal and molecular structure of [bis(diphenylphosphino)ethane]tricarbonyliron(0) *

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Abstract

[Bis(diphenylphosphino)ethane]tricarbonyliron(0), $\text{Fe}(\text{CO})_3\text{-(Ph}_2\text{PCH}_2\text{CH}_2\text{-PPh}_2)$, has been prepared by reducing FeCl_2 with metallic manganese under an atmosphere of CO in the presence of the diphosphine at room temperature in THF. The results of an X-ray diffraction study (room temperature, Mo- K_α) are: $P2_1/n$, a 12.260(6), b 15.890(7), c 14.227(6) Å, β 110.57(3)°, $Z = 4$, D_c 1.378, D_m 1.40 Mg m^{-3} , $R_F(2957/413) = 0.0393$.

The iron is pentacoordinate, with a geometry intermediate between trigonal bipyramidal, with a phosphorus and a carbonyl apical, and square pyramidal with a carbonyl apical. No significant differences are observed between the Fe–P distances (av. 2.224(2) Å) or between the Fe–CO distances (av. 1.770(5) Å). Comparison with the analogous bis(diphenylphosphino)methane derivative shows that the main differences in the coordination polyhedra arise from the difference in the P···P bite distance, which is 2.981(2) Å in the ethane derivative but only 2.650(3) Å in the methane derivative. The five-membered Fe–P–C–C–P chelate ring shows an unsymmetrical conformation, with one carbon atom tending to lie in the P–Fe–P plane, the corresponding torsion about the Fe–P bond being almost zero (1.3(2)°). This kind of conformation is common for bis(diphenylphosphino)ethane chelating rings, suggesting a limited flexibility of that ring. The orientations of the phenyl groups are somewhat different from those in the corresponding bis(diphenylphosphino)methane complex.

* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

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Introduction

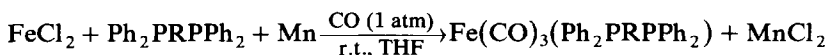
The importance of iron(0) carbonyl complexes as catalysts or promoters of organic syntheses is well known. In particular, the mixed ligand complexes derived by substitution of carbonyls in iron pentacarbonyl by ligands containing phosphorus have been recognized as effective models of catalysts for nitrogen fixation and carbon monoxide hydrogenation [1]. Of particular interest are the chelating phosphines containing aromatic rings. The steric arrangement of these rings can affect the reactivity by providing unique environments for incoming substrates. Hence the importance of examining differences and analogies within a series of analogous complexes.

As part of a research on this theme, the bis(diphenylphosphino)ethane (dppe) derivative has been prepared by a new procedure [2], and in the present paper its crystal structure is described and compared with that of the analogous bis(diphenylphosphino)methane(dppm) derivative studied by Cotton et al. [3]. This offers an opportunity for more general consideration of the behaviour of dppe as a ligand in metal complexes.

Results and discussion

Preparation

The title compound was prepared by the following general reaction [2] involving use of powdered manganese metal as reducing agent in a one step process carried out under mild conditions (room temperature, atmospheric pressure):



(R = CH₂, CH₂CH₂, *cis*-CH=CH, *o*-C₆H₄)

The Fe⁰ complex is easily isolated from the reaction mixture by extraction with toluene followed by precipitation with n-hexane (yield 40%, for R=CH₂CH₂). In spite of its low yield, this turns out to be one of the simplest preparations of metal carbonyls, since cumbersome separation procedures are not required.

Description of the structure

The crystals are built up by neutral Fe(CO)₃(dppe) complex molecules in which Fe⁰ is pentacoordinate, as shown in the ORTEP projection of Fig. 1. From the data in Table 1, where bond distances and angles in the metal coordination sphere are compared with those of the analogous dppm derivative, it can be seen that the coordination geometry is intermediate between that of a trigonal bipyramid (tbp), with P(1) and C(28) at the apices, and that of a square pyramid (spy), with C(27) at the apex.

The angular deformations associated with these geometries are best appreciated by considering the differences, Δ, between the observed and expected angles. The expected angles are uniquely defined in the case of the trigonal pyramid arrangement, but are undefined for the square pyramid where in the ideal case all the apex to basal plane angles should be equal (as they should for the basal plane), the first being greater and the second less than 90°. In terms of these requirements and

