1,1′,2,2′-Tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, a new *cisoid* arrangement of phosphino groups

Roland Broussier [a], Emmanuelle Bentabet [a], Régine Amardeil [a], Philippe Richard [a], Philippe Meunier [a],*, Philippe Kalck [b], Bernard Gautheron [a]

[a] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (UMR 5632), Université de Bourgogne, 6, boulevard Gabriel, 21000 Dijon, France*
[b] *Laboratoire de Catalyse, Chimie fine et Polymères, Ecole Nationale Supérieure de Chimie de Toulouse, 118, route de Narbonne, 31077 Toulouse Cedex, France*

Abstract

The action of two equivalents of 1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyllithium on $FeCl_2$ led to the corresponding 1,1′,2,2′-tetraphosphinoferrocene. The X-ray structure of this bulky ferrocene is described. The spectroscopic results reveal a conformational chirality with a *cisoid* disposition of the phosphino groups. The first results about the complexation with representative elements of Group IX and X (Rh, Pd, Ir) are reported. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Phosphinoferrocene; Group IX and X complexes; *Cisoid*; Arrangement

1. Introduction

In the field of the ferrocene derivatives and their coordination chemistry, di or polyphosphines, as the dppf, are powerful auxiliaries [1]. Several types of di or polyphosphines can be imagined [2] with different substitution patterns on Cp rings and various steric and electronic properties. We have been interested in the 1,2-disubstitution and original representative examples of this class have been synthesized and studied: 1,2-bis(-diphenylphosphino)-3,4,5-trimethylferrocene [3] and 1,2-bis(diphenylphosphino)-4-*tert*-butylferrocene [4]. These ferrocenes were obtained from a mixture of the corresponding substituted and unsubstituted cyclopentadienyl lithium salts and $FeCl_2$. Using this approach and exclusively 1,2-bis(diphenylphosphino)cyclopentadienyl salts, a tetraphosphine of 1,2 and 1′,2′ substitution pattern was expected. Only two ferrocenyltetraphosphines are available: the 1,1′,2,2′-tetrakis(diphenylphosphino)ferrocene recently reported by Butler et al. [2] and its hexamethyl analogue [3]. The

availability of phosphorus atoms and their coordination capacities are in part directed by the backbone rigidity of the ligand as shown in the following polyphosphines. Structurally characterized examples of two biligate coordination modes are reported for branched tetradentate phosphines as 2,3-bis[(diphenylphosphino)methyl] - 1,4 - bis(diphenylphosphino)-butane [5], 1,2,4,5-tetrakis[(diphenylphosphino)methyl] or [diphenyl-phosphino]benzene [6] and *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane [7]. The linear tetradentate $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P$-$(Ph)CH_2CH_2PPh_2$ [8] or $MeHP(CH_2)_3P(Me)(CH_2)_2P$-$(Me)(CH_2)_3PMeH$ [9] and the tripodal tetradentate $P(CH_2CH_2PPh_2)_3$ [10], $P(o\text{-}C_6H_4PPh_2)_3$ [11] or $P(CH_2CH_2CH_2PMe_2)_3$ [12] are tetracoordinated to the metal center. The specific geometry of ferrocene and the independance of the two Cp rings can make a tetraphosphine equivalent to two diphosphines or allow a higher coordination number due to the rings rotation. At this time, the highlighted behavior are of type 1,2-diphosphine for 1,1′,2,2′ tetraphosphine [3] and of type 1,2 or 1,1′ for the 1,2,1′ triphosphine [13]. In this paper, we report a new example of ferrocenic tetraphosphine as well as its behavior towards Pd, Rh and Ir salts leading to various coordination modes.

* Corresponding author. Fax: + 33-3-8039-6100.
E-mail address: philippe.meunier@u-bourgogne.fr (P. Meunier).

Scheme 1.
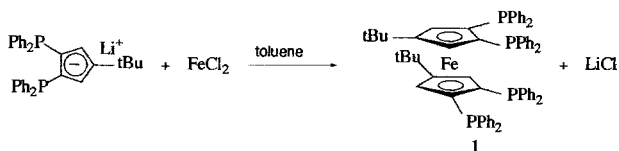
2. Results and discussion

2.1. Synthesis and structure

The reaction of two equivalents of 1,2-bis(diphenylphosphino) - 4 - *tert* - butylcyclopentadienyllithium [4] with $FeCl_2$ in toluene at reflux produces 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene **1** in excellent yield (70% of orange crystals in toluene) (Scheme 1).

