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Chiral biphosphole iron complexes. Synthesis and characterization of the biphosphaferrocene $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4HMe_2P)]_2$. X-ray characterization of the dinuclear complex $[Fe(\eta^5\text{-}C_5H_5)(C_4HMe_2PhP)(CO)]_2$[†]

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Summary — 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole **1** reacts with $[FeCp(CO)_2]_2$ to yield as a major product the dinuclear complex $[Fe(\eta^5\text{-}C_5H_5)(C_4HMe_2PhP)(CO)]_2$ **4** which was fully characterized. Its X-ray structure displays a C_2-symmetry. The 2,2′-biphosphaferrocene **2** was synthesised from the 2,2′-biphosphole **1** and complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ $[PF_6]$ via a 2,2′-biphospholyl intermediate. Compound **2** was obtained as a mixture of two diastereoisomers in a 60:40 ratio.

2,2′-biphosphole / diiron complex / 2,2′-biphosphaferrocene / chiral complex / C_2-symmetry

Résumé — Complexes du fer avec un biphosphole chiral. Synthèse et caractérisation du biphosphaferrocène $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4HMe_2P)]_2$. Structure par diffraction des rayons X du complexe $[Fe(\eta^5\text{-}C_5H_5)(C_4HMe_2PhP)(CO)]_2$. La réaction du 1,1′-diphényl-3,3′,4,4′-tétraméthyl-2,2′-biphosphole **1** avec $[FeCp(CO)_2]_2$ conduit majoritairement au complexe dinucléaire $[Fe(\eta^5\text{-}C_5H_5)(C_4HMe_2PhP)(CO)]_2$ **4** qui a été entièrement caractérisé. Sa structure, établie par diffraction des rayons X, met en évidence un axe de symétrie C_2. La synthèse du 2,2′-biphosphaferrocène **2** a été effectuée à partir du 2,2′-biphosphole **1** et du complexe $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ $[PF_6]$ via l'intermédiaire 2,2′-biphospholyl. Le composé **2** est obtenu sous forme d'un mélange de deux diastéréoisomères **2a** et **2b** dans le rapport 60:40.

2,2′-biphosphole / complexe dinucléaire du fer / 2,2′-biphosphaferrocène / complexe chiral / symétrie C_2

Introduction

Chiral bidentate ligands, in particular those belonging to the C_2-symmetry class, have been proved to be powerful auxiliaries in catalytic asymmetry processes. In the framework of a project concerning the design and synthesis of new C_2-symmetry chiral bidentate ligands, we were interested in exploring the possibility of using 2,2′-biphosphaferrocene as a chiral ligand in transition metal complexes.

The chemistry of η^5-phospholyl-iron complexes, phosphaferrocenes and 1,1′-diphosphaferrocenes has been extensively studied [1]. However, the coordination chemistry of 2,2′-biphospholyl first described by Mathey is less developed [2] and only one example of 2,2′-biphosphaferrocene [3] has been reported so far.

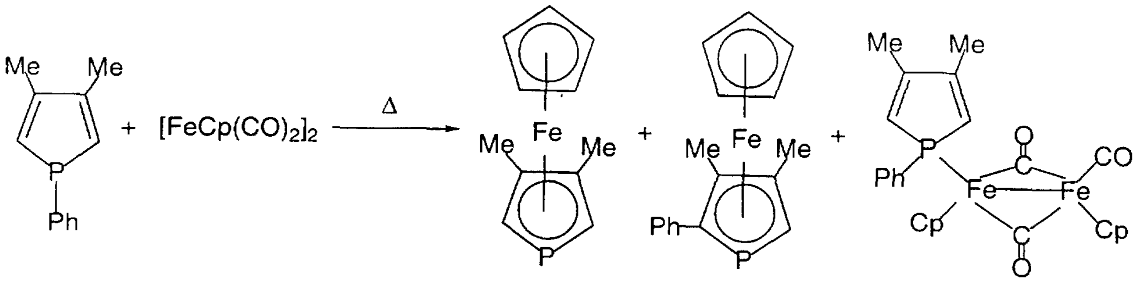
Recent studies in our laboratory [4] have focused on the chemistry of 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole **1**. We have characterized the different diastereoisomers of this compound [4] in which the axial chirality, resulting from a dihedral angle between the two phosphole rings, combines with the central chirality of phosphorus atoms. We have studied the coordination chemistry of this C_2-symmetric chiral bidentate ligand to transition metals [5]. We report here the synthesis and spectroscopic characterization of 2,2′-biphosphaferrocene $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4HMe_2P)]_2$ **2** and the synthesis, spectroscopic and X-ray characterizations of the dinuclear complex $[Fe(\eta^5\text{-}C_5H_5)(C_4HMe_2PhP)(CO)]_2$ **4**.