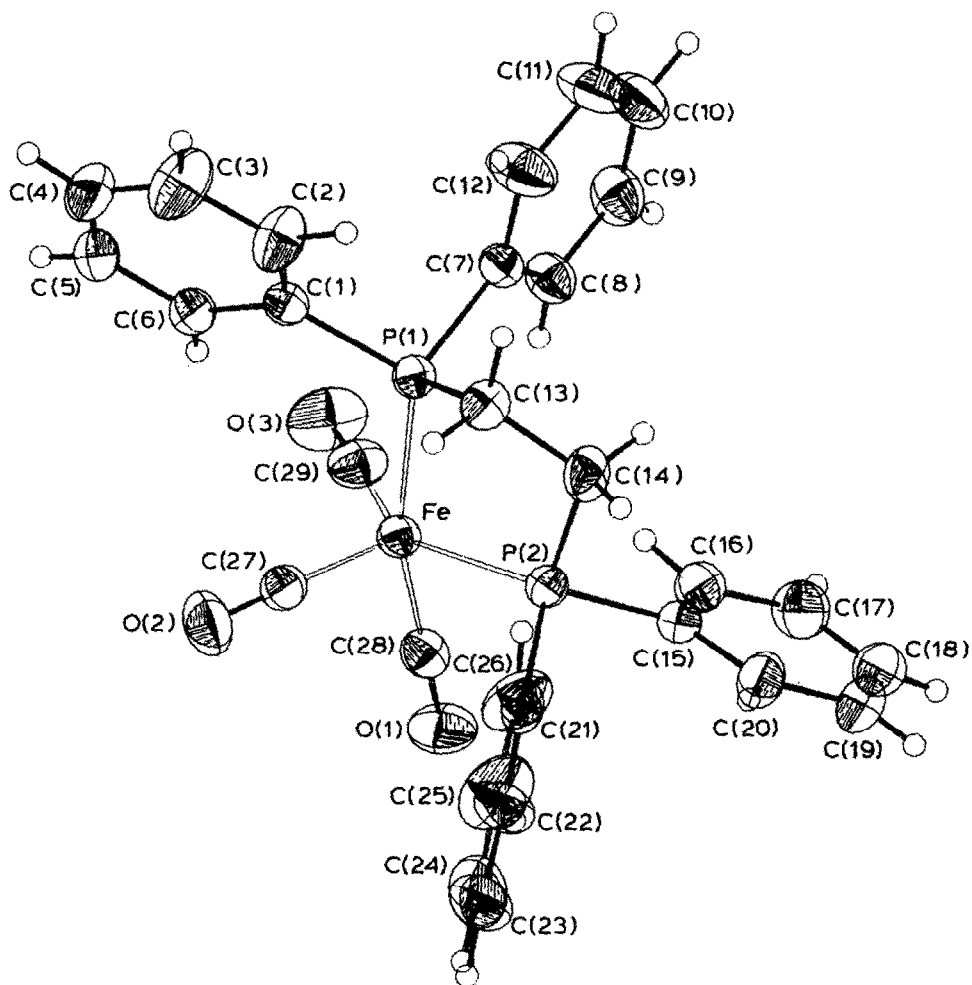


Fig. 1. ORTEP drawing of the molecular structure of $\text{Fe}(\text{CO})_3(\text{dppe})$. Ellipsoids at 50% probability level.

taking account of the fact that the sum of the deformed angles is usually near to the sum of the undeformed ones, the averaged values can be considered equal to the expected values.

Simple trigonometric considerations show that for a regular tetragonal pyramid the equation $\sin \beta = \sqrt{1 - \cos \alpha}$ ($\beta = \text{L}_{\text{apical}} - \text{Fe} - \text{L}_{\text{basal}}$, $\alpha = \text{L}_{\text{basal}} - \text{Fe} - \text{L}'_{\text{basal}}$, L = ligand atom) applies. Application of this equation to the observed angles gives the following calculated values (av.) (Δ are the ranges of the differences from the observed values):

	dppe		dppm	
	av.	Δ	av.	Δ
β	$103.3 + 2.8^\circ$	$0.7-9.3^\circ$	$107.8 + 14.4^\circ$	$1.3-10.5^\circ$
α	$86.5 + 1.8$	$0.9-3.8$	$85.2 + 2.3$	$5.2-11.1$

Comparison of these values and the differences quoted in Table 1, reveals that the coordination polyhedron is a little nearer to a square pyramid than to a trigonal bipyramid, and that the displacements from that ideal polyhedron are a little

Table 1

Bond distances (Å) and angles (°) in the metal coordination sphere. (The quantities accompanying the average are: the first (in parentheses) the averaged standard deviations $[\Sigma(\frac{1}{2}\sigma)^2]^{-1/2}$ the second the r.m.s. deviation from the mean $[\Sigma(x - \langle x \rangle)^2/(n-1)]^{1/2}$. When only one value is quoted (in parenthesis), this is the larger of the two values)

	dppe	dppm		dppe	dppm
Fe-P(1)	2.223(1)	2.225(3)	Fe-C(27)	1.777(4)	1.77(1)
Fe-P(2)	2.227(2)	2.209(3)	Fe-C(28)	1.770(4)	1.74(1)
av.	2.224(2)	2.217(8)	Fe-C(29)	1.758(5)	1.77(1)
			av.	1.770(5)	1.76(1)
P(1) ... P(2)	2.981(2)	2.650(3)			

(a) Trigonal bipyramidal (tbp)

Apex to trigonal plane ($\Delta = \text{angle} - 90^\circ$)

	dppe		dppm	
	Δ		Δ	
P(1)-Fe-P(2)	84.1(1)	-6.0(1)	73.5(1)	-16.5(1)
P(1)-Fe-C(27)	95.8(2)	5.7(2)	99.2(3)	9.2(3)
P(1)-Fe-C(29)	90.3(2)	0.2(2)	89.8(3)	0.2(3)
av.	87.1(1) ± 3.2	5.0(1) ± 1.5	77.3(1) ± 5.9	14.4(1) ± 3.5

