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Ferrocenic polyphosphines and polythioethers: synthesis, reactivity and structure

Roland Broussier *, Serge Ninoreille, Cyrille Bourdon, Olivier Blacque, Corinne Ninoreille, Marek M. Kubicki, Bernard Gautheron

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS, UMR 5632, 6 boulevard Gabriel, BP 138, 21004 Dijon Cedex, France

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Abstract

The new ferrocenic polyphosphines $[C_5Me_3\text{-}1,2\text{-}(PPh_2)_2](C_5H_5)Fe$ **2**, $[C_5Me_3\text{-}1,2\text{-}(PPh_2)_2]_2Fe$ **3**, $[C_5Me_3\text{-}1,2\text{-}(PPh_2)_2][C_5Me_4(PPh_2)]Fe$ **4** and polythioethers $[C_5Me_3\text{-}1,2\text{-}(SCH_2CH_2CH_3)2]_2Fe$ **6** and $[C_5Me_3\text{-}1,2\text{-}(SCH_2CH_2CH_3)_2](C_5H_5)Fe$ **7** have been prepared. The X-ray crystal structures of **3** and **6** have been determined. Some aspects of the reactivity of compounds **2**, **3** and **4** are reported (P(III) → P(V) transformation, chelating properties) as well as the X-ray structure of $[C_5Me_3\text{-}1,2\text{-}(PPh_2)_2W(CO)_4](C_5H_5)Fe$ **15**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Ferrocene; Phosphine; Thioether; Group 6 metal carbonyl

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1. Introduction

The ferrocenic polyphosphine chemistry deals mostly with 1,1′ diphosphines which are not ordinary diphosphine ligands as exemplified by many descriptions [1]. We have already reported on the synthesis of mono and 1,2-diphosphinotrimethylcyclopentadienes [2] which may be used for preparation of new ferrocenylphosphines with 1,2-disubstituted rings. The potentiality of these 1,2 diphosphines could be a novelty in the role of the ferrocenyl moiety. We have also developped the synthesis of analogous alkylsulfanylcyclopentadienes [3,4], thus allowing an access to new sulfur containing ferrocenes with potential 1,2-chelating properties.

We report here on the synthesis of some new ferrocenes together with a study of their chelating abilities toward the group 6 metal carbonyls.

2. Results and discussion

2.1. Synthesis of substituted ferrocenes

Ferrocenic polyphosphines **2**, **3** and **4** (Scheme 1) were obtained from 1,2-bis(diphenylphosphino)-3,4,5-trimethylcyclopentadienyllithium **1**.

However, the usual pathway of synthesis of ferrocenes may be perturbed by the presence of potentially coordinating phosphino groups. The addition of yellow solution of $C_5Me_3(PPh_2)_2Li$ **1** in tetrahydrofuran to a suspension of $FeCl_2$ in the same solvent resulted in a violet solution. After removal of the tetrahydrofuran and refluxing of the violet residue in toluene the ferrocenic species **3** is readily formed. It is noteworthy that the hydrolysis of the initial tetrahydrofuran violet solution does not lead to a substituted ferrocene. In addition the ^{31}P-NMR spectrum recorded for this solution (it was not possible to obtain the ^{1}H-NMR spectra) exhibits two signals close to 80 ppm, which may be attributed to phosphorus atoms in diamagnetic complexes with phosphorus–iron bond [5,6]. This suggests

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* Corresponding author. Tel.: +33 3 80396100; fax: +33 3 80396098.

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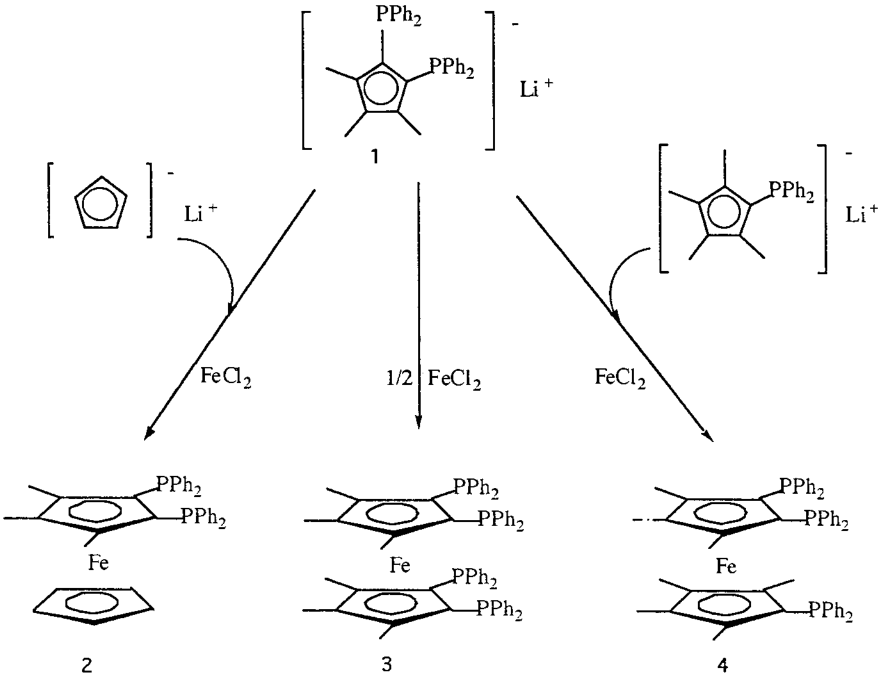


Scheme 1.

that $C_5Me_3(PPh_2)_2Li$ **1** reacts initially as a phosphorus donor and that the usual nucleophily of the ring appears upon warming.

When a suspension of $FeCl_2$ is treated at r.t. successively with one equivalent of $C_5Me_3(PPh_2)_2Li$ **1** and one equivalent of C_5H_5Li, the dissymmetric ferrocene **2** is obtained as the main product after usual treatment. This may suggest that a species with σ FeP bonded ligand **1** is also present in solution at room temperature and that the σ FeP-π FeCp equilibrium shifts toward π complex either on heating (like for **3**) or on addition of other cyclopentadienyl reagent (like for **2**).

The above strategy may be generalized, and the permethylated 1,2,1′-triphosphine **4** has been isolated by this way. Butler and coll. have described the related non methylated triphosphine [7].

The dipropylsulfanyl sodium salt $C_5Me_3(SCH_2CH_2CH_3)_2Na$ **5**, equivalent to **1**, is prepared from the trimethylcyclopentadienylsodium salt. The action of an appropriate mixture of disulfane and sodium hydride leads to the 'one pot' substitution of both hydrogen atoms of the cyclopentadienyl ring (Scheme 2). In boiling THF, the reaction between two equivalents of **5** and one equivalent of $FeCl_2$ gives the corresponding substituted ferrocene **6.**

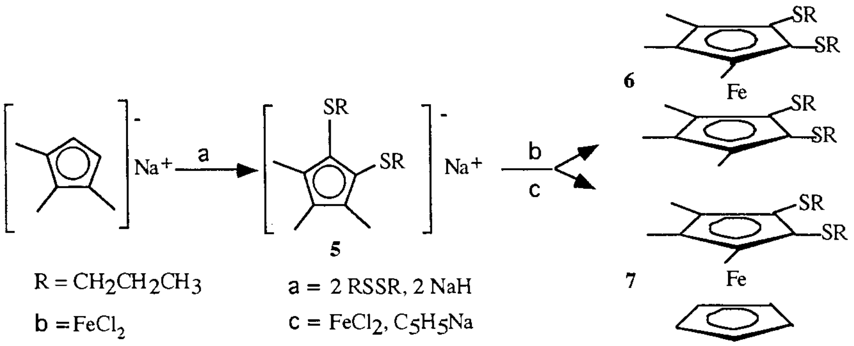
The use of two different sodium salts, **5** and C_5H_5Na, leads to the mixture of dissymmetric ferrocene **7** together with the two corresponding symmetric species. The respective proportions (2/1/1 determined by ^1H-NMR analysis) imply a statistic distribution of the ligands, even if they are introduced successively (**5** first and then C_5H_5Na).