Results and discussion

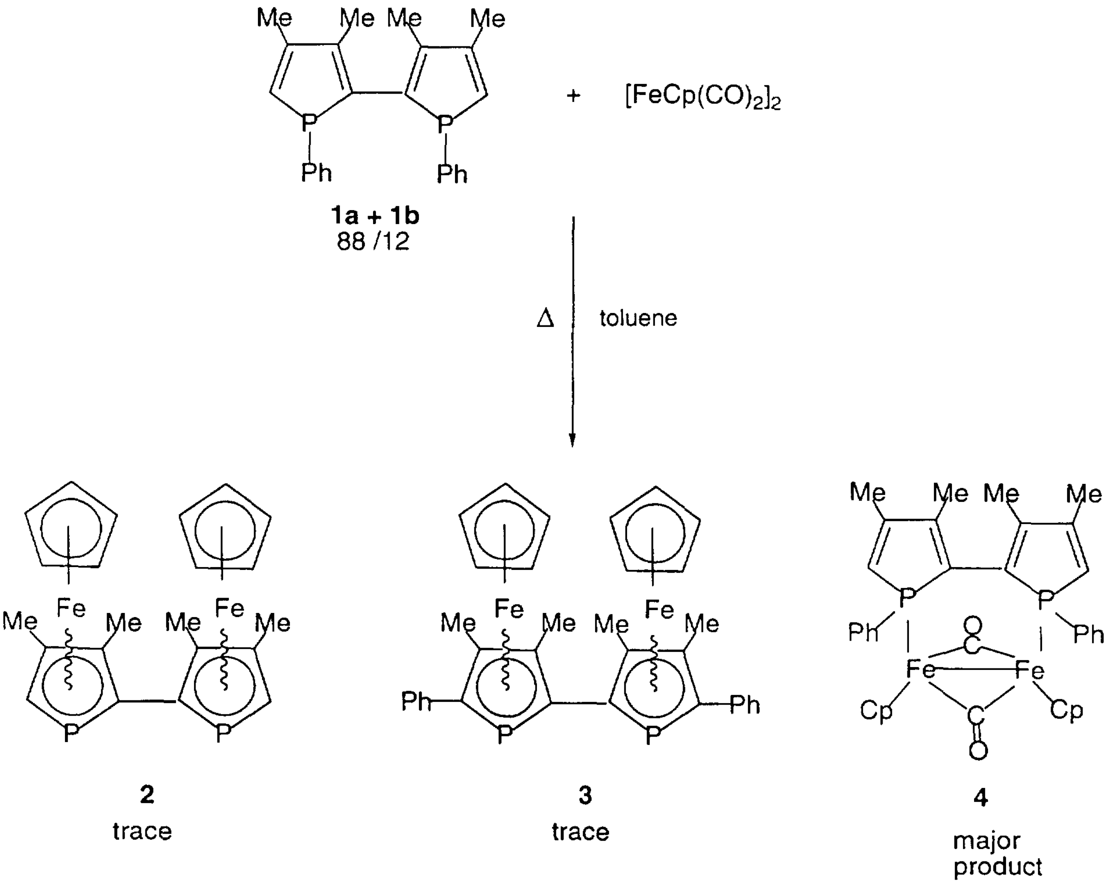
The synthetic approach of phosphaferrocene, published by Mathey et al [6], involved thermal cleavage of the phosphorus–phenyl bond of 1-phenylphosphole by $[FeCp(CO)_2]_2$. In the case of 1-phenyl-3,4-dimethylphosphole, 3,4-dimethylphosphaferrocene is formed in 20% yield along with phenyl-subsituted phosphaferrocene and a σ-complex in which phosphole replaces one terminal CO (eq 1). Using this procedure, we attempted to synthesize 2,2′-biphosphaferrocene **2** starting from 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole **1**.

