# Synthesis, coordination behaviour, structural features and use in asymmetric hydrogenations of bifep-type biferrocenes<sup>†</sup>

Gustavo Espino,<sup>b</sup> Li Xiao,<sup>a</sup> Michael Puchberger,<sup>c</sup> Kurt Mereiter,<sup>c</sup> Felix Spindler,<sup>d</sup> Blanca R. Manzano,<sup>e</sup> Félix A. Jalón<sup>e</sup> and Walter Weissensteiner<sup>\*a</sup>

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A protocol for the synthesis of C<sub>2</sub>- and C<sub>1</sub>-symmetric 2,2"-diarylphosphino-substituted biferrocenes (bifep-type ligands) is presented and the preparation of four representatives is described  $[(S_p,S_p)-2-R^1_2P-2"-R^2_2P-1,1"-biferrocene; 1 (bifep): R^1 = R^2 = Ph; 2: R^1 = Ph, R^2 = Cy; 3: R^1 = R^2 = 3,5-Me_2C_6H_3; 4: R^1 = 3,5-Me_2-4-OMe-C_6H_2, R^2 = 3,5-(CF_3)_2C_6H_3].$  In addition, the synthesis of three palladium(II) complexes ([PdX<sub>2</sub>(L)], 10: L = 1, X = Cl; 11: L = 4, X = Cl; 12: L = 1, X = C\_6F\_5 and of four bifep ruthenium complexes (13: [RuCl(*p*-cymene)(1)]PF<sub>6</sub>; 14: [RuI(*p*-cymene)(1)]PF<sub>6</sub>; 15: [RuCl(benzene)(1)]PF<sub>6</sub>; 16: [RuI(*p*-cymene)(1)]I) is reported. In the solid state the biferrocene unit of complexes 10, 11 and 15 adopt either a (*P*)-shaped (10) or an (*M*)-shaped (11, 15) conformation. In solution, palladium complexes 10 and 11 are present as equilibrium mixtures of rapidly interconverting (*P*)- and (*M*)-shaped conformers. Rhodium- and iridium-mediated asymmetric hydrogenations of a number of olefins and one imine give products with only low to moderate enantiomeric excess, while in the ruthenium-catalyzed hydrogenation of ketones a maximum e.e. of 82% is obtained. The low enantioselectivities are assumed to be related to the conformational flexibility of bifep-type ligands.

# Introduction

Diphosphines based on C<sub>2</sub>-symmetric biaryl backbones are widely used as ligands for enantioselective catalysts, with 2,2'bis(diphenylphosphino)-1,1'-binaphthyl (binap) certainly being one of the most prominent examples.<sup>1</sup> In addition to binaphthyl, a number of alternative biaryl-type backbones<sup>2</sup> (including biphenyl, bispyridyl and other bisheteroaromatic ligand scaffolds) have been investigated. This concept has further been extended to 2,2"-disubstituted biferrocenes and the synthesis of 2,2"bis(diphenylphosphino)-1,1"-biferrocene (bifep)<sup>3</sup> and some of its P-stereogenic analogues<sup>4</sup> have been described (*e.g.* I, Fig. 1). On using the latter type of ligand, catalytic allylic amination reactions resulted in products with up to 93% e.e.<sup>4</sup>

In a previous communication, we briefly described a protocol for the synthesis of 2,2"-disubstituted biferrocenes that allowed not only the preparation of  $C_2$ - but also of  $C_1$ -symmetric biferrocenes.<sup>5</sup> In addition, the use of a few bifep-type ligands in rutheniumcatalyzed asymmetric hydrogenations of ethyl acetoacetate was



Fig. 1 Binap, bifep, and P-chiral analogues I and II.

described as well as structural features of dichloro palladium(II) complexes of bifep and one  $C_1$ -symmetric analogue. We noticed with interest that in the solid-state the helicity of the biferrocene backbone in these complexes changed on changing the type of phosphino substituents and this observation was interpreted as being the result of conformational flexibility of the biferrocene backbone.

We now describe in detail the synthesis of  $C_{2}$ - and  $C_{1}$ -symmetric bifep-type biferrocenes, their coordination behaviour and additional rhodium- and ruthenium-mediated asymmetric hydrogenations of alkenes and ketones. These catalytic reactions were carried out with catalysts obtained either *in situ* 

<sup>&</sup>lt;sup>a</sup>Faculty of Chemistry, University of Vienna, Währinger Straße 38, 1090, Wien, Austria. E-mail: walter.weissensteiner@univie.ac.at

<sup>&</sup>lt;sup>b</sup>Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Pza Misael Bañuelos s/n., 09001, Burgos, Spain. E-mail: gespino@ubu.es <sup>c</sup>Faculty of Technical Chemistry, Vienna University of Technology, Getreidemarkt 9/164SC, 1060, Wien, Austria. E-mail: mpuchber@mail. zserv.tuwien.ac.at, kurt.mereiter@tuwien.ac.at

<sup>&</sup>lt;sup>d</sup>Solvias AG, Catalysis & Synthesis, P.O. Box, CH-4002, Basel, Switzerland. E-mail: felix.spindler@solvias.com

<sup>&</sup>lt;sup>e</sup>Departamento de Química Inorgánica, Orgánica y Bioquímica, IRICA, Universidad de Castilla-La Mancha, Avda. C. J. Cela, 10, 13071, Ciudad Real, Spain. E-mail: blanca.manzano@uclm.es, felix.jalon@uclm.es

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Fig. 2 Synthesis of ligands 1–4.

from ligands and an appropriate metal source or from isolated metal ligand complexes. In addition, a more extensive study on the structural features of palladium and ruthenium complexes of bifep-type ligands is reported.

#### Results

#### Synthesis of ligands and complexes

C<sub>2</sub>- and C<sub>1</sub>-symmetric ligands 1-4 were prepared in three steps from  $(S, R_p)$ -5 (Fig. 2), which was easily available from (S)-(4methylphenyl)sulfinyl ferrocene.6 An Ullmann-type reaction of iodide  $(S, R_p)$ -5 with Cu powder gave enantiopure  $(S, S, S_p, S_p)$ -2,2"-bis-(p-tolylsulfinyl)-1,1"-biferrocene (6, 77%), which served as the key intermediate that allowed the stepwise replacement of both *p*-tolylsulfinyl units. Intermediates 7-9 were obtained by treatment of 6 with t-BuLi (1.2 equiv.) and subsequent quenching with the appropriate chloro(diaryl)phosphine  $[(S,S_p,S_p)-7, \text{ chloro}(\text{diphenyl})\text{phosphine}, 60\% \text{ yield}; (S,S_p,S_p)-7)$ 8, chlorobis(3,5-dimethylphenyl)phosphine, 80%,  $(S,S_p,S_p)$ -9, chlorobis(3,5-dimethyl-4-methoxyphenyl)phosphine, 66%]. In the final step, the second sulfinyl group was removed by reaction of 7, 8, or 9 with t-BuLi followed by addition of either a chloro(diaryl)phosphine or a chloro(dialkyl)phosphine, resulting in ligands  $(S_n, S_n)$ -1 [chloro(diphenyl)phosphine, 49%],  $(S_n, S_n)$ -2 [chloro(dicyclohexyl)phosphine, 10%],  $(S_p, S_p)$ -3 [chlorobis(3,5dimethylphenyl)phosphine, 30%], and  $(S_{p}, S_{p})$ -4 [chlorobis[3,5bis(trifluoromethyl)phenyl]phosphine, 42%]. Interestingly, all attempts to transform 6 directly into the C2-symmetric ligands 1 and 3 failed [e.g. by treatment of 6 with 2.2 equiv. of t-BuLi followed by quenching with a chloro(diaryl)phosphine]. In neither case could both sulfinyl groups of 6 be replaced in one step by phosphino substituents.

In order to study the coordination behaviour of bifep-type ligands, three palladium(II) complexes of ligands **1** and **4**, as well as four ruthenium(II) complexes of bifep (1), were prepared as model compounds (Fig. 3). In addition, all bifep-ruthenium complexes were tested as pre-catalysts in asymmetric hydrogenation reactions.

The dichloro palladium(II) complexes [PdCl<sub>2</sub>(1)], 10 and [PdCl<sub>2</sub>(4)], 11, were prepared by treating the respective ligands with [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] in benzene while reaction of ligand 1 with [Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(COD)] in CH<sub>2</sub>Cl<sub>2</sub> gave the bis(pentafluorophenyl) palladium(II) complex [Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(1)], 12. All monocationic ruthenium complexes [RuX(arene)(1)]PF<sub>6</sub> were obtained by reaction of

1 or 4	+ [PdCl <sub>2</sub> (MeCN) <sub>2</sub> ]	<b>_</b>	[PdCl <sub>2</sub> (L)]	10 [PdCl <sub>2</sub> (1)] 11 [PdCl <sub>2</sub> (4)]
1 +	$[Pd(C_6F_5)_2(COD)]$	$\rightarrow$	$[{\sf Pd}({\sf C}_6{\sf F}_5)_2({\bf 1})]$	12
21+	[RuX <sub>2</sub> (arene)] <sub>2</sub> X = Cl, I arene = <i>p</i> -cymene,	<u>AgPF<sub>6</sub></u> benzene	2 [RuX(arene)( <b>1</b> )]PF <sub>6</sub>	<ol> <li>RuCl(<i>p</i>-cymene)(1)]PF<sub>6</sub></li> <li>[Rul(<i>p</i>-cymene)(1)]PF<sub>6</sub></li> <li>[RuCl(benzene)(1)]PF<sub>6</sub></li> </ol>
21 +	[Rul <sub>2</sub> (p-cymene)]	<b>→</b>	2 [Rul(p-cymene)(1)]	16

Fig. 3 Preparation of palladium and ruthenium complexes 10-16.

ligand 1 (2 equiv.) in THF with the respective  $[RuX_2(arene)]_2$  dimer (1 equiv.) in the presence of AgPF<sub>6</sub> (13:  $[RuCl(p-cymene)(1)]PF_6$ ; 14:  $[RuI(p-cymene)(1)]PF_6$ ; and 15:  $[RuCl(benzene)(1)]PF_6$ ). Complex 16, [RuI(p-cymene)(1)]I, was obtained by reacting 2 equiv. of ligand 1 with  $[RuI_2(p-cymene)]_2$  in a mixture of  $CH_2Cl_2$  and MeOH (4 : 1) in the absence of AgPF<sub>6</sub>.

The structural integrity of all ligands (1–4) and complexes (10– 16) was assessed by NMR spectroscopy and for ligand 1 and complexes 10, 11, and 15 single crystals were also studied by X-ray diffraction (see below). The absolute  $(S_p, S_p)$ -configuration of ligands 1–4 follows from the known absolute configuration of the starting material (*S*)-(4-methylphenyl)sulfinyl ferrocene.<sup>6</sup> Furthermore, the X-ray data for ligand 1 and complexes 10, 11, and 15 also confirmed the absolute  $(S_p, S_p)$ -configuration of ligands 1 and 4.

