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Pd(0) and Pd(II) derivatives with heteroannularly bridged chiral ferrocenyl diphosphine ligands – A stereochemical analysis

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Dedicated to Dr. Antonio Abad on the occasion of his retirement for his contribution to the palladium chemistry.

Abstract

The ligands (S_c, S_p)-1-diphenylphosphino-2,1′-(1-dicyclohexylphosphinopropanediyl)ferrocene, (S_c, S_p)-PP^{Cy}PF, and (S_c, S_p)-1-diphenylphosphino-2,1′-(1-diphenylphosphinopropanediyl)ferrocene, (S_c, S_p)-PP^{Ph}PF, have been used in the synthesis of the new Pd(0) and Pd(II) derivatives [Pd(PP^{Cy}PF)(DMFU)] (**1**) (DMFU = dimethylfumarate), [Pd(PP^{Cy}PF)(MA)] (**2**) (MA = maleic anhydride), [Pd(η^3-2-Me-C_3H_4)(PP)]OTf (PP = PP^{Cy}PF, **3**; PP^{Ph}PF, **4**) (OTf = triflate), [PdRR′(PP)] (R = Me, R′ = Cl, PP = PP^{Cy}PF, **5**, PP^{Ph}PF, **6**; R = R′ = Me, PP = PP^{Cy}PF, **7**, PP^{Ph}PF, **8**; R = R′ = C_6F_5, PP = PP^{Cy}PF, **9**, PP^{Ph}PF, **10**). The molecular structure of **7** has been determined by X-ray diffraction. In the cases of complexes **1**–**4** two isomers are formed depending on the orientation of the ancillary ligand with respect to the ferrocenyl core. The stereochemistry of these complexes has been determined. In complex **6** the two possible isomers are obtained whereas in complex **5** the derivative with the Me group *trans* to PPh_2 is selectively formed. Restricted rotation of the pentafluorophenyl groups with respect to the Pd–C bond has been found in **9** and **10**. In all derivatives the conformation of the ferrocenyl ligand is the same as that seen by X-ray diffraction and deduced from NMR data.

Keywords: Diphosphines; Ferrocenyl ligands; Chirality; Palladium; Stereochemistry

1. Introduction

Chiral nonracemic ferrocenyl ligands have been successfully used in a wide variety of catalytic asymmetric processes [1]. A huge number of ferrocenyl aminoalcohols and aminophosphines have originally been obtained from 1-(dimethylamino)ethyl-ferrocene [1a,2]. In addition, ferrocenyl pyrazole and oxazoline derivatives have been successfully used as P–N coordinating ligands [3,4]. Besides aminophosphines, ferrocenyl diphosphines have been studied extensively and several types of ligand families have been developed, many of which exhibit excellent catalytic behaviour [5]. In particular, Josiphos-type ligands not only show outstanding performance in a number of distinct catalytic processes [5b,5c,6] such as hydrogenations, hydroborations, polymerisations, allylic alkylations and others, but have also found an industrial application in asymmetric hydrogenation [7].

Recently, we described the synthesis of several homoannularly and heteroannularly bridged ferrocenyl diphosphines that represent ligands with different degrees of conformational flexibility (see Scheme 1) [8,9]. The behaviour of these systems in asymmetric hydrogenations was analysed and compared with that of the related Josiphos

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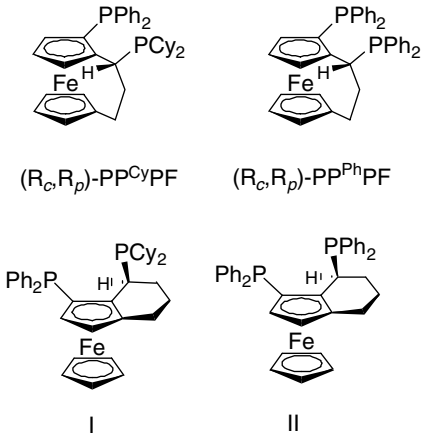


Scheme 1.

ligands [8]. In addition, we tested some of our ligands in palladium-catalysed asymmetric allylic alkylations and aminations [10] as well as in platinum-catalysed carbonylation reactions [11]. For the hydrogenation and allylic alkylation (amination) reactions we concluded that – in comparison to Josiphos-type ligands – the increased backbone rigidity, which is especially pronounced for the heteroannularly bridged derivatives, was not beneficial [8]. However, in very recent studies, Erker's group showed that – like Josiphos itself – some heteroannularly bridged ferrocenyl diphosphines are very active catalysts for CO/alkene copolymerisations and can be successfully used for the asymmetric alternating copolymerisation of CO and propene [12].

In the study described here, we investigated the stereochemical behaviour of a number of Pd(II) and Pd(0) complexes of two heteroannularly bridged ferrocenyl diphosphine ligands [8]: (S_c, S_p)-1-diphenylphosphino-2,1′-(1-dicyclohexylphosphinopropanediyl)ferrocene, (S_c, S_p)-PP^{Cy}PF, and (S_c, S_p)-1-diphenylphosphino-2,1′-(1-diphenylphosphinopropanediyl)ferrocene, (S_c, S_p)-PP^{Ph}PF. Palladium complexes with ancillary ligands that have different electronic and steric properties were investigated. Maleic anhydride and dimethyl fumarate were used as ligands in the Pd(0) complexes and methyl, chloride, and pentafluorophenyl ligands were used in the Pd(II) complexes. We previously described the structural and dynamic properties of the palladium(0) dibenzylideneacetone complex of PP^{Cy}PF [13].

It was of interest to investigate how such rigid ligands can adapt to the changing oxidation states of palladium or to changes in the electronic and steric properties of coordinating ligands; such changes would be expected to occur during the course of catalytic cycles, e.g., in catalytic allylic alkylations. The ligand conformations and, where possible, the stereochemistries and isomer ratios were therefore analysed, mainly by NMR spectroscopy. In addition, the steric and electronic differences between the two ferrocenyl ligands and their likely influence on the observed isomer ratios will be discussed.

2. Results and discussion

2.1. Synthesis

The palladium(0) complexes were synthesised by the reaction in toluene of $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone) with PP^{Cy}PF and olefins, L, dimethylfumarate (DMFU) and maleic anhydride (MA) according to Eq. (1). These electron-poor olefins are expected to stabilise the low oxidation state of the palladium centre.

$$[Pd_2(dba)_3]\cdot CHCl_3 + 2PP^{Cy}PF + 2L \rightarrow 2[Pd(PP^{Cy}PF)(L)] + 3dba \quad L = DMFU,\ \mathbf{1};\ MA,\ \mathbf{2} \tag{1}$$

The allyl complexes were obtained according to a literature method [14] from $[Pd(\eta^3\text{-2-Me-}C_3H_4)Cl]_2$ and silver trifluoromethylsulfonate (AgOTf) in the presence of the corresponding ferrocene ligand, PP (see Eq. (2)).

$$[Pd(\eta^3\text{-2-Me-}C_3H_4)Cl]_2 + 2PP + 2AgOTf \rightarrow 2[Pd(\eta^3\text{-2-Me-}C_3H_4)(PP)]OTf + 2AgCl \quad PP = PP^{Cy}PF,\ \mathbf{3};\ PP^{Ph}PF,\ \mathbf{4} \tag{2}$$

Displacement of the weekly coordinating ligands 1,5-cyclooctadiene (COD) or tetramethylethylenediamine (TMEDA) from the appropriate starting materials led to the palladium(II) derivatives **5**–**10** (see Eqs. (3) and (4)).

$$[PdRR'(COD)] + PP \rightarrow [PdRR'(PP)] + COD \quad R = Cl,\ R' = Me,\ (PP = PP^{Cy}PF\ (\mathbf{5});\ PP^{Ph}PF\ (\mathbf{6})) \quad R = R' = C_6F_5,\ (PP = PP^{Cy}PF\ (\mathbf{9});\ PP^{Ph}PF\ (\mathbf{10})) \tag{3}$$

$$[PdMe_2(TMEDA)] + PP \rightarrow [PdMe_2(PP)] + TMEDA \quad PP = PP^{Cy}PF\ (\mathbf{7});\ PP^{Ph}PF\ (\mathbf{8}) \tag{4}$$

2.2. Complex characterisation

The elemental analysis data for the new products are given in Section 4. The IR spectra contain bands due to the ν(CO) vibration for complexes **1** and **2**. Bands due to the allyl group, the triflate anion, the ν(Pd–Cl) and ν(Pd–C) vibrations or those corresponding to the C_6F_5 groups were also observed in the respective spectra (see Section 4).

In complexes **1**–**4** two diastereomers exist in solution in different ratios (**M** = major isomer, **m** = minor isomer, see Table 1 for the isomer ratio). These isomers differ in the way that either the alkene or the allyl group is oriented with respect to the asymmetric diphosphine ligand (see Scheme 2). In the case of the DMFU derivative (alkene symmetry: C_{2h}) the diastereomers differ in the face (*Re* or *Si*) that is coordinated to the metallic centre. On the other hand, in the MA or allyl complexes (alkene or allyl symmetry: C_{2v}) the orientation of the endocyclic oxygen or the

Table 1
^{31}P NMR data at room temperature for the ligands and complexes **1**–**10**

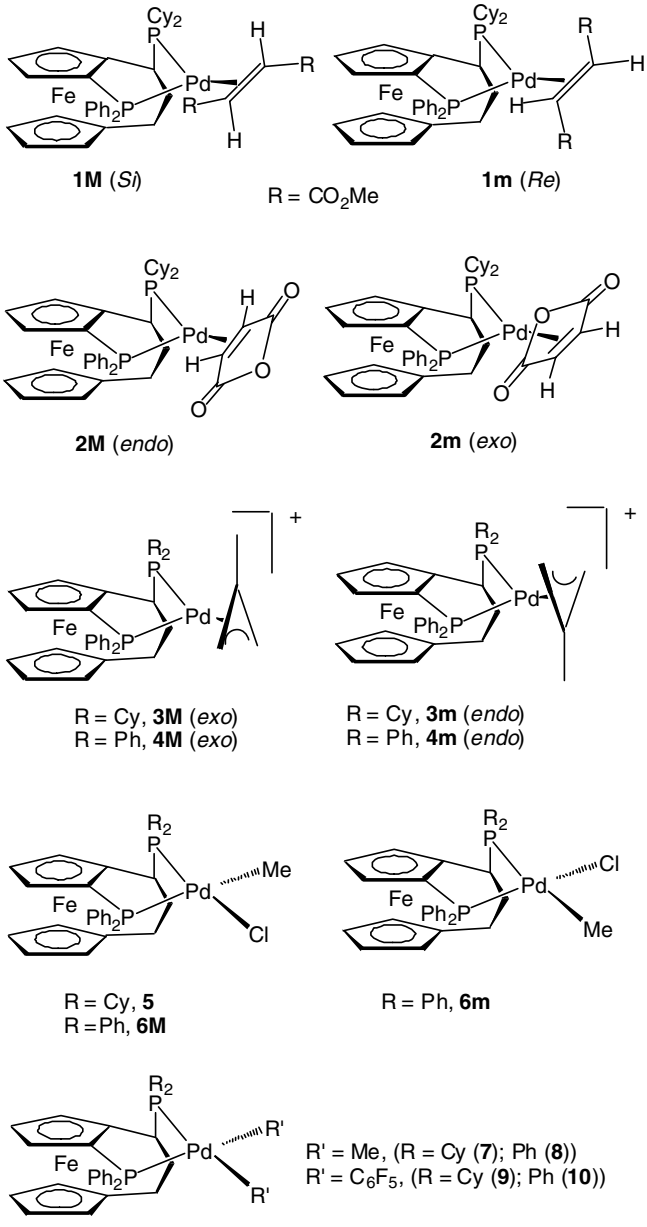
Derivative	**M**		**m**		**M/m** ratio[c]
	P^2	P^1	P^2	P^1	
$PP^{Cy}PF$[a]	6.38(d) $J_{PP} = 72.9$	−27.08(d)			
$PP^{Ph}PF$[a]	−9.78(d) $J_{PP} = 81.2$	−25.42(d)			
1[a]	45.33(d) $J_{PP} = 28.1$	13.02(d)	50.19(d) $J_{PP} = 29.0$	10.66(d)	52/48
2[a]	45.57(d) $J_{PP} = 43.3$	11.88(d)	49.91(d) $J_{PP} = 40.3$	13.40(d)	60/40
3[a]	57.10(d) $J_{PP} = 49.4$	10.22(d)	58.06(d) $J_{PP} = 49.7$	13.98(d)	67/33
4[a]	41.18(d) $J_{PP} = 54.3$	8.52(d)	42.77(d) $J_{PP} = 54.6$	13.11(d)	71/29
5[a]	62.84(d) $J_{PP} = 38.2$	−0.43(d)			
6[a]	54.68(d) $J_{PP} = 45.2$	−2.44(d)	24.38(d) $J_{PP} = 42.7$	22.82(d)	51/49
7[b]	40.00(d) $J_{PP} = 28.4$	8.99(d)			
8[b]	34.87(d) $J_{PP} = 28.7$	7.09(d)			
9[a]	38.78(d) $J_{PP} = 33.3$	5.67(d)			
10[a]	34.20(m)	4.46(m)			

M = major isomer; **m** = minor isomer.
[a] $CDCl_3$.
[b] [D_6]benzene.
[c] Determined from ^1H NMR spectra.

allylic methyl group with respect to the ferrocenyl core (*endo* or *exo*) determines the isomer formation. Such a mixture of diastereomers has been observed previously in related palladium diphosphine and aminophosphine derivatives by us [10,13,15,16] and others [17]. The stereochemical assignment of the complexes is described below. In complexes **5** and **6**, two isomers are also possible depending on the relative disposition of the methyl and chloride with respect to the two distinct phosphorus atoms. When the ligand is $PP^{Cy}PF$ (**5**) the two P atoms are sufficiently different that only one isomer is observed. In contrast, the complex with $PP^{Ph}PF$ (**6**), which contains two PPh_2 groups, exists as two isomers that are formed in a very similar ratio (see Table 1).

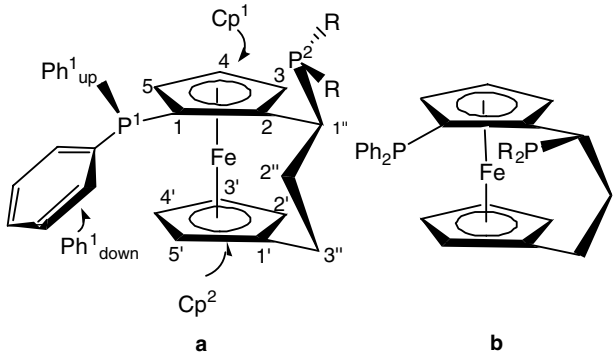
The ^{31}P NMR data for the ligands and the new complexes are collected in Table 1. In all compounds, apart from **10**, two doublets are observed for each single isomer. In the case of complex **10**, two multiplets are observed and this is due to the existence of small couplings with the fluorine atoms. Two main changes are observed in the spectra upon complexation: (i) the P–P couplings become smaller (the values are especially low for the DMFU or dimethyl derivatives) and (ii) the resonances are shifted towards higher frequencies. The analysis of partially ^{31}P decoupled ^1H NMR spectra (mainly considering the effect on the *ortho* phenyl protons) allowed the resonance at higher frequencies to be assigned to P^2 (bonded to the heteroannular chain) and the more shielded one to P^1. For complexes **7**–**10**, the ^{31}P chemical shifts have low values and this reflects the *trans* influence of the methyl or pentafluorophenyl groups. In the case of complex **5**, given that the PCy_2 group has a higher *trans* influence than the PPh_2 group, it is expected that the only isomer formed would be that with the methyl group *trans* to P^1Ph_2 [18]. According to that, the analysis of the proton resonance of the methyl group after ^{31}P selective decoupling showed that complex **5** and the major isomer of complex **6** have the Me group and the P^1 atom mutually *trans*, a situation that leads to negative chemical shifts for these P atoms (see Scheme 2 and Table 1). In contrast, the low *trans* influence of the chloride gives rise to resonances of particularly high frequency for the P^2 atoms in these derivatives. The positions of the resonances for the minor isomer of complex **6**, in which the disposition of the ligands is reversed, also reflect the effect of the relative *trans* influence of the chloride and methyl groups. These arrangements lead to a difference of 57 ppm between the chemical shifts of the two phosphorus atoms in **6M** whereas in the case of **6m** the difference is less than 2 ppm.

Prior to analysing the ^1H NMR data, it is necessary to state that two conformations are possible for the free ligands (see Scheme 3). Force field calculations performed previously indicate that conformation (a) is more stable in the free ligands [8]. This type of behaviour was also deduced for similar aminophosphino derivatives [9b,16]. In this orientation the heteroannular chain has the central carbon pointing towards the P^1 atom and, as a consequence, the P^2R_2 group is located above Cp^1. We studied other complexes with these ligands or the aminophosphine counterpart [9b,11,16] and found that when the ligands are coordinated to a transition metal in a chelate fashion, the Ph^1_{down} group is very effective at shielding the cyclopentadienyl $H^{5'}$ proton of Cp^2 and this signal therefore appears at very low frequency ($\delta = 2$–2.7 ppm). In fact, this anomalous chemical shift indicates the coordination of the ligands and also reflects their high level of rigidity. In the free ligands the signal for this proton appears in the normal range for cyclopentadienyl protons. This proton resonance was identified for all of the complexes. In cases where the resonance is obscured by the cyclohexyl proton signals, its position was deduced from ^1H–^1H COSY spectra (correlation with other Cp^2 protons) and confirmed from the NOE observed with the *ortho* protons of Ph^1_{down}. COSY spectra were used to assign the seven cyclopentadienyl protons, with some exceptions, to Cp^1 and Cp^2. In cases where two isomers are formed, the signals are assigned to a specific isomer except in cases where both are present in a similar ratio (complexes **1** and **6**). In the vast majority of the complexes the resonances corresponding to the *ortho* protons of the two phenyl groups (up and down) of



Scheme 2.

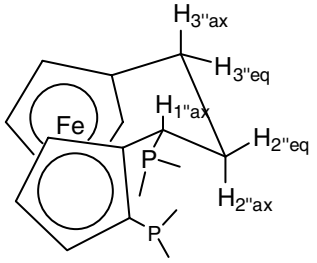
P^1Ph_2 were assigned, with the $H_{ortho}Ph^1_{down}$ signals always appearing at higher frequencies than $H_{ortho}Ph^1_{up}$. In the pentafluorophenyl derivatives the resonance of the $H_{ortho}Ph^1_{down}$ is particularly broad and this is possibly a consequence of interannular coupling with fluorine atoms. This coupling has already been observed for a similar complex with an aminophosphine ligand [16]. In some complexes, the *ortho* protons of the other P^2Ph_2 group were also located. With respect to the protons of the heteroannular chain that connects the two cyclopentadienyl groups, when the ligand is $PP^{Cy}PF$ the signals are usually overlapped with the resonances of the cyclohexyl group and only one or two could be detected. The assignment is less difficult for complexes with the $PP^{Ph}PF$ ligand. Considering that the H–H coupling constants provide information about the conformation of



Scheme 3. Conformations of ligands (S_c, S_p)-PP^RPF with R = Cy, Ph. Numbering scheme (a).

the chain, we attempted the complete assignment of these resonances (see Section 4). The expected conformation for the chain is shown in Scheme 4. The fact that $H^{1''}$ has a J_{H-H} value of 12.2–12.9 Hz (it appears in some complexes as a triplet because of the existence of coupling with P^2) indicates that it occupies an *axial* position (*axial–axial* coupling). Consequently, and according with our proposal the P^2Ph group is pointing straight above Cp^1. The shape and the couplings observed in the rest of the resonances are also consistent with the proposed conformation. Complex **10** is the easiest case to analyse because of the absence of overlapping signals and the presence of only one isomer.

The resonances of the alkene protons of complexes **1** and **2** appear between 3.50 and 4.22 ppm, which implies a shift towards lower frequencies with respect to the corresponding signals in the free olefins [19]. This change is due to the π back donation from the metal. These signals appear in the range usually found for $[ML_2(alkene)]$ derivatives of palladium and platinum [15b,16,20,21]. As expected, these resonances exhibit two couplings of different values with the two phosphorus atoms (8.7–10.1 Hz for the *trans* coupling and 1.5–2.5 Hz for the *cis* coupling). An *ABXY* system is observed in the case of complex **1M**. In complexes **3** and **4**, the allylic protons were assigned on the basis of the characteristic chemical shifts [22] and coupling constants as well as the information obtained from ^1H–^1H COSY, ^{31}P selective decouplings and NOE experiments. Four different allylic protons were observed for each complex and this reflects the asymmetric environ-



Scheme 4.

ment. The H_{anti} protons appear as doublets due to the coupling with the phosphorus atoms in *trans* ($J_{H-P} = 9$–11 Hz) and the H_{syn} signals give rise to multiplets or broad singlets, possibly due to the presence of small H_{syn1}–H_{syn2} couplings and a smaller value for $J_{H-Ptrans}$ [23]. It is worth noting that the allylic methyl resonance of one isomer of each allylic complex appears at an unusual low frequency. Bearing in mind that this signal is observed for both ferrocenyl ligands and also in a similar complex with a dimethylamino group instead of the PR_2 group [16], the chemical shift should be due to the effect of the anisotropy of a phenyl ring of the P^1Ph_2 group. The resonances of the methyl groups of complexes **5**–**8** appear in the region 0.71–0.93 ppm as doublet of doublets.

The $^{13}C\{^1H\}$ NMR data for the new complexes are listed in Section 4. In some cases *g*-HSQC twodimensional spectra were used in the assignment. The majority of the resonances were assigned to the two isomers where possible. The Cp carbon resonances appear between 92.2 and 68.2 ppm and the one corresponding to the carbon atom bonded to the P^1Ph_2 appears at around 90 ppm as a doublet of doublets. Coupling with one phosphorus atom is observed in the phenylic carbons. In both bispentafluorophenyl derivatives (**9** and **10**) one of the doublets of the *ortho* resonances is especially broad and this provides evidence – in a similar way to the ^1H NMR spectra and observations on other complexes [16] – for the existence of interannular couplings with fluorine atoms. The signals for the carbon atoms of the chain, which sometimes overlap with the cyclohexyl resonances, usually appear as doublets. In some complexes, a second and smaller coupling is also observed for the $C^{1''}$ or $C^{2''}$ carbons. The alkene carbon resonances are observed between 48.7 and 56.5 ppm. These signals are shifted towards lower frequency with respect to those in the free olefins, with the shift slightly higher for the MA derivative. These values are consistent with those found for other zerovalent alkene palladium or platinum complexes [19]. The methyl groups of complexes **5**–**8** appear between 1.81 and 17.56 ppm. Selective ^{31}P decouplings allowed the relative dispositions of these groups to be determined with respect to the different phosphorus atoms. A J_{C-P} value of around 100 Hz is observed with the phosphorus atom in the *trans* position. The *cis* coupling is only observed in the dimethyl derivatives and has a value of around 10 Hz.

The ^{19}F NMR spectra of complexes **9** and **10** were also recorded (see Table 2). The existence of two distinct resonances for F_{para} is indicative of the presence of two different pentafluorophenyl groups. These signals appear as triplets or doublet of doublets. Considering that the coordination plane is not a symmetry plane, the existence of one or two types of F_{ortho} per ring is indicative of free or restricted rotation around the Pd–C_{ipso} bond, respectively. The same applies to F_{meta}. Although there is some overlap of the corresponding resonances, the fact that three signals are observed for F_{meta} in complex **9** and F_{ortho} in **10** (both in a 2:1:1 ratio) is indicative of the existence of a restricted rotation of the pentafluorophenyl rings at room temperature. It is possible that there is steric hindrance with the phosphine substituents in both complexes. This situation has previously been observed in other *cis* palladium and platinum complexes [16,24] but free rotation of these groups is usually seen [25].

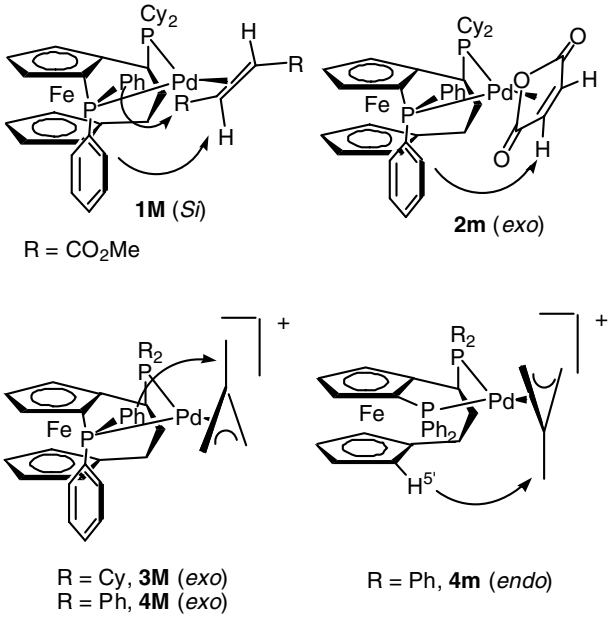
Table 2
^{19}F NMR data at room temperature for complexes **9** and **10** in $CDCl_3$

Complex	F_{ortho}	F_{meta}	F_{para}
9	−115.23(m, 2F) −115.84(m, 2F)	−164.09(m, 2F) −164.54(m, 1F) −165.04(m, 1F)	−162.42(t, 1F) $J_{F-F} = 19.8$ −162.97(t, 1F) $J_{F-F} = 19.8$
10	−114.91(m, 2F) −115.67(m, 1F) −117.51(m, 1F)	−164.49(m, 3F) −164.91(m, 1F)	−162.40(dd, 1F) $J_{F-F} = 21.4$ $J_{F-F} = 18.3$ −163.17(dd, 1F) $J_{F-F} = 21.4$ $J_{F-F} = 18.3$

2.3. Stereochemical assignment of complexes *1–4*

Considering the importance of the specific arrangement of the ligands around the metal centre, especially in enantioselective homogeneous catalysis, we attempted to establish the orientation of the alkene and allyl groups of the isomers of complexes **1**–**4**. This goal was achieved by means of NOE studies and the previous thorough assignment of the different proton resonances. The determination of the positions of $H_{ortho}Ph^1_{down}$ and $H_{ortho}Ph^1_{up}$ proved particularly useful in this respect. The rigidity of our diphosphine ligands favours the application of this strategy.

The NOEs that allowed the stereochemical assignment for complexes **1M**, **2m**, **3M**, **4M** and **4m** are indicated by arrows in Scheme 5. In the case of complex **1**, the major



Scheme 5.

isomer (**1M**) has an NOE between $H_{ortho}Ph^1_{down}$ and the olefinic proton at 4.10 ppm, which indicates that in this isomer the alkene is coordinated by the *Si* face. Coincidentally, for isomer **1M** an NOE was found between the $H_{ortho}Ph^1_{up}$ and the methyl of one of the ester groups. In complex **2**, the information required to determine the structures of the two isomers was obtained from an NOE found in the minor isomer (**2m**), namely that between $H_{ortho}Ph^1_{down}$ and one alkene proton (4.14 ppm). This indicates that the isomer has the endocyclic oxygen pointing away from the ferrocene core (*exo* isomer). This type of NOE was not found in the case of **2M**. In the allyl complexes, the same disposition of the allyl group was found for the two major isomers. An NOE was observed between $H_{ortho}Ph^1_{up}$ and the methyl allyl, indicating that **3M** and **4M** are the *exo* isomers (a similar correlation was not found for the minor isomers). Interestingly, the resonance for this methyl group was the one that exhibited an anomalously low chemical shift and this phenomenon has been ascribed to the effect of a phenyl ring on the P^1 atom. In the minor isomers, the methyl allyl must point towards the ferrocene core. In accordance with this situation, an NOE was found for **4m** between the allylic methyl and $H^{5'}$ of the Cp^2 (a similar comparison cannot be made for **3m** due the similar chemical shift of the two types of protons). Other NOEs found between $H_{ortho}Ph^1_{down}$ or $H_{ortho}Ph^1_{up}$ and allylic protons proved useful in determining their position with respect to the P atoms.

It is worth noting that in both allylic complexes (**3** and **4**) the allyl group in the major isomer has an *exo* orientation and that the isomer ratio does not change significantly when the PPh_2 group was replaced by the more sterically demanding PCy_2. This result was found despite the fact that, in principle, steric factors could influence the relative stabilisation of these stereoisomers. In contrast, the nature of the ferrocenyl ligand has a strong influence on the isomers formed in the case of the chloromethyl derivatives. As stated, when the ligand is $PP^{Cy}PF$ only one isomer is formed while with $PP^{Ph}PF$ both isomers are obtained in a very similar ratio. In this case, the electronic effects seem to dominate in the isomer stabilisation process.

2.4. X-ray structural characterization of complex $7 \cdot CH_3C_6H_5$

Suitable crystals for an X-ray diffraction study were obtained for the dimethyl complex **7**. Crystallographic data are given in Section 4, selected geometric data are compiled in Table 3. An ORTEP plot is shown in Fig. 1. As expected, the absolute configuration of the ligand is (S_c, S_p). The compound is a stable toluene solvate. Toluene occupies channel-like spaces in the framework of the Pd complexes. These channels extend at $x \approx 1/2$, $z \approx 0$ parallel to **b**-axis. The toluene molecules are ordered and oriented with their CH_3 groups approximately parallel to the positive **b**-axis (polar axis, chiral space group $P2_1$) forming a chain-like arrangement. The geometry around the palladium atom is distorted square-planar with the smallest angle of the coordination plane being C5–Pd–C4. The bite angle (P1–Pd–P2 = 93.84(2)°) is slightly smaller than that found in the derivative [$PtCl_2(PP^{Cy}PF)$] (97.14(3)°) [11]. Salient features of the PdP_2C_2 moiety are two short and strong Pd–C bonds of 2.159 Å (C4) and 2.103 Å (C5), whereas the Pd–P bonds Pd–P1 = 2.2950(7) Å *trans* to C4 and Pd–P2 = 2.3186(7) Å *trans* to C5 are somewhat elongated in comparison to *cis*-configured $PdCl_2P_2$ moieties (a representative value from Cambridge Crystallographic Data Base is Pd–P ~ 2.28 Å). The relative values for the Pd–P bond distances are not as one would expect considering the relative donor character of the PR_2 groups. Thus, although PCy_2 is considered a stronger donor than PPh_2, the corresponding Pd–P2 distance is longer than Pd–P1. However, this unexpected fact is observed in nearly all solved X-ray structures of Pd(II) compounds with PPh_2 and PCy_2 groups in relative *cis* position [26]. This characteristic has also been found in the Pt compound [$PtCl_2(PP^{Cy}PF)$] [11]. Bearing in mind that the fact is found with Josiphos type ligands that do not contain the heteroannular bridge, the effect should not be related to the

Table 3
Selected bond lengths (Å) and angles (°) for $7 \cdot CH_3C_6H_5$ with estimated standard deviations in parentheses

Pd–C5	2.103 (2)	C5–Pd–C4	83.93 (9)
Pd–C4	2.159 (2)	C5–Pd–P1	88.70 (7)
Pd–P1	2.2950 (7)	C4–Pd–P1	168.77 (6)
Pd–P2	2.3186 (6)	C5–Pd–P2	177.19 (7)
P1–C22	1.819 (2)	C4-Pd–P2	93.38 (6)
P1–C31	1.824 (2)	P1–Pd–P2	93.84 (2)
P1–C41	1.829 (2)	C1–C2–C3	114.2 (2)
P2–C51	1.863 (2)	*Torsion angle* (°)	
P2–C1	1.864 (2)	P2–C1–C21–C22	57.5(2)
P2–C61	1.864 (2)		

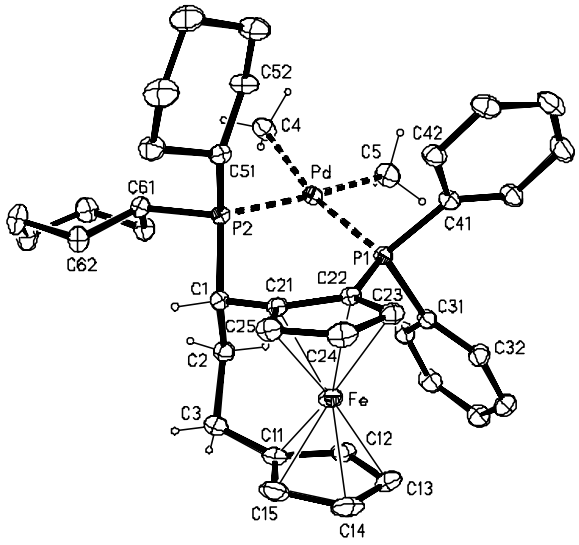


Fig. 1. ORTEP plot of **7** showing atom labelling; some hydrogen atoms have been omitted for clarity.

rigidity of the ligands but to the steric difference between PPh_2 and PCy_2. The relative values of the Pd–C bond distances are neither in accordance with the relative *trans* influence of the phosphine moieties and Pd–C4 is longer than Pd–C5 (Table 3). This anomalous fact is not generally found in similar structures [26]. In the ferrocenyl ligand, bond lengths and bond angles are within the usual range, showing average Fe–C_{Cp} and C_{Cp}–C_{Cp} bond lengths of 2.039(16) and 1.426(11) Å, respectively. The Cp rings are essentially planar and are approximately eclipsed. However, the heteroannular bridge imposes considerable strain on the ferrocene unit, which leads to a significant tilt of the cyclopentadienyl groups with a tilt angle of 9.3° (8.4° in the free ligand) [8]. The strain also forces the benzylic bridge carbons C1 and C3 to move out of plane, towards the inner bridge carbon C2. C1 is displaced by 0.093(3) Å below Cp^1 (Cp^1 is formed by C21–C25) and C3 above Cp^2 by 0.166(4) Å (Cp^2 is formed by C11–C15). As in free $PP^{Cy}PF$ and a similar aminophosphine derivative ligand [8,16] the bridge carbon C2 is oriented toward the side of the diphenylphosphine group attached to the Cp ring and the C1–P2 bond is pointing above the Cp^1 plane (torsion angle P2–C1–C21–C22 = 57.5(2)°). The position adopted by P2 means that the palladium atom is situated above the plane of the Cp^1 ring, the inclination angle between the Cp^1 ring and the least squares plane of the PdP_2C_2 moiety being 29.0(1)°. All of the features discussed above are consistent with our proposal concerning the conformation adopted by the ligands (conformation (a) in Scheme 3) and their rigidity. A comparison of the structure of **7** with that of the free ferrocenyl ligand (see Fig. 2) [8] indicates that the formation of the P–P chelate ring after coordination to the palladium atom imposes conformational changes that mainly affect the diphenylphosphine part. A rotation of the PPh_2 group about the C22–P1 bond and a distinct upward bending of the C22–P1 bond take place. That makes that in the complex one phenyl ring is situated in close proximity to Cp^2, a fact that explains the observed shielding of the $H^{5'}$ proton (crystallographic atom designation H12, bonded to C12). The PCy_2 group also rotates, although in a smaller degree, to approach the palladium atom. It is worth noting that there exist a close stereochemical similarity of complex **7** with $[PtCl_2(PP^{Cy}PF)]$ [11]. It indicates that the coordination of the ligand in a square-planar geometry leads to similar conformational changes.

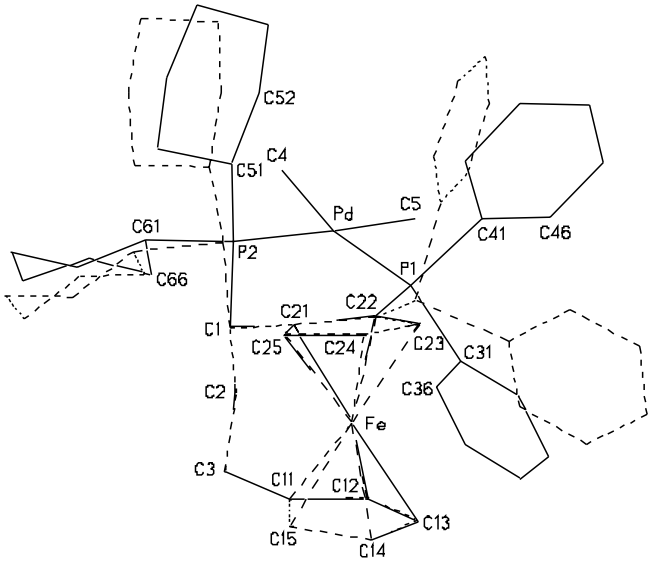


Fig. 2. Superposition of the molecular structures of **7** (—) and the corresponding free ligand $PP^{Cy}PF$ (---).

3. Conclusions

The ligands $PP^{Cy}PF$ and $PP^{Ph}PF$, although rigid, have proven to be capable of adapting to the geometry of palladium(II) and (0) derivatives, even when they bear ancillary ligands of high steric hindrance (e.g., pentafluorophenyl groups). In both oxidation states the conformation of the ferrocenyl ligands is the same and the ligand coordination produces a rotation in the ferrocenyl–PPh_2 bond that is seen by X-ray diffraction (complex **7**) and can be deduced from NMR data. For the allyl-Pd(II) and alkene-Pd(0) derivatives, two isomers have been found in solution and their respective stereochemistries deduced. In the allyl-Pd complexes, the isomer ratio is not clearly influenced by the type of ferrocenyl ligand. However, the type of diphosphine ligand has a marked influence, probably electronic in nature, over the isomers formed in the case of the chloromethyl derivatives, with complete diastereoselectivity achieved when $PP^{Cy}PF$ is used. It has been found that the pentafluorophenyl groups in the corresponding derivatives are in a situation of restricted rotation with respect to the Pd–C bonds.

4. Experimental

4.1. General methods

All manipulations which are described in this section were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were pre-dried and distilled over appropriate drying agents and degassed before use.

^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on a VARIAN UNITY INOVA 500, VARIAN UNITY 300 and a GEMINI FT-200 spectrometers. Chemical shifts (ppm) and coupling constants (in Hz) are given relative to TMS (^1H, ^{13}C NMR), taking as reference the signal of the deuterated solvent which has been used. For the ^{31}P NMR, H_3PO_4 (85%) has been used as reference. ^1H–^1H COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. The NOE difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5–10 dB. ^1H–^{13}C *g*-HSQC spectra: standard pulse sequence with an acquisition time of 0.128 s, pulse width 11 ms, relaxation delay 1 s, number of scans 8,

number of increments 256. IR spectra were recorded as KBr pellets or dispersion of the product in Nujol with a Perkin–Elmer PE 883 IR spectrometer. All data are quoted in wavenumbers (cm^{-1}). Elemental analyses were performed with a Perkin–Elmer 2400 microanalyzer. **M** = major isomer, **m** = minor isomer; δ_{oop} = deformation out of plane (IR); s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. If not specified, the $^{13}C\{^1H\}$ NMR resonances are singlets. Ph^1 and Ph^2 refer to the phenyl groups bonded to P^1 or P^2, respectively. In the allyl derivatives **3** and **4**, the subscripts "s" and "a" refer to H_{syn} or H_{anti}, respectively and the subscripts "1" and "2" refer to the CH_2 groups trans to P^2 and P^1, respectively.

The starting materials $[Pd_2(dba)_3]\cdot CHCl_3$ [27], $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)Cl]_2$ [28], [PdClMe(cod)] [29], $[Pd(C_6F_5)_2(COD)]$ [30] and $[PdMe_2(TMEDA)]$ [31] were synthesised according to literature procedures. The ligands $PP^{Cy}PF$ and $PP^{Ph}PF$ were also reported in a previous paper [8].

4.2. Synthesis

4.2.1. [Pd($PP^{Cy}PF$)(DMFU)] (1)

Toluene (15 mL) was added to a mixture of $PP^{Cy}PF$ (50.0 mg, 0.082 mmol), DMFU (15.7 mg, 0.109 mmol), and $[Pd_2(dba)_3]\cdot CHCl_3$ (38.8 mg, 0.037 mmol). The mixture was vigorously stirred for five hours. The initially brownish-red solution turned orange and a bit cloudy. It was filtered, and the resulting clear solution was concentrated under reduced pressure to the minimum volume where the product was still solved. This solution was purified in a silica-gel column using toluene as eluent (first product is dba and second **1**). Finally, the fraction containing the product was dried to afford **1** as a brownish-orange solid. Yield: 80% (56 mg, 0.066 mmol). $C_{43}H_{52}FeO_4P_2Pd$ (857.08): calc. C 60.26, H 6.11; found C 60.11, H 6.27%. IR (KBr): $\bar{\nu} = 1684\ cm^{-1}$ ν(C=O), 887 cm^{-1} δ_{oop}(C–H). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): some signals are common or not clearly assignable to one of the two isomers: $\delta = 0.86$–2.55 (PCy_2 and interannular chain), 2.84 (s, 3H, CO_2CH_3), 3.38 (s, 6H, 2 CO_2CH_3), 3.68 (s, 3H, CO_2CH_3) ppm. (**1M**, *Si*): $\delta = 2.22$ (s, 1H, $H^{5'}$ Cp^2), 3.47 (s, 1H, Cp^2), 3.82 (s, 2H, Cp^2), 3.92 (s, 1H, Cp^2), 4.10 and 4.02 (ABXY system, $J_{HP} = 10.0$, 2.5 Hz, $J_{HH} = 9.8$ Hz, 2H, AB = alkene protons), 4.27 (s, 2H, Cp^1), 4.37 (1, 1H, Cp^1), 6.99–8.06 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 7.02$ (m, $H_{ortho}Ph^1_{up}$), 8.02 (m, $H_{ortho}Ph^1_{down}$) ppm. (**1m**, *Re*): $\delta = 2.42$ (s, 1H, $H^{5'}$ Cp^2), 3.21 (ddd, $J_{HP} = 10.7$, 2.4 Hz, $J_{HH} = 9.7$ Hz, 1H, alkene $H_{transP2}$), 3.52 (s, 1H, Cp^2), 3.82 (s, 1H, Cp^2), 3.92 (s, 1H, Cp^2), 4.15 (d, assigned in the ^{31}P decoupled spectra, alkene $H_{transP1}$), 4.22 (s, 1H, Cp^1), 4.27 (s, 1H, Cp^1), 4.31 (s, 1H, Cp^1) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): Several signals are not assigned to a one specific isomer $\delta = 25.79$–38.12 (PCy_2), 127.55 (d, $J_{CP} = 8.5$ Hz, $C_{meta}Ph$), 127.81 (d, $J_{CP} = 11.0$ Hz, Ph), 128.07 (d, $J_{CP} = 10.7$ Hz, Ph), 130.39 (s, $C_{para}Ph$), 136.86 (d, $J_{CP} = 34.8$ Hz, $C_{ipso}Ph$), 137.89 (d, $J_{CP} = 33.4$ Hz, $C_{ipso}Ph$), 138.16 d, $J_{CP} = 33.0$ Hz, $C_{ipso}Ph$), 139.56 (d, $J_{CP} = 37.4$ Hz, $C_{ipso}Ph$), 172.20 (m, CO_{DMFU}), 174.27 (m, CO_{DMFU}), 174.55 (m, CO_{DMFU}), 174.71 (m, CO_{DMFU}) ppm. (**1M**, *Si*): $\delta = 24.21$ (d, $J_{CP} = 7.3$ Hz, $C^{3''}$), 32.26 (d, $J_{CP} = 10.1$ Hz, $C^{1''}$), 42.15 (d, $J_{CP} = 19.2$ Hz, $C^{2''}$), 50.38 (s, CO_2CH_3), 50.49 (s, CO_2CH_3), 51.81 (d, $J_{CP} = 26.0$ Hz, CH(alkene)), 51.98 (d, $J_{CP} = 26.2$ Hz, CH(alkene)), 68.21 (s, Cp^2), 68.98 (d, $J_{CP} = 4.9$ Hz, Cp^1), 69.38 (s, Cp^1), 70.88 (s, Cp^2), 71.71 (s, Cp^2), 72.06 (s, $C^{5'}$ Cp^2), 73.07(s, Cp^1), 75.94 (s, Cp^1), 86.51 (s, Cp^2), 91.90 (dd, $J_{CP} = 23.0$, 5.6 Hz, C_{Cp}-P), 131.16 (d, $J_{CP} = 13.1$, $C_{ortho}Ph$), 136.23 (d, $J_{CP} = 17.3$ Hz, $C_{ortho}Ph$) ppm. (**1m**, *Re*): $\delta = 24.36$ (d, $J_{CP} = 7.3$ Hz, $C^{3''}$), 32.87 (d, $J_{CP} = 8.2$ Hz, $C^{1''}$), 41.46 (d, $J_{CP} = 16.7$ Hz, $C^{2''}$), 48.97 (d, $J_{CP} = 25.0$ Hz, CH(alkene)), 50.13 (s, CO_2CH_3), 51.18 (s, CO_2CH_3), 52.67 (d, $J_{CP} = 29.0$ Hz, CH(alkene)), 69.3 (d, $J_{CP} = 4.5$ Hz, Cp^1), 68.35 (s, Cp^2), 71.04 (s, Cp^2), 71.63 (s, Cp^1), 71.67(s, Cp^2), 71.90 (s, $C^{5'}$ Cp^2), 73.10 (overlapped signal, Cp^1), 76.50 (s, Cp^1), 86.85 (s, Cp^2), 91.70 (dd, $J_{CP} = 22.9$, 5.2 Hz, C_{Cp}-P), 130.99 (d, $J_{CP} = 13.1$, $C_{ortho}Ph$), 135.97 (d, $J_{CP} = 17.7$ Hz, $C_{ortho}Ph$) ppm.

4.2.2. [Pd($PP^{Cy}PF$)(MA)] (2)

Toluene (15 mL) was added to a mixture of $PP^{Cy}PF$ (50.0 mg, 0.082 mmol), MA (10.65 mg, 0.109 mmol), and $Pd_2(dba)_3\cdot CHCl_3$ (38.8 mg, 0.037 mmol). The mixture was vigorously stirred for seven hours. The initially brownish-red solution turned orange and a bit cloudy. It was filtered, and the resulting solution was concentrated under reduced pressure to the minimum volume where the product was still dissolved. This solution was purified in a silica-gel column using toluene as eluent (first product is dba) and after THF (to obtain **2**). The fraction containing the product was dried to afford an oily product, which was washed with hexane to obtain finally **2** as an orange-yellow solid. Yield: 60% (42 mg, 0.049 mmol,). $C_{43}H_{50}FeO_3P_2Pd\cdot 1/4C_7H_8$ (862.14): calc. C 62.35, H 6.08; found C 62.45, H 5.93%. IR (KBr): $\bar{\nu} = 1784, 1719\ cm^{-1}$ ν(C=O). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.84$–2.66 (PCy_2 and interannular chain), 6.99–8.25 (PPh_2) ppm. (**2M**): $\delta = 2.61$ (s, 1H, $H^{5'}Cp^2$), 3.43 (s, 1H, Cp^2), 3.50 (m, $J_{HP2} = 9.5$, $J_{HP1} = 1.5$ Hz, $J_{HH} = 3.9$ Hz, 1H, CH(alkene) *trans* P^2), 3.86 (s, 1H, Cp^2), 3.99 (s, 1H, Cp^2), 4.22 (m, $J_{HP1} = 10.2$, $J_{HP2} = 1.0$ Hz, $J_{HH} = 3.9$ Hz, 1H, CH(alkene) *trans* P^1), 4.33 (s, 1H, Cp^1), 4.34 (s, 1H, Cp^1), 4.44 (s, 1H, Cp^1), 7.16 (m, $H_{ortho}Ph^1_{up}$), 7.71 (m, $H_{ortho}Ph^1_{down}$). (**2m**): $\delta = 2.50$ (s, 1H, $H^{5'}$ Cp^2), 3.50 (s, 1H, Cp^2), 3.87 (s, 1H, Cp^2), 3.99 (s, 1H, Cp^2), 4.06 (m, $J_{HP} = 9.3$, 2.5 Hz, $J_{HH} = 3.9$ Hz, 1H, CH(alkene) *trans* P^1), 4.14 (m, $J_{HP} = 8.1$, 1.5 Hz, $J_{HH} = 3.6$ Hz, 1H, CH(alkene) *trans* P^2), 4.36 (s, 1H, Cp^1), 4.37 (s, 1H, Cp^1), 4.41 (s, 1H, Cp^1), 7.03 (m, $H_{ortho}Ph^1_{up}$), 7.88 (m, $H_{ortho}Ph^1_{down}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): some signals are common or not clearly assignable to one of the two isomers: $\delta = 24.05$–41.07 (PCy_2) ppm. (**2M**): $\delta = 24.16$ (d, $J_{CP} = 12.1$ Hz, $C^{3''}$), 28.62 (d, $J_{CP} = 5.4$ Hz, $C^{1''}$), 41.73 (d,

$J_{CP} = 17.5$ Hz, $C^{2''}$), 49.02 (dd, $J_{CP} = 28.2$, 1.6 Hz, *C*H(alkene) *trans*P^1), 49.73 (dd, $J_{CP} = 27.8$, 2.4, *C*H(alkene) *trans*P^2), 68.47 (s, Cp^2), 69.70 (d, $J_{CP} = 4.9$ Hz, Cp^1), 70.97 (s, Cp^2), 71.67 (s, Cp^2), 72.13 (s, $C^{5'}$ Cp^2), 73.46 (s, Cp^1), 73.47 (s, Cp^1), 75.86 (s, Cp^1), 86.94 (s, Cp^2), 91.78 (dd, $J_{CP} = 21.7$, 4.7 Hz, C_{Cp}-P), 128.23 (d, $J_{CP} = 9.3$ Hz, C_{meta}Ph), 128.64 (d, $J_{CP} = 11.3$ Hz, C_{meta}Ph), 131.43 (d, $J_{CP} = 15.5$ Hz, C_{ortho} Ph_{up}), 135.45 (d, $J_{CP} = 16.6$ Hz, C_{ortho} Ph_{down}), 138.61 (d, $J_{CP} = 39.7$ Hz, C_{ipso}Ph), 172.02 (d, $J_{CP} = 6.9$ Hz, CO_{AM}), 172.72 (d, $J_{CP} = 4.4$ Hz, CO_{AM}) ppm. (**2m**): $\delta = 24.23$ (d, $J_{CP} = 12.1$ Hz, $C^{3''}$), 42.42 (d, $J_{CP} = 14.6$ Hz, $C^{2''}$), 49.40 (dd, $J_{CP} = 28.2$, 2.4 Hz, *C*H(alkene) *trans*P^1), 49.24 (dd, $J_{CP} = 28.6$, 2.0 Hz, *C*H(alkene) *trans*P^2), 69.01 (s, Cp^2), 69.9 (d, $J_{CP} = 14.9$, Cp^1), 71.11 (s, Cp^2), 71.62 (s, Cp^1), 71.82 (s, $C^{5'}$ Cp^2), 72.05 (s, Cp^2), 73.33 (d, $J_{CP} = 3.2$ Hz, Cp^1), 76.25 (s, Cp^1), 86.46 (s, Cp^2), 91.64 (dd, $J_{CP} = 22.2$, 4.8 Hz, C_{Cp}-P), 128.15 (d, $J_{CP} = 9.7$ Hz, C_{meta}Ph), 128.5 (d, $J_{CP} = 10.9$ Hz, C_{meta}Ph), 131.2 (d, $J_{CP} = 14.5$ Hz, C_{ortho} Ph_{up}), 135.23 (d, $J = 16.6$ Hz, C_{ortho}Ph$_{down}$), 136.70 (d, $J_{CP} = 36.7$ Hz, C_{ipso}Ph), 170.54 (d, $J_{CP} = 6.9$ Hz, CO_{AM}), 172.71 (overlapped signal, CO_{AM}) ppm.

4.2.3. [Pd(η^3-2-Me-C_3H_4)($PP^{Cy}PF$)]OTf (**3**)

[Pd(η^3-2-Me-C_3H_4)Cl]$_2$ (22.0 mg, 0.056 mmol) was solved in acetone (10 mL). This solution was transferred to another schlenk flask containing AgOTf (28.7 mg, 0.112 mmol) in methanol (10 mL) protected from light. This mixture was vigorously stirred for three hours, and filtered with celite in order to eliminate the AgCl formed. To the yellow filtrate was added $PP^{Cy}PF$ (67.9 mg, 0.112 mmol), and immediately the solution turned orange. The solution is stirred for two and a half hours, and finally dried at reduced pressure. A brownish-orange solid of **3** is obtained. Yield: 70% (71 mg, 0.078 mmol,). $C_{42}H_{51}F_3FeO_3P_2PdS$ (917.16): calc. C 55.00, H 5.60, S 3.50; found C 54.72, H 5.89, S 3.95%. IR (KBr): $\bar{\nu} = 1262$, 1220, 1146, 637 cm^{-1} (CF_3SO_3), 1433, 1029 cm^{-1} (η^3-2-Me-C_3H_4). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): some signals are common or not clearly assignable to a specific isomer: $\delta = 0.82$–2.40 (PCy_2 and some of the interannular chain protons) ppm. (**3M**, *exo*): $\delta = 1.05$ (s, 3H, CH_3-allyl), 2.23 (s, 1H, $H^{5'}$ Cp^2), 2.89 (t, $J_{HP} = J_{HH} = 13.2$ Hz, $H^{1''}$), 3.14 (d, $J = 10.7$ Hz, 1H, H_{a2}), 3.66 (m, 1H, Cp^2), 3.67 (d, $J = 9.0$ Hz, 1H, H_{a1}), 3.70 (bs, 1H, H_{s1}), 3.91 (s, 1H, Cp^2), 4.13 (s, 1H, Cp^2), 4.32 (bs, 1H, H_{s2}), 4.37 (s, 1H, Cp^1), 4.42 (m, 1H, Cp^1), 4.60 (s, 1H, Cp^1), 6.94–7.95 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 7.01$ (m, $H_{ortho}Ph^1_{up}$), 7.94 (m, $H_{ortho}Ph^1_{down}$). (**3m**, *endo*): $\delta = 2.07$ (s, 3H, CH_3-allyl), 2.09 (s, 1H, $H^{5'}$ Cp^2), 2.88 (overlapped signal H_{a1}), 2.98 (t, $J_{HP} = J_{HH} = 13.2$ Hz, $H^{1''}$), 3.64 (m, 1H, Cp^2), 3.91 (s, 1H, Cp^2), 4.20 (s, 1H, Cp^2), 4.22 and 4.27 (bs, 2H, H_{s1}/H_{s2}), 4.45 (s, 1H, Cp^1), 4.47 (m, 1H, Cp^1), 4.74 (s, 1H, Cp^1), 6.98–7.98 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 7.08$ (m, $H_{ortho}Ph^1_{up}$), 7.69 (m, $H_{ortho}Ph^1_{down}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): some signals are common or not clearly assignable to one of the two isomers: $\delta =$ 25.5–25.8 (overlapped signals, Cy); 133.31 (d, $J_{CP} = 48.7$, C_{ipso}Ph), 134.32 (d, $J_{CP} = 49.9$, C_{ipso}Ph), 135.22 (d, $J_{CP} = 49.5$, C_{ipso}Ph), 137.01 (d, $J_{CP} = 39.6$, C_{ipso}Ph). (**3M**, *exo*): 22.85 (s, *Me*-allyl), 23.74 (d, $J_{CP} = 12.1$ Hz, $C^{3''}$), 28.23 (d, $J_{CP} = 15.5$ Hz, $C^{1''}$), 41.83 (d, $J_{CP} = 9.7$ Hz, $C^{2''}$), 65.13 (d, $J_{CP} = 32.2$ Hz, $CH_{2allyl}{}^2$), 68.72 (dd, $J_{CP} = 43.9$ Hz, 6.8, Cp^1), 69.23 (s, Cp^2), 70.22 (d, $J_{CP} = 6.4$, Cp^1), 71.12 (s, Cp^2), 72.34 (s, $C^{5'}$ Cp^2), 72.42 (s, Cp^2), 73.45 (dd, $J_{CP} = 8.5$, 3.3 Hz, Cp^1), 75.62 (s, Cp^1), 77.84 (d, $J_{CP} = 25.3$ Hz, CH^1_{2allyl}), 86.73 (s, Cp^2), 91.02 (t, $J_{CP} = 5.3$ Hz, C_{Cp}-P), 128.61 (d, $J_{CP} = 10.1$, $C_{meta}Ph_{up}$), 129.22 (d, $J_{CP} = 15.7$ Hz, $C_{meta}Ph_{down}$), 129.84 (d, $J_{CP} = 2.0$ Hz, $C_{para}Ph_{down}$), 130.42 (d, $J_{CP} = 12.7$ Hz, $C_{ortho}Ph_{up}$), 132.21 (d, $J_{CP} = 2.0$ Hz, $C_{para}Ph_{down}$), 135.43 (d, $J_{CP} = 14.9$ Hz, $C_{ortho}Ph_{down}$), 135.85 (t, $J_{CP} = 5.6$ Hz, –*C*=CH_2) ppm. (**3m**, *endo*): 23.58 (d, $J_{CP} = 12.1$ Hz, $C^{3''}$), 23.96 (s, *Me*-allyl), 28.2 (d, $J_{CP} = 22.4$ Hz, $C^{1''}$), 41.62 (d, $J_{CP} = 11.7$ Hz, $C^{2''}$), 66.55 (d, $J_{CP} = 32.7$, CH^2_{2allyl}), 67.83 (dd, $J_{CP} = 46.3$, 6.8 Hz, Cp^1), 69.42 (s, Cp^2), 70.53 (d, $J_{CP} = 6.8$ Hz, Cp^1), 71.12 (s, Cp^2), 72.0 (s, $C^{5'}$ Cp^2), 72.76 (s, Cp^2), 73.80 (dd, $J_{CP} = 9.5$ Hz, 2.8, Cp^1), 75.12 (d, $J_{CP} = 24.2$ Hz, CH^1_{2allyl}), 75.71 (s, Cp^1), 86.4 (s, Cp^2), 90.84 (t, $J_{CP} = 4.9$ Hz, C_{Cp}-P), 128.72 (d, $J_{CP} = 10.1$ Hz, $C_{meta}Ph_{up}$), 128.01 (d, $J_{CP} = 11.3$ Hz, $C_{meta}Ph_{down}$), 130.14 (s, $C_{para}Ph_{down}$), 130.80 (d, $J_{CP} = 10.9$ Hz, $C_{ortho}Ph_{up}$), 132.45 (d, $J_{CP} = 2.5$ Hz, $C_{para}Ph_{down}$), 134.32 (d, $J_{CP} = 49.9$ Hz, Ph_{ipso}), 135.01 (d, $J_{CP} = 15.7$ Hz, $C_{ortho}Ph_{down}$), 135.91 (t, $J_{CP} = 5.6$ Hz, –*C*=CH_2) ppm.

4.2.4. [Pd(η^3-2-Me-C_3H_4)($PP^{Ph}PF$)]OTf (**4**)

The method is similar to that used for complex **3**. Amounts are as follows: [(η^3-2-Me-C_3H_4)PdCl]$_2$ (22.0 mg, 0.056 mmol) in acetone (10 mL), AgOTf (28.7 mg, 0.112 mmol) in methanol (10 mL), $PP^{Ph}PF$ (66.5 mg, 0.112 mmol). There was not an appreciable change of the colour. After drying at reduced pressure, the solid was extracted with CH_2Cl_2 (2 × 10 mL) in order to eliminate a small amount of black precipitate. After evaporation to dryness of the solution a yellow solid of **4** is obtained. Yield: 60% (61 mg, 0.067 mmol). $C_{42}H_{39}F_3FeO_3P_2PdS$ (905.03): calc. C 55.74, H 4.34, S 3.54; found C 56.19, H 4.68, S 3.56%. IR (KBr): $\bar{\nu} = 1260$, 1220, 1148, 637 cm^{-1} (CF_3SO_3), 1028 and 1433 cm^{-1} (η^3-2-Me-C_3H_4). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): (**4M**, *exo*): $\delta = 1.21$ (s, 3H, CH_3-allyl), 1.61 (t, $J_{HH} = 13.8$ Hz, $H^{3''ax}$), 2.27 and 2.34 (overlapped signals, $H^{3''eq}$ and $H^{2''ax}$), 2.51 (m, $H^{2''eq}$), 3.19 (t, $J_{HP} = J_{HH} = 12.2$ Hz, $H^{1''ax}$), 2.67 (s, $H^{5'}$ Cp^2), 3.42 (s, 1H, Cp^2), 3.51 (d, $J_{HH} = 10.3$ Hz, 1H, H_{a2}), 3.80 (bs, 1H, H_{s1}), 3.84 (s, 1H, Cp^2), 3.94 (d, $J_{HH} = 9.8$ Hz, 1H, H_{a2}), 4.08 (overlapped signal, 1H, H_{s2}), 4.09 (s, 1H, Cp^2), 4.16 (s, 1H, Cp^1), 4.26 (m, 1H, Cp^1), 4.61 (s, 1H, Cp^1), 6.52–8.15 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 6.54$ (dd, $J = 11.7$, 8.3 Hz, $H_{ortho}Ph^1_{up}$), 8.12 (dd, $J = 12.4$, 7.1 Hz, $H_{ortho}Ph^1_{down}$). (**4m**, *endo*): $\delta =$ 1.75 (t, $J_{HH} = 13.2$ Hz, $H^{3''ax}$), 1.76 (m, $H^{2''eq}$), 2.30 (s, 3H, CH_3-allyl), 2.71 (s, 1H, $H^{5'}$ Cp^2), 3.32 (t,

$J_{HP} = J_{HH} = 13.3$ Hz, $H^{1''ax}$), 3.48 (s, 1H, Cp^2), 3.19 (overlapped signal, 1H, H_{a1}), 3.84 (overlapped signal, Cp^2), 4.41 (bs, 1H, H_{s1}), 4.19 (s, 1H, Cp^1), 4.21 (s, 1H, Cp^2), 4.31 (s, 1H, Cp^1), 4.40 (bs, 1H, H_{s2}), 4.85 (s, 1H, Cp^1), 6.52–8.15 (P*Ph*$_2$) ppm. Identified signals: $\delta = 6.64$ (dd, $J = 11.7$, 7.8 Hz, $H_{ortho}Ph^1_{up}$), 7.81 (m, $H_{ortho}Ph^1_{down}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): (**4M**, *exo*): $\delta = 22.88$ (s, *Me*-allyl), 23.60 (d, $J_{CP} = 14.6$ Hz, $C^{3''}$), 33.79 (dd, $J_{CP} = 26.0$, 2.0 Hz, $C^{1''}$), 41.57 (bd, $J = 17.1$ Hz, $C^{2''}$), 67.2 (dd, $J_{CP} = 47.0$, 9.1 Hz, C^1), 69.10 (Cp^2), 70.40 (dd, $J_{CP} = 20.0$, 6.0 Hz, Cp^1), 70.82 (dd, $J_{CP} = 30.2$, 2 Hz, CH^2_{2allyl}), 71.08 (Cp^2), 71.76 ($C^{5'}$ Cp^2), 72.37 (Cp^2), 74.01 (dd, $J_{CP} = 8.2$, 4.3 Hz, C^1), 74.83 (s, Cp^1), 77.01 (overlapped signal, CH^1_{2allyl}), 87.62 (Cp^2), 90.66 (dd, $J = 20.1$, 6.0 Hz, Cp^1-P), 137.20 (t, $J_{CP} = 6.2$, $-C{=}CH_{2allyl}$), 127.78- 137.32 (P*Ph*$_2$) ppm. Some of the Ph signals have been identified: $\delta = 129.60$ (s, C_{para}Ph), 130.5 (d, $J_{CP} = 11.5$, $C_{ortho}Ph_{up}$), 131.30 (s, C_{para}Ph), 131.60 (s, C_{para}Ph), 132.20 (s, C_{para}Ph), 133.2 (d, $J_{CP} = 13.0$ Hz, C_{ortho}Ph), 134.7 (d, $J_{CP} = 13.4$ Hz, 2C, C_{ortho}Ph), 135.4 (d, $J_{CP} = 15.3$ Hz, $C_{ortho}Ph_{down}$). (**4m**, *endo*): $\delta = 23.40$ (d, $J_{CP} = 14.0$ Hz, $C^{3''}$), 24.23 (s, *Me*-allyl), 33.34 (dd, $J_{CP} = 17.0$, 2.0 Hz, $C^{1''}$), 41.79 (d, $J_{CP} = 17.0$ Hz, $C^{2''}$), 67.10 (dd, $J_{CP} = 48.4$, 9.1 Hz, C^1), 69.40 (s, Cp^2), 70.65 (d, $J_{CP} = 6.2$ Hz, Cp^1), 71.14 (s, Cp^2), 71.40 (s, $C^{5'}$ Cp^2), 75.07 (s, Cp^2), 72.74 (s, Cp^1), 73.5 (dd, $J_{CP} = 36.8$, 2.0 Hz, CH^1_{2allyl}), 74.10 (overlapped signal, CH^2_{2allyl}), 74.56 (dd, $J_{CP} = 8.6$, 4.31 Hz, Cp^1), 87.31 (s, Cp^2), 90.70 (dd, $J_{CP} = 20.0$, 6.0 Hz, C_{Cp}-P), 127.78–137.32 (P*Ph*$_2$), 137.38 (t, $J_{CP} = 5.8$ Hz, $-C{=}CH_2$) ppm. Some of the Ph signals have been identified: $\delta = 129.92$ (s, C_{para}Ph), 130.82 (d, $J_{CP} = 11.5$ Hz, $C_{ortho}Ph_{up}$), 131.60 (s, C_{para}Ph), 131.92 (s, C_{para}Ph), 132.51 (s, C_{para}Ph), 132.92 (d, $J_{CP} = 12.9$ Hz, C_{ortho}Ph), 135.40 (d, $J_{CP} = 15.3$ Hz, $C_{ortho}Ph_{down}$) ppm. Other PPh_2 signal not assigned to a concrete isomer: $\delta = 128.22$ (d, $J_{CP} = 10.1$ Hz, C_{meta}Ph), 132.53 (C_{para}Ph), 132.15 (C_{para}Ph), 131.55 (C_{para}Ph), 131.22 (d, $J_{CP} = 2.2$ Hz, C_{para}Ph), 133.13 (d, $J_{CP} = 13.1$ Hz, C_{ortho}Ph), 133.78 (d, $J_{CP} = 50.34$ Hz, C_{ipso}Ph), 134.65 (d, $J_{CP} = 13.6$ Hz, C_{ortho}Ph), 134.71 (d, $J_{CP} = 51.3$ Hz, C_{ipso}Ph), 136.70 (d, $J_{CP} = 49.9$ Hz, C_{ipso}Ph), 135.35 (d, $J_{CP} = 15.1$ Hz, C_{ortho}-Ph), 136.60 (d, $J_{CP} = 49.6$ Hz, C_{ipso}Ph) ppm.

4.2.5. [PdClMe(PP^{Cy}PF)] (5)

[PdClMe(cod)] (21.85 mg, 0.082 mmol) and PP^{Cy}PF (50.0 mg, 0.082 mmol) were dissolved in toluene (15 mL). This solution was stirred for 17 h. It was observed the precipitation of a yellow solid. The solvent was filtered off and the solid dried at reduced pressure. Yield: 70% (51 mg, 0.057 mmol,). $C_{38}H_{47}ClFeP_2Pd \cdot 3/2C_7H_8$ (901.69): calc. C 64.61, H 6.59; found C 64.97, H 6.67%. IR (KBr): $\bar{\nu} = 292$ cm^{-1} (Pd–Cl). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.76$ (d, $J_{HP} = 7.6$ Hz, *Me*-Pd), 1.08–2.47 (P*Cy*$_2$), 2.56 (t, $J_{HH} = 12.9$ Hz, $H^{1''ax}$), 2.03 (s, 1H, $H^{5'}$ Cp^2), 3.69 (s, 1H, Cp^2), 3.86 (s, 1H, Cp^2), 3.97 (s, 1H, Cp^2), 4.29 (s, 1H, Cp^1), 4.35 (s, 2H, Cp^1), 7.16–7.56 (P*Ph*$_2$) ppm. One Ph signal has been identified: $\delta = 8.10$ (m, $H_{ortho}Ph^1_{down}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 5.78$ (d, $J_{CP} = 102.7$ Hz, *Me*-Pd), 24.20 (d, $J_{CP} = 11.6$ Hz, $C^{3''}$), 21.40–39.29 (P*Cy*$_2$ and $C^{1''}$), 41.23 (d, $J_{CP} = 9.1$ Hz, $C^{2''}$), 68.41 (s, Cp^2), 68.86 (d, $J_{CP} = 2.3$ Hz, Cp^1), 70.95 (s, Cp^2), 71.51 (s, Cp^2), 71.52 (dd, $J_{CP} = 28.0$, 4.0 Hz, Cp^1), 72.23 (dd, $J_{CP} = 6.0$, 1.0 Hz, Cp^1), 72.42 (s, Cp^2), 76.02 (s, Cp^1), 85.53 (s, Cp^2), 89.96 (dd, $J_{CP} = 22.2$, 4.5 Hz, C_{Cp}-P), 127.21 (d, $J_{CP} = 9.1$ Hz, C_{meta}Ph), 127.86 (d, $J_{CP} = 10.1$ Hz, C_{meta}Ph), 128.53 (d, $J_{CP} = 1.7$ Hz, C_{para}Ph), 130.54 (d, $J_{CP} = 1.7$ Hz, C_{para}Ph), 132.87 (d, $J_{CP} = 10.1$ Hz, C_{ortho}Ph), 134.96 (d, $J_{CP} = 36.3$ Hz, C_{ipso}Ph), 136.10 (d, $J_{CP} = 42.3$ Hz, C_{ipso}Ph), 137.02 (d, $J_{CP} = 14.0$ Hz, C_{ortho}Ph) ppm.

4.2.6. [PdClMe(PP^{Ph}PF)] (6)

The method is similar to that used for complex **5**. Amounts are as follows: [PdClMe(cod)] (22.3 mg, 0.084 mmol) and PP^{Ph}PF (50.0 mg, 0.084 mmol) in toluene (15 mL). Complex **6** was obtained as a yellow solid. Yield: 60% (41 mg, 0.050 mmol,). $C_{38}H_{35}ClFeP_2Pd \cdot 2/3C_7H_8$ (812.73): calc. C 63.05, H 5.00; found C 63.24, H 5.23%. IR (KBr): $\bar{\nu} = 289$ cm^{-1} (Pd–Cl). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): some signals are common or not clearly assignable to one of the two isomers: $\delta = 6.69$–8.89 (P*Ph*$_2$) ppm. (**6M**): $\delta = 0.77$ (dd, $J_{HP} = 8.3$, 3.2 Hz, *Me*-Pd), 1.52 (t, $J_{HH} = 15.4$ Hz, $H^{3''ax}$), 2.22 (m, 1H, $H^{2''eq}$), 2.32 (m, 1H, $H^{3''eq}$), 2.34 (s, 1H, $H^{5'}$ Cp^2), 2.60 (bd, $J_{HH} = 13.1$ Hz, $H^{2''ax}$), 2.86 (t, $J_{HH} = 12.2$ Hz, $H^{1''ax}$), 3.51 (s, 1H, Cp^2), 3.79 (s, 1H, Cp^2), 3.96 (s, 1H, Cp^2), 4.09 (s, 1H, Cp^1), 4.11 (s, 1H, Cp^1), 4.31 (s, 1H, Cp^1), 6.73 (q, $J = 9.5$ Hz, $H_{ortho}Ph^1_{up}$), 7.87 (m, $H_{ortho}Ph^2_{down}$), 8.43 (m, $H_{ortho}Ph^1_{down}$) ppm. (**6m**): $\delta = 0.74$ (dd, $J_{HP} = 7.9$, 3.5 Hz, *Me*-Pd), 1.47 (t, $J_{HH} = 13.7$, 1H, $H^{3''ax}$), 2.15 (m, 1H, $H^{2''eq}$), 2.15 (s, 1H, $H^{5'}$ Cp^2), 2.73 (d, $J_{HH} = 12.0$ Hz, 1H, $H^{2''ax}$), 2.32 (m, 1H, $H^{3''eq}$), 2.81 (t, $J_{HH} = 12.9$ Hz, 1H, $H^{1''ax}$), 3.52 (s, 1H, Cp^2), 3.79 (s, 1H, Cp^2), 4.00 (m, 2H, Cp^{1and2}), 4.11 (m, 1H, Cp^1), 4.40 (s, 1H, Cp^1), 8.07 (t, $J = 8.9$ Hz, $H_{ortho}Ph^2_{down}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): Ph signals were not clearly assignable to one of the two isomers: 125.25–137.00 (P*Ph*$_2$) ppm. (**6M**): $\delta = 13.46$ (d, $J_{CP} = 99.8$ Hz, *Me*-Pd), 24.31 (d, $J_{CP} = 14.5$ Hz, $C^{3''}$), 35.74 (dd, $J_{CP} = 29.0$, 6.3 Hz, $C^{1''}$), 41.01 (dd, $J_{CP} = 14.0$, 3.3 Hz, $C^{2''}$), 68.8 (s, Cp^2), 69.4 (s, Cp^1), 70.95 (d, $J_{CP} = 6.9$ Hz, Cp^1), 71.5 (s, Cp^2), 72.0 (s, $C^{5'}$ Cp^2), 72.05 (d, $J_{CP} = 6.4$ Hz, Cp^2), 73.1 (dd, $J_{CP} = 7.7$, 4.9 Hz, Cp^1), 76.0 (s, Cp^1), 86.8 (s, Cp^2), 89.9 (dd, $J_{CP} = 22.1$, 5.2 Hz, C_{Cp}-P) ppm. Some of the phenyl signals have been identified: $\delta = 127.19$ (d, $J_{CP} = 9.2$ Hz, C_{meta}Ph), 128.06 (d, $J_{CP} = 10.7$ Hz, C_{meta}Ph), 128.18 (d, $J_{CP} = 10.8$ Hz, C_{meta}Ph), 128.48 (d, $J_{CP} = 2.8$ Hz, C_{para}Ph), 128.88 (d, $J_{CP} = 2.6$ Hz, C_{para}Ph), 130.78 (d, $J_{CP} = 2.1$ Hz, C_{para}Ph), 131.40 (d, $J_{CP} = 2.0$ Hz, C_{para}Ph), 132.84 (d, $J_{CP} = 10.5$ Hz, $C_{ortho}Ph_{up}$),133.56 (d, 10.5 Hz, C_{ortho}Ph), 136.02 (d, $J_{CP} = 12.9$ Hz, C_{ortho}Ph), 137.10 (d, $J_{CP} = 14.1$ Hz, $C_{ortho}Ph_{down}$) ppm. (**6m**): $\delta =$ 17.56 (d, $J_{CP} = 100.0$ Hz, *Me*-Pd), 24.03 (d, $J_{CP} = 13.3$ Hz,

$C^{3''}$), 33.00 (dd, $J_{CP} = 18.0$, 2.2 Hz, $C^{1''}$), 41.48 (d, $J_{CP} = 18.2$ Hz, $C^{2''}$), 68.9 (s, Cp^2), 69.5 (s, Cp^2), 69.6 (s, Cp^1), 70.70 (d, $J_{CP} = 6.9$ Hz, Cp^1), 71.7 (s, Cp^2), 72.3 (s, $C^{5'}$ Cp^2), 72.4 (d, $J_{CP} = 11.1$ Hz, Cp^2), 73.4 (dd, $J_{CP} = 8.0$, 3.8 Hz, Cp^1), 76.8 (d, $J_{CP} = 2.9$ Hz, Cp^1), 87.6 (s, Cp^2), 91.0 (dd, $J_{CP} = 17.7$, 8.1 Hz, C_{Cp}-P) ppm. Some of the phenyl signals have been identified: $\delta = 127.48$ (d, $J_{CP} = 10.4$ Hz, C_{meta}Ph), 134.82 (d, $J_{CP} = 11.1$ Hz, C_{ortho}Ph), 135.10 (d, 11.6 Hz, C_{ortho}Ph) ppm.

4.2.7. [$PdMe_2(PP^{Cy}PF)$] (7)

[$PdMe_2$(TMEDA)] (20.8 mg, 0.082 mmol) and $PP^{Cy}PF$ (50.0 mg, 0.082 mmol) were dissolved in toluene (15 mL). This solution was stirred for 16 h. It was observed a change in the colour of the solution, from yellow to yellow-orange. The volume of the solution was reduced at vacuum, and hexane was added (10 mL). After 2 days in the refrigerator, orange crystals were obtained. Yield: 76% (46 mg, 0.062 mmol,). $C_{39}H_{50}FeP_2Pd$ (743.02): calc. C 63.04, H 6.78; found C 62.97, H 6.71%. IR (KBr): $\bar{\nu} = 514$ cm^{-1} (Pd-Me). ^1H NMR (300 MHz, [D_6]benzene, 25 °C): $\delta = 0.71$ (dd, $J_{HP2} = 8.6$ Hz, $J_{HP1} = 6.6$ Hz, $Me_{transP2}$-Pd), 0.98 (dd, $J_{HP2} = 6.6$ Hz, $J_{HP1} = 7.1$ Hz, $Me^{transP1}$-Pd), 0.83–2.26 (PCy_2 and interannular chain), 2.16 (bs, 1H, $H^{5'}$ Cp^2), 2.50 (m, 1H, $H^{1''ax}$), 3.59 (bs, 1H, Cp^2), 3.69 (bs, 2H, Cp^2), 3.85 (bs, 1H, Cp^1), 3.95 (pt, $J = 2.4$ Hz, 1H, Cp^1), 4.06 (m, 1H, Cp^1), 6.91–7.18 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 7.35$ (m, $H_{ortho}Ph^1_{up}$), 8.12 (m, $H_{ortho}Ph^1_{down}$). $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): $\delta = 3.10$ (dd, $J_{CP} = 106.4$, 10.6 Hz, $Me^{transP1}$-Pd), 9.01 (dd, $J = 102.8$, 10.0 Hz, $Me^{transP2}$), 24.90 (d, $J_{CP} = 10.8$ Hz, $C^{3''}$), 26.85–39.44 (PCy_2), 34.83 (dd, $J_{CP} = 7.2$, 2.8 Hz, $C^{1''}$), 42.09 (dd, $J_{CP} = 15.9$, 3.2 Hz, $C^{2''}$), 68.80 (Cp), 68.93 (Cp), 71.75 (Cp), 72.10 (Cp), 72.84 (dd, $J = 7.7$, 2.5 Hz, Cp^1), 73.19 (Cp), 77.68 (Cp^1), 86.70 (Cp^2), 92.20 (dd, $J_{CP} = 7.0$, 24.0 Hz, C_{Cp}-P), 126.10–139.06 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 130.81$ (d, $J = 2.1$ Hz, C_{para}Ph), 132.70 (d, $J = 10.5$ Hz, Ph), 138.07 (d, $J = 15.0$ Hz, C_{ortho}Ph) ppm.

4.2.8. [$PdMe_2(PP^{Ph}PF)$] (8)

The method is similar to that used for complex **7**. Amounts are as follows: [$PdMe_2$(TMEDA)] (21.2 mg, 0.084 mmol) and $PP^{Ph}PF$ (50.0 mg, 0.084 mmol) in toluene (15 mL). There was not an appreciable change in the colour of the solution, and the product is finally obtained as orange crystals. Yield: 60% (41 mg 0.050 mmol,). $C_{39}H_{38}FeP_2Pd.C_7H_8$ (823.111): calc. C 67.13, H 5.63; found C 66.99, H 5.78%. IR (KBr): $\bar{\nu} = 506$ cm^{-1} (Pd-Me). ^1H NMR (300 MHz, [D_6]benzene, 25 °C): $\delta = 0.93$ (dd, $J_{HP2} = 8.6$ Hz, $J_{HP1} = 6.4$ Hz, $Me^{transP2}$-Pd), 1.00 (overlapped signal, $H^{2''ax}$), 1.06 (dd, $J_{HP1} = 7.9$ Hz, $J_{HP2} = 6.4$ Hz, $Me^{transP1}$-Pd), 1.91 (dt, $J_{HH} = 14.2$, 2.9 Hz, $H^{2''eq}$), 2.28 (m, $H^{3''ax} + H^{1''ax}$), 2.33 (m, 1H, $H^{5'}$ Cp^2), 2.47 (m, $H^{3''eq}$), 3.37 (m, 1H, Cp^2), 3.56 (m, 1H, Cp^2), 3.60 (m, 1H, Cp^2), 3.71 (m, 1H, Cp^1), 3.76 (m, 1H, Cp^1), 3.79 (m, 1H, Cp^1), 6.80–7.13 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 7.74$ (t, $J = 7.7$ Hz, $H_{ortho}Ph^2_{down}$), 8.12 (pt, $J = 6.5$ Hz, $H_{ortho}Ph^1_{down}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene, 25 °C): $\delta = 7.20$ (dd, $J_{CP} = 103.6$, 9.0 Hz, *Me*-Pd), 8.29 (dd, $J_{CP} = 107.4$, 9.0 Hz, *Me*-Pd), 24.20 (d, $J_{CP} = 12.3$ Hz, $C^{3''}$), 34.73 (dd, $J_{CP} = 17.0$, 4.0 Hz, $C^{1''}$), 41.70 (d, $J_{CP} = 19.6$ Hz, $C^{2''}$), 68.39 (s, Cp^2), 68.79 (d, $J_{CP} = 4.0$ Hz, Cp^1), 71.44 (s, Cp), 71.74 (s, Cp), 72.02 (s, Cp), 73.15 (dd, $J_{CP} = 6.0$, 2.0 Hz, Cp^1), 76.51 (s, Cp^1), 87.17 (Cp^2), 91.50 (dd, $J_{CP} = 6.0$, 21.0 Hz, C_{Cp}-P), 125.63–137.47 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 129.77$ (d, $J_{CP} = 2.0$ Hz, C_{para}Ph), 130.16 (d, $J_{CP} = 2.0$ Hz, C_{para}Ph), 130.49 (d, $J_{CP} = 2.0$ Hz, C_{para}Ph), 131.97 (d, $J_{CP} = 10.6$ Hz, C_{meta}Ph), 132.70 (d, $J_{CP} = 30.0$ Hz, C_{ipso}Ph), 134.63 (d, $J_{CP} = 12.1$ Hz, C_{meta}Ph), 135.60 (d, $J_{CP} = 33.0$ Hz, C_{ipso}Ph), 135.71 (d, $J_{CP} = 13.6$ Hz, C_{ortho}Ph), 137.37 (d, $J_{CP} = 15.1$ Hz, C_{ortho}Ph), 138.00 (d, $J_{CP} = 41.0$ Hz, C_{ipso}Ph), 139.00 (d, $J_{CP} = 41.0$ Hz, C_{ipso}Ph) ppm.

4.2.9. [$Pd(C_6F_5)_2(PP^{Cy}PF)$] (9)

[$Pd(C_6F_5)_2$(cod)] (54.3 mg, 0.099 mmol) and $PP^{Cy}PF$ (60.0 mg, 0.099 mmol) were dissolved in toluene (15 mL). This solution was vigorously stirred for 16 h, and dried at reduced pressure to afford a yellow-orange oil, which was transformed into a solid with hexane to obtain finally, after filtering and drying at reduced pressure, a yellow-orange solid. Yield: 97% (119 mg, 0.096 mmol,). $C_{49}H_{44}F_{10}FeP_2Pd \cdot 2C_7H_8$ (1237.43): calc. C 61.15, H 4.89; found C 60.91, H 4.68%. IR (KBr): $\bar{\nu} = 1494$, 953, 772 cm^{-1} (C_6F_5). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.60$–2.76 (PCy_2 and interannular chain), 0.88 (q, $J_{HH} = 6.9$ Hz, $H^{2''ax}$), 2.14 (s, 1H, $H^{5'}$ Cp^2), 2.62 (t, $J_{HH} = 12.2$ Hz, $H^{1''ax}$), 3.72 (s, 1H, Cp^2), 3.90 (s, 1H, Cp^2), 4.02 (s, 1H, Cp^2), 4.37 (s, 1H, Cp^1), 4.42 (s, 2H, Cp^1), 7.17–7.50 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 6.92$ (t, $J_{HH} = 7.2$ Hz, $H_{ortho}Ph^1_{up}$), 8.08 (bm, $H_{ortho}Ph^1_{down}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 24.16$ (d, $J_{CP} = 12.6$ Hz, $C^{3''}$), 41.17 (d, $J_{CP} = 13.6$ Hz, $C^{2''}$), 26.01–41.26 (PCy_2 and $C^{1''}$), 68.72 (d, $J_{CP} = 10.6$ Hz, Cp^2), 69.05 (s, Cp^2), 70.76 (d, $J_{CP} = 8.1$ Hz, Cp^1), 71.24 (d, $J_{CP} = 4.0$ Hz, Cp^1), 71.59 (dd, $J_{CP} = 7.8$, 34.5 Hz, Cp^1), 72.71 (d, $J_{CP} = 3.0$ Hz, Cp^1), 72.80 (s, Cp^2), 76.16 (s, Cp^1), 86.59 (Cp^2), 90.04 (dd, $J_{CP} = 20.1$, 5.0 Hz, C_{Cp}-P), 127.51 (d, $J_{CP} = 9.6$ Hz, C_{meta}Ph), 127.92 (d, $J_{CP} = 10.6$ Hz, C_{meta}Ph), 129.74 (s, C_{ipso}Ph), 131.15 (s, C_{ipso}Ph), 132.54 (d, $J_{CP} = 10.6$ Hz, C_{ortho}Ph), 133.61 (d, $J_{CP} = 48.3$ Hz, C_{ipso}Ph), 134.84 (d, $J_{CP} = 49.9$ Hz, C_{ipso}Ph), 135.63 (bd, $J = 13.6$ Hz, C_{ortho}Ph) ppm.

4.2.10. [$Pd(C_6F_5)_2(PP^{Ph}PF)$] (10)

The method is similar to that used for complex **9**. Amounts are as follows: [$Pd(C_6F_5)_2$(cod)] (55.4 mg, 0.101 mmol) and $PP^{Ph}PF$ (60.0 mg, 0.101 mmol) in toluene (15 mL). The complex was obtained as a yellow-orange solid. Yield: 86% (94 mg 0.087 mmol,). $C_{49}H_{32}F_{10}FeP_2Pd \cdot 1/2C_7H_8$ (1081.05): calc. C 58.33, H 3.36; found C

58.50, H 3.84%. IR (KBr): $\bar{\nu} = 1495$, 952 cm^{-1} (C_6F_5). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.87$ (q, $J_{HH} = 7.3$ Hz, $H^{2''ax}$), 1.87 (t, $J_{HH} = 13.6$ Hz, $H^{3''ax}$), 2.01 (s, 1H, $H_{5'}$ Cp^2), 2.52 (dd, $J_{HH} = 13.5$, $J^2_{HP} = 6.4$Hz, $H^{2''eq}$), 2.59 (dd, $J_{HH} = 13.5$, $J^2_{HP} = 3.2$Hz, $H^{3''eq}$), 3.17 (t, $J_{HH} = 12.7$ Hz, $H^{1''ax}$), 3.61 (s, 1H, Cp^2), 3.81 (s, 1H, Cp^2), 4.01 (s, 1H, Cp^2), 4.01 (m, 1H, Cp^1), 4.19 (s, 1H, Cp^1), 4.21 (s, 1H, Cp^1), 6.88–7.83 (PPh_2) ppm. Some of the Ph signals have been identified: $\delta = 6.52$ (dd, $J_{HH} = 10.9$, 7.4 Hz, $H_{ortho}Ph^1_{up}$), 7.92 (dd, $J_{HH} = 11.0$, 7.1 Hz, $H_{ortho}Ph^2_{down}$), 8.18 (bm, $H_{ortho}Ph^1_{down}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 24.27$ (d, $J_{CP} = 14.1$ Hz, $C^{3''}$), 33.36 (d, $J_{CP} = 18.6$ Hz, $C^{1''}$), 42.61 (d, $J_{CP} = 15.0$ Hz, $C^{2''}$), 68.50 (d, $J_{CP} = 8.0$ Hz, Cp^2), 68.80 (d, $J_{CP} = 8.0$ Hz, Cp^2), 70.71 (d, $J_{CP} = 11.1$ Hz, Cp^1), 71.22 (d, $J_{CP} = 11.1$ Hz, Cp^1), 71.59 (dd, $J_{CP} = 9.1$, 20.6 Hz, Cp^1), 72.60 (d, $J_{CP} = 5.0$ Hz, Cp^2), 72.83 (d, $J_{CP} = 5.0$ Hz, Cp^1), 75.89 (s, Cp^1), 85.92 (Cp^2), 90.08 (dd, $J_{CP} = 19.6$, 6.5 Hz, C_{Cp}-P), 127.27 (d, $J_{CP} = 10.1$ Hz, C_{meta}Ph), 127.81 (d, $J_{CP} = 9.6$ Hz, C_{meta}Ph), 128.18 (d, $J_{CP} = 9.4$ Hz, C_{meta}Ph), 128.44 (d, $J_{CP} = 10.6$ Hz, C_{meta}Ph), 129.70 (d, $J_{CP} = 2$ Hz, C_{para}Ph), 129.74 (C_{para}Ph), 131.00 (s, C_{para}Ph), 131.12 (s, C_{para}Ph), 131.40 (d, $J_{CP} = 10.1$ Hz, C_{ortho}Ph), 131.58 (d, $J_{CP} = 46.8$ Hz, C_{ipso}Ph), 131.98 (d, $J_{CP} = 38.8$ Hz, C_{ipso}Ph), 132.65 (bd, $J_{CP} = 9.3$ Hz, C_{ortho}Ph), 133.10 (d, $J_{CP} = 49.9$ Hz, C_{ipso}Ph), 135.18 (d, $J_{CP} = 49.3$ Hz, C_{ipso}Ph), 135.43 (d, $J_{CP} = 12.1$ Hz, C_{ortho}Ph), 136.02 (d, $J_{CP} = 14.2$ Hz, C_{ortho}Ph) ppm.

4.3. Crystal structure determination of compound $7 \cdot CH_3C_6H_5$

Crystal data: $C_{39}H_{50}FeP_2Pd \cdot C_6H_5CH_3$, fw 835.11, orange pyramid, $0.76 \times 0.42 \times 0.40$ mm^3; monoclinic, space group $P2_1$ (No. 3), $a = 10.235(3)$ Å, $b = 15.040(4)$ Å, $c = 13.916(4)$ Å, $\beta = 108.90(1)°$, $V = 2026.7(10)$ $Å^3$. $Z = 2$, $\rho = 1.369$ g/cm^3, $\mu = 0.911$ mm^{-1}. A total of 36 588 reflections were measured up to $\theta = 29.9°$ on a Bruker Smart CCD diffractometer with a sealed X-ray tube (Mo Kα, $\lambda = 0.71073$ Å, graphite monochromator) at room temperature (297 K) using 5 swings of ω-scan frames with $\Delta\omega = 0.3°$ and 10 s per frame. A multi-scan absorption correction was applied (correction factors 0.65–0.77) before the data were merged to 11 553 unique reflections ($R_{int} = 0.021$) of which 10848 with $I > 2$ (I) were observed [32]. The structure was solved with direct methods using program SHELXS97 and refined with the program SHELXL97 against F^2 of all reflections [33]. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were inserted in calculated positions and refined riding with the atoms to which they were bonded. Methyl groups were optimized in orientation using AFIX 137 of SHELXL97. There were 455 refined parameters and 1 restraint. R ($I > 2$ (I)): $R_1 = 0.0219$, $wR_2 = 0.0545$. R(all reflections): $R_1 = 0.0246$, $wR_2 = 0.0549$. GOF = 1.006. The residual electron density was between −0.27 and 0.29 e/$Å^3$; Flack absolute structure parameter was −0.010(8) and gave prove for the (S_c, S_p) configuration of the enantiopure ligand.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-285340 for compound **7**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax. (int code) +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www.cccd.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.023.

References

[1] (a) I. Ojima (Ed.), Catalytic Asymmetric Synthesis, Wiley–VCH, New York, 2000;
(b) A. Togni, T. Hayashi (Eds.), Ferrocenes, Homogeneous Catalysis, Organic Synthesis, Material Science, VCH, Weinheim, 1995.
[2] (a) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, Bull. Chem. Soc. Jpn. 53 (1980) 1138;
(b) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, J. Am. Chem. Soc. 92 (1970) 5389.
[3] (a) O.B. Sutcliffe, M.R. Bryce, Tetrahedron: Asymmetry 14 (2003) 2297;
(b) A. Togni, N. Bieler, U. Burckhardt, C. Kollner, G. Pioda, R. Schneider, A. Schnyder, Pure Appl. Chem. 71 (1999) 1531;
(c) A. Togni, R. Dorta, C. Kollner, G. Pioda, Pure Appl. Chem. 70 (1998) 1477.
[4] L.X. Dai, T. Tu, S.L. You, W.P. Deng, X.L. Hou, Acc. Chem. Res. 36 (2003) 659.
[5] (a) P. Barbaro, C. Bianchini, G. Giambastiani, S.L. Parisel, Coord. Chem. Rev. 248 (2004) 2131;
(b) R.C.J. Atkinson, V.C. Gibson, N.J. Long, Chem. Soc. Rev. 33 (2004) 313;
(c) T.J. Colacot, Chem. Rev. 103 (2003) 3101;
(d) C.J. Richards, A.J. Locke, Tetrahedron: Asymmetry 9 (1998) 2377.
[6] A. Togni, Angew. Chem., Int. Ed. Engl. 35 (1996) 1475.
[7] H.U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Adv. Synth. Catal. 345 (2003) 103.
[8] T. Sturm, W. Weissensteiner, F. Spindler, K. Mereiter, A.M. López-Agenjo, B.R. Manzano, F.A. Jalón, Organometallics 21 (2002) 1766.
[9] (a) E.M. Cayuela, L. Xiao, T. Sturm, B.R. Manzano, F.A. Jalón, W. Weissensteiner, Tetrahedron: Asymmetry 11 (2000) 861;
(b) A. Mernyi, C. Kratky, W. Weissensteiner, M. Widhalm, J. Organomet. Chem. 508 (1996) 209;
(c) G. Kutschera, C. Kratky, W. Weissensteiner, M. Widhalm, J. Organomet. Chem. 508 (1996) 195.
[10] T. Sturm, W. Weissensteiner, B. Abad, K. Mereiter, B.R. Manzano, F.A. Jalón, unpublished.

[11] T. Sturm, W. Weissensteiner, K. Mereiter, T. Kégl, G. Jeges, G. Petolz, L. Kollár, J. Organomet. Chem. 595 (2000) 93.
[12] (a) P. Liptau, L. Tebben, G. Kehr, R. Fröhlich, G. Erker, F. Hollmann, B. Rieger, Eur. J. Org. Chem. 9 (2005) 1909;
(b) P. Liptau, D. Carmona, L.A. Oro, F.J. Lahoz, G. Kehr, G. Erker, Eur. J. Inorg. Chem. 23 (2004) 4586;
(c) L. Tebben, G. Kehr, R. Fröhlich, G. Erker, Synthesis 12 (2004) 1971;
(d) P. Liptau, M. Neumann, G. Erker, G. Kehr, R. Fröhlich, S. Grimme, Organometallics 23 (2004) 21;
(e) P. Liptau, L. Tebben, G. Kehr, B. Wibbeling, R. Fröhlich, G. Erker, Eur. J. Inorg. Chem. 23 (2003) 4261;
(f) P. Liptau, L. Tebben, G. Kehr, B. Wibbeling, R. Fröhlich, G. Erker, Eur. J. Inorg. Chem. 19 (2003) 3590;
(g) P. Liptau, T. Seki, G. Kehr, A. Abele, R. Fröhlich, G. Erker, S. Grimme, Organometallics 22 (2003) 2226;
(h) P. Liptau, S. Knuppel, G. Kehr, O. Kataeva, R. Fröhlich, G. Erker, J. Organomet. Chem. 637–639 (2001) 621.
[13] F.A. Jalón, B.R. Manzano, F. Gómez-de la Torre, A.M. López-Agenjo, A.M. Rodríguez, W. Weissensteiner, T. Sturm, J. Mahía, M. Maestro, Dalton Trans. (2001) 2417.
[14] C. Breutel, P.S. Pregosin, R. Salzmann, A. Togni, J. Am. Chem. Soc. 116 (1994) 4067.
[15] (a) B. Jedlicka, R.E. Rülke, W. Weissensteienr, R. Fernández-Galán, F.A. Jalón, B.R. Manzano, J. Rodríguez-de la Fuente, N. Veldman, H. Koijman, A.L. Spek, J. Organomet. Chem. 508 (1996) 69;
(b) R. Fernández-Galán, F.A. Jalón, B.R. Manzano, J. Rodríguez-de la Fuente, M. Vrahami, B. Jedlicka, W. Weissensteiner, G. Jogl, Organometallics 16 (1997) 3758.
[16] F. Gómez-de la Torre, F.A. Jalón, A. López-Agenjo, B.R. Manzano, A. Rodríguez, T. Sturm, W. Weissensteiner, M. Martínez-Ripoll, Organometallics 17 (1998) 4634.
[17] (a) U. Burckhart, V. Gramlich, P. Hofmann, R. Nesper, P.S. Pregosin, R. Salzmann, A. Togni, Organometallics 15 (1996) 3496;
(b) A. Togni, U. Burckhart, V. Gramlich, P.S. Pregosin, R. Salzmann, J. Am. Chem. Soc. 118 (1996) 1031;
(c) A. Albinati, J. Eckert, P.S. Pregosin, H. Rüegger, R. Salzmann, C. Stössel, Organometallics 16 (1997) 579;
(d) P.S. Pregosin, R. Salzmann, A. Togni, Organometallics 14 (1995) 842.
[18] This effect has been called antisymbiotic effect by some authors: (a) R.G. Pearson, Inorg. Chem. 12 (1973) 712;
(b) R.R. Cooke, J.L. Burmeister, J. Organomet. Chem. 63 (1973) 471;
(c) F. Strobel, D.P. Ridge, Inorg. Chem. 27 (1988) 891;
(d) J.A. Casares, S. Coco, P. Espinet, Y.-S. Lin, Organometallics 14 (1995) 3058;
(e) J.N. Harvey, K.M. Heslop, A.G. Orpen, P.S. Pringle, Chem. Commun. (2003) 278;
(f) L. Battan, S. Fantasia, M. Manassero, A. Pasini, M. Sansoni, Inorg. Chim. Acta 358 (2005) 555;
(g) P. Braunstein, F. Naud, A. Dedieu, M.-M. Rohmer, A. DeCian, S.J. Rettig, Organometallics 20 (2001) 2966;
(h) or transphobia by others: J. Vicente, A. Arcas, D. Bautista, P.G. Jones, Organometallics 16 (1997) 2127;
(i) J. Vicente, J.A. Abad, A.D. Frankland, M.C. Ramírez de Arellano, Chem. Eur. J. 5 (1999) 3067;
(j) J. Vicente, A. Arcas, D. Bautista, M.C. Ramirez de Arellano, J. Organomet. Chem. 663 (2002) 164.
[19] ^{1}H (^{13}C) NMR data for the free alkenes in $CDCl_3$: MA, 7.04 (137.1) ppm; DMFU, 6.86 (133.9) ppm.
[20] (a) S. Otsuka, T. Yoshida, Y. Tatsuno, J. Am. Chem. Soc. 93 (1971) 6462;
(b) M.T. Chicote, M. Green, J.L. Spencer, F.G.A. Stone, J. Vicente, J. Chem. Soc., Dalton Trans. (1979) 536;
(c) K.J. Cavell, D.J. Stufkens, K. Vrieze, Inorg. Chim. Acta 47 (1980) 67.
[21] (a) J. Krause, W. Bonrath, K.R. Pörschke, Organometallics 11 (1992) 1158;
(b) R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 33 (1994) 1521;
(c) M. Tschoerner, G. Trabesinger, A. Albinati, P.S. Pregosin, Organometallics 16 (1997) 3447;
(d) P. Dotta, A. Magistrato, U. Rothlisberger, P.S. Pregosin, A. Albinati, Organometallics 21 (2002) 3033.
[22] G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 6, Pergamon Press, Oxford, UK, 1982, p. 409.
[23] (a) R. Fernández-Galán, B.R. Manzano, A. Otero, J. Organomet. Chem. 577 (1999) 271;
(b) F. Gómez-de la Torre, Y. Gutiérrez, F.A. Jalón, B.R. Manzano, A. Rodríguez, Monast. Chem. 131 (2000) 1267.
[24] See, for example: (a) J. Forniés, F. Martínez, R. Navarro, E. Urriolabeitia, A.J. Welch, J. Chem. Soc., Dalton Trans. (1995) 2805;
(b) I. Ara, E. Delgado, J. Forniés, E. Hernández, E. Lalinde, N. Mansilla, M.T. Moreno, J. Chem. Soc., Dalton Trans. (1996) 3201;
(c) B.R. Manzano, F.A. Jalón, F. Gómez-de la Torre, A.M. López-Agenjo, A.M. Rodríguez, K. Mereiter, W. Weissensteiner, T. Sturm, Organometallics 21 (2002) 789;
(d) M.C. Carrión, A. Díaz, A. Guerrero, F.A. Jalón, B.R. Manzano, A. Rodríguez, New J. Chem. 26 (2002) 305;
(e) A.C. Albéniz, J.C. Cuevas, P. Espinet, J. de Mendoza, P. Prados, J. Organomet. Chem. 410 (1991) 257;
(f) L.R. Falvello, J. Forniés, C. Fortuño, A. Martín, A.P. Martínez-Sariñena, Organometallics 16 (1997) 5849;
(g) J. Forniés, M.A. Gómez-Saso, A. Martín, F. Martínez, B. Menjón, J. Navarrete, Organometallics 16 (1997) 6024;
(h) J.A. Casares, S. Coco, P. Espinet, Y.-S. Lin, Organometallics 14 (1995) 3058.
[25] See for example: (a) J.M. Casas, L.R. Falvello, J. Forniés, A. Martín, M. Tomás, J. Chem. Soc., Dalton Trans. (1993) 1107;
(b) J. Forniés, E. Lalinde, A. Martín, M.T. Moreno, A.J. Welch, J. Chem. Soc., Dalton Trans. (1995) 1333;
(c) A.C. Albéniz, A.L. Casado, P. Espinet, Organometallics 16 (1997) 5416;
(d) L.R. Falvello, J. Forniés, R. Navarro, A. Rueda, E.P. Urrialobeitia, Organometallics 15 (1996) 309;
(e) J. Forniés, B. Menjón, N. Gómez, M. Tomás, Organometallics 11 (1992) 1187;
(f) G. López, J. Ruiz, C. Vicente, J.M. Martí, G. García, P.A. Chaloner, P.B. Hitchcock, R.M. Harrison, Organometallics 11 (1992) 4090;
(g) J.M. Casas, L.R. Falvello, J. Forniés, A. Martín, Inorg. Chem. 35 (1996) 56;
(h) I. Ara, L.R. Falvello, S. Fernández, J. Forniés, E. Lalinde, A. Martín, M.T. Moreno, Organometallics 16 (1997) 5923.
[26] (a) C. Gambs, G. Consiglio, A. Togni, Helv. Chim. Acta 84 (2001) 3105;
(b) H.C.L. Abbenhuis, U. Burckhardt, V. Gramlich, A. Martelletti, J. Spencer, I. Steiner, A. Togni, Organometallics 15 (1996) 1614;
(c) A. Togni, C. Breutel, M.C. Soares, N. Zanetti, T. Gerfin, V. Gramlich, F. Spindler, G. Rihs, Inorg. Chim. Acta 222 (1994) 213.
[27] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, J. Organomet. Chem. 65 (1994) 253.
[28] W.T. Dent, R. Long, A.J. Wilkinson, J. Chem. Soc. (1964) 1585.
[29] R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, Inorg. Chem. 32 (1993) 5769.
[30] P. Espinet, J.M. Martínez-Ilarduya, C. Pérez-Briso, A.L. Casado, M.A. Alonso, J. Organomet. Chem. 551 (1998) 9.
[31] W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 8 (1989) 2907.
[32] Bruker, Programs SMART, version 5.054; SAINT, version 6.2.9; SADABS version 2.03; XPREP, version 5.1; SHELXTL, version 5.1, Bruker AXS Inc, Madison, WI, USA, 2001.
[33] G.M. Sheldrick, SHELX97: Program System for Crystal Structure Determination, University of Göttingen, Germany, 1997.