

Tertiary Phosphine Complexes of Iron Porphyrins: Synthesis, Molecular Stereochemistry, and Crystal Structure of Bis(dimethylphenylphosphine)-(meso-5,10,15,20-tetraphenylporphyrinato)iron(II)†

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The bonding properties of phosphines ($\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$, and PH_2Ph) in iron(II) porphyrin complexes have been studied. The six-co-ordinate complexes $[\text{Fe}^{\text{II}}(\text{tpp})(\text{PR}_3)_2]$ and $[\text{Fe}^{\text{II}}(\text{tpp})(\text{PMe}_3)(\text{mim})]$ ($\text{tpp} = \text{meso-5,10,15,20-tetraphenylporphyrinate}$, $\text{mim} = N\text{-methylimidazole}$) have been prepared. The ^1H and ^{31}P n.m.r. properties of these compounds are discussed in comparison with previous studies on the binding of phosphines to haemoglobins. Carbon monoxide binding to $[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ has also been studied and followed by i.r. spectroscopy. The crystal structure of $[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$ has been determined by three-dimensional, single-crystal X-ray diffraction methods. The complex crystallizes in the triclinic space group $P\bar{1}$ in a cell of dimensions $a = 10.305(5)$, $b = 11.149(7)$, $c = 12.839(5)$ Å, $\alpha = 65.67(4)^\circ$, $\beta = 63.34(3)^\circ$, $\gamma = 79.25(4)^\circ$, and $Z = 1$. Refinement based on 3 968 observed [$I > \sigma(I)$] diffractometer data converged at $R = 0.030$ and $R' = 0.032$. The Fe–P distance is 2.284(1) Å and the average Fe–N distance 2.000(1) Å. The porphyrin core is planar and all bond parameters in the core are consistent with a low-spin iron(II) complex.

Binding of small molecules has been frequently exploited in studies of haemoproteins and porphyrin derivatives. These studies have focused particularly on exploring O_2 , CO, NO, and RNC ($\text{R} = \text{alkyl or aryl}$) ligation¹ and X-ray crystal structures of iron porphyrin complexes are available for all these ligands.² In contrast, only a few phosphine derivatives of haems^{3–6} and haemoproteins have been described. The phosphine complexes have been considered as probes for the catalytic site of cytochrome P_{450} ⁷ and chloroperoxidase⁸ and provide a sensitive test for the presence of thiolate ligand. Recently we have obtained evidence that small phosphines like trimethylphosphine can bind to both valence states of haemoglobins (Fe^{II} and Fe^{III}) and consequently can be used as structural probes for haem environments.⁹ The size of the ligand-binding 'pocket' in haemoglobins can be probed more sensitively with phosphine ligands than with other small molecules such as O_2 , CO, and NO because the steric demands of the phosphine ligand PR_3 may be varied by changing R. We have recently shown that perturbations in the β haem pocket induced by a thiol reagent can be detected both by ^1H and ^{31}P n.m.r. spectra.⁹

As an essential complement to haemoprotein studies, the present paper describes the synthesis and properties of iron(II) porphyrin complexes with phosphine axial ligands. In view of the utility of model compounds‡ for understanding the binding of molecules to haemoproteins and because of the absence of structural studies on model phosphine complexes of iron(II), full structural details for $[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$ ($\text{tpp} = \text{meso-5,10,15,20-tetraphenylporphyrinate}$) have also been determined.§

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

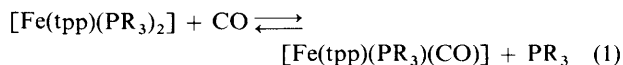
Non-S.I. unit employed: atm = 101 325 Pa.

‡ We have recently demonstrated the analogy between the bonding properties of *N*-acyl isocyanides and CO as ligands of iron(II) porphyrins, see ref. 10.

Results and Discussion

The complexes $[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ ($\text{R}_3 = \text{Me}_3, \text{Me}_2\text{Ph}, \text{MePh}_2$, or H_2Ph) and $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{mim})]$ ($\text{mim} = N\text{-methylimidazole}$) were obtained as crystalline solids and characterized by ^{31}P and ^1H n.m.r. (Table 1), visible spectroscopy, and elemental analysis. The syntheses of the symmetric bisphosphine species are variations of the method of Ohya *et al.*,³ but the reduction of Fe^{III} to Fe^{II} was carried out with zinc amalgam. Addition of PMe_3 to a solution of $[\text{Fe}(\text{tpp})(\text{mim})_2]$ containing excess of *N*-methylimidazole gave the mixed-coordinate complex $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{mim})]$. Under the conditions used the bis-ligand species $[\text{Fe}(\text{tpp})(\text{mim})_2]$ and $[\text{Fe}(\text{tpp})(\text{PMe}_3)_2]$ are present in negligible amounts. Because of the leaving group order $\text{mim} > \text{PMe}_3$ ^{4,12} the build up of the $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{mim})]$ intermediate is easy in the presence of excess mim. The reverse of this reaction was also investigated but reaction of $[\text{Fe}(\text{tpp})(\text{PMe}_3)_2]$ with mim is much slower and does not result in a clean reaction to give $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{mim})]$.