Apex to trigonal plane ($\Delta = \text{angle} - 90^\circ$)

	dppe		dppm	
	Δ		Δ	
C(28)-Fe-P(2)	87.4(1)	-2.6(1)	92.3(3)	2.3(3)
C(28)-Fe-C(27)	99.3(2)	9.3(2)	97.3(4)	7.3(4)
C(28)-Fe-C(29)	88.6(2)	-1.4(2)	91.6(4)	1.6(4)
av.	89.6(1) ± 3.8	3.5(1) ± 1.8	93.4(2) ± 1.6	3.4(2) ± 1.6

Trigonal plane ($\Delta = \text{angle} - 120^\circ$)

	dppe		dppm	
	Δ		Δ	
P(2)-Fe-C(27)	104.0(2)	-16.0(2)	109.1(3)	-10.9(3)
P(2)-Fe-C(29)	143.3(2)	23.3(2)	134.2(3)	14.2(3)
C(27)-Fe-C(29)	112.6(2)	-7.4(2)	115.7(4)	-4.3(4)
av.	120.0(1) ± 11.9	15.6(1) ± 4.6	120.3(2) ± 8.0	10.7(2) ± 2.6

Apex to apex ($\Delta = \text{angle} - 180^\circ$)

	dppe		dppm	
	Δ		Δ	
P(1)-Fe-C(28)	164.1(2)	-15.9(2)	161.0(3)	-19.0(3)

Table 1 (continued)

(b) Square pyramidal (*spy*)

Apex to basal plane ($\Delta = \text{angle} - \langle \text{angle} \rangle$)				
	dppe		dppm	
		Δ		Δ
C(27)–Fe–P(1)	95.8(2)	–7.1(2)	99.2(3)	–6.1(4)
C(27)–Fe–P(2)	104.0(2)	1.1(2)	109.1(3)	3.8(4)
C(27)–Fe–C(28)	99.3(2)	–3.6(2)	97.3(4)	–8.0(4)
C(27)–Fe–C(29)	112.6(2)	9.7(2)	115.7(4)	10.4(4)
av.	102.9(1) ± 3.6	5.4(1) ± 1.9	105.0(2) ± 4.0	7.1(2) ± 1.4
Basal plane ($\Delta = \text{angle} - \langle \text{angle} \rangle$)				
	dppe		dppm	
		Δ		Δ
C(28)–Fe–C(29)	88.6(2)	1.0(2)	91.6(4)	4.8(4)
C(29)–Fe–P(1)	90.3(2)	2.7(2)	89.8(3)	3.0(4)
P(1)–Fe–P(2)	84.1(1)	–3.5(1)	73.5(1)	–13.3(2)
P(2)–Fe–C(28)	87.4(1)	–0.2(1)	92.3(3)	5.5(4)
av.	86.5(1) ± 1.2	1.8(1) ± 0.9	77.4(1) ± 4.2	9.5(2) ± 2.6
P(2)–Fe–C(29)	143.3(2)	–10.4(2)	134.2(3)	–13.4(4)
P(1)–Fe–C(28)	164.1(2)	10.4(2)	161.0(3)	13.4(4)
av.	153.7(1) ± 10.4		147.6(2) ± 13.4	

smaller in the dppe than in the dppm derivative. The steric constraint inherent in the diphosphine ligand is itself, of course, the major cause of the observed deformation. The P...P bite distance is larger (2.981(2) Å) for dppe than for dppm (2.650(3) Å), while the Fe–P distances are not significantly changed; consequently the P–Fe–P angle is larger (84.1(1)°) in the dppe than in the dppm complex (73.5(1)°), and the deformation with respect to a regular coordination is reduced.

The deformations from trigonal bipyramid coordination are also shown by the displacements of Fe from the (P(2),C(27),C(29)), (P(1),C(27),C(28)) and (P(1),P(2),C(28)) planes, which are 0.023(1), 0.075(1), 0.245(1) Å, respectively.

As pointed out by Cotton et al. [3], only relatively slight bends or twists are needed to change the configurations of these compounds from those actually observed, in which the three CO groups are all non-equivalent, into those in which different pairs become equivalent, i.e. these complexes are stereochemically non rigid, and fluxional behaviour of the CO groups can be predicted [4].