The metallocenic species **2**, **3**, **4** and **6** are air stable solids while **7** is isolated as an oily product. They have been characterized by elemental analysis, mass spectrometry and ^1H-, ^{31}P- and ^{13}C-NMR.

The ^1H-NMR spectra of the three polyphosphines **2**, **3** and **4** confirm the assignment of signals of the methyl groups we have already proposed for the 1,1′-diphenylphosphinooctamethylferrocene (dppomf) [8]. In all cases, the ^1H-NMR spectra display for the $C_5Me_3(PPh_2)_2$ ligand a singlet of intensity three near 3 ppm and a second singlet of intensity six near 1,5 ppm. The signal at the highest field corresponds to the isochronic methyl groups bonded to the carbon atoms in α position with respect to the phosphorus atoms. The intensities of the singlets (methyl protons) are inversed in the spectra of **6** and **7** indicating different electronic influence of PR_2 and SR substituents. Morphology of multiplets observed for the propyl groups claims for an ABM_2X_3 spin system.

The ^{31}P-NMR chemical shifts for **2**, **3** and **4** are close to those observed for the dppf [9] and the dppomf [8]. The triphosphine **4** exhibits a singlet (intensity two) at -18.8 ppm and another one (intensity one) at -22.3 ppm. Thus the chemical shift of a phosphorus atom included in a monophosphorated ring (dppomf) is shifted to a higher field than those observed for the phosphorus atoms of a 1,2-diphosphorated ring. Contrary to dppomf, there is no P–P inter-ring interaction because the P–P couplings are not detected on the ^{31}P-NMR spectra of **3** and **4**.

The ^{13}C-NMR show the resonances expected for the different structures (see Section 3). The parts of the



Scheme 2.

spectra standing for the PPh_2 groups show the isotopic effect. The *ipso* and *ortho* carbon atoms of **2**, **3** and **4** giving pseudotriplets, confirm the resulting diastereotopy.

2.2. Oxidation reactions $P(III) \rightarrow P(V)$

We have recently reported on an easy oxidation of dppomf [8] with H_2O_2 and elemental sulfur leading to the P(V) substituted ferrocenes. Analogous reactions have been carried out with new ferrocenic polyphosphines **2** and **3**.

The oxidation takes place rapidly when hydrogen peroxide is added to a dichloromethane solution of the polyphosphine. By this way, the dioxide **8** and the tetraoxide **9** are isolated directly and in a quite quantitative yields (Scheme 3). These compounds are air stable and sparingly soluble in common solvents. Their structure was confirmed by elemental analysis, mass spectrometry and NMR spectroscopy. In ^{31}P-NMR, the shift of about 50 ppm of the P signal to lower field (-17.9 to $+32.0$ ppm for **28** and -19.8 to $+29.7$ ppm for **3** → **9**) is indicative of $P(III) \rightarrow P(V)$ transformation.

Polyphosphines are very reactive toward sulfur. However, we did not detect the formation of the sulfides (analogous to **8** and **9**) from the reaction of **2** and **3** with sulfur. Only the cyclopentadienes **10** and **11** were isolated in this case (Scheme 3). These compounds were identified by comparison with the samples obtained from direct synthesis [2]. Other products present in the reaction mixture could not be identified.

The destruction of the ferrocenic structure is uncommon and may be tentatively ascribed to the steric requirements of bulky substituents. The intramolecular migration of one phosphorus group (formation of **11** as major product) may support this idea. Other intramolecular interactions e.g. Fe–S leading to the mineral compounds can not be ruled out.

2.3. Chelating properties

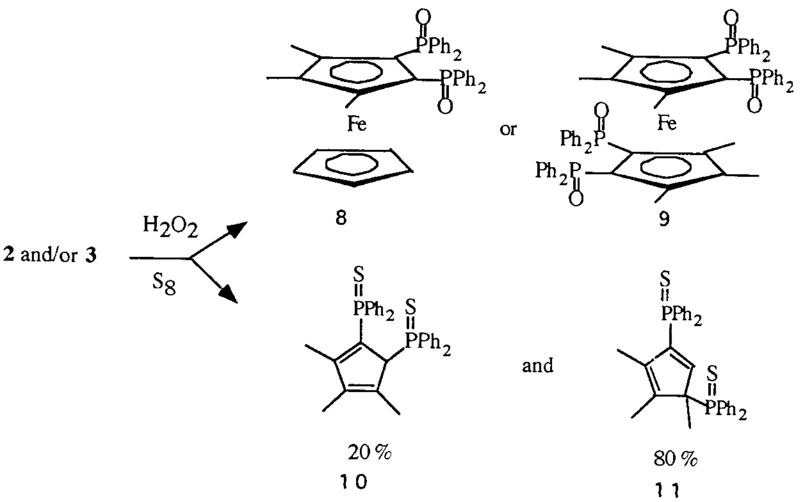
Polyphosphines may bind the carbonyl metal fragments in different ways. The chelating properties of tri and tetra functionalized ferrocenes can lead to the homo or heteroannular coordinations.

Polyphosphines **2**, **3** and **4** react with $M(CO)_4L_2$ ($M = Cr,W$) metal carbonyls under 1/1 stoechiometric conditions giving the bimetallic complexes **12**–**15** (Scheme 4). The yields of bimetallic compounds are very high: **12** (85%), **13** (76%), **14** (86%) and **15** (88%). The phosphorus atoms of one ring are involved in the bonding with the metal carbonyl (homoannular coordination).

The ^{31}P-NMR spectra confirm the 1,2-homoannular coordination (Table 1). The resonances of phosphorus atoms bound to the carbonyl metal fragments are shifted to lower fields than those reported for heteroannular complexes dppomf$M(CO)_4$ [8]. Such a shift is indicative of the difference between the phosphorus-metal bond distances (strengths) and C–P–W angles [9,10]. It has already been observed that the coordination of chromium atom causes a larger low field shift than does the heavier tungsten atom [11]. This result is roughly due to the non local diamagnetic contribution ($Z_{Cr} < Z_W$) of the metallic fragment to the overall shielding [12].

The main modifications observed in the ^{1}H-NMR spectra of homoannular with respect to heteroannular series consist of an extent of the field of resonance of the benzenic hydrogen atoms what is representative of changes in anisotropy effects.

Thus, our polyphosphines behave as the current chelating diphosphines showing that the homoannular coordination is more favourable than the heteroannular one. This agrees well with the results of Butler and colleagues [7] reported on the homoannular complexation of the non methylated equivalent of **4** with the palladium atom upon the action of $Pd(COD)Cl_2$. In the case of dppomf, which bears only one PPh_2 substituent on each cyclopentadienyl ring, the unique heteroannular chelation on $W(CO)_4$ is allowed resulting in some strained metric parameters over the W–P bonds [8].



Scheme 3.

When **13** is heated in boiling heptane for 48 h with an excess of $Cr(CO)_4NBD$, another compound is formed. Because of its very poor solubility, only its ^{31}P-NMR spectrum ($CDCl_3$, + 71.2 ppm, singlet) could be recorded. This compound could be the trimetallic complex because no ^{31}P resonance appears in the field corresponding to the non complexed phosphorus atoms.