1 leads to a well-resolved but complicated ^{31}P-NMR spectrum which cannot be compared with the spectra observed for the others di, tri or tetraferrocenylphosphines [2–4,14], exhibiting only singlets. Fig. 1 shows a diastereotopy for the phosphorus atoms which form an AA′BB′ spin system [14]. The complete spectrum is centrosymetric about 1/2 ($v_A + v_B$) and shows an overlap of twice 12 expected lines. On the basis of calculated spectrum [15], we propose the following coupling constants: $J_{AB} = 75$ Hz, $J_{AA'} = 40$ Hz, $J_{AB'} = 3$ Hz and $J_{BB'} = 2$ Hz. The magnetic nonequivalence between the two groups of phosphorus atoms exists if the molecular symmetry is reduced by the presence of a conformational chirality. A mixture of two enantiomeric conformers not interconnecting rapidly on the NMR time

scale should give AA′BB′ spectrum. The energy barrier to ring rotation in bulky substituted ferrocenes is generally quite low (< 13 kcal mol^{-1} [16]) and the resonance of nonequivalent ring or substituents protons are resolved only in the conformationally 'frozen' molecule when the solution was cooled. In our case, for **1**, the AA′BB′ spectrum remained constant when the temperature was increased up to 90 °C. X-ray structural analysis confirms the NMR observations. The solid-state structure corresponds to a racemic mixture.

The molecular structure of **1** is shown in Fig. 2. This structural study shows an example of conformational chirality or atropoisomery. The two enantiomers are present in the unit cell. The complex is located on a C_2 axis which is bisecting the P(1)–Fe–P(1)* angle. In the ferrocenyl part the two symmetrically related Cp planes are nearly parallel and exhibit a small deviation from an eclipsed conformation (8°) and the observed Fe-centroid (CNT) distance is 1.670 Å.

Several relative orientations can be considered for 1,2,4 substituted cyclopentadienyl rings in the molecule [16]. The minimum energy configuration judging from the X-ray diffraction structure shows four staggered and two eclipsed substituents. This is quite similar to the situation encountered in the 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)ferrocene [17] with two eclipsed Me_3Si groups. In our case, two conformations corresponding to a minimum energy with either two PPh_2 or two *tert*-Bu eclipsed groups are expected. The source of the conformational preferences for in the actually eclipsed PPh_2 groups, P(1) and P(1)*, becomes clear from the view of the molecular structure. The phenyl substituents
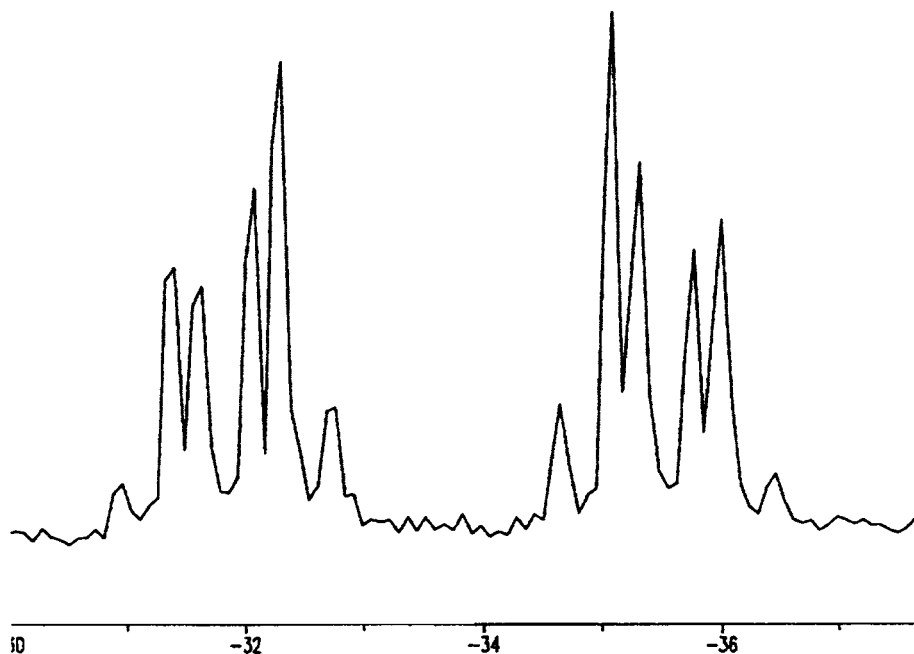

Fig. 1. ^{31}P-NMR signals (AA′BB′ spin system) of **1** in $CDCl_3$.

are tightly interlocked so as to give a conformationally stable arrangement with both parallel and orthogonal phenyl rings. At the same time, the *tert*-Bu groups are sufficiently distant from each other to minimize the steric effects. The *tert*-butyl substituents are staggered (twist angle: 66°). All the phosphorus atoms exhibit an *exo* (outside) deviation: the displacement from the average plan of the ring is different for each atom: P(1) 0.186(2) Å, P(2) 0.254(2) Å. For the two eclipsed phosphorus atoms, the variation from the perfect eclipse is of 6°. One originality of the structure lies in this relative arrangement of the phosphorus atoms. Indeed in the tetraphosphine $[C_5Me_3(PPh_2)_2]_2Fe$ [3] a very different arrangement of the phosphorus atoms is observed: the two PPh_2 substituents of a Cp ring are as distant as possible from the two PPh_2 groups carried by the other ring.