The new carbonyl complexes $[\text{Fe}(\text{tpp})(\text{PR}_3)(\text{CO})]$ were obtained *in situ* by stirring CO-saturated methylene chloride solution with the corresponding $[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ complexes, equation (1), and were characterized by their visible and i.r.



spectra (Table 2). Dilute solutions (10^{-5} mol dm^{-3}) were required to drive the equilibria to the right at 1 atm of CO and the formation of the desired mixed species depended on the nature of the leaving group. The leaving group order is $\text{PMePh}_2 > \text{PMe}_2\text{Ph} > \text{PMe}_3$. The i.r. spectra for

§ The synthesis and X-ray structure analysis of $[\text{Fe}(\text{tpp})(\text{P}^n\text{Bu}_3)_2]$, as well as its catalytic activity of the decarbonylation of aldehydes *via* the intermediate $[\text{Fe}(\text{tpp})(\text{P}^n\text{Bu}_3)(\text{CO})]$ has been reported in ref. 11.

Table 1. Proton and ^{31}P n.m.r. data for $[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ complexes^a

Complex	Porphyrin ($^1\text{H}^b$)			PR_3		Temp. ($^\circ\text{C}$)
	NC ₄ Ring	<i>o</i> -Ph	<i>m</i> - and <i>p</i> -Ph	$^1\text{H}^b$	$^{31}\text{P}^c$	
$[\text{Fe}(\text{tpp})(\text{PMe}_3)_2]$	8.21	7.91	7.53	-2.61	13.5	25
$[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$	8.19	7.82	7.55	-2.45 ^d	14.5	25
$[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{mim})]^e$	7.89	7.78	7.49	-2.87	25.5	-40
$[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{py})]^f$	8.40	7.41	7.26	-2.93	25.7	-40
$[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{Him})]$					23.7	-40 ^g
$[\text{NBu}_4][\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{im})]$					20.2	-40 ^g

^a Solutions 0.05 mol dm⁻³ in deaerated CD₂Cl₂ containing an excess of phosphine. ^b Values in p.p.m.; reference SiMe₄. ^c Values in p.p.m.; reference 85% H₃PO₄. ^d PPh: *ortho*, 4.26 (d); *meta*, 6.43 (t); *para*, 6.75 (m). ^e Data not obtained for mim. ^f Pyridine: 2,6-H, 2.49 (d); 3,5-H, 5.43 (t), 4-H, 6.14 (t). ^g Dimethylformamide solvent.

Table 2. I.r. spectroscopic data for carbonyl complexes of iron(II) porphyrins, $[\text{Fe}(\text{tpp})\text{L}(\text{CO})]^a$

Ligand L	$\nu_{\text{CO}}/\text{cm}^{-1}$	Ref.
PMe ₃	1 975	<i>b</i>
PMe ₂ Ph	1 988	<i>b</i>
PMePh ₂	1 990	<i>b</i>
Pyridine	1 980	19

^a In CH₂Cl₂; values ± 2 cm⁻¹. ^b This work.

Table 3. Bond distances (\AA)

Fe-P	2.284(1)	C(14)-H(14)	0.93(2)
Fe-N(1)	2.000(1)	C(15)-C(16)	1.388(3)
Fe-N(2)	2.000(1)	C(15)-H(15)	0.90(2)
P-C(23)	1.814(2)	C(16)-H(16)	0.89(2)
P-C(24)	1.818(2)	C(17)-C(18)	1.390(3)
P-C(25)	1.824(2)	C(17)-C(22)	1.387(3)
N(1)-C(1)	1.384(2)	C(18)-C(19)	1.378(3)
N(1)-C(4)	1.379(2)	C(18)-H(18)	0.95(2)
N(2)-C(6)	1.378(2)	C(19)-C(20)	1.360(4)
N(2)-C(9)	1.387(2)	C(19)-H(19)	0.85(2)
C(1)-C(2)	1.435(2)	C(20)-C(21)	1.365(3)
C(1)-C(10)	1.390(2)	C(20)-H(20)	0.93(2)
C(2)-C(3)	1.341(3)	C(21)-C(22)	1.388(3)
C(2)-H(2)	0.95(2)	C(21)-H(21)	0.24(2)
C(3)-C(4)	1.439(2)	C(22)-H(22)	0.90(2)
C(3)-H(3)	0.95(2)	C(23)-H(23A)	1.00(2)
C(4)-C(5)	1.399(2)	C(23)-H(23B)	0.89(2)
C(5)-C(6)	1.399(2)	C(23)-H(23C)	0.94(2)
C(5)-C(17)	1.495(2)	C(24)-H(24A)	0.88(2)
C(6)-C(7)	1.440(2)	C(24)-H(24B)	0.96(2)
C(7)-C(8)	1.339(3)	C(24)-H(24C)	0.94(2)
C(7)-H(7)	0.93(2)	C(25)-C(26)	1.380(3)
C(8)-C(9)	1.436(2)	C(25)-C(30)	1.368(3)
C(8)-H(8)	0.90(2)	C(26)-C(27)	1.365(4)
C(9)-C(10)	1.387(2)	C(26)-H(26)	0.91(2)
C(10)-C(11)	1.503(2)	C(27)-C(28)	1.344(5)
C(11)-C(12)	1.379(3)	C(27)-H(27)	0.99(2)
C(11)-C(16)	1.382(3)	C(28)-C(29)	1.355(5)
C(12)-C(13)	1.389(3)	C(28)-H(28)	0.87(2)
C(12)-H(12)	0.84(2)	C(29)-C(30)	1.389(4)
C(13)-C(14)	1.354(3)	C(29)-H(29)	0.84(2)
C(13)-H(13)	0.88(2)	C(30)-H(30)	0.90(2)
C(14)-C(15)	1.369(4)		

$[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ with CO were obtained with 4×10^{-3} mol dm⁻³ solutions since these measurements required higher concentration.

The reactions are very slow. For example, reaction of $[\text{Fe}(\text{tpp})(\text{PMePh}_2)_2]$ with CO results in a clean reaction to give $[\text{Fe}(\text{tpp})(\text{PMePh}_2)(\text{CO})]$ and needs 3 h while formation of significant amounts of $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{CO})]$ required 1 d (25 $^\circ\text{C}$). Assuming that π -bonding effects dominate, this agrees with the π -acceptor order $\text{PMePh}_2 > \text{PMe}_2\text{Ph} > \text{PMe}_3$. A similar order $[\text{P}(\text{OBu})_3 > \text{PBu}_3]$ is found in iron(II) dimethylglyoxime complexes¹² and in iron(II) protoporphyrin IX dimethyl ester complexes.⁴ Since a more detailed study of rate in a related porphyrin system is described by Stynes and co-workers^{4,12} this aspect will not be discussed at length here.

The solution i.r. spectra of the new complexes $[\text{Fe}(\text{tpp})(\text{PR}_3)(\text{CO})]$ exhibit an intense band between 1 970 and 2 000 cm⁻¹, the ν_{CO} values for $[\text{Fe}(\text{tpp})(\text{PMePh}_2)(\text{CO})]$ and $[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})(\text{CO})]$ being the highest. This is consistent with a greater π -acceptor ability of aromatic phosphines compared with those of trialkylphosphines¹³ and a concomitant decrease in π back bonding from iron to the CO bond because of *trans* π competition.

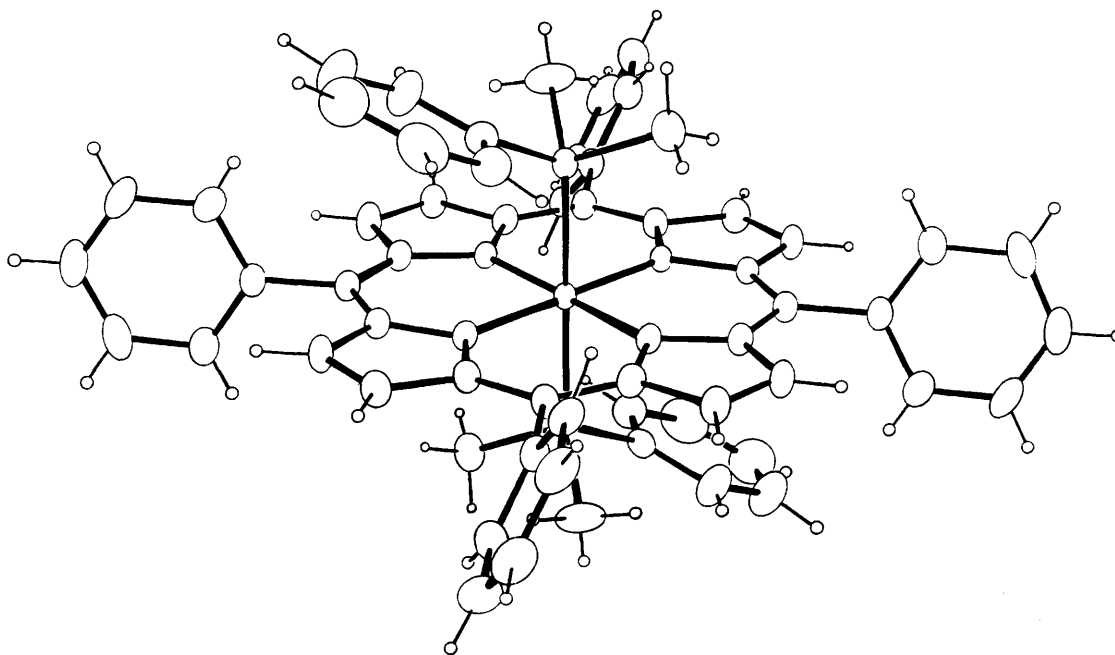
The ^1H n.m.r. spectra of $[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ ($\text{R} = \text{Me}_3$ or Me_2Ph) display two groups of signals corresponding to the porphyrin ring protons (7–9 p.p.m.) and to the phosphine $[\text{PMe}_3 - 2.61; \text{PMe}_2\text{Ph}, -2.45 (\text{Me})]$ (see Table 1). The chemical shifts of the former are very similar to those of $[\text{Fe}(\text{tpp})(\text{py})_2]$ ($\text{py} = \text{pyridine}$)¹⁴ and are expected for diamagnetic iron(II) porphyrin derivatives. Of more interest is the resonance at high field (δ ca. -2.5 p.p.m.) which has been assigned to the protons of alkylphosphines bound to iron. A similar upfield spectral feature is observed with the mixed species $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{mim})]$ ($\delta -2.87$ p.p.m.) and $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{py})]$ ($\delta -2.93$ p.p.m.) and is due to the shielding effect of porphyrin ring current. This property makes phosphines particularly attractive n.m.r. probes of haemoproteins since the ligand signal appears outside the 0–10 p.p.m. envelope.⁹

The ^{31}P n.m.r. spectra of complexes $[\text{Fe}(\text{tpp})(\text{PR}_3)_2]$ exhibit two sharp peaks in the presence of excess phosphine: a signal

due to free phosphine and a signal due to bound phosphine. This implies slow ligand exchange on the n.m.r. time-scale under the experimental conditions used. The ^{31}P resonances of the mixed phosphine species generated *in situ* have very similar but usually distinguishable chemical shifts. Of particular relevance to our studies on haemoproteins is the observation that the haem-bound $^{31}\text{PMe}_3$ resonance is sensitive to the nature of the *trans* ligand. For example, the proximal ligand in horseradish peroxidase is thought to be a histidyl residue that is strongly hydrogen bonded to another amino acid at the imidazole 1-H site¹⁵ giving it imidazole character. In order to test the possible influence of a *trans* imidazolate ligand on the chemical shift value of bound $^{31}\text{PMe}_3$, a model iron porphyrin compound was examined (see Experimental section). The mixed PMe_3 -imidazole (Him) complex of iron(II) 5,10,15,20-tetraphenylporphyrin exhibited a signal at 23.7 p.p.m. in dimethyl-

Table 4. Bond angles (°)

P-Fe-N(1)	91.45(4)	C(6)-C(5)-C(17)	118.6(1)	C(13)-C(14)-C(15)	119.2(2)	C(17)-C(22)-H(22)	119(1)
P-Fe-N(2)	90.90(4)	N(2)-C(6)-C(5)	125.6(1)	C(13)-C(14)-H(14)	122(1)	C(21)-C(22)-H(22)	120(1)
N(1)-Fe-N(2)	89.25(5)	N(2)-C(6)-C(7)	109.8(1)	C(15)-C(14)-H(14)	118(1)	H(23A)-C(23)-H(23B)	105(2)
Fe-P-C(23)	115.35(9)	C(5)-C(6)-C(7)	124.6(2)	C(14)-C(15)-C(16)	121.0(2)	H(23A)-C(23)-H(23C)	106(2)
Fe-P-C(24)	114.12(9)	C(6)-C(7)-C(8)	107.6(2)	C(14)-C(15)-H(15)	120(1)	H(23B)-C(23)-H(23C)	117(2)
Fe-P-C(25)	118.43(6)	C(6)-C(7)-H(7)	123(1)	C(16)-C(15)-H(15)	119(1)	H(24A)-C(24)-H(24B)	109(2)
C(23)-P-C(24)	101.2(2)	C(8)-C(7)-H(7)	129(1)	C(11)-C(16)-C(15)	120.3(2)	H(24A)-C(24)-H(24C)	105(2)
C(23)-P-C(25)	102.6(1)	C(7)-C(8)-C(9)	107.3(2)	C(11)-C(16)-H(16)	119(1)	H(24B)-C(24)-H(24C)	113(2)
C(24)-P-C(25)	102.8(1)	C(7)-C(8)-H(8)	127(1)	C(15)-C(16)-H(16)	120(1)	C(26)-C(25)-C(30)	117.2(2)
C(1)-N(1)-C(4)	105.1(1)	C(9)-C(8)-H(8)	126(1)	C(5)-C(17)-C(18)	121.4(2)	C(25)-C(26)-C(27)	121.9(3)
C(6)-N(2)-C(9)	105.4(1)	N(2)-C(9)-C(8)	109.9(2)	C(5)-C(17)-C(22)	120.9(2)	C(25)-C(26)-H(26)	117(1)
N(1)-C(1)-C(2)	110.4(1)	N(2)-C(9)-C(10)	125.9(1)	C(18)-C(17)-C(22)	117.7(2)	C(27)-C(26)-H(26)	121(1)
N(1)-C(1)-C(10)	125.3(2)	C(8)-C(9)-C(10)	124.3(2)	C(17)-C(18)-C(19)	120.3(2)	C(26)-C(27)-C(28)	120.3(3)
C(2)-C(1)-C(10)	124.3(2)	C(1)-C(10)-C(9)	124.8(2)	C(17)-C(18)-H(18)	110(1)	C(26)-C(27)-H(27)	116(1)
C(1)-C(2)-C(3)	106.9(2)	C(1)-C(10)-C(11)	117.8(2)	C(19)-C(18)-H(18)	122(1)	C(20)-C(27)-H(27)	123(1)
C(1)-C(2)-H(2)	124(1)	C(9)-C(10)-C(11)	117.4(1)	C(18)-C(19)-C(20)	121.5(2)	C(27)-C(28)-C(29)	119.4(3)
C(3)-C(2)-H(2)	129(1)	C(10)-C(11)-C(12)	121.2(2)	C(18)-C(19)-H(19)	119(2)	C(27)-C(28)-H(28)	116(1)
C(2)-C(3)-C(4)	107.6(2)	C(10)-C(11)-C(16)	120.9(2)	C(20)-C(19)-H(19)	119(2)	C(29)-C(28)-H(28)	124(1)
C(2)-C(3)-H(3)	129(1)	C(12)-C(11)-C(16)	117.9(2)	C(19)-C(20)-C(21)	119.3(2)	C(28)-C(29)-C(30)	120.8(3)
C(4)-C(3)-H(3)	124(1)	C(11)-C(12)-C(13)	121.1(2)	C(19)-C(20)-H(20)	121(1)	C(28)-C(29)-H(29)	123(2)
N(1)-C(4)-C(3)	110.0(1)	C(11)-C(12)-H(12)	121(2)	C(21)-C(20)-H(20)	120(1)	C(30)-C(29)-H(29)	116(2)
N(1)-C(4)-C(5)	125.8(1)	C(13)-C(12)-H(12)	117(2)	C(20)-C(21)-C(22)	120.3(2)	C(25)-C(30)-C(29)	120.3(3)
C(3)-C(4)-C(5)	124.1(2)	C(12)-C(13)-C(14)	120.5(2)	C(20)-C(21)-H(21)	124(2)	C(25)-C(30)-H(30)	118(1)
C(4)-C(5)-C(6)	123.2(2)	C(12)-C(13)-H(13)	119(1)	C(22)-C(21)-H(21)	116(2)	C(29)-C(30)-H(30)	122(1)
C(4)-C(5)-C(17)	118.2(1)	C(14)-C(13)-H(13)	121(1)	C(17)-C(22)-C(21)	120.9(2)		

**Figure 1.** A perspective view of the $[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$ molecule

formamide. Titration of the $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{Him})]$ complex at 23.7 p.p.m. with tetrabutylammonium hydroxide led to the imidazolate complex $[\text{NBu}_4][\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{im})]$, which showed a large upfield shift to 20.2 p.p.m. Thus a chemical shift difference of 3.5 p.p.m. is seen in the deprotonation of the imidazole complex $[\text{Fe}(\text{tpp})(\text{PMe}_3)(\text{Him})]$. This strong *trans* effect can be related to the ^{31}P n.m.r. sensitivity of the PMe_3 ligand to electronic variation around the iron atom.

Structure of $[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$.—The crystal structure

consists of monomeric molecules of bis(dimethylphenylphosphine)(*meso*-5,10,15,20-tetraphenylporphyrinato)iron(II) as illustrated in Figure 1. The atomic numbering scheme employed is shown in Figure 2, together with bond lengths in the porphyrinate core and the principal bond lengths of the axial ligand. Other bond lengths and angles for the molecules are given in Tables 3 and 4.

The requirement of C_i symmetry for the molecule leads to rigorous centring of the iron atom in the porphyrinate plane. The geometry of the tpp moiety is very similar to that found in other metalloporphyrins.² The averaged bond distances for the

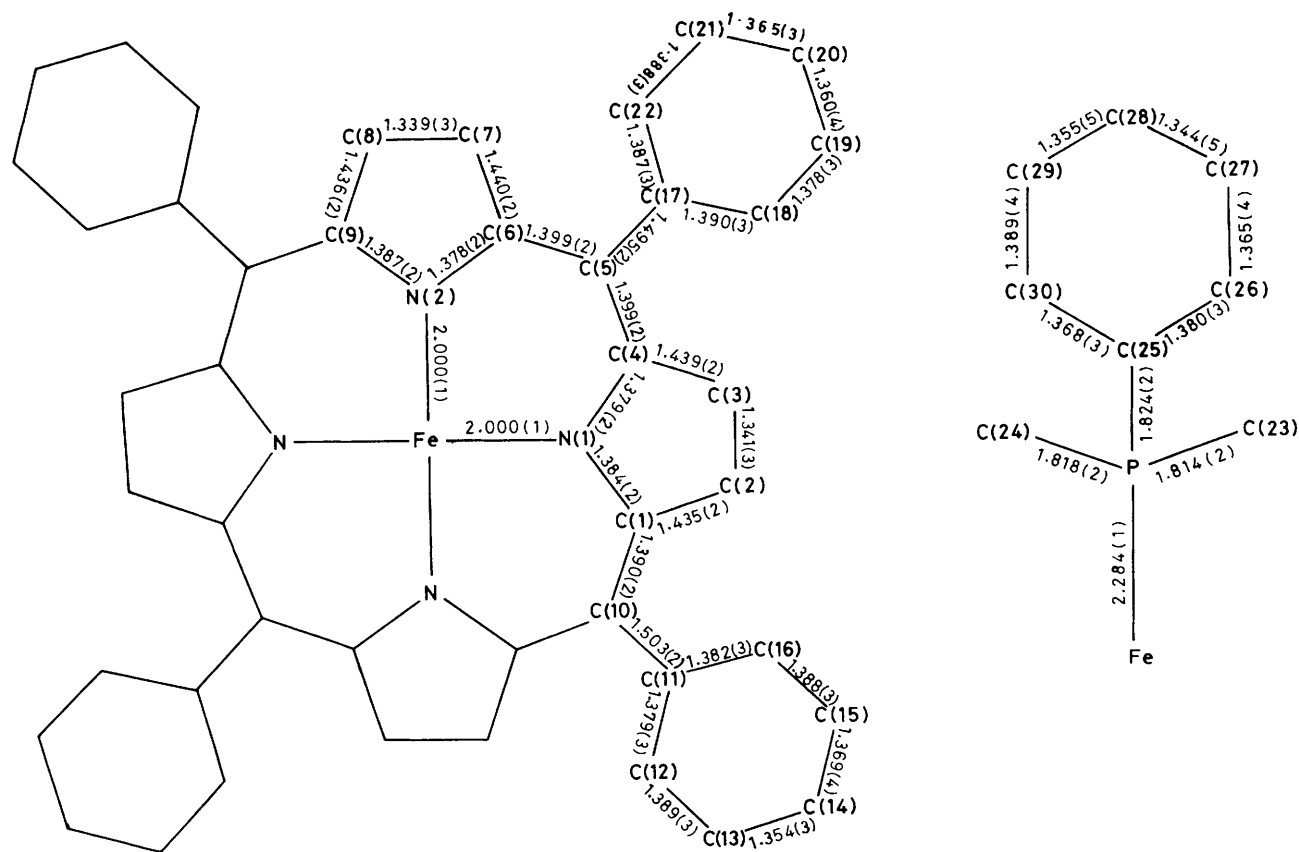


Figure 2. Atom labelling scheme for $[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$ and the bond distances (Å) of the co-ordination group

two crystallographically non-equivalent pyrrole rings lie within the range of those found for other low-spin iron(II) porphyrin structures.² The four equivalent Fe–N(pyrrole) distances average to 2.000(1) Å in agreement with those observed in a number of other low-spin iron porphyrin structures: 2.004(4) Å for $[\text{Fe}(\text{tpp})(\text{pip})_2]$ (pip = piperidine),¹⁶ 2.001(3) Å for $[\text{Fe}(\text{tpp})(\text{NO})]$,¹⁷ 2.005(4) Å for $[\text{Fe}(\text{tpp})(\text{Bu}^i\text{NC})_2]$,¹⁸ 2.02(3) Å for $[\text{Fe}(\text{tpp})(\text{CO})(\text{py})]$,¹⁹ and 1.98(3) Å for $[\text{Fe}(\text{tmpdpa})(\text{CO})(\text{thf})]$ (tmpdpa = 3,7,12,17-tetramethylporphyrin-2,18-dipropionate, thf = tetrahydrofuran).²⁰

The P–C distances in PMe_2Ph [*ca.* 1.81(1) Å] are in good agreement with those found in other metal phosphine complexes.^{21–25} The axial Fe–PMe₂Ph distance is 2.284(1) Å. This distance is slightly longer than the Fe–P distance in iron complexes containing PMe_2Ph as ligand: 2.270(1) Å for $[\text{Fe}\{\text{COCH}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{OMe})\}(\text{CO})_3(\text{PMe}_2\text{Ph})]$,²¹ 2.228(1) Å for $[\text{Fe}(\text{CO})_2(\text{PMe}_2\text{Ph})(\text{bda})]$ (bda = benzylideneacetone),²² 2.264(2) and 2.260(2) Å for $[\text{Fe}(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\text{CS}_2)\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$,²³ 2.242 Å for $[\text{Fe}(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\text{H})(\text{SMe})]\text{PF}_6$.²⁴ As expected, the metal–phosphorus bond length is much shorter than those observed in $[\text{Ru}(\text{tpp})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ [Ru–P 2.398(3) Å]²⁵ and in $[\text{V}(\text{oep})(\text{PMe}_2\text{Ph})_2]$ [V–P 2.523(1) Å; oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate].²⁶ From these structural results we can conclude that the axial co-ordination of two strong field ligands leads to low-spin six-co-ordination.

The dihedral angles between the porphyrinate plane and the plane of the two phenyl rings (porphyrin) are 70[C(11)] and 63°[C(17)]; they are well removed from 90° but these values are not unusual.² The phenyl ring of the axial ligand is oriented such that it minimizes the steric interaction with two adjacent porphyrinate phenyl rings.

Conclusions

$[\text{Fe}(\text{tpp})(\text{PMe}_2\text{Ph})_2]$ is the first structurally characterized model compound for protein phosphine complexes. A similar stereochemistry is expected for six-co-ordinate low-spin complexes where one of the PMe_2Ph ligands is replaced by a nitrogenous base such as *N*-methylimidazole and by analogy, similar structures may be expected for myoglobin and haemoglobin complexes. In addition the spectroscopic studies demonstrate that the bonding between phosphine and iron is sensitive to the *trans* ligand and suggest that the distinct n.m.r. signals observed for $^{31}\text{PMe}_3$ bound to the α and β chains of haemoglobin⁹ could result from modulation of the bonding of the proximal histidine *trans* to PMe_3 .

Experimental

Synthesis and Spectroscopic Measurements.—As a precaution against the formation of the μ -oxo dimer $[\{\text{Fe}(\text{tpp})\}_2\text{O}]$ ²⁷ all reactions were carried out in dried solvents in Schlenk tubes under Ar or N₂ atmosphere. Solvents were distilled from appropriate drying agents and stored under nitrogen. Infrared spectra were recorded on a Unicam SP 1100 i.r. spectrophotometer. The ^1H and proton-decoupled ^{31}P spectra were recorded in pulse Fourier-transform mode with a Bruker AM 300 WB spectrometer operating at 300 MHz for ^1H and at 121.49 MHz for ^{31}P . Ultraviolet–visible spectra were recorded with a Jobin-Yvon–Hitachi spectrophotometer; absorption coefficients ($10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) are given in parentheses following λ_{max} (nm).

Elemental analyses were performed by the Service Central d'Analyses (CNRS) at Vernaison (France).

Table 5. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Fe	0.0000	0.0000	0.0000	C(14)	0.221 1(3)	-0.362 7(2)	0.553 5(2)
P	-0.178 89(5)	-0.148 83(5)	0.008 16(4)	C(15)	0.097 0(3)	0.601 3(3)	0.559 7(2)
N(1)	0.070 2(2)	-0.005 7(2)	-0.170 6(1)	C(16)	0.053 1(3)	0.666 3(2)	0.462 5(2)
N(2)	0.138 3(2)	-0.145 3(2)	0.037 4(1)	C(17)	0.366 1(2)	-0.259 6(2)	-0.233 3(2)
C(1)	0.016 5(2)	0.066 2(2)	-0.268 1(2)	C(18)	0.356 7(2)	-0.395 3(2)	-0.193 3(2)
C(2)	0.085 6(2)	0.026 3(2)	-0.365 8(2)	C(19)	0.463 6(3)	-0.463 0(2)	-0.260 2(2)
C(3)	0.181 9(2)	-0.067 8(2)	-0.342 0(2)	C(20)	0.578 7(3)	-0.400 0(3)	-0.367 7(2)
C(4)	0.173 2(2)	-0.088 4(2)	-0.228 7(2)	C(21)	0.589 4(3)	-0.266 6(3)	-0.409 7(2)
C(5)	0.253 1(2)	-0.183 7(2)	-0.161 4(2)	C(22)	0.484 5(2)	-0.196 3(2)	-0.342 7(2)
C(6)	0.233 6(2)	-0.210 0(2)	-0.038 9(2)	C(23)	-0.362 3(3)	-0.093 4(3)	0.156 0(3)
C(7)	0.315 4(2)	-0.305 9(2)	0.024 1(2)	C(24)	-0.169 4(3)	-0.298 1(3)	0.209 9(2)
C(8)	0.271 1(2)	-0.299 5(2)	0.137 8(2)	C(25)	-0.194 3(2)	-0.212 1(2)	-0.022 1(2)
C(9)	0.161 8(2)	-0.198 7(2)	0.146 0(2)	C(26)	-0.294 6(3)	-0.164 4(3)	-0.073 5(2)
C(10)	0.090 8(2)	-0.162 3(2)	0.249 4(2)	C(27)	-0.301 5(3)	-0.209 7(4)	-0.154 7(3)
C(11)	0.134 6(2)	0.768 9(2)	0.357 1(2)	C(28)	-0.208 3(4)	-0.302 7(3)	-0.188 2(2)
C(12)	0.250 8(2)	0.004 2(3)	0.352 8(2)	C(29)	-0.107 7(4)	-0.351 4(3)	-0.140 2(3)
C(13)	0.301 6(3)	0.737 9(3)	0.450 6(2)	C(30)	-0.099 4(3)	-0.306 1(3)	-0.057 6(2)

Reagents.—[Fe(tpp)Cl] was prepared according to a literature procedure;²⁷ PMe₃, PMe₂Ph, PMePh₂, and PH₂Ph were used as commercially available (Strem Chemicals, Inc.).

Synthesis.—[Fe(tpp)(PMe₃)₂]. A solution of [Fe(tpp)Cl] (0.3 g, 0.42 mmol) in toluene (50 cm³) was reduced under argon by Zn–Hg amalgam.²⁸ The solution was then filtered through a coarse frit and a large excess of PMe₃ (ca. 10 mol equiv.) was added by syringe to the *in situ* Fe^{II}(tpp) species. Hexane (30 cm³) was added gradually and the solution set aside overnight for crystallization. Fine crystals of [Fe(tpp)(PMe₃)₂] were collected by filtration and washed with hexane. Yield 0.25 g (75%) (Found: C, 73.15; H, 5.50; N, 6.10; P, 7.30. Calc. for C₅₀H₄₈FeN₄P₂: C, 73.10; H, 5.60; N, 6.80; P, 7.5%; λ_{max} (toluene) 450 (129), 560 (12.9), and 600 (15.8).

[Fe(tpp)(PR₃)₂] (R₃ = Me₂Ph, MePh₂, or H₂Ph) were prepared as described above. [Fe(tpp)(PMe₂Ph)₂]. Yield 84% (Found: C, 75.90; H, 5.30; N, 5.35; P, 6.55. Calc. for C₆₀H₅₀FeN₄P₂: C, 76.20; H, 5.30; N, 5.90; P, 6.50%; λ_{max} (toluene) 452 (126), 557 (14), and 600 (15.8). [Fe(tpp)(PMePh₂)₂]. Yield 79% (Found: C, 78.15; H, 5.10; N, 5.15; P, 5.35. Calc. for C₇₀H₅₄FeN₄P₂: C, 78.60; H, 5.00; N, 5.20; P, 5.85%; λ_{max} (toluene) 452 (170), 551 (20), and 593 (15.5).

[Fe(tpp)(PMe₃)(mim)]. To a solution of [Fe(tpp)(mim)₂]² (0.3 g, 0.37 mmol) and mim (3 mol equiv.) in CH₂Cl₂ (50 cm³) was added gradually PMe₃ (1.5 mol equiv.) in CH₂Cl₂ (5 cm³). The mixture was stirred for 10 min. After concentration to 5 cm³, methanol (10 cm³) was then added and the solution left overnight at room temperature. The resulting purple crystals were collected by filtration and washed with methanol. Yield 0.27 g (87%) (Found: C, 75.60; H, 4.70; N, 6.35; P, 6.90. Calc. for C₅₁H₄₃FeN₄P: C, 75.60; H, 4.70; N, 6.35; P, 6.90%; λ_{max} (toluene) 431 (130), 538 (18.4), and 572 (12.6).

[Fe(tpp)(PMe₃)(py)] [λ_{max} (toluene) 433, 535, and 573] was prepared as described above but was contaminated with [Fe(tpp)(PMe₃)₂] (ca. 10%). Dimethylformamide solvent was used for imidazolate salt preparation. Sufficient imidazole and [Fe(tpp)Cl] to make respectively 15 and 3 mmol dm⁻³ solutions were placed in a 10-mm n.m.r. tube with dimethylformamide (2.0 cm³). After a nitrogen purge of the tube, sodium dithionite (2.0 mol equiv.) in water (30 μ l) was injected through a septum cap. The PMe₃ was introduced by syringe and the ³¹P n.m.r. spectrum was recorded. Tetrabutylammonium hydroxide (1.0 mol dm⁻³, 2 mol equiv.) in methanol (60 μ l) was then added to effect deprotonation of the imidazole ligand.

[Fe(tpp)(CO)(PR₃)] (PR₃ = PMe₃, PMe₂Ph, or PMePh₂).

Samples of solid [Fe(tpp)(PR₃)₂] (ca. 0.1 g) were dissolved in CO-saturated dichloromethane (30 cm³). The solution was stirred at 25 °C under CO and the exchange reaction was followed by spectral changes as a function of time. In these cases, the mixed species [Fe(tpp)(PR₃)(CO)] has a Soret band at λ = 438 nm.

Crystallography.—Crystal data. C₆₀H₅₀FeN₄P₂, triclinic, space group $P\bar{1}$, a = 10.305(5), b = 11.149(7), c = 12.839(5) Å, α = 65.67(4), β = 63.34(3), γ = 79.25(4)°, U = 1 201.4 (6) Å³, Z = 1, D_c = 1.31 Mg m⁻³, $F(000)$ = 494, μ = 4.2 cm⁻¹, T = 297 K.

X-Ray data collection. A single dark purple crystal (0.15 × 0.20 × 0.25 mm) of the title compound was mounted under a thin layer of paste and studied on an Enraf–Nonius CAD4 automatic diffractometer [λ (Mo- K_α) = 0.710 69 Å, graphite monochromator]. A preliminary study established a one-molecule triclinic cell. The unit-cell parameters were obtained from a least-squares refinement of 25 high-angle reflections. Intensities were gathered in an $\omega/2\theta$ scan mode ($\omega/2\theta$ = 1) with a variable scan rate set to measure weak reflections more slowly to minimize counting errors (t_{max} = 60 s). Three standard reflections were measured each 1 800 s without appreciable decay. All data in the range $2 < 2\theta < 50^\circ$ (h 0,12; k 13,13; l 15,15) were measured, giving 4 380 reflections, of which 3 968 were unique (R_{int} = 0.017) with $I > \sigma(I)$.

Resolution and refinement of the structure. After Lorentz and polarization corrections²⁹ (no absorption correction), the iron atom was set at the unit-cell origin (multiplicity = 0.5). The remaining non-hydrogen atoms of the molecule were located after several scale factor refinements and Fourier difference syntheses. After refinements in isotropic mode (R = 0.086) then anisotropic mode (R = 0.054), the hydrogen atoms were located in a Fourier difference synthesis between electronic densities 0.58 and 0.26 e Å⁻³ and their co-ordinates were refined in further calculations. The best full-matrix least-squares refinement of the molecule [x , y , z , β_{ij} for Fe, P, C, N atoms and x , y , z (B = 4 Å²) for H atoms] gave $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.030$, $R' = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 = 0.032$, $w = 4|F_o|^2 [\sigma^2(|F|^2) + (0.04|F|^2)^2]^{-1}$, S = 1.36, Δe = 0.24 e Å⁻³.

All the calculations were performed on a Digital PDP 11/60 computer with the SDP package;³⁰ Figure 1 was drawn using the ORTEP program.³¹ Atomic co-ordinates are listed in Table 5. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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