# Molecular structures of bifep, 1, and complexes $[PdCl_2(1)]$ (10), $[PdCl_2(4)]$ (11) and $[RuCl(benzene)(1)]PF_6$ (15), in the solid-state

Single crystals were obtained by vapour-liquid diffusion of diethyl ether into a solution of the respective ligand or complex in either CHCl<sub>3</sub> (1) or CH<sub>2</sub>Cl<sub>2</sub> (11) or by liquid–liquid diffusion of ethanol into a solution of 10 in CHCl<sub>3</sub>, and liquid–liquid diffusion of hexane into a solution of 15 in acetone. Details for the X-ray crystallography experiments are given in Table 1 and in the Experimental. Views of the molecular structures of these compounds are shown in Fig. 4 and selected geometrical data are given in Table 2. The absolute configuration of each compound was determined from the X-ray anomalous dispersion effects and was consistent with the chemical evidence.

Ligand  $(S_p, S_p)$ -1 crystallizes in the orthorhombic space group  $P2_12_12_1$  and contains one molecule per asymmetric unit. Although in the crystal 1 is found in an asymmetric environment, it adopts a clear C<sub>2</sub> pseudosymmetry when viewed perpendicular to the

	$(S_{p}, S_{p})$ -1	$(S_{p}, S_{p}) - [PdCl_{2}(1)] \cdot 2CHCl_{3} \cdot H_{2}O(10)$	$(S_{p},S_{p})$ -[PdCl <sub>2</sub> (4)]· solv (11) <sup><i>a</i></sup>	$(S_p, S_p)$ -[RuCl(C <sub>6</sub> H <sub>6</sub> )(1)]PF <sub>6</sub> · solv (15) <sup><i>a</i></sup>
Formula	$C_{44}H_{36}Fe_2P_2$	$C_{44}H_{36}Cl_2Fe_2P_2Pd{\cdot}2CHCl_3{\cdot}H_2O$	$C_{54}H_{44}Cl_2F_{12}Fe_2O_2P_2Pd$	$C_{50}H_{42}ClF_6Fe_2P_3Ru$
FW	738.37	1172.42	1303.83	1097.97
Crystal size/mm	$0.52 \times 0.34 \times 0.28$	$0.74 \times 0.56 \times 0.50$	$0.80 \times 0.20 \times 0.08$	$0.24 \times 0.06 \times 0.04$
Space group	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	<i>C</i> 2 (no. 5)
a/Å	8.5119(7)	10.270(3)	13.883(3)	26.087(6)
b/Å	18.2877(15)	22.142(6)	15.914(3)	10.143(2)
c/Å	22.2993(19)	10.282(3)	26.242(5)	22.461(5)
$\beta/^{\circ}$	_ ``	100.96(2)	_	123.957(3)
$V, Å^3$	3471.2(5)	2295.5(11)	5798(2)	4929.6(18)
Z	4	2	4	4
$ ho_{ m calcd}/ m g~ m cm^{-3}$	1.413	1.696	1.494	1.479
T/K	173(2)	223(2)	297(2)	297(2)
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.960	1.583	1.024	1.090
F(000)	1528	1176	2616	2216
$\theta_{\rm max}/^{\circ}$	30.0	30.0	25.0	23.0
No. of reflections measured	27 639	33 075	60 296	16994
$R_{ m int}$	0.0315	0.0510	0.0682	0.0799
No. of unique reflections	10101	12764	10183	6755
No. of reflections $I > 2\sigma(I)$	9347	12 440	8145	5010
No. of parameters	433	549	687	530
$R_1 (I > 2\sigma(I))^b$	0.0472	0.0461	0.0405	0.0482
$R_1$ (all data)	0.0519	0.0483	0.0590	0.0725
$wR_2$ (all data)	0.1064	0.1086	0.1056	0.1080
Flack parameter	-0.017(12)	-0.04(2)	-0.07(2)	-0.04(3)
$\Delta$ -Fourier peaks min/max/e Å <sup>-3</sup>	-0.26/0.79	-1.11/1.36	-0.41/0.42	-0.53/0.59

**Table 1** Details for the crystal structure determinations of complexes  $(S_p, S_p)$ -1,  $(S_p, S_p)$ -[PdCl<sub>2</sub>(1)] (10),  $(S_p, S_p)$ -[PdCl<sub>2</sub>(4)] (11), and  $(S_p, S_p)$ -[RuCl( $C_6H_6$ )(1)]PF<sub>6</sub> (15)

<sup>*a*</sup> Solvent squeezed with program PLATON and not contained in chemical formula and quantities derived thereof. <sup>*b*</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$ .

biferrocene axis. A view along the biferrocene axis (C1–C6, Fig. 4) shows the biferrocene unit in an (M)-shaped arrangement with the substituted Cp-rings Cp (C1-C5) and Cp" (C6–C10) tilted with respect to one other by 61°. In this arrangement P2 is located 2.62 Å above Cp and P1 2.63 Å above Cp".

It is interesting to note that a change in the diphenylphosphino units of bifep to naphthyl(phenyl)phosphino groups induces a marked change in the conformation of the biferrocenyl backbone. For  $(S, S, R_p, R_p)$ -2,2"-[bis(1-naphthyl(phenyl)phosphino)]-1,1"-biferrocene (I, Fig. 1) in the solid state a  $C_2$  symmetric molecular structure has been reported,<sup>5</sup> but with the biferrocene unit adopting a totally different conformation than bifep itself. In this conformation both substituted Cp rings are tilted with respect to each other by 142°, an arrangement that places P1 and P2 1.33 Å below Cp" and Cp, respectively (for a schematic representation see Fig. 5, conformer C).

According to simple force field calculations,<sup>7</sup> four arrangements of the biferrocene backbone seem to be feasible for C<sub>2</sub>-symmetric bifep-type ligands. All of these conformers are expected to be interconvertible through rotation of the ferrocene units about the biferrocene axis (Fig. 5). Experimental evidence for this model comes from the X-ray diffraction data of biferrocenes 1, I, and II. Diphosphine  $(S_p, S_p)$ -1 (bifep) adopts conformation A, the P-stereogenic analogue I conformation C and its bis(phosphineoxide)  $(R, R, R_p, R_p)$ -2,2"-[bis(1-naphthyl(phenyl)phosphinyl)]-1,1"-biferrocene (II, Fig. 1) conformation D. For geometric reasons it is obvious that for *cis*-coordinated chelate complexes only ligands adopting either conformation A or B are feasible.

The dichloro palladium(II) complex  $[PdCl_2((S_p, S_p)-1)]$ -2CHCl<sub>3</sub>· H<sub>2</sub>O (10) crystallizes in the monoclinic space group  $P2_1$  and contains one molecule per asymmetric unit. Both chloroform molecules form a non-classical hydrogen bond to chloride Cl1 while one water molecule bridges both chlorides (Cl1 and Cl2) through two classical hydrogen bonds. The  $[PdCl_2(1)]$  unit adopts C<sub>2</sub> pseudosymmetry but with the coordinated ligand 1 surprisingly present in conformation B and not in conformation A, as in the free ligand. In this conformation the biferrocene backbone is (*P*)-shaped with Cp and Cp" tilted against each other by 20° and the phosphorus atoms P1 and P2 positioned 1.1 Å below Cp" and Cp, respectively.

Complex  $[PdCl_2((S_p,S_p)-4)]$ -solv. (11) crystallizes in the orthorhombic space group  $P2_12_12_1$  and contains one molecule per asymmetric unit. This palladium complex is asymmetric but in this case the *cis*-coordinated ligand **4** is present in conformation A. The biferrocene unit is (*M*)-shaped with the substituted Cp rings rotated against each other by 65° (P2 2.7 Å above Cp and P1 2.7 Å above Cp"). At the peripheral parts of the molecule significant thermal motion and disorder is observed and this mainly concerns the trifluoromethyl groups. Interestingly, one aryl ring of the bis[3,5-bis(trifluoromethyl)phenyl]phosphino unit, C21-C26, shows clear  $\pi$ - $\pi$ -stacking with Cp" while the corresponding ring of the bis(3,5-dimethyl-4-methoxyphenyl)phosphino unit, C37-C42, lacks such an interaction with Cp.

The ruthenium complex [RuCl(benzene)( $(S_p, S_p)$ -1)]PF<sub>6</sub>·solv. (15) crystallizes in the monoclinic space group C2 and contains one molecule per asymmetric unit. The overall structural features of this asymmetric cationic complex are as expected. Chloride,

	$(S_{p}, S_{p})$ -1	$(S_p, S_p)$ -[PdCl <sub>2</sub> (1)]·2CHCl <sub>3</sub> ·H <sub>2</sub> O (10)	$(S_p, S_p)$ -[PdCl <sub>2</sub> (4)]·solv (11)	$(S_p, S_p)$ -[RuCl(C <sub>6</sub> H <sub>6</sub> )(1)]PF <sub>6</sub> ·solv (15)
Bond lengths/Å				
$\langle Fe1-C(Cp) \rangle$ $\langle Fe1-C(Cp') \rangle$ $\langle Fe2-C(Cp'') \rangle$	2.050(3) 2.052(3) 2.051(3)	2.050(6) 2.046(7) 2.054(6)	2.042(5) 2.058(6) 2.044(5)	2.037(8) 2.032(8) 2.041(8)
(Fe2–C(Cp'')) (Fe2–C(Cp''')) C1–C6	2.056(3) 1.477(3)	2.056(6) 1.481(7)	2.035(5) 1.451(6)	2.033(8) 1.484(10)
Pd,Ru–P1 Pd,Ru–P2 Pd,Ru–C11 Pd–C12		2.274(2) 2.267(2) 2.366(2) 2.367(2)	2.248(1) 2.284(1) 2.346(2) 2.341(2)	2.352(2) 2.341(2) 2.363(2)
$\langle Ru-(C_{benzene})\rangle$	_	_	_	2.210(7)
Bond angles/°				
C2–P1–Pd,Ru C7–P2–Pd,Ru P1–Pd,Ru–P2 P1–Pd Ru–C11		124.7(2) 125.8(2) 98.83(5) 86.34(6)	110.8(2) 118.4(2) 93.45(5) 91.74(6)	124.0(2) 114.3(2) 91.8(1) 87 5(1)
P2–Pd,Ru–Cl2 Cl1–Pd–Cl2		86.64(6) 88.55(6)	85.56(6) 90.34(6)	86.3(1) —
Normal distance of a	tom from L.S.	plane through ring Cp (Cl to C5) or Cp"	(C6 to C10)/Å	
Pd,Ru/Cp P1/Cp P2/Cp Cl1/Cp	 0.047(4) 2.621(4) 	-0.686(16) 0.246(10) -1.060(14) -0.211(21)	2.553(8) 0.345(8) 2.739(8) 2.502(12)	0.857(20) 0.196(13) 1.914(16) -1.108(20)
Cl2/Cp Pd,Ru/Cp" P1/Cp" P2/Cp"	 2.627(4) 0.059(4)	-1.874(22) -0.630(16) -1.056(15) 0.256(10)	4.889(9) 1.957(10) 2.656(7) 0.119(7)	
Cl1/Cp″ Cl2/Cp″	_	-1.691(23) -0.112(21)	3.953(13) 1.053(14)	3.059(6)
Interplanar angles/°				
$\overline{Cp \wedge Cp''}$	61.4(1)	19.8(3)	65.0(2)	50.1(3)
Dihedral angles/°				
C2-C1-C6-C7 C6-C1-C2-P1 C1-C6-C7-P2 C1-C2-P1-Pd,Ru C6-C7-P2-Pd,Ru	-115.3(3) -0.9(3) -0.9(3) 	28.7(10) 6.7(10) 2.1(11) -46.1(7) -41.9(7)	-58.5(6) 9.2(6) -3.3(6) 77.1(4) 57.6(4)	-52.6(11) 10.4(12) 14.5(10) 10.4(9) 63.9(6)
	_	т. <i>Э</i> ( <i>i</i> )	57.0(7)	00.0(0)