Considering the molecular structure, the tetraphosphine **1** allows several different chelating geometry at the metal center, as a consequence of the appropriate orientation of the coordinating phosphorus lone pairs. The conformation of PPh_2 groups and the degree of distortion of Cp rings can control the coordination
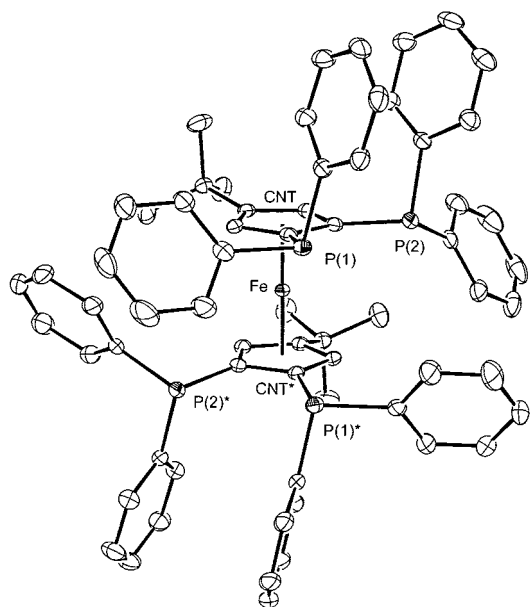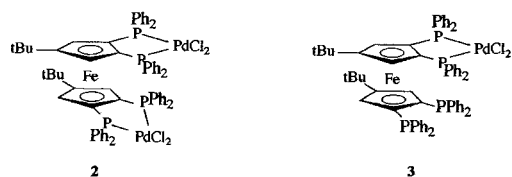

Fig. 2. ORTEP view of **1**. Thermal ellipsoids are drawn at the 50% probability level. For clarity hydrogen atoms and solvate molecules are omitted. The starred labels are symmetrically related (C_2) to the non-starred one.

Scheme 2.

number, stoichiometry and stereochemistry of the resulting metal complexes: 1,2 mononuclear biligate, 1,1′ mononuclear biligate, 1,2 and 1′,2′ bis(mononuclear biligate) and 1,1′,2 mononuclear triligate. We have explored the coordination behavior of the tetraphosphine with Rh(I), Pd(II) and Ir(I) for which planar structure and tetracoordination have been reported associated with either 1,1′ or 1,2 ferrocenyldiphosphines.

2.2. Palladium coordination

Studies from NMR experiments on the coordination chemistry of 1,2,1′-tris(diphenylphosphino)ferrocene with $Pd(COD)Cl_2$ were described by Butler et al. [13]. Both 1,2 and 1,1′ coordination occurs, the high intensity signals being associated to 1,2 coordination. A similar reaction conducted with our tetraphosphine **1** and $PdCl_2(PhCN)_2$ leads exclusively to 1,2 coordination mode. Addition of two equivalents of palladium salt to a dichloromethane solution of tetraphosphine **1** gives the dipalladate complex **2** in quantitative yield (Scheme 2). Spectroscopic data, as the low-field shift of the phosphorus resonances at δ 39.1 and 41.0 ppm, support the proposed coordination. Reaction of the tetraphosphine with an equimolar amount of palladium dichloride gives more complicated mixture as indicated by ^{31}P-NMR analysis: both **1** and **2** were identified and, in addition, four signals were observed due to the monopalladate complex **3** (Fig. 3). The appearance of the signals suggests an overlap, which occurs for the eight resonances relative to the four anisochronous phosphorus atoms in two diastereoisomeric conformers. From the mixture, it has not been possible to isolate the dissymmetric complex **3**. **3** reacts readily with Pd(COD)Cl_2 yielding **2**. Therefore, only the 1,2 and 1′,2′ bis(mononuclear biligate) coordination is observed and fully characterized.

2.3. Rhodium coordination

Contrary to palladium, a remarkable feature of the coordination of **1** with $[RhCl(CO)_2]_2$ is the number of isomers obtained. The tetraphosphine ligand **1** coordinates Rh(I) to give complexes with all coordination modes which can be deduced from the molecular structure of the ligand. The different possibilities, as **4**, **5** and **6**, are depicted in Scheme 3. These complexes were synthesized independently under particular conditions to reach a single coordination mode. Characterizations were conducted by elemental analysis, NMR, IR and mass spectroscopies as well as reaction chemistry investigations of the complexes.

The reaction of an equimolar amount of tetraphosphine **1** with $[RhCl(CO)_2]_2$ in toluene at room temperature gave a mixture of products of the type tetraphosphine bis(chlorocarbonylrhodium) as indi-
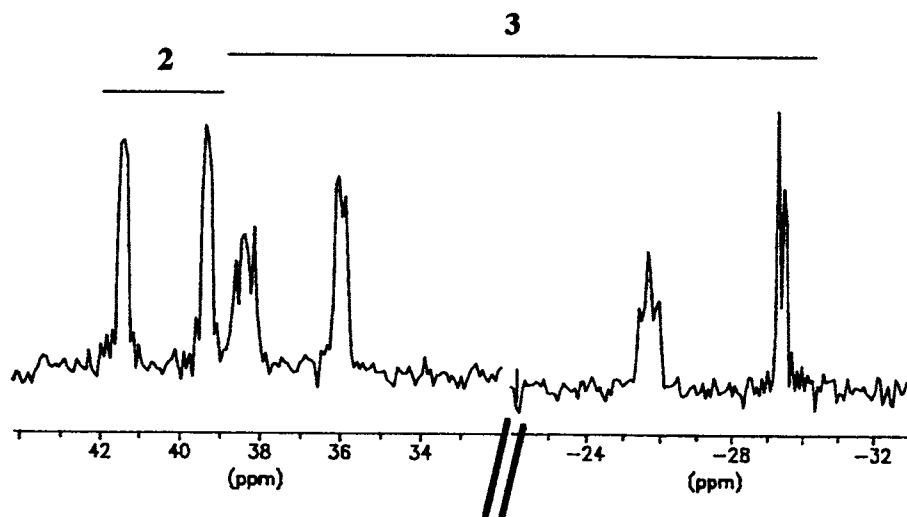
Fig. 3. ^{31}P-NMR spectrum (CDCl₃) corresponding to the reaction of **1** with one equimolar amount of PdCl₂(PhCN)₂.

cated by mass spectroscopy and elemental analysis. In such a situation, with two different substituents on the Rh atom, the complexes can exist theoretically in three diastereoisomeric forms **6a**–**c** (Schemes 3 and 4). The evidence for the 1,2 and 1′,2′ bis(coordination) shown in Scheme 4 is clearly demonstrated by ^{31}P-NMR spectrum (Fig. 4). Four ABX pattern (A = B = [31]P; X = Rh) are observed: one for each racemic form for which the phosphorus atoms belonging to each of Cp rings are magnetically equivalent, and two others for the meso form resulting from the chlorocarbonyl dissymmetry at the rhodium atom. Although clearly observable by NMR (rac–rac–meso 8:2:6), all attempts to separate the different diastereoisomers failed.

With the aim to isolate the 1,2 coordinated complex, the stoichiometry **1**: [RhCl(CO)₂]₂ was varied from 1:1 to 2:1. The reaction running under the same conditions leads to five products: **6a**–**c** and two other compounds, **4** and **5**. Both are formed from **1** with only one rhodium atom, but spectroscopic evidence for the formation of the 1,2 coordinate species could not be provided. The separation of the various species from the mixture has not been successful. In addition, ^{31}P-NMR spectrum of the reaction mixture reveals that after a few hours, the 1,2,1′ species **5** associated with [RhCl₂(CO)₂]⁻ afford **6a**–**c**.

The synthesis of 1,1′-coordinate tetraphosphine-rhodium complex **4** has been successfully achieved independently, performing the reaction under a carbon monoxide atmosphere. The ^{31}P-NMR of **4** at room temperature exhibits a singlet at −28.0 ppm and a broad signal centred at −4 ppm, suggesting that an exchange process occurs between species with different coordination. The existence of a fast equilibrium in solution for a triphosphine such as [(triphos)RhCl(CO)] has been already discussed [18] and attributed to inter-
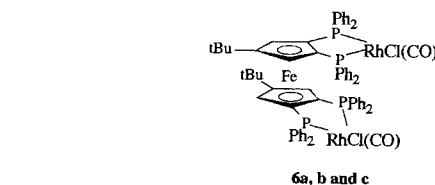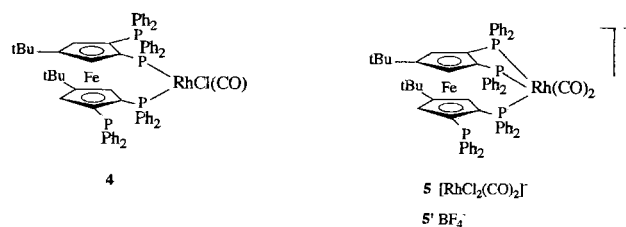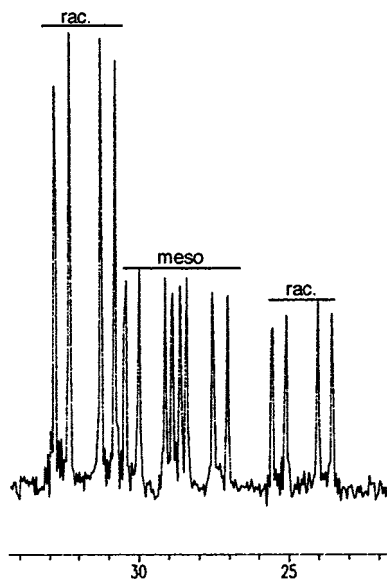

Scheme 3.
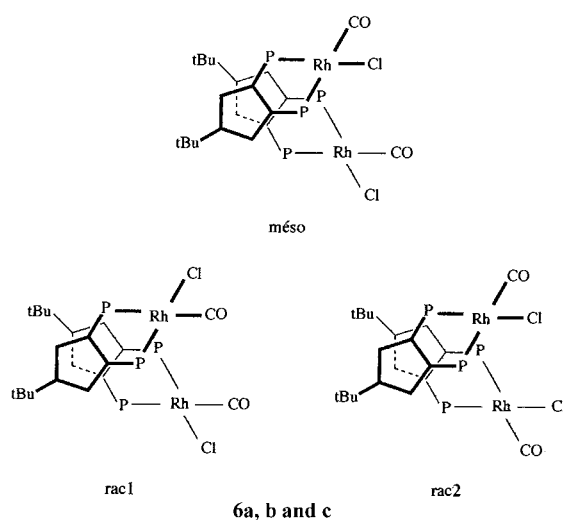
Scheme 4.

Fig. 4. ^{31}P-NMR (CDCl$_3$) spectrum of **6a**–**c** showing the resonance attributed to the ^{31}P *trans* to the carbonyl group.

conversion between a geometry in which the rhodium is pentacoordinated and another in which it is tetracoordinated. This assumption is based on the observation of very different v_{CO} vibrational bands in solution for each species (1920 and 2005 cm^{-1}). In the present case, for **4**, with regard to the infrared spectrum in the CO region only one vibration band is detected. Thus, the equilibrium observed in NMR exhibits species which for the infrared absorption is almost unaffected. We propose that a $1,1' \Leftrightarrow 1,2'$ reversible process occurs, concerning the Rh–P bond in *trans* position of the Rh–Cl bond.

Compound **5** was prepared by modification of the experimental conditions: using 1:3 toluene–hexane mixture instead of toluene, precipitation of **5** associated with [RhCl$_2$(CO)$_2$]$^-$ was observed. The ^{31}P-NMR spectrum of the cationic rhodium complex **5** indicates a (1,1', 2) coordination. One resonance at -30.4 ppm characteristic of free phosphino group and an ABCX system (A = B = C = ^{31}P; X = ^{103}Rh) in the area of the coordinated phosphorus atom are detected.

The complete spectroscopic characterization of all these complexes is reported in Section 3.

2.4. Iridium coordination

The behavior of the tetraphosphine **1** toward the iridium salt [IrI$_2$(CO)$_2$][N(PPh$_3$)$_2$] has also been examined. The reaction leads to the complexes **7** and **8** iridium analogous of the rhodium complexes **4** and **5**. They were characterized by ^{1}H- and ^{31}P-NMR spectroscopy, mass spectroscopy, IR and elemental analysis (see Section 3).

In conclusion, we have shown a new example for chirality phenomena in ferrocenic complexes, which are specifically attributable to the bulky substituted Cp ligands. Thus, the new ferrocenyltetraphosphine **1** generate different isomeric complexes with planar tetracoordination. In order to extend these studies the coordination chemistry concerning tetrahedral and octahedral surrounded metals is currently in progress and will be reported in due course.

3. Experimental

3.1. General considerations

Reactions were carried out under an atmosphere of argon by means of conventional Schlenck techniques. Solvents were dried and deoxygenated before distillation from sodium benzophenone ketyl or Na–K alloy. Elemental analyses were performed by the analytical service of LSEO of the Université de Bourgogne (Eager 200). Mass spectra were recorded on a Kratos concept IS machine. For Rh, Pd and Ir complexes the fragmentation of non-polymetallic species are omitted. ^{1}H- and ^{31}P{^{1}H} -NMR spectra were recorded on a Bruker AC200 spectrometer. The 1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyllithium was prepared according a previous report [4].

3.2. Preparation of **1**

A yellow solution of 1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyllithium (1.5 g, 3 mM) in 20 ml toluene was added to iron dichloride (250 mg, 1.9 mM) in 10 ml of toluene at room temperature (r.t.). The mixture was refluxed for 16 h and filtered. The brown–red solution was concentrated and kept in the refrigerator for two days. Orange crystals of **1** (1.1 g, 1.06 mM, yield = 71%) were obtained, m.p. = 228 °C. Anal. Found: C, 76.33; H, 6.03. Calc. for C$_{66}$H$_{62}$FeP$_4$: C, 76.59; H, 6.04%. ^{1}H-NMR (CDCl$_3$): δ 0.70 (s, 18H, *t*-Bu), 4.04 (m, 2H, Cp), 4.14 (m, 2H, Cp), 6.4–7.6 (m, 40H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ -31.5 (m), -35.5 (m, J_{PP} = 75, 40, 3 and 2 Hz). EIMS (200 °C); m/z (%): 1034 (100) [M$^+$], 1019 (5) [M$^+$ − CH$_3$], 849 (30) [M$^+$ − PPh$_2$], 665 (5) [M$^+$ − 2PPh$_2$].

3.3. Preparation of **2**

A mixture of **1** (32 mg, 0.031 mM) and (PhCN)$_2$PdCl$_2$ (24 mg, 0.062 mM) in 15 ml of CH$_2$Cl$_2$ was stirred three days at r.t. The solvent was removed under reduced pressure and **2** was obtained as a red powder. The yield was essentially quantitative, m.p. > 260 °C. Anal. Found: C, 56.81; H, 4.55. Calc. for C$_{66}$H$_{62}$ Cl$_4$FeP$_4$Pd$_2$: C, 57.05; H, 4.50%. ^{1}H-NMR

(CDCl$_3$): δ 0.86 (s, 18H, t-Bu), 4.29 (m, 4H, Cp), 6.5–8.2 (m, 40H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 39.1 (s), 41.0 (s). EIMS (200 °C); m/z (%): 1386 (5) [M$^+$], 1298 (5) [M$^+$ − 2HCl − CH$_4$], 1262 (100) [M$^+$ − 3HCl − CH$_3$], 1247 (50) [M$^+$ − 3HCl − 2CH$_3$].

3.4. Preparation of 4

A yellow solution of [RhCl(CO)$_2$]$_2$ (31 mg, 0.159 mM) in 5 ml of toluene was added under CO, at r.t., to a solution of **1** (166 mg, 0.16 mM) in 15 ml toluene. After 45 min of stirring under CO, the solvent was evaporated to dryness and **4** was obtained as a red powder. The yield was essentially quantitative, m.p.149 °C (dec.). Anal. Found: C, 66.65; H, 5.06. Calc. for C$_{67}$H$_{62}$ClFeOP$_4$Rh: C, 66.99; H, 5.20%. ^{1}H-NMR (CDCl$_3$): δ 0.81 (s, 18H, t-Bu), 3.95 (m, 1H, Cp), 4.43 (m, 2H, Cp), 4.60 (m, 1H, Cp), 6.5–8.3 (m, 40H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ − 28 (s), − 2 to − 5 (m). FABMS; m/z (%): 1165 (90) [M$^+$ − Cl], 1137 (100) [M$^+$ − CO − Cl], 1059 (40) [M$^+$ − CO − Cl − C$_6$H$_6$]. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 1956.

3.5. Preparation of 5 and 5′

(a) A yellow solution of [RhCl(CO)$_2$]$_2$ (41 mg, 0.106 mM) in 5 ml of hexane was added at r.t. to a red solution of **1** (110 mg, 0.106 mM) in a mixture of toluene–hexane 5:14. An orange precipitate of **5** was immediately formed and isolated by filtration. The counter-ion was [RhCl(CO)$_2$]$^-$. The yield was essentially quantitative. Anal. Found: C, 58.87; H, 4.39. Calc. for C$_{70}$H$_{62}$Cl$_2$Fe O$_4$P$_4$Rh$_2$: C, 59.04; H, 4.39%. ^{1}H-NMR (CDCl$_3$): δ 0.81 (s, 9H, t-Bu), 0.86 (s, 9H, t-Bu), 3.97 (m, 1H, Cp), 4.57 (m, 1H, Cp), 4.71 (m, 1H, Cp), 5.06 (m, 1H, Cp), 6.4–8.3 (m, 40H, Ph). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ − 29.7 (s), 17.8 (ddd, J_{Rh-P} = 110 Hz, J_{PP} = 12, 8 Hz), 40.7 (ddd, J_{Rh-P} = 94 Hz, J_{PP} = 23, 8 Hz), 43.8 (ddd, J_{Rh-P} = 92 Hz, J_{PP} = 23, 12 Hz). FABMS; m/z (%): 1193 (40) [M$^+$], 1165 (80) [M$^+$ − CO], 1137 (100) [M$^+$ − 2CO]. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2005, 2054 ([RhCl$_2$(CO)$_2$]$^-$: 1990, 2068).

(b) **1** (109 mg, 0.105 mM) is dissolved in 15 ml of toluene. To this red solution were added, at r.t, AgBF$_4$ (20.5 mg, 0.105 mM) in 5 ml of methanol followed by a solution of [RhCl(CO)$_2$]$_2$ (41 mg, 0.105 mM) in 5 ml of toluene. After stirring for 30 min, the mixture was filtered and the solvent was evaporated to dryness. **5′** was obtained as a red powder. The counter-ion was BF$_4^-$. The yield was essentially quantitative.

3.6. Preparation of 6

A yellow solution of [RhCl(CO)$_2$]$_2$ (58.6 mg, 0.15 mM) in 10 ml of toluene was added at r.t. to a solution of **1** (156 mg, 0.15 mM) in 15 ml of toluene. A

precipitate was immediately formed. After 14 h stirring at r.t., the solvent was evaporated to dryness and **6** was obtained as an orange powder. The yield was essentially quantitative. Anal. Found C, 60.09; H, 4.96. Calc. for C$_{68}$H$_{62}$Cl$_2$FeO$_2$P$_4$Rh$_2$: C, 59.72; H, 4.57%. ^{1}H-NMR (CDCl$_3$): δ 0.74, 0.79, 0.85, 0.94 (four s, t-Bu), 4.55–3.96 (m, Cp), 8.75–6.65 (m, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 24.5, 28.1, 29.4, 31.8 (four dd, J_{RhP} = 126 Hz, J_{PP} = 40 Hz), 51.4, 53.4, 54.0, 54.6 (four dd, J_{RhP} = 162 Hz, J_{PP} = 40 Hz). FABMS; m/z (%): 1310 (50) [M$^+$ − 2CO], 1275 (100) [M$^+$ − 2CO − Cl]. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2013.

3.7. Preparation of 7

A yellow solution of [(PPh$_3$)$_2$N][IrI$_2$(CO)$_2$] (124 mg, 0.12 mM) in 5 ml of CH$_2$Cl$_2$ was added at r.t. to a solution of **1** (124 mg, 0.12 mM) in 10 ml of CH$_2$Cl$_2$. The solvent was removed under reduced pressure and replaced by 10 ml of hexane. We then obtained **7** as a red precipitate, which is isolated by filtration (14 mg, 0.011 mM, yield = 9%). The solution contained **8**. Anal. Found: C, 58.50; H, 4.75. Calc. for C$_{67}$H$_{62}$FeIIrOP$_4$: C, 58, 22; H, 4.52%. ^{1}H-NMR (CDCl$_3$): δ 0.75 (s, 9H, t-Bu), 0.81 (s, 9H, t-Bu), 3.73 (m, 1H, Cp), 4.42 (m, 1H, Cp), 4.64 (m, 1H, Cp), 4.90 (m, 1H, Cp), 6.2–8.3 (m, 40H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ − 28.6 (s), 5,0 (m). FABMS; m/z (%): 1353 (98) [M$^+$ − CO − H], 1338 (65) [M$^+$ − CO − CH$_4$], 1172 (80), 1157 (100). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 1929.

3.8. Preparation of 8

A solution of [(PPh$_3$)$_2$N][IrI$_2$(CO)$_2$] (170 mg, 0.165 mM) in 5 ml of CH$_2$Cl$_2$ was added at r.t. under CO to a solution of **1** (170 mg, 0.165 mM) in 20 ml of toluene. After 45 min of stirring under CO, the mixture was filtered and the solvent was evaporated to dryness. **8** was obtained as an orange powder. Anal. Found: C, 58.02; H, 4.50. Calc. for C$_{68}$H$_{62}$FeI$_2$IrO$_2$P$_4$: C, 57.91; H, 4.44%. ^{1}H-NMR (CDCl$_3$): δ 0.83 (s, 9H, t-Bu), 0.90 (s, 9H, t-Bu), 3.96 (m, 1H, Cp), 4.62 (m, 1H, Cp), 4.78 (m, 1H, Cp), 5.14 (m, 1H, Cp), 6.3–8.2 (m, 40H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ − 30.7 (s), 1.8 (dd, J_{PP} = 8, 6 Hz), 10.4 (dd, J_{PP} = 22, 6 Hz), 12.9 (dd, J_{PP} = 22, 8 Hz). FABMS; m/z (%): 1283 (30) [M$^+$], 1255 (100) [M$^+$ − CO], 1225 (95) [M$^+$ − C$_4$H$_{10}$]. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2031, 1981.

3.9. X-ray structure determination of 1

An orange crystal of **1** suitable for X-ray crystallographic study was obtained from a saturated toluene solution of **1**. The data were collected on a Nonius Kappa-CCD diffractometer at 110 K using an Oxford Cryostream low temperature attachment. The structure

was solved by direct methods using SHELXS-97 [19] and refined by full least-squares methods using SHELXL-97 [19] with the aid of the WINGX program [20]. Except for one disordered toluene solvate molecule, non-hydrogen atoms were anisotropically refined. Two toluene solvate molecules were found: one is located around an inversion centre and then refined with an occupancy factor fixed to $m = 0.5$; the other one is disordered over two positions with occupancies refined to $m_1 = 0.77$ and $m_2 = 1 - m_1 = 0.23$. The carbon atoms of the smaller contribution to this disorder were isotropically refined. Hydrogen atoms of the toluene methyl groups were not included in the model, the other hydrogen atoms were included in their calculated positions and refined with a riding model. Crystallographic data are reported in Table 1.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{66}H_{62}P_4Fe \cdot 3(C_7H_8)$
Formula weight	1311.28
Temperature (K)	110(2)
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	21.9229(4)
b (Å)	14.4138(3)
c (Å)	22.5460(5)
β (°)	94.035(1)
V (Å^3)	7106.7(3)
Z	4
D_{calc} (g cm^{-3})	1.226
$F(000)$	2776
Diffractometer	Enraf–Nonius Kappa CCD
Scan type	Mixture of ϕ rotations and ω scans
λ (Å)	0.71073
μ (mm^{-1})	0.348
Crystal size (mm^3)	$0.37 \times 0.17 \times 0.15$
$\mathrm{Sin}(\theta)/\lambda_{max}$ (Å^{-1})	0.65
Index ranges	$-28 \leq h \leq 28$, $0 \leq k \leq 18$, $-29 \leq k \leq 29$
Absorption correction	SCALEPACK
Reflections collected (RC)	15 965
Independent reflections (IRC)	8152 [$R_{int} = 0.0247$]
IRCGT = IRC and [$I > 2\sigma(I)$]	6726
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8152/2/460
R for IRCGT	R_1 [a] $= 0.0349$, wR_2 [b] $= 0.0911$
R for IRC	R_1 [a] $= 0.0470$, wR_2 [b] $= 0.0964$
Goodness-of-fit [c]	1.049
Largest difference peak and hole (e Å^{-3})	0.532 and -0.317

[a] $R_1 = \Sigma \left(||F_o| - |F_c|| \right)/\Sigma |F_o|$.
[b] Weighting scheme calc. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma [w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 4.98P]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.
[c] Goodness of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 150996 for compound **1**, 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butyl-ferrocene. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] A. Togni, T. Hayashi, Ferrocenes, VCH, Weinheim, 1995.
[2] I.R. Butler, M.G.B. Drew, C.H. Greenwell, E. Lewis, M. Plath, S. Mussig, J. Szewczyk, Inorg. Chem. Commun. 2 (1999) 576.
[3] R. Broussier, S. Ninoreille, C. Bourdon, O. Blacque, C. Ninoreille, M.M. Kubicki, B. Gautheron, J. Organomet. Chem. 561 (1998) 85.
[4] R. Broussier, E. Bentabet, P. Mellet, O. Blacque, P. Boyer, M.M. Kubicki, B. Gautheron, J. Organomet. Chem. 598 (2000) 365.
[5] M.R. Mason, C.M. Duff, L.L. Miller, R.A. Jacobson, J.G. Verkade, Inorg. Chem. 31 (1992) 2746.
[6] (a) P. Steenwinkel, S. Kolmschot, R.A. Gossage, P. Dani, N. Veldman, A.L. Spek, G.V. Koten, Eur. J. Inorg. Chem. (1998) 477;
(b) G. Hogarth, J. Organomet. Chem. 406 (1991) 391.
[7] W. Oberhauser, C. Bachmann, T. Stampfl, R. Haid, C. Langes, H. Kopacka, A. Rieder, P. Brüggeller, Inorg. Chim. Acta 290 (1999) 167.
[8] M. Bacci, C.A. Ghilardi, A. Orlandini, Inorg. Chem. 23 (1984) 2798.
[9] M. Baacke, S. Hietkamp, S. Morton, O. Stelzer, Chem. Ber. 115 (1982) 1389.
[10] (a) W.H. Hohman, D.J. Kountz, D.W. Meek, Inorg. Chem. 25 (1986) 616;
(b) C. Bianchini, C. Mealli, A. Meli, M. Peruzzini, F. Zanobini, J. Am. Chem. Soc. 110 (1988) 8725;
(c) C.A. Ghilardi, S. Midollini, L. Sacconi, Inorg. Chem. 14 (1975) 1790;
(d) M.D. Vaira, S. Midollini, L. Sacconi, Inorg. Chem. 16 (1977) 1518;
(e) M.D. Vaira, M. Peruzzini, P. Stoppioni, Inorg. Chem. 30 (1991) 1001;
(f) C. Bianchini, M. Peruzzini, A. Vacca, F. Zanobini, Organometallics 10 (1991) 3697;
(g) M. Di Vaira, J. Chem. Soc. Dalton Trans. (1975) 2360;
(h) A. Orlandini, L. Sacconi, Inorg. Chem. 15 (1976) 78;
(i) C. Bianchini, C. Mealli, M. Peruzzini, F. Zanobini, J. Am. Chem. Soc. 109 (1987) 5548;
(j) C. Bianchini, M. Peruzzini, F. Zanobini, P. Frediani, A. Albinati, J. Am. Chem. Soc. 113 (1991) 5453;
(k) C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca, F. Zanobini, Inorg. Chem. 32 (1993) 2366;

(l) L. Dahlenburg, K.M. Frosin, Chem. Ber. 121 (1988) 865;

(m) C. Bianchini, P. Frediani, D. Masi, M. Peruzzini, F. Zanobini, Organometallics 13 (1994) 4616;

(n) M. Di Vairi, D. Rovai, P. Stoppioni, M. Peruzzini, J. Organomet. Chem. 420 (1991) 135;

(o) L. Dahlenburg, K.M. Frosin, S. Kerstan, D. Werner, J. Organomet. Chem. 407 (1991) 115.

[11] (a) T.L. Blundell, H.M. Powell, L.M. Venanzi, Chem. Commun. (1967) 763;

(b) T.L. Blundell, H.M. Powell, Acta Crystallogr. Sect. B 27 (1971) 2304.

[12] (a) L. Dahlenburg, K.M. Frosin, Polyhedron 12 (1993) 427;

(b) M. Antberg, L. Dahlenburg, Acta Crystallogr. Sect. C 42 (1986) 997.

[13] I.R. Butler, L.J. Hobson, S.M.E. Macan, D.J. Williams, Polyhedron 12 (1993) 1901.

[14] F.A. Bovey (Ed.), Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1969.

[15] (a) M.L. Martin, G.J. Martin, Manuel de Résonance Magnétique Nucléaire, Azoulay, Paris, 1971 (chap. 4);

(b) H. Günther, La spectroscopie de RMN, Masson, Paris, 1993 (chap. 5).

[16] C. Janiak, H. Schumann, Adv. Organomet. Chem. 33 (1991) 291.

[17] J. Okuda, E. Herdtweck, Chem. Ber. 121 (1988) 1899.

[18] (a) J. Ott, L.M. Venanzi, C.A. Ghilardi, S. Midollini, A. Orlandini, J. Organomet. Chem. 291 (1985) 89;

(b) W.O. Siegl, S.J. Lapporte, J.P. Collman, Inorg. Chem. 10 (1971) 2158;

(c) A.R. Sanger, J. Chem. Soc. Dalton Trans. (1977) 120.

[19] G.M. Sheldrick, SHELX-97 (Includes SHELXS-97, SHELX-97), Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Tammanstraße 4, D-3400 Göttingen, Germany, 1998.

[20] L.J. Farrugia, WINGX, J. Appl. Crystallogr. 32 (1985) 837.