Structural Aspects of Palladium and Platinum Complexes With Chiral Diphosphinoferrocenes Relevant to the Regio- and Stereoselective Copolymerization of CO with Propene

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Dedicated to the memory of *Luigi M. Venanzi*, mentor, colleague, and friend

A series of chiral diphosphinoferrocene ligands **3a**–**i**, derived from josiphos (=(2*R*)-1-[(1*R*)-1-(dicyclohexylphosphino)ethyl]-2-(diphenylphosphino)ferrocene, formerly called {(*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl}dicycloxexylphosphine) where the electronic properties of the ligand are systematically varied, were prepared. X-Ray studies of five of these new ligands confirmed that these compounds display very similar conformations in the solid state and that no structural criteria could be found indicating the modified electronic properties. These ligands find application in the Pd-catalyzed highly regio- and stereoselective CO/propene copolymerization reaction, where the electronic properties of the ligand show a great impact on the catalyst activity. Coordination-chemical aspects of these diphosphinoferrocenes relevant to the CO/propene copolymerization reaction were addressed by the preparation and characterization of Pd- and Pt-complexes of the general formula $[PdCl_2(P-P)]$ (**5**), $[PdMe_2(P-P)]$ (**6**), [PdClMe(P–P)] (**7**), $[PdMe(MeCN)(P-P)]PF_6$ (**8**), and [PtClMe(P–P)] (**9**) (P–P = chiral diphosphinoferrocene ligand (**3a**–**h**), four of which were characterized by X-ray crystallography.

1. Introduction. – Among the different classes of chiral phosphine ligands available for asymmetric catalysis, planar chiral phosphinoferrocenes (= ferrocenylphosphines) belong to the most important ones. They have been successfully used in a variety of transition metal catalyzed reactions [1–5]. In particular, ligands of the josiphos type [6] (josiphos = (2*R*)-1-[(1*R*)-1-(dicyclohexylphosphino)ethyl]-2-(diphenylphosphino)ferrocene[1]; **3a**), *i.e.*, chelating diphosphines comprising two different phosphino groups, have reached the stage of large-scale industrial applications [7–9].

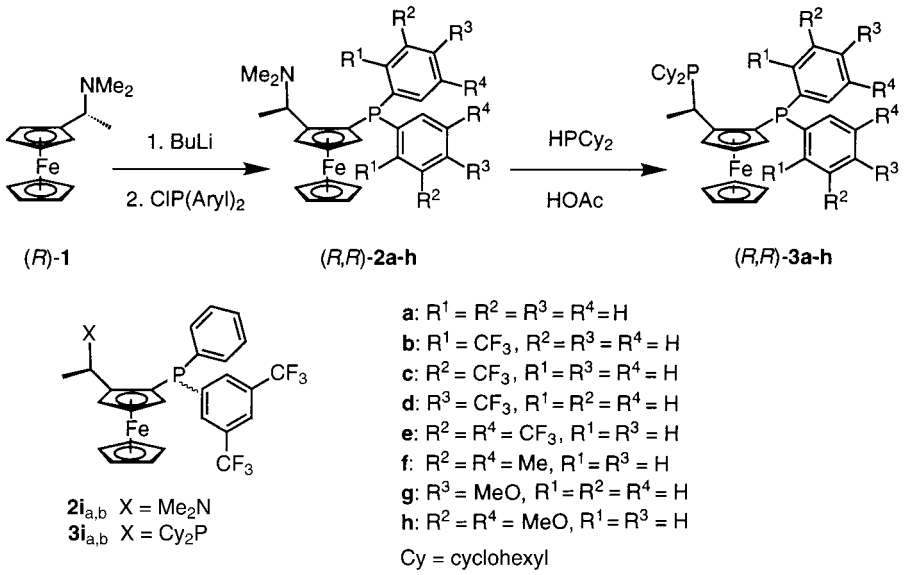
Very recently, *Blaser et al.* reported a study of the tuning of ligands of the josiphos family for the Ir-catalyzed hydrogenation of imines [10]. We had previously demonstrated that the introduction of peripheral substituents into such ligands may drastically influence the stereoselectivity of various reactions [11–13]. The diphenylphosphino group is easily amenable to directed modifications of the donor properties of the P-atom *via* introduction of electron-donating or -withdrawing groups at the Ph rings, therefore increasing or diminishing the 'electronic asymmetry' [11] of the ligand. For small substituents, typically placed in *para* position, one can assume a negligible effect on the overall steric features of the ligand, and one is thus in the situation of investigating, from a purely empirical point of view, ligand electronic effects in

[1] josiphos was formerly called {(*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl}dicyclohexylphosphine [6].

asymmetric catalysis. As we recently reported, the electronic nature of such modified josiphos ligands in the stereoselective Pd-catalyzed CO/propene copolymerization [14][15] is of great importance in determining the relative activity of the corresponding catalyst. This means that ligand modifications in electronic terms may seriously alter the kinetics of the catalytic process. However, to pinpoint the nature of such an electronic effect, one would need a very detailed knowledge of the reaction mechanism, unfortunately often not available. Nevertheless, discernable structural – ground state, thermodynamic – effects concerning the involved species may be expected [12]. In this context, we report the preparation and structural characterization of a series of modified josiphos ligands, as well as of their Pd^{II} and Pt^{II} complexes which are model compounds relevant to the Pd-catalyzed CO/propene copolymerization.

2. Results and Discussion. – 2.1. *Synthesis and Characterization of Ligands.* The planar-chiral diphosphinoferrocene ligands **3a**–**h** (*Scheme 1*) were prepared by a two-step procedure [6] starting from the commercially available, enantiomerically pure (aminoethyl)ferrocene **1**. *ortho*-Lithiation of **1** occurred diastereoselectively [16], and subsequent treatment with a diaryl(chloro)phosphine generated in moderate to fair yield (33–64%) the expected derivatives **2a**–**h** that were isolated each as single stereoisomer after chromatography and/or recrystallization [17] (*Scheme 1*). We limited our attention to Me, CF_3, and MeO substituents at the aryl moieties because of their relatively small size, relative inertness, and availability of the required precursors. However, the nature of the substituents may significantly influence the yield of the functionalization step of (aminoethyl)ferrocene **1**, with the more basic diaryl(chloro)phosphines giving poorer yields. This can be partially explained by the increased sensitivity to oxidation and, therefore, loss of product during workup, as no

Scheme 1



specific precaution was adopted. On the other hand, the presence of electron-donating groups renders the diaryl(chloro)phosphine less electrophilic and thus less prone to react with the ferrocene nucleophile. Upon reaction of the racemic chlorophosphane ClPPh[3,5-$(CF_3)_2C_6H_3$] with the lithiated form of **1**, the corresponding diastereoisomeric products $\mathbf{2i}_a$ and $\mathbf{2i}_b$, containing a stereogenic P-atom, were formed in equal amounts; they could easily be separated by column chromatography.

The introduction of the second phosphino fragment was achieved by nucleophilic substitution at the ethyl group of **2**, which is known to proceed with retention of configuration at the stereogenic C-center [18]. Derivatives **2a**–**h** were treated in AcOH at 100° with the secondary phosphine $HPCy_2$ (Cy = cyclohexyl) giving the corresponding diphosphino ligands **3a**–**h** in good to high yields (up to 93%). The diphosphinoferrocenes **3a**–**h** are air-stable and can be stored for a long time without noticeable oxidation or decomposition.

When the diastereoisomerically pure $\mathbf{2i}_b$ was reacted at 100° with $HPCy_2$ in AcOH, it did not retain completely its stereochemical integrity, as partial epimerization at the P-atom occurred, due to the high temperature required for the reaction. The $^{31}P\{^1H\}$-NMR spectrum of the resulting diastereoisomer mixture $\mathbf{3i}_a/\mathbf{3i}_b$ revealed a degree of epimerization of *ca.* 20%. Attempts to separate the pairs of diastereoisomeric diphosphinoferrocenes by column chromatography failed. After conversion to the bis(borane) adduct, a stereochemically pure derivative **4** (= $[\mathbf{3i}_b \cdot 2\ BH_3]$ could be obtained as the major product after chromatography, which was structurally characterized (*vide infra*, *Fig. 3*). However, attempts at deprotecting this compound with morpholine under mild conditions, in order to avoid epimerization, failed, as the PCy_2 group always retained the borane. Due to these synthetic difficulties, the chemistry with this new P-stereogenic phosphine was not pursued.

Table 1 collects a selection of characteristic spectroscopic features of the modified josiphos ligands, as compared to the parent compound **3a** [6]. In their ^{31}P-NMR spectra,

Table 1. *Selected Spectroscopic Properties of the Diphosphino Derivatives* **3a**–**i** (all of absolute configuration (*R*,*R*)). δ in ppm, *J* in Hz.

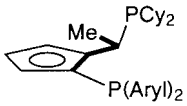
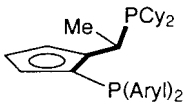
Ligand	$^{31}P\{^1H\}$-NMR[a])			^1H-NMR		$[\alpha]_D^{20}$[c])
	$\delta(P)$ PCy_2	PAr_2	$^4J(P,P)$	$\delta(C_5H_5)$	$\delta(MeCHP)$[b])	
3a (josiphos)[d])	15.6	– 25.1	36.9	3.93	3.68	– 352
3b (*o*-CF_3)[e])	15.8	– 34.8	58.7	3.91	3.59	– 360
3c (*m*-CF_3)[e])	16.7	– 24.2	47.3	3.82	3.54	– 267
3d (*p*-CF_3)[e])	16.2	– 24.9	46.0	3.83	3.56	– 349
3e ((*m*-$CF_3)_2$)[e])	15.6	– 25.1	52.0	3.75	3.42	– 288
3f ((*m*-Me)$_2$)[e])	15.6	– 25.1	37.5	3.97	3.72	– 305
3g (*p*-MeO)[e])	15.6	– 25.1	32.0	4.01	3.69	– 338
3h ((*m*-MeO)$_2$)[e])	15.6	– 25.1	37.9	4.05	3.71	– 281
$\mathbf{3i}_a$ (Ph/(*m*-$CF_3)_2$)[e])	14.3	– 25.9	42.9	3.83	3.57	n.d.[f])
$\mathbf{3i}_b$ (Ph/(*m*-$CF_3)_2$)[e])	15.9	– 24.1	47.9	3.86	3.35	n.d.[f])

[a]) Each P-signal appears as a *d* (except, for **3b**). [b]) MeC*H*P appear as *dq*. [c]) $c = 0.46 - 0.62$ g/cm^3 in $CHCl_3$. [d]) Data from [19]. [e]) The peripheral substituents at the aryl moieties are indicated in parentheses. [f]) Not determined.

3a–**i** display an *AX* spin system, with a relatively large four-bond coupling constant ^4J(P,P), ranging from 32.0 Hz for the *p*-MeO derivative **3g** to 58.7 Hz for the *o*-CF_3 derivative **3b**. This latter compound also shows an anomalous high-field shift of *ca.* 10 ppm of the P(Aryl)$_2$ P-atom with respect to the corresponding signal of all other derivatives, as well as coupling of this P-atom to the F-atoms of the CF_3 groups.

2.2. *Solid-State Structure of the Diphosphino Derivatives* **3b**, **3d**, **3e**, **3g**, **3h**, *and* **4**. To define possible structural consequences of the introduction of peripheral substituents at the diphosphinoferrocenes of type **3**, X-ray crystallographic studies were carried out. Suitable single crystals could be obtained for the ligands **3b**, **3d**, **3e**, **3h**, and **4** by recrystallization from EtOH and for **3g** from a ^{t}BuOMe/EtOH solution layered with hexane. Due to the structural similarities between these derivatives, only two representative ORTEP views of the diphosphinoferrocenes **3b** and **3h** are presented in *Figs. 1* and *2*, respectively. The bonding parameters fall in the expected ranges and are well comparable to those of the parent compound josiphos [19]. From a conformational point of view, the five diphosphinoferrocenes **3** analyzed are very similar as far as the conformation of the substituted common backbone is concerned. In fact, in all compounds, the two aryl groups, here defined as '*endo*' (pointing toward the ferrocene moiety) and '*exo*' (away from the ferrocene) can be viewed as assuming a pseudoequatorial and pseudoaxial orientation, respectively, as is the case of josiphos. The position of the PCy_2 group can also be viewed as being pseudoaxial and pointing away from the ferrocene. Furthermore, in all ligands, the Me group at the stereogenic center is positioned below the plane of the substituted Cp ring (*i.e.*, '*endo*'). This conformational preference is well illustrated by the torsion angles given in *Table 2*. Significant differences are, however, observed when focusing on the Cy and, to a lesser extent, on the aryl groups, as visualized by the two structures of *Figs. 1* and *2*. This means that there appear to be essentially no restrictions to rotations around the P–Cy bonds, and that, therefore, this peripheral part of the molecule is conformationally very flexible. Furthermore, one observes slight displacements of the stereogenic C-atom (0.013–0.038 Å) and of the PAr_2 P-atom (0.02–0.1 Å) from the plane of the Cp ring away from the Fe-atom. The small dislocation of the P-atom indirectly implies that the

Table 2. *Relevant Torsions Angles* [°] *and Sum of Bond Angles for the* PAr_2 *Group in Compounds* **3a**, **3b**, **3d**, **3e**, **3g**, *and* **3h**

	3a[a])	**3b**	**3d**	**3e**	**3g**	**3h**
	– 24	– 29	– 34	– 15	– 14	– 17
	– 70	– 76	– 80	– 59	– 62	– 64
Sum of C–P–C angles for Cp–P(Aryl)$_2$ group	302.5	302.2	303.4	304.5	302.1	302.2

[a]) Data for comparison from [19].

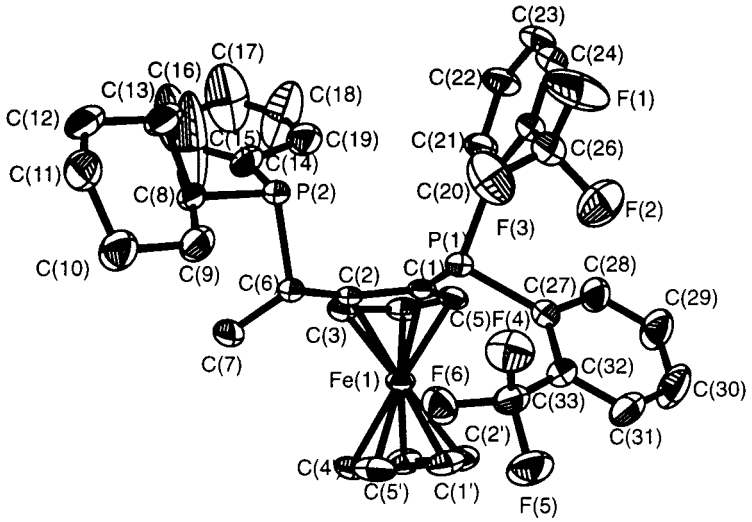


Fig. 1. *ORTEP Drawing* (30% probability ellipsoids) *and atom-numbering scheme of ligand* **3b**

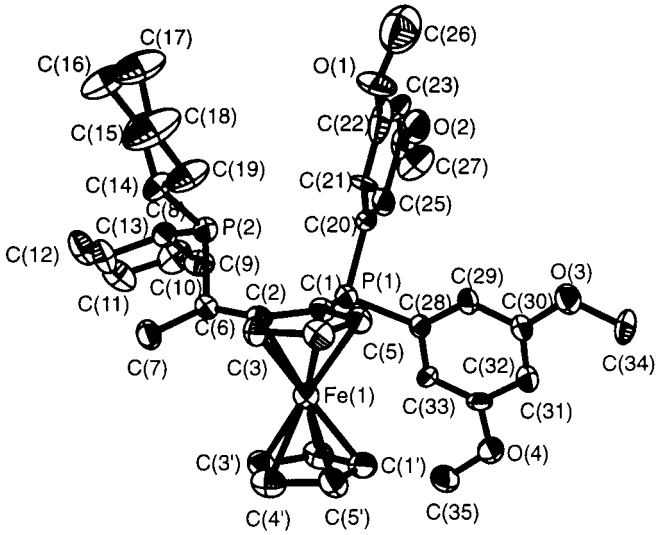


Fig. 2. *ORTEP Drawing* (30% probability ellipsoids) *and atom-numbering scheme of ligand* **3h**

repulsion between the '*endo*' aryl group and the ferrocene fragment is negligible, as it does not lead to a significant distorsion.

The introduction of substituents altering the electronic properties of the PAr_2 group could, in principle, change the degree of pyramidalization of the P-atom, as expressed by the sum of the corresponding three C–P–C angles (*Table 2*). A larger sum of the C–P–C angles, *i.e.*, a less pyramidalized P-atom, should correlate with a decreasing s-character of the P lone-pair, and this should be expected in the case of electron-

withdrawing substituents. The experimental data in *Table 2*, however, show that the ligands examined cover a very narrow range of C–P–C angles, between 302.1 and 304.4°. Although the least degree of pyramidalization is shown, as expected from the simple considerations made above, by derivative **3e** bearing four CF_3 groups, the observed differences are too small and cannot be used as a reliable structural criterion for judging the electronic effect of the substituents.

The crystal structure of **4** (*Fig. 3*) allows the assignment of the absolute configuration (*R*) of its stereogenic P-atom (therefore, (R_P,R_C,R_{Cp})-**4**). In this compound, the '*exo*'-axial and '*endo*'-equatorial orientation of the two aryl groups is more pronounced than for the other derivatives, probably due to the presence of BH_3 attached to the corresponding P-atom. The relative position of the second BH_3 is indicative of the high conformational flexibility of the PCy_2 group. In fact, as shown by the relatively small torsion angle C(7)–C(6)–P(2)–B(2) of 38.4°, the B-atom and the Me group (C(7)) are *syn*-clinal, whereas a metal center coordinated to both P-atoms assumes an almost *anti*-periplanar position with respect to C(7).

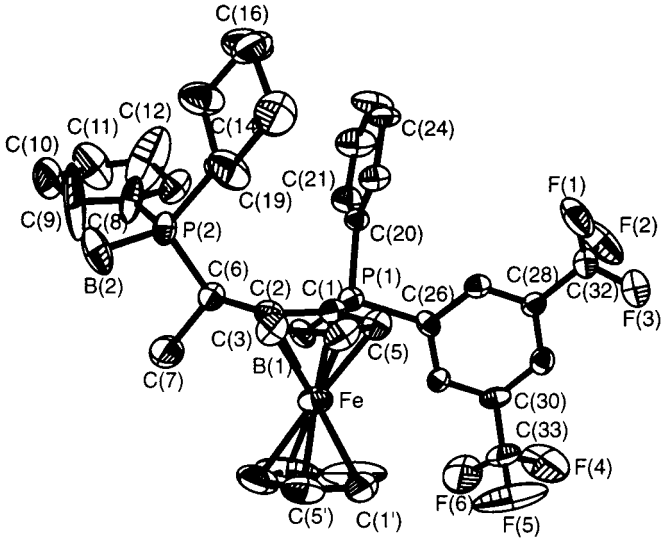


Fig. 3. *ORTEP Drawing* (30% probability ellipsoids) *and atom-numbering scheme of compound* **4** (= [**3i**$_b$ · 2 BH_3])

2.3. *Synthesis and Characterization of Pd and Pt Complexes.* 2.3.1. *Syntheses.* The rate of reaction in the CO/propene copolymerization reaction is drastically influenced by the electronic characteristics of the *P*-aryl substituents of the ligand [15]. Typically, the highest productivity was obtained with the Pd^{II} system modified with ligand **3e**, bearing the electron-withdrawing CF_3 substituents. Thus, a series of Pd- and Pt-complexes of general formula [$PdCl_2$(P–P)] (**5**), [$PdMe_2$(P–P)] (**6**), [PdClMe(P–P)] (**7**), [PdMe(MeCN)(P–P)]PF_6 (**8**), and [PtClMe(P–P)] (**9**) – where P–P is one of the chiral diphosphinoferrocene ligands **3a**–**h** – were prepared by conventional ligand substitution reactions (see *Scheme 2* and *Table 3*). In the case of **5**, **7** [21][22], and **9** [23], the corresponding cod (cod = cycloocta-1,5-diene) derivatives

Scheme 2

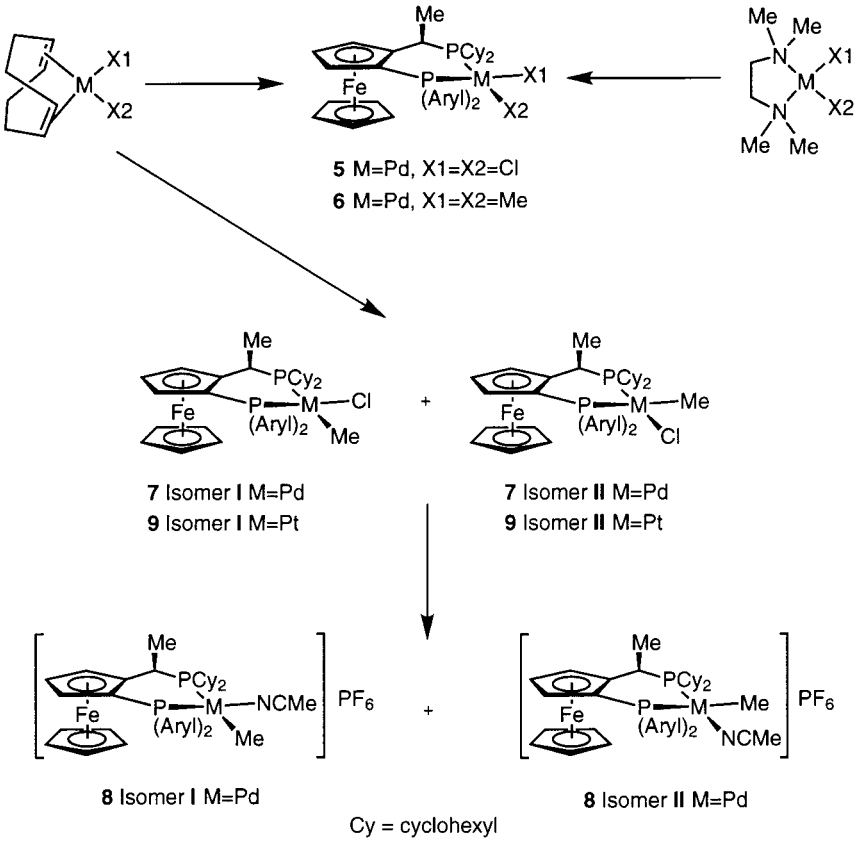


Table 3. *Numbering Scheme for All Prepared and Characterized Pd- and Pt-Complexes Containing Ligands* **3a**–**h**[a])

Ligand	[$PdCl_2$(P–P)]	[$PdMe_2$(P–P)]	[PdClMe(P–P)]	[PdMe(MeCN)(P–P)]PF_6	[PtClMe(P–P)]
3a (josiphos)	**5a**[a])[b])	**6a**[a])	**7a**[a])	**8a**	**9a**
3b (*o*-CF_3)[c])					**9b**
3c (*m*-CF_3)[c])					**9c**
3d (*p*-CF_3)[c])			**7d**	**8d**	**9d**
3e ((*m*-$CF_3)_2$)[c])	**5e**[a])	**6e**	**7e**	**8e**	**9e**
3f ((*m*-$Me)_2$)[c])			**7f**		**9f**
3g (*p*-MeO)[c])			**7g**[a])	**8g**	
3h ((*m*-$MeO)_2$)[c])					**9h**

[a]) An X-ray crystal structural study was carried out for **5a**, **5e**, **6a**, **7a**, and **7g**. [b]) See [20]. [c]) The peripheral substituents at the aryl moieties are indicated in parentheses.

were used as starting materials, whereas [$PdMe_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) [24] served as precursor of **6**. The ^{1}H-NMR spectra for the dimethylpalladium complexes **6a** and **6e** show the two Me ligands as a *dd* due to the coupling with the two nonequivalent P-atoms. Their ^{13}C-NMR spectra exhibit

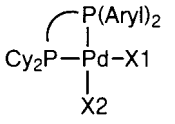
nonequivalent Me signals with ^2J(P,C) coupling constants of *ca.* 10 and *ca.* 100 Hz for *cis* and *trans* relationships of the P and Me ligands, respectively. The cationic complexes **8** were obtained in high yields as a mixture of stereoisomers **I** and **II** by ligand-abstraction reaction with $TlPF_6$ from **7** in CH_2Cl_2 in the presence of a small amount of MeCN.

The complexes **5**–**9**, generally isolated as air-stable solid materials in good to high yields, are either possible catalyst precursors or constitute models of intermediates in the CO/propene copolymerization reaction. A comparative characterization of these compounds, both in solution and in the solid state, is therefore desirable. The Pd complexes **8** are particularly interesting because of the possible influence of the ligands onto the ratio of the two different diastereoisomers **I** and **II** existing for these derivatives. These species have been shown to be directly involved as catalysts in the copolymerization reaction [25][26]. Before reporting on these aspects, we describe the solid-state structure of four different complexes illustrating the general behavior of modified josiphos ligands from a conformational point of view.

2.3.2. *Solid-State Structure of Neutral Dichloro-, Dimethyl-, and Chloro(methyl)-palladium Complexes.* For the four new complexes [$PdCl_2$(**3e**)] (**5e**), [$PdMe_2$(**3a**)] (**6a**), [PdClMe(**3a**)] (**7a**), and [PdClMe(**3g**)] (**7g**), suitable single crystals could be obtained and routine X-ray crystallographic studies were carried out. *Table 4* provides a selection of bonding parameters defining the geometry around the Pd centers, and in *Table 5* important torsion angles are presented. These latter assist in quantifying the conformational features of the chelate ring. Due to the structural similarities between these complexes, only the representative ORTEP view of the dimethyl complex **6a** is shown in *Fig. 4*, whereas *Fig. 5* displays a schematic superposition of **5a**, **5e**, **6a**, **7a**, and **7g**.

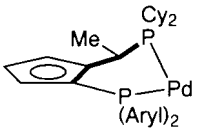
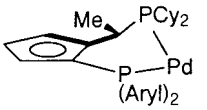
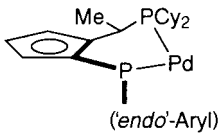
For all complexes examined, the geometry around the Pd-atom is slightly distorted square planar. The coordination distances to the Pd-atom fall within the expected ranges [27]. In the two dichloro complexes **5a** and **5e**, the Pd–Cl distances are very

Table 4. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for the Complexes* **5a**, **5e**, **6a**, **7a**, *and* **7g**

	**5a**[a]) [$PdCl_2$(**3a**)]	**5e** [$PdCl_2$(**3e**)]	**6a** [$PdMe_2$(**3a**)]	**7a**[b]) [PdClMe(**3a**)][b])	**7g**[b]) [PdClMe(**3g**)][b])
Pd–PAr_2	2.253(4)	2.275(3)	2.298(3)	2.198(9)	2.2369(13)
Pd–PCy_2	2.281(4)	2.237(3)	2.327(3)	2.343(3)	2.3639(16)
Pd–X1	2.358(4)	2.359(3)	2.102(8)	2.097(7)	2.138(6)
Pd–X2	2.332(4)	2.338(2)	2.080(8)	2.346(8)	2.3802(17)
Cy_2P–Pd–PAr_2	94.46(13)	96.01(8)	93.26(9)	97.24(12)	97.08(5)
Cy_2P–Pd–X1	172.59	172.65(9)	171.6(3)	171.4(2)	176.7(2)
Cy_2P–Pd–X2	83.73(13)	84.65(10)	95.1(3)	92.27(15)	91.25(6)
Ar_2P–Pd–X1	176.94	174.21(11)	174.6(3)	162.5(1)	169.66(7)
Ar_2P–Pd–X2	92.95(14)	87.98(10)	87.4(3)	86.9(2)	85.79(19)
X1–Pd–X2	88.26(14)	92.00(10)	84.3(4)	85.7(2)	86.08(19)

[a]) Data for comparison from [20]. [b]) For complexes **7a** and **7g** X1=Me and X2=Cl.

Table 5. *Relevant Torsions Angles* [°] *for the Complexes* **5a**, **5e**, **6a**, **7a**, *and* **7g**

	5a[a]) [$PdCl_2$(**3a**)]	**5e** [$PdCl_2$(**3e**)]	**6a** [$PdMe_2$(**3a**)]	**7a** [PdClMe(**3a**)]	**7g** [PdClMe(**3g**)]
	– 65 (– 70 in **3a**)	– 68	– 61	– 64	– 61
	– 10 (– 24 in **3a**)	– 13	– 14	– 21	– 14
	– 103 (– 145 in **3a**)	– 96 (– 150 in **3e**)	– 110	– 98	– 103 (– 158 in **3g**)

[a]) Data for comparison from [20].

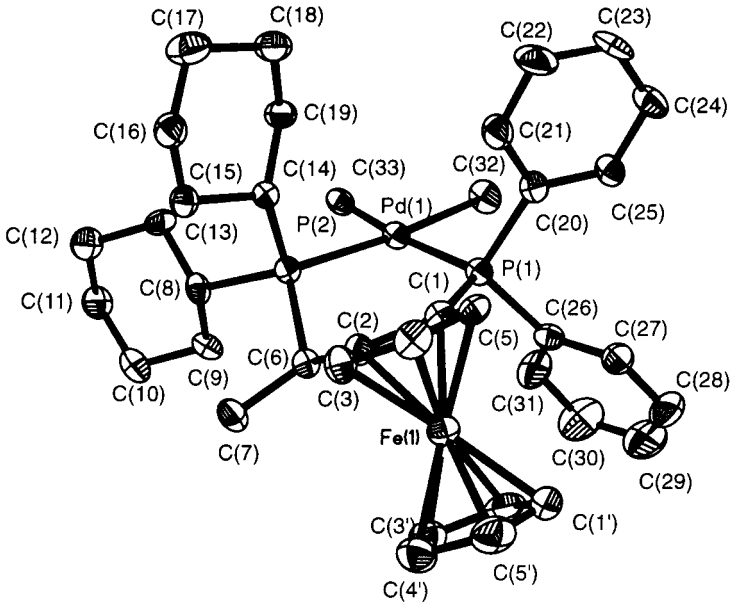


Fig. 4. *ORTEP Drawing* (30% probability ellipsoids) *and atom-numbering scheme of complex* **6a** (= [$PdMe_2$(**3a**)]

similar to those in related derivatives, such as [$PdCl_2$(dppe)] (dppe = 1,2-(diphenylphosphino)ethane = (ethane-1,2-diyl)bis[phosphine]) [28] and [$PdCl_2$(dppb)] (dppb = 1,4-(diphenylphosphino)butane = (butane-1,4-diyl)bis[phosphine]) [29], with the differ-

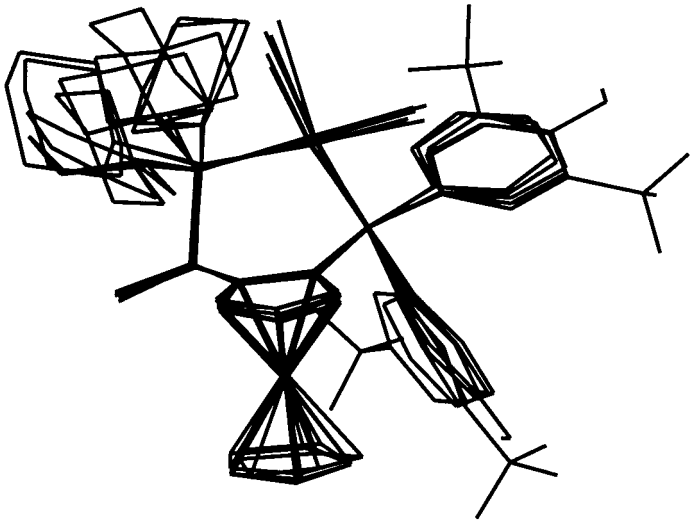


Fig. 5. *Schematic superposition of the structures of complexes* **5a**, **5e**, **6a**, **7a**, *and* **7g**

ence that the Cl ligand in *trans* position to the PCy_2 group displays a significantly larger distance from Pd, as one would expect from *trans*-influence considerations [30]. The same applies to the Pd–C separations in dimethyl complex **6a**, although the difference between the two Pd–C distances fall within the experimentally observed standard deviations. The bite angle (P–Pd–P) of the coordinated diphosphino moieties varies between 93 and 97° and is thus significantly larger than for other typical chelating phosphines. The combination of large P–Pd–P angles with conformational flexibility of the ligand backbone has been considered to be an important factor in increasing the rate of the CO/propene copolymerization process [31]. However, the large differences in catalytic activity observed with our system [15], for which the bite angle [32] is essentially constant, clearly show that other factors also play a very important role.

The two torsion angles defining the relative position of the Me group at the stereogenic center and of the PCy_2 fragment given in *Table 5* are very similar in all five complexes examined, and are also comparable within less than ±10° to those of the free ligands (*Table 2*). On the other hand, the orientations of the two aryl groups in the complexes are clearly different from those observed in the free ligands, as shown by the torsion angle involving the '*endo*'-aryl group. The values of this angle given in *Table 5* deviate by *ca.* 50° with respect to those of the free ligands. The two aryl groups, in the free ligands described as '*endo*'-equatorial and '*exo*'-axial, are now better referred to as '*endo*'-axial and '*exo*'-equatorial, respectively, this coinciding with the only prominent conformational change occurring upon coordination. The resulting repulsion between the ferrocene and the '*endo*'-axial aryl manifests itself in a distorsion involving a displacement of the corresponding P-atom out of the plane of the 'upper' Cp ring. This 'lifting' of the P-atom ranges from a minimum of 0.3 Å in dichloro complex **5a** to a maximum of 0.37 Å for compounds **5e** and **7a**. The schematic superposition of the five complexes of *Fig. 5* shows that the structural fitting between the different complexes extends from the ferrocene unit over the chelate ring to the aryl groups. The flexible

parts of the molecules are restricted to the Cy groups that can be viewed as forming a bulky, however adaptable aliphatic region. Overall, it can be said that the conformational features of the coordinated ligands do not depend upon the electronic nature of the peripheral substituents at the aryl groups.

Finally, it is interesting to note that the configuration observed in the solid state for the chloro(methyl) complexes **7a** and **7g** is such that the Me ligand is in both cases *trans* to the PCy_2 fragment. As these two ligands (an alkyl and a trialkylphosphine) possess the highest *trans*-influence [30], one would not have expected them in mutual *trans*-position.

2.3.3. *Chloro(methyl)palladium, Chloro(methyl)platinum, and Cationic Methylpalladium Complexes in Solution*. The neutral chloro(methyl)palladium complexes **7**, their corresponding cationic derivatives **8**, as well as the analogous chloro(methyl)platinum compounds **9** containing the ligands **3a**–**h** were prepared (see *Table 3*), with the aim of ascertaining the influence of the different diphosphinoferrocenes on the distribution of the two possible isomers **I** and **II** (see *Scheme 2*). In isomer **I** the Me ligand is located *trans* to the trialkylphosphino ligand, and in isomer **II**, it is *trans* to the PAr_2 fragment. Isomer identification was straightforward for all three complex types, based on the NMR parameters of the Pd(Me)(P–P) and Pt(Me)(P–P) units, respectively. Relevant NMR-spectroscopic data are collected in *Table 6* (complexes **7** and **8**), and *Table 7* (complexes **9**) and were obtained with the help of 2D NMR experiments (P,H and C,H correlations). For compounds **7a**, **7f**, and **7g**, only isomer **I**, corresponding to the structure observed in the solid state (*vide supra*), was detected by NMR (*Table 6*). For the two complexes displaying CF_3 substituents at the PAr_2 moiety, both isomers could be identified. Whereas in the case of **7d**, isomer **I** was still predominant with a ratio **I/II** of 2.2 : 1, the proportion was reversed for **7e**. An entirely different situation was encountered for the analogous Pt complexes **9** (*Table 7*). Here isomer **II**, with the Me ligand *trans* to the PAr_2 group, was the prevailing species in all seven cases

Table 6. *Selected NMR-Spectroscopic Data for Complexes* **7** ([PdClMe(P–P)]) *and* **8** ([PdMe(MeCN)(P–P)]PF_6). δ in ppm, J in Hz.

	^{1}H-NMR		^{31}P{^{1}H}-NMR		Ratio **I/II**
	δ(Pd–Me)	^3J(P,H)	δ(P)	^2J(P,P)	
7aI	0.44	7.2, 3.7	40.9, 28.9	39.8	> 100 : 1
7dI	0.42	7.0, 3.9	40.9, 29.9	40.5	2.2 : 1
II	0.85	7.9, 1.9	60.6, 4.9	36.0	
7eI	0.46	7.2, 4.2	42.3, 32.2	41.2	1 : 2
II	0.92	7.9, 2.2	60.5, 6.9	36.0	
7fI	0.42	7.3, 3.7	41.7, 28.9	39.1	> 100 : 1
7gI	0.42	7.3, 3.6	41.7, 26.7	39.7	> 100 : 1
8aI	0.30	6.4, 2.2	44.5, 29.8	40.7	2 : 1
II	0.58	7.5, 1.5	67.9, 8.3	34.3	
8dI	0.32	6.7, 2.8	43.7, 30.4	41.6	1.3 : 1
II	0.66	7.2, 1.4	66.8, 8.5	35.3	
8eI	0.31	6.7, 3.0	44.6, 33.8	42.0	1 : 1.8
II	0.74	7.4, 1.6	66.9, 11.3	35.9	
8gI	0.34	6.8, 2.6	44.0, 27.3	40.1	1.6 : 1
II	0.57	7.2, 1.5	68.9, 5.8	34.2	

Table 7. *Selected NMR-Spectroscopic Data for Complexes* **9** ([PtClMe(P–P)]). δ in ppm, J in Hz.

	^{1}H-NMR		^{31}P{^{1}H}-NMR			Ratio **I/II**
	δ (Pt–Me)	^3J(P,H)	δ(P)	^1J(Pt,P)	^2J(P,P)	
9aI	0.24	6.8, 2.0	44.0, 8.1	1841, 4315	17.6	1:4
II	0.78	7.5, 2.0	39.2, 11.2	1680, 4186	17.0	
9bII	0.90	9.2, <2	46.7, 36.2	1694, 4278	15.0	1: >100
9cI	0.22	7.5, 2.5	44.1, 9.7	1825, 4322	17.8	1:7
II	0.82	6.8, 2.5	39.0, 12.7	1664, 4134	16.7	
9dI	0.23	6.8, 2.5	43.5, 9.3	1822, 4308	17.9	1:13
II	0.83	7.5, 2.4	39.1, 12.1	1641, 4137	16.7	
9eI	0.22	6.9, 4.3	44.9, 7.8	1852, 4328	17.5	1:17
II	0.86	7.3, 2.4	39.1, 10.5	1688, 4206	16.7	
9fI	0.23	6.9, 4.3	44.9, 7.8	1852, 4328	17.5	1:2.5
II	0.75	7.3, 2.4	39.1, 10.5	1688, 4206	16.7	
9hI	0.32	6.9, 4.2	44.4, 11.9	1834, 4372	17.9	1:4.5
II	0.77	7.4, 2.5	39.1, 14.5	1699, 4176	17.0	

examined. The ratios **I/II** varied between 1:2.5 for **9f** and 1:17 for **9e**. Interestingly, for derivative **9b** containing *o*-CF_3 groups, only isomer **II** could be detected. Although ligands containing electron-withdrawing groups seem to favor the formation of isomer **II**, no clear trend can be recognized.

The main species of the cationic Pd-complexes **8** was isomer **I** in the case of **8a**, **8d**, and **8g**, and of isomer **II** in the case of **8e**. However, in all cases, the observed mixtures displayed similar fractions of the two isomers, indicating only very small differences in stability. Despite the absence of any simple trend with respect to the isomer distribution in complexes **8**, it has nevertheless to be noted that the complex containing ligand **3e** is the one most strongly favoring the isomeric form **II**, with a *trans* relationship between the Me ligand and the PAr_2 moiety. Ligand **3e** is the one with the (supposedly) most π-acidic PAr_2 group, by virtue of the four CF_3 substituents, and therefore the highest 'electronic asymmetry'.

2.4. *CO/Propene Copolymerization with Isolated Pd Complexes as Catalyst Precursors.* The dimethylpalladium complexes **6a** and **6e** reacted with $HBF_4 \cdot OEt_2$ to afford highly efficient catalyst precursors for the CO/propene copolymerization reaction (*Table 8*). The CO/propene copolymers formed were obtained with almost perfect head-to-tail regioselectivity (>99% of head-to-tail enchainments) and with high stereoselectivity, in both cases more than 98% of isotactic diads. Among these two catalyst systems, the most efficient one contained the ligand **3e**. This catalyst showed a very high productivity reaching up to 956 $g_{Cop}/g_{Pd} \cdot h$. In these systems, the steric demand and the electronic properties of the ligand are essential to produce highly regio- and stereoregular materials. Moreover, large electronic differentiation of the two phosphino moieties is very important to enhance the rate of the reaction, as previously shown [15]. The Pd^{II} complex containing **3e** was about four times more active than the one with **3a**. NMR Studies indicated that when an excess of acid ($HBF_4 \cdot OEt_2$) was added to a solution containing a dimethylpalladium complex **6**, a dicationic species of type $[Pd(P–P)(S)_2]^{2+}$ (S = solvent molecule) was formed by protonolytic cleavage of the Pd–Me bonds. However, it must be noted that the productivity of the catalyst thus

Table 8. *CO/Propene Copolymerization in the Presence of Isolated Complexes as Catalyst Precursors*

Catalyst system	Productivity [$g_{cop}/g_{Pd} \cdot h$]	Regioregularity [% H–T enchainments]	Stereoregularity [% *l*-diads]	$[\alpha]_D$[a])	$\Delta\varepsilon$ (CD)[b])	M_n[c])
6a/$HBF_4 \cdot OEt_2$	224	> 99	98.3	– 32.0	1.37	10970
6e/$HBF_4 \cdot OEt_2$	956	> 99	98.8	– 33.0	1.55	13680
8a	4.3	> 99	97.5	– 21.7	0.86	25300
8a + MeOH	74.5	> 99	97.6	– 26.0	1.01	9600

[a]) Measured in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). [b]) Measured in HFIP; 1–2 mg/ml concentration range. [c]) Determined by integration of end-group signals in the ^{1}H-NMR spectrum.

generated from the isolated complexes **6a** and **6e** was only about half with respect to the corresponding *in situ* systems.

The monocationic complex [PdMe(MeCN)(**3a**)]PF_6 (**8a**) was used as well as catalyst precursor in the copolymerization process (see *Table 8*). In the absence of MeOH, the system showed a very poor activity. In contrast, when a small amount of MeOH was added, an increase in activity was obtained, though the productivity level of the *in situ* generated catalyst could not be reached. It is interesting to note that when complex **8a** was used in the absence of MeOH as the activator, the small amount of copolymer formed was isolated in the solid state in the form of a 1,4-polyketone, exclusively. These experiments clearly show that the performance of a catalyst generated *in situ* from [$Pd(OAc)_2$], the corresponding ligand, and $BF_3 \cdot OEt_2$ cannot be matched by the use of isolated complexes.

3. Conclusion. – A series of new chiral diphosphinoferrocenes of the josiphos type and their Pd- and Pt-complexes were prepared and characterized. The degree of pyramidalization at the PAr_2 P-atom and the overall conformational features of the free ligands are essentially insensitive to the presence of electron-withdrawing or donating substituents at the aryl groups. The structural analyses reported for Pd and Pt complexes reveal that the steric environment of the metal center imposed by the ligand is not influenced by the electronic nature of the peripheral substituents at the aryl groups to any significant extent. In other words, there are no clearly recognizable structural criteria that would allow one to pinpoint the reactivity differences observed when modifying the ligand properties by virtue of such substituents. Also, the factors determining the isomeric composition displayed by complexes of type **7**–**9** are not apparent based solely on simple *trans*-influence considerations. Therefore, an interpretation and understanding of the observed effects on the catalyst activity [15] can only be achieved with a detailed knowledge of the entire reaction mechanism, as well as of the electronic structure of the intermediate complexes involved, implying the necessity of computational studies, so far not yet available for our system.

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Experimental Part

General. Diaryl(chloro)phosphines [33][34] were prepared by the reaction of Et_2NPCl_2 with 2 equiv. of the corresponding arylmagnesium bromide followed by treatment of the intermediate Et_2NPAr_2 with a soln. of HCl in THF. Dicyclohexylphosphane was obtained from *Strem*. Monophosphanyl intermediates **2** [17][35], as well as josiphos derivatives **3** [6][19] were prepared according to reported general procedures; therefore, only yield and characterization data will be provided here. $[PdCl_2(cod)]$ [21], $[PdClMe(cod)]$ [22], $[PdMe_2(tmeda)]$ [24], and $[PtCl_2(cod)]$ [23] were prepared as described. CC = Column chromatography. NMR Spectra: *Bruker Avance-250* and *-300* spectrometers; chemical shifts δ in ppm rel. to internal $SiMe_4$ (^1H and ^{13}C) or to external 85% H_3PO_4 (^{31}P), coupling constants J in Hz. MS: in m/z (rel. %).

Crystallographic data (excluding structure factors) for the routine structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications no. CCDC 163613 (**3b**), CCDC 163610 (**3d**), CCDC 163608 (**3e**), CCDC 163612 (**3g**), CCDC 163609 (**3h**), CCDC 163607 (**4**), CCDC 163787 (**5e**), CCDC 163786 (**6a**), CCDC 163785 (**7a**), and CCDC 165115 (**7g**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

*(1*R*)-1-{Bis[2-(trifluoromethyl)phenyl]phosphino}-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2b**). CC (silica gel, hexane/AcOEt 1:1 + 0.5% Et_3N; R_f 0.29): 2.81 g (35%) of **2b**. Orange solid. $[\alpha]_D^{20} = -360$ (c = 0.46, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.84–7.79 (*m*, 1 arom. H); 7.75–7.21 (*m*, 6 arom. H); 7.13–7.10 (*m*, 1 arom. H); 4.44 (*m*, 1 H, Cp); 4.36 (*m*, 1 H, Cp); 4.09 (*dq*, J = 6.75, 2.99, MeC*H*N); 3.97 (*s*, C_5H_5); 3.94 (*m*, 1 H, Cp); 1.63 (*s*, Me_2N); 1.21 (*d*, J = 6.75, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 140.7–122.4 (arom. C); 97.2 (*d*, J = 24, Cp); 77.1 (Cp (under solvent signal)); 70.9 (*d*, J = 4, Cp); 69.9 (*d*, J = 4, Cp); 69.5 (*s*, Ph); 68.2 (*s*, Cp); 56.6 (*d*, J = 8, Me*C*H); 38.7 (*s*, Me_2N); 8.5 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −35.6 (*m*). FAB-MS: 577 (88, M^+), 562 (30, $[M - Me]^+$), 532 (100, $[M - Me_2NH]^+$), 432 (23), 389 (7), 255 (13), 212 (35). Anal. calc. for $C_{28}H_{26}F_6FeNP$ (577.33): C 58.25, H 4.54, N 2.43; found: C 57.91, H 4.66, N 2.66.

*(1*R*)-1-{Bis[3-(trifluoromethyl)phenyl]phosphino}-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2c**). CC (silica gel, hexane/AcOEt 2:1; R_f 0.58): 6.27 g (54%) of **2c**. Thick orange oil. $[\alpha]_D^{20} = -267$ (c = 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.99 (*d*, J = 7.76, 1 arom. H); 7.65–7.30 (*m*, 7 arom. H); 4.42 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 4.14 (*dq*, J = 6.73, 2.38, MeC*H*N); 3.98 (*s*, C_5H_5); 3.72 (*m*, 1 H, Cp); 1.71 (*s*, Me_2N); 1.21 (*d*, J = 6.73, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 142.5–118.9 (arom. C); 97.1 (*d*, J = 23, Cp); 75.2 (*d*, J = 9, Cp); 70.8 (*d*, J = 5, Cp); 69.4 (*s*, C_5H_5); 69.3 (*d*, J = 4, Cp); 68.5 (*s*, Cp); 56.9 (*d*, J = 7, Me*C*HN); 38.0 (*s*, Me_2N); 6.9 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −20.7 (*s*). FAB-MS: 577 (100, M^+), 532 (78, $[M - Me_2NH]^+$), 389 (5), 212 (24). Anal. calc. for $C_{28}H_{26}F_6FeNP$ (577.33): C 58.25, H 4.54, N 2.43; found: C 58.13, H 4.70, N 2.64.

*(1*R*)-1-{(Bis[4-(trifluoromethyl)phenyl]phosphino}-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2d**). CC (silica gel, hexane/AcOEt 2:1 → 1:1; R_f 0.49): 4.594 g (50%) of **2d**. Orange solid. $[\alpha]_D^{20} = -272$ (c = 0.51, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.70–7.62 (*m*, 4 arom. H); 7.47–7.45 (*m*, 2 arom. H); 7.30–7.25 (*m*, 2 arom. H); 4.43 (*m*, 1 H, Cp); 4.29 (*m*, 1 H, Cp); 4.16 (*dq*, J = 6.75, 2.30, MeC*H*N); 3.99 (*s*, C_5H_5); 3.77 (*m*, 1 H, Cp); 1.59 (*s*, Me_2N); 1.23 (*d*, J = 6.75, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 145.1–122.1 (arom. C); 97.1 (*d*, J = 23, Cp); 74.6 (*d*, J = 8, Cp); 71.1 (*d*, J = 6, Cp); 69.4 (*s*, C_5H_5); 8.3 (*s*, Cp); 56.9 (*d*, J = 6, Me*C*HN); 38.3 (*s*, Me_2N); 7.6 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −21.0 (*s*). FAB-MAS: 577 (84, M^+); 534 (100, $[M - Me_2N]^+$), 212 (18). Anal. calc. for $C_{28}H_{26}F_6FeNP$ (577.33): C 58.25, H 4.54, N 2.43; found: C 58.59, H 4.92, N 2.37.

*(1*R*)-1-{Bis[3,5-bis(trifluoromethyl)phenyl]phosphino}-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2e**). FC (silica gel, hexane/AcOEt 10:1; R_f 0.32): 9.84 g (64%) of **2e**. Orange oil that solidified upon standing. $[\alpha]_D^{20} = -194$ (c = 0.53, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 8.12 (*d*, J = 6.8, 2 arom. H); 7.88 (*d*, J = 6.3, 2 arom. H); 7.80 (*s*, 1 arom. H); 7.74 (*s*, 1 arom. H); 4.14 (*m*, 1 H, Cp); 4.08 (*dq*, J = 6.8, 2.4, MeC*H*N); 3.99 (*m*, 1 H, Cp); 3.83 (*s*, C_5H_5); 3.54 (*m*, 1 H, Cp); 1.73 (*s*, Me_2N); 1.00 (*d*, J = 6.8, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 143.4–116.7 (arom. C); 97.6 (*d*, J = 24, Cp); 73.3 (*d*, J = 6, Cp); 70.3 (*d*, J = 6, Cp); 70.2 (*d*, J = 4, Cp); 69.7 (*s*, C_5H_5); 68.2 (*s*, Cp); 57.3 (*d*, J = 7, Me*C*H); 11.2 (*s*, Me_2N); 7.3 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −20.2 (*s*). MALDI-TOF-MS: 713 (M^+). Anal. calc. for $C_{30}H_{24}F_{12}FeNP$ (713.33): C 50.51, H 3.39, N 1.96; found: C 50.29, H 3.49, N 1.84.

*(1*R*)-1-[Bis(3,5-dimethylphenyl)phosphino]-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2f**). CC (silica gel, hexane/AcOEt 2:1 → 1:1): 1.224 g (33%) of **2f**. Orange oil that solidified upon standing. $[\alpha]_D^{20} = -277$ (c = 0.475, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.29 (*s*, 1 arom. H); 7.02 (*s*, 1 arom. H); 6.84–6.81 (*m*, 4 arom. H); 4.39 (*m*, 1 H, Cp); 4.26 (*m*, 1 H, Cp); 4.12 (*dq*, J = 6.81, 2.74, MeC*H*N); 3.96 (*s*, C_5H_5); 3.92 (*m*, 1 H, Cp); 2.35 (*s*, 2 *Me*C_6H_3); 2.22 (*s*, 2 *Me*C_6H_3); 1.85 (*s*, Me_2N); 1.32 (*d*, J = 6.75, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 141.4–127.2 (arom. C); 97.1 (*d*, J = 23, Cp); 77.7 (*d*, J = 12, Cp); 71.8 (*d*, J = 6, Cp); 69.5 (*s*, C_5H_5); 68.8 (*d*, J = 4, Cp); 67.9

(*s*, Cp); 57.3 (*d*, *J* = 7, Me*C*HN); 38.7 (*s*, Me_2N); 20.9 (*s*, *Me*C_6H_3); 20.8 (*s*, *Me*C_6H_3); 8.2 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −22.68 (*s*). FAB-MS (pos.): 497 (73, M^+), 453 (100, $[M-Me_2N]^+$), 212 (24). Anal. calc. for $C_{30}H_{36}FeNP$ (497.44): C 72.44, H 7.29, N 2.82; found: C 72.41, H 7.29, N 2.66.

*(1*R*)-1-[Bis(4-methoxyphenyl)phosphino]-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2g**). CC (silica gel, hexane/AcOEt 2:1 → 1:1): 2.755 g (36%) of **2g**. Orange solid. ^{1}H-NMR ($CDCl_3$): 7.82–7.76 (*m*, 2 arom. H); 7.48–7.42 (*m*, 2 arom. H); 6.88–6.82 (*m*, 4 arom. H); 4.44 (br. *m*, MeC*H*N); 4.31 (*m*, 1 H, Cp); 4.20 (*m*, 1 H, Cp); 4.09 (*m*, 1 H, Cp); 4.04 (*s*, C_5H_5); 3.38 (*s*, 1 MeO); 3.35 (*s*, 1 MeO); 2.03 (*s*, Me_2N); 1.26 (*d*, *J* = 6.7, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −26.0 (*s*).

*(1*R*)-1-[Bis(3,5-dimethoxyphenyl)phosphino]-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2h**). CC (silica gel, hexane/AcOEt 2:1 → 1:1): 1.70 g (39%) of **2h**. Orange solid. $[\alpha]_D^{20} = -240$ (*c* = 0.44, $CHCl_3$). ^{1}H-NMR (C_6D_6): 7.33–7.32 (*m*, 1 arom. H); 7.32–7.29 (*m*, 1 arom. H); 6.91–6.90 (*m*, 1 arom. H); 6.89–6.86 (*m*, 1 arom. H); 6.69–6.68 (*m*, 1 arom. H); 6.58–6.56 (*m*, 1 arom. H); 4.43 (*qd*, *J* = 6.8, 2.6, MeC*H*N); 4.29 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 4.17 (*m*, 1 H, Cp); 4.04 (*s*, C_5H_5); 3.42 (*s*, 2 MeO); 3.35 (*s*, 2 MeO); 2.06 (*s*, Me_2N); 1.23 (*d*, *J* = 6.8, *Me*CHN). ^{13}C-NMR (C_6D_6): 160.9–100.2 (arom. C); 97.3 (*d*, *J* = 23.4, Cp); 77.2 (*d*, *J* = 9.7, Cp); 72.0 (*d*, *J* = 5.7, Cp); 69.9 (*s*, C_5H_5); 69.2 (*d*, *J* = 4, Cp); 68.3 (*s*, Cp); 57.2 (*d*, *J* = 4, Me*C*HN); 54.6 (*s*, 2 MeO); 54.5 (*s*, 2 MeO); 38.9 (*s*, Me_2N); 8.1 (br. *s*, *Me*CHN). $^{31}P\{^1H\}$-NMR (C_6D_6): −17.7 (*s*). FAB-MS: 561 (100, M^+), 517 (83, $[M-Me_2N]^+$). Anal. calc. for $C_{30}H_{36}FeNO_4P$ (561.44): C 64.18, H 6.46, N 2.49; found: C 64.07, H 6.28, N 2.46.

*(1*R*)-1-[Bis[3,5-bis(trifluoromethyl)phenyl]phenylphosphino]-2-[(1*R*)-1-(dimethylamino)ethyl]ferrocene* (**2i**). CC (silica gel, hexane/AcOEt 4:1 → 3:1) allowed the separation of the two isomers (total yield, 3.54 g (44%): 1.87 g of $\mathbf{2i}_a$ and 1.66 g of $\mathbf{2i}_b$.

Isomer $\mathbf{2i}_a$: Orange oil. $[\alpha]_D^{20} = -251$ (*c* = 0.465, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.65–7.40 (*m*, 8 arom. H); 4.42 (*m*, 1 H, Cp); 4.29 (*m*, 1 H, Cp); 4.14 (*dq*, *J* = 6.8, 2.8, MeC*H*N); 3.95 (*s*, C_5H_5); 3.84 (*m*, 1 H, Cp); 1.78 (*s*, Me_2N); 1.23 (*d*, *J* = 6.8, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 146.0–120.5 (arom. C); 97.6 (*d*, *J* = 24, Cp); 74.5 (*d*, *J* = 7, Cp); 71.3 (*d*, *J* = 6, Cp); 69.7 (*s*, C_5H_5); 68.9 (*s*, Cp); 68.3 (*s*, Cp); 57.0 (*d*, *J* = 8, Me*C*HN); 38.6 (*s*, Me_2N); 7.58 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −19.54 (*s*).

Isomer $\mathbf{2i}_b$: Orange solid. $[\alpha]_D^{20} = -264$ (*c* = 0.575, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 7.98 (*d*, *J* = 5.5, 2 arom. H); 7.81 (*s*, 1 arom. H); 7.27–7.19 (*m*, 5 arom. H); 4.42 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 4.17 (*dq*, *J* = 6.7, 2.0, MeC*H*N); 4.03 (*s*, C_5H_5); 3.64 (*m*, 1 H, Cp); 1.66 (*s*, Me_2N); 1.20 (*d*, *J* = 6.7, *Me*CHN). ^{13}C-NMR ($CDCl_3$): 144.2–121.2 (arom. C); 97.0 (*d*, *J* = 22, Cp); 75.8 (*d*, *J* = 8, Cp); 71.2 (*d*, *J* = 6, Cp); 69.6 (*s*, C_5H_5); 69.6 (C of Cp, partially under the C_5H_5 signal); 68.3 (*s*, Cp); 57.4 (*d*, *J* = 5, Me*C*HN); 38.3 (*s*, Me_2N); 7.9 (*s*, *Me*CHN). $^{31}P\{^1H\}$-NMR ($CDCl_3$): −20.7 (*s*). Anal. calc. for $C_{28}H_{26}F_6FeNP$ (577.33): C 58.25, H 4.54, N 2.4; found: C 58.14, H 4.75, N 2.37.

*(1*R*)-1-[Bis[2-(trifluoromethyl)phenyl]phosphino]-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3b**). CC (silica gel, hexane/AcOEt 20:1; R_f 0.28): 723 mg (48%) of **3b**. Orange solid. $[\alpha]_D^{20} = -360$ (*c* = 0.46, $CHCl_3$). Single crystals suitable for X-ray-analysis were grown from an EtOH soln., by slow evaporation of the solvent. ^{1}H-NMR (C_6D_6): 7.71–7.62 (*m*, 2 arom. H); 7.47–7.43 (*m*, 2 arom. H); 7.20–7.15 (*m*, 1 arom. H); 7.01–6.91 (*m*, 3 arom. H); 4.33 (*m*, 1 H, Cp); 4.31 (*m*, 1 H, Cp); 4.21 (*m*, 1 H, Cp); 3.91 (*s*, C_5H_5); 3.59 (*dq*, *J* = 7.3, 3.3, MeC*H*P); 1.96–1.21 (*m*, 25 H, Cy, *Me*CHP). ^{13}C-NMR (C_6D_6): 140.2–118.2 (arom. C); 102.8 (*dd*, *J* = 30, 20, Cp); 74.2 (*d*, *J* = 17, Cp); 70.2 (*d*, *J* = 5, Cp); 69.5 (*s*, C_5H_5); 69.3 (*dd*, *J* = 5, 2, Cp); 68.9 (*s*, Cp); 33.2–26.5 (Cy, Me*C*HP); 15.9 (br. *s*, *Me*CHP). $^{31}P\{^1H\}$-NMR (C_6D_6): 15.8 (*d*, *J* = 58.9, PCy_2); −34.8 (*ds*, PAr_2). FAB-MS: 731 (29, M^+), 647 (54, $[M-Cy]^+$), 585 (76, $[M-Ar]^+$), 533 (100, $[M-HPCy_2]^+$), 373 (6), 212 (5). Anal. calc. for $C_{38}H_{42}F_6FeP_2$ (730.53): C 62.48, H 5.79; found: C 62.48, H 5.80.

*(1*R*)-1-[Bis[3-(trifluoromethyl)phenyl]phosphino]-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3c**). CC (silica gel, hexane/AcOEt 10:1). Due to phosphine oxide traces, a second CC was necessary (Alox, short column, hexane/AcOEt 20:1): 5.89 g (81%) of **3c**. Orange oil. $[\alpha]_D^{20} = -267$ (*c* = 0.5, $CHCl_3$). ^{1}H-NMR (C_6D_6): 8.37 (*d*, *J* = 8.84, 1 arom. H); 7.91 (*d*, *J* = 5.61, 1 arom. H); 7.56–7.26 (*m*, 4 arom. H); 6.96–6.91 (*m*, 2 arom. H); 4.25 (*m*, 1 H, Cp); 4.17 (*m*, 1 H, Cp); 3.96 (*m*, 1 H, Cp); 3.82 (*s*, C_5H_5); 3.54 (*dq*, *J* = 7.17, 2.26, MeC*H*P); 1.99–1.02 (*m*, 25 H, Cy, *Me*CHP). $^{13}C\{^1H\}$-NMR (C_6D_6): 138.5–122.6 (arom. C); 101.7 (*dd*, *J* = 28, 20, Cp); 72.4 (*dd*, *J* = 10, 4, Cp); 70.7 (*d*, *J* = 5, Cp); 69.4 (*s*, C_5H_5); 69.3 (*s*, Cp); 69.0 (*dd*, *J* = 5, 2, Cp); 69.3 (*s*, Cp); 33.1–26.5 (Cy, Me*C*HP); 15.0 (br. *s*, *Me*CHP). $^{31}P\{^1H\}$-NMR (C_6D_6): 16.7 (*d*, *J* = 47.3, PCy_2); −24.2 (*d*, *J* = 47.3, PAr_2). FAB-MS: 731 (14, M^+), 647 (100, $[M-Cy]^+$), 533 (56, $[M-HPCy_2]^+$), 388 (5), 212 (42). Anal. calc. for $C_{38}H_{42}F_6FeP_2$ (730.53): C 62.48, H 5.79; found: C 62.50, H 5.80.

*(1*R*)-1-[Bis[4-(trifluoromethyl)phenyl]phosphino]-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3d**). CC (silica gel, hexane/AcOEt 20:1). Due to phosphine oxide traces, a second CC was necessary (Alox, short column, hexane/AcOEt 20:1): 1.61 g (63%) of **3d**. Orange solid. Single crystals suitable for X-ray-analysis were grown from EtOH by slow evaporation of the solvent. $[\alpha]_D^{20} = -349$ (*c* = 0.47, $CHCl_3$). ^{1}H-NMR (C_6D_6):

7.60–7.55 (*m*, 2 arom. H); 7.42–7.34 (*m*, 6 arom. H); 4.27 (*m*, 1 H, Cp); 4.21 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 3.82 (*s*, C_5H_5); 3.54 (*dq*, *J* = 7.5, 2.9, MeC*H*P); 1.95–1.18 (*m*, 25 H, Cy, *Me*CHP). ^{13}C-NMR (C_6D_6): 146.6–122.6 (arom. C); 101.7 (*dd*, *J* = 28, 20, Cp); 72.4 (*dd*, *J* = 10, 4, Cp); 70.7 (*d*, *J* = 5, Cp); 69.4 (*s*, C_5H_5); 69.3 (*s*, Cp); 69.0 (*dd*, *J* = 5, 2, Cp); 33.0–26.5 (Cy, Me*C*HP); 15.3 (*d*, *J* = 1, *Me*CHP). ^{31}P{^{1}H}-NMR (C_6D_6): 16.3 (*d*, *J* = 46.0, PCy_2); −24.8 (*d*, *J* = 46.0, PAr_2). FAB-MS: 731 (14, M^+), 647 (100, $[M - Cy]^+$), 533 (56, $[M - HPCy_2]^+$), 388, 212. Anal. calc. for $C_{38}H_{42}F_6FeP_2$ (730.53): C 62.48, H 5.79: found: C 62.40, H 5.78.

*(1*R*)-1-{Bis[3,5-bis(trifluoromethyl)phenyl]phosphino}-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3e**). CC (silica gel, hexane/AcOEt 10:1). Due to phosphine oxide traces, a second CC was necessary (Alox, short column, hexane/AcOEt 20:1): 2.225 g (91.5%) of **3e**. Orange solid. Single crystals suitable for X-ray analysis were grown from EtOH by slow evaporation of the solvent. $[\alpha]_D^{20} = -288$ (*c* = 0.49, $CHCl_3$). ^{1}H-NMR (C_6D_6): 8.20 (*d*, *J* = 6.6, 2 arom. H); 7.99 (*d*, *J* = 5.7, 2 arom. H); 7.79 (*s*, 1 arom. H); 7.75 (*s*, 1 arom. H); 4.18 (*m*, 1 H, Cp); 4.08 (*m*, 1 H, Cp); 3.81 (*m*, 1 H, Cp); 3.75 (*s*, C_5H_5); 3.42 (*dq*, *J* = 7.25, 2.15, MeC*H*P); 1.98–1.25 (*m*, 22 H, Cy); 1.50 (*dd*, *J* = 7.12, 3.55, *Me*CHP). ^{13}C-NMR (C_6D_6): 145.0–120.4 (arom. C); 101.9 (*dd*, *J* = 28, 20, Cp); 70.9 (*dd*, *J* = 9, 4, Cp); 70.1 (*d*, *J* = 5, Cp); 70.0 (*s*, Cp); 69.6 (*s*, C_5H_5); 33.2–26.4 (Cy, Me*C*HP); 14.6 (*d*, *J* = 2, *Me*CHP); 1 C of Cp missing. ^{31}P{^{1}H}-NMR (C_6D_6): 17.8 (*d*, *J* = 52.0, PCy_2); −22.6 (*d*, *J* = 52.0, PAr_2). FAB-MS: 867 (34, M^+), 783 (100, $M - HCy]^+$), 700.9 (6), 669 (85, $[M - HPCy_2]^+$), 456 (3), 212 (40). Anal. calc. for $C_{40}H_{40}F_{12}FeP_2$ (866.53): C 55.44, H 4.65; found: C 55.41, H 4.82.

*(1*R*)-1-[Bis(3,5-dimethylphenyl)phosphino]-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3f**). CC (Alox, hexane/AcOEt 7:1): 1.168 g (89%) of **3f**. Orange oil that solidified upon standing. $[\alpha]_D^{20} = -305$ (*c* = 0.505, $CHCl_3$). ^{1}H-NMR (C_6D_6): 7.69 (*d*, *J* = 8.35, 2 arom. H); 7.31 (*d*, *J* = 7.44, 2 arom. H); 6.87 (*s*, 1 arom. H); 6.78 (*s*, 1 arom. H); 4.44 (*m*, 1 H, Cp); 4.37 (*m*, 1 H, Cp); 4.29 (*m*, 1 H, Cp); 3.97 (*s*, C_5H_5); 3.72 (br. *dq*, MeC*H*P); 2.19 (*s*, 2 *Me*C_6H_3); 2.18 (*s*, 2 *Me*C_6H_3); 1.97–1.21 (*m*, 25 H, Cy, *Me*CHP). ^{13}C-NMR (C_6D_6): 137.2–127.4 (arom. C); 101.1 (*dd*, *J* = 28, 9, Cp); 75.3 (*dd*, *J* = 13, 3, Cp); 71.7 (*d*, *J* = 5, Cp); 69.6 (*s*, C_5H_5); 68.8–68.6 (*m*, 2 C, Cp); 33.1–26.6 (Cy, Me*C*HP); 21.2 (*s*, *Me*C_6H_3); 21.0 (*s*, *Me*C_6H_3); 16.5 (*s*, *Me*CHP). ^{31}P{^{1}H}-NMR (C_6D_6): 14.8 (*d*, *J* = 37.4, PCy_2); −25.9 (*d*, *J* = 37.5, PAr_2). FAB-MS: 651 (13, M^+), 567 (100, $[M - HCy]^+$), 453 (50, $[M - HPCy_2]^+$), 387 (5), 212 (32). Anal. calc. for $C_{40}H_{52}FeP_2$ (650.65): C 73.84, H 8.06; found: C 73.98, H 7.94.

*(1*R*)-1-[Bis(4-methoxyphenyl)phosphino]-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3g**). CC (Alox, hexane/AcOEt 6:1; R_f 0.46): 1.8474 g (72%) of **3g**. Orange solid. Single crystals suitable for X-ray analysis were grown from ^{t}BuOMe/EtOH/hexane by slow evaporation of the solvent mixture. $[\alpha]_D^{20} = -338$ (*c* = 0.49, $CHCl_3$). ^{1}H-NMR (C_6D_6): 7.80 (*dd*, *J* = 7.6, 2, 2 arom. H); 7.52 (*dd*, *J* = 6.7, 1.9, 2 arom. H); 6.85 (*d*, *J* = 8.1, 4 arom. H); 4.36, 4.28, 4.26 (3*m*, 3 H, Cp); 4.01 (*s*, C_5H_5); 3.69 (*dq*, *J* = 7.3, 3.2, MeC*H*P); 3.37 (*s*, 1 MeO); 3.32 (*s*, 1 MeO); 1.93–1.18 (*m*, 25 H, Cy, *Me*CHP). ^{13}C-NMR (C_6D_6): 160.5–113.2 (arom. C); 101.3 (*dd*, *J* = 27, 20, Cp); 76.1 (*dd*, *J* = 12, 3, Cp); 71.2 (*d*, *J* = 6, Cp); 69.45 (*s*, C_5H_5); 68.7–68.6 (*m*, 2 C, Cp); 54.4 (*s*, MeO); 54.2 (*s*, MeO); 33.3–26.5 (Cy, Me*C*HP); 16.6 (*s*, *Me*CHP). ^{31}P{^{1}H}-NMR (C_6D_6): 15.3 (*d*, *J* = 32.0, PCy_2); −28.6 (*d*, *J* = 32.0, PAr_2). FAB-MS: 654 (11, M^+), 571 (100, $[M - HCy]^+$), 457 (56, $[M - HPCy_2]^+$), 391 (6), 350 (6), 245 (33), 212 (33). Anal. calc. for $C_{38}H_{48}FeO_2P_2$ (654.59): C 69.73, H 7.39; found: C 69.29, H 7.07.

*(1*R*)-1-[Bis(3,5-dimethoxyphenyl)phosphino]-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3h**). CC (Alox, hexane/AcOEt 6:1): 349 mg (86%) of **3h**. Orange solid. Single crystals suitable for X-ray analysis were grown from EtOH by slow evaporation of the solvent. $[\alpha]_D^{20} = -281$ (*c* = 0.49, $CHCl_3$). ^{1}H-NMR (C_6D_6): 7.36 (*d*, *J* = 2.2, 1 arom. H); 7.33 (*d*, *J* = 2.2, 1 arom. H); 6.99 (*d*, *J* = 2.1, 1 arom. H); 6.96 (*d*, *J* = 2.2, 1 arom. H); 6.68–6.67 (*d*, 1 arom. H); 6.55–6.54 (*m*, 1 arom. H); 4.45 (*m*, 1 H, Cp); 4.35 (*m*, 1 H, Cp); 4.25 (*m*, 1 H, Cp); 4.05 (*s*, C_5H_5); 3.71 (*dq*, *J* = 7.6, 3.2, MeC*H*P); 3.40 (*s*, 2 MeO); 3.38 (*s*, 2 MeO); 2.00–1.21 (*m*, 25 H, Cy, *Me*CHP). ^{31}P{^{1}H}-NMR (C_6D_6): 15.6 (*d*, *J* = 38.0, PCy_2); −20.7 (*d*, *J* = 37.8, PAr_2). FAB-MS: 716 (8, M^+), 632 (100, $[M - HCy]^+$), 517 (34, $[M - HPCy_2]^+$), 212 (5). Anal. calc. for $C_{40}H_{52}FeO_4P_2$ (714.64): C 67.23, H 7.33; found: C 67.17, H 7.41.

*(1*R*)-1-{Bis[3,5-bis(trifluoromethyl)phenyl]phenylphosphino}-2-[(1*R*)-1-(dicyclohexylphosphino)ethyl]ferrocene* (**3i**). From enantiomerically pure **2i**$_b$ ((*R*,*R*); 0.91 g, 1.58 mmol, 1 equiv.) and 350 µl of dicyclohexylphosphine (1.73 mmol, 1.1 equiv.) according to the general method. The residue was purified by CC (silica gel, hexane/AcOEt 30:1): 902 mg (78%) of the diastereoisomers **3i**$_a$/**3i**$_b$ which could not be separated by CC. Orange solid. FAB-MS: 731 (12, M^+), 647 (100, $[M - HCy]^+$), 533 (49, $[M - HPCy_2]^+$), 212 (21). Anal. calc. for $C_{38}H_{42}F_6FeP_2$ (730.53): C 62.48, H 5.79; found: C 62.24, H 5.97.

Isomer **3i**$_a$: ^{1}H-NMR (C_6D_6): 8.04 (*d*, *J* = 5.2, 2 arom. H); 7.74 (*s*, 1 arom. H); 7.68–7.62 (*m*, 2 arom. H); 7.14–7.12 (*m*, 3 arom. H); 4.25, 4.19, 4.06 (3*m*, 3 H, Cp); 3.83 (*s*, C_5H_5); 3.57 (*dq*, *J* = 7.2, 2.5, MeC*H*P); 1.99–1.21 (*m*, 25 H, Cy, *Me*CHP). ^{31}P{^{1}H}-NMR (C_6D_6): 15.9 (*d*, *J* = 42.9, PCy_2); −24.1 (*d*, *J* = 42.9, PAr_2).

Isomer **3i**$_b$: ^{1}H-NMR (C_6D_6): 8.31 (*d*, *J* = 8.2, 2 arom. H); 7.83 (*s*, 1 arom. H); 7.47–7.42 (*m*, 2 arom. H); 7.14–7.12 (*m*, 3 arom. H); 4.36, 4.12, 3.92 (3*m*, 3 H, Cp); 3.86 (*s*, C_5H_5); 3.37–3.34 (br. *dq*, MeC*H*P); 1.99–1.21 (*m*, 25 H, Cy, *Me*CHP). ^{31}P{^{1}H}-NMR (C_6D_6): 14.3 (*d*, *J* = 47.7, PCy_2); −25.9 (*d*, *J* = 48.1, PAr_3).

*(*SP*-4-3)-{(1*R*)-1-{Bis[3,5-bis(trifluoromethyl)phenyl]phosphino-*κ*P}-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]ferrocene}dichloropalladium* ([$PdCl_2$(**3e**)]; **5e**). CH_2Cl_2 (10 ml) was added to a *Schlenk* flask containing [$PdCl_2$(cod)] (50 mg, 0.175 mmol) and a slight excess of **3e** (159.35 mg, 0.2 mmol). The mixture was stirred at r.t. for 3 h. After filtration through *Celite* to remove traces of Pd^0, the soln. was concentrated *in vacuo*. Cold pentane was added to precipitate the complex, which was filtered off, washed with additional pentane (10 ml), and dried overnight *in vacuo:* 167.1 mg (91%) of **5e**. Orange powder. Single crystals suitable for X-ray analysis were grown from a CH_2Cl_2 soln. layered with pentane at 4°. ^{1}H-NMR ($CDCl_3$): 8.59 (*d*, *J* = 12.23, 2 arom. H); 8.17 (*s*, 1 arom. H); 7.95–7.90 (*m*, 3 arom. H); 4.82 (*m*, 1 H, Cp); 4.58 (*m*, 1 H, Cp); 4.23 (*m*, 1 H, Cp); 3.68 (*s*, 1 H, C_5H_5); 3.54–3.41 (*m*, 1 H, Cy); 3.22 (*m*, MeC*H*P); 2.49–1.12 (*m*, 24 H, Cy, *Me*CHP). ^{13}C-NMR ($CDCl_3$): 136.92–116.08 (arom. C); 94.17 (*dd*, *J* = 20.41, 3.35, Cp); 77.2 (C(*q*) of Cp under $CDCl_3$ signal); 74.49 (*d*, *J* = 3.65, Cp); 70.69 (C of Cp partially under C_5H_5 signal); 70.38 (*d*, *J* = 7.61, Cp); 37.63 (*d*, *J* = 22.84, Cy(CH)); 35.21 (*d*, *J* = 18.88, Cy(CH)); 30.94–25.39 (Cy, Me*C*HP); 16.42 (*d*, *J* = 6.70, *Me*CHP). ^{31}P{^{1}H}-NMR ($CDCl_3$): 80.47 (br. *s*, PCy_2), 22.67 (br. *s*, PAr_2). FAB-MS: 2051 (100, [2*M* − Cl]$^+$), 1550 (5), 1009 ([*M* − Cl]$^+$), 669 (8), 349 (4). Anal. calc. for $C_{40}H_{40}Cl_2F_{12}FeP_2Pd$ (1043.86): C 46.03, H 3.86; found: C 46.16, H 4.11.

Dimethylpalladium Complexes: General Procedure 1 (*G.P. 1*). [$PdMe_2$(tmeda)] (1 equiv.) and the diphosphine ligand (1–1.1 equiv.) were dissolved in benzene. The orange soln. was stirred for 3 h at r.t. After filtration through *Celite* to remove traces of Pd^0, the soln. was concentrated *in vacuo*. A mixture of cold Et_2O/pentane was added to precipitate the complex, which was filtered off, washed with additional pentane (10 ml), and then dried overnight *in vacuo:* orange solid.

*(*SP*-4-3)-{(2*R*)-1-[(1*R*)-1-(Dicyclohexylphosphino-*κ*P)ethyl]-2-(diphenylphosphino-*κ*P)ferrocene}dimethylpalladium* ([$PdMe_2$(**3a**)]; **6a**). According to the *G.P. 1* from [$PdMe_2$(tmeda)] (60 mg, 0.237 mmol, 1 equiv.) and **3a** (144 mg, 0.242 mmol, 1.02 equiv.): 154.2 mg (89%) of **6a**. Orange solid. Single crystals suitable for X-ray analysis were obtained from a warm soln. of benzene and Et_2O. ^{1}H-NMR (C_6D_6): 8.27–8.22 (*m*, 2 arom. H); 7.63–7.58 (*m*, 2 arom. H); 7.32–7.12 (*m*, 6 arom. H); 4.25 (*m*, 1 H, Cp); 4.14 (*m*, 1 H, Cp); 4.05 (*m*, 1 H, Cp); 3.62 (*s*, C_5H_5); 3.28 (*dq*, *J* = 7.28, 4.15, MeC*H*P); 2.68–2.64 (br. *m*, 1 H, Cy); 2.47–2.41 (br. *m*, 1 H, Cy); 2.23–1.00 (*m*, 27 H, Cy, *Me*CHP, 1 MePd); 0.83 (*dd*, *J* = 8.73, 6.42, 1 MePd). ^{13}C-NMR (C_6D_6): 137.2–126.5 (arom. C); 95.0 (*dd*, *J* = 23, 6, Cp); 77.2 (*dd*, *J* = 24, 8, Cp); 75.0 (*s*, Cp); 70.0 (*s*, C_5H_5); 68.7 (*d*, *J* = 8, Cp); 67.7 (*d*, *J* = 5, Cp); 34.0–26.1 (Cy, Me*C*HP); 16.2 (*d*, *J* = 6, *Me*CHP); 8.4 (*dd*, *J* = 102, 10, 1 MePd); 3.65 (*dd*, *J* = 107, 10, 1 MePd). ^{31}P{^{1}H}-NMR (C_6D_6): 40.8 (*d*, *J* = 28.0, PCy_2); 13.2 (*d*, *J* = 28.0, PPh_2). FAB-MS (pos.): 699 (83, [*M* − 2 Me]$^+$), 637 (100). Anal. calc. for $C_{38}H_{50}FeP_2Pd$ (731.03): C 62.44, H 6.89; found: C 62.24, H 7.02.

*(*SP*-4-3)-{(1*R*)-1-{Bis[3,5-bis(trifluoromethyl)phenyl]phosphino-*κ*P}-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]ferrocene}dimethylpalladium* ([$PdMe_2$(**3e**); **6e**). According to the *G.P. 1* from [$PdMe_2$(tmeda)] (40 mg, 0.158 mmol, 1 equiv.) and **3e** (138.5 mg, 0.159 mmol, 1.01 equiv.). The filtrate was evaporated to give **6e** quantitatively. ^{1}H-NMR (C_6D_6): 8.67 (*d*, *J* = 9.43, 2 arom. H); 7.97 (*d*, *J* = 8.40, 1 arom. H); 7.82 (*s*, 1 arom. H); 7.75 (*s*, 1 arom. H); 4.20 (*m*, 1 H, Cp); 3.94 (*m*, 1 H, Cp); 3.56 (*m*, 1 H, Cp); 3.45 (*s*, C_5H_5); 3.13 (*dq*, *J* = 6.82, 2.13, MeC*H*P); 2.65–2.55 (br. *m*, 1 H, Cy); 2.35–1.04 (*m*, 27 H, Cy, *Me*CHP, 1 MePd); 0.64 (*dd*, *J* = 7.03, 1.25, 1 MePd). ^{13}C-NMR (C_6D_6): 140.1–121.4 (arom. C); 95.8 (*dd*, *J* = 25, 6, Cp); 74.1 (*s*, Cp); 73.0 (*dd*, Cp); 70.2–70.0 (Cp, C_5H_5); 69.0 (*d*, *J* = 5, Cp); 33.7–26.0 (Cy, Me*C*HP); 15.9 (*d*, *J* = 6, *Me*CHP); 7.7 (*dd*, *J* = 100, 10, 1 MePd); 5.6 (*dd*, *J* = 107, 10, 1 MePd). ^{31}P{^{1}H}-NMR (C_6D_6): 41.6 (*d*, *J* = 26.8, PCy_2); 16.9 (*d*, *J* = 26.8, PAr_2). FAB-MS (pos.): 973 (23, [*M* − 2Me]$^+$), 773 (65), 212 (100). Anal. calc. for $C_{42}H_{46}Cl_2F_{12}FeP_2Pd$ (1003.02): C 50.29, H 4.62; found: C 50.24, H 4.66.

Chloromethylpalladium Complexes: General Procedure 2 (*G.P. 2*). To a soln. of [PdClMe(cod)] (1 equiv.) in CH_2Cl_2, the diphosphino ligand (1–1.1 equiv.), was added and the mixture was stirred at r.t. After 3 h, the soln. was filtered through a *Celite* filter aid. The filtrate was evaporated until 0.5 ml of CH_2Cl_2 was left, and the product was precipitated by addition of hexane/Et_2O or pentane/Et_2O, washed with hexane or pentane, and dried *in vacuo:* orange solid.

*(*SP*-4-2)-{(2*R*)-1-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]-2-(diphenylphosphino-*κ*P)ferrocene}chloro(methyl)palladium* ([PdClMe(**3a**)]; **7a**). According to the *G.P. 2*, from [PdClMe(cod)] (200 mg, 0.754 mmol, 1 equiv.) and **3a** (493 mg, 0.82 mmol, 1.1 equiv.): 527 mg (93%) of **7a**. Red-orange crystals. Single crystals suitable for X-ray analysis were grown from a CH_2Cl_2 soln. layered with Et_2O and pentane. Crystallization afforded a single stereoisomer. ^{1}H-NMR ($CDCl_3$): 8.15–8.08 (*m*, 2 arom. H); 7.57–7.54 (*m*, 3 arom. H); 7.37–7.26 (*m*, 5 arom. H); 4.52 (*m*, 1 H, Cp); 4.26 (*m*, 1 H, Cp); 4.11 (*m*, 1 H, Cp); 3.64 (*s*, C_5H_5); 3.12 (*dq*, *J* = 7.0, 4.6, MeC*H*P); 3.00–2.84 (br. *m*, 1 H, Cy); 2.35–2.22 (br. *m*, 1 H, Cy); 1.97–1.10 (*m*, 23 H, Cy, *Me*CHP); 0.44

(*dd*, *J* = 7.28, 3.73, MePd). ^{13}C-NMR ($CDCl_3$): 136.0–127.4 (arom. C); 94.6 (*dd*, *J* = 18, 6, Cp); 75.3 (*d*, *J* = 4, Cp); 70.3 (*s*, C_5H_5); 70.1 (*s*, Cp); 69.1 (*dd*, *J* = 8, 1, Cp); 68.0 (*d*, *J* = 7, Cp); 33.6–25.8 (Cy, Me*C*HP); 16.5 (*d*, *J* = 103, MePd); 15.9 (*s*, *Me*CHP). ^{31}P{^{1}H}-NMR ($CDCl_3$): 40.9 (*d*, *J* = 39.9, PCy_2); 29.0 (*d*, *J* = 39.8, PPh_2). FAB-MS (pos.): 1467 (64.5, $[2M - Cl]^+$), 737 (100, $[M - Me]^+$), 700 (23, $[M - MeCl]^+$). Anal. calc. for $C_{37}H_{47}ClFeP_2Pd$ (751.45): C 59.14, H 6.30; found: C 58.52, H 6.45.

*(*SP*-4)-{(1*R*)-1-[Bis[4-(trifluoromethyl)phenyl]phosphino-*κ*P]-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]-ferrocene}chloro(methyl)palladium* ([PdClMe(**3d**)]; **7d**). According to the *G.P. 2*, from [PdClMe(cod)] (100 mg, 0.377 mmol, 1 equiv.) and **3d** (281 mg, 0.385 mmol, 1.02 equiv.): 291 mg (87%) of **7d** as isomer mixture **I**/**II** 1: 0.45. Small orange crystals. FAB-MS (pos.): 1742 (50, $[2M - Me_2]^+$), 871 (33, $[M - Me]^+$), 837 (22, $[M - ClMe]^+$). Anal. calc. for $C_{39}H_{45}ClF_6FeP_2Pd$ (887.44): C 52.78, H 5.11; found: C 52.72, H 5.30.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR ($CDCl_3$): 8.23–8.17 (*m*, 2 arom. H); 7.86 (*d*, *J* = 7.67, 2 arom. H); 7.57–7.37 (*m*, 4 arom. H); 4.61 (*m*, 1 H, Cp); 4.34 (*m*, 1 H, Cp); 4.05 (*m*, 1 H, Cp); 3.64 (*s*, C_5H_5); 3.09 (*dq*, *J* = 7.02, 5.26, Me*CH*P); 3.02–2.86 (*m*, 1 H, Cy(CH)); 2.25–1.05 (*m*, 24 H, Cy, *Me*CHP); 0.42 (*dd*, *J* = 7.02, 3.95, MePd). ^{31}P{^{1}H}-NMR ($CDCl_3$): 40.9 (*d*, *J* = 40.5, PCy_2); 29.9 (*d*, *J* = 40.5, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ($CDCl_3$): 8.23–8.17 (*m*, 2 arom. H); 7.77 (*d*, *J* = 7.67, 2 arom. H); 7.57–7.37 (*m*, 4 arom. H); 4.59 (*m*, 1 H, Cp); 4.42 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 3.61 (*s*, C_5H_5); 3.23 (br. *dq*, *J* = 7.45, Me*CH*P); 2.48–2.41 (*m*, 1 H, Cy); 2.25–1.04 (*m*, 24 H, Cy, *Me*CHP); 0.85 (*dd*, *J* = 7.89, 1.97, MePd). ^{31}P{^{1}H}-NMR ($CDCl_3$): 60.6 (*d*, *J* = 36.0, PCy_2); 4.9 (*d*, *J* = 36.0, PAr_2).

*(*SP*-4)-{(1*R*)-1-[Bis[3,5-bis(trifluoromethyl)phenyl]phosphino-*κ*P]-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]ferrocene}chloro(methyl)palladium* ([PdClMe(**3e**)]; **7e**). According to the *G.P. 2*, from [PdClMe-(cod)] (61.2 mg, 0.23 mmol, 1 equiv.) and **3e** (200 mg, 0.23 mmol, 1 equiv.). The filtrate was evaporated to give **7e** quantitatively as isomer mixture **I**/**II** 1:2. Due to the high solubility of **7e** even in pentane, purification attempts by precipitation were unsuccessful. FAB-MS (pos.): 2009 (100, $[M - Cl]^+$), 971 (8, $[M - MeCl]^+$), 773 (21), 669 (7), 471 (8), 351 (5), 212 (8). Anal. calc. for $C_{41}H_{43}ClF_{12}FeP_2Pd \cdot 25C_8H_{12}$ (1022.07): C 49.11, H 4.41; found: C 49.23, H 4.91.

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ^{1}H-NMR ($CDCl_3$): 8.48 (*s*, 1 arom. H); 8.45 (*s*, 1 arom. H); 8.09 (*s*, 1 arom. H); 7.85 (*s*, 1 arom. H); 7.80 (*d*, *J* = 8.99, 2 arom. H); 4.68 (*m*, 1 H, Cp); 4.53 (*m*, 1 H, Cp); 4.30 (*m*, 1 H, Cp); 3.61 (*s*, C_5H_5); 3.31–3.21 (*m*, 1 H, Cy(CH)); 3.16–3.01 (br. *m*, Me*CH*P); 2.58–1.03 (*m*, 24 H, Cy, *Me*CHP); 0.92 (*dd*, *J* = 7.89, 2.19, MePd). ^{31}P{^{1}H}-NMR ($CDCl_3$): 60.5 (*d*, *J* = 36.0, PCy_2); 6.9 (*d*, *J* = 36.0, PAr_2).

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2): ^{1}H-NMR ($CDCl_3$): 8.45 (*s*, 1 arom. H); 8.41 (*s*, 1 arom. H); 8.16 (*s*, 1 arom. H); 7.92 (*s*, 1 arom. H); 7.68 (*d*, *J* = 8.99, 2 arom. H); 4.72 (*m*, 1 H, Cp); 4.46 (*m*, 1 H, Cp); 4.05 (*m*, 1 H, Cp); 3.66 (*s*, C_5H_5); 3.31–3.21 (*m*, 1 H, Cy); 3.16–3.01 (br. *m*, Me*CH*P); 2.58–1.03 (*m*, 24 H, Cy, *Me*CHP); 0.46 (*dd*, *J* = 7.23, 4.17, MePd). ^{31}P{^{1}H}-NMR ($CDCl_3$): 42.3 (*d*, *J* = 41.2, PCy_2); 32.2 (*d*, *J* = 41.2, PAr_2).

*(*SP*-4-2)-{(1*R*)-1-[Bis(3,5-dimethylphenyl)phosphino-*κ*P]-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]-ferrocene}chloro(methyl)palladium* ([PdClMe(**3f**)]; **7f**). According to the *G.P. 2*, from [PdClMe(cod)] (100 mg, 0.378 mmol, 1 equiv.) and **3f** (250.2 mg, 0.385 mmol, 1.02 equiv.): 247.8 mg (81.4%) of **7f**. Light orange solid as a single isomer **I** (Me *trans* to PCy_2; (*SP*-4-2). ^{1}H-NMR ($CDCl_3$): 7.74 (*d*, *J* = 12.79, 2 arom. H); 7.17 (*s*, 1 arom. H); 6.96–6.92 (*m*, 3 arom. H); 4.49 (*m*, 1 H, Cp); 4.25 (*m*, 1 H, Cp); 4.14 (*m*, 1 H, Cp); 3.67 (*s*, C_5H_5); 3.07 (*dq*, *J* = 6.92, 4.16, Me*CH*P); 2.87–2.83 (br. *m*, 1 H, Cy); 2.44 (*s*, 6 H, *Me*C_6H_3); 2.24 (*s*, 6 H, *Me*C_6H_3); 1.92–0.85 (*m*, 24 H, Cy, *Me*CHP); 0.42 (*dd*, *J* = 7.29, 3.70, MePd). ^{13}C-NMR ($CDCl_3$): 137.7–130.4 (arom. C); 94.5 (*dd*, *J* = 18, 6, Cp); 77.20 (C of Cp under $CDCl_3$ signal); 75.5 (*d*, *J* = 5, Cp); 70.2 (*s*, C_5H_5), 68.9 (*dd*, *J* = 8, 1, Cp); 67.8 (*d*, *J* = 7, Cp); 33.7 (*d*, *J* = 12, Cy(CH)); 32.9 (*d*, *J* = 9, Cy(CH)); 31.6–26.0 (Cy, Me*C*HP); 21.6 (*s*, *Me*C_6H_3); 21.5 (*s*, *Me*C_6H_3); 16.8 (*d*, *J* = 6, *Me*CHP); 9.3 (MePd); 7.7 (MePd). ^{31}P{^{1}H}-NMR ($CDCl_3$): 41.7 (*d*, *J* = 39.1, PCy_2); 28.9 (*d*, *J* = 39.1, PAr_2). FAB-MS (pos.): 1580 (37, $[2M - Cl]^+$), 793 (55, $[M - Me]^+$), 757 (17, $[M - MeCl]^+$), 665 (100). Anal. calc. for $C_{41}H_{55}ClFeP_2Pd$ (807.55): C 60.98, H 6.86; found: C 61.16, H 6.78.

*(*SP*-4-2)-{(1*R*)-1-[Bis(4-methoxyphenyl)phosphino-*κ*P]-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]ferrocene}chloro(methyl)palladium* ([PdClMe(**3g**)]; **7g**). According to the *G.P. 2*, from [PdClMe(cod)] (50 mg, 0.188 mmol, 1 equiv.) and **3g** (130 mg, 0.198 mmol, 1.05 equiv.): 126.9 mg (83%) of **7g**. Orange solid. Single crystals suitable for an X-ray study were grown from a CH_2Cl_2 soln. layered with hexane and *t*BuOMe. Crystallization afforded a single isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)). ^{1}H-NMR ($CDCl_3$): 8.06 (*dd*, *J* = 11.51, 8.74, 1 arom. H); 7.26 (*dd*, *J* = 10.66, 8.95, 1 arom. H); 7.07 (*dd*, *J* = 8.74, 1.49, 1 arom. H); 6.83 (*dd*, *J* = 8.95, 1.92, 1 arom. H); 4.50 (*m*, 1 H, Cp); 4.25 (*m*, 1 H, Cp); 4.08 (*m*, 1 H, Cp); 3.89 (*s*, 1 MeO); 3.81 (*s*, 1 MeO); 3.73 (*s*, C_5H_5); 3.07 (*dq*, *J* = 7.03, 4.26, Me*CH*P); 2.96–2.83 (br. *m*, 1 H, Cy); 2.29–1.11 (*m*, 24 H, Cy, *Me*CHP); 0.42 (*dd*, *J* = 7.25, 3.62, MePd). ^{13}C{^{1}H}-NMR ($CDCl_3$): 161.5–113.0 (arom. C); 74.9 (*d*, *J* = 5, Cp); 70.0 (*s*, C_5H_5), 68.9 (*dd*, *J* = 9, 2, Cp); 67.5 (*d*, *J* = 7, Cp); 55.2 (*s*, MeO); 55.0 (*s*, MeO); 33.4 (*d*, *J* = 12, Cy(CH)); 32.5 (*d*, *J* = 9,

Cy(CH)); 30.5–25.7 (Cy, Me*C*HP); 16.5 (*d*, *J* = 89, MePd); 15.8 (*d*, *J* = 2, *Me*CHP). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 41.7 (*d*, *J* = 39.7, PCy_2); 26.7 (*d*, *J* = 39.7, PAr_2). Anal. calc. for $C_{39}H_{51}ClFeO_2P_2Pd$ (811.50): C 57.72, H 6.33; found: C 57.83, H 6.52.

Cationic Pd Complexes [PdMe(P–P)(MeCN)]PF$_6$: General Procedure 3 (*G.P. 3*). To a soln. of the chloromethylpalladium complex [PdClMe(P–P)] (1 equiv.) in CH_2Cl_2/MeCN 9.5 : 0.5 (*v*/*v*), $TlPF_6$ (1.1 equiv.) was added. After stirring overnight, the soln. was filtered over *Celite* to remove TlCl. The filtrate was first concentrated *in vacuo* to *ca*. 0.5–1.0 ml, then cooled pentane (30 ml) was added with rapid stirring, to allow precipitation of the product. The material was filtered off, washed with additional pentane (10 ml), and dried *in vacuo* to afford product [PdMe(P–P)(MeCN)]PF_6 as a mixture of the two isomers.

*SP-4)-(Acetonitrile){(2*R*)-1-[(1*R*)-1-(dicyclohexylphosphino-κ*P*)ethyl]-2-(diphenylphosphino-κ*P*)ferrocene}methylpalladium(+) Hexafluorophosphate* ([PdMe(**3a**)(MeCN)]PF_6; **8a**). According to the *G.P. 3*, from [PdClMe(**3a**)] (89.4 mg, 0.119 mmol, 1 equiv.) and 41.6 mg of $TlPF_6$ (41.6 mg, 0.130 mmol, 1.1 equiv.): 97.6 mg (90%) of **8a** as isomer mixture **I**/**II** 1.95 : 1. Dark orange powder. FAB-MS (pos.): 699 (72, $[Pd(\mathbf{5a})]^+$), 637 (87), 205 (100). Anal. calc. for $C_{39}H_{60}F_6FeNP_3Pd$ (912.09): C 51.36, H 6.63, N 1.54; found: C 51.34, H 6.52, N 1.28.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR (CD_3CN): 8.13–7.30 (*m*, 10 arom. H); 4.73 (*m*, 1 H, Cp); 4.42 (*m*, 1 H, Cp); 4.16 (*m*, 1 H, Cp); 3.74 (*s*, C_5H_5); 3.36–3.26 (*m*, 1 H); 2.47–2.36 (*m*, 1 H, Cy); 2.16–0.88 (*m*, 27 H, Cy, *Me*CHP, MeCNPd); 0.30 (*dd*, *J* = 6.36, 2.19, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 44.5 (*d*, *J* = 40.7, PCy_2); 29.8 (*d*, *J* = 40.7, PPh_2).

Isomer **II** (Me *trans* to PPh_2; (*SP*-4-3)): ^{1}H-NMR (CD_3CN): 8.13–7.30 (*m*, 10 arom. H); 4.77 (*m*, 1 H, Cp); 4.51 (*m*, 1 H, Cp); 4.46 (*m*, 1 H, Cp); 3.77 (*s*, C_5H_5); 3.22–3.13 (*m*, 1 H); 2.63–2.51 (*m*, 1 H, Cy); 2.16–0.88 (*m*, 27 H, Cy, *Me*CHP, MeCNPd); 0.58 (*dd*, *J* = 7.45,1.53, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 67.9 (*d*, *J* = 34,3, PCy_2); 8.3 (*d*, *J* = 34.3, PPh_2).

*(*SP*-4)-(Acetonitrile){(1*R*)-1-{bis[4-(trifluoromethyl)phenyl]phosphino-κ*P*}-2-[(1*R*)-1-(dicyclohexylphosphino-κ*P*)ferrocene}methylpalladium(+) Hexafluorophosphate* ([PdMe(**3d**)(MeCN)]PF_6; **8d**). According to the *G.P. 3*, from [PdClMe(**3d**)] (150 mg, 0.169 mmol, 1 equiv.) and $TlPF_6$ (64.95 mg, 0.186 mmol, 1.1 equiv.): 163 mg (93%) of **8d** as isomer mixture **I**/**II** 1.3 : 1. Dark red powder. FAB-MS (pos.): 1750 (100), 834 (82), 704 (87), 212 (31). Anal. calc. for $C_{41}H_{48}F_{12}FeNP_3Pd$ (1038.01): C 47.44, H 4.66, N 1.35; found: C 47.62, H 4.76, N 1.18.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR (CD_3CN): 8.27–8.18 (*m*, 2 arom. H); 8.03–8.00 (*m*, 2 arom. H); 7.76–7.73 (*m*, 2 arom. H); 7.54–7.39 (*m*, 2 arom. H); 4.80 (*m*, 1 H, Cp); 4.50 (*m*, 1 H, Cp); 4.18 (*m*, 1 H, Cp); 3.75 (*s*, C_5H_5); 3.31 (*dq*, *J* = 7.23, 4.82, MeC*H*P); 2.62–2.50 (*m*, 1 H, Cy); 2.14–1.12 (*m*, 27 H, Cy, *Me*CHP, MeCNPd); 0.32 (*dd*, *J* = 6.72, 2.83, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 43.7 (*d*, *J* = 41.6, PCy_2); 30.4 (*d*, *J* = 41.6, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ^{1}H-NMR (CD_3CN): 8.27–8.18 (*m*, 2 arom. H); 8.03–8.00 (*m*, 2 arom. H); 7.76–7.73 (*m*, 2 arom. H); 7.54–7.39 (*m*, 2 arom. H); 4.83 (*m*, 1 H, Cp); 4.58 (*m*, 1 H, Cp); 4.50 (*m*, 1 H, Cp); 3.77 (*s*, C_5H_5); 3.18 (br. *dq*, MeC*H*P); 2.44–2.34 (*m*, 1 H, Cy); 2.14–1.12 (*m*, 27 H, Cy, *Me*CHP, MeCNPd); 0.66 (*dd*, *J* = 7.24, 1.38, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 66.8 (*d*, *J* = 35.3, PCy_2); 8.5 (*d*, *J* = 35.3, PAr_2).

*(*SP*-4)-(Acetonitrile){(1*R*)-1-{bis[3,5-bis(trifluoromethyl)phenyl]phosphino-κ*P*}-2-[(1*R*)-1-(dicyclohexylphosphino-κ*P*)ethyl]ferrocene}palladium(+) Hexafluorophosphate* ([PdMe(**3e**)(MeCN)]PF_6; **8e**). According to the *G.P. 3*, from [PdClMe(**3e**)] (178 mg, 0.174 mmol, 1 equiv.) and $TlPF_6$ (63.8 mg, 0.183 mmol, 1.05 equiv.): **8e** as isomer mixture **I**/**II** 1 : 1.8 in quant. yield. Dark red powder.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR (CD_3CN): 8.55–8.51 (*m*, 2 arom. H); 8.38 (*s*, 1 arom. H); 8.17 (*s*, 1 arom. H); 7.77 (*d*, *J* = 11.08, 2 arom. H); 4.89 (*m*, 1 H, Cp); 4.58 (*m*, 1 H, Cp); 4.44 (*m*, 1 H, Cp); 3.74 (*s*, C_5H_5); 3.35–3.21 (*m*, MeC*H*P); 2.61–2.45 (*m*, 1 H, Cy); 2.16–1.11 (*m*, 27 H, Cy, *Me*CHP, MeCNPd); 0.31 (*dd*, *J* = 6.67, 3.04, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 44.6 (*d*, *J* = 42.0, PCy_2); 33.8 (*d*, *J* = 42.0, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-2)): ^{1}H-NMR (CD_3CN): 8.55–8.51 (*m*, 2 arom. H); 8.41 (*s*, 1 arom. H); 8.14 (*s*, 1 arom. H); 7.71 (*d*, *J* = 9.62, 2 arom. H); 4.89 (*m*, 1 H, Cp); 4.67 (*m*, 1 H, Cp); 4.65 (*m*, 1 H, Cp); 3.75 (*s*, C_5H_5); 3.35–3.21 (*m*, MeC*H*P); 2.61–2.45 (*m*, 1 H, Cy); 2.16–1.11 (*m*, 27 H, Cy, *Me*CHP, MeCNPd); 0.74 (*dd*, *J* = 7.36, 1.61, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 66.9 (*d*, *J* = 36.0, PCy_2); 11.3 (*d*, *J* = 36.0, PAr_2).

*(*SP*-4)-(Acetonitrile){(1*R*)-1-[bis(4-methoxyphenyl)phosphino-κ*P*]-2-[(1*R*)-1-(dicyclohexylphosphino-κ*P*)ethyl]ferrocene}palladium(+) Hexafluorophosphate* ([PdMe(**3g**)(MeCN)]PF_6; **8g**). According to the *G.P. 3*, from [PdClMe(**3g**)] (145 mg, 0.179 mmol, 1 equiv.) and $TlPF_6$ (65.5 mg, 0.187 mmol, 1.05 equiv.): **8g** as isomer mixture **I**/**II** 1.6 : 1 in quant. yield. Dark red powder.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR (CD_3CN): 8.00–7.93 (*m*, 2 arom. H); 7.29–7.14 (*m*, 4 arom. H); 6.99–6.92 (*m*, 2 arom. H); 4.61 (*m*, 1 H, Cp); 4.40 (*m*, 1 H, Cp); 4.15 (*m*, 1 H, Cp); 3.93

(*s*, 1 MeO); 3.86 (*s*, C_5H_5); 3.80 (*s*, 1 MeO); 3.22–3.14 (*m*, 1 H); 2.52–1.05 (*m*, 28 H, Cy, *Me*CHP, MeCNPd); 0.34 (*dd*, *J* = 6.80, 2.63, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 44.0 (*d*, *J* = 40.1, PCy_2); 28.3 (*d*, *J* = 40.1, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ^{1}H-NMR (CD_3CN): 8.00–7.93 (*m*, 2 arom. H); 7.29–7.14 (*m*, 4 arom. H); 6.99–6.92 (*m*, 2 arom. H); 4.64 (*m*, 1 H, Cp); 4.47 (*m*, 1 H, Cp); 4.40 (*m*, 1 H, Cp); 3.94 (*s*, 1 MeO); 3.84 (*s*, C_5H_5); 3.80 (*s*, 1 MeO); 3.02–2.94 (*m*, 1 H); 2.52–1.05 (*m*, 28 H, Cy, *Me*CHP, MeCNPd); 0.57 (*dd*, *J* = 7.23, 1.53, MePd). $^{31}P\{^1H\}$-NMR (CD_3CN): 68.89 (*d*, *J* = 34.2, PCy_2); 5.80 (*d*, *J* = 34.2, PAr_2).

Chloromethylplatinum Complexes [PtClMe(P–P)]: General Procedure 4 (*G.P. 4*). A mixture of [PtClMe(cod)] (1 equiv.) and the corresponding diphosphine ligand (P–P) (1–1.1 equiv.) was stirred in CH_2Cl_2 at r.t. for 3–5 h. The resulting clear orange soln. was filtered through *Celite*. The filtrate was concentrated to *ca*. 0.5–1.0 ml, and cold Et_2O or pentane was added to precipitate the complex. The complex was filtered off, washed with additional Et_2O or pentane (10 ml), and dried *in vacuo*.

*(*SP*-4)-{(2*R*)-1-[(1*R*)-1-(Dicyclohexylphosphino-κP)ethyl]-2-(diphenylphosphino-κP)ferrocene}chloro(methyl)platinum* ([PtClMe(**3a**)]; **9a**). According to the *G.P. 4*, from [PtClMe(cod)] (100 mg, 0.28 mmol, 1 equiv.) and **3a** (166 mg, 0.28 mmol, 1 equiv.): 225 mg (96%) of **9a** as isomer mixture **I**/**II** 1:4. Orange solid. FAB-MS (pos.): 1665 (100, $[2M - Me]^+$), 824 (70, $[M - Me]^+$), 788 (76, $[M - MeCl]^+$). Anal. calc. for $C_{37}H_{47}ClFeP_2Pt$ (840.11): C 52.90, H 5.64; found: C 52.95, H 5.89.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2): ^{1}H-NMR ($CDCl_3$): 8.21–8.14 (*m*, 2 arom. H); 7.56–7.27 (*m*, 8 arom. H); 4.53 (*m*, 1 H, Cp); 4.35 (*m*, 1 H, Cp); 4.12 (*m*, 1 H, Cp); 3.63 (*s*, C_5H_5); 3.52–3.28 (*m*, MeC*H*P); 2.71–2.61 (br. *m*, 1 H, Cy); 2.37–2.29 (br. *m*, 1 H, Cy); 2.09–1.10 (*m*, 23 H, Cy, *Me*CHP); 0.24 (*dd*, ^3J(P,H) = 6.8, ^3J(P,H) = 2.0, MePt). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 44.0 (*d*, ^1J(Pt,P) = 1841, ^2J(P,P) = 17.6, PCy_2); 8.1 (*d*, ^1J(Pt,P) = 4315, ^2J(P,P) = 17.6, PPh_2).

Isomer **II** (Me *trans* to PPh_2; (*SP*-4-3)): ^{1}H-NMR ($CDCl_3$): 8.21–8.14 (*m*, 2 arom. H); 7.56–7.27 (*m*, 8 arom. H); 4.50 (*m*, 1 H, Cp); 4.31 (*m*, 1 H, Cp); 4.30 (*m*, 1 H, Cp); 3.60 (*s*, C_5H_5); 3.52–3.28 (br. *m*, MeC*H*P); 2.71–2.61 (br., 1 H, Cy); 2.37–2.29 (br., 1 H, Cy); 2.09–1.10 (*m*, 23 H, Cy, *Me*CHP); 0.78 (*dd*, ^3J(P,H) = 7.5, ^3J(P,H) = 2.0, MePt). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 39.2 (*d*, ^1J(Pt,P) = 4186, ^2J(P,P) = 17.0, PCy_2); 11.2 (*d*, ^1J(Pt,P) = 1680, ^2J(P,P) = 17.0, PPh_2).

*(*SP*-4-2)-{(1*R*)-1-{Bis[2-(trifluoromethyl)phenyl]phosphino-κP}-2-[(1*R*)-1-(dicyclohexylphosphino-κP)ethyl]ferrocene}chloro(methyl)platinum* ([PtClMe(**3b**)]; **9b**). According to the *G.P. 4*, from [PtClMe(cod)] (100 mg, 0.28 mmol, 1 equiv.) and **3b** (204 mg, 0.28 mmol, 1 equiv.): 246 mg (90%) of **9b** as a single isomer **I** (Me *trans* to $P(Cy)_2$; (*SP*-4-2)). Orange solid. ^{1}H-NMR ($CDCl_3$): 9.37 (*dd*, *J* = 18.4, 6.6, 1 arom. H); 7.90–7.32 (*m*, 7 arom. H); 4.53 (*m*, 1 H, Cp); 4.49 (*m*, 1 H, Cp); 4.37 (*m*, 1 H, Cp); 3.68 (*s*, C_5H_5); 3.27–3.21 (*m*, MeC*H*P); 2.69–2.61 (br. *m*, 1 H, Cy); 2.16–1.12 (*m*, 27 H, Cy, *Me*CHP); 0.90 (*dd*, ^3J(P,H) = 9.2, ^3J(P,H) < 2, MePt). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 46.7 (br. *m*, ^1J(Pt,P) = 1694, PAr_2); 36.2 (*d*, ^1J(Pt,P) = 4278, ^2J(P,P) = 15.0, PCy_2). FAB-MS (pos.): 1915 (46, $[2M - Cl]^+$), 960 (100, $[M - Me]^+$), 940 (72, $[M - Cl]^+$). Anal. calc. for $C_{39}H_{45}ClF_6FeP_2Pt \cdot 0.125C_8H_{12}$ (976.10): C 48.57, H 4.69; found: C 48.51, H 4.93.

*(*SP*-4)-{(1*R*)-1-{Bis[3-(trifluoromethyl)phenyl]phosphino-κP}-2-[(1*R*)-1-(dicyclohexylphosphino-κP)ethyl]ferrocene}chloro(methyl)platinum* ([PtClMe(**3c**)]; **9c**). According to *G.P. 4*, from [PtClMe(cod)] (100 mg, 0.28 mmol, 1 equiv.) and **3c** (204 mg, 0.28 mmol, 1 equiv.): 248 mg (91%) of **9c** as isomer mixture **I**/**II** 1:7. Orange solid. FAB-MS (pos.): 1915 (100, $[2M - Cl]^+$), 960 (21, $[M - Me]^+$), 924 (43, $[M - MeCl]^+$). Anal. calc. for $C_{39}H_{45}ClF_6FeP_2Pt \cdot 0.2C_8H_{12}$ (840.11): C 48.87, H 4.79; found: C 48.56, H 5.05.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)). ^{1}H-NMR ($CDCl_3$): 8.46–8.39 (*m*, 1 arom. H); 8.26 (*d*, *J* = 11.2, 1 arom. H); 7.86–7.32 (*m*, 6 arom. H); 4.62 (*m*, 1 H, Cp); 4.34 (*m*, 1 H, Cp); 4.09 (*m*, 1 H, Cp); 3.62 (*s*, C_5H_5); 3.39–3.28 (br. *dq*, MeC*H*P); 2.76–2.73 (br. *m*, 1 H, Cy); 2.42–2.35 (br. *m*, 1 H, Cy); 2.02–0.86 (*m*, 23 H, Cy, *Me*CHP); 0.22 (*dd*, *J* = 6.7, 4.5, MePt). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 44.0 (*d*, ^1J(Pt,P) = 1825, ^2J(P,P) = 17.8, PCy_2); 9.7 (*d*, ^1J(Pt,P) = 4322, ^2J(P,P) = 17.8, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)). ^{1}H-NMR ($CDCl_3$): 8.59–8.53 (*m*, 1 arom. H); 8.14 (*d*, *J* = 9.5, 1 arom. H); 7.86–7.32 (*m*, 6 arom. H); 4.59 (*m*, 1 H, Cp); 4.39 (*m*, 1 H, Cp); 4.31 (*m*, 1 H, Cp); 3.58 (*s*, C_5H_5); 3.44 (*dq*, *J* = 7.3, 3.9, MeC*H*P); 2.76–2.73 (br. *m*, 1 H, Cy); 2.42–2.35 (br. *m*, 1 H, Cy); 2.02–0.86 (*m*, 23 H, Cy, *Me*CHP); 0.82 (*dd*, *J* = 7.5, 2.5, MePt). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 39.0 (*d*, ^1J(Pt,P) = 4134, ^2J(P,P) = 16.7, PCy_2); 12.7 (*d*, ^1J(Pt,P) = 1644, ^2J(P,P) = 16.7, PPh_2).

*(*SP*-4)-{(1*R*)-1-{Bis[4-(trifluoromethyl)phenyl]phosphino-κP}-2-[(1*R*)-1-(dicyclohexylphosphino-k;P)-ethyl]ferrocene}chloro(methyl)platinum* ([PtClMe(**3d**)]; **9d**. According to the *G.P. 4*, from [PtClMe(cod)] (100 mg, 0.28 mmol, 1 equiv.) and **3d** (204 mg, 0.28 mmol, 1 equiv.): 258 mg (95%) of **9d** as isomer mixture **I**/**II** 1:13. Orange solid. FAB-MS (pos.): 1915 (100, $[2M - Cl]^+$), 924 (36, $[M - MeCl]^+$). Anal. calc. for $C_{39}H_{45}ClF_6FeP_2Pt$ (976.10): C 47.99, H 4.65; found: C 48.20, H 4.89.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR ($CDCl_3$): 8.29 (*dd*, *J* = 8.6, 2.0, 2 arom. H); 7.86–7.79 (*m*, 2 arom. H); 7.59–7.41 (*m*, 4 arom. H); 4.63 (*m*, 1 H, Cp); 4.33 (*m*, 1 H, Cp); 4.07 (*m*, 1 H, Cp); 3.65 (*s*, C_5H_5); 3.37–3.26 (br. *dq*, MeC*H*P); 2.79–2.72 (br. *m*, 1 H, Cy); 2.37 (br. *m*, 1 H, Cy); 1.98–0.88 (*m*, 23 H, Cy, *Me*CHP); 0.23 (*dd*, *J* = 6.5, 4.3, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 43.5 (*d*, ^1J(Pt,P) = 1822, ^2J(P,P) = 17.8, PCy_2); 9.3 (*d*, ^1J(Pt,P) = 4308, ^2J(P,P) = 17.9, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)). ^{1}H-NMR ($CDCl_3$): 8.29 (*dd*, *J* = 8.6, 2.0, 2 arom. H); 7.86–7.79 (*m*, 2 arom. H); 7.59–7.41 (*m*, 4 arom. H); 4.59 (*m*, 1 H, Cp); 4.38 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 3.61 (*s*, C_5H_5); 3.41 (*dq*, *J* = 7.5, 4.0, MeC*H*P); 2.79–2.72 (br. *m*, 1 H, Cy); 2.37 (br. *m*, 1 H, Cy); 1.98–0.88 (*m*, 23 H, Cy, *Me*CHP); 0.83 (*dd*, *J* = 7.5, 2.4, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 39.1 (*d*, ^1J(Pt,P) = 4137, ^2J(P,P) = 16.7, PCy_2); 12.1 (*d*, ^1J(Pt,P) = 1641, ^2J(P,P) = 16.7, PAr_2).

*(*SP*-4)-{(1*R*)-1-[Bis[3,5-bis(trifluoromethyl)phenyl]phosphino-*κ*P}-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]ferrocene}chloro(methyl)platinum* ([PtClMe(**3e**)]; **9e**). According to the *G.P. 4*, from [PtClMe(cod)] (100 mg, 0.28 mmol, 1 equiv.) and **3e** (243 mg, 0.28 mmol, 1 equiv.). The resulting clear orange soln. was evaporated to dryness: **9e** as isomer mixture **I/II** 1:17 quantitatively. Pure orange solid. FAB-MS (pos.): 2189 (100, $[2M - Cl]^+$). Anal. calc. for $C_{41}H_{43}ClF_{12}FeP_2Pt$ (1112.10): C 44.28, H 3.90; found: C 44.50, H 4.01.

Isomer **I** (Me *trans* to PCy_2; (SP-4-2)): ^{1}H-NMR ($CDCl_3$): 8.53–8.50 (*d*, 2 arom. H, (under arom. H of isomer **II**)); 8.14 (*s*, 1 arom. H); 7.90 (*s*, 1 arom. H); 7.70 (*d*, *J* = 10.0, 2 arom.H); 4.72 (*m*, 1 H, Cp); 4.43 (*m*, 1 H, Cp); 4.06 (*m*, 1 H, Cp); 3.63 (*s*, C_5H_5); 3.29–3.22 (br. *dq*, MeC*H*P); 2.78–2.75 (br. *m*, 1 H, Cy); 2.39–2.32 (br. *m*, 1 H, Cy); 2.03–1.10 (*m*, 23 H, Cy, *Me*CHP); 0.22 (*dd*, *J* = 6.4, 4.8, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 44.4 (*d*, ^1J(Pt,P) = 1810, ^2J(P,P) = 17.7, PCy_2); 11.7 (*d*, ^1J(Pt,P) = 4332, ^2J(P,P) = 17.6, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ^{1}H-NMR ($CDCl_3$): 8.53–8.50 (*d*, *J* = 10.4, 2 arom. H); 8.09 (*s*, 1 arom. H); 7.84 (*s*, 1 arom. H); 7.78 (*d*, *J* = 9.6, 2 arom. H); 4.68 (*m*, 1 H, Cp); 4.48 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 3.57 (*s*, C_5H_5); 3.42 (*dq*, *J* = 7.1, 4.1, MeC*H*P); 2.78–2.75 (br. *m*, 1 H, Cy); 2.39–2.32 (br. *m*, 1 H, Cy); 2.03–1.10 (*m*, 23 H, Cy, *Me*CHP); 0.86 (*dd*, *J* = 7.2, 1.7, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 39.3 (*d*, ^1J(Pt,P) = 4076, ^2J(P,P) = 16.1, PCy_2); 14.7 (*d*, ^1J(Pt,P) = 1603, ^2J(P,P) = 16.1, PAr_2).

*(*SP*-4)-{(1*R*)-1-[Bis(3,5-dimethylphenyl)phosphino-*κ*P]-2-[(1*R*)-(dicyclohexylphosphino-*κ*P)ethyl]ferrocene}chloro(methyl)platinum* ([PtClMe(**3f**)]; **9f**. According to the *G.P. 4*, from [PtClMe(COD)] (100 mg, 0.28 mmol, 1 equiv.) and **3f** (182 mg, 0.28 mmol, 1 equiv.): **9f** as isomer mixture **I/II** 1:2.5 in quant. yield. Orange solid.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR ($CDCl_3$): 7.79–7.74 (*m*, 2 arom. H); 7.10–6.90 (*m*, 4 arom. H); 4.49 (*m*, 1 H, Cp); 4.23 (*m*, 1 H, Cp); 4.14 (*m*, 1 H, Cp); 3.64 (*s*, C_5H_5); 3.29–3.24 (br. *dq*, MeC*H*P); 2.70–2.67 (br. *m*, 1 H, Cy); 2.44 (*s*, 2 *Me*C_6H_3); 2.35–2.28 (br. *m*, 1 H, Cy); 2.42 (*s*, 2 *Me*C_6H_3); 1.84–0.86 (*m*, 23 H, Cy, *Me*CHP); 0.23 (*dd*, *J* = 6.9, MePt. ^{31}P{^{1}H}-NMR ($CDCl_3$): 44.9 (*d*, ^1J(Pt,P) = 1852, ^2J(P,P) = 17.5, PCy_2); 7.8 (*d*, ^1J(Pt,P) = 4328, ^2J(P,P) = 17.5, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ^{1}H-NMR ($CDCl_3$): 7.79–7.74 (*m*, 2 arom. H); 7.10–6.90 (*m*, 4 arom. H); 4.47 (*m*, 1 H, Cp); 4.32 (*m*, 1 H, Cp); 4.27 (*m*, 1 H, Cp); 3.59 (*s*, C_5H_5); 3.41 (*dq*, *J* = 7.2, 3.8, MeC*H*P); 2.70–2.67 (br. *m*, 1 H, Cy); 2.41 (*s*, 2 *Me*C_6H_3); 2.35–2.28 (br. *m*, 1 H, Cy); 2.22 (*s*, 2 *Me*C_6H_3); 1.89–0.86 (*m*, 23 H, Cy, *Me*CHP); 0.75 (*dd*, *J* = 7.3, 2.4, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 39.1 (*d*, ^1J(Pt,P) = 4206, ^2J(P,P) = 16.7, PCy_2); 10.5 (*d*, ^1J(Pt,P) = 1688, ^2J(P,P) = 16.7, PAr_2).

*(*SP*-4)-{(1*R*)-1-[Bis(3,5-dimethoxyphenyl)phosphino-*κ*P]-2-[(1*R*)-1-(dicyclohexylphosphino-*κ*P)ethyl]-ferrocene}chloro(methyl)platinum* ([PtClMe(**3h**)]; **9h**). According to the *G.P. 4*, from [PtClMe(cod)] (62.6 mg, 0.175 mmol, 1 equiv.) and **3h** (125 mg, 0.175 mmol, 1 equiv.): 147.3 mg (88%) of **9h** as isomer mixture **I/II** 1:4.5. Orange solid. FAB-MS (pos.): 945 (100, $[M - Me]^+$), 907 (76, $[M - MeCl]^+$), 825 (5), 741 (7), 467 (5), 307 (19), 212 (8), 154 (39). Anal. calc. for $C_{41}H_{55}ClFeO_4P_2Pt$ (960.21): C 51.29, H 5.77; found: C 51.38, H 6.00.

Isomer **I** (Me *trans* to PCy_2; (*SP*-4-2)): ^{1}H-NMR ($CDCl_3$): 7.37–7.33 (*m*, 2 arom. H); 6.66–6.55 (*m*, 3 arom. H); 6.39–6.38 (*m*, 1 arom. H); 4.51 (*m*, 1 H, Cp); 4.23 (*m*, 1 H, Cp); 4.15 (*m*, 1 H, Cp); 3.86 (*s*, 2 MeO); 3.73 (*s*, C_5H_5); 3.68 (*s*, 2 MeO); 3.33–3.23 (br. *dq*, MeC*H*P); 2.52–2.46 (br. *m*, 1 H, Cy); 2.34–2.25 (br. *m*, 1 H, Cy); 1.98–1.09 (*m*, 23 H, Cy, *Me*CHP); 0.32 (*dd*, *J* = 6.9, 4.2, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 44.4 (*d*, ^1J(Pt,P) = 1834, ^2J(P,P) = 17.9, PCy_2); 11.9 (*d*, ^1J(Pt,P) = 4372, ^2J(P,P) = 17.9, PAr_2).

Isomer **II** (Me *trans* to PAr_2; (*SP*-4-3)): ^{1}H-NMR ($CDCl_3$): 7.37–7.33 (*m*, 2 arom. H); 6.66–6.55 (*m*, 3 arom. H); 6.39–6.38 (*m*, 1 arom. H); 4.49 (*m*, 1 H, Cp); 4.32 (*m*, 1 H, Cp); 4.29 (*m*, 1 H, Cp); 3.85 (*s*, 2 MeO); 3.71 (*s*, C_5H_5); 3.68 (*s*, 2 MeO); 3.39 (*dq*, *J* = 14.7, 7.3, MeC*H*P); 2.71–2.68 (br. *m*, 1 H, Cy); 2.34–2.25 (br. *m*, 1 H, Cy); 1.98–1.09 (*m*, 23 H, Cy, *Me*CHP); 0.77 (*dd*, *J* = 7.4, 2.5, MePt). ^{31}P{^{1}H}-NMR ($CDCl_3$): 39.1 (*d*, ^1J(Pt,P) = 4176, ^2J(P,P) = 17.0, PCy_2); 14.5 (*d*, ^1J(Pt,P) = 1699, ^2J(P,P) = 17.0, PAr_2).

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