**Table 2** Geometrical parameters of complexes  $(S_p, S_p)$ -1,  $(S_p, S_p)$ -[PdCl<sub>2</sub>(1)] (10),  $(S_p, S_p)$ -[PdCl<sub>2</sub>(4)] (11), and  $(S_p, S_p)$ -[RuCl(C<sub>6</sub>H<sub>6</sub>)(1)]PF<sub>6</sub> (15)

benzene and bifep are coordinated to Ru(II) in a tetrahedral fashion to form a three-legged piano stool complex. The biferrocene backbone is (*M*)-shaped and the ligand adopts conformation A with a Cp/Cp" tilt angle of 50°, P1 is 1.9 Å above Cp" and P2 is 2.1 Å above Cp.

# Molecular structures of complexes $[PdCl_2(1)]$ (10), $[PdCl_2(4)]$ (11), $[RuCl(p-cymene)(1)]PF_6$ (13), $[RuI(p-cymene)(1)]PF_6$ (14), $[RuCl(benzene)(1)]PF_6$ (15), and [RuCl(benzene)(1)]I (16), in solution

The molecular structures of complexes 10, 11, 13–16 in solution were determined by NMR spectroscopy, mainly by analyzing nuclear Overhauser interactions. The assignment of <sup>1</sup>H, <sup>13</sup>C and

<sup>31</sup>P signals was made using standard one- and two-dimensional techniques. The main structural information was obtained from proton spectra and, predominately, from NOESY and ROESY spectra.

On the basis of the <sup>1</sup>H NMR spectrum (250 MHz,  $CD_2Cl_2$ , 300 K), in solution complex [PdCl<sub>2</sub>(1)] appears to adopt a twofold symmetry consistent with the pseudo  $C_2$  symmetric solid state structure. However, for some of the signals severe line broadening was observed, indicating the presence of dynamic exchange. Indeed, variable temperature measurements in the range 300– 190 K showed that on cooling the sample from 300 K to 240 K each of the Cp-proton signals split into two signals in a 5 : 1 ratio. Since both interconverting species exhibit twofold symmetry, the observed exchange phenomenon is likely to be caused by the





 $(S_p, S_p)$ -[PdCl<sub>2</sub>(1)] 10

 $(S_p, S_p)$ -[PdCl<sub>2</sub>(4)] 11

**Fig. 4** Molecular structures of bifep (1), and complexes  $[PdCl_2(1)]$  (10),  $[PdCl_2(4)]$  (11), and  $[RuCl(benzene)(1)]PF_6$  (15) in the solid state. Cp: C1–C5, Cp': C11–C15; Cp'': C6–C10; Cp''': C16–C20.

interconversion of the two  $C_2$  symmetric conformers of complex  $[PdCl_2(1)]$  with the biferrocene backbone adopting either a (P)or an (M)-shaped conformation (Fig. 5). On further cooling the sample from 240 K to 190 K, a second dynamic process was observed that only affected the phenyl proton signals. This second process is assigned to a slowed rotation of the phenyl rings about their respective P-C bond. The conformer interconversion is also clearly observed in the VT- ${}^{13}C{}^{1}H$  and  ${}^{31}P{}^{1}H$  spectra. In the <sup>13</sup>C spectrum at 300 K only one signal for the carbons of the unsubstituted Cp rings was observed while at 240 K two barely separated signals in a ratio of approximately 5:1 were seen. Two phosphorus signals are seen in the <sup>31</sup>P spectrum at 240 K and on raising the temperature these broaden and finally coalesce at about 300 K. From the proton spectra the free energy of activation for the conformer exchange process was calculated to be approximately  $\Delta G^{\neq} = 58 \pm 3 \text{ kJ mol}^{-1}$  (260 K, major to minor conformer) and  $\Delta G^{\neq} = 54 \pm 3 \text{ kJ mol}^{-1}$  (minor to major conformer).<sup>8</sup>

The NMR spectra of complex [PdCl<sub>2</sub>(4)] are consistent with the presence of one  $C_1$  symmetric conformer but, as in the case of [PdCl<sub>2</sub>(1)], the r.t. proton NMR spectrum (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K) points to an exchange process. In comparison to all other resonances the signals of both unsubstituted Cp rings and of all aryl *ortho* protons are significantly broadened. VT-<sup>1</sup>H NMR spectroscopy in the range 300–200 K again showed two independent exchange processes. When the sample was cooled from 300 K to 280 K, further broadening of the Cp' and aryl *ortho* proton signals occurred but signal splitting could not be

**Fig. 5** Schematic representation of feasible conformers of  $C_2$ -symmetric bifep-type ligands.

observed. Below 280 K all exchanging signals sharpened again (without a detectable decoalescence) and at 260 K the Cp' ( $\delta$  3.98 and 4.09 ppm) as well as two aryl *ortho* proton signals had fully reappeared while the remaining aryl *ortho* signals of one 3,5-dimethyl-4-methoxyphenyl ( $\delta$  8.09 ppm) and one 3,5-bis(trifluoromethyl)phenyl ring ( $\delta$  8.43 ppm) had started to broaden again. In addition, below 240 K one aryl methyl signal was also affected by an exchange process. Finally, at 200 K this methyl signal as well as the aforementioned aryl *ortho* proton signals had split into two signals of equal intensity (3,5-dimethyl-4-methoxyphenyl ring: CH<sub>3</sub>  $\delta$  2.21 and 2.36 ppm; *ortho* protons  $\delta$  6.92 and 7.89 ppm; 3,5-bis(trifluoromethyl)phenyl ring: *ortho* protons  $\delta$  7.62 and 8.77 ppm).

In a similar way to complex  $[PdCl_2(1)]$ , we consider that the exchange process observed at higher temperature (300–260 K) is the result of two interchanging conformers of complex  $[PdCl_2(4)]$  having either a (*P*)- or an (*M*)-shaped biferrocene backbone but with one conformer present in only a very small amount.

The second exchange process observed below 260 K relates to a slowed rotation of one 3,5-dimethyl-4-methoxyphenyl and one 3,5-bis(trifluoromethyl)phenyl ring about their respective P–C(aryl) bond. Free energy of activation values of  $\Delta G^{\neq} = 44 \pm 2 \text{ kJ mol}^{-1}$  (230 K, 3,5-dimethyl-4-methoxyphenyl ring) and  $\Delta G^{\neq} = 42 \pm 2 \text{ kJ mol}^{-1}$  (220 K, 3,5-bis(trifluoromethyl)phenyl ring) have been calculated for these processes.

In solution, the ruthenium complexes 13–16 adopt a  $C_1$  symmetric molecular structure. The <sup>1</sup>H NMR spectra (400 MHz, acetone-d<sub>6</sub>, 300 K) of these complexes showed a uniform pattern for all ferrocene signals but, unlike the dichloro palladium complexes [PdCl<sub>2</sub>(1)] and [PdCl<sub>2</sub>(4)], the variable temperature spectra recorded *e.g.* for complex [RuI(*p*-cymene)(1)]PF<sub>6</sub> (14) in

the temperature range 300-200 K did not show any evidence of an exchange process related to a conformer equilibrium. A conformational analysis showed that in solution the biferrocene backbone of complexes 13-15 prefer an (M)-shaped arrangement, which is consistent with the (M)-shaped molecular structure found for  $[RuCl(benzene)(1)]PF_6$  (15) in the solid-state. The (M)-shaped biferrocene conformation could be deduced from NOE interactions of selected ferrocene proton signals. For a given complex all of the ferrocene signals could be unequivocally ascribed to the individual ferrocene units (of the biferrocene backbone) and, as a result, we were able to record NOE interactions between these units. In each case, the ROESY spectra of complexes 13-15 showed rather intense cross peaks between protons from the unsubstituted Cp-ring of one ferrocene unit to one proton of the substituted Cp-ring of the second ferrocene unit (e.g. from Cp-H5 to Cp<sup>'''</sup>-H; for a graphical representation see Fig. 6) and such interactions are only consistent with the  $(S_p, S_p)$ -configured bifep ligand adopting an (M)-shaped conformation.

In summary, in palladium and ruthenium coordination compounds of  $(S_p, S_p)$ -bifep-type ligands the biferrocene unit can adopt either a (*P*)- or an (*M*)-shaped conformation. In the solid-state, for dichloro palladium complexes both (*P*)- and (*M*)-shaped conformers were found, while in the ruthenium complex [RuCl(benzene)(1)]PF<sub>6</sub> the biferrocene unit prefers the (*M*)-shaped arrangement. In solution, the palladium complexes are present as an equilibrium mixture of rapidly interconverting (*P*)- and (*M*)-shaped conformers. In all of the investigated ruthenium arene complexes the bifep ligand adopts exclusively an (*M*)-shaped conformation.

#### **Enantioselective hydrogenations**

Diphosphine ligands  $(S_p, S_p)$ -1, 3, and 4 were tested in catalytic hydrogenations of several olefins, ketones and one imine (for the catalytic results see Tables 3 and 4, for substrates tested see Fig. 7). In these cases all catalysts were formed *in situ* using an appropriate



Fig. 6 Numbering scheme and main Overhauser interactions used for NMR signal and structural assignment (schematic representation of [RuCl(*p*-cymene)(1)]\*).

Rh, Ru, or Ir source and ligands of  $(S_p, S_p)$  configuration. In most hydrogenations (except for the substrate MCA) conversion ranged from acceptable to nearly quantitative. However, for all olefins and the imine tested, products with very low enantiomeric excess values were obtained. Only the ruthenium-promoted hydrogenation of ethyl acetoacetate (EAA, entry 9) gave a product with reasonably high e.e. (82%). Therefore, further hydrogenation experiments were carried out with EAA as well as with two additional  $\beta$ -keto derivatives (ethyl benzoylacetate, EBA, and acetylacetone, ACA). For this purpose not only catalysts prepared *in situ* but also the isolated ruthenium complexes **13–16** were used as pre-catalysts. However, preparatively useful results could not be obtained in either case. Interestingly, for all three substrates tested, catalysts prepared *in situ* gave products with significantly higher e.e. values.