[†] Dedicated to Professor H Kagan in recognition of his pioneering work on asymmetric synthesis

* Correspondence and reprints



Equation 1



Equation 2

Compound **1**, prepared according to a previously described method [7], was obtained in solution at room temperature as a mixture of two inseparable stereoisomers **1a** and **1b** in a ratio of 88:12 [4]. This mixture reacted with [FeCp(CO)$_2$]$_2$ in refluxing toluene to afford a small amount of 2,2′-biphosphaferrocenes, **2** and **3**, the major product of the reaction being the σ-complex **4** (eq 2). The phenyl-substituted biphosphaferrocene **3**, already obtained by another procedure [3], results here from a classical P–Ph bond cleavage and a Ph [1, 5] shift around the phosphole ring as observed in the monophosphole series (eq 1). The formation of the dinuclear complex **4** requires the displacement of the two terminal carbonyl ligands of [FeCp(CO)$_2$]$_2$ by the diphosphine ligand **1**, without rupture of the metal–metal bond. Complex **4** was stable and did not lose CO upon heating at 150 °C in xylene to give the expected biphosphaferrocene **2**. **4**, isolated by alumina column chromatography of the reaction mixture, was characterized by elemental analysis, infrared, ^{1}H, ^{31}P, ^{13}C NMR spectroscopy and mass spectroscopy. Its structure was confirmed by X-ray diffraction analysis.

Complex **4** crystallizes in a monoclinic space group, $C2/c$, with two molecules of dichloromethane in the

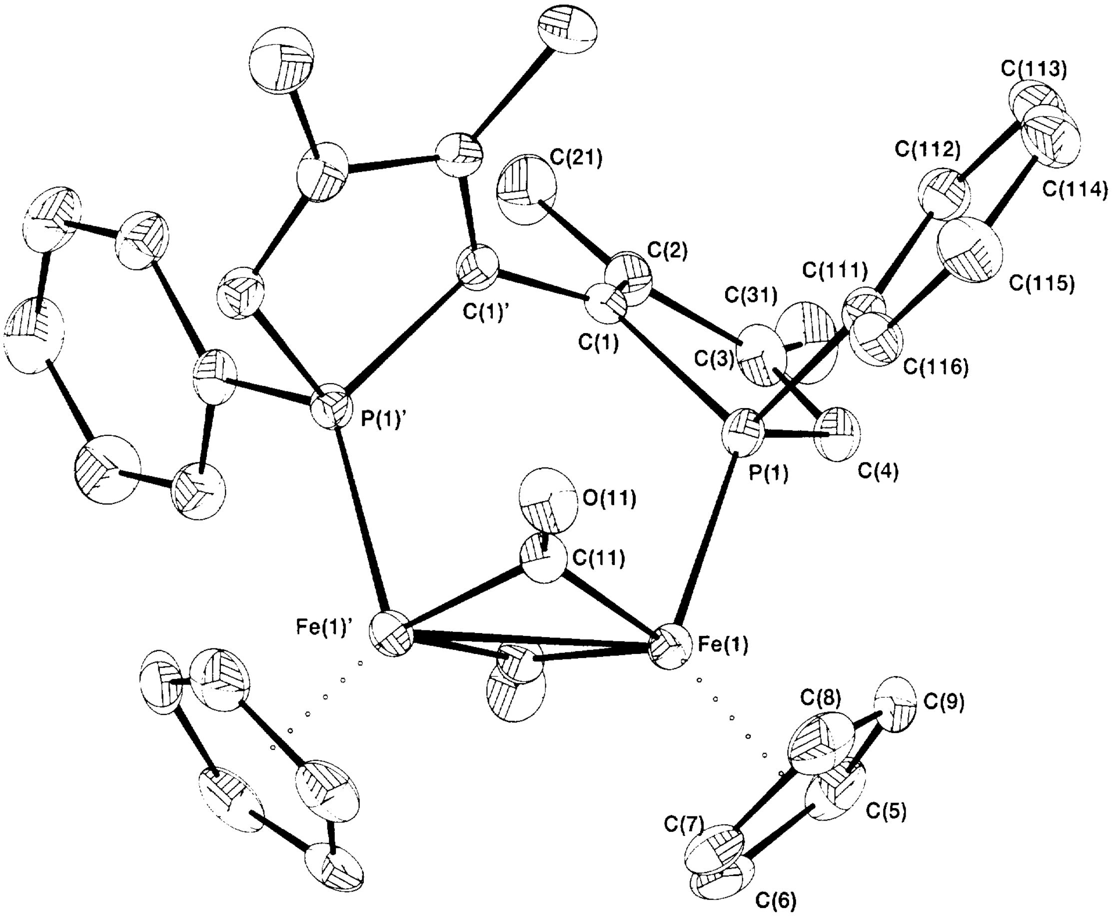


Fig 1. Molecular view of complex **4**. Thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted.

