

New 1,1'- or 1,2- or 1,3-bis(diphenylphosphino)ferrocenes

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Abstract

The syntheses of ferrocenyl phosphines with bulky substituents are reported using the reaction between FeCl_2 and the suitably substituted cyclopentadienyl salts, $\text{LiC}_5\text{H}_3\text{-1,3-(PPh}_2)_2$, $\text{LiC}_5\text{H}_3\text{-1-PPh}_2\text{-3-'Bu}$, $\text{LiC}_5\text{H}_2\text{-1,2-(PPh}_2)_2\text{-4-'Bu}$. This strategy leads to bi-, tri- and tetraphosphines, which cannot be obtained by the other access paths used to prepare substituted ferrocenes. $[\text{C}_5\text{H}_3\text{-1,3-(PPh}_2)_2](\text{C}_5\text{H}_5)\text{Fe}$, $[\text{C}_5\text{H}_3\text{-1-PPh}_2\text{-3-'Bu}]_2\text{Fe}$ racemic and *meso* and $[\text{C}_5\text{H}_2\text{-1,2-(PPh}_2)_2\text{-4-'Bu}](\text{C}_5\text{H}_5)\text{Fe}$ have been characterized by single-crystal X-ray diffraction studies. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Phosphine; Ferrocene

1. Introduction

Molecular architecture is an essential factor in the behavior of bridging or chelating diphosphines. Ferrocene exhibits architecture leading to various diphosphines species. Most of these derivatives contain two identical diphenylphosphino fragments directly attached at the 1,1' positions on the ferrocene [1]. The approach to create this 1,1' disubstitution was based on the successful metalation of ferrocene itself or pre-formed ferrocene with a specific side chain. Currently, the search for synthetic methods is based on the use of an adequate ferrocenic precursor, especially bromo- [2] or silyl- [3] substituted products. For ferrocenes, with a disposition of phosphino groups other than 1,1', the synthesis of 1,2-diphosphinoferrocene has been realized only recently [4]. Previous attempts by direct metalation of diphenylphosphinoferrocene were unsuccessful [5].

We report here the access paths to new ferrocenylphosphines using a complementary methodology, i.e. the reaction of the appropriate cyclopentadienyl salts with FeCl_2 . We have already performed a chemical pathway leading to ferrocenylphosphines with 1,2-diphosphino-substituted rings from the corresponding 1,2-bis(diphenylphosphino)trimethylcyclopentadienyl

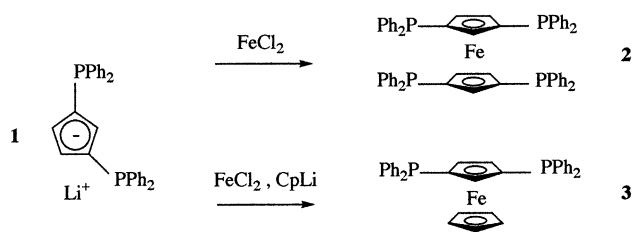
salt [6]. Analogous 1,2-phosphorylated cyclopentadiene, 1,2-(methylphenylphosphinoborane)cyclopentadiene, has been described, but the preparation of the corresponding ferrocene failed [7]. This paper is the result of investigations on the diphosphino substitution of cyclopentadienyllithium itself and experiments on an alternative cyclopentadienyl ligand obtained from the tertibutylcyclopentadienyllithium. The synthesis and crystal structures of $[\text{C}_5\text{H}_3\text{-1,3-(PPh}_2)_2](\text{C}_5\text{H}_5)\text{Fe}$, $[\text{C}_5\text{H}_3\text{-1-PPh}_2\text{-3-'Bu}]_2\text{Fe}$ racemic and *meso* and $[\text{C}_5\text{H}_2\text{-1,2-(PPh}_2)_2\text{-4-'Bu}](\text{C}_5\text{H}_5)\text{Fe}$ are hereafter reported.

2. Results and discussion

2.1. 1,3-Diphenylphosphinocyclopentadienyllithium and corresponding ferrocenes

We have reinvestigated the synthesis of ferrocenes with two or more diphenylphosphino substituents. The lithiation of ferrocenylphosphines is easy, but with the increasing number of substituents, a difficulty arises with the isolation of pure compounds from mixtures of isomers [8]. We then postulated that the problems of isomers may be overcome if the ferrocenes were produced from the corresponding substituted cyclopentadienes.

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Very little is known about the chemistry of bis-(diphenylphosphino)cyclopentadiene. Nevertheless the most characteristic feature of the 1,5-bis(diphenylphosphino)-2,3,4-trimethylcyclopenta-1,3-diene is the sigma-tropic migration of one diphenylphosphino group leading to a mixture of 1,2- and 1,3-diphosphino-substituted cyclopentadienes [9]. In the light of these results an attractive hypothesis is to imagine that a 1,2–1,3 equilibrium takes place in the analogous non-methylated cyclopentadienes.

Promising information has been obtained from the reaction in THF of diphenylphosphinocyclopentadienyllithium with successively chlorodiphenylphosphine and butyllithium solutions. In the $^1\text{H-NMR}$ spectrum (THF- d_8 solution), two sets of multiplets, consistent with two disubstituted species, are observed. It is the only indication we got in speculating on the existence of a mixture of 1,2 and 1,3 type. The signals of the minor set disappear during treatment and only one species (**1**) is extractable and isolable from the reaction mixture. Moreover **1** is the only product obtained in toluene instead of THF mixture. Unfortunately the shape of signals in the $^1\text{H-NMR}$ spectrum of **1** (heptuplet, quadruplet) is not consistent with the predicted resonance lineshapes [5] for both the 1,2- and 1,3-diphenylphosphinocyclopentadienyl rings. Because the

recognition of the mode of substitution on the cyclopentadienyl ring in **1** from $^1\text{H-NMR}$ data is not clear, its 1,3-diphenylphosphinocyclopentadienyllithium structure will be definitely proved by the synthesis of corresponding ferrocenes.