Table 3 Results obtained in the ruthenium-, rhodium-, and iridium-catalyzed hydrogenation of olefins, ketones, and one imine with ligands 1, 3, and 4

Entry	Substrate <sup>a</sup>	Ligand	Catalyst precursor <sup>b</sup>	S/C	Solvent <sup>c</sup>	$p(H_2)/bar$	T∕°C	Time/h	Conv. (%)	e.e. (%)	Product configuration
1	MAC	1	[Rh(NBD) <sub>2</sub> ]BF <sub>4</sub>	200	MeOH	1	25	16	>99	37	S
2	MAC	4	[Rh(NBD)]]BF4	200	MeOH	1	25	16	>99	48	S
3	MCA	1	[Rh(NBD)]]BF4	200	MeOH	5	25	15	9	32	S
4	MCA	3	[Rh(NBD)]]BF4	200	MeOH	5	25	15	21	8	R
5	MCA	4	Rh(NBD), BF4	200	MeOH	5	25	15	5	N.d.	N.d.
6	PCA	1	[Rh(NBD) <sub>2</sub> ]BF <sub>4</sub>	200	MeOH	80	25	14.5	95	35	S
7	DMI	1	$[Rh(NBD)_2]BF_4$	200	MeOH	1	25	17.5	>99	23	R
8	DMI	4	$[Rh(NBD)_2]BF_4$	200	MeOH	1	25	18	>99	13	R
9	EAA	1	$[RuI_2(p-cymene)]_2$	1000	EtOH	80	80	19	>99	82	R
10	EAA	3	$[RuI_2(p-cymene)]_2$	1000	EtOH	80	80	19	>99	68	R
11	EAA	4	$[RuI_2(p-cymene)]_2$	1000	EtOH	80	80	16	96	20	R
12	EPY	1	[RhCl(COD) <sub>2</sub> ] <sub>2</sub>	10	Toluene	40	25	18	26	33	R
13	EPY	3	[RhCl(COD) <sub>2</sub> ] <sub>2</sub>	100	Toluene	40	25	16	98	57	R
14	MEAI	1	[IrCl(COD) <sub>2</sub> ] <sub>2</sub>	1000	Toluene	80	25	15.5	41	33	S
15	MEAI	3	[IrCl(COD) <sub>2</sub> ] <sub>2</sub>	1000	Toluene	80	25	15.5	71	21	S
16	MEAI	4	[IrCl(COD) <sub>2</sub> ] <sub>2</sub>	1000	Toluene	80	25	15.5	>99	28	S

<sup>*a*</sup> For substrates see Fig. 7, NBD = norbornadiene, COD = cycloocta-1,5-diene. <sup>*b*</sup> Ligand/catalyst precursor: [Rh(NBD)<sub>2</sub>]BF<sub>4</sub>: 1.05; [RuI<sub>2</sub>(*p*-cymene)]<sub>2</sub>: 2.2; [RhCl(COD)<sub>2</sub>]<sub>2</sub> and [IrCl(COD)<sub>2</sub>]<sub>2</sub>: 2.1. <sup>*c*</sup> Additives: substrates EAA and EPY (entries 9–13): 1 M HCl (60  $\mu$ L); MEAI (entries 14–16): CF<sub>3</sub>COOH (30  $\mu$ L); tetrabutylammonium iodide (TBAI): 2 equiv./Ir.

Entry	Substrate	Catalyst precursor	Additives 1 M HCl/µL	Time/h	Conv. (%)	e.e. (%)	Product configuration	dl : meso
9	EAA	$1 + [RuI_2(p-cymene)]_2$	60	19	>99	82	R	_
17	EAA	$[RuCl(p-cymene)_2(1)]PF_6$	60	21	>99	65	R	
18	EAA	$[RuI(p-cymene)_2(1)]PF_6$	60	21	>99	69	R	
19	EAA	$[RuI(p-cymene)_2(1)]PF_6$	60/TBAI	20.5	>99	66	R	
20	EAA	[Rul(p-cymene) <sub>2</sub> (1)]I	60	20.5	>99	61	R	
21	EBA	$1 + [RuI_2(p-cymene)]_2$	60	16	>99	54	S	
22	EBA	$[Rul(p-cymene)_2(1)]PF_6$	60	16	>99	46	S	
23	EBA	[Rul(p-cymene) <sub>2</sub> (1)]I	60	20.5	>99	43	S	
24	ACA	$1 + [RuI_2(p-cymene)]_2$	60	19	>99	72	2R,4R	97:3
25	ACA	$[Rul(p-cymene)_2(1)]PF_6$	60	18	>99	63	2R,4R	96:4
26	ACA	[RuI(p-cymene) <sub>2</sub> (1)]I	60	20	61	59	2R, 4R	97:3
Substrate: 6.45 mmol; S/C: 1000; solvent: EtOH (15 mL); p(H <sub>2</sub> ): 80 bar; T: 80 °C.								





Fig. 7 Substrates used in enantioselective hydrogenation reactions.

Overall, in hydrogenations of ketones the bifep-type ligands tested (1, 3, and 4) did not perform anywhere near as well as binaptype or comparable biaryl-based ligands. It seems reasonable to assume that the performance of bifep-based catalysts is strongly influenced by the lack of conformational stability of the biferrocene ligand backbone resulting in a severe drop in enantioselectivity.

# **Concluding remarks**

A method for the synthesis of  $C_2$ - and  $C_1$ -symmetric bifep-type ligands has been developed and four representative derivatives have been synthesized. The coordination behaviour of these compounds has been studied as along with structural features of the dichloro palladium and ruthenium arene complexes. In both the solid-state and in solution, bifep-based complexes were found to adopt different conformations with the biferrocene backbone present either in a (*P*)- or an (*M*)-shaped conformation. Variabletemperature NMR measurements indicate that in solution the dichloro palladium complexes in particular are present as equilibria of rapidly interconverting (*P*)- and (*M*)-shaped conformers. The use of three bifep-type ligands in rhodium-, ruthenium- and iridium-catalyzed asymmetric hydrogenations of olefins, ketones and one imine resulted in products with poor to moderate enantioselectivities. The use of ethyl acetoacetate as the substrate did provide a product with 82% e.e. It is assumed that the overall poor to moderate performance of bifep-based catalysts is—at least in part—caused by the lack of conformational stability of the biferrocene ligand backbone.

# Experimental

#### General comments

Melting points were determined on a Kofler melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker DRX 400, Varian Unity Inova-400 or a Bruker DPX 250 spectrometer. Chemical shifts  $\delta$  are reported in ppm and are referenced relative to CHCl<sub>3</sub> (7.26 and 77.00 ppm for <sup>1</sup>H and <sup>13</sup>C), CHDCl<sub>2</sub> (5.32 for <sup>1</sup>H), CD<sub>2</sub>Cl<sub>2</sub> (53.8 ppm for <sup>13</sup>C), TMS (acetone-d<sub>6</sub>, 0 ppm for <sup>1</sup>H and <sup>13</sup>C), CFCl<sub>3</sub> (0 ppm for <sup>19</sup>F), and 85% H<sub>3</sub>PO<sub>4</sub> (0 ppm for <sup>31</sup>P), coupling constants are reported in Hz. In the <sup>1</sup>H NMR data, br s, d, t, q, and spt refer to broad singlet, doublet, triplet, quartet and septet, respectively, and  $C_{\alpha}$  in <sup>13</sup>C NMR data stands for quaternary carbon atom. Coupling constants listed in <sup>13</sup>C NMR data refer to <sup>13</sup>C-<sup>31</sup>P couplings, unless stated otherwise. Mass spectra were measured on a Varian MAT-CH7 or a Finnigan MAT 8230 spectrometer (E.I., 70 eV, unless stated otherwise). FAB+ mass spectra were recorded on a Micromass AutoSpec instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter in CHCl<sub>3</sub> at 20 °C. CD spectra were recorded on a dichrograph JOBIN YVON CD 6 in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Wien (Mag. J. Theiner) or were measured on a LECO CHNS932 microanalyser. All reactions requiring inert conditions were conducted under Ar or N<sub>2</sub>, using standard Schlenk techniques. Diethyl ether was distilled from lithium aluminium hydride, acetonitrile and benzene were distilled from calcium hydride, and THF was dried over potassium/benzophenone prior to use. Chromatographic separations were performed under gravity either on silica gel (MERCK, 40–63 µm) or on alumina (MERCK, activity II–III, 0.063–0.200 mm). Petroleum ether (PE) with a boiling range of 55-65 °C was used for chromatography. Copper was activated

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according to ref. 9, (*S*)-(4-methylphenyl)sulfinyl-ferrocene<sup>6</sup> and complexes  $[RuCl_2(p-cymene)]_2$ ,  $[RuCl_2(benzene)]_2$  and  $[RuI_2(p-cymene)]_2^{10}$  were prepared as described previously.

#### General procedure for the preparation of biferrocenes 1-4

To a solution of compound 7, 8 or 9 (1 mmol) in THF was added dropwise *t*-BuLi (0.71 mL, 1.7 M in pentane, 1.2 mmol) under Ar at -78 °C. After stirring for an additional 5 min, the appropriate chloro(diaryl)- or chloro(dialkyl)phosphine (1.3 mmol) was added at the same temperature. The reaction mixture was allowed to warm to r.t. and was stirred for 2–16 h. After quenching with saturated NaHCO<sub>3</sub> solution, the organic phase was separated, and washed with water and brine. After drying over MgSO<sub>4</sub> the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica or alumina.

 $(S_p,S_p)$ -2,2"-Bis(diphenylphosphino)-1,1"-biferrocene 1. Compound 1 was synthesized from  $(S,S_p,S_p)$ -7 (400 mg, 578 mmol, in 150 mL THF) and Ph<sub>2</sub>PCl (166 mg, 754 mmol). Reaction time: 16 h. Chromatography on alumina; elution with PE/Et<sub>2</sub>O/Et<sub>3</sub>N (100/2/1  $\rightarrow$  60/3/1  $\rightarrow$  20/3/1) afforded  $(S_p,S_p)$ -1 as a yellow solid (209 mg, 49%).