In coordinating to metal the dppe ligand forms a puckered five-membered ring in an envelope conformation, with a pseudo mirror along C(13) at the flap, a little deformed towards half-chair, with a local pseudo twofold axis along P(2) and the middle of the P(1)–C(13) bond, as indicated by the following values of the puckering [5] and asymmetry [6] parameters; Q 0.508(4) Å, ϕ 186.8(3)°, $\Delta_5(\text{C}(13)) = 0.0275(13)$, $\Delta_2(\text{P}(2)) = 0.0589(11)$. Bond distances and angles in it are consistent with a pseudo C_2 local symmetry along Fe and the midpoint of the C(13)–C(14)

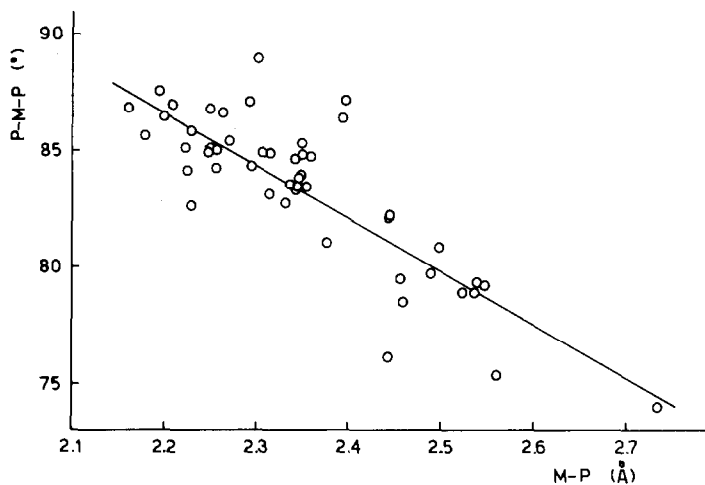


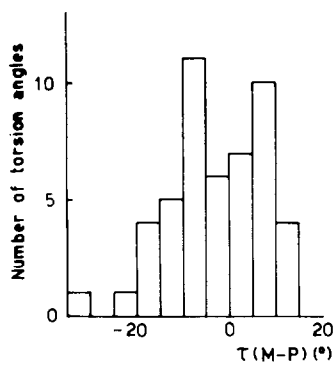
Fig. 2. Scatter plot of the P-M-P angle ($^{\circ}$) vs. the M-P distance (\AA) in metal-dppe chelate complexes (from crystal structures with $R < 0.06$). The equation of the straight line is: $(\text{P-M-P}) = 136.562 - 22.707 (\text{P-M})$, ($r = 0.912$). (Literature references for data used in the plot are available from the authors.)

bond. Except for the P-Fe-P angle, whose value is determined by the P...P bite and Fe-P bond distances, the endocyclic angles deviate by only a few degrees (max. 3.7°) from the tetrahedral value.

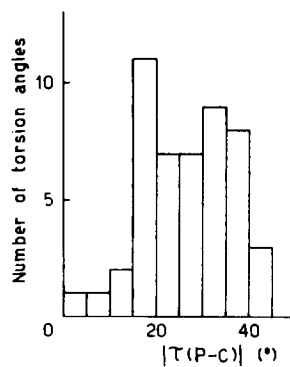
In coordinating to metal atoms the dppe ligand can behave as a chelating agent or as a bridging ligand. Examination of the literature data reveal the following features: (i) bridging dppe together with chelating dppe has been found only in Cu^{I} tetrahedral complexes [7,8], (ii) if these complexes, where the P-Cu-P angle is larger owing to tetrahedral coordination [8], are disregarded, the P-M-P angle is inversely related to the M-P distance, as shown in Fig. 2, and this can be related to a tendency to maintain the P...P bite distance unchanged in the ligand, (iii) except for $[\text{Ir}(\text{CH}_3)(\text{C}_8\text{H}_{12})(\text{dppe})]$ [9], where the chelating dppe ligand has $C_s(m)$ crystallographic symmetry with a $\tau(\text{C-C})$ torsion angle of exactly zero, in all cases of chelating dppe the total puckering amplitude is roughly the same, with an average value of $0.538(9) \text{\AA}$, and the values of the endocyclic torsion angles are as shown in the histograms of Fig. 3, indicating that the ring shows a tendency to assume an unsymmetrical conformation with one P-C bond almost in the P-M-P plane (the $\tau(\text{M-P})$ torsion angle tends to be near to zero). The endocyclic torsion angles found in the title compound fall within the most populated ranges of the histograms: $\tau(\text{Fe-P}) - 1.3(2)$, $\tau(\text{P-C}) - 28.3(3)$, $\tau(\text{C-C}) 47.2(3)$, $\tau(\text{C-P}) - 48.6(3)$ and $\tau(\text{P-Fe}) 25.1(2)^{\circ}$.

According to Hall et al. [10], in these chelate rings the energy barrier to torsion about the P-C bond is probably lower than that about the other bonds, while the most relevant barrier is that about the C-C bond (ca. 3 kcal mol^{-1}). In addition the histograms of Fig. 3 show that the flexibility of the ligand is limited, and seem to confirm the observation that the conformation of the ring must be influenced more by the intramolecular interactions between the aromatic rings than by any influence of the metal atom or of the packing.