The symmetrically (**2**) and unsymmetrically substituted (**3**) ferrocenes were synthesized as shown in Scheme 1. The best route to **3** consists of a low-temperature reaction (-78 to 20°C). This is mainly because **1** and FeCl_2 initially form a 1/1 complex preventing the formation of **2** or ferrocene itself [6] and that CpLi further reacts with such a 1/1 complex on heating. Literature data report on the failure [10] or at best on formation of an intractable reaction mixture of tetraphosphine isomers [8] in attempts of preparing compound **2**.

Single-crystal X-ray diffraction analysis of complex **3** (see Fig. 1 and Table 1) has been carried out in order to recognize the substitution pattern. It reveals the presence of two independent ferrocenic molecules in the asymmetric unit of $C2/c$ space group.

An analysis of the shapes (heptuplet, quadruplet) of proton resonances in the $^1\text{H-NMR}$ spectrum of 1,3-diphenylphosphinocyclopentadienyllithium (**1**) has been attempted in the light of the X-ray structure of **3**. For **1**, the values of the coupling constants $J(\text{H-P})_{\text{ortho}}$, $J(\text{H-P})_{\text{meta}}$ and $J(\text{H-H})_{\text{meta}}$ for the protons bound to carbons 4 and 5 are essentially the same (2.2 Hz). The coupling constant $J(\text{H-P})_{\text{ortho}}$ of the proton carried by carbon 2 is roughly double this value (3.8 Hz).

Referring to the 1,2 orientation effect of the thiophosphino group observed during the preparation of thiodiphenylphosphinocyclopentadiene derivatives [11], we have also investigated an alternative preparative scheme using this cyclopentadiene as a precursor. Unfortunately, the sequence of reactions leading to **3**,

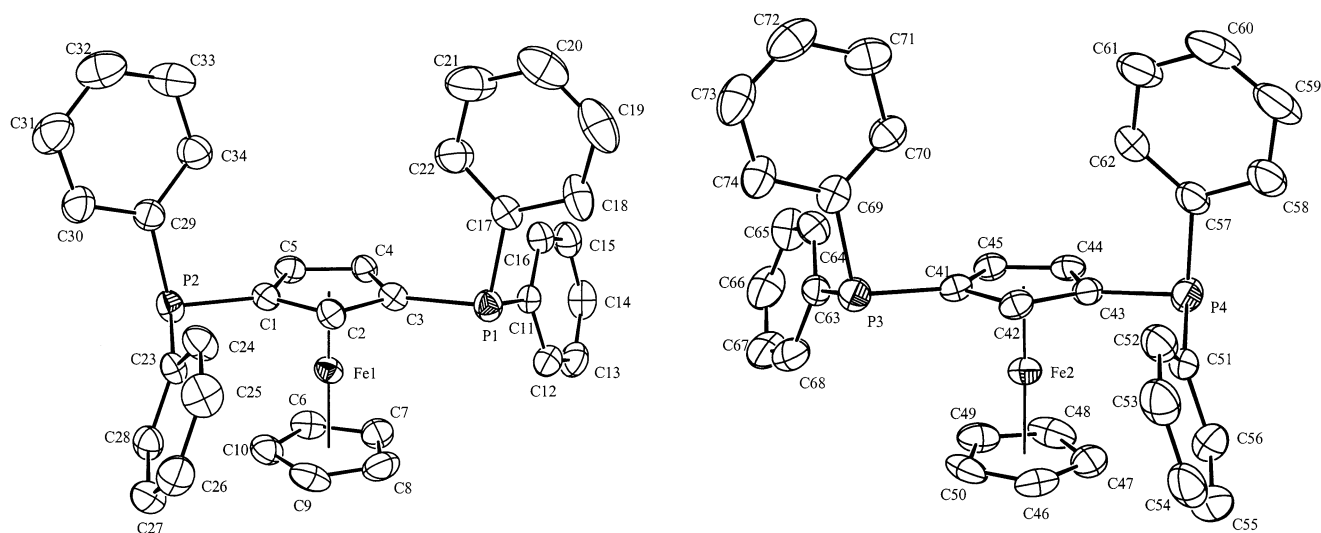


Fig. 1. ORTEP drawing of two independent molecules of **3**: 30% probability level.

Table 1
Molecular geometries of complexes **3**, **5**, **6** and **8**

Complex	3		5	6	8	
	Molecule 1	Molecule 2			Molecule 1	Molecule 2
Fe–CP ₁ ^a	1.645	1.641	1.659	1.660	1.647	1.648
Fe–C _{CP} (mean)	2.044(5) ^b	2.041(5)	2.056(3)	2.050(6)	2.046(7)	2.048(6)
Fe–C _{CP} (P ₁)	2.057(5)	2.052(5)	2.048(3)	2.052(6)	2.045(6)	2.045(6)
Fe–C _{CP} (P ₂)	2.041(5)	2.047(5)			2.037(6)	2.026(6)
Fe–C _{CP} (tBu)			2.083(3)	2.081(6)	2.070(7)	2.073(7)
C _{CP} –C _{CP} (C ₅) mean	1.425(7)	1.420(8)	1.427(4)	1.413(7)	1.429(8)	1.429(8)
(C _{CP} –C _{CP} –C _{CP}) mean	108.0	108.0	108.0	108.0	108.0	108.0
Fe–CP ₂	1.660	1.648	1.659	1.664	1.660	1.662
Fe–C _{CP} (mean)	2.041(6)	2.030(6)	2.054(3)	2.055(6)	2.037(9)	2.041(8)
Fe–C _{CP} (P ₁)			2.054(3)	2.066(6)		
Fe–C _{CP} (tBu)			2.078(3)	2.078(6)		
C _{CP} –C _{CP} (C ₅) mean	1.396(7)	1.393(9)	1.424(4)	1.419(7)	1.388(11)	1.392(11)
(C _{CP} –C _{CP} –C _{CP}) mean	108.0	108.0	108.0	108.0	108.0	108.0
C _{CP1} –P	1.806(6)	1.814(6)	1.823(3)	1.813(6)	1.806(7)	1.815(7)
	1.813(6)	1.811(6)			1.810(7)	1.825(7)
C _{CP2} –P			1.819(3)	1.810(6)		
C _{CP1} –C'Bu			1.517(4)	1.512(8)	1.511(9)	1.523(9)
C _{CP2} –C'Bu			1.520(4)	1.501(8)		
CP–Fe–CP (°)	179.7		178.4	176.3	179.2	178.7
Tilt of C ₅ planes (°)	0.67	2.02	4.49	4.03	2.28	3.23
Deviations of substituents from C ₅ planes ^c						
P ₁ (CP ₁)	–0.081	–0.057	–0.088	+0.124	–0.126	–0.111
P ₂ (CP ₁)	–0.021	–0.119			+0.037	+0.012
P ₁ (CP ₂)			–0.003	+0.188		
C'Bu _(CP1)			+0.178	+0.173	+0.173	+0.148
C'Bu _(CP2)			+0.188	+0.174		
Conformation	Interm	Interm	Eclipsed	Staggered	Staggered	Staggered
Twist angle ^d	19.2	16.7	7.3	25.6	26.3	27.7

^a CP are the geometrical centers of C₅ rings.