Mp 221 °C. Found: C 71.26, H 4.83. C<sub>44</sub>H<sub>36</sub>Fe<sub>2</sub>P<sub>2</sub> requires C 71.57, H 4.91%. <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>) δ 3.97 (2 H, m, Cp-H), 4.04 (10 H, s, Cp'-H), 4.53 (2 H, m, Cp-H), 4.94 (2 H, m, Cp-H), 6.66-6.72 (8 H, m, Ph-H), 6.78-6.83 (2 H, m, Ph-H), 7.34–7.38 (6 H, m, Ph–H), 7.52–7.57 (4 H, m, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>) δ 69.95 (10 C, 2 Cp'-CH), 69.98 (2 C, 2 Cp–CH), 71.5 (2 C, d, J = 5.3, 2 Cp–CH), 76.12 (2 C, dd, J = 4.6, J = 8.4, 2 Cp-CH), 78.4 (2 C, d, J = 10.6, 2 Cp-Cq), 91.1 (2 C, dd, J = 3.0, J = 32.7, 2 Cp-Cq), 126.8 (2 C, 2 Ph-CH),127.3 (4 C, d, J = 5.3, 4 Ph–CH), 128.0 (4 C, d, J = 8.4, 4 Ph– CH), 129.0 (2 C, 2 Ph–CH), 131.4 (4 C, d, J = 16.7, 4 Ph–CH), 135.4 (4 C, d, J = 22.8, 4 Ph–CH), 139.5 (2 C, d, J = 9.1, 2 Ph– Cq), 139.8 (2 C, d, J = 7.6, 2 Ph–Cq). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta = -23.2$ . MS (EI, 230 °C) m/z (rel%) = 738 (42, M<sup>+</sup>), 661 (100, M<sup>+</sup> – Ph), 552 (8, M<sup>+</sup> – Ph<sub>2</sub>P). HRMS found: 738.0967; calcd (for C<sub>44</sub>H<sub>36</sub>Fe<sub>2</sub>P<sub>2</sub>): 738.0991.  $[\alpha]_{\lambda}^{20} = +151$  (589 nm), +182 (578 nm), +377 (546 nm) (c = 0.22 in CHCl<sub>3</sub>). CD  $\Delta \varepsilon (\lambda_{max}) =$ +469 (244 nm), +35.0 (312 nm), -20.3 (351 nm), +33.2 (478 nm)  $(c = 1.06 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ in } \text{CH}_2\text{Cl}_2).$ 

 $(S_p, S_p)$ -2-Dicyclohexylphosphino-2"-diphenylphosphino-1,1"biferrocene 2. Compound 2 was synthesized from  $(S, S_p, S_p)$ -7 (825 mg, 1.19 mmol, in 320 mL THF) and Cy<sub>2</sub>PCl (360 mg, 1.55 mmol). Reaction time: 2 h. Chromatography on alumina; elution with PE/Et<sub>2</sub>O/Et<sub>3</sub>N (100/2/1  $\rightarrow$  60/6/1) afforded  $(S_p, S_p)$ -2 as a yellow solid (89 mg, 10%).

Mp 196 °C. Found: C 70.29, H 6.42.  $C_{44}H_{48}Fe_2P_2$  requires C 70.42, H 6.45%. <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  0.60–0.69 (4 H, m, Cy), 0.83–0.90 (3 H, m, Cy), 1.21–1.43 (8 H, m, Cy), 1.51–1.56 (1 H, m, Cy), 1.71–1.75 (1 H, m, Cy), 1.81–1.89 (2 H, m, Cy), 2.00–2.17 (3 H, m, Cy), 3.92 (5 H, s, Cp'–H), 4.15 (1 H, m, Cp–H), 4.28 (1 H, m, Cp–H), 4.34 (5 H, s, Cp'–H), 4.51 (1 H, m, Cp–H), 4.56 (1 H, m, Cp–H), 4.79 (1 H, m, Cp–H), 4.89 (1 H, m, Cp–H), 7.09–7.12 (3 H, m, Ph–H), 7.15–7.20 (2 H, m, Ph–H), 7.36–7.38 (3 H, m, Ph–H), 7.60–7.65 (2 H, m, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>)  $\delta$  25.9 (1 C, CH<sub>2</sub>), 26.5 (1 C, CH<sub>2</sub>), 26.7 (1 C, d, J = 21.3, CH<sub>2</sub>), 26.7 (1 C, CH<sub>2</sub>), 27.8 (1 C, d, J = 4.6, CH<sub>2</sub>), 28.4 (1 C, d,

 $J = 16.0, CH_2$ , 29.6 (1 C, CH<sub>2</sub>), 29.7 (1 C, d,  $J = 13.7, CH_2$ ), 31.1 (1 C, d, J = 16.7, CH<sub>2</sub>), 34.0 (1 C, d, J = 25.9, CH<sub>2</sub>), 34.9 (1 C, d, J = 10.6, CH), 37.1 (1 C, d, J = 12.9, CH), 68.8 (1 C, Cp–CH), 69.8 (5 C, Cp'-CH), 69.9 (5 C, Cp'-CH), 70.0 (1 C, Cp-CH), 71.1 (1 C, d, J = 3.8, Cp–CH), 71.6 (1 C, d, J = 4.6, Cp–CH), 74.8 (1 C, dd, J = 3.8, J = 8.4, Cp–CH), 75.8 (1 C, dd, J = 4.8, J = 8.4, Cp–CH), 77.6 (1 C, d, J = 12.2, Cp–Cq), 82.6 (1 C, d, J = 21.3, Cp-Cq, 91.0 (1 C, dd, J = 3.0 and 25.8, Cp-C), 92.7 (1 C, dd, J =3.0, J = 31.9, Cp–C), 127.1 (1 C, Ph–CH), 127.6 (2 C, d, J = 5.3, 2 Ph–CH), 128.0 (2 C, d, J = 8.4, 2 Ph–CH), 129.0 (1 C, Ph–CH), 132.4 (2 C, d, J = 17.5, 2 Ph–CH), 135.4 (2 C, d, J = 22.8, 2 Ph–CH), 140.2 (1 C, d, J = 7.6, Ph–C), 140.5 (1 C, d, J = 9.9, Ph–C). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>) δ –23.9 (PPh<sub>2</sub>), –31.1 (PCy<sub>2</sub>). MS (EI, 210 °C) m/z (rel%) = 667 (100, M<sup>+</sup> – Cy), 584 (18,  $M^+ - 2Cy$ ). HRMS found: 750.1952; calcd (for  $C_{44}H_{48}Fe_2P_2$ ): 750.1933.  $[\alpha]_{\lambda}^{20} = +166 (589 \text{ nm}), +201 (578 \text{ nm}), +416 (546 \text{ nm})$  $(c = 0.50 \text{ in CHCl}_3)$ . CD  $\Delta \varepsilon (\lambda_{max}) = +4.0 (300 \text{ nm}), -1.7 (353 \text{ nm}),$ +3.4 (481 nm) ( $c = 9.99 \times 10^{-4}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).

 $(S_p,S_p)$ -2,2"-Bis[bis(3,5-dimethylphenyl)phosphino]-1,1"-biferrocene 3. Compound 3 was synthesized from  $(S,S_p,S_p)$ -8 (1.414 g, 1.89 mmol, in 40 mL THF) and chloro-bis(3,5-dimethylphenyl)phosphine (680 mg, 2.46 mmol, in 10 mL THF). Reaction time: 2 h. Chromatography on alumina; elution with PE/Et<sub>2</sub>O/Et<sub>3</sub>N (100/4/1) afforded  $(S_p,S_p)$ -3 as a yellow solid (482 mg, 30%; in solution this compound is very sensitive to air).

Mp 190 °C (dec). Found: C 72.98, H 6.22.  $C_{52}H_{52}Fe_2P_2$  requires C 73.42, H 6.16%.

<sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  1.78 (12 H, s, 4 CH<sub>3</sub>), 2.34 (12 H, s, 4 CH<sub>3</sub>), 3.97 (2 H, m, 2 Cp–H), 4.00 (10 H, s, Cp'–H), 4.51 (2 H, m, 2 Cp–H), 4.90 (2 H, m, 2 Cp–H), 6.26 (4 H, d, J = 7.3, Ph-H), 6.45 (2 H, s, Ph-H), 7.03 (2 H, s, Ph-H), 7.20 (4 H, d, J = 8.3, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>)  $\delta$  20.9 (4 C, 4 CH<sub>3</sub>), 21.4 (4 C, 4 CH<sub>3</sub>), 69.8 (12 C, br s, 10 Cp'-CH + 2 Cp-CH), 70.7 (2 C, d, J = 4.5, 2 Cp–CH), 75.8 (2 C, dd, J = 4.6, J = 7.6, 2 Cp–CH), 79.6 (2 C, d, J = 11.4, 2 Cp–Cq), 91.3 (2 C, dd, J = 3.0, J = 29.7, 2 Cp–Cq), 128.4 (2 C, 2 Ph–CH), 129.2 (4 C, d, J = 16.7, 4 Ph–CH), 130.7 (2 C, 2 Ph–CH), 133.3 (4 C, d, J = 22.0, 4 Ph–CH), 136.5 (4 C, d, J = 5.3, 4 Ph–Cq); 137.2 (2 C, d, J = 8.4, 4 Ph–Cq), 139.6 (2 C, d, J = 9.1, 2 Ph–Cq), 139.8 (2 C, d, J = 7.8, 2 Ph–Cq). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta$  –22.4. MS (EI,  $100 \,^{\circ}\text{C}) \, m/z \, (\text{rel}\%) = 850 \, (8, \, \text{M}^+), \, 745 \, (14, \, \text{M}^+ - \text{C}_6\text{H}_3(\text{CH}_3)_2), \, 58$ (100). HRMS found: 850.2309; calcd (for C<sub>52</sub>H<sub>52</sub>Fe<sub>2</sub>P<sub>2</sub>): 850.2243.  $[\alpha]_{\lambda}^{20} = +126 (589 \text{ nm}), +145 (578 \text{ nm}), +272 (546 \text{ nm}) (c = 0.40)$ in CHCl<sub>3</sub>). CD  $\Delta \varepsilon$  ( $\lambda_{max}$ ) = +31.5 (251 nm), +2.5 (307 nm), -1.3 (352 nm), +2.1 (478 nm) ( $c = 8.80 \times 10^{-4} \text{ mol } L^{-1} \text{ in } CH_2Cl_2$ ).

 $(S_p, S_p)$ -2-Bis(3,5-dimethyl-4-methoxyphenyl)phosphino-2"-bis-[3,5-bis(trifluoromethyl) phenyl]phosphino-1,1"-biferrocene 4. Compound 4 was synthesized from  $(S, S_p, S_p)$ -9 (1.596 g, 1.97 mmol, in 40 mL THF) and chloro-bis[(3,5-bis(trifluoromethyl)phenyl]phosphine (1.26 g, 2.56 mmol, in 10 mL THF). Reaction time: 16 h. Chromatography on alumina; elution with PE/acetone (100/4) afforded  $(S_p, S_p)$ -4 as a yellow solid (931 mg, 42%).