2.4. Crystallographic studies

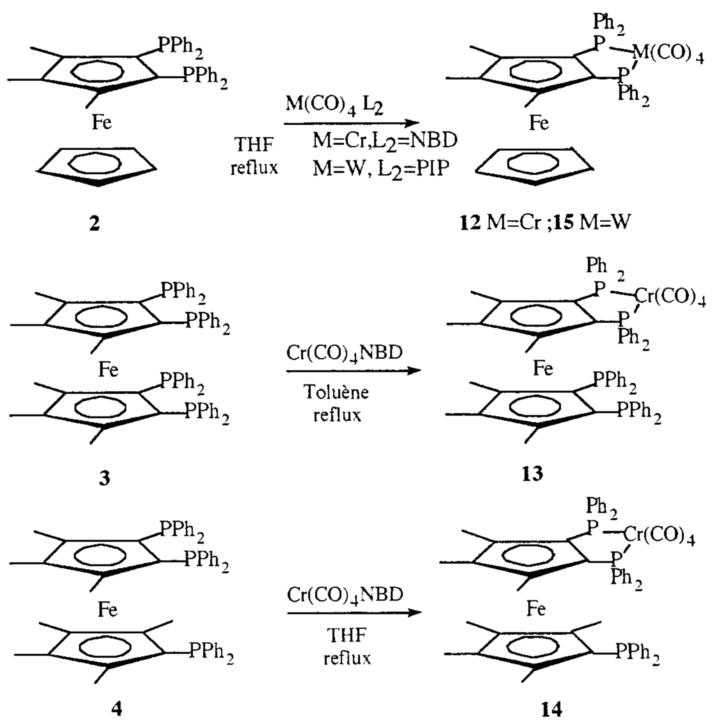
2.4.1. Structure of $[C_5Me_3(PPh_2)_2]_2Fe$ **3**

Complex **3** crystallizes in the monoclinic system (space group $P2_1/c$) with two organometallic molecules in the unit cell. Thus, the iron atoms occupy a set of special positions on the symmetry centers. The centrosymmetric geometries have been also found for 1,1′-ferrocenes such as dppf $(C_5H_4PPh_2)_2Fe$ [13] and dppomf $(C_5Me_4PPh_2)_2Fe$ [14].

The molecular structure of **3** is shown on Fig. 1. 1,2-substitutions on cyclopentadienyl rings in **3** have some geometrical consequencies. The phosphorus atoms exhibit a greater displacement from the ring plane outside the iron atom (0.38 and 0.09 Å, *exo*-type) than in the case of monosubstituted rings in dppomf (0.07 Å, *exo*-type) [14]. The orientations of phosphorus lone pairs may be estimated from Fig. 2. Their repulsions may explain the 0.38 Å displacement of P1 atom from Cp plane. The four phenyl groups of two PPh_2 substituents on the same Cp cycle form two pairs of nearly parallel rings. The dihedral angles are equal to 4° for Ph6 (C6–C65)/Ph8 (C8–C85) pair and 10.6° for Ph7 (C7–C75)/Ph9 (C9–C95) one. The Ph7 and Ph9 planes are separated by some 3.4 Å which corresponds roughly to the usual distance between two parallel π-systems.

2.4.2. Structure of $[C_5Me_3(SCH_2CH_2CH_3)_2]_2Fe$ **6**

Complex **6** crystallizes in the triclinic system (space group P-1) with one organometallic molecule per unit cell. Thus, like in the structure of **3**, the molecules have crystallographic center of symmetry. The presence of this center has been also observed in the structure of 1,1′-diphenylsulfanylferrocene $Fe(C_5H_4SPh)_2$ [15]. The molecular structure of **6** is shown on Fig. 3. All n-propyl groups of SR substituents on the C_5 rings are pushed outside from the $Fe(C_5)_2$ building block, as it was the case of the phenyl groups in $Fe(C_5H_5)(C_5H_4SPh)$ and $Fe(C_5H_4SPh)_2$ [15]. The dihedral angles between the (C1–C5) plane and the planes formed by C1/S1/C6 and C2/S2/C9 atoms are equal to 91.1(2) and 81.8(2)°, respectively. These observations agree with our previous EHMO study carried out on $Fe(C_5H_4SMe)_2$ which favours the out-of-plane *exo* conformation of *R* with respect to the out-of-plane *endo* one [3]. Contrary to the phosphorus atoms in **3** (*exo* structure), the sulfur atoms in **6** are displaced from the Cp ring best planes toward the iron atom by − 0.065 Å for S1 and by − 0.074 Å for S2 (*endo* structure). Such subtleties should account for an estimation of the mutual importance of steric and electronic effects in complexes in which the PR_2 and SR groups are present. The PR_2 substituted ligand is bulkier than that bearing SR groups. Thus, the cyclopentadienyl planes are separated by 3.34 Å in **3** and by 3.30 Å in **6**. The smaller separation of these planes observed in **6** may suggest that, because of steric requirements, the sulfur atoms should exhibit an *exo* displacement from the ring planes which is not a case. In addition, the electronic effects seem to agree with displacements observed. It has been suggested, that the electronic effect of one PPh_2 substituent on the ring is equivalent to that of one methyl group [16] and behaves so as electron donor. Moreover, the repulsions between two lone pairs of phosphorus



Scheme 4.

atoms from one cycle (Fig. 2) and the π -electrons cloud of the second one push the phosphorus atoms outside the rings. In the case of SR substituents, such repulsions may be compensated by activation of the d atomic orbitals of sulfur able to accept an excedent electron density and to form a weak bonding interaction with iron atom [4,17]. The energy of empty d orbitals is lower in sulfur than in phosphorus, so the partial population of these orbitals should be more easily reached in the thiolate SR than in the phosphide PR_2.

2.4.3. Structure of $(CO)_4W[C_5Me_3(PPh_2)_2]_2[C_5H_5]Fe$ **15**

The crystal structure of **15** is built of dinuclear organometallic molecules and of disordered molecules of chloroform. The structure of organometallic molecule is shown on Fig. 4 and some selected bond distances and angles are reported in Table 2. The metallic fragments exhibit their usual 'sandwich' (Fe) and distorted octahedral (W) geometries.

The Fe–Cp plane distances (1.66 and 1.65 Å) found in **15** fall well in the range of values previously observed for dppomfW$(CO)_4$ [8] (1.64 and 1.65Å), **3** (1.67 Å) and dppf [13] (1.65 Å). It is, however, very interesting that the distance of the iron atom from the non-substituted cycle (Cp2, C10–C14) is longer than that involving the bulky Cp1 (C5–C9) one. Different factors explain this apparent contradiction. The lone pairs of phosphorus atoms in the metalloligand (complex **2**) are now involved in the bonding with $M(CO)_4$ fragment. Because of the presence of electron-withdrawing carbonyl ligands in this fragment, the electron density retained on C5–C9 ring should be lower than in the non-complexed phosphinoferrocenes like **2** and **3**. The complexation with $W(CO)_4$ modifies the geometry of 1,2-$(PPh_2)_2C_5Me_3$ ligand (Fig. 5). The Ph21 and Ph33 phenyl rings, corresponding to the Ph7 and Ph9 in the structure of **3** (Fig. 2), are no longer close and parallel. Consequently, two other phenyl groups Ph15 and Ph27 (Ph6 and Ph8 in **3**) move toward the *endo* positions (between the cyclopentadienyl rings) pushing the C_5H_5 ring away from the iron atom. The presence of C_2O_2 carbonyl group in this *endo* space may also contribute to the remoteness of C_5H_5 ring.

The tungsten-phosphorus distances of 2.506(5) Å are slightly shorter than those usually observed for tungsten–phosphine or diphosphine bonds (2.52–2.54 Å) [18,19] but correspond well to the Mo–P bond lengths reported for the molybdenum carbonyl complexes with 1,2-bis(diphenylphosphino)ethylene ligand (2.50 Å) [20]. These W–P distances are clearly shorter than those observed in the structure of dppomfW$(CO)_4$ (2.602(3) Å) [8] where the chelation occurs in heteroannular manner. The bite angle P–W–P of 80.0° in **15** is more acute than in dppomfW$(CO)_4$ (97.9(2)°), as expected, and corresponds well to that found in *cis*-Mo$(CO)_4$ complex with 1,2-bis(diphenylphosphino)ethylene (78.6°).

Like in the structure of **3**, the phosphorus atoms P1 and P2 exhibit an *exo* displacement from the best cyclopentadienyl plane (C5–C9, Cp1) by + 0.29 and + 0.09 Å, while the tungsten atom is found in an *endo*

Table 1
$^{31}P\{H^1\}$-NMR data, δ (ppm)

		M = Cr		M = W	
dppomf	−22.6	dppomf$Cr(CO)_4$	45.6	dppomf$W(CO)_4$	17.2
2	−17.9	**12**	65.8	15	29.4
3	−19.8	**13**	69.0		
			−19.4		
4	−18.8	**14**	67.3		
	−22.3		−23.9		

position with respect to this plane by −0.07 Å. Consequently, the C5/P1/W/P2/C9 fragment adopts a very flat chair conformation.

3. Experimental details

3.1. 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. $Cr(CO)_4$NBD (NBD = norbornadiene) [21] and $W(CO)_4$PIP (PIP = piperidine) [22] were prepared by literature procedures. 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 spectra were recorded on a Bruker AC 200. The spectra were referenced to TMS or H_3PO_4. ^{13}C spectra were recording using the JMOD technique. The following abbreviations appear in the text I, II, II and IV for the primary, secondary, tertiary and quaternary carbon atoms, respectively.

*3.2. $[C_5Me_3(PPh_2)_2](C_5H_5)Fe$ **2***

A yellow solution of the 1,2-bis(diphenylphosphino)-3,4,5-trimethylcyclopentadienyllithium salt **1** (5.6 g; 8.8 mmol) in THF (100 ml) was added dropwise to an orange suspension of $FeCl_2$ (1.13 g; 8.8 mmol) in THF (100 ml) previously cold to 0°C. The mixture took an intense violet coloration. After the end of the addition, the mixture was cooled to −80°C and a solution of cyclopentadienyllithium (0.65 g; 9.0 mmol) in THF (50 ml) was then added dropwise. The cold bath was then removed and the mixture led to warm to r.t.. THF was removed and replaced with toluene (100 ml). The brown mixture thus obtained was heated at reflux for 3 h. It was filtered in air on silica (2–3 cm high) by elution with toluene. The solvent was removed and the residue was chromatographied on a silica column with toluene as eluent. Three successive fractions were observed: the first one (yellow) contained the ferrocene, the second (bright red) contained the bis[1,2-bis-(diphenylphosphino)trimethylcyclopentadienyl]iron **3**, and the last one, (orange) contained the expected product. The solvent was removed from the last one and the residue was recrystallized from a dichloromethane/pentane mixture (3.5 g; 67% yield). M.p. = 168°C.

Anal. Found: C, 74.44; H, 5.64; P, 10.72. $C_{37}H_{34}P_2Fe$. Calc.: C, 74.51; H, 5.75; P, 10.39. Mass spectrum (EI): 596 [M^+, 100]; 519 [$(M\text{-}Ph)^+$, 10]; 475 [$(M\text{-}Cp\text{–}Fe)^+$, 10]; 411 [$(M\text{-}PPh_2)^+$, 20]. ^1H-NMR, $CDCl_3$: 1.54 (s, 6H, Me); 1.96 (s, 3H, Me); 3.80 (s, 5H, Cp); 7.05-7.13 (m, 12H, phenyl); 7.25–7.33 (m, 4H, phenyl); 7.53–7.59 (m, 4H, phenyl). ^{13}C-NMR, $CDCl_3$: (I) 11.9 (pt, βMe, $|J_{PC}| = 4.5$ Hz); 13.3 (pt, αMe, $|J_{PC}| = 4.5$ Hz); (III) 72.5 (pt, Cp, $|J_{PC}| = 7.4$ Hz); 127,5 (s, *meta*); 127.7 (very broad s, *meta′* + *para*); 128.3 (s, *para*); 133.2 (pt, *ortho*, $|^2J_{PC} + {}^5J_{PC}| = 20.2$ Hz); 135.8 (pt, *ortho′*, $|^2J_{PC} + {}^5J_{PC}| = 21.6$ Hz); (IV) 80.2 (pt, *ipso* Cp, $|^1J_{PC} + {}^2J_{PC}| = 14.4$ Hz); 87.9 (s, α Cp); 88.3 (s, β Cp); 137.4 (pt, *ipso* phenyl, $|^1J_{PC} + {}^4J_{PC}| = 7.6$ Hz); 138.7 (pt, *ipso′* phenyl, $|^1J_{PC} + {}^4J_{PC}| = 7.8$ Hz). ^{31}P-NMR, $CDCl_3$: −17.9 (s).

*3.3. $[C_5Me_3(PPh_2)_2]_2Fe$ **3***

A yellow green solution of the 1,2-bis(diphenylphosphino)-3,4,5-trimethyl-cyclopentadienyllithium anion **1** (4.42 g; 7.0 mmol) in toluene (100 ml) was added at r.t. to Fe_2Cl_4, 3THF (0.82 g; 1.75 mmol). The mixture was heated to reflux for 3 h after which time it had become red. It was then filtered in air on 2–3 cm of silica and eluted with toluene. The filtrate was concentrated and then kept at 0°C for two days. 2.92 g (2.9 mmol; 83% yield) of thin bright red crystals were isolated. M.p. = 218°C (decomposition). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a chloroform/hexane mixture.

Anal. Found: C, 76.32; H, 5.73; P, 12.00. $C_{64}H_{58}P_4Fe$. Calc.: C, 76.34; H, 5.81; P, 12.30. Mass spectrum (EI): 1006 [M^+, 100]; 821 [$(M\text{-}PPh_2)^+$, 25]; 744 [$(M\text{-}PPh_2\text{–}Ph)^+$, 10]. ^1H-NMR, $CDCl_3$: 1.58 (s, 12H, Me); 1.86 (s, 6H, Me); 7.03–7.54 (m, 40H, phenyl). ^{13}C-NMR, $CDCl_3$: (I) 11.2 (s, βMe); 13.8 (s, αMe); (III) 127.5 (broad s, *meta*); 127.6 (broad s,

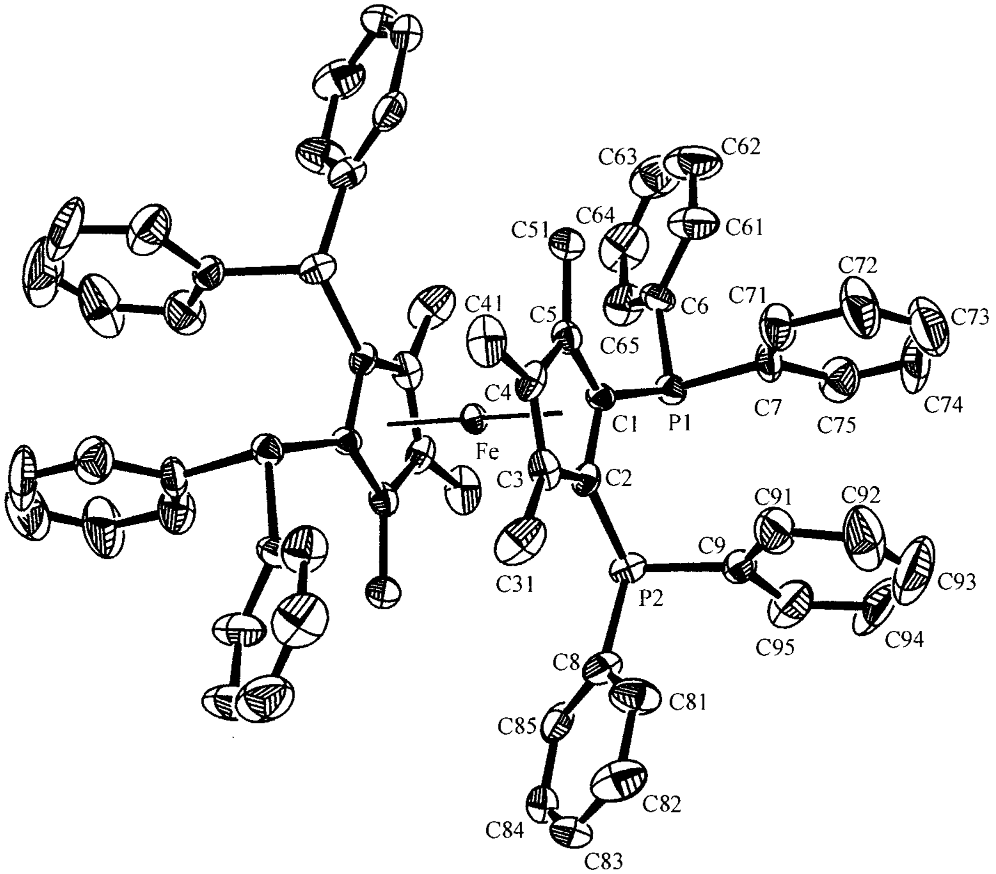


Fig. 1. ORTEP drawing of the structure of **3**. 50% Probability level. The Fe–C_5 plane distances are equal to 1.67 Å.

meta'); 128.1 (s, *para* and *para'*); 134.6 (pt, *ortho*, $|^2J_{PC}+{}^5J_{PC}| = 24.0$ Hz); 136.6 (pt, *ortho'*, $|^2J_{PC}+{}^5J_{PC}| = 24.0$ Hz); (IV) 80.6 (s, *ipso* Cp); 88.1 (s, $\alpha+\beta$ Cp); 137.9 (pt, *ipso* phenyl, $|^1J_{PC}+{}^4J_{PC}| = 6.6$ Hz); 138.6 (pt, *ipso'* phenyl, $|^1J_{PC}+{}^4J_{PC}| = 5.0$ Hz). ^{31}P-NMR, $CDCl_3$: -19.8 (s).

3.4. *$[C_5Me_3(PPh_2)_2][C_5Me_4(PPh_2)]Fe$* **4**

The procedure was the same used for the preparation of the diphosphine **2**. The resulting mixture contained three different polyphosphines which were separated from each other by silica-chromatography using a toluene/hexane eluent (1/1). The first fraction (orange) contained the dppomf, the second one (bright red) contained the symmetric species **3** and the last one (orange) led, after removal of the solvents, to an orange solid. After recrystallization from a toluene/pentane mixture, thin orange crystals of **4** were isolated (63% yield). M.p. = 170°C.

Anal. Found: C, 76.09; H, 6.14; P, 9.80. $C_{53}H_{51}P_3Fe$. Calc.: C, 76.08; H, 6.14; P, 11.10. Mass spectrum (EI): 836 [M^+, 100]; 759 [$(M\text{-}Ph)^+$, 10]; 651 [$(M\text{-}PPh_2)^+$, 20]; 361 [$(M\text{-}C_5Me_3(PPh_2)_2)^+$, 10]. ^{1}H-NMR, $CDCl_3$: 1.26 (s, 6H, Me); 1.64 (s, 6H, Me); 1.73 (s, 6H, Me); 1.93 (s, 3H, Me); 6.85–7.45 (m, 30H, phenyl). ^{13}C-NMR, $CDCl_3$: (I) 10.5 (s, Me); 10,9 (s, 2C, Me); 12.5 (s, 2C, Me); 12.9 (s, 2C, Me); (III) 127.4 (broad s, *meta* or *para*); 127.9 (broad s, *meta* or *para*); 128.1 (broad s, *meta* or *para*); 128.2 (broad s, *meta* or *para*); 128.4 (broad s, *meta* or *para*); 134.3 (pt, *ortho*A, $|^2J_{PC}+{}^5J_{PC}| = 23.0$ Hz); 135.0 (d, *ortho*B, $^2J_{PC} = 21.2$ Hz); 136.6 (pt, *ortho*A', $|^2J_{PC}+{}^5J_{PC}| = 24.6$ Hz); (IV) 74.1 (d, *ipso* CpB, $^1J_{PC} = 17.2$ Hz); 79.2 (broad s, *ipso* CpA); 84.3 (d, α CpB, $^2J_{PC} = 1.6$ Hz); 84.5 (d, β CpB, $^3J_{PC} = 8.3$ Hz); 86.8 (pt, α CpA, $|^2J_{PC}+{}^3J_{PC}| = 10.0$ Hz); 87.5 (broad s, β CpA), 137.9 (d, *ipso*B phenyl, $J_{PC} = 12.9$ Hz); 138.1 (pt, *ipso*A phenyl, $|^1J_{PC}+{}^4J_{PC}| = 13.0$ Hz); 138.9 (pt, *ipso*A' phenyl, $|^1J_{PC}+{}^4J_{PC}| = 8.8$ Hz). ^{31}P-NMR, $CDCl_3$: -22.3 (s, 1P); -18.8 (s, 2P).

3.5. *$C_5Me_3(SCH_2CH_2CH_3)_2Na$* **5**

A 2.60 ml volume (165 mmol) of dipropyldisulfane were added to a suspension of 1,2,3-trimethylcyclopentadienylsodium (1.07 g; 8.2 mmol) and sodium hydride (0.80 g; 33.3 mmol) in THF (80 ml). A thick white suspension quick appeared and the mixture was heated to 50°C for 40 h. The white solid and the excess of NaH were separated by filtration, washed by two times 20 ml of THF and eliminated. The solvent was removed from the brown orange filtrate and the residue was

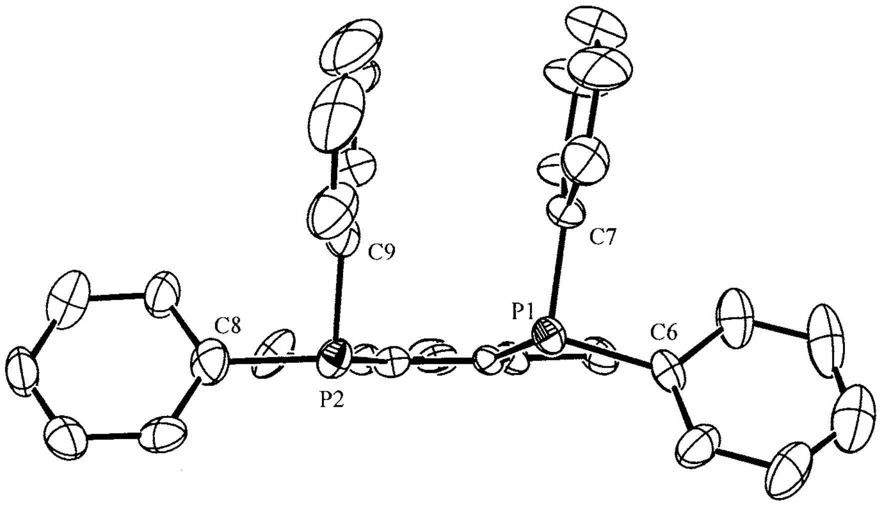


Fig. 2. Geometry of one ligand in the structure of **3**.

washed with diethyl ether to give compound **5** as a very air sensitive white solid (0.94 g; 41% yield).

^1H-NMR, THF-d_8: 0.93 (t, 3H, CH_3, 7.3 Hz); 1.48 (sx, 2H, CH_2, 7.3 Hz); 1.98 (s, 3H, βCH_3); 2.15 (s, 6H, αCH_3); 2.37 (t, 2H, SCH_2, 7.3 Hz).

3.6. $[C_5Me_3(SCH_2CH_2CH_3)_2]_2Fe$ **6**

A solution of 3,4,5-trimethyl-1,2-di(propylsulfanyl)cyclopentadienylsodium (1.28 g; 4.6 mmol) in THF (20 ml) was added to a suspension of Fe_2Cl_4, 3 THF (0.54 g; 1.15 mmol) in THF (20 ml). The resulting brown suspension was heated at reflux overnight. The solvent was removed under reduced pressure and replaced by diethyl ether (30 ml). The mixture was then hydrolysed and the organic layer was collected. The aqueous layer was extracted several times with diethyl ether and the various organic layers were put together and dried over $MgSO_4$. After filtration, the solvent was removed and the residue was recrystallized from pentane leading to compound **6** as a red solid (0.71 g; 54% yield). M.p. = 124°C.

Anal. Found: C, 59.2; H, 8.1; S, 22.5. $C_{28}H_{46}S_4Fe$ C. Calc.: C, 59.3; H, 8.2; S, 22.6. Mass spectrum (EI): 566[M^+, 100], 480[$(M-2C_3H_7+H)^+$, 8]; 448[$(M-2C_3H_7-S+H)^+$, 9]; 394[$(M-4C_3H_7)^+$, 20]; 362[$(M-3C_3H_7-S)^+$, 6]. ^1H-NMR, C_6D_6: 0.85 (t, 12H, CH_3, 7.3 Hz); 1.47 (sx, 8H, CH_2, 7.3 Hz); 2.08 (s, 6H, βMe); 2.21 (s, 12H, αMe); 2.40 (m, 4H, SCH_a, 7.3 Hz, 21.6 Hz); 2.51 (m, 4H, SCH_b, 7.3 Hz, 21.6 Hz). ^{13}C-NMR, C_6D_6: 10.5 (αMe or βMe); 10.8 (αMe or βMe); 13.5 (CH_3); 23.3 (CH_2); 38.4 (SCH_2); 82.9 (Cp); 84.8 (Cp), 88.3 (Cp).

3.7. $[C_5Me_3(SCH_2CH_2CH_3)2](C_5H_5)Fe$ **7**

A solution of a mixture of **5** (1.96 g; 7.04 mmol) and cyclopentadienylsodium (0.62 g; 7.04 mmol) in THF (20 ml) was added dropwise to a boiling suspension of Fe_2Cl_4,3THF (1.65 g; 3.51 mmol) in THF (20 ml). The reflux was maintained for 12 h. The solvent was removed and replaced by diethyl ether and the mixture was then hydrolysed. After removal of the solvent from the organic layer, the oily residue contains a mixture of ferrocene (25%), compound **6** (25%) and compound **7** (50%). The residue was then chromatographied with a toluene/hexane eluent (1/1). The last collected fractions gave, after removal of the solvents, 0.65 g (24%) of compound **7** isolated as an oily product.

Anal. Found: C, 60.16; H, 7.54; S, 14.47. $C_{19}H_{28}FeS_2$. Calc.: C, 60.63; H, 7.50; S, 14.84. ^1H-NMR, C_6D_6: 0.89 (t, 6H, CH_3, 7.3 Hz); 1.52 (sx, 4H, CH_2, 7.3 Hz); 1.77 (s, 3H, βMe); 2.09 (s, 6H, αMe); 2.54 (m, 4H, SCH_2); 3.83 (s, 5H, Cp). ^{13}C-NMR, C_6D_6: 12,7 (αMe or βMe); 13.3 (αMe or βMe); 14.4 (CH_3); 24.2 (CH_2); 40.6 (SCH_2); 73.6 (C_5H_5); 84.2 (Cp); 84.3 (Cp); 88.1 (Cp).

3.8. $[C_5Me_3(PPh_2O)_2](C_5H_5)Fe$ **8**

Five drops of a 30% hydrogen peroxide solution were added to an orange solution of complex **2** (0.1 g; 0.17 mmol) in dichloromethane (15 ml). After 30 min stirring, the solution was washed by 3 × 10 ml of distilled water. The organic layer was then dried over $MgSO_4$ and the solvent removed led to compound **8** as a yellow powder (0.1 g; 0.16 mmol; 94% yield). M.p. = 220°C (decomposition).

Anal. Found: C, 67.99; H, 5.43; P, 9.08. $C_{37}H_{34}O_2P_2Fe$. Calc.: C, 70.71; H, 5.45; P, 9.86.

Mass spectrum (EI): 628 [M^+, 10]; 429 [$(M-PPh_2O)^+$, 10]; 201 [$(PPh_2O)^+$, 100]. ^1H-NMR, $CDCl_3$: 1.76 (s, 6H, Me); 1.98 (s, 3H, Me); 3.99 (s, 5H, Cp); 7.17–6.65 (m, 20H, phenyl). ^{13}C-NMR, $CDCl_3$: (I) 12.1

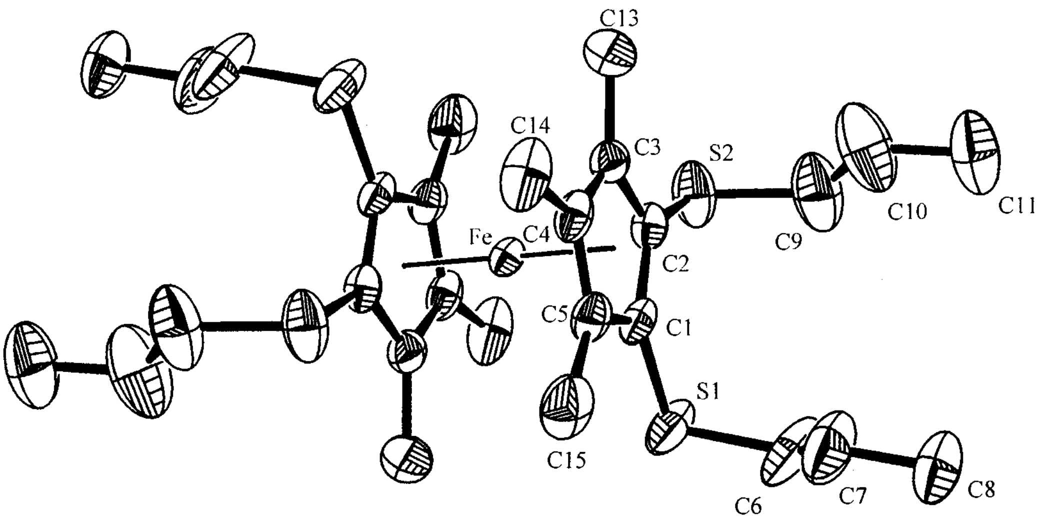


Fig. 3. ORTEP drawing of the structure of **6**. 30% Probability level. The Fe–C_5 plane distances are equal to 1.648 Å.

(s, β Me); 14.6 (s, α Me); (III) 73.9 (s, Cp); 127.6 (t, *meta*, $^3J_{PC} = 12.5$ Hz); 131.1 (s, *para*); 132.4 (d, *ortho*, $^2J_{PC} = 10.0$ Hz); (IV) 74.4 (d, *ipso* Cp, $^1J_{PC} = 12.5$ Hz); 76.6 (d, *ipso′* Cp, $^1J_{PC} = 12.0$ Hz); 89.9–90.1 (m, α Cp, α' Cp, β Cp, β' Cp); 134.3 (d, *ipso* phenyl, $^1J_{PC} = 56.0$ Hz); 136.4 (d, *ipso′* phenyl, $^1J_{PC} = 54.5$ Hz). ^{31}P-NMR, $CDCl_3$: + 32.0 (s).

3.9. *[$C_5Me_3(PPh_2O)_2]_2Fe$* **9**

Fifteen drops of a 30% hydrogen peroxide solution were added to a red solution of the tetraphosphine **3** (0.1 g; 0.1 mmol) in dichloromethane (18 ml). After 30 min stirring, the solution was washed three times with 10 ml of distilled water. The organic layer was then dried over $MgSO_4$ and the solvent was removed, leading to compound **9** isolated as a dark red solid (0.11 g; 0.1 mmol; 100% yield). Recrystallization from a dichloromethane/pentane mixture gave red parallelepipedic crystals which turned into a thin powder when separated from the mother solution. M.p. = 190°C (decomposition).

Anal. Found: C, 69.46; H, 5.17; P, 11.84. $C_{64}H_{58}O_4P_4Fe$. Calc.: C, 71.78; H, 5.46; P, 11.57. Mass spectrum (EI): 1070 [$M^{+\cdot}$ 60]; 869 [$(M\text{-}PPh_2O)^+$, 10]; 508 [$(M\text{-}C_5Me_3(PPh_2O)_2\text{–}Fe)^{+\cdot}$ 60]; 417 [$(M\text{-}C_5Me_3(PPh_2O)_2\text{–}Fe\text{–}Me\text{–}O)^+$, 15]; 307 [$(M\text{-}C_5Me_3(PPh_2O)_2\text{–}Fe\text{–}PPh_2O)^+$, 90]; 201 [$(PPh_2O)^+$, 90]; 183 [$(PPh_2)^+$, 75]; 77 [$(Ph)^+$, 100]. ^{1}H-NMR, $CDCl_3$: 2.13 (s, 6H, Me); 2.87 (s, 3H, Me); 6.75-7.33 (m, phenyl). ^{31}P-NMR, $CDCl_3$: + 29.7 (s).

3.10. *[$C_5Me_3(PPh_2)_2Cr(CO)_4](C_5H_5)Fe$* **12**

An orange solution of **2** (0.1 g; 0.17 mmol) and $Cr(CO)_4$ NBD (0.12 g; 0.47 mmol) in toluene (40 ml) was heated at reflux for 4 h [7]. Toluene was then removed and the orange solid thus obtained was chromatographied on a silica column with a toluene/hexane (1/1) eluent. The first yellow fraction contained the excess of $Cr(CO)_4$ NBD. After removal of the solvent from the second fraction, 0.11 g (1.4 mmol; 85% yield) of a yellow solid was isolated and recrystallized from a dichloromethane/pentane mixture. M.p. > 280°C.

Anal. Found: C, 60.67; H, 4.14; P, 7.70. $C_{41}H_{34}O_4P_2CrFe$. Calc.: C, 59.67; H, 4.29; P, 7.33. Mass spectrum (EI): 760 [M^+, 10]; 705 [$(M\text{-}2CO)^+$, 5]; 676 [$(M\text{-}3CO)^+$, 30]; 648 [$(M\text{-}4CO)^+$, 100]; 596 [$(M\text{-}Cr(CO)_4)^+$, 5]; 463 [$(M\text{-}4CO\text{-}PPh_2)^+$, 10]. IR (THF) νCO (cm^{-1}): 1879 broad; 1922; 2007. ^{1}H-NMR, $CDCl_3$: 1.67 (s, 6H, Me); 2.03 (s, 3H, Me); 3.76 (s, 5H, Cp); 7.00–7.20 (m, phenyl), 7.48 (s, broad, phenyl); 8.01–8.12 (m, phenyl). ^{31}P-NMR, $CDCl_3$: + 65.8 (s).

3.11. *[$C_5Me_3(PPh_2)_2Cr(CO)_4][C_5Me_3(PPh_2)_2]Fe$* **13**

A mixture of tetraphosphine **3** (0.20 g; 0.19 mmol) and $Cr(CO)_4NBD$ (0.072 g; 0.28 mmol) in toluene (20 ml) was heated at reflux for 5 h. The solvent was then removed and the oily residue was chomatographied on a silica column with a toluene/hexane (2/1) eluent. Three fractions were successively eluted from which $Cr(CO)_4NBD$, tetraphosphine **3** and complex **13** were characterized respectively. After removal of the solvents, the product was isolated as red solid (0.16 g; 0.14 mmol; 76% yield). M.p. > 300°C.

^{1}H-NMR, $CDCl_3$: 1.24 (s, 6H, Me); 1.84 (s, 6H, Me); 2.13 (s, 3H, Me); 2;67 (s, 3H, Me); 6.69-8.14 (m, 40H, phenyl). ^{31}P-NMR, $CDCl_3$: − 19.4 (s); + 69.1 (s). IR (THF) νCO (cm^{-1}): 1979 (broad); 1923; 2008.

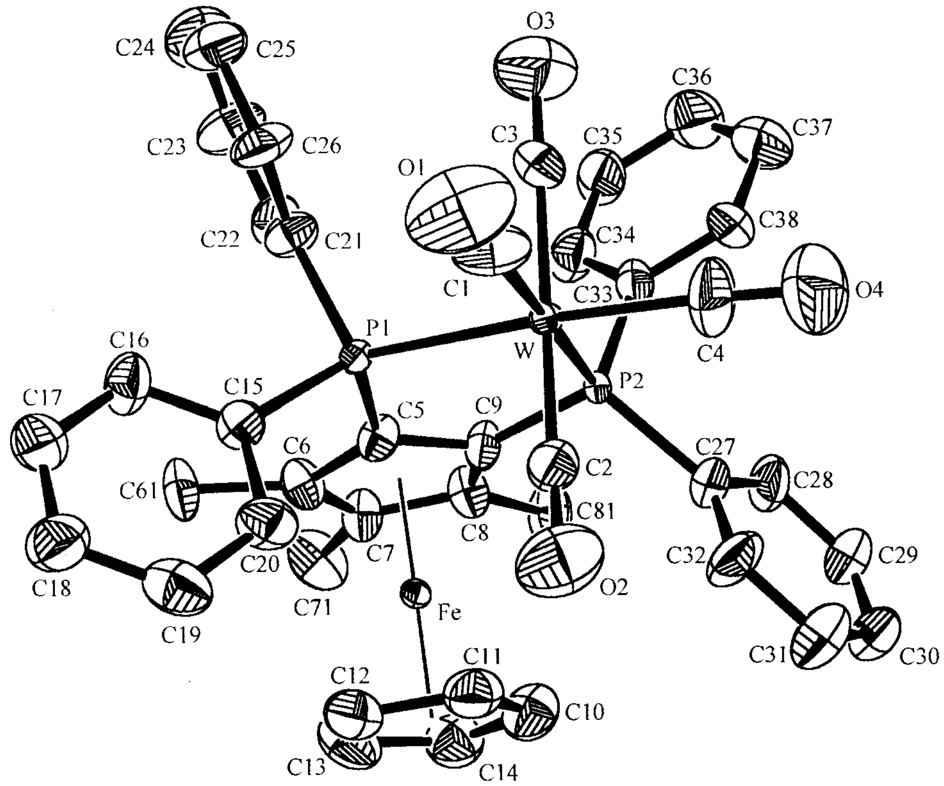


Fig. 4. ORTEP drawing of the molecular structure of **15**. 30% Probability level.

3.12. $[C_5Me_3(PPh_2)_2Cr(CO)_4][C_5Me_4(PPh_2)]Fe$ **14**

A solution of a mixture of the triphosphine **4** (0.12 g; 0.14 mmol) and $Cr(CO)_4NBD$ (0.037 g; (0.14 mmol) in THF (20 ml) was heated at reflux for 4 h. The solvent was then removed and the residue was recrystallized from a chloroform/hexane mixture. Complex **14** was isolated as bright red crystals (0.12 g; 0.12 mmol; 86% yield). M.p. > 300°C (decomposition).

Mass spectrum (EI): 888 [$(M\text{-}4CO)^+$, 80]; 836 [$(M\text{-}Cr(CO)_4)^+$, 20]; 651 [$(M\text{-}Cr(CO)_4)\text{–}PPh_2)^+$, 20]. IR (THF) νCO (cm^{-1}): 1877; 1923; 2007. ^1H-NMR $CDCl_3$: 0.69 (s, 6H, Me); 1.33 (s, 6H, Me); 2.02 (s, 6H, Me); 2.19 (s, 3H, Me); 6.75–7.63 (m, phenyl); 8.17–8.28 (m, phenyl). ^{31}P-NMR, $CDCl_3$: -23.9 (s, 1P); $+67.3$ (s, 2P).

Table 2
Selected bonds (Å) and angles (°) for **15**

Distances		Bonds	
W–Fe	4.708(3)	P1–W–P2	80.0(2)
W–P1	2.506(5)	C1–W–C2	86.6(8)
W–P2	2.506(5)	C3–W–C4	89.5(9)
W–C1	1.97(2)	P1–W–C1	97.1(8)
W–C2	1.98(2)	P2–W–C1	175.6(8)
W–C3	1.98(2)	P1–W–C2	92.9(6)
W–C4	2.01(3)	P2–W–C2	96.8(6)
Fe–CP1	1.648	P1–W–C3	89.6(7)
Fe–CP2	1.656	P2–W–C3	91.0(7)
		P1–W–C4	169.6(8)
		P2–W–C4	89.9(8)
		CP1–Fe–CP2	173

CP1 and CP2 are the geometrical centres of C5–C9 and C10–C14 rings, respectively.

3.13. $[C_5Me_3(PPh_2)_2W(CO)_4](C_5H_5)Fe$ **15**

An orange solution of compound **2** (0.20 g; 0.34 mmol) in THF (20 ml) was added to a suspension of $W(CO)_4$ $(PIP)_2$ (0.164 g; 0.36 mmol) [8] in THF (10 ml). The mixture was heated with reflux for 4 h and was then filtered in air. The solvent was removed and the resulting orange solid was recrystallized from a chloroform/hexane mixture. The product was isolated as orange crystals (0.32 g; 0.30 mmol; 88% yield) containing one molecule of chloroform per bimetallic unit. M.p. > 300°C.

Anal. Found: C, 50.24; H, 3.56; P, 6.29; W, 17.90. $C_{41}H_{34}O_4P_2FeW$, $CHCl_3$.Calc.: C, 49.86; H, 3.49; P, 6.12; W, 18.17. Mass spectrum (EI): 892 [M^+, 70]; 864 [$(M\text{-}CO)^+$, 90]; 836 [$(M\text{-}2CO)^+$, 10]; 808 [$(M\text{-}3CO)^+$, 100]; 780 [$(M\text{-}4CO)^+$, 30]; 596 [$(M\text{-}W(CO)_4)^+$, 25]. IR (THF) νCO en cm^{-1}: 1880 (large); 1919; 2015. ^1H-NMR, $CDCl_3$: 1.71 (s, 6H, Me); 2.04 (s, 3H, Me); 3.76 (s, 5H, Cp); 7.06–7.25 (m, phenyl); 7.50 (broad s, phenyl); 7.98-8.07 (m, phenyl). ^{13}C-NMR, $CDCl_3$: (I) 13.1 (pt, β Me, $|J_{PC}| = 4.2$ Hz); 13.5 (pt, α Me, $|J_{PC}| = 4.2$ Hz); (III) 73.4 (pt, Cp, $|J_{PC}| = 7.0$ Hz); 128.2–128.7

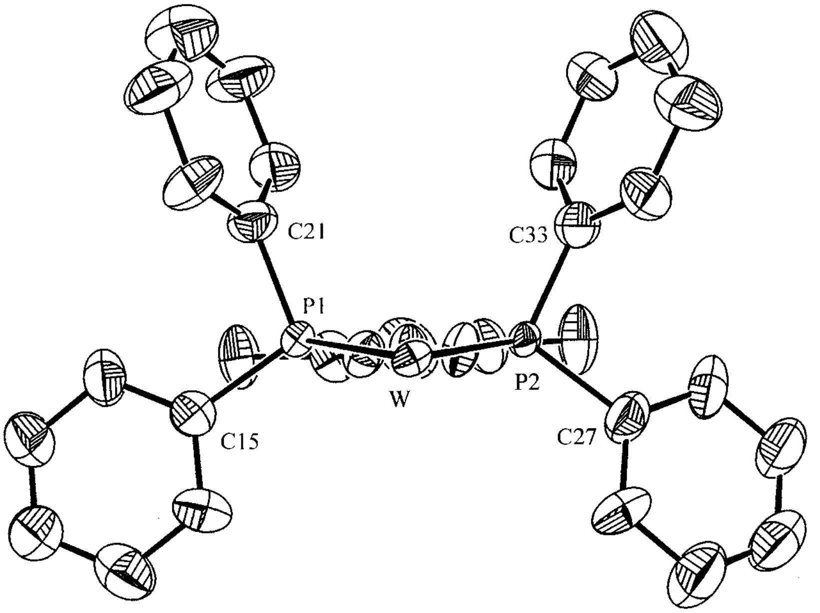


Fig. 5. Geometry of the ligand complexed to the W atom in the structure of **15**.

Table 3
Crystallographic data

Compound	**3**	**6**	**15**
Formula	$C_{64}H_{58}P_4Fe$	$C_{28}H_{46}S_4Fe$	$C_{42}H_{35}Cl_3O_4P_2FeW$
Formula weight (g mol^{-1})	1006.92	566.78	1011.75
Crystal: color, size (mm)	Yellow; 0.3, 0.2, 0.1	Yellow; 0.3, 0.3, 0.1	Yellow; 0.4, 0.2, 0.15
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a (Å)	14.200(2)	8.794(1)	20.837(4)
b (Å)	14.006(1)	9.856(2)	10.197(2)
c (Å)	13.910(3)	10.368(2)	21.108(4)
α (°)		67.58(1)	
β (°)	112.24(2)	88.82(1)	112.76(1)
γ (°)		68.40(1)	
V (Å^3)	2560.8	764.8	4135.8
Z	2	1	4
D_{calcd} (g cm^{-3})	1.306	1.231	1.625
F(000)	1056	304	2000
Radiation, Mo–Kα, λ, (Å)	0.71073	0.71073	0.71073
Lin. abs., μ(Mo–K$_\alpha$) (cm^{-1})	4.560	7.685	35.009
Reflections measured	5957	3272	9115
Linear decay (%)	−2.2, corrected	−3.3, corrected	−9.3, corrected
Abs.cor.,DIF ABS,min/max	0.8596/1.0596		0.7077/1.3654
Ψ scan, min/max		90.654/99.780	
Cutoff for obsd data	$I \geq 3\sigma(I)$	$I \geq 3\sigma(I)$	$I \geq 3\sigma(I)$
Unique obsd data	2702	1994	4678
No. of variables	319	178	470
$R(F)$	0.088	0.048	0.074
$R_w(F)$	0.099	0.047	0.086
Weight, $w^{-1} = [\sigma^2(I) + (pF_o^2)^2]^{1/2}$, p	0.05	0.04	0.06
Goodness of Fit		0.731	0.950
ρ_{max}/ρ_{min} (eÅ^{-3})	0.57/−0.24	0.43/−0.11	2.41[a]/−0.23

[a] Close to the tungsten atom.

(m, *meta* and *meta'*); 129.4 (s, *para*); 130.9 (s, *para'*); 131.5 (pqt, *ortho*, $|^{2}J_{PC} + {}^{4i}\mathrm{J}_{PC}| = 15.9$ Hz); 135.9 (pqt, *ortho'*, $|^{2}J_{PC} + {}^{4}J_{PC}| = 14.3$ Hz); (IV) 86.7 (pt, *ipso* Cp, $|^{1}J_{PC} + {}^{2}J_{PC}| = 80.2$ Hz); 86.8 (pt, β Cp, $|^{3}J_{PC} + {}^{3}J_{PC}| = 9.0$ Hz); 95.2 (pt, α Cp, $|^{2}J_{PC} + {}^{3}J_{PC}| = 7.6$ Hz); 135.7 (pdd, *ipso* phenyl, $|^{1}J_{PC} + {}^{3}J_{PC}| = 43.9$ Hz); 138.6 (pdd, *ipso'* phenyl, $|^{1}J_{PC} + {}^{3}J_{PC}| = 46.2$ Hz); 198.7 (pt, CO, $|^{2}J_{PC}| = 16.2$ Hz); 209.0 (pt, CO, $|^{2}J_{PC}| = 17.1$ Hz); 209.4 (pt, CO, $|^{2}J_{PC}| = 17.3$ Hz); 209.9 (pt, CO, $|^{2}J_{PC}| = 16.0$ Hz). ^{31}P-NMR, $CDCl_3$: +29.4 (s) $J_{(^{31}P-^{183}W)} = 232$ Hz.

3.14. X-ray structure analyses

Crystals suitable for X-ray diffraction studies were grown from chloroform/hexane (**3** and **15**) or cold pentane (**6**) solutions. The pertinent crystallographic data are gathered in Table 3. All measurements have been carried out on an Enraf-Nonius CAD4 diffractometer at r.t.. The unit cells were determined for each crystal from 25 reflections selected by the CAD4 routines. All calculations were carried out by use of the MOLEN package [23] with neutral-atom scattering factors [24]. Intensities were corrected for Lorentz and polarization effects as well as for linear decay. The Ψ-scan empirical absorption correction was applied for **6**.

The structures were solved and refined by conventional Patterson, difference Fourier, and full-matrix least-squares methods. In the case of **15** a disordered molecule of chloroform was found. Refinement of this molecule led to the ratio 0.8/1 (with respect to the organometallic one) and to an occupation of 0.5 for one set of three chlorine atoms and 0.3 for a second set of these atoms. An empirical absorption correction DIFABS [25] was applied for **3** and **15** after isotropic refinement. All non-hydrogen atoms of organometallic molecules were further refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and included in the final cycles of refinements in a riding model.

4. Supplementary material

Tables of atomic coordinates, anisotropic thermal parameters, and interatomic distances and angles for **3**, **6** and **15** (11 pages).

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