^b Estimated S.D. for individual bonds.

^c Sign (–) means the *endo* displacement (towards Fe atom), while (+) indicates the *exo* one.

^d Twist angle is equal to 0° for ideal eclipsed, and 36° for ideal staggered conformations.

applied to thiodiphenylphosphinocyclopentadienyllithium does not produce the 1,2 but the 1,3 isomer: the 1-thiophosphino-3-phosphino analog of **3**.

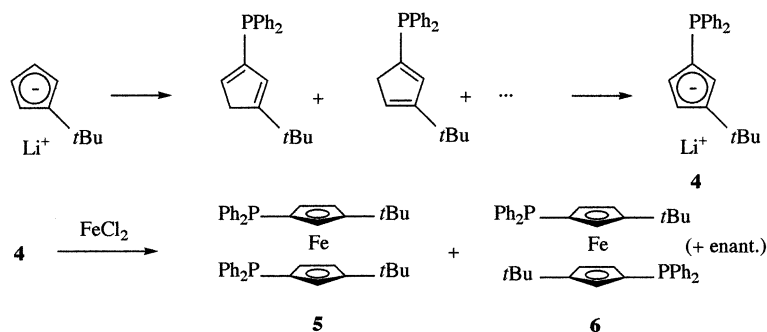
2.2. 1-Diphenylphosphino-3-tertiobutylcyclopentadienyllithium and 1,1'-bis(diphenylphosphino)-3,3'-ditertio-butylferrocene racemic and meso

This investigation on the dissymmetrically disubstituted cyclopentadienyl ligand area was performed with the aim of obtaining the two diastereoisomeric forms of sterically crowded ferrocenic phosphines. Previously reported studies [12] show the inability of the sequence metalation-reaction with electrophile applied to ferrocene in the preparation of the two diastereoisomeric forms of 1,1'-bis(diphenylphosphino)-3,3'-bis(trimethylsilyl)ferrocene. We can consider that such a behavior will be the same with the known 3,3' dilithiated 1,1'-bis(tertiobutyl)ferrocene [13]. On the other hand, a large number of ferrocenes with bulky substituents have

been prepared from the corresponding cyclopentadienyl salts [14].

Using this approach and starting from the tertio-butylcyclopentadienyllithium, we have prepared a cyclopentadiene with both tertio-butyl and diphenylphosphino substituents (Scheme 2). In the presence of tertio-butyl group the subsequent substitution occurs at the β position and the 1,3-disubstituted cyclopentadiene is obtained as a mixture of four tautomers: 1-diphenylphosphino-4-tertiobutylcyclopenta-1,4-diene (45%), 1-diphenylphosphino-3-tertiobutylcyclopenta-1,3-diene (45%), 1-diphenylphosphino-3-tertiobutylcyclopenta-2,4-diene (3%) and 1-diphenylphosphino-3-tertiobutylcyclopenta-1,4-diene or 1-diphenylphosphino-4-tertiobutylcyclopenta-1,3-diene (7%). The isomers exhibit small but significant differences of the chemical shifts for substituents in ³¹P- or ¹H-NMR spectra (see Section 4).

Treatment of the above mixture of phosphines with *n*-butyllithium in THF gave 1-diphenylphosphino-3-ter-



Scheme 2.

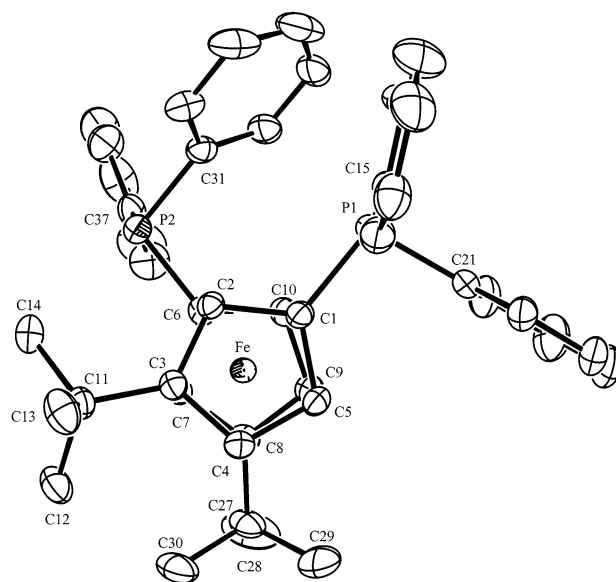
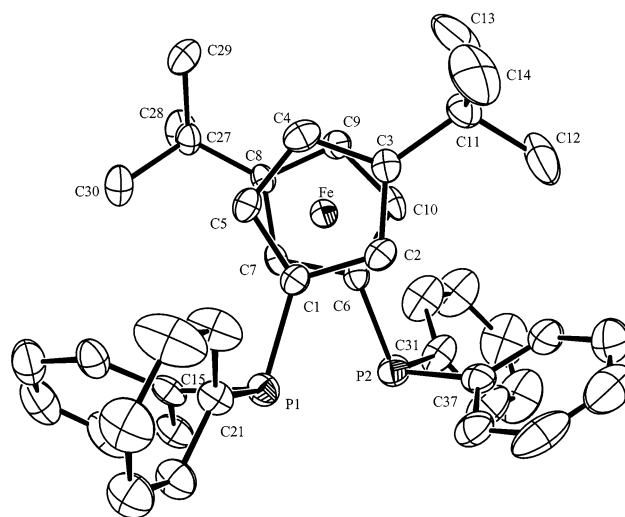
tiobutylcyclopentadienyllithium (**4**) in quantitative yield. This salt has proven to be a convenient starting material for the preparation of two diastereoisomeric iron metallocenes (166 and 177°C melting points) in 60/40 ratio. Analytical and spectroscopic data (^1H -, ^{31}P - and ^{13}C -NMR) support the formulation presented in Scheme 2, but despite the differences observed, the attribution of *meso* form **5** or racemic form **6** could not be achieved. We can only state at this point that species F166°C displays a more complicated ^{13}C -NMR spectrum than that of F177°C, for which long-range phosphorus–carbon coupling is seen as in racemic 1,1'-bis-(diphenylphosphino) - 3,3' - bis(trimethylsilyl)ferrocene [12]. The structures of these products (**5** and **6**) have been definitively recognized on the basis of X-ray analyses (Figs. 2 and 3 and Table 1).