Mp 124 °C. Found: C 57.52, H 3.95.  $C_{54}H_{44}F_{12}Fe_2O_2P_2$  requires C 57.57, H 3.94%. <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  1.75 (6 H, s, CH<sub>3</sub>), 2.29 (6 H, s, CH<sub>3</sub>), 3.38 (3 H, s, OCH<sub>3</sub>), 3.75 (3 H, s, OCH<sub>3</sub>), 3.85 (1 H, m, Cp–H), 3.96 (6 H, br s, 5 Cp'–H + 1 Cp–H), 4.05 (5 H, s, Cp'–H), 4.56 (1 H, m, Cp–H), 4.68 (1 H, m, Cp–H),

4.80 (1 H, m, Cp–H), 5.06 (1 H, m, Cp–H), 6.26 (2 H, d, J = 7.0, Ph–H), 7.06 (2 H, d, *J* = 5.6, Ph–H), 7.13 (2 H, d, *J* = 8.1, Ph–H), 7.43 (1 H, s, Ph–H), 7.91 (2 H, d, J = 7.0, Ph–H), 7.98 (s, 1 H, Ph–H).  ${}^{13}C{}^{1}H{}$  NMR (100.6 MHz; CDCl<sub>3</sub>)  $\delta$  15.6 (2 C, 2 CH<sub>3</sub>), 16.14 (2 C, 2 CH<sub>3</sub>), 59.1 (1 C, OCH<sub>3</sub>), 59.8 (1 C, OCH<sub>3</sub>), 69.8 (5 C, Cp'-CH), 69.9 (5 C, Cp'-CH), 70.0 (1 C, Cp-CH), 70.2 (1 C, d, J = 5.3, Cp–CH), 71.5 (1 C, Cp–CH), 71.9 (1 C, d, J = 4.6, Cp-CH), 76.0 (1 C, br m, Cp-Cq), 76.0 (1 C, br m, Cp-CH), 77.4 (1 C, d, J = 6.4, Cp–CH), 81.0 (1 C, d, J = 10.6, Cp–Cq), 89.9 (1 C, dd, J = 3.3, J = 30.2, Cp-Cq), 92.8 (1 C, dd, J = 3.6, J =34.8, Cp–Cq), 121.3 (1 C, m, Ph–CH), 122.8 (2 C, d, J = 271.5, 2 Ph–CF<sub>3</sub>), 123.0 (2 C, d, J = 271.5, 2 Ph–CF<sub>3</sub>), 123.4 (1 C, m, Ph-CH), 129.5 (2 C, d, J = 5.3, 2 Ph-Cq), 130.4 (2 C, d, J = 9.1, 2 Ph–Cq), 130.9 (2 C, m, 2 Ph–CH), 131.7 (2 C, d, J = 17.1, 2 Ph–CH), 131.8 (1 C, q, J = 33.5, Ph-meta [Ph–CF<sub>3</sub>]), 131.9 (1 C, q, J = 34.0, Ph-meta [Ph-CF<sub>3</sub>]), 133.8 (1 C, d, J = 9.1, Ph-Cq), 134.4 (1 C, d, J = 6.8, Ph–Cq), 134.8 (2 C, m, 2 Ph–CH), 135.7 (2 C, d, J = 22.8, 2 Ph–CH), 142.6 (2 C, d, J = 16.7, 2 Ph-Cq), 143.1 (2 C, d, J = 15.2, 2 Ph-Cq), 155.9 (1 C, Ph-C), 158.0 (1 C, Ph–Cq). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta$  –25.9, -19.1. <sup>19</sup>F{<sup>1</sup>H} NMR (282.2 MHz; CDCl<sub>3</sub>)  $\delta$  -62.5, -62.6. MS (FAB) m/z (rel%) = 1126 (M<sup>+</sup>). HRMS found: 1126.1327; calcd (for  $C_{54}H_{44}F_{12}Fe_2O_2P_2$ ): 1126.1324.  $[\alpha]_{\lambda}^{20} = +1.63$  (589 nm), +8.60 (578 nm), +62.8 (546 nm) (c = 0.43 in CHCl<sub>3</sub>). CD  $\Delta \varepsilon (\lambda_{max}) =$ +287 (243 nm), +283 (251 nm), +37.2 (285 nm), +27.3 (311 nm),  $-11.0 (352 \text{ nm}), -3.7 (423 \text{ nm}), +15.2 (481 \text{ nm}) (c = 9.90 \times 10^{-4})$ mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).

 $(S,R_p)$ -1-Iodo-2-[(4-methylphenyl)sulfinyl]-ferrocene 5. To a solution of diisopropylamine (7.54 g, 74.7 mmol) in THF (40 mL) was added dropwise n-BuLi (46.7 mL, 1.6 M in hexane, 74.7 mmol) at -25 °C. After stirring for an additional 30 min this solution was transferred within 100 min via a cannula into a stirred suspension of enantiopure (S)-(4-methylphenyl)sulfinyl-ferrocene (22 g, 67.9 mmol) in THF (400 mL) at -78 °C. During this procedure the sulfoxide dissolved, and stirring of the resulting red-orange solution was continued for another 30 min before a solution of iodine (22.7 g, 89.3 mmol) in THF (100 mL) was added dropwise. After stirring at the same temperature for additional 20 min, the reaction was quenched with water (50 mL). The aqueous phase was extracted with three portions of Et<sub>2</sub>O (50 mL each) and the combined organic layers were washed with aqueous sodium sulfite, water and brine. After drying with MgSO<sub>4</sub> the solvent was removed under reduced pressure. The crude product was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give 12.0 g of  $(S, R_p)$ -1 as yellow crystals. The solvents of the mother liquor were removed under reduced pressure and the residue purified by column chromatography on silica gel. Elution with PE/acetone/Et<sub>3</sub>N  $(50/10/1 \rightarrow 10/10/1)$  afforded additional 6.3 g of  $(S, R_p)$ -1. Total yield: 18.3 g (60%). Product 1 is light-sensitive in solution and it is therefore recommended to carry out chromatography with the exclusion of light.

Mp 148 °C. Found: C 45.54, H 3.35.  $C_{17}H_{15}FeIOS$  requires C 45.36, H 3.36%. <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  2.44 (3 H, s, CH<sub>3</sub>), 4.08 (1 H, m, Cp–H), 4.24 (5 H, s, Cp'–H), 4.35 (1 H, m, Cp–H), 4.66 (1 H, m, Cp–H), 7.34 (2 H, d, J = 8.1, Ph–H), 7.70 (2 H, d, J = 8.1, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>)  $\delta$  21.5 (1 C, CH<sub>3</sub>), 39.4 (1 C, Cp–Cq), 68.6 (1 C, Cp–CH), 70.9 (1 C, Cp–CH), 72.7 (5 C, Cp'–CH), 78.1 (1 C, Cp–CH), 94.0 (1 C,

Cp–Cq), 125.5 (2 C, 2 Ph–CH), 129.5 (2 C, 2 Ph–CH), 140.1 (1 C, Ph–C), 141.5 (1 C, Ph–C). MS (EI, 110 °C) m/z (rel%) = 450 (100, M<sup>+</sup>), 434 (9, M<sup>+</sup> – O), 324 (11, M<sup>+</sup> – I). HRMS found: 449.9251; calcd (for C<sub>17</sub>H<sub>15</sub>FeIOS): 449.9238. [ $\alpha$ ]<sub> $\lambda$ <sup>20</sup></sub> = –3.9 (589 nm), –4.0 (578 nm), –5.4 (546 nm) (c = 0.52 in CHCl<sub>3</sub>). CD  $\Delta \varepsilon$  ( $\lambda_{max}$ ) = –0.7 (258 nm), –3.9 (287 nm), +1.8 (304 nm), –0.5 (354 nm), –0.6 (427 nm) (c = 1.04 × 10<sup>-3</sup> mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).

 $(S,S,S_p,S_p)-2,2''$ -Bis[(4-methylphenyl)sulfinyl]-1,1''-biferrocene 6. A mixture of finely powdered  $(S,R_p)$ -5 (18.3 g, 40.7 mmol) and activated copper bronze (200 g) was heated under Ar to 130 °C for 16 h. The mixture was cooled to r.t. and was washed repeatedly with CHCl<sub>3</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel. Elution with PE/acetone/Et<sub>3</sub>N (10/10/1) resulted in 4.9 g of starting material 5 (first band), and biferrocene  $(S,S,S_p,S_p)$ -6 (8.5 g, 65%; 88% based on recovered 1) as a yellow solid.

Mp 182 °C (dec). Found: C 63.07, H 4.69.  $C_{34}H_{30}Fe_2O_2S_2$  requires C 63.17, H 4.68%.

<sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  2.44 (6 H, s, CH<sub>3</sub>), 4.01 (2 H, m, Cp–H), 4.37 (12 H, br s, 10 Cp'–H + 2 Cp–H), 5.14 (2 H, m, Cp–H), 7.31 (4 H, d, J = 7.9, Ph–H), 7.68 (4 H, d, J = 7.9, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>)  $\delta$  21.5 (2 C, 2 CH<sub>3</sub>), 68.96 (2 C, 2 Cp–CH), 68.97 (2 C, 2 Cp–CH), 71.2 (10 C, Cp'–CH), 76.08 (2 C, 2 Cp–CH), 84.60 (2 C, 2 Cp–Cq), 92.64 (2 C, 2 Cp–Cq), 125.64 (4 C, 4 Ph–CH), 129.32 (4 C, 4 Ph–CH), 140.02 (2 C, 2 Ph–Cq), 141.27 (2 C, 2 Ph–Cq). MS (EI, 200 °C) m/z (rel%) = 646 (48, M<sup>+</sup>), 630 (100, M<sup>+</sup> – O), 614 (38, M<sup>+</sup> – 2O), 581 (48, M<sup>+</sup> – Cp). HRMS found: 646.0342; calc. (for C<sub>34</sub>H<sub>30</sub>Fe<sub>2</sub>O<sub>2</sub>S<sub>2</sub>): 646.0388. [ $\alpha$ ]<sub> $\lambda$ <sup>20</sup></sub> = –393 (589 nm), –425 (578 nm), –574 (546 nm) (c = 0.50 in CHCl<sub>3</sub>). CD  $\Delta \epsilon$  ( $\lambda_{max}$ ) = +16.0 (258 nm), +9.6 (283 nm), –1.0 (364 nm), –2.0 (429 nm), +1.2 (485 nm) (c = 9.59 × 10<sup>-4</sup> mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>).

# General procedure for the preparation of $(S, S_p, S_p)$ -2diarylphosphino-2"-(4-methylphenyl)sulfinyl-1,1"-biferrocene 7–9

To a solution of biferrocene derivative  $(S,S,S_p,S_p)$ -6 (1.94 g, 3 mmol) in THF (360 mL) was added dropwise *t*-BuLi (2.1 mL, 1.7 M solution in pentane, 3.6 mmol) under Ar at -78 °C. Upon addition of *t*-BuLi the colour of the reaction mixture turned red. After stirring for an additional 5 min, the appropriate chlorodiarylphosphine (4.5 mmol) was added at the same temperature. The mixture was allowed to warm up to r.t. and stirring was continued for 16 h. After quenching with an saturated aqueous NaHCO<sub>3</sub>, the organic phase was separated, washed with water and brine and was dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified on silica gel.

