Synthesis and structure of new chiral ferrocenylphosphines for asymmetric catalysis

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Abstract

The reaction of (*R*)-1-[(*S*)-(diphenylphosphino)ferrocenyl]ethyl acetate (**1**) or *N,N*-dimethyl-(*R*)-1-[(*S*)-(diphenylphosphino)ferrocenyl]ethylamine (**2a**) with secondary phosphines in acetic acid leads to the diphosphines **5** in moderate to good yields. Two of these ligands, (*R*)=1[(*S*)-(diphenylphosphino)ferrocenyl]ethyl-dicyclohexylphosphine (**5a**) and (R_P,*R*)-1[(*S*)-(diphenylphosphino)ferrocenyl]ethyl-phenyl-(2-methoxyphenyl)phosphine (**5g**), as well as the complexes [Rh(**5a**)(NBD)]$BF_4 \cdot 2CH_2Cl_2$ (**9**), [Pd(η^3-C_3H_5) (**5a**)]OTf (**10**) and [$PtCl_2$(**5a**)] (**11**), have been characterized by X-ray diffraction. Crystals of **5a**, **9**, **10** and **11** are orthorhombic, space group $P2_12_12_1$, with four molecules in the unit cell. **5a**: $a=10.772(1)$, $b=15.278(1)$, $c=21.069(2)$ Å; **9**: $a=18.166(2)$, $b=17.540(2)$, $c=14.564(1)$; **10**: $a=10.995(4)$, $b=14.021(8)$, $c=25.410(11)$ Å; **11**: $a=15.077(14)$, $b=15.122(16)$, $c=16.188(11)$ Å. The stereogenic-at-phosphorus derivative **5g** crystallizes in the monoclinic system, space group $P2_1$, with two pairs of symmetry independent molecules per the unit cell with $a=7.896(1)$, $b=25.667(2)$, $c=15.654(1)$ Å and $\beta=92.39(1)°$. Very similar conformations of the chelate rings in the complexes **9–11** are observed, this being indicative of the relative rigidity of the ligand **5a**.

Key words: Crystal structures; Asymmetric catalysis; Palladium complexes; Ferrocenyl phosphine complexes; Chiral ligand complexes

Introduction

Chiral ferrocenylphosphines of type **2** have been successfully applied to a variety of transition-metal-catalyzed asymmetric reactions [1]. The important and unique feature of these ligands is the presence of a stereogenic, functionalized side chain which can be modeled to fulfil specific purposes, in particular a secondary interaction with substrates [2]. Thus, the phosphino substituents have been invariably attached to the ferrocenyl moiety, whereas the stereospecific nucleophilic substitution reactions of the acetate derivative **1** [3] have been used to introduce the desired side chain. For the vast majority of derivatives known, the nucleophilic synthons have been restricted to secondary amines (**2**), and to a lesser extent to alcohols (**3**, see Scheme 1) [4]. We have recently shown [5] that it is possible to introduce sulfur substituents via the S_N1 reaction of the acetate **1** with KSAc in anhydrous acetic (or formic) acid to afford **4**. The same reaction conditions can be applied to the smooth formation of the diphosphines **5** by using the corresponding secondary phosphines as reagents. This synthetic pathway allows access to ferrocenyldiphosphines in which the electronic and steric properties of the two phosphorus ligands can be varied almost indefinitely. This is notoriously not the case for 1,1'-bisphosphino-ferrocene ligands, because the phosphino groups are usually introduced at the same time in a one-pot reaction [4]. It has been previously shown that the possibility of selectively varying the nature of the substituent at phosphorus in chelating diphosphines has advantageous effects, in particular in the asymmetric hydrogenation reaction [6].

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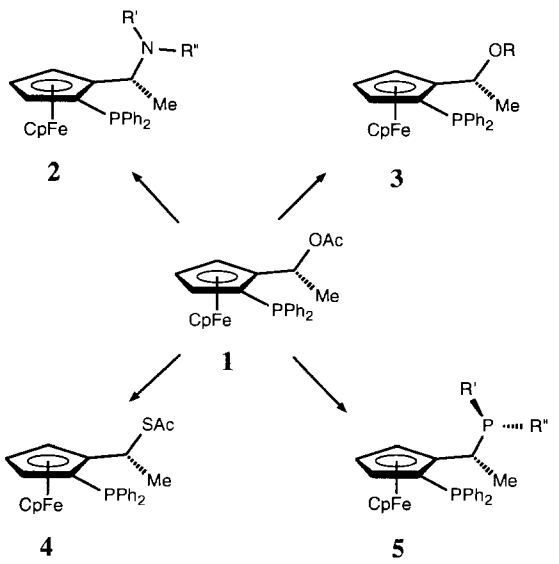
We describe herein the synthesis, structure and coordination behavior of a series of novel asymmetric diphosphines of type **5**. To our knowledge the only derivative in this series so far described in the literature has been prepared by the reaction of acetate **1** with an excess of diphenylphosphine in methanol [4], but no catalytic applications thereof have been reported. We previously described the successful use of this type of ligand in catalytic hydrogenation, hydroboration and allylic alkylation reactions [7].

Results and discussion

Synthesis

The new asymmetric diphosphines were prepared by the smooth reaction of the ferrocenyl acetate **1** [4] with a slight excess of a secondary phosphine in glacial acetic acid at 50–60 °C, to reflux temperature. The reaction generally goes to completion in *c.* 2–4 h under these conditions. The products were isolated in good yields by extraction and were purified by column chromatography and/or recrystallization from ethanol. They were obtained in pure form as orange, air-stable powders, and were characterized by conventional methods. Table 1 collects the compounds prepared. The same ligands are also accessible directly from *N*,*N*-dimethyl-(*R*)-1-[(*S*)-(diphenylphosphino)ferrocenyl]ethylamine (**2a**), in part in even better yields [7].

The retentive substitution reactions the acetate **1** undergoes [3] have been exploited for the introduction of phosphino groups bearing electronically as well as sterically different substituents. Thus, for example, $HPCy_2$ and $HP(4\text{-}F_3C\text{–}Ph)_2$ were qualitatively found to display very similar reactivities toward **1**. This is clearly indicative of the typical S_N1 type behavior of this precursor in such substitution reactions [3].

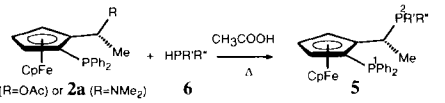


Scheme 1.

Chiral, racemic secondary phosphines, i.e. phenyl-(2-methoxy-phenyl)phosphine and phenyl-cyclohexyl-phosphine, have also been employed as nucleophiles. The corresponding derivatives (the diastereomeric pairs **5g,h** and **5i,j**) now contain three elements of chirality, i.e. the substituted ferrocenyl moiety, the stereogenic carbon atom of the side chain, as well as the contiguous phosphorus atom. It was therefore of interest to see whether a kinetic resolution [8] of the racemic secondary phosphine would take place. By reacting **1** with three equivalents of *rac*-HPPh(2-OMe–Ph) in acetic acid, there was no indication whatsoever that this would be the case. The same negative result was obtained upon reaction of **1** with ten equivalents of HPCyPh in methanol. Both reactions afforded nearly perfect 1 to 1 mixtures of the two diastereomeric diphosphines, as revealed by NMR spectroscopy (Scheme 2). Attempts to separate the pairs of diastereomers by column chromatography failed. The only successful approach to stereoisomerically pure, stereogenic-at-phosphorus ligands was found to be the rather tedious methodology of diastereomeric Pd complexes of type **8**, already successfully applied to the separation of enantiomeric diphosphines [9]. Scheme 3 illustrates the reaction sequence for the derivatives **5g,h**. By this procedure, the pure stereoisomeric forms of the ligands could be obtained in moderate yields. The absolute configuration at phosphorus could only be determined by an X-ray crystallographic study of the compound **5g** (*vide infra*), whereas for the derivatives **5i,j** it is still unknown.