Like other X-ray structures reported in this paper, those of **5** and **6** bear the symmetry center excluding any speculation about the polar properties of these molecules. The crystals of **5** are built of (*S*, *R*) and (*R*, *S*) molecules (*meso* structure), while those of **6** contain the (*S*, *S*) and (*R*, *R*) isomeric set of racemic molecules.

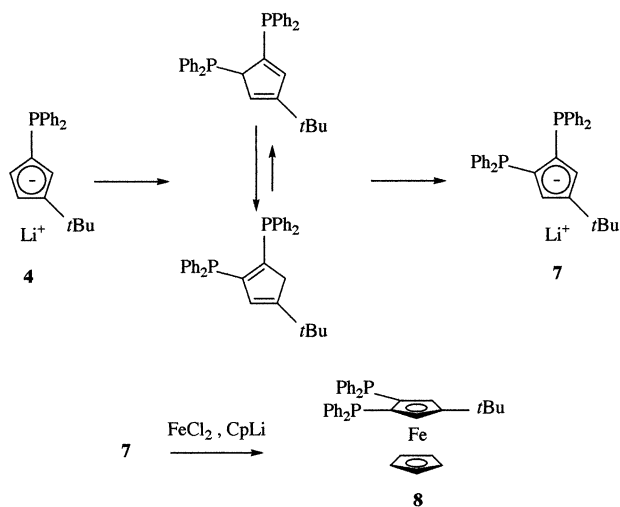
2.3. 1,2-Bis(diphenylphosphino)-4-tertbutylferrocene

We have shown the marked preference for 3-substitution in the orientation effects of $-\text{PPh}_2$ versus $-\text{PPh}_2$ and $-\text{tBu}$ versus $-\text{PPh}_2$. The combined directive influence of the two substituents in 1-diphenylphosphino-3-tertbutylcyclopentadienyllithium upon the reaction site for a subsequent attack by Ph_2PCl gave the exclusive formation of 1,2-bis(diphenylphosphino)-4-tertbutyl arrangement. This route allows a new and easy access to cyclopentadienes with two diphenylphosphino groups in vicinal position. 1,2,3-Trimethylcyclopentadienyl salts already proved that they were good candidates for this preparation [6].

The reaction of **4** (Scheme 3) with chlorodiphenylphosphine gives a trisubstituted cyclopentadiene as a mixture of two isomers, 1,2-bis(diphenylphosphino)-4-tertbutylcyclopenta-2,4-diene and 1,2-bis-

Fig. 2. ORTEP drawing of **5**: 30% probability levelFig. 3. ORTEP drawing of **6**: 30% probability level

(diphenylphosphino)-4-tertbutylcyclopenta-2,4-diene, in a 80/20 ratio. The mixture is then deprotonated with



Scheme 3.

BuLi yielding **7**. After the coupling of **7** with FeCl_2 , the resulting 1/1 intermediate reacts cleanly with CpLi affording **8**. It is noteworthy that **8** thus formed, is only contaminated by a very small amount of unsubstituted ferrocene and that no of symmetrical tetraphosphine species has been detected.

X-ray structure analysis of **8** has been carried out. As in the case of unsymmetrical complex **3**, **8** crystallizes with two independent molecules in the asymmetric unit (Fig. 4 and Table 1).

3. Crystallographic studies

All organometallic molecules have usual ferrocenic geometries. Their selected metric parameters are gathered in Table 1. All of them bear two PPh_2 substituents in 1,3 (**3**), 1,1' (**5** and **6**) or 1,2 (**8**) positions reached with 3,3' (**5** and **6**) and 4 (**8**) $t\text{Bu}$ substitutions. Both unsymmetrical (two different Cp rings) complexes **3** and **8** crystallize with two independent molecules in the asymmetric units of the corresponding $C2/c$ and $P2_1/c$ monoclinic space groups. One observes that the $\text{Fe}-\text{CP}$ (geometrical center of C_5 ring) distances in asymmetrical complexes **3** and **8** are shorter (except molecule **2** in **3**) for substituted rings than for the non-substituted C_5H_5 ones. Intuitively, one would expect an inverse relation. An explanation for this is furnished by the C–C bond lengths found for substituted (1.42–1.43 Å) and non-substituted (1.39–1.40 Å) rings. The substituted rings are larger, and consequently may be closer to the metal than the smaller C_5H_5 ones. The C_5 planes are roughly parallel in all molecules. However, one states that the corresponding tilt angles increase clearly (from 0.7 to 4.5°) with the degree of substitution i.e. **3** < **8** < **5** and **6**. The $t\text{Bu}$ substituents exhibit an *exo* (outside) deviation with respect to the $(\text{C}_5)_2\text{Fe}$ fer-

rocenic core as generally reported for alkyl-substituted ferrocenes, while the PPh_2 ones may give rise either to the *exo* (**6**) or to the *endo* (or in plane) deviations (**3**, **5**, **8**). Steric hindrances are thus responsible for the deviations observed: bulky and rigid $t\text{Bu}$ group bound to the carbon atom of C_5 ring with short $\text{C}(\text{Cp})-\text{C}(t\text{Bu})$ (1.51 Å) moves outside, while the larger and more flexible PPh_2 groups with $\text{C}(\text{Cp})-\text{PPh}_2$ distances close to 1.81 Å are able to deviate in both the *exo* and the *endo* positions.