 $(S, S_p, S_p)$ -2-Diphenylphosphino-2"-(4-methylphenyl)sulfinyl-1,1"-biferrocene 7. Lithiated 6 (3 mmol) was reacted with Ph<sub>2</sub>PCl (995 mg, 4.5 mmol). Chromatography: elution with PE/acetone/Et<sub>3</sub>N (100/20/1  $\rightarrow$  10/10/1) afforded ( $S, S_p, S_p$ )-7 as a yellow solid (1.24 g, 60%).

Mp 210 °C (dec). <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  2.45 (3 H, s, CH<sub>3</sub>), 3.79 (1 H, m, Cp–H), 3.89 (1 H, m, Cp–H), 4.18 (5 H, s, Cp'–H), 4.26 (1 H, m, Cp–H), 4.27 (5 H, s, Cp'–H), 4.48 (1 H, m, Cp–H), 4.77 (1 H, m, Cp–H), 5.06 (1 H, m, Cp–H), 7.06–7.11 (2 H, m, Ph–H), 7.13–7.20 (3 H, m, Ph–H), 7.33 (2 H, d, J = 7.9, Ph–H), 7.39–7.44 (3 H, m, Ph–H), 7.58–7.63 (2 H, m, Ph–H),

7.77 (2 H, d, J = 7.9, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>) δ 21.5 (1 C, CH<sub>3</sub>), 67.6 (1 C, Cp–CH), 68.7 (1 C, Cp–CH), 70.1 (1 C, Cp-CH), 70.3 (5 C, Cp'-CH), 70.8 (5 C, Cp'-CH), 72.2 (1 C, d, J = 4.6, Cp–CH), 74.8 (1 C, d, J = 9.2, Cp–CH), 75.0 (1 C, d, J = 3.8, Cp-CH), 77.6 (1 C, d, J = 11.4, Cp-Cq), 87.5 (1 C, Cp–Cq), 88.2 (1 C, d, J = 25.1, Cp–Cq), 93.5 (1 C, Cp–Cq), 125.9 (2 C, 2 Ph–CH), 127.3 (1 C, Ph–CH), 127.9 (2 C, d, J = 5.3, 2 Ph-CH), 128.1 (2 C, d, J = 8.4, 2 Ph-CH), 129.2 (1 C, Ph-CH), 129.3 (2 C, 2 Ph–CH), 132.1 (2 C, d, J = 17.5, 2 Ph–CH), 135.6 (2 C, d, J = 22.0, 2 Ph–CH), 138.4 (1 C, d, J = 10.6, Ph–Cq), 139.5 (1 C, d, J = 9.9, Ph-Cq), 140.7 (1 C, Ph-Cq), 141.4 (1 C, Ph–Cq). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta$  –19.34. MS (FAB,  $120^{\circ}C$ ) m/z (rel%) = 692 (100, M<sup>+</sup>). HRMS found: 692.0671; calcd (for  $C_{39}H_{33}Fe_2OPS$ ): 692.0690.  $[\alpha]_{\lambda}^{20} = +60.6$  (589 nm), +77.6 (578 nm), +188.6 (546 nm) (c = 0.50 in CHCl<sub>3</sub>). CD  $\Delta \varepsilon (\lambda_{max}) =$ +29.9 (251 nm), +5.6 (310 nm), -1.7 (354 nm), +4.5 (476 nm) (c = $1.04 \times 10^{-3} \text{ mol } L^{-1}, CH_2Cl_2$ ).

 $(S, S_p, S_p)$ -2-Bis(3,5-dimethylphenyl)phosphino-2"-(4-methylphenyl)sulfinyl-biferrocene 8. Lithiated 6 (3 mmol) was reacted with chloro-bis(3,5-dimethylphenyl)phosphine (1.24 g, 4.5 mmol) in THF (20 mL). Chromatography: elution with PE/acetone/Et<sub>3</sub>N (120/20/1) afforded  $(S, S_p, S_p)$ -8 as a yellow solid (1.79 g, 80%).

Mp 139 °C. <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>) δ 2.19 (6 H, s, CH<sub>3</sub>), 2.35 (6 H, s, CH<sub>3</sub>), 2.45 (3 H, s, CH<sub>3</sub>), 3.77 (1 H, m, Cp-H), 3.92 (1 H, m, Cp-H), 4.18 (5 H, s, Cp'-H), 4.23 (1 H, m, Cp-H), 4.25 (5 H, s, Cp'-H), 4.47 (1 H, m, Cp-H), 4.69 (1 H, m, Cp-H), 5.04 (1 H, m, Cp–H), 6.71 (2 H, d, *J* = 7.4, Ph–H), 6.78 (1 H, s, Ph–H), 7.05 (1 H, s, Ph–H), 7.23 (2 H, d, J = 8.3, Ph–H), 7.34 (2 H, d, J = 8.1, Ph–H), 7.79 (2 H, d, J = 8.1, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>) δ 21.2 (2 C, 2 CH<sub>3</sub>), 21.4 (2 C, 2 CH<sub>3</sub>), 21.5 (1 C, CH<sub>3</sub>), 67.4 (1 C, Cp–CH), 68.6 (1 C, Cp–CH), 69.9 (1 C, Cp–CH), 70.4 (5 C, Cp'–CH), 70.9 (5 C, d, J = 1.5, 5 Cp'–CH), 72.5 (1 C, d, J = 4.6, Cp–CH), 74.8 (1 C, d, J = 9.1, Cp–CH), 74.9 (1 C, d, J = 3.8, Cp–CH), 77.6 (1 C, d, J = 12.9, Cp–Cq), 87.9 (1 C, Cp-Cq), 88.2 (1 C, d, J = 25.1, Cp-Cq), 93.4 (1 C, Cp-Cq),126.0 (2 C, 2 Ph–CH), 129.3 (2 C, 2 Ph–CH), 129.3 (1 C, Ph–CH), 129.7 (2 C, d, J = 17.5, 2 Ph–CH), 130.8 (1 C, Ph–CH), 133.3 (2 C, d, J = 22.1, 2 Ph-CH), 137.3, 137.3, 137.4 (4 C, 4 Ph-C), 138.3 (1 C, d, J = 9.1, Ph–Cq), 139.4 (1 C, d, J = 9.9, Ph–Cq), 140.9 (1 C, Ph-Cq), 141.5 (1 C, Ph-Cq). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta$  -20.0. MS (EI, 140 °C) m/z (rel%) = 748 (89, M<sup>+</sup>), 733 (47, M<sup>+</sup> – CH<sub>3</sub>), 683 (100, M<sup>+</sup> – Cp). HRMS found: 748.1358; calcd (for C<sub>43</sub>H<sub>41</sub>Fe<sub>2</sub>OPS): 748.1314.  $[\alpha]_{\lambda}^{20} = -27.0 (589 \text{ nm}), -20.6$ (578 nm), +32.2 (546 nm) (c = 0.52 in CHCl<sub>3</sub>). CD  $\Delta \varepsilon (\lambda_{max}) =$ +27.2 (252 nm), -0.9 (292 nm), +5.1 (308 nm), -1.2 (355 nm),  $+3.16 (477 \text{ nm}) (c = 8.82 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ in } \text{CH}_2\text{Cl}_2).$ 

 $(S, S_p, S_p)$ -2-Bis(3,5-dimethyl-4-methoxyphenyl)phosphino-2"-(4-methylphenyl)sulfinyl-1,1"-biferrocene 9. Lithiated 6 (3 mmol) was reacted with chloro-bis(3,5-dimethylphenyl-4methoxyphenyl)phosphine (1.52 g, 4.5 mmol) in THF (20 mL). Chromatography: elution with PE/acetone/Et<sub>3</sub>N (120/20/1) afforded  $(S, S_p, S_p)$ -9 as a yellow solid (1.61 g, 66%).

Mp 100 °C. <sup>1</sup>H NMR (400.1 MHz; CDCl<sub>3</sub>)  $\delta$  2.16 (6 H, s, CH<sub>3</sub>), 2.32 (6 H, s, CH<sub>3</sub>), 2.46 (3 H, s, CH<sub>3</sub>), 3.66 (3 H, s, OCH<sub>3</sub>), 3.75 (1 H, m, Cp–CH), 3.78 (3 H, s, OCH<sub>3</sub>), 3.93 (1 H, m, Cp–H), 4.17 (5 H, s, Cp'–H), 4.23 (1 H, m, Cp–H), 4.25 (5 H, s, Cp'–H), 4.46 (1 H, m, Cp–H), 4.68 (1 H, m, Cp–H), 5.02 (1 H, m, Cp–H), 6.72 (2 H, d, J = 7.3, Ph-H), 7.25 (2 H, d, J = 6.3, Ph-H), 7.34 (2 H, 100)d, J = 8.1, Ph–H), 7.78 (2 H, d, J = 8.1, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz; CDCl<sub>3</sub>) δ 16.0 (2 C, 2 CH<sub>3</sub>), 16.2 (2 C, 2 CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 59.5 (1 C, OCH<sub>3</sub>), 59.8 (1 C, OCH<sub>3</sub>), 67.3 (1 C, Cp-CH), 68.5 (1 C, Cp-CH), 69.9 (1 C, Cp-CH), 70.3 (5 C, Cp'-CH), 70.9 (5 C, Cp'-CH), 72.4 (1 C, d, J = 3.8, Cp-CH), 74.8, 74.8, 74.9 (2 C, 10.4)2 Cp–CH), 78.3 (1 C, d, J = 12.2, Cp–Cq), 87.9 (1 C, d, J = 1.5, Cp–Cq), 88.1 (1 C, d, J = 25.1, Cp–Cq), 93.5 (1 C, Cp–Cq), 126.0 (2 C, 2 Ph–CH), 129.3 (2 C, 2 Ph–CH), 130.3 (2 C, d, J = 3.8, 2 Ph–Cq), 130.4 (2 C, d, J = 6.1, 2 Ph–Cq), 132.5 (2 C, d, J = 18.2, 2 Ph–CH), 133.3 (1 C, d, J = 9.1, Ph–Cq), 134.3 (1 C, d, J = 8.4, Ph– Cq), 136.0 (2 C, d, J = 22.8, 2 Ph–CH), 140.9 (1 C, Ph–Cq), 141.5 (1 C, Ph–Cq), 156.6 (1 C, Ph–Cq), 158.0 (1 C, Ph–Cq). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta$  –21.5. MS (EI, 120 °C) m/z (rel%) = 808 (100, M<sup>+</sup>), 792 (53, M<sup>+</sup> – O), 776 (13, M<sup>+</sup> – 2O), 760 (11, M<sup>+</sup> - SO), 743 (98, M<sup>+</sup> - Cp). HRMS found: 808.1596; calcd (for  $C_{45}H_{45}Fe_2O_3PS$ ): 808.1528.  $[\alpha]_{\lambda}^{20} = -14.4 (589 \text{ nm}), -8.0 (578 \text{ nm}),$  $+46.0 (546 \text{ nm}) (c = 0.50, \text{CHCl}_3). \text{CD} \Delta \varepsilon (\lambda_{\text{max}}) = +21.0 (252 \text{ nm}),$ -0.42 (291 nm), +5.3 (305 nm), -1.1 (355 nm), +2.8 (477 nm) (c = $9.65 \times 10^{-4} \text{ mol } L^{-1}, CH_2Cl_2).$ 

# General procedure for the synthesis of the dichloropalladium complexes $(S_p, S_p)$ - [PdCl<sub>2</sub>(1)] and $(S_p, S_p)$ -[PdCl<sub>2</sub>(4)] 10, 11

Ligand 1 or 4 (0.1 mmol) in dry benzene (2 mL) was degassed and transferred into a degassed solution of  $[PdCl_2(CH_3CN)_2]$  (24.6 mg, 0.095 mmol) in benzene (2 mL). The resulting mixture was stirred under Ar for 16 h at r.t. The precipitate was filtered off and dried under vacuum to give complex  $[PdCl_2(1)]$  or  $[PdCl_2(4)]$ .