All derivatives **5a–j** give in the ^{31}P NMR spectra the expected AB quartet pattern, but show surprisingly large phosphorus–phosphorus coupling constants (^4J(P1–P2) from 14 to 50 Hz in $CDCl_3$). These large values are indicative of a preferred time-averaged conformation in solution similar to that found in the solid state for the ligands **5a** and **5g** (*vide infra*). One can look at the ligand system as a 1,3-bis(phosphino) allylic fragment (P1–C1=C2–C3–P2). It is known that for such fragments the absolute value for the ^4J allylic coupling reaches a maximum when the vector of the bond connecting the allylic substituent (here C3–P2) lies in a plane perpendicular to the allylic moiety [10]. The large ^4J(P1–P2) values observed are also in accordance with phosphorus lone-pair effects on such four-bond coupling constants [11], assuming a conformation such that the two phosphorus lone-pair vectors are nearly parallel and approximately face each other, as is the case in the solid state. The two largest values of this coupling observed for the derivatives **5a** and **5b**, bearing bulky cyclohexyl and t-butyl groups, respectively (compared to the compounds **5c–j** containing aryl substituents), also reflect the restricted conformational free-

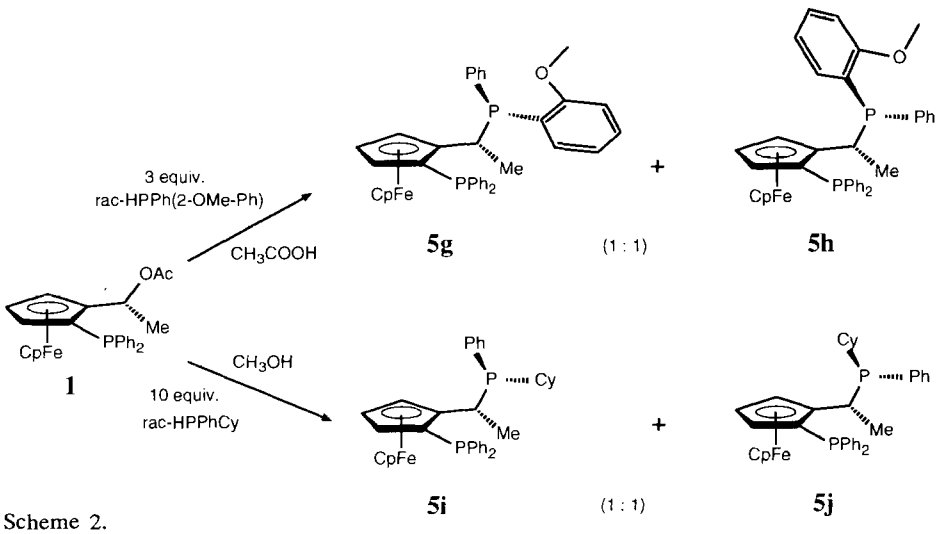
TABLE 1. The new ferrocenyl diphosphines prepared and their ^{31}P NMR data



1 (R=OAc) or **2a** (R=NMe$_2$) **6** **5**

Ligand	Yield (%)	δ P^1 (ppm)	δ P^2 (ppm)	^4J(P^1,P^2) (Hz)
5a (R′ = R″ = Cy)	88[a]	−25.8	15.7	30
5b (R′ = R″ = t-Bu)	81[a]	−26.1	45.9	50
5c (R′ = R″ = 2,4,6-Me$_3$Ph)	35	−25.0	−6.8	17
5d (R′ = R″ = 2-OMe-Ph)	71	−24.9	−21.2	14
5e (R′ = R″ = 4-OMe-Ph)	70	−25.5	2.5	16
5f (R′ = R″ = 4-CF$_3$-Ph)	76	−26.4	6.6	24
(R_P)-**5g** (R′ = Ph, R″ = 2-OMe-Ph)	82[b]	−25.5	−6.1	16
(S_P)-**5h** (R′ = Ph, R″ = 2-OMe-Ph)		−25.1	−7.9	14
(R_P or S_P)-**5i** (R′ = Ph, R″ = Cy)	49[b]	−25.8	7.0	18
(S_P or R_P)-**5j** (R′ = Ph, R″ = Cy)		−25.7	9.0	26

[a]Prepared from the amine **2a**. [b]Total yield of diastereomers before separation.



Scheme 2.

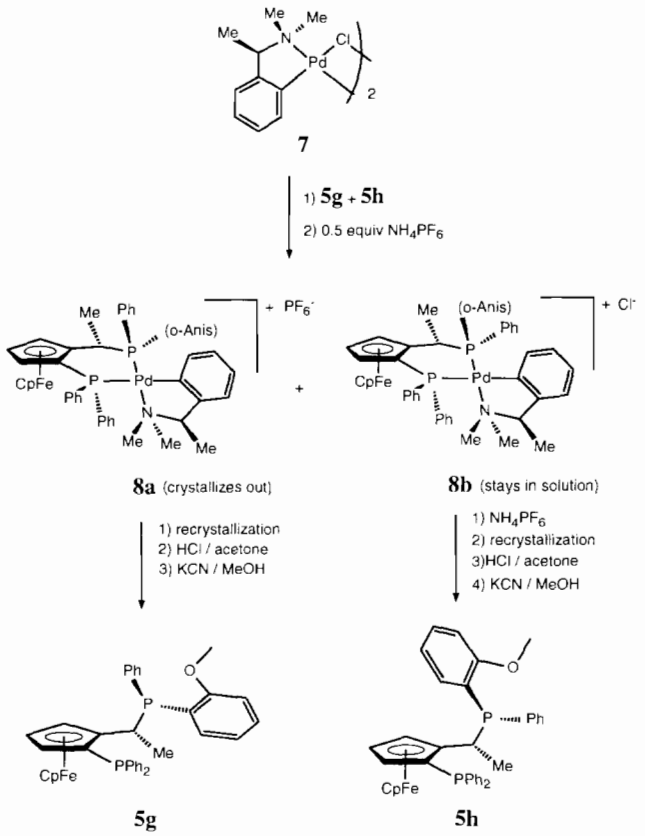
dom due to these substituents [12]. It is interesting to note that, whereas the values of ^2J(P–P) of 36 and 51 Hz for the complexes **9** and **10**, respectively, are comparable to, but larger than the one of the free ligand, this coupling constant is much smaller in **11** (17 Hz).

Complex **9** was prepared by the reaction of equivalent amounts of **5a** and [Rh(NBD)$_2$]BF$_4$ [13] in CH_2Cl_2 and is a catalyst precursor for hydrogenation reactions [7]. Crystalline samples of **9**, obtained after recrystallization in a layered mixture of CH_2Cl_2/n-Bu$_2$O, were found to contain two CH_2Cl_2 solvent molecules per complex (*vide infra*). Compound **10** was obtained from the reaction of the ligand and [Pd$_2$(η^3-C$_3$H$_5$)$_2$Cl$_2$] and serves as a useful catalyst precursor for allylic alkylation reactions [7]. The reaction of [PtCl$_2$(COD)] [14] with **5a** in benzene afforded **11** in high yield.

Solid state structures of 5a, 5g, 9, 10 and 11

In view of the successful applications of ligand **5a** in several catalytic reactions [7], X-ray crystallographic studies of **5a** and its Rh, Pd and Pt complexes **9–11** were carried out in order to better understand the coordination behavior of this ligand. Furthermore, in order to determine the absolute configuration of the diastereoisomeric pair **5g,h** a crystal structure was necessary. Table 2 gives the data collection parameters and a selection of bond lengths and angles for the ligands **5a** and **5g** is shown in Table 3. Tables 4, 5, 6 and 7 collect similar data for the complexes **9–11**. The overall geometry and the adopted atom numbering schemes of the five compounds are depicted in the ORTEP representations of Figs. 1–5.

Compound **5g** crystallizes with two independent molecules in the asymmetric unit. Because there are no



Scheme 3.

relevant differences in the bonding parameters between the two molecules, the data reported in Table 3 and in the present discussion refer to molecule A (arbitrarily chosen). All bonding parameters of the ligands **5a** and **5g** fall in the expected range and are rather routine [15]. The important aspects of these two structures are of conformational and configurational nature. Given the absolute configuration of the starting material **1** (*R*–*S*), the present crystal structures confirm the expected retention of configuration at the stereogenic center upon substitution. Although there are no reasons to expect significant stereochemical differences when phosphorus nucleophiles are used, this is the first time that the absolute configuration has been determined for this type of product. Furthermore, in compound **5g** the relative and, therefore, also the absolute configuration at the stereogenic phosphorus atom (P(3)) turns out to be *R*.

The two ligands show in the solid state very similar conformations. The diphenylphosphino group directly attached to the cyclopentadienyl ring is oriented in such a way that the phosphorus lone-pair points toward the region between the Cp rings. Relevant torsion angles are: C(8)–C(4)–P(2)–C(14) (−65(1)°) and C(8)–C(4)–P(2)–C(20) (37(1)°) for **5a**, and C(18)–C(14)–P(4)–C(19) (−63(1)°) and C(18)–C(14)–P(4)–C(25) (40(1)°)

TABLE 2. Crystal data, collection data and details of refinement of **5a** and **5g**

	5a	**5g**
Chemical formula	$C_{36}H_{44}FeP_2$	$C_{37}H_{34}FeOP_2$
Formula weight	594.54	612.47
Crystal size (mm)	0.75×0.72×0.54	0.63×0.36×0.06
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	10.772(1)	7.896(1)
b (Å)	15.278(2)	25.667(2)
c (Å)	21.069(2)	15.654(2)
β (°)		92.39(1)
V (Å^3)	3467(1)	3170(2)
Z	4	4
D_{calc} (g/cm^3)	1.139	1.283
Diffractometer	Philips PW1100	Philips PW1100
Radiation, λ(Å) (monochromated)	Mo Kα, 0.70926	Mo Kα, 0.70926
$F(000)$	1264	1280
μ (cm^{-1})	5.446	6.002
Temperature (°C)	21	21
Scan range, 2θ	6–60	6–56
Scan time (s)	41–50	36–45
Scan width (°)	1.6	1.4
Structure solution	Patterson method	Patterson method
No. variables	352	738
No. unique reflections	5657	8136
No. observed reflections ($I>3\sigma(I)$)	3490	4747
Refinement	full-matrix	full-matrix
R	0.055	0.038
R_w	0.062	0.043
Weighting scheme, w	$1/\sigma^2(\|F_o\|)$	$1/\sigma^2(\|F_o\|)$
Residual electron density, max./min. (e/Å^3)	0.873/−0.765	0.614/−0.592

TABLE 3. Selected interatomic distances (Å)[a] and angles (°)[a] for **5a** and **5g**

5a		**5g**	
Bond distances			
P(2)–C(4)	1.81(1)	P(4)–C(14)	1.81(1)
P(2)–C(14)	1.87(1)	P(4)–C(19)	1.81(1)
P(2)–C(20)	1.87(1)	P(4)–C(25)	1.83(1)
P(3)–C(26)	1.90(1)	P(3)–C(31)	1.91(1)
P(3)–C(28)	1.84(2)	P(3)–C(33)	1.88(1)
P(3)–C(34)	1.87(1)	P(3)–C(39)	1.83(1)
P(2)–P(3)	3.70(1)	P(3)–P(4)	3.75(1)
Bond angles			
C(4)–C(5)–C(26)	128(1)	C(14)–C(15)–C(31)	124(1)
C(5)–C(26)–P(3)	109.4(9)	C(14)–C(15)–C(31)	105.4(8)
C(26)–P(3)–C(28)	102.4(7)	C(31)–P(3)–C(33)	100.7(5)
C(26)–P(3)–C(34)	102.2(6)	C(31)–P(3)–C(39)	101.0(5)
C(28)–P(3)–C(34)	104.9(6)	C(33)–P(3)–C(39)	101.3(6)
C(5)–C(4)–P(2)	123.3(8)	C(15)–C(14)–P(4)	124.5(9)
C(4)–P(2)–C(14)	100.5(6)	C(14)–P(4)–C(19)	102.3(6)
C(4)–P(2)–C(20)	102.6(6)	C(14)–P(4)–C(25)	100.2(6)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4. Crystal data, collection parameters and details of refinement of **9**, **10** and **11**

	9	**10**	**11**
Chemical formula	$C_{43}H_{51}P_2FeRhBF_4 \cdot 2CH_2Cl_2$	$C_{40}H_{49}F_3FeO_3P_2PdS$	$C_{36}H_{44}Cl_2FeP_2Pt \cdot CH_2Cl_2$
Formula weight	1045.25	891.09	945.48
Crystal size (mm)	$0.50 \times 0.33 \times 0.27$	$0.1 \times 0.05 \times 0.05$	$0.15 \times 0.25 \times 0.30$
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	18.166(2)	10.995(4)	15.077(14)
b (Å)	17.540(2)	14.021(8)	15.122(16)
c (Å)	14.564(1)	25.410(11)	16.188(11)
V (Å^3)	4641(1)	3917(3)	3691(1)
Z	4	4	4
D_{calc} (g/cm^3)	1.496	1.511	1.703
Diffractometer	Philips PW1100	Syntex P21	Siemens R3m/V
Radiation, λ (Å)	Mo Kα, 0.70926	Mo Kα, 0.71073	Mo Kα, 0.71073
$F(000)$	2140	1832	1884
μ (cm^{-1})	10.06	10.15	45.82
Temperature (°C)	21	25	25
Scan range, 2θ (°)	6–56	3–45	3–50
Scan width (°)	1.2	1.1	1.05
Structure solution	Patterson method	Direct methods	Direct methods
No. variables	523	460	406
No. unique reflections	6207	2925	3641
No. observed reflections ($I > 3\sigma(I)$)	3815	2393	3170
R	0.068	0.030	0.036
R_w	0.072	0.031	0.037
Weighting scheme	$w = 1/\sigma^2(\lvert F_o \rvert)$	unit weights	$w^{-1} = \sigma^2(F) + 0.0000F^2$
Residual electron density, max./min. (e/Å^3)	0.921/−0.811	0.47/−0.51	1.53/−1.15

TABLE 5. Selected interatomic distances (Å)[a] and angles (°)[a] for **9**

Bond distances			
Rh(1)–P(3)	2.330(3)	Rh(1)–P(4)	2.300(3)
Rh(1)–MP(1)[b]	2.07(1)	Rh(1)–MP(2)[b]	2.05(1)
Rh(1)–C(12)	2.15(1)	Rh(1)–C(13)	2.21(1)
Rh(1)–C(10)	2.17(1)	Rh(1)–C(15)	2.14(1)
P(3)–C(17)	1.85(1)	P(3)–C(23)	1.87(2)
P(3)–C(46)	1.87(1)	P(4)–C(29)	1.82(1)
P(4)–C(35)	1.89(2)	P(4)–C(41)	1.81(1)
C(12)–C(13)	1.38(3)	C(10)–C(15)	1.31(3)
Bond angles			
P(3)–Rh(1)–P(4)	93.3(1)	P(3)–Rh(1)–MP(1)	102.0(3)
P(4)–Rh(1)–MP(2)	95.6(3)	MP(1)–Rh(1)–MP(2)	69.4(6)
P(3)–Rh(1)–MP(2)	169.4(3)	P(4)–Rh(1)–MP(1)	164.6(3)
Rh(1)–P(3)–C(17)	120.6(4)	Rh(1)–P(3)–C(46)	112.4(4)
Rh(1)–P(3)–C(23)	108.1(5)	C(17)–P(3)–C(23)	103.7(7)
C(23)–P(3)–C(46)	111.0(7)	C(17)–P(3)–C(46)	100.4(7)
Rh(1)–P(4)–C(29)	112.9(5)	Rh(1)–P(4)–C(35)	108.7(4)
Rh(1)–P(4)–C(41)	117.0(5)	C(29)–P(4)–C(41)	108.4(8)
C(29)–P(4)–C(35)	101.7(7)	C(35)–P(4)–C(41)	106.9(7)

[a]Numbers in parentheses are e.s.d.s in the least significant digits. [b]MP(1) and MP(2) denote the midpoints of the olefinic bonds C(12)–C(13) and C(10)–C(15), respectively.