The conformations of the C_5 rings are intermediate between the eclipsed and staggered, being closer to the eclipsed one in **5**, the staggered one in **6** and **8** and clearly intermediate in **3**.

4. Experimental

4.1. General considerations

Reactions were carried out in an atmosphere of argon by means of conventional Schlenk techniques. Solvents were dried and deoxygenated before distillation from sodium benzophenone ketyl or Na–K alloy. Elemental analyses were performed by the Service central d'analyses du CNRS. Mass spectra (electronic ionization 70 eV) were recorded on a Kratos concept IS machine. ^1H -, ^{31}P - and ^{13}C -NMR spectra were recorded on a Bruker AC 200 (special abbreviations: pqd, pseudo quadruplet; pt, pseudo triplet; pd, pseudo doublet; numerotation of Cp ring refer to ORTEP drawing numerotation; for **2**, **6** and **8**, the spin system for each of the carbon atoms of phenyl (*i*, *o*, *m*, *p*) is of the $\text{AA}'\text{X}$ ($\text{A} = \text{A}' = ^{31}\text{P}$, $\text{X} = ^{13}\text{C}$) limiting type [12,15]).

4.2. Preparation of **1**

To 10.05 g (39.2 mmol) of diphenylphosphinocyclopentadienyllithium [16] in 200 ml toluene was added at -80°C , 6.3 ml (35 mmol) of chlorodiphenylphosphine. The solution turned orange after stirring for 2 h at room temperature (r.t.). The mixture was filtered, the lithium chloride was washed with 40 ml of hexane and the solution was evaporated in vacuo leading to an orange oil. To the toluene solution of oil were added at -80°C , 28 ml of butyllithium (1.39 M in diethyl ether, 39 mmol). Upon this addition, butane was evolved and the solution turned yellow. After stirring at r.t. for 14 h, a precipitate appeared. The mixture was filtered and the precipitate was washed twice with 30 ml hexane. Then, the solution was evaporated in vacuo and 13.04 g (29.5 mmol, yield = 90%) of a white air-sensitive powder **1**, was isolated. ^1H -NMR ($\text{THF}-d_8$): δ 6.06 (pqd, 2H, $^3J_{\text{H-P}} = 2.2$, $^4J_{\text{H-H}} = 2.2$, $^4J_{\text{H-P}} = 2.2$ Hz), 6.32 (hept, 1H, $^3J_{\text{H-P}} = 3.8$, $^4J_{\text{H-H}} = 2.2$ Hz). ^{31}P -NMR ($\text{THF}-d_8$): δ –15.83 (s).

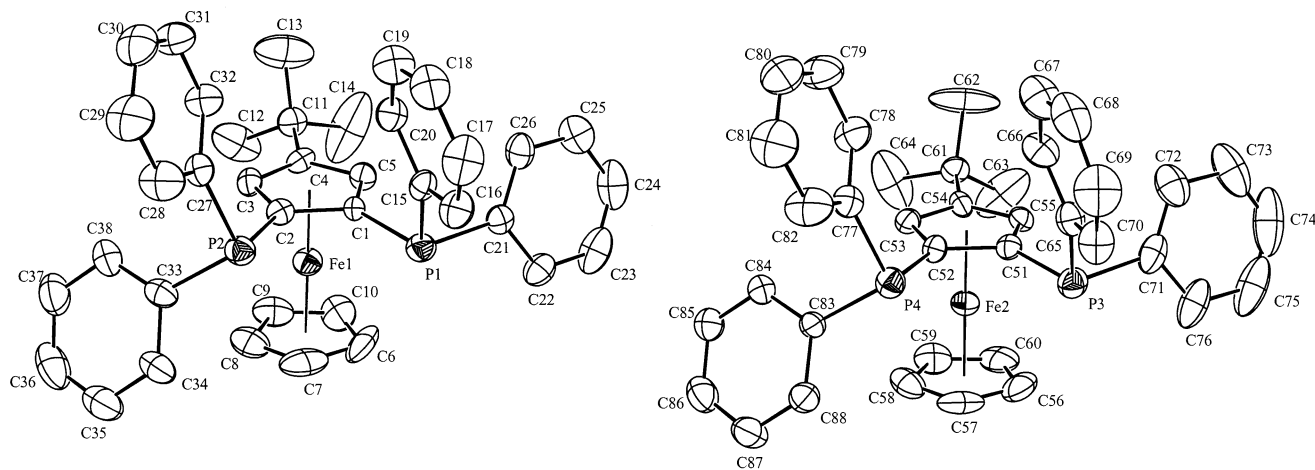


Fig. 4. ORTEP drawing of two independent molecules of **8**: 30% probability level.

4.3. Preparation of **2**

To 0.38 g (2.99 mmol) of iron dichloride in 20 ml THF were added at r.t. 2.64 g (5.99 mmol, two molar equivalent) of **1** in 50 ml THF. After refluxing for 4 h, the reaction mixture was filtered on 2 cm of a silica gel and the solvent was evaporated in vacuo. The oil was chromatographed on a silica gel column with toluene–hexane (1:1), and an orange solution was obtained. Then the solvent was removed to give 2 g of **2** (2.16 mmol, yield = 73%) as an orange air stable solid, m.p. = 180°C. Anal. Calc. for $C_{58}H_{46}FeP_4$: C, 75.50; H, 5.02. Found C, 75.30; H, 4.93%. 1H -NMR (C_6D_6): δ 3.97 (s, 2H, Cp), 4.40 (s, 1H, Cp), 7.03–7.50 (m, 20H, Ph). ^{31}P -NMR (C_6D_6): δ –22.46 (s). ^{13}C -NMR (C_6D_6): δ 76.2 (m, C_1 Cp), 81.0 (m, C_2/C_3 Cp), 83.0 (m, C_5 Cp), 128.2 (pt, $J_{PC+P'C} = 7$ Hz, *p*-Ph), 128.5 (pd, $J_{PC+P'C} = 23$ Hz, *m*-Ph), 133.1 (pt, $J_{PC+P'C} = 30$ Hz, *o*-Ph), 134.0 (pt, $J_{PC+P'C} = 30$ Hz, *o'*-Ph), 133.3 (pt, $J_{PC+P'C} = 60$ Hz, *o''*-Ph), 133.7 (pt, $J_{PC+P'C} = 60$ Hz, *o'''*-Ph), 139.3 (m, *i*-Ph). EI-MS (200°C): m/z (%): 923 (100) [M^+], 845 (10) [$M^+ - Ph$], 737 (10) [$M^+ - PPh_2$].