Dichloro-{ $(S_p, S_p)$ -[2,2"-bis(diphenylphosphino- $\kappa P$ )-1,1"-biferrocene]} palladium(II) 10.  $(S_n, S_n)$ -[PdCl<sub>2</sub>(1)] (73 mg, 80%), red prisms (from CHCl<sub>3</sub>/EtOH). Mp 230 °C (dec). NMR: at 240 K two conformers in a 5:1 ratio are observed, only the resonances of the major conformer are given. <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 240 K) δ 3.47 (10 H, s, Cp'-H), 3.55 (2 H, m, Cp-H), 4.41 (2 H, m, Cp-H), 4.79 (2 H, m, Cp-H), 6.80 (2 H, br s, Ph-H), 7.23-7.99 (16 H, m, Ph–H), 8.25 (2 H, br s, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (62.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 240 K) δ 70.0 (2 C, 2 Cp–CH), 70.6 (2 C, d, J = 36.1, 2 Cp–C), 70.7 (10 C, Cp'–CH), 72.3 (2 C, 2 Cp–CH), 78.7 (2 C, 2 Cp-CH), 85.3 (2 C, m, 2 Cp-C), 127.1 (4 C, m, 4 Ph-CH), 128.1 (2 C, m, 2 Ph-C), 129.0 (4 C, m, 4 Ph-CH), 129.9 (2 C, 2 Ph-CH), 132.2 (2 C, 2 Ph-CH), 133.2 (4 C, br m, 4 Ph-CH), 134.8 (2 C, dd, J = 3.7, J = 69.4, 2 Ph–C); 136.6 (4 C, br m, 4 Ph–CH).  ${}^{31}P{}^{1}H$  NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300K)  $\delta$  27.8 (br s).  ${}^{31}P{}^{1}H$ NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 258 K) δ 22.3 (major), 29.0 (minor). MS (EI, 300 °C) m/z (rel%) = 738 (M<sup>+</sup> – PdCl<sub>2</sub>).  $[\alpha]_{\lambda}^{20} = +658$ (589 nm), +789 (578 nm), +1141 (546 nm) (c = 0.046 in CH<sub>2</sub>Cl<sub>2</sub>). CD  $\Delta \varepsilon$  ( $\lambda_{max}$ ) = -18.5 (240 nm), +43.2 (281 nm), +6.1 (331 nm), +6.52 (511 nm) ( $c = 1.00 \times 10^{-4} \text{ mol } L^{-1} \text{ in } CH_2Cl_2$ ).

**Dichloro-** {( $S_p$ , $S_p$ )-[2-bis(3,5-dimethyl-4-methoxyphenyl)phosphino-κP-2"-bis[3,5-bis (trifluoromethyl) phenyl] phosphino-κP-1,1"-biferrocene]} palladium(II) 11. ( $S_p$ , $S_p$ )-[PdCl<sub>2</sub>(4)] (110 mg, 84%), red needles (from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O). Mp 210 °C (dec). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 260 K)  $\delta$  2.25 (6 H, s, CH<sub>3</sub> (A)), 2.31 (6 H, s, CH<sub>3</sub> (B)), 3.23 (1 H, m, Cp–H3), 3.56 (1 H, m, Cp–H3"), 3.66 (3 H, s, OCH<sub>3</sub> (A)), 3.76 (3 H, s, OCH<sub>3</sub> (B)), 3.97 (5 H, s, Cp'–H), 4.08 (5 H, s, Cp<sup>\*\*</sup>–H), 4.35 (1 H, m, Cp–H4"), 4.56 (1 H, m, Cp–H4), 4.90 (1 H, m, Cp–H5"), 5.08 (1 H, m, Cp–H5), 7.34–7.48 (2 H, br

d, Ar-H-*ortho* (B)), 7.57 (2 H, d, J = 13.0, Ar-H-*ortho* (A)), 7.95 (1 H, s, Ar-H-para (C)), 8.08 (1 H, s, Ar-H-para (D)), 8.21 (2 H, d, J = 11.2, Ar-H-ortho (D)), 8.42 (2 H, d, J = 11.6, Ar-H-ortho (C)). A, B: aryl rings 3,5-Me<sub>2</sub>-4-MeO-C<sub>6</sub>H<sub>2</sub>; C, D: aryl rings 3,5- $(CF_3)_2$ -C<sub>6</sub>H<sub>3</sub>. <sup>13</sup>C{<sup>1</sup>H} NMR (62.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 260 K)  $\delta$  15.9 (2 C, 2 CH<sub>3</sub> (A)), 16.1 (2 C, 2 CH<sub>3</sub> (B)), 59.7 (1 C, OCH<sub>3</sub>), 59.8 (1 C, OCH<sub>3</sub>), 70.4 (1 C, d, *J* = 8.7, Cp–C4"), 70.8 (1 C, d, *J* = 9.6, Cp-C4); 71.1 (5 C, Cp'''-C), 71.3 (5 C, Cp'-C), 71.7 (1 C, Cp-C), 74.8 (1 C, d, J = 12.3, Cp–C3), 75.2 (1 C, Cp–Cq), 76.0 (1 C, d, J = 11.0, Cp-C3"), 76.9 (1 C, Cp-C5"), 77.0 (1 C, Cp-C5), 85.3 (1 C, d, J = 10.5, Cp–Cq), 87.8 (1 C, d, J = 12.3, Cp–Cq), 121.8 (1 C, d, J = 67.6, MeO-Ph-C-meta), 122.8 (2 C, q, J = 272.2),2 Ph– $CF_3$ ), 122.9 (2 C, q, J = 272.2, 2 Ph– $CF_3$ ), 124.1 (1 C, d, J = 59.8, MeO-Ph-C-meta), 125.0-125.4 (2 C, br m, 2 CF<sub>3</sub>-Ph-C-para (C + D)), 129.7-132.6 (8 C, Ph-Cq), 133.5 (2 C, br m, 2 CF<sub>3</sub>-Ph-C-*ortho* (C)), 134.3 (1 C, d, *J* = 12.8, CH<sub>3</sub>O-Ph-C-*ortho* (B)), 134.6 (2 C, br m, 2 CF<sub>3</sub>-Ph-C-ortho (D)), 135.8 (2 C, br m,  $2 \text{ CF}_3$ -Ph-C-*ortho* (C)), 159.3 (1 C, d, J = 3.8, MeO-Ph-C-*para* (A)), 159.6 (1 C, d, J = 3.8, MeO-Ph-C-para (B)). A, B: aryl rings 3,5-Me-4-MeO-C<sub>6</sub>H<sub>2</sub>; C, D: aryl rings 3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 300K) δ 21.5 [s, P-(3,5-Me<sub>2</sub>-4-MeO- $C_6H_2_2$ ], 24.2 [s, P-(3,5-(CF\_3)\_2-C\_6H\_3)\_2]. [ $\alpha$ ]<sub> $\lambda$ </sub><sup>20</sup> = +1118 (589 nm), +1287 (578 nm), +1741 (546 nm) (c = 0.043 in CHCl<sub>3</sub>). CD  $\Delta \varepsilon$  $(\lambda_{\rm max}) = -2.2$  (248 nm), +48.6 (279 nm), +6.3 (362 nm), +8.9  $(459 \text{ nm}), +13.9 (518 \text{ nm}) (c = 1.00 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ in } \text{CH}_2\text{Cl}_2).$ 

**Bis(pentafluorophenyl) - {** $(S_p, S_p)$ **- [2, 2" - bis (diphenylphosphino-** $\kappa P$ **)-1,1"-biferrocene] palladium(II) 12.** Ligand  $(S_p, S_p)$ **-1** (50 mg, 0.068 mmol) was added to a solution of [Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(COD)] (37.1 mg, 0.068 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the mixture was heated under reflux for 10 h. After cooling to r.t. the solvent was removed under reduced pressure. The resulting solid was washed with pentane (3×5 mL) and dried under vacuum. The final product was obtained as an orange-red solid that was soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> (64 mg, 0.060 mmol, 88%).

Found: C 55.7, H 3.5. C<sub>56</sub>H<sub>36</sub>P<sub>2</sub>Fe<sub>2</sub>F<sub>10</sub>Pd·1.5H<sub>2</sub>O requires C 55.8, H 3.3%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 293 K) δ 3.8 (10 H, s, Cp–H), 4.02 (2 H, br s, Cp–H3), 4.34 (2 H, br t, Cp–H4), 4.65 (2 H, br s, Cp-H5), 7.2 (4 H, m, Ph-H), 7.32 (2 H, br t, Ph-H), 7.4 (6 H, br s, Ph-H), 7.5 (4 H, br s, Ph-H), 8.08 (4 H, br s, Ph–H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  69.8 (2 C, br s, Cp-CH), 71.0 (10 C, br s, Cp-CH), 73.2 (2 C, br s, Cp-CH), 76.5 (2 C, br s, Cp-CH), 127.3 (4C, m, Ph-C-meta), 128.8 (4C, m, Ph-C-meta), 130.0 (2C, s, Ph-C-para), 131.7 (2C, s, Ph-Cpara), 133.0 (4C, br s, Ph-C-ortho), 135.7 (4C, br s, Ph-C-ortho). Signals for quaternary carbons have not been observed.  ${}^{31}P{}^{1}H{}$ NMR (161.9 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  13.71 (2 P, s). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>, 293 K) δ-164.1 (2 F, m, F-meta), -163.0 (4 F, m, 2 F-meta + 2 F-para), -116.2 (2 F, m, F-ortho); -112.5 (2F, m, F-ortho). Assignment based on COSY <sup>19</sup>F-<sup>19</sup>F. MS (FAB+)  $m/z = 1115 [M - (C_5H_5) + 2 \cdot H]^+, 1011 [M - (C_6F_5)]^+, 844 [M - (C_6F_5)]^+, 844$  $(C_6F_5) - (C_6F_5)^+$ .

**Chloro-**{ $(S_p, S_p)$ -[2, 2"-bis(diphenylphosphino- $\kappa P$ )-1, 1"-biferrocene]-( $\eta^6$ -*p*-cymene)} ruthenium(1) hexafluