

Priority communication

# The molecular structure of 2,2',5,5'-tetraphenyl-1,1'-diphosphaferrocene

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Received 26 March 1996; revised 22 April 1996

## Abstract

The molecular structure of 2,2',5,5'-tetraphenyl-1,1'-diphosphaferrocene **1** has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic space group  $P2_1/n$ . The phosphole rings are completely eclipsed.

**Keywords:** X-ray diffraction; Group 15; Molecular structure

The ever increasing availability of five membered rings incorporating Group 15 elements has led to the synthesis and the structural characterization of several ferrocene analogues, such as monophospha- [1,2], diphospha- [3–7], diarsa- [8–11], distiba- [11–14] and dibisferrocenes [14,15] (Table 1).

Although the first diphosphaferrocene was reported almost two decades ago, only one  $\eta^5, \eta^5$ -1,1'-diphosphaferrocene, 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **2**, has been structurally characterized [4]. This study revealed that the phosphole rings were roughly parallel to one another, but that the phosphorus atoms were staggered by  $145^\circ$  ( $C_1$  conformation) (see Fig. 1).

A study based on Fenske–Hall calculations concluded that the  $C_1$  conformation was the most stable for unsubstituted 1,1'-diphosphaferrocene, by about  $6 \text{ kcal mol}^{-1}$  with respect to both the  $C_{2v}$  and  $C_{2h}$  conformations, which were found to have the same energies (Fig. 1) [16]. Two later studies, based on extended Hückel calculations, also agreed that the  $C_1$  conformation was the lowest in energy ( $9.6 \text{ kcal mol}^{-1}$  [11] and  $8.8 \text{ kcal mol}^{-1}$  [17]). For the As, Sb and Bi analogues, however, the  $C_{2v}$  conformation was found to be the most stable and indeed five eclipsed As [9], Sb [11,13,14] and Bi [15] analogues have been structurally characterized. The eclipsed conformation has not, however, been previously observed for phosphorus.

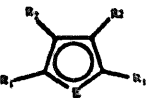
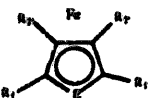



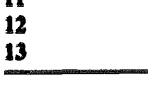
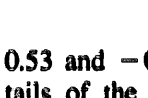

Herein we report the determination of the molecular structure of 2,2',5,5'-tetraphenyl-1,1'-diphosphaferrocene **1** which shows the presence of perfectly eclipsed discrete sandwich units, as shown in Fig. 2.

The compound was prepared by the previously reported method [4] purified by sublimation, precipitation from cold benzene and finally recrystallization from toluene at  $-30^\circ\text{C}$ .  $^1\text{H}$  and  $^{31}\text{P}$  NMR data agreed with the published data [4].  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR (100.61 MHz,  $\text{CDCl}_3$ )  $\delta$  84.6 (ring  $\beta$  carbons,  $J_{\text{P-C}} = 6 \text{ Hz}$ ), 102.6 (ring  $\alpha$  carbons,  $J_{\text{P-C}} = 60 \text{ Hz}$ ), 126.9 (phenyl  $p$ -carbons), 127.2 (phenyl  $o$ -carbons,  $J_{\text{P-C}} = 11 \text{ Hz}$ ), 128.6 (phenyl  $m$ -carbons) and 138.9 ppm (*ipso*-phenyl carbons,  $J_{\text{P-C}} = 16 \text{ Hz}$ ). Elemental analysis for  $\text{C}_{32}\text{H}_{24}\text{FeP}_2$ : C, 73.02 (73.02); H, 4.57 (4.60).

Summary of crystal structure data for **1**:  $M = 526.3$ , monoclinic,  $P2_1/n$  (non-standard no.14),  $a = 14.114(7)$ ,  $b = 6.159(3)$ ,  $c = 26.977(6) \text{ \AA}$ ,  $\beta = 95.65(3)^\circ$ ,  $V = 2334(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.50 \text{ g cm}^{-3}$ ,  $T = 173(2) \text{ K}$ , crystal dimensions =  $0.20 \times 0.20 \times 0.10 \text{ mm}^3$ ,  $\mu = 0.80 \text{ mm}^{-1}$ ,  $\lambda = 0.71073 \text{ \AA}$ ; 2982 reflections (2862 independent) were collected ( $2\theta_{\text{max}} = 44^\circ$ ) of which 1643 independent reflections with  $I > 2\sigma(I)$  were used in refinement. The structure was solved by direct methods and refined by full-matrix least squares (on  $F^2$ ). All non-hydrogen atoms were refined anisotropically, except C(1) and C(5) which became non-positive and were reset isotropic. H atoms were included in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Final residuals  $R1 = 0.073$  and  $wR2 = 0.141$  for 2861 data and 306 parameters. Largest difference peak and hole:

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Table 1  
Di-phospha-, arsa-, stiba- and bismaferrocenes

									Ref.
	E	E	R <sub>1</sub>	R <sub>2</sub>	R <sub>1'</sub>	R <sub>2'</sub>			
1	P	P	Ph	H	Ph	H	[3,4]		
2	P	P	H	Me	H	Me	[3,4]		
3	P	P	H	H	H	H	[4]		
4	P	CH	H	Me	H	H	[1]		
5	P	CH	Ph	Ph	Me	Me	[2]		
6	As	As	H	H	H	H	[10]		
7	As	As	Me	H	Me	H	[8,9]		
8	As	As	Me	Me	Me	Me	[11]		
9	Sb	Sb	Me	H	Me	H	[13]		
10	Sb	Sb	SiMe <sub>3</sub>	Me	SiMe <sub>3</sub>	Me	[14]		
11	Sb	Sb	Me	Me	Me	Me	[11]		
12	Bi	Bi	SiMe <sub>3</sub>	Me	SiMe <sub>3</sub>	Me	[14]		
13	Bi	Bi	Me	H	Me	H	[15]		

0.53 and  $-0.48 e \text{ \AA}^{-3}$ .  $\text{GOF}(F^2) = 1.081$ . Further details of the crystal structure investigation can be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

The phospholyl rings are planar within experimental error. It has been observed that the deviation from planarity increases with the size of the heteroatom [13]. The average Fe–P bond length, 2.307(3) Å, is significantly longer than in other mono- and diphosphaferrocenes (Table 2).

The Fe–C distances range from 2.051(9) to 2.125(9) Å, while the ring centroids have an average distance from Fe of 1.676(3) Å, which is only slightly longer than that of 1.653(3) Å found in 1,1',4,4'-tetraphenylferrocene 14. [18] The C–C distances in the rings range from 1.40(1) to 1.49(1) Å, and the average C–C–C angle is 113.3(9)°, in agreement with the values found for other  $\eta^5$ -five-membered rings.

The phospholyl rings are almost parallel. The ring centroids, Cp<sub>1</sub> and Cp<sub>2</sub>, exhibit a Cp<sub>1</sub>–Fe–Cp<sub>2</sub> angle of 171.9(10)°, which is a little less than normally observed in non-eclipsed phosphoferrocenes. The average inter-ring distances between the phosphorus atoms, (P<sub>1</sub>–P<sub>2</sub>, 3.49 Å), the  $\alpha$  carbon atoms, (C<sub>1</sub>–C<sub>17</sub>, C<sub>4</sub>–C<sub>20</sub>, 3.35 Å) and the  $\beta$  carbon atoms (C<sub>2</sub>–C<sub>18</sub>, C<sub>3</sub>–C<sub>19</sub>, 3.21 Å) indicate a slight tilting of the rings away from the eclipsed P atoms. As previously postulated from H/D exchange studies [19], the phenyl ring substituents are not coplanar with respect to the cyclopentadienyl rings (23.9(3)° and 20.9(3)° respectively) but are essentially parallel to one another and, furthermore, parallel to the corresponding 2'- and 5'-phenyl rings (4.3(5)° and 4.4(5)° respectively).

The short distance between the phosphorus atoms indicates the existence of a secondary interaction (i.e.

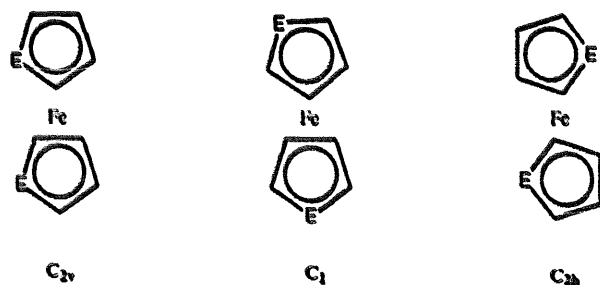


Fig. 1. Conformations of a 1,1'-diheterocene.

Table 2  
Fe–P and P–P bond lengths for some mono- and diphosphaferrocenes

Compound	P–P (Å)	Fe–P (Å)	Ref.
1	3.490	2.307	this work
2	4.457	2.276	[4]
4	—	2.276	[1]
5	—	2.274	[2]
[Ru(PPh <sub>3</sub> )X(DPF)(μ-Cl)] <sub>2</sub> <sup>a</sup>	3.376	2.256	[19]
[Ag(DPF) <sub>2</sub> ] <sup>+</sup> <sup>a</sup>	3.717 (av.)	2.344 (av.)	[20]
15	3.154	2.359	[21]

<sup>a</sup> DPF = 3,3',4,4'-tetramethyldiphosphaferrocene 2.

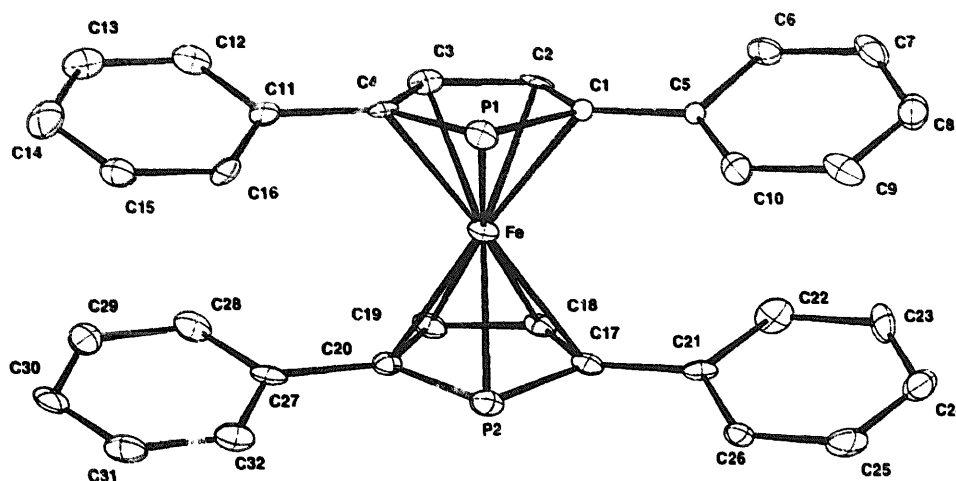


Fig. 2. The molecular structure of 2,2',5,5'-tetraphenyl-1,1'-diphosphaferrocene and atom numbering scheme. Selected bond lengths (Å) and angles (deg): Fe–P(1) 2.303(3), Fe–P(2) 2.311(3), Fe–C(1) 2.110(9), Fe–C(2) 2.052(9), Fe–C(3) 2.052(9), Fe–C(4) 2.110(9), Fe–C(17) 2.125(9), Fe–C(18) 2.053(9), Fe–C(19) 2.051(9), Fe–C(20) 2.103(9), Fe–Cp1 1.667(2), Fe–Cp2 1.685(2), P(1)–C(4) 1.776(10), P(1)–C(1) 1.783(10), P(2)–C(17) 1.787(10), P(2)–C(20) 1.797(9), C(1)–C(2) 1.414(13), C(1)–C(5) 1.452(12), C(2)–C(3) 1.416(12), C(3)–C(4) 1.405(13), C(4)–C(11) 1.491(12), C(17)–C(18) 1.425(13), C(17)–C(21) 1.457(12), C(18)–C(19) 1.401(12), C(19)–C(20) 1.412(13), C(20)–C(27) 1.500(12); P(1)–Fe–P(2) 99.48(12), C(4)–P(1)–C(1) 90.2(4), C(17)–P(2)–C(20) 89.9(4), C(2)–C(1)–C(5) 123.8(9), C(2)–C(1)–P(1) 111.5(7), C(5)–C(1)–P(1) 124.6(8), C(1)–C(2)–C(3) 113.0(7), C(4)–C(3)–C(2) 113.1(9), C(3)–C(4)–C(11) 124.6(9), C(3)–C(4)–P(1) 112.1(7), C(11)–C(4)–P(1) 123.2(7), C(18)–C(17)–C(21) 124.5(9), C(18)–C(17)–P(2) 111.1(7), C(21)–C(17)–P(2) 124.4(8), C(19)–C(18)–C(17) 114.1(9), C(18)–C(19)–C(20) 112.9(9), C(19)–C(20)–C(27) 125.7(9), C(19)–C(20)–P(2) 112.0(7), C(27)–C(20)–P(2) 122.3(8).

the distance between two atoms is longer than the sum of the covalent radii, but shorter than the sum of the van der Waals radii) which should destabilize this conformation. [11] The eclipsed structure of this molecule is stabilized by the intramolecular interaction of the phenyl substituents. This stabilization energy has been calculated to be 6.5 kcal mol<sup>-1</sup> [20], thereby providing an upper limit for the conformational energy. A similar eclipsed configuration is also displayed by the recently reported carbon analogue 14 [18].

Eclipsed P atoms have been previously reported for two other diphosphaferrocenes [21,22] (in which the eclipsed conformation is due to the ligation of both lone pairs of the phosphorus atoms to a secondary metal centre) and for one polyphosphaferrocene, 2,2',5,5'-tetra-*t*-butyl-1,1',3,3',4,4'-hexaphosphaferrocene 15 [23] (the two phosphorus atoms which eclipse one another do so in order to minimize the steric repulsion between the *t*-butyl substituents resulting in a remarkably short P–P distance of 3.154 Å).

Finally, differential scanning calorimetry studies on 1 show that this molecule undergoes an irreversible transition at 164 K (2.7 kcal mol<sup>-1</sup>). The nature of this transformation is being investigated by solid state NMR [24].

#### Acknowledgements

We thank the School of Chemistry and Molecular Sciences at University of Sussex for a bursary (I.M.),

Dr. M.P. Waugh and Mr. P. Garcia for technical support and Professor D. Braga, Dr. F. Grepioni and Mr. E. Tedesco for useful discussions.

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