TABLE 6. Selected interatomic distances (Å)[a] and angles (°)[a] for **10**

Bond distances			
Pd–P(1)	2.313(3)	Pd–P(2)	2.297(2)
Pd–C(1)	2.179(10)	Pd–C(2)	2.129(15)
Pd–C(3)	2.184(10)	P(1)–C(33)	1.879(8)
P(1)–C(10)	1.831(9)	P(1)–C(4)	1.850(9)
P(2)–C(29)	1.807(8)	P(2)–C(16)	1.825(8)
P(2)–C(22)	1.817(8)	C(28)–C(33)	1.514(10)
C(1)–C(2)	1.235(17)	C(2)–C(3)	1.251(18)
Bond angles			
P(1)–Pd–P(2)	95.7(1)	Pd–P(2)–C(29)	115.1(3)
P(2)–C(29)–C(28)	125.5(6)	C(29)–C(28)–C(33)	126.5(7)
P(1)–C(33)–C(28)	108.5(5)	C(1)–C(2)–C(3)	146.9(14)
P(1)–Pd–C(3)	102.4(3)	P(2)–Pd–C(1)	95.4(3)
P(1)–Pd–C(1)	168.2(3)	P(1)–Pd–C(3)	160.9(3)
P(1)–Pd–C(2)	135.8(4)	P(2)–Pd–C(2)	128.5(4)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

for **5g**. The conformation of the side chain allows the bulky PCy_2 and PPh(2-OMe–Ph) groups, respectively, to avoid important steric interactions with the rest of the molecule. The consequence is that the two smaller substituents attached to the stereogenic carbon atom (H and CH_3) are forced below the functionalized Cp ring. This is illustrated by the torsion angles C(6)–C(5)–C(26)–C(27) of −24(1)° and (C16)–C(15)–C(31)–C(32) of −21(1)°. Furthermore, the position of the phosphorus atoms of the side chain is best reflected by the torsion angles C(4)–C(5)–C(26)–P(3) of −70(1)°

TABLE 7. Selected interatomic distances (Å)[a] and angles (°)[a] for **11**

Bond distances			
Pt–P(1)	2.237(3)	Pt–P(2)	2.247(3)
Pt–Cl(1)	2.325(4)	Pt–Cl(2)	2.350(3)
P(1)–C(1)	1.792(13)	P(1)–C(111)	1.805(14)
P(1)–C(121)	1.827(15)	P(2)–C(7)	1.883(12)
P(2)–C(211)	1.808(15)	P(2)–C(221)	1.830(14)
Bond angles			
Cl(1)–Pt–Cl(2)	86.4(1)	Cl(1)–Pt–P(1)	171.1(1)
Cl(2)–Pt–P(1)	85.8(1)	Cl(1)–Pt–P(2)	92.6(1)
Cl(2)–Pt–P(2)	178.9(1)	P(1)–Pt–P(2)	95.2(1)
Pt–P(1)–C(1)	116.3(4)	P(1)–C(1)–C(2)	124.4(10)
C(1)–C(2)–C(7)	123.9(11)	P(2)–C(7)–C(2)	106.5(8)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

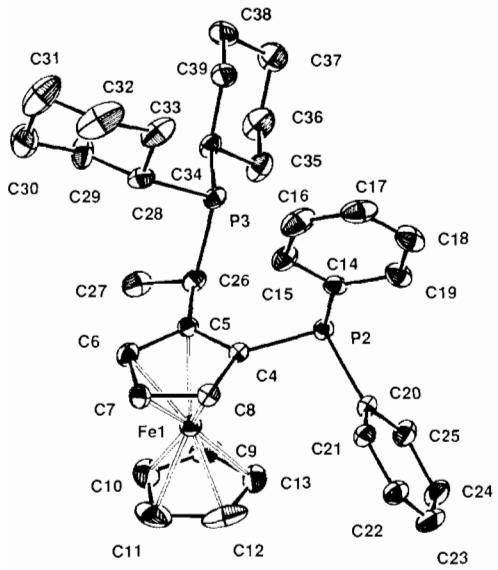


Fig. 1. ORTEP view and atom numbering scheme of **5a**.

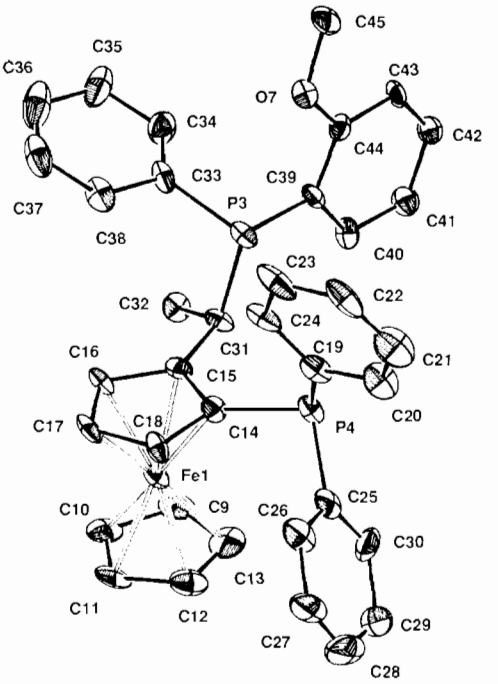


Fig. 2. ORTEP view and atom numbering scheme of **5g**.

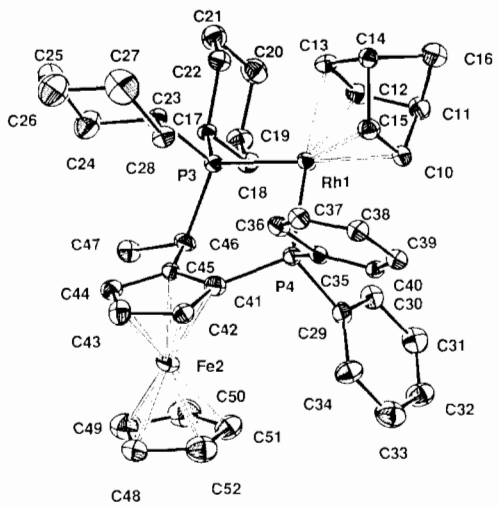


Fig. 3. ORTEP view and atom numbering scheme of **9**.

for **5a** and C(14)–C(15)–C(31)–P(3) of −77(1)° for **5g**. A qualitatively similar conformation has been found by 2D NMR methods for related systems in solution [16]. Given the relative position and orientation of the phosphino groups in these molecules, one can deduce that, in order to accommodate a metal center in a chelating fashion, relatively modest conformational changes will be required. This is indeed confirmed by the structure of the complex cations **9** and **10**, as well as for the neutral complex **11**. A detailed discussion of such conformational aspects will be given only for **9**, since the trends for **10** and **11** are very similar. A collection of the crucial torsion angles defining the conformation of the chelate rings is given in Table 8.

For **9** one observes a value of −69(1)° for the diagnostic torsion angle C(41)–C(45)–C(46)–P(3), equal to the corresponding parameter of the free ligand **5a**. A relatively small clockwise rotation of 8° around the C(26)–P(3) bond in **5a** is sufficient to accommodate the metal atom (compare, for example, the torsion angle C(28)–P(3)–C(26)–C(5) of −64(1)° in **5a** with C(23)–P(3)–C(46)–C(45) of −56(1)° for **9**). However, the rather rigid nature of the side chain indirectly causes a significant and, for similar systems, previously unobserved distortion of the diphenylphosphino group upon complexation. Thus, P(4) is situated 0.41 Å above the Cp ring. In order to coordinate to the metal center a clockwise rotation of *c.* 45° around the Cp–P bond of the free ligand is required (see the torsion angles C(5)–C(4)–P(2)–C(20) of −145(1)° in **5a** and C(45)–C(41)–P(4)–C(29) of −101(2)° in **9**). This takes

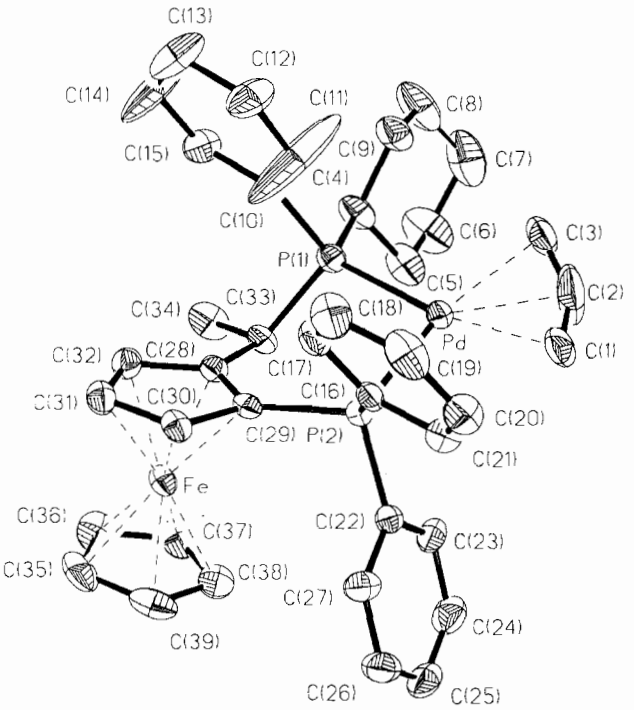


Fig. 4. ORTEP view and atom numbering scheme of **10**.

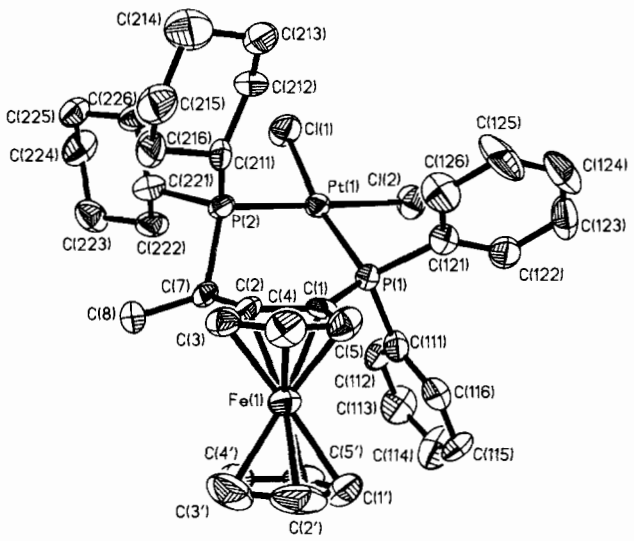
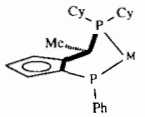
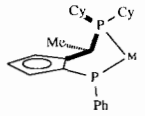
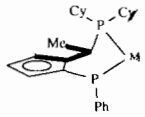
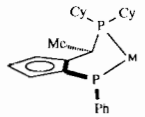


Fig. 5. ORTEP view and atom numbering scheme of **11**.

one of the phenyl groups in a pseudo axial position and, thus, in closer vicinity to the unsubstituted Cp ring (see, for example, the relatively short interatomic distance C(34)–C(51) of 3.18(1) Å), thus leading to severe steric repulsion. The observed displacement of the phosphorus atom out of the Cp plane can be viewed as the tendency of the system to release this steric hindrance. On the same line one can interpret the two different distances of the Cp rings from the Fe atom. The plane of the 'upper' Cp is situated 1.64(1) Å (versus

TABLE 8. Comparison between selected torsion angles for the compounds **5a**, **9**–**11**. Involved atoms are connected by highlighted bonds

Torsion angle	Compound			
	5a	**9**	**10**	**11**
	−70	−69	−62	−65
	−64	−56	−47	−43
	−24	−15	−15	−20
	−145	−101	−108	−104

1.63(1) Å in **5a**) from the iron, whereas the corresponding distance of the 'lower' Cp ring is significantly longer and amounts to 1.73(1) Å.

Taking the midpoints of the two coordinated olefinic bonds as virtual monodentate ligands (MP(1)/C(12)–C(13) and MP(2)/C(10)–C(15)), the geometry around the Rh atom is best described as distorted square-planar. Thus, the plane defined by the Rh and the two phosphorus atoms forms an angle of 6.9(2)° with the plane containing Rh and the two olefin midpoints. As a consequence, Rh(1), P(3), P(4), MP(1) and MP(2) are within 0.09(1) Å coplanar. The bonding parameters of the Rh atom do not show any peculiarity and compare well with data previously reported for complexes having the same coordination sphere at Rh [17]. The Rh atom is situated above the Cp ring, in a position one could qualitatively define as-far-as-possible from the Fe atom. For complexes of ferrocenyl ligand systems of this type, forming six-membered chelate rings, relatively few structural data are available, but both relative positions of the metal center, 'above' and 'below', have already been observed. In the cationic complex $[(CpFe(\eta^5\text{-}C_5H_3(PPh_2)(CH(Me)NMe_2))\text{-}Rh(NBD)]^+$, reported by Cullen *et al.* [18], the rhodium atom is found to reside above the Cp ring. Conversely, the trimeric copper(I) thiolato complex $[(CpFe(\eta^5\text{-}C_5H_3(PPh_2)(CH(Me)S)Cu]_3$, from our laboratories, adopts a conformation of the thiolato side chain such that the copper atoms lie in the region between the Cp rings [5]. Because the PR_2 and NMe_2 groups are

sterically more demanding than the thiolato fragment, it is obvious that they will enforce a conformation of the ligands in which they are placed above the Cp ring. It can be speculated that such conformational aspects will have an important impact on the stereoselectivity of catalytic reactions involving these ligands.

For complex **10** basically the same considerations just made for **9** concerning the conformation of the chelate ring apply (for comparison, see the torsion angles in Table 8). The similar conformation also induces comparable distortions of the molecule. Thus, P(2) is situated 0.29 Å above the plane of the Cp ring and this is, in turn, a consequence of the repulsive interaction between the pseudo axial phenyl fragment and the lower Cp ring, the shortest intramolecular distance being C(38)–C(27) = 3.38 Å. The lower Cp ring also shows a slightly larger distance from the iron atom (1.66 versus 1.63 Å). The geometry around palladium can be viewed as pseudo square-planar, with the palladium and the two phosphorus atoms defining the coordination plane. The three carbon atoms of the allyl fragment, C(1), C(2) and C(3), are located on the same side of this plane (at distances of 0.15, 0.02 and 0.23 Å, respectively). Thus, there is no indication of significant distortions in the coordination sphere of palladium. The central allylic carbon C(2) is disordered and this explains the very short distances found to the terminal partners C(1) and C(3).

For the platinum complex **11**, as was the case for derivatives **9** and **10**, the same qualitative arguments concerning the conformation of the chelate ring apply, thus these aspects will not be discussed here in detail (compare the values of some important torsion angles in Table 8). Also in **11** one observes a large displacement of the aryl substituted phosphorus out of the Cp plane (the distance of P(1) form this plane is 0.40 Å), as well as a short intramolecular contact involving the lower Cp and the pseudo axial phenyl group (shortest non-bonding C–C distance: C(5')–C(116) = 3.34 Å). Much less pronounced, indeed almost insignificant now, is the difference in the distances of the iron atom from the two Cp rings, as compared to the above discussed cases (to the upper Cp, 1.62 Å and to the lower, 1.64 Å). The coordination geometry around the platinum atom is only slightly distorted square-planar, with almost perfect coplanarity of the four atoms Pt, P(1), P(2) and Cl(2). Cl(1) is placed 0.18 Å from the best plane defined by the former four atoms. The chloride *trans* to the dicyclohexylphosphino fragment shows a bond length to Pt significantly longer than the corresponding distance of Cl(1) (2.350(3) versus 2.325(4)). This could be indicative of the higher *trans* influence [19] due to the trialkylphosphino group.

Finally, a further feature common to the three complexes is the bite angle of the ligand which varies within a very narrow range (93.3(1), 95.7(1) and 95.2(1)° for **9**, **10** and **11**, respectively).

Conclusions

We have shown that ligands of type **5** are easily prepared either from the acetate **1** or from the amine **2a**. The possibility of varying the phosphino groups in a chiral chelating diphosphine, independently from one another and in such an easy way, should open new avenues of exploration addressing the important issue of steric and electronic effects of ligands used in asymmetric catalysis. With the compound **5a** we have found a successful representative which has already been shown to ensure high enantioselectivities in a variety of catalytic reactions [7]. The structural work presented here provides evidence that **5a** behaves as a conformationally rather rigid ligand, thus being able to dictate a very similar coordination environment to different metal centers. Because the two ligating fragments are not equal, the two ligands in *trans* positions, e.g. in a square-planar complex, should display different reactivities, and hence stereochemical control. Studies along these lines are currently being carried out in our laboratories.

Experimental

General considerations

All reactions with air- or moisture-sensitive materials were carried out under Ar using standard Schlenk techniques. Freshly distilled solvents were used throughout. Routine ^{1}H NMR (250.133 MHz) and ^{31}P NMR (101.256 MHz) spectra were recorded with a Bruker AC 250 spectrometer. Chemical shifts are given in ppm relative to internal TMS and to external 85% H_3PO_4, respectively, and coupling constants (J) are given in Hz. Merck silica gel 60, 70–230 or 230–400 mesh ASTM was used for flash column chromatography. Thin-layer chromatography (TLC) was performed with Macherey-Nagel Polygram SIL G/UV254 pre-coated plastic sheets. Elemental analyses were done by Analytical Research Services, Ciba-Geigy Ltd. Secondary phosphines were either commercially available ($HPCy_2$ and $HP(tBu)_2$ from Strem Chemicals Ltd.), or were prepared by adaptation of published procedures [20]. Selected protocols have been included here for convenience. The general method for the preparation of the diphosphines of type **5** from the amine **2a** has already been reported [7]. For those compounds which have been obtained from the acetate **1**, the procedure is essentially the same. Complex **10** has been previously reported [7].

*Synthesis of P(2-MeOPh)$_2$H (**6d**)*

A solution of n-BuLi (26.7 ml, 1.6 M) was added by a syringe to a solution of 10 g of 2-(OCH_3)C_6H_4I in 20 ml of hexane. The resulting white suspension was stirred for 4 h at room temperature. Filtration, washing with hexane and drying *in vacuo* afforded a white powder. 10 ml of THF and 30 ml of diethyl ether were added. The concentration of the aryl lithium solution was determined by titration with isopropanol using phenanthroline as an indicator ($c = 0.47$ M). 30 ml of this solution (14.1 mmol) were added at −78 °C to a solution of 0.61 ml of PCl_3 (7.0 mmol) in 100 ml of diethyl ether. The resulting white suspension was allowed to warm to room temperature. After filtration, 0.3 g of $LiAlH_4$ (7.9 mmol) were added at 0 °C. The grey suspension was allowed to warm up over night and hydrolyzed with 100 ml of hydrochloric acid (1 M) giving two phases. The aqueous phase was further extracted with CH_2Cl_2; the organic phase was dried over $MgSO_4$, filtered and evaporated yielding a white powder. Recrystallization from ethanol afforded 1.17 g (68.0%) of the pure product as white needles. ^{1}H NMR ($CDCl_3$): δ 3.84 (s, CH_3O), 5.22 (vbr d, J(P,H) = 220 Hz), 6.86–7.36 (m, Ph H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −72.9 (s) (d, J(P,H) = 220.0).

*Synthesis of (R)-1-[(S-2-diphenylphosphino)ferrocenyl]-ethyldi(ortho-anisyl)phosphine (**5d**)*

This compound was prepared analoguously to **5a** from **2a**. Yield 1.29 g (71.1%). ^{1}H NMR ($CDCl_3$): δ 1.58 (dd, J = 10.8, J = 7.11, CH_3CHP), 3.54 (s, 3H, OCH_3), 3.63 (m, 1H, CH_3CHP), 3.67 (s, 3H, OCH_3), 3.91 (s, 6H, C_5H_5 and Cp H), 4.20 (m, 1H, Cp H), 4.44 (s, 1H, Cp H), 7.65–6.66 (m, 18H, Ph H). ^{31}P NMR ($CDCl_3$): δ −25.36 (d, J = 10.9), −21.68 (d, J = 10.9).

Synthesis of P(4-MeOPh)$_2$OH

16.8 ml of P(OH)$(OEt)_2$ (0.13 mmol, 0.33 equiv.) were added over a period of 2 h to a freshly prepared solution of *p*-(CH_3O)C_6H_4MgBr (50 ml, 0.4 mol) in diethyl ether. The resulting grey, thick suspension was refluxed overnight. Hydrolysis with hydrochloric acid (200 ml, 5 M) gave two phases. The aqueous phase was further extracted with CH_2Cl_2, and the combined organic phase was dried over $MgSO_4$ and filtered. The colorless solution was concentrated to a volume of 10 ml. The pure product crystallized on standing overnight. Filtration and repeated washings with cold diethyl ether and drying *in vacuo* yielded a white powder (23.9 g, 70.1%). ^{1}H NMR ($CDCl_3$): δ 3.85 (s, OCH_3), 6.96–7.01 (m, Ph H), 7.60 (m, Ph H), 8.03 (d, J(PH) = 477.8). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.3 (s).

*Synthesis of P(4-MeOPh)$_2$H (**6e**)*

4.7 g of $LiAlH_4$ (excess) were slowly added at 0 °C to a solution of 9.0 g of P(*p*-An)$_2$OH (34.3 mmol) in 250 ml of THF. The grey suspension was allowed to warm up to room temperature overnight. Hydrolysis with hydrochloric acid (250 ml, 5M) gave two phases. The aqueous phase was further extracted with CH_2Cl_2, and the organic phases were dried over $MgSO_4$, filtered and evaporated. The resulting oil was distilled under reduced pressure (0.1 bar, 175 °C) to give 3 g (35.5%) of the product as a viscous liquid. ^{1}H NMR ($CDCl_3$): δ 3.80 (s, OCH_3), 5.20 (d, J(P,H) = 215), 6.83–6.91 (m, Ph H), 7.20–7.44 (m, Ph H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −45.25 (s).

*Synthesis of (R)-1-[(S-2-diphenylphosphino)ferrocenyl]-ethyldi(para-anisyl)phosphine (**5e**)*

This compound was prepared analogously to **5a** from **2a**. The pure product was obtained after chromatography on silica (hexane/toluene), 1:2 vol./vol.) R_f = 0.13. Yield 70%. ^{1}H NMR ($CDCl_3$): δ 1.48 (dd, J = 9.1, J = 7.1, 3H, CH_3CHP), 3.66 (m, 1H, CH_3CHP), 3.73 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.84 (s, 5H, Cp), 4.03 (m, 1H, Cp H), 4.14 (m, 1H, Cp H), 4.25 (m, 1H, Cp H), 6.68 (d, J = 8.2, Ph H), 6.83 (d, J = 8.4, 2H, Ph H), 7.11–7.40 (m, 12H, Ph H),7.60–7.67 (m, 2H, Ph H). ^{31}P NMR ($CDCl_3$): δ −25.67 (d, J = 15.9), 2.22 (d, J = 15.9). *Anal.* Calc. for $C_{38}H_{36}O_2P_2Fe$: C, 71.04; H, 5.65. Found: C, 70.93; H, 5.67%.

*Synthesis of (R)-1-[(S-2-diphenylphosphino)ferrocenyl]-ethyldi(para-trifluoromethylphenyl)phosphine (**5f**)*

This compound was prepared analogously to **5a** from **2a**. Yield 76%, starting from 1.2 g (2.73 mmol) of (*R*,*S*)-PPFOAc (**1**). ^{31}P NMR ($CDCl_3$): δ −26.4 (d, J = 24), −6.6 (d, J = 24). *Anal.* Calc. for $C_{38}H_{30}F_6P_2Fe$: C, 63.53; H, 4.21; P, 8.62; F, 15.87. Found: C, 62.96; H, 4.23; P, 8.58; F, 15.68%.

*Synthesis of racemic HP(2-MeOPh)Ph (**6g**)*

A solution of *ortho*-anisylmagnesiumbromide (100 ml, 0.25 mol/l in THF) was added to a stirred solution of 3.4 ml (23.6 mmol) phenyldichlorophosphine in THF (100 ml) at −78 °C over a period of 3 h, followed by an excess of $LiAlH_4$ (1.6 g) at −78 °C, yielding a grey suspension. The mixture was allowed to warm up to room temperature and stirred for 2 h. After hydrolysis with 1 N HCl (200 ml), THF was evaporated *in vacuo*. The residual aqueous phase was extracted with CH_2Cl_2 (400 ml). The organic phase was dried over $MgSO_4$ and evaporated leaving a pale yellow oil. Distillation under reduced pressure (0.1 mbar) at 130 °C yielded 3.5 g of the product (67.9%) as a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 3.84 (s, OCH_3), 5.22 (vbr d, J = 190.3,

PH), 6.87–7.55 (m, Ph H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −55.97.

*Synthesis of the diastereoisomeric mixture of (R_P and S_P)-(R)-1-[(S-2-diphenylphosphino)ferrocenyl]-ethyl(ortho-anisyl)phenylphosphine (**5g, 5h**)*

0.39 ml (2.3 mmol, 1.1 equiv.) of *ortho*-anisylphenylphosphine was added to a stirred solution of 0.967 g (2.12 mmol) (*R,S*)-PPFOAc (**1**) in acetic acid (16 ml) at room temperature. The resulting clear orange solution was stirred for 4 h at 60 °C. After cooling to room temperature, CH_2Cl_2 (20 ml) was added. The acetic acid was neutralized by adding a saturated solution of $NaHCO_3$ until pH = 5. The organic phase was separated and washed twice with H_2O (10 ml). Drying over $MgSO_4$ and evaporation of the solvent yielded an orange foam. The diastereomeric mixture was purified by chromatography on silica (hexane/EtOAc, 9:1 vol./vol.) R_f = 0.3. The ratio of the diastereoisomers was 1/1. Yield 1.07 g (82.3%); m.p. 78–80 °C. ^1H NMR ($CDCl_3$): δ 1.46–1.59 (m, $CHCH_3$), 3.59 (s, OCH_3), 3.63 (s, OCH_3), 3.70–3.85 (m, $CHCH_3$), 3.88 (s, Cp), 3.88 (s, Cp), 3.99 (m, CH, 2H), 4.11 (m, Cp H), 4.21 (m, CH), 4.25 (m, Cp H), 4.33 (m, Cp H), 6.68–6.90 (m, Ph H), 7.1–7.4 (m, Ph H), 7.55–7.66 (m, Ph H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.40 (d, J = 15.9), −7.91 (d, J = 12.8), −25.12 (d, J = 12.8), −25.55 (d, J = 15.9). *Anal.* Calc.: C, 72.56; H, 5.6. Found: C, 72.34; H, 5.78%.

*Synthesis of [Pd(R(+)-$C_6H_4CHCH_3N(CH_3)_2$)-((R,S,Rp)-**5g**)][PF_6] (**8a**, diastereomer A)*

2.797 g of the diastereomeric mixture of PPF(*o*-An)Ph (**5g,h**) (4.6 mmol) were added to a suspension of 1.325 g [Pd_2Cl_2(*R*(+)-$C_6H_4CHCH_3N(CH_3)_2)_2$] (**7**, 2.3 mmol) in 25 ml of methanol. The resulting red solution was stirred for 30 min at room temperature. After filtering off traces of an unknown black impurity a solution of 0.372 g [NH_4][PF_6] (2.3 mmol) in 6 ml of H_2O was slowly added. The resulting orange suspension was further stirred for 16 h. The yellow precipitate was filtered off and thoroughly washed with 20 ml of 50% aqueous methanol and 20 ml diethyl ether. Recrystallizations from acetone/diethyl ether afforded the pure product. Yield 1.4 g (31% based on the diastereomeric mixture; d.e. = 100%). ^1H NMR ($CDCl_3$): δ 1.18 (d, J = 6.6, CH_3CHN), 1.37 (d, J = 1.7, CH_3N), 1.50 (d×d, J = 7.3, J = 14.1, CH_3CHP), 2.66 (t, J = 3.2, CH_3N), 3.56 (s, Cp), 3.91 (m, Cp H), 3.93 (m, Cp H), 3.94 (m, Cp H), 4.07 (m, CH_3CHP), 4.22 (s, OCH_3), 4.74 (q, J = 6.6), 6.34–8.30 (m, Ph H); ^{31}P NMR ($CDCl_3$): δ 57.01 (d, J = 43.8), 4.72 (d, J = 43.8).

*Synthesis of [Pd(R(+)-$C_6H_4CHCH_3N(CH_3)_2$)-((R,S,Sp)-**5h**)][PF_6] (**8b**, diastereomer B)*

A solution of 0.5 g [NH_4][PF_6] (3.1 mmol, 34% excess) in 6 ml of water was added to the filtrate from the isolation of diastereomer A. The resulting brown–red precipitate was filtered off and washed with 20 ml of 50% aqueous methanol and 20 ml of diethyl ether. Two recrystallizations from acetone/diethyl ether afforded red crystals. Yield 1.2 g (26% based on the diastereomeric mixture; d.e. = 75%). ^1H NMR ($CDCl_3$): δ 1.10 (dd, J = 7.2, J = 11.0, CH_3CHP), 1.37 (d, J = 6.6, CH_3CHN), 1.66 (d, J = 2, NCH_3), 2.60 (t, J = 2.7, NCH_3), 3.0 (q, J = 6.6, CH_3CHP), 3.62 (s, CH_3O), 4.05 (s, Cp), 3.75 (m, Cp H), 3.79 (m, Cp H), 4.32 (m, Cp H), 4.48 (q, J = 7.2, CH_3CHN), 6.30–8.30 (m, Ph H). ^{31}P NMR ($CDCl_3$): δ 24.9 (broad s), 30.6 (d, J = 43.5), 36.2 (d, J = 43.5).

*Synthesis of pure **5g** and **5h***

The same procedure was used for both diastereomeric products. A solution of 1.2 g of the Pd(II) complex (1.19 mmol) in 9 ml of acetone containing 0.8 ml of hydrochloric acid (1 M) was refluxed for 10 min. After cooling to room temperature, 20 ml of H_2O were added. The resulting orange suspension was concentrated to a volume of 20 ml. Filtration, followed by washing with water and drying *in vacuo* afforded an orange–red powder. To a suspension of this powder in 20 ml of methanol was added KCN (3.0 g, 46.1 mmol, 38 equiv.). The resulting yellow suspension was stirred for 15 min at room temperature. The addition of 10 ml of H_2O and 15 ml of CH_2Cl_2 gave two phases. The organic phase was separated, dried over $MgSO_4$, and evaporated affording an orange powder. Purification by chromatography (basic aluminum oxide, hexane/EtOAc, 9:1 vol./vol.) gave the free ligands. The diastereomeric pure ligands could be obtained after recrystallization from ethanol. In one case (diastereomer A) the crystals were suitable for X-ray analysis (*vide infra*).

(*R,S,R$_p$*)-*PPF(o-An)Ph*: yield 589.2 mg (81.4%) thin orange plates. ^1H NMR ($CDCl_3$): δ 1.48 (dd, J = 7.1, J = 8.7, 3H, CH_3CHP), 3.58 (s, 3H, OCH_3), 3.75 (m, 1H, CH_3CHP), 3.87 (s, 5H, Cp), 3.98 (m, 1H, Cp H), 4.11 (m, 1H, Cp H), 4.19 (m, 1H, Cp H), 6.69–6.81 (m, 2H, Ph H), 7.05–7.39 (m, 16H, Ph H), 7.61–7.68 (m, 2H, Ph H). ^{31}P NMR ($CDCl_3$): δ −25.58 (d, J = 14.9), −6.42 (d, J = 14.9). *Anal.* Calc. for $C_{37}H_{34}OP_2Fe$: C, 72.56; H, 5.60. Found: C, 72.39; H, 5.70%.

(*R,S,S$_P$*)-*PPF(o-An)Ph*: yield 616.9 mg (84.9%) thin orange needles. ^1H NMR ($CDCl_3$): δ 1.54 (*dd*, J = 7.1, J = 9.8, 3H, CH_3CHP), 3.62 (s, 3H, OCH_3), 3.74 (m, 1H, CH_3CHP), 3.86 (s, 5H, Cp), 3.97 (m, 1H, Cp H), 4.24 (m, 1H, Cp H), 4.32 (m, 1H, Cp H), 6.79–6.88 (m, 2H, Ph H), 7.10–7.39 (m, 16H, Ph H), 7.59–7.66 (m, 2H, Ph H). ^{31}P NMR ($CDCl_3$): δ −25.12 (d, J = 13.4),

−7.86 (d, J=13.4). *Anal.* Calc. for $C_{37}H_{34}OP_2Fe$: C, 72.56; H, 5.60. Found: C, 72.44; H, 5.57%.

*Synthesis of HPCyPh (**6h**)*

A solution of $C_6H_{11}MgBr$ (154 ml, 0.48 M in THF) was added at −78 °C over a period of 2 h to a solution of 10 ml of $PPhCl_2$ (73.7 mmol) in 200 ml of THF. The resulting suspension was allowed to warm up to room temperature, stirred for 15 min and cooled again to −78 °C. 3.5 g of $LiAlH_4$ (92.0 mmol) were added. The suspension was then allowed to warm up to room temperature and stirred overnight. Hydrolysis with 100 ml of hydrochloric acid (1 M) gave two phases. After separation, the aqueous phase was further extracted with CH_2Cl_2 (100 ml). The combined extracts were dried over $MgSO_4$, filtered and evaporated yielding a yellow oil. After distillation under reduced pressure 5.3 g (37.8%) of the pure product were obtained as a colorless viscous liquid. ^{1}H NMR ($CDCl_3$): δ 1.01–1.27 (m, cyclohexyl H), 1.66–1.82 (m, cyclohexyl H), 3.99 (d, J(P,H)=211.5), 7.26–7.51 (m, Ph H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −30.51 (s) (d, J(P,H)=211.4).

*Synthesis of the diastereoisomeric mixture of (R_P or S_P)-(R)-1-[(S-2-diphenylphosphino)ferrocenyl]-ethyl(cyclohexyl)phenylphosphine (**5i,5j**)*

An orange solution of 0.238 g of (*R,S*)-PPFOAc (**1**) (0.52 mmol) and 0.75 ml of HPCyPh (5.2 mmol) in methanol (6 ml) were refluxed for 7 h. The solvent was evaporated and the resulting orange oil purified by chromatography on silica (hexane/EtOAc 20/1 vol./vol.) R_f=0.17, 0.15 g (49.0%) of the diastereomeric mixture was obtained as an orange powder; m.p. 74–76 °C. ^{1}H NMR ($CDCl_3$): δ 0.78–2.10 (m, 28H, cyclohexyl and CHCH_3), 3.50 (m, 2H, CHCH$_3$), 3.80 (s, 5H, Cp), 3.82 (s, 5H, Cp), 3.9 (s, 1H, Cp H), 4.1 (s, 2H, Cp H), 4.19 (s, 1H, Cp H), 4.23 (s, 2H, Cp H), 7.12–7.80 (m, 30H, Ph H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −25.63 (br s), −25.20 (br d, J=13.8), 9.50 (br d, J=13.8), 11.72 (br d, J=18.4). *Anal.* Calc. for $C_{36}H_{38}P_2Fe$: C, 73.48; H, 6.51. Found: C, 73.31; H, 6.68%.

*Synthesis of [Rh(NBD)((R)-(S)-**5a**)]BF_4 (**9**)*

74.8 mg (0.2 mmol) of $[Rh(NBD)_2]BF_4$ were dissolved in a 1:1 mixture of MeOH and CH_2Cl_2 (10 ml). After the addition of 119.0 mg (0.2 mmol) of **5a** the mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in 2 ml of CH_2Cl_2. Addition of 20 ml of diethyl ether precipitated the product which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 129 mg (74%) of an orange powder. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ +23.2 (PPh_2, dd, J(P,Rh)=152, J(P,P)=36); +52.8 (PCy_2, dd).

*Synthesis of [$PtCl_2$((R)-(S)-**5a**)] (**11**)*

A mixture of 141.5 mg (0.38 mmol) of [$PtCl_2$(COD)] and 224.8 mg (0.38 mmol) of **5a** was stirred overnight in 25 ml of toluene giving a quantitative yield of the product which was recrystallized from toluene/hexane. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.6 (PPh_2, J(P,P)=16.5, J(P,Pt)=3552); +43.6 (PCy_2, J(P,P)=16.5, J(P,Pt)=3559). *Anal.* Calc. for $C_{36}H_{44}Cl_2P_2FePt$: C, 50.25; H, 5.15. Found: C, 50.27; H, 5.61%.

X-ray crystallography

The main goal of the X-ray crystallographic studies was to confirm the structure, as well as several stereochemical aspects of the compounds **5a**, **5g**, **9**, **10** and **11**. Because the structures turn out to be rather routine in nature, most of the crystallographic data has been deposited, see 'Supplementary material'. Pertinent crystal and collection and refinement, as well as bonding parameters are given in Tables 2–8.

Suitable crystals for X-ray diffraction were grown from ethanolic solutions (**5a** and **5g**), a concentrated CH_2Cl_2 solution layered with n-Bu_2O (**9**), a CH_2Cl_2 solution layered with hexane (**10**), or from toluene/hexane (**11**). For all five compounds the crystals chosen were glued at the tip of a MARK glass fiber using ARALDIT RAPID and covered with a thin film of the same glue. The unit cell, crystal system and space group were determined on the diffractometer, and the same crystals were then used for data collection. The $\theta/2\theta$ scan mode was used. There was no significant intensity variation for three standard reflections measured every 2 h. Intensity data were reduced by routine procedures and all calculations were performed using the commercial package SDP DIRDIF for **5a**, **5g** and **9**, and the Siemens SHELX PLUS package for **10** and **11**. The structures were solved by Patterson (**5a**, **5g** and **9**) or direct methods (**10** and **11**) and all non-hydrogen atoms were refined anisotropically. Only in the case of compound **5a**, could 24 hydrogen atoms (of a total of 44) be localized in a difference Fourier map. For all five structures hydrogen atoms were inserted at calculated positions with fixed isotropic U.

Supplementary material

For compounds **5a**, **5g**, **9**, **10** and **11** tables of atomic coordinates, displacement parameters, bond distances and angles and torsion angles, as well as listings of observed and calculated structure factors, are available from the authors upon request.

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