unit cell. The molecular structure is shown in figure 1 with an atom labelling scheme. Selected bond distances and angles are given in table I. The whole molecule is arranged around a two-fold axis passing through the middle of the C(1)-C(1)′ and Fe(1)-Fe(1)′ bonds. Complex **4** is a new example of a complex with chiral 2,2′-biphosphole in which there is a combination of central chirality of the phosphorus atom and axial chirality of the biphosphole (fig 2). As observed for mononuclear complexes [5], the solid state structure of **4** corresponds to a racemic mixture of the S_{RR} and R_{SS} forms of the ligand. The phosphole rings are planar within the range of experimental error, but they are twisted towards each other along the C(1)-C(1′) bond making a dihedral angle of 86.0°. This much larger angle, compared to the one observed in other mononuclear complexes [5] or in the free ligand [4], may be related to the fact that in this case the biphosphole ligand should accommodate coordination on two metal centers. Surprisingly, the Fe-P bond length of 2.161(1) Å is significantly shorter than the values of 2.172-2.183(2) Å observed in the related complex, $[Fe_2(dppe)(Cp)_2(CO)_2]$ [8], although the Fe-Fe bond of 2.520(1) Å is identical, within experimental error, to that of 2.528(2) Å for the dppe complex. This difference in metal-phosphorus bond length was not observed in the mononuclear series of Ni, Pd and Pt complexes of dppe and 2,2′-biphosphole, respectively. It might indicate that the biphosphole ligand is slightly less sterically demanding than the diphenylphosphino ethane ligand. Finally, the geometry of the phosphole ring is not modified by the coordination on the iron atoms as observed in the other mononuclear complexes [5]. Bond lengths and angles are, within experimental error, identical to those found in the free ligand [4]. To the best of our knowledge, complex **4** is the first crystal structure of a dinuclear complex reported containing the 2,2′-biphosphole ligand. This result allows to clarify the stereochemistry of the complexes of 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole and to demonstrate the flexibility of this ligand, which can also accommodate a dinuclear system.

In order to improve the yield of **2**, we next considered the method described by Wells et al [9] for the preparation of monophosphaferrocenes. This procedure involves the nucleophilic attack of phospholyl anions at the iron center of the η^6-arene-η^5-cyclopentadienyliron(II) cation. The 2,2′-biphospholyl anion [2] was accessible from 2,2′-biphosphole **1** via the reductive cleavage of the exocyclic phosphorus-phenyl bonds with

Table I. Important interatomic distances (Å) and bond angles (°) with Esd's in parentheses.

Fe(1)-Fe(1)*	2.520(1)	O(11)-C(11)	1.186(5)
Fe(1)-P(1)	2.161(1)	C(1)-C(1)	1.466(8)
Fe(1)-C(5)	2.113(5)	C(1)-C(2)	1.357(6)
Fe(1)-C(6)	2.110(5)	C(2)-C(3)	1.474(7)
Fe(1)-C(7)	2.139(5)	C(2)-C(21)	1.510(7)
Fe(1)-C(8)	2.130(5)	C(3)-C(4)	1.329(7)
Fe(1)-C(9)	2.092(5)	C(3)-C(31)	1.502(7)
Fe(1)-C(11)	1.899(4)	C(5)-C(6)	1.375(8)
Fe(1)-C(11)*	1.921(4)	C(5)-C(9)	1.382(9)
P(1)-C(1)	1.812(4)	C(6)-C(7)	1.411(8)
P(1)-C(4)	1.801(4)	C(7)-C(8)	1.378(8)
P(1)-C(111)	1.847(4)	C(8)-C(9)	1.406(9)
Fe(1)-Fe(1)*-P(1)	106.24(3)	C(1)-C(2)-C(21)	125.0(5)
P(1)-Fe(1)-C(11)	93.9(1)	C(3)-C(2)-C(21)	121.7(4)
P(1)-Fe(1)-C(11)*	90.4(1)	C(2)-C(3)-C(4)	114.6(4)
C(11)-Fe(1)-C(11)*	94.7(2)	C(2)-C(3)-C(31)	121.6(5)
Fe(1)-P(1)-C(1)	118.9(1)	C(4)-C(3)-C(31)	123.8(5)
Fe(1)-P(1)-C(4)	117.3(2)	P(1)-C(4)-C(3)	111.1(3)
C(1)-P(1)-C(4)	90.4(2)	C(6)-C(5)-C(9)	107.6(5)
Fe(1)-P(1)-C(111)	118.8(2)	C(5)-C(6)-C(7)	108.6(5)
C(1)-P(1)-C(111)	103.2(2)	C(6)-C(7)-C(8)	107.6(5)
C(4)-P(1)-C(111)	103.7(2)	C(7)-C(8)-C(9)	107.4(5)
P(1)-C(1)-C(1)	118.4(3)	C(5)-C(9)-C(8)	108.8(5)
P(1)-C(1)-C(2)	110.4(3)	Fe(1)-C(11)-Fe(1)*	82.6(2)
C(1)'-C(1)-C(2)	130.0(4)	Fe(1)-C(11)-O(11)	140.4(4)
C(1)-C(2)-C(3)	113.3(4)	Fe(1)-C(11)'-O(11)*	136.5(4)

* Refers to atoms related by the two-fold axis.

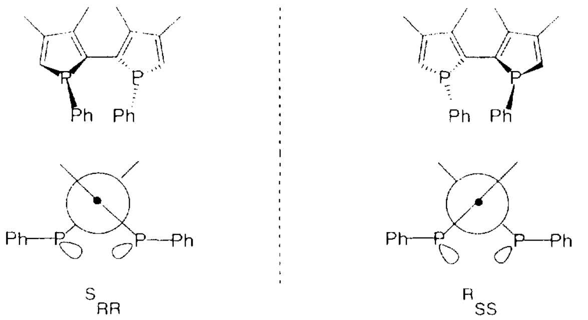


Fig 2. Configuration of the 2,2'-biphosphole ligand in complex **4**. The projection is along the axis of the C–C bond linking the phosphole rings. Superscript refers to axial chirality, subscript refers to central chirality.

metallic lithium. Reaction of this dianion with a large excess of η^6-benzene-η^5-cyclopentadienyliron(II) hexafluorophosphate in refluxing THF yields biphosphaferrocene **2** (eq 3). The ^{31}P-NMR spectrum of this reaction mixture reveals the complete disparition of the signal at $\delta = +62$ ppm corresponding to the dianion and the apparition of two high-field signals at $\delta = -69.5$ and -71.9 in a 60:40 ratio. This is indicative of the formation of the biphosphaferrocene **2**, as a mixture of two isomers **2a** and **2b**. These two isomers were isolated in 55% yield as an air- and moisture-sensitive orange solid. The minor isomer could be obtained by flash chromatography on deoxygenated silica gel.

If we consider the conformation of biphosphaferrocene in which the phospholyl rings are coplanar, stereochemical analysis reveals the existence of diastereoisomers **2a**, **2a'** and **2b**, **2b'** (fig 3). According to our study on the 2,2'-biphosphole [4], a free rotation around the the C–C bond bridge may be considered. So the conformers **2a** and **2a'** as well as **2b** and **2b'** might interconvert rapidly on the NMR time scale, thus explaining the sharp ^{31}P resonances. **2a** and **2a'** are achiral and possess a plane of symmetry and a center of symmetry, respectively; **2b** and **2b'** are chiral and possess a two-fold axis. In solution, due to the free rotation around the C–C bond bridge, the phospholyl rings are probably not coplanar, as is the case in the biphosphole **1** [4], and it is difficult on the basis of a single stereochemical analysis to assign a structure to the mi-

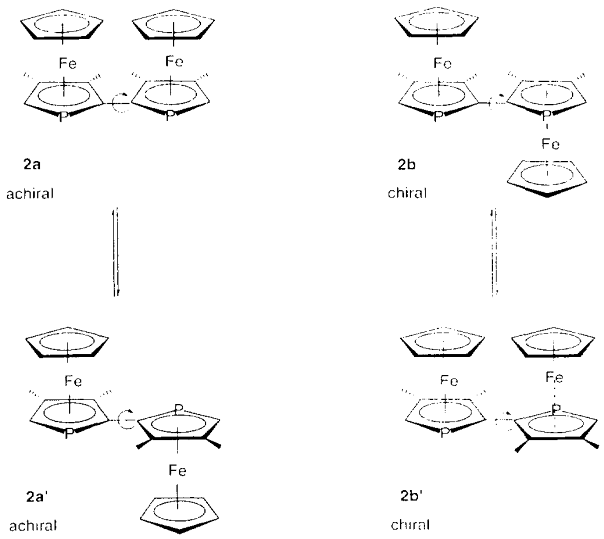
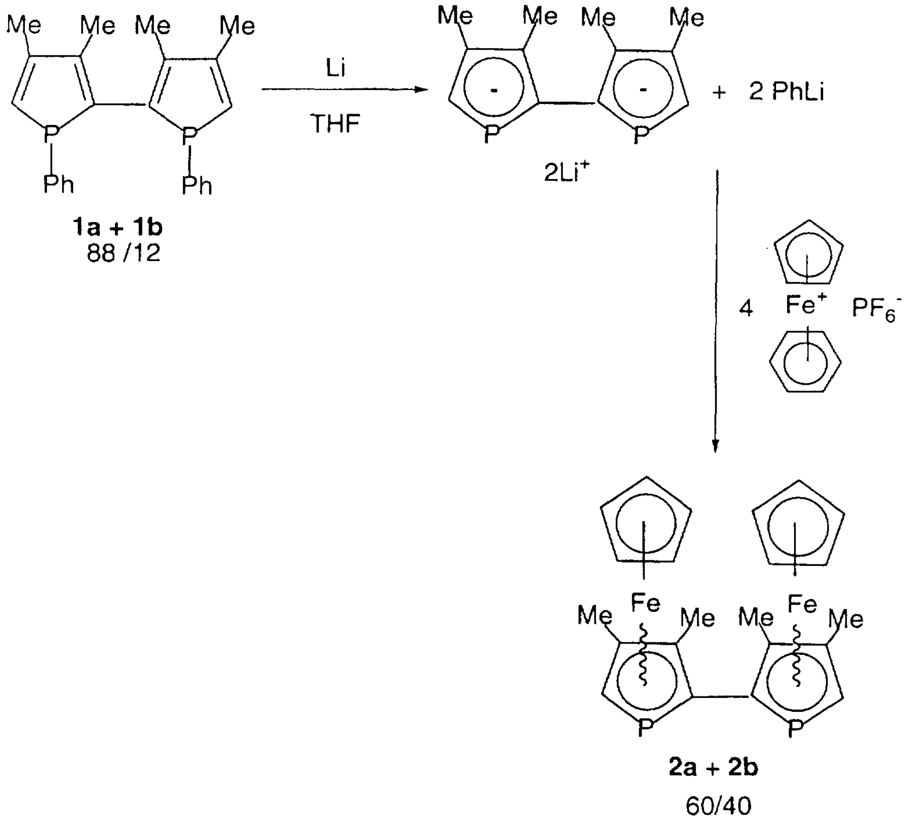


Fig 3. The four stereoisomers of biphosphaferrocene **2**.



Equation 3

nor isomer isolated by chromatography. **2b** is the chiral stereoisomer having phosphorus lone pairs in the right direction to coordinate a transition-metal atom. Work concerning the complexing properties and resolution of these compounds is in progress.

Experimental section

General procedures

All reactions were carried out under an inert atmosphere of dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. Preparative column chromatography was performed on Merck alumina, freshly deactivated with 8% H_2O (wt/wt). Flash chromatography was carried out under argon on Merck silica gel (230–400 mesh). $[FeCp(CO)_2]_2$ was purchased from Aldrich Chemical Co. The starting materials biphosphole **1** [7] and η^6-benzene-η^5-cyclopentadienyliron(II) hexafluorophosphate [10] were prepared as described in the literature. ^1H, ^{13}C $\{^1H, ^{31}P\}$ and ^{31}P $\{^1H\}$ NMR spectra were recorded on a Bruker WMX 400 instrument operating at 400, 162, 100 MHz respectively. Chemical shifts are reported in ppm relative to Me_4Si (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). Elemental analyses were performed by the 'Service d'Analyse du Laboratoire de Chimie de Coordination' at Toulouse and the 'Service Central d'Analyse du CNRS', Lyon, France. Mass spectra were obtained on a Nermag R10-10 instrument. Infrared spectra (KBr pellet) were recorded on a Perkin–Elmer 1725X FT-IR spectrometer.

- *Synthesis of 3,3′,4,4′-tetramethyl-2,2′-biphosphaferrocene* **2**

A 100 mL Schlenk was charged with 1.06 g of lithium dispersion in mineral oil. After extraction of oil with small portions of pentane (3 × 10 mL), a solution of biphosphole **1** (0.54 g, 1.44 mmol) in 40 mL of THF was added and the reaction mixture was stirred at room temperature. After 35 min, ^{31}P NMR reveals the quantitative formation of the dianion at δ $^{31}P = +62$. The red solution was added to 1.98 g (5.1 mmol) of η^6-benzene-η^5-cyclopentadienyliron(II) hexafluorophosphate and the mixture refluxed for 2 h and 30 min. After elimination of the precipitate by filtration through celite, the solvent was removed. The residue was dissolved in CH_2Cl_2 and filtered on silica gel. Compound **2** was isolated by evaporation of the solvent (0.37 g, 55%) as a mixture of two diastereoisomers (60:40), according to the ^{31}P and ^1H NMR data.

Main isomer:

^1H NMR (CD_2Cl_2): 2.23 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 3.80 (m, 2H, CH), 4.36 (s, 10H, Cp).

^{31}P NMR (THF-D8): −69.5.

Minor isomer:

^1H NMR (CD_2Cl_2): 1.89 (s, 6H, CH_3), 2.17 (s, 6H, CH_3), 3.70 (m, 2H, CH), 4.15 (s, 10H, Cp).

^{31}P NMR (THF-D8): −71.9.

MS (DCI, CH_4), m/z 463 (MH^+, 100).

Flash chromatography on silica gel (hexane/dichloromethane: 90:10) afforded the minor isomer.

• *Synthesis of di-μ-carbonyl bis (η^5-cyclopentadienyl) [1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole]diiron* **4**

$[FeCp(CO)_2]_2$ (0.657 g, 1.85 mmol) was added to a solution of biphosphole **1** (0.347 g, 0.93 mmol) in toluene (50 mL). The reaction mixture was heated under reflux for 10 h, during which the solution slowly changed colour from dark red to green. The solvent was then evaporated. The residue was chromatographed on alumina using first hexane/dichloromethane (80:20), which allowed elution of a first fraction containing unreacted biphosphole, biphosphaferrocenes **2** and **3** and impurities. Elution with pure dichloromethane led to a second green fraction. Dark green crystals of **4** were obtained by slow evaporation of a dichloromethane solution (0.187 g, 30%).

IR: ν C=O = 1 691 cm^{-1}.

^{1}H NMR (CD_2Cl_2): 0.73 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 6.34 (d, $^2J_{HP}$ = 27.2 Hz, 2H, CH), 7.25 (m, 6H, Ph), 7.75 (m, 4H, Ph).

^{13}C {^{1}H, ^{31}P} NMR (CD_2Cl_2): 12.02 (C_{21}, C'_{21}), 16.94 (C_{31}, C'_{31}), 85.30 (Cp), 125.87 (C_4, C'_4), 127.23 (C_{113}, C'_{113}), 128.92 (C_{114}, C'_{114}), 131.40 (C_{112}, C'_{112}), 133.69 (C_{111}, C'_{111}), 136.75 (C_1, C'_1), 140.72 (C_2, C'_2), 150.46 (C_3, C'_3), 295.00 (broad, CO).

^{31}P NMR (CD_2Cl_2): 99.06.

MS (FAB, MNBA matrix), m/z 672 (M^+, 100).

Anal calc for $C_{36}H_{34}Fe_2O_2P_2$ + 2 CH_2Cl_2: C, 54.20; H, 4.55. Found: C, 54.20; H, 4.53.

• *X-ray structure determination*

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite oriented monochromator utilizing MoKα radiation (λ = 0.71073). The final unit cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections that had been accurately centered on the diffractometer. Only statistical fluctuations were observed in the intensities monitored during data collections.

The structure was solved by direct methods (SIR92) [11] and refined by least-squares procedures on F_{obs}. H atoms could be located by difference Fourier syntheses, but they were introduced in the calculation in idealized positions (d(CH) = 0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Least-squares refinements were carried out by minimizing the function $\sum w(F_o - F_c)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - \Delta F/6\sigma F_o^2]^2$ where $w' = 1/\sum_1{}^n A_r T_r(x)$ with 3 coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was $F_c/F_c(\max)$ [12]. The model reached convergence with $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum_w (|F_o| - |F_c|)^2 / \sum_w (|F_o|)^2]^{1/2}$, having values listed in table II. Criteria for a satisfactory complete analysis were the ratios of root-mean-square shift to standard deviation less than 0.1 and no significant features in the final difference maps. Details of data collection and refinement are given in table II. Fractional atomic coordinates appear in table III.

The calculations were carried out with the CRYSTALS package programs [13] running on a PC. A molecular view was drawn using CAMERON [14].

Table II. Crystal data.

Crystal parameters	*Compound* **4**
Formula	$C_{36}H_{34}O_2P_2Fe_2,(CH_2Cl_2)_2$
fw (g)	421.1
Shape (color)	Box (dark green)
Size (mm)	0.8 × 0.5 × 0.5
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	15.816(3)
b (Å)	14.121(3)
c (Å)	18.330(2)
β (°)	112.80(1)
V (Å^3)	3773(1)
Z	4
F(000)	–
ρ, calc (g, cm^{-3})	1.482
μ, MoKα (cm^{-1})	11.71
Data Collection	
Diffractometer	Enraf Nonius CAD4F
Monochromator	Graphite
Radiation	MoKα (λ = 0.71073)
Scan type	$\omega/2\theta$
Scan range θ (deg)	0.9 + 0.345 tg θ
2θ range (deg)	$3 < 2\theta < 50$
No. of reflections collected	3581 (± h, k, l)
No. of unique reflections	3326
Merging R factor	0.028
Reflections used, ($I > 3\sigma(I)$)	2429
Refinement	
R	0.062
R_w	0.058
Weighting scheme	Chebyshev
Coefficient Ar	2.70, 3.96
Goodness of fit	1.06
l.s. parameters	219

Table III. Fractional atomic coordinates and equivalent isotropic thermal parameter U(eq). Esd's in parentheses refers to the last significant digit. U(eq) is defined as the cube root of the product of the principal axes.

Atom	x/a	y/b	z/c	$U(eq)$
Fe(1)	0.44572(4)	0.08156(4)	0.17836(3)	0.0330
P(1)	0.41456(7)	0.22839(8)	0.14559(6)	0.0337
Cl(1)	0.3849(2)	−0.3031(2)	0.2121(2)	0.1238
Cl(2)	0.2590(2)	−0.3784(2)	0.0642(2)	0.1244
O(11)	0.6386(2)	0.1117(3)	0.2085(2)	0.0502
C(1)	0.4519(3)	0.3180(3)	0.2224(2)	0.0350
C(2)	0.3784(3)	0.3636(3)	0.2267(3)	0.0427
C(3)	0.2902(3)	0.3324(4)	0.1661(3)	0.0468
C(4)	0.2973(3)	0.2657(3)	0.1175(3)	0.0415
C(5)	0.3193(4)	0.0191(4)	0.1066(4)	0.0597
C(6)	0.3720(4)	−0.0468(4)	0.1603(3)	0.0524
C(7)	0.4524(4)	−0.0631(3)	0.1463(3)	0.0511
C(8)	0.4491(5)	−0.0054(5)	0.0846(4)	0.0583
C(9)	0.3668(5)	0.0463(4)	0.0607(3)	0.0573
C(10)	0.2770(5)	−0.2934(7)	0.1371(5)	0.0951
C(11)	0.5743(3)	0.1022(3)	0.2260(2)	0.0361
C(21)	0.3828(4)	0.4354(4)	0.2892(4)	0.0628
C(31)	0.2007(4)	0.3739(5)	0.1610(4)	0.0654
C(111)	0.4478(3)	0.2787(3)	0.0675(2)	0.0393
C(112)	0.4102(3)	0.3637(4)	0.0310(3)	0.0480
C(113)	0.4341(4)	0.4003(4)	−0.0281(3)	0.0560
C(114)	0.4952(4)	0.3520(5)	−0.0514(4)	0.0634
C(115)	0.5343(4)	0.2688(5)	−0.0152(3)	0.0617
C(116)	0.5104(3)	0.2316(4)	0.0446(3)	0.0484

Acknowledgments

We thank Professor F Mathey for advice and fruitful discussions, and the CNRS for financial support.

Supplementary material available

Anisotropic thermal parameters for non-hydrogen atoms and atomic coordinates for H atoms have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication No SUP 90453 and are available upon request from the Document Supply Centre.

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