4.4. Preparation of **3**

To 0.291 g (2.3 mmol) of iron dichloride in 15 ml THF was added a mixture of 1.02 g (2.3 mmol) of **1** and 0.166 g (2.3 mmol) of cyclopentadienyllithium in 40 ml THF at –80°C. After stirring for 2 h at r.t., the solution turned violet–brown. Then the mixture was filtered on 2 cm of celite and, following solvent removal, an oil was obtained. This oil was chromatographed on a silica gel column with toluene–hexane (2:3). In the order of elution and after the solvent was evaporated in vacuo from each fraction, three products were obtained: ferrocene, 495 mg (0.89 mmol, yield = 39%) of **3** and finally 74 mg (8×10^{-2}

mmol) of **2**. The solid was recrystallized in hot hexane and orange crystals of **3** were obtained, m.p. = 109°C. Anal. Calc. for $C_{34}H_{28}FeP_2$: C, 73.66; H, 5.09. Found C, 73.85; H, 5.12%. 1H -NMR ($CDCl_3$): δ 3.98 (s, 5H, Cp), 4.13 (s, 1H, Cp), 4.28 (s, 2H, Cp), 7.35 (m, 20H, Ph). ^{31}P -NMR ($CDCl_3$): δ –19.37 (s). ^{13}C -NMR (C_6D_6): δ 70.3 (s, Cp), 75.4 (dd, $^2J_{PC} = 14$, $^3J_{PC} = 3.5$ Hz, C_4/C_5 Cp), 77.7 (pt, $^2J_{PC} = 15$ Hz, C_2 Cp), 79.5 (dd, $^1J_{PC} = 8$, $^3J_{PC} = 3$ Hz, C_1/C_3 Cp), 128.3 (d, $^3J_{PC} = 6.5$ Hz, *m*-Ph), 128.7 (d, $^4J_{PC} = 4$ Hz, *p*-Ph), 133.4 (d, $^2J_{PC} = 9.5$ Hz, *o*-Ph), 133.7 (d, $^2J_{PC} = 9.5$ Hz, *o'*-Ph), 138.8 (m, *i*-Ph/*i'*-Ph). EI-MS (200°C): m/z (%): 554 (100) [M^+], 477 (20) [$M^+ - Ph$].

4.5. Preparation of **4**

To 3.1 g (24 mmol) of tertiotbutylcyclopentadienyllithium in 70 ml toluene were added at –80 °C, 4.2 ml (23.4 mmol) of chlorodiphenylphosphine. The solution turned orange after stirring for 2 h at r.t. The mixture was filtered and lithium chloride was washed with 30 ml of hexane. The solution was evaporated in vacuo and 6.5 g (21.2 mmol, yield = 91%) of an orange oil, mixture of cyclopentadienes, were isolated.

1H -NMR (C_6D_6) non-assigned signals for ethylenic and phenyl protons: δ 6.00 (m, 1H), 6.05 (m, 1H), 6.25 (m, 1H), 6.62 (m, 1H), 7.30–8.05 (m, 20H).

1-Diphenylphosphino-4-tertiotbutylcyclopenta-1,4-diene: 1H -NMR (C_6D_6): δ 0.98 (s, t Bu), 2.93 (m, CH_2); ^{31}P -NMR (C_6D_6): δ –19.14 (s).

1-Diphenylphosphino-3-tertiotbutylcyclopenta-1,3-diene: 1H -NMR (C_6D_6): δ 1.06 (s, t Bu), 3.02 (m, CH_2); ^{31}P -NMR (C_6D_6): δ –19.14 (s).

1-Diphenylphosphino-3-tertiotbutylcyclopenta-2,4-diene: ^{31}P -NMR (C_6D_6): δ –10.86 (s).

1-Diphenylphosphino-3-tertiotbutylcyclopenta-1,4-diene or 1-diphenylphosphino-4-tertiotbutylcyclopenta-1,3-diene: ^{31}P -NMR (C_6D_6): δ –20.12 (s).

To 6.5 g (21.2 mmol) of the previous oil in 100 ml toluene were added at -20°C , 18 ml of butyllithium (1.46 M in diethylether, 26 mmol). Upon this addition, butane was evolved and the solution turned yellow. After stirring at r.t. for 14 h, a precipitate appeared. The mixture was filtered and the precipitate was washed with 30 ml of toluene. Then, the solution was evaporated in vacuo and 5.73 g (18.3 mmol, yield = 87%) of a white air sensitive powder, **4**, was isolated. $^1\text{H-NMR}$ ($\text{THF-}d_8$): δ 1.24 (s, 9H, $t\text{-Bu}$), 5.73 (m, 1H, Cp), 5.88 (m, 1H, Cp), 5.97 (m, 1H, Cp), 7.12–7.31 (m, 10H, Ph). $^{31}\text{P-NMR}$ ($\text{THF-}d_8$): δ –15.5 (s).

4.6. Preparation of **5** and **6**

To 0.45 g (3.5 mmol) of iron dichloride in 40 ml THF were added at 0°C , 2.10 g (6.7 mmol, two molar equivalent) of **4** in 80 ml THF. After stirring at 0°C for 30 min and at r.t. for 15 h, the solvent was removed and the resulted brown oil was extracted with 60 ml of pentane. The brown mixture was then filtered and the solvent was evaporated in vacuo. The oil was chromatographed on a silica gel column with toluene–hexane (1:2). In order of elution and after the solvent was evaporated in vacuo from each fraction, two products were obtained: 320 mg (0.48 mmol, yield = 14%) of an orange solid, **5** and 200 mg (0.3 mmol, yield = 9%) of an orange solid, **6**.

Data for **5**: m.p. = 177°C . Anal. Calc. for $\text{C}_{42}\text{H}_{44}\text{FeP}_2$: C, 75.66; H, 6.65. Found C, 75.64; H, 6.89%. $^1\text{H-NMR}$ (C_6D_6): δ 1.23 (s, 18H, $t\text{-Bu}$), 3.83 (m, 2H, Cp), 3.98 (m, 2H, Cp), 4.30 (m, 2H, Cp), 7.01–7.64 (m, 20H, Ph). $^{31}\text{P-NMR}$ (C_6D_6): δ –19.52 (s). $^{13}\text{C-NMR}$ (C_6D_6): δ 31.0 (s, $\text{C}(t\text{-Bu})$), 32.0 (s, $\text{Me}(t\text{-Bu})$), 68.5 (s, C_4Cp), 71.4 (s, $\text{C}_2/\text{C}_5\text{Cp}$), 74.0 (d, $^1J_{\text{P-C}} = 32$ Hz, C_1Cp), 76.3 (m, $\text{C}_2/\text{C}_5\text{Cp}$), 105.8 (s, C_3Cp), 129.3 (s, $p\text{-Ph}$), $m\text{-Ph}$ not observed (solvent), 132.6 (d, $^2J_{\text{PC}} = 18$ Hz, $o\text{-Ph}$), 135.4 (d, $^2J_{\text{PC}} = 21$ Hz, $o'\text{-Ph}$), 138.5 (d, $^1J_{\text{PC}} = 11.5$ Hz, $i\text{-Ph}$), 141.0 (d, $^1J_{\text{PC}} = 13$ Hz, $i'\text{-Ph}$). EI-MS (200°C): m/z (%): 666 (100) [M^+], 589 (30) [$\text{M}^+ - \text{Ph}$], 481 (20) [$\text{M}^+ - \text{PPh}_2$], 361 (10) [$\text{M}^+ - \text{C}_5\text{H}_2\text{BuPPh}_2$].

Data for **6**: m.p. = 166°C . Anal. Calc. for $\text{C}_{42}\text{H}_{44}\text{FeP}_2$: C, 75.66; H, 6.65. Found C, 75.46; H, 6.66%. $^1\text{H-NMR}$ (C_6D_6): δ 0.96 (s, 18H, $t\text{-Bu}$), 3.95 (m, 2H, Cp), 4.16 (m, 2H, Cp), 4.20 (m, 2H, Cp), 7.02–7.85 (m, 20H, Ph). $^{31}\text{P-NMR}$ (C_6D_6): δ –22.01 (s). $^{13}\text{C-NMR}$ (C_6D_6): δ 30.7 (s, $\text{C}(t\text{-Bu})$), 31.5 (s, $\text{Me}(t\text{-Bu})$), 69.0 (s, C_4Cp), 71.3 (s, $\text{C}_2/\text{C}_5\text{Cp}$), 74.5 (m, C_1Cp), 76.1 (m, $\text{C}_2/\text{C}_5\text{Cp}$), 105.7 (s, C_3Cp), 129.3 (s, $p\text{-Ph}$), $m\text{-Ph}$ not observed (solvent), 132.6 (pt, $J_{\text{PC}+\text{P'C}} = 18$ Hz, $o\text{-Ph}$), 136.0 (pt, $J_{\text{PC}+\text{P'C}} = 23$ Hz, $o'\text{-Ph}$), 138.9 (pt, $J_{\text{PC}+\text{P'C}} = 12$ Hz, $i\text{-Ph}$), 142.5 (pt, $J_{\text{PC}+\text{P'C}} = 11.5$ Hz, $i'\text{-Ph}$). EI-MS (200°C): m/z (%): 666 (100) [M^+], 589 (30) [$\text{M}^+ - \text{Ph}$], 481 (20) [$\text{M}^+ - \text{PPh}_2$], 361 (10) [$\text{M}^+ - \text{C}_5\text{H}_2\text{BuPPh}_2$].

4.7. Preparation of **7**

To 5.73 g (18 mmol) of **4** in 50 ml toluene were added at -80°C , 3.2 ml (17.8 mmol) of chlorodiphenylphosphine. The solution turned orange after stirring for 4 h at r.t. The mixture was filtered and lithium chloride was washed twice with 10 ml of toluene. The solution was evaporated in vacuo and 6.4 g (13 mmol, yield = 73%) of trisubstituted cyclopentadienes as an orange oil, were isolated.

1,2-Bis(diphenylphosphino)-4-tertiobutyl-1,3-diene: $^1\text{H-NMR}$ (C_6D_6): δ 0.83 (s, 9H, $t\text{-Bu}$), 3.24 (s, 1H, CHPPh_2), 6.30 (m, 2H, $\text{CH}=\text{C}$), 6.9–7.2 (m, 20H, Ph). $^{31}\text{P-NMR}$ (C_6D_6): δ –26 (pqd, 2P, $^3J_{\text{P-P}} = 84$ Hz).

1,2-Bis(diphenylphosphino)-4-tertiobutyl-2,4-diene: $^1\text{H-NMR}$ (C_6D_6): δ 0.84 (s, 9H, $t\text{-Bu}$), 3.24 (s, 2H, CH_2), 6.34 (m, $\text{CH}=\text{C}$), 7.41–7.54 (m, 20H, Ph). $^{31}\text{P-NMR}$ (C_6D_6): δ –1.5 (d, 1P, $^3J_{\text{P-P}} = 84$ Hz), –20.5 (d, 1P, $^3J_{\text{P-P}} = 84$ Hz).

To 6.4 g (13 mmol) of the previous oil in 70 ml toluene were added at 0°C , 10 ml of butyllithium (1.46 M in diethylether, 14.6 mmol). Upon this addition, butane was evolved and the solution turned yellow. After stirring at r.t. for 14 h, a precipitate appeared. The mixture was filtered and the precipitate was washed with 15 ml of hexane. Then, the solution was evaporated in vacuo and 4.12 g (8.3 mmol, yield = 57%) of a white air sensitive powder **7**, were isolated. $^1\text{H-NMR}$ ($\text{THF-}d_8$): δ 1.17 (s, 9H, $t\text{-Bu}$), 5.88 (m, 2H, Cp), 7.00–7.34 (m, 20H, Ph). $^{31}\text{P-NMR}$ ($\text{THF-}d_8$): δ –18.82 (s).

4.8. Preparation of **8**

At -40°C , a yellow solution of 4.1 g of **7** (8.25 mmol) in 40 ml THF was added to 1.1 g (8.7 mmol) of iron dichloride in 20 ml THF. After stirring for 2 h at r.t., the solution turned violet. Then, 0.67 g (9.3 mmol) of cyclopentadienyllithium in 20 ml THF was added to the reaction mixture at -40°C , and agitation was maintained during 1 h at r.t. The THF was evaporated and replaced by 70 ml of toluene. The brown mixture was refluxed for 16 h and filtered. Following solvent removal, washing with hexane and drying under reduce pressure, a yellow solid identified as **8** was obtained. The product was crystallized in ethanol–water to obtain 3.4 g (5.6 mmol, yield = 68%) of orange crystals, m.p. = 176°C . Anal. Calc. for $\text{C}_{38}\text{H}_{36}\text{FeP}_2$: C, 74.76; H, 5.94. Found C, 74.47; H, 6.03%. $^1\text{H-NMR}$ (C_6D_6): δ 1.07 (s, 9H, $t\text{-Bu}$), 4.05 (s, 5H, Cp), 4.25 (s, 2H, Cp), 6.87–7.76 (m, 20H, Ph). $^{31}\text{P-NMR}$ (C_6D_6): δ –24.3 (s). $^{13}\text{C-NMR}$ (C_6D_6): δ 31.0 (s, $\text{C}(t\text{-Bu})$), 31.6 (s, $\text{Me}(t\text{-Bu})$), 71.2 (s, Cp), 83.0 (pt, $^{1+2}J_{\text{PC}+\text{P'C}} = 19$ Hz, $\text{C}_1/\text{C}_2\text{Cp}$), 106.3 (s, $\text{C}_3/\text{C}_5\text{Cp}$), 129.2 (s, $p\text{-Ph}$), $m\text{-Ph}$ not observed (solvent), 133.6 (pt, $^{2+5}J_{\text{PC}+\text{P'C}} = 20$ Hz, $o\text{-Ph}$), 135.5 (pt, $^{2+5}J_{\text{PC}+\text{P'C}} = 22$ Hz, $o'\text{-Ph}$), 139.5 (pt, $^{1+4}J_{\text{PC}+\text{P'C}} = 8$ Hz, $i\text{-Ph}$), 140.4 (pt, $^{1+4}J_{\text{PC}+\text{P'C}} = 12$

Table 2
Crystallographic data for complexes **3**, **5**, **6** and **8**.

Complex	3	5	6	8
Molecular formula	C ₃₄ H ₂₈ FeP ₂	C ₄₂ H ₄₄ FeP ₂	C ₄₂ H ₄₄ FeP ₂	C ₃₈ H ₃₆ FeP ₂
Formula weight (g)	554.35	666.56	666.56	610.46
Colour, shape	Amber, irregular	Amber, prism	Amber, prism	Amber, irregular
Dimensions (mm)	0.5 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.2 × 0.2 × 0.15	0.25 × 0.2 × 0.15
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c (15)	P $\bar{1}$	P2 ₁ /c (14)	P2 ₁ /c (14)
<i>a</i> (Å)	42.279(5)	10.9097(6)	15.744(3)	16.946(4)
<i>b</i> (Å)	11.378(3)	11.777(1)	11.033(2)	13.566(6)
<i>c</i> (Å)	28.966(5)	15.276(1)	20.803(3)	29.427(7)
α (°)		79.31		
β (°)	126.75(1)	69.99(1)	96.63(1)	105.49(2)
γ (°)		79.20(1)		
<i>V</i> (Å ³)	11165(4)	1795.8(3)	3589(1)	6519(4)
<i>Z</i>	16	2	4	8
<i>F</i> (000)	4608	704	1408	2560
ρ_{calc} (g cm ^{−3})	1.319	1.233	1.233	1.244
Radiation, λ (Mo–K α) (Å)	0.71073	0.71073	0.71073	0.7073
Linear absorption, μ (mm ^{−1})	0.676	0.537	0.537	0.585
Temperature (K)	296(1)	296(1)	296(1)	296(1)
Linear decay (%)	−0.7	−1.0	−4.0	0.0
Scan type	ω	$\omega-2\theta$	ω	$\omega-2\theta$
θ range (°)	2.31–24.64	2.49–26.28	2.09–19.98	2.08–22.77
Measured	9730	7665	3764	9057
Unique	5299	7268	3334	7788
With [<i>I</i> > 2 σ (<i>I</i>)]	4537	5423	1944	3236
Parameters	667	406	406	739
Final <i>R</i> (<i>F</i> ²): <i>R</i> ₁	0.048	0.043	0.042	0.051
<i>wR</i> ₂	0.099	0.114	0.080	0.137
Goodness-of-fit	1.060	1.134	0.986	0.943
$\rho_{\text{max}}/\rho_{\text{min}}$ (e Å ^{−3})	+0.29/−0.24	+0.30/−0.27	+0.24/−0.25	+0.29/−0.24

Hz, *i*'-Ph). EI-MS (200°C): *m/z* (%): 610 (100) [M⁺], 595 (70) [M⁺ − CH₃], 553 (30) [M⁺ − 'Bu], 425 (30) [M⁺ − PPh₂], 240 (10) [M⁺ − 2PPh₂], 183 (70) [M⁺ − 'Bu2PPh₂].

4.9. X-ray crystallography

All measurements have been carried out at 296 K on an Enraf–Nonius CAD4 diffractometer. The pertinent crystallographic data are given in Table 2. The unit cells have been determined from 25 randomly selected reflections (CAD4-EXPRESS) [17]. Intensity data have been reduced with PROCESS in MOLEN package [18] with neutral-atom scattering factors taken from the usual source. All structures were solved by direct methods (SHELXS97) [19] and refined by using the SHELXL97 library [20].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-

117661 (structure of **3**), CCDC-117662 (structure of **5**), CCDC-117663 (structure of **6**) and CCDC-117664 (structure of **8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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