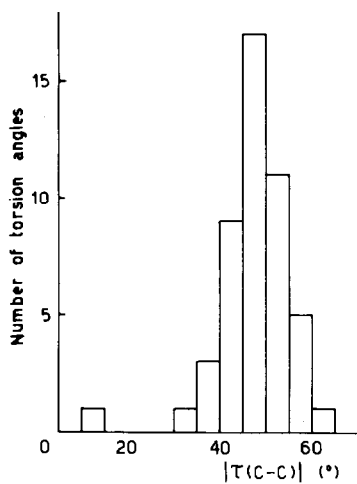
Bond distances and angles in diphosphine and carbonyls are given in Table 2. The orientation of the phosphine ligand with respect to the other ligands is best



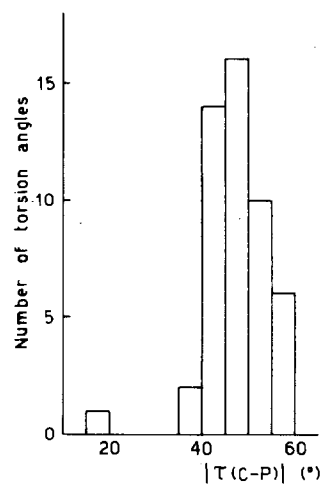
(a)



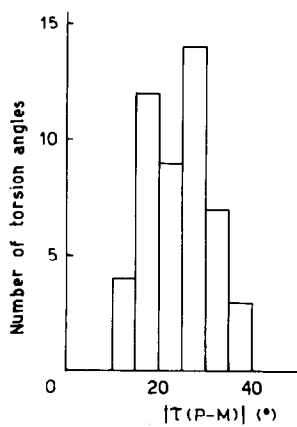
(b)



(c)



(d)



(e)

Fig. 3. Distribution of the endocyclic torsion angles in 49 metal-dppe chelation cycles (from crystal structures with $R < 0.06$). The sequence of the signs for $\tau(\text{P-C})$, $\tau(\text{C-C})$, $\tau(\text{C-P})$, $\tau(\text{P-M})$ is $- + - +$ or vice versa. In the cases of centrosymmetric space groups both sequences are present in the same crystal. (Literature references for the data used are available from the authors.)

Table 2

Bond distances (Å) and angles (°) involving diphosphine and carbonyls in Fe(CO)₃(dppe)

P(1)–C(1)	1.826(4)	P(2)–C(15)	1.832(4)
P(1)–C(7)	1.841(4)	P(2)–C(21)	1.836(5)
P(1)–C(13)	1.837(4)	P(2)–C(14)	1.835(4)
C(13)–C(14)	1.520(6)	C(27)–O(2)	1.149(5)
C(28)–O(1)	1.146(5)	C(29)–O(3)	1.156(7)
C(1)–C(2)	1.383(6)	C(15)–C(16)	1.370(6)
C(2)–C(3)	1.390(6)	C(16)–C(17)	1.386(6)
C(3)–C(4)	1.365(7)	C(17)–C(18)	1.361(8)
C(4)–C(5)	1.352(7)	C(18)–C(19)	1.376(8)
C(5)–C(6)	1.370(6)	C(19)–C(20)	1.375(6)
C(6)–C(1)	1.387(5)	C(20)–C(15)	1.382(6)
C(7)–C(8)	1.379(6)	C(21)–C(22)	1.371(7)
C(8)–C(9)	1.390(7)	C(22)–C(23)	1.435(9)
C(9)–C(10)	1.364(7)	C(23)–C(24)	1.362(11)
C(10)–C(11)	1.373(8)	C(24)–C(25)	1.362(11)
C(11)–C(12)	1.388(8)	C(25)–C(26)	1.382(11)
C(12)–C(7)	1.379(6)	C(26)–C(21)	1.371(7)
C(sp ²)–H	0.917(15) av.	C(sp ³)–H	0.956(18) av.
Fe–P(1)–C(1)	118.3(1)	Fe–P(2)–C(15)	121.2(1)
Fe–P(1)–C(7)	118.5(1)	Fe–P(2)–C(21)	114.0(2)
Fe–P(1)–C(13)	108.1(2)	Fe–P(2)–C(14)	110.4(2)
C(1)–P(1)–C(7)	103.2(2)	C(15)–P(2)–C(21)	102.2(2)
C(1)–P(1)–C(13)	104.9(2)	C(15)–P(2)–C(14)	102.3(2)
C(7)–P(1)–C(13)	102.0(2)	C(21)–P(2)–C(14)	105.0(2)
P(1)–C(1)–C(2)	122.2(3)	P(2)–C(15)–C(16)	120.0(3)
P(1)–C(1)–C(6)	118.8(3)	P(2)–C(15)–C(20)	121.8(3)
P(1)–C(7)–C(8)	121.0(3)	P(2)–C(21)–C(22)	118.0(4)
P(1)–C(7)–C(12)	121.5(3)	P(2)–C(21)–C(26)	123.3(4)
C(6)–C(1)–C(2)	118.0(4)	C(20)–C(15)–C(16)	118.2(4)
C(1)–C(2)–C(3)	120.6(4)	C(15)–C(16)–C(17)	121.2(4)
C(2)–C(3)–C(4)	120.1(4)	C(16)–C(17)–C(18)	119.5(5)
C(3)–C(4)–C(5)	119.3(5)	C(17)–C(18)–C(19)	120.5(5)
C(4)–C(5)–C(6)	121.9(4)	C(18)–C(19)–C(20)	119.4(5)
C(5)–C(6)–C(1)	120.1(4)	C(19)–C(20)–C(15)	121.2(4)
C(12)–C(7)–C(8)	117.5(4)	C(26)–C(21)–C(22)	118.6(5)
C(7)–C(8)–C(9)	121.5(4)	C(21)–C(22)–C(23)	119.7(5)
C(8)–C(9)–C(10)	120.0(5)	C(22)–C(23)–C(24)	119.4(6)
C(9)–C(10)–C(11)	119.6(5)	C(23)–C(24)–C(25)	120.6(7)
C(10)–C(11)–C(12)	120.1(5)	C(24)–C(25)–C(26)	119.6(6)
Fe–C(28)–O(1)	179.0(4)	Fe–C(27)–O(2)	176.7(4)
Fe–C(29)–O(3)	176.9(5)	C(sp ²)–C(sp ²)–H	119.8(7) av.
P–C–H	108(2) av.	C(sp ³)–C(sp ³)–H	114(1) av.
H–C–H	106(2) av.		

illustrated by the Newman projections in Fig. 4, which show that, except for the P–C and Fe–P bonds whose orientation is determined by the conformation of the diphosphine, the bonds tend to be staggered. The mutual orientation of the phenyl rings is such that the planes of these rings make the dihedral angles quoted in Table 3. These angles show differences from the corresponding angles in the dppm complex, indicating that chelation to metal influences the orientations of the phenyl

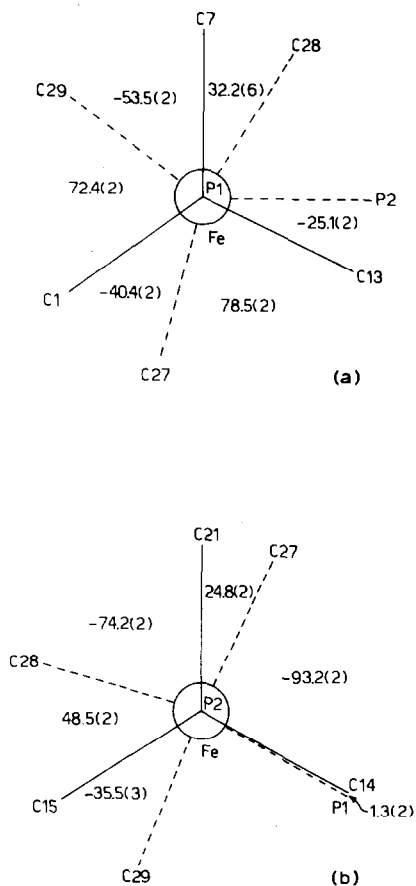


Fig. 4. Newman projections along: (a) P(1)–Fe, (b) P(2)–Fe.

groups. In the iron complex of dppe these orientations are also related to the non-bonded intermolecular contacts shown in Table 4.

The exocyclic C–P–C angles do not show systematic differences when $C(sp^2)$ or $C(sp^3)$ is involved, and their mean value, $103.3(6)^\circ$ for dppe and $104.7(8)^\circ$ for dppm, is lower than the ideal tetrahedral value (109.5°). In contrast, the

Table 3

Comparison of the dihedral angles ($^\circ$) between the phenyl rings in $\text{Fe}(\text{CO})_3(\text{dppe})$ and $\text{Fe}(\text{CO})_3(\text{dppm})$

	$\text{Fe}(\text{CO})_3(\text{dppe})$	$\text{Fe}(\text{CO})_3(\text{dppm})$
$\text{C}(1) \cdots \text{C}(6) \wedge \text{C}(7) \cdots \text{C}(12)$	71.6(2)	76.8(3)
$\text{C}(15) \cdots \text{C}(20) \wedge \text{C}(21) \cdots \text{C}(26)$	77.2(2)	98.0(3)
$\text{C}(1) \cdots \text{C}(6) \wedge \text{C}(15) \cdots \text{C}(20)$	128.0(2)	99.2(3)
$\text{C}(1) \cdots \text{C}(6) \wedge \text{C}(21) \cdots \text{C}(26)$	97.0(2)	76.2(3)
$\text{C}(7) \cdots \text{C}(12) \wedge \text{C}(15) \cdots \text{C}(20)$	85.6(2)	63.5(3)
$\text{C}(7) \cdots \text{C}(12) \wedge \text{C}(21) \cdots \text{C}(26)$	27.4(2)	35.1(3)

Table 4

Intermolecular non-bonded contacts (Å) related to the orientation of the phenyl rings in Fe(CO)₃(dppe)

H(2)···H(12)	2.47(5)	H(26)···H(142)	2.10(6)
H(2)···H(132)	2.27(5)	C(28)···H(16)	2.98(4)
H(8)···H(16)	2.76(6)	C(28)···H(22)	2.86(4)
H(12)···H(132)	2.42(6)	C(29)···H(6)	2.74(3)
H(26)···H(131)	2.62(6)	C(29)···H(8)	2.67(3)

Fe–P–C(*sp*²) angles are all significantly larger (av. 118.9(1.1)° for dppe and 121.4(1.8)° for dppm) than the Fe–P–C(*sp*³) ones (av. 109.2(1.2)° for dppe and 97.8(2)° for dppm), the latter being quite close to the tetrahedral value in the case of the dppe complex and much smaller in the case of the dppm derivative. This pattern of larger Fe–P–C(*sp*²) and narrower C–P–C angles is general both for free phosphines and for phosphine complexes of the transition metals, as observed by Churchill and O'Brien [11].

The data quoted in Table 5 show that the deformations of the phenyl rings, even if small and not always significant, show regular trends. Thus the averaged distances are in the sequence:

$$d(C_o - C_m) > d(C_i - C_o) > d(C_m - C_p)$$

both in the dppe and dppm derivative, even though the corresponding values for the two compounds are slightly different, probably as a consequence of uncorrected thermal motion. The endocyclic angles at the *meta* and *para* carbon atoms are practically equal, while the angle at the *ipso* carbon is narrower than that at the *ortho* carbon in the case of the dppe derivative and the opposite is the case for the dppm derivative. The exocyclic P–C–C angles range from 118.0(4) to 123.3(4)°, mean 121.0(5)°, in agreement with the requirement of planarity at the *ipso* carbon atoms, where the average endocyclic angle is 118.2(2)°.

As usually observed, the carbonyl groups are not exactly colinear with the Fe–C bonds, the angles Fe–C–O being in the range 179.0(4)–176.9(5)°. The Fe–C distances are not significantly different and their mean value 1.770(5) Å agrees well with that observed in the dppm derivative (1.76(1) Å). The C–O distances are also in quite good agreement for both dppe (1.149(3) Å) and dppm (1.150(6) Å) compounds.

Table 5

Comparison of averaged distances (Å) and angles (°) in the phenyl rings (*i* = *ipso*, *o* = *ortho*, *m* = *meta*, *p* = *para*)

	dppe	dppm
C _{<i>i</i>} –C _{<i>o</i>}	1.380(2)	1.395(6)
C _{<i>o</i>} –C _{<i>m</i>}	1.388(5)	1.418(7)
C _{<i>m</i>} –C _{<i>p</i>}	1.366(3)	1.388(4)
C–C _{<i>i</i>} –C	118.2(2)	120.5(4)
C–C _{<i>o</i>} –C	120.8(3)	119.4(4)
C–C _{<i>m</i>} –C	119.8(2)	120.1(3)
C–C _{<i>p</i>} –C	119.9(4)	120.3(4)

The CH₂–CH₂ distance of 1.520(6) Å (after correction for riding motion, 1.525 Å) within the diphosphine ligand is a little shorter than the theoretical value for a C(sp³)–C(sp³) bond of 1.542(1) Å [12], but the difference is just at the limit of significance ($\Delta/\sigma = 2.8$).

Conclusions

The X-ray investigation of the dppe complex reveals analogies with the known dppm complex and shows that the ring formed by dppe with Fe exhibits the conformation more generally observed when this ligand chelates transition metals, and so it can be argued that this conformation is not as flexible as has been previously assumed. The aromatic rings in the dppe complex are oriented somewhat differently from those in the dppm derivative.

Experimental

Preparation procedure

Anhydrous FeCl₂ (Merck) (1 g, 7.9 mmol), dppe (Strem) (3.2 g, 8 mmol), and an excess of Mn powder (Alfa) (1.4 g) were placed into a 250 cm³ flask under dry nitrogen. After addition of tetrahydrofuran (60 cm³), N₂ was replaced by CO at atmospheric pressure and the mixture was then stirred at room temperature overnight. After filtration the yellow solution was reduced to dryness under vacuum and the residue extracted with toluene. Addition of n-hexane to the extract and storage at low temperature (–20 °C) led to separation of the title compound as yellow crystals suitable for the X-ray study (yield 40%, not optimized). Analytical data: Found: C, 64.89; H, 4.61. calc: C, 64.71; H, 4.49%. m.p. 130 °C (dec.).

Crystal data

C₂₉H₂₄FeO₃P₂, $M = 538.3$, monoclinic $P 2_1/n$ (from systematic absences), a 12.260(6), b 15.890(7), c 14.227(6) Å, β 110.57(3)°, V 2595(2) Å³, D_m 1.40 (by flotation), D_c 1.378 Mg m^{–3}, $Z = 4$, μ 0.726 mm^{–1}, $F(000) = 1112$, Mo-K α_1 radiation, λ 0.709300 Å, room temperature (~293 K). The unit cell parameters were determined, from 18 accurately diffractometer measured reflections with θ values in the 11.2–18.6° range; an extrapolation least-squares procedure based on the method proposed by Vogel and Kempter [13].

Intensity measurements

A prismatic crystal with main size 0.33 × 0.52 × 0.85 mm was used to collect 4983 independent reflections on a Philips PW 1100 diffractometer with Mo-K α graphite monochromated radiation in the 2.5–25.0° θ range ($-13 \leq h \leq 13$, $0 \leq k \leq 18$, $0 \leq l \leq 16$). A standard reflection (3 4 1), checked every hour to monitor the crystal alignment and decomposition and the equipment stability, showed intensity variations not greater than 4.7%. The measurements were made at room temperature by the $\omega - 2\theta$ scan technique, with a scan speed of 0.10°/s and a scan width of (1.60 + 0.30 tan θ)°.

All the reflections were corrected for Lorentz and polarization effects, but not for absorption and extinction. 1986 reflections having $I < 3\sigma(I)$ were considered unobserved, so the total number of independent reflections used in the structure analysis was 2957.

Solution of the structure and refinement

The structure was solved by Patterson and Fourier methods and refined by least-squares using the SHELX76 program [14]. All the hydrogen atoms were located from difference Fourier syntheses and refined isotropically in a separate least-squares block. The total number of refined parameters was 413.

The final values of the residual error indices are $R = \Sigma |\Delta F| / \Sigma |F_o| = 0.0393$, $R_w = [\Sigma w |\Delta F|^2 / \Sigma w F_o^2]^{1/2} = 0.0495$, and the goodness of fit is $S = [\Sigma w |\Delta F|^2 / (N - P)]^{1/2} = 1.2901$. The weighting scheme used in the refinement was $w = [\sigma^2(F_o) + 0.000641 F_o^2]^{-1}$. At the end of the refinement the least-squares shift to error ratio had an average value of 0.30, while the minimum and maximum heights in final difference Fourier synthesis were -0.10 and $0.17 \text{ e } \text{\AA}^{-3}$, respectively.

Table 6

Fractional atomic coordinates and U_{eq} ($\times 10^4$)

Atom	x	y	z	U_{eq}^a
Fe	2232.2(4)	1255.7(3)	297.9(4)	363(2)
P(1)	3419.9(8)	2360.4(6)	691.3(7)	354(4)
P(2)	2855.8(8)	1051.9(6)	1951.3(7)	380(3)
C(1)	2973(3)	3316(2)	-59(3)	388(16)
C(2)	3296(5)	4109(3)	342(3)	626(20)
C(3)	2952(5)	4823(3)	-255(4)	774(25)
C(4)	2293(4)	4746(3)	-1248(4)	670(22)
C(5)	1969(4)	3971(3)	-1639(3)	610(19)
C(6)	2291(3)	3257(3)	-1068(3)	492(17)
C(7)	4939(3)	2216(2)	770(3)	407(16)
C(8)	5316(3)	1456(2)	528(3)	478(15)
C(9)	6465(4)	1337(4)	596(4)	620(21)
C(10)	7255(4)	1972(3)	937(4)	720(23)
C(11)	6910(4)	2725(3)	1213(5)	842(27)
C(12)	5752(4)	2850(3)	1109(4)	719(23)
C(13)	3603(4)	2683(2)	1978(3)	450(15)
C(14)	3883(4)	1883(3)	2602(3)	503(16)
C(15)	3646(3)	94(2)	2519(3)	419(14)
C(16)	4164(4)	-389(3)	1997(3)	518(17)
C(17)	4797(4)	-1102(3)	2419(4)	658(21)
C(18)	4883(4)	-1340(3)	3361(4)	705(20)
C(19)	4380(4)	-862(3)	3907(4)	687(23)
C(20)	3769(4)	-149(3)	3483(3)	558(18)
C(21)	1698(4)	1091(3)	2490(3)	510(17)
C(22)	873(4)	466(4)	2233(3)	743(22)
C(23)	-73(5)	494(5)	2605(4)	950(30)
C(24)	-130(6)	1136(6)	3221(5)	1040(36)
C(25)	692(7)	1754(4)	3473(5)	1054(37)
C(26)	1588(5)	1731(3)	3096(4)	809(26)
C(27)	926(4)	1842(2)	44(3)	449(15)
C(28)	1648(3)	225(3)	165(3)	460(16)
C(29)	2584(4)	1080(2)	-782(3)	538(17)
O(1)	1284(3)	-447(2)	78(2)	692(16)
O(2)	53(3)	2192(2)	-152(2)	716(14)
O(3)	2763(3)	957(2)	-1516(2)	852(18)

$$^a U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

The atomic scattering factors and the anomalous scattering coefficients are from ref. 15.

The final atomic coordinates are given in Table 6 together with the equivalent isotropic thermal parameters. Lists of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen coordinates are available from the authors.

The calculations were carried out on the CYBER 76 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna) with the financial support of the University of Parma, and the Gould-Sell 32/77 computer of the Centro di Studio per la Strutturistica Diffattometrica del CNR (Parma). In addition to the quoted programs, LQPARM [16], PARST [17], ORTEP [18] were used. Extended use of the files of the Cambridge Crystallographic Database was made through the Servizio Italiano per la Diffusione dei Dati Cristallografici (CNR, Parma).

Throughout the paper an averaged value, $\langle x \rangle$, is a weighted mean and the corresponding e.s.d., σ , is the largest of the values of the external and internal standard deviations [19]. When two values, x_1 and x_2 , are compared, the ratio $\Delta/\sigma = |x_1 - x_2|/(\sigma_1^2 + \sigma_2^2)^{1/2}$ is considered, where σ_1 and σ_2 are the e.s.d.'s of x_1 and x_2 , respectively. The e.s.d.'s are given, within parentheses, in units of the last decimal place of the numbers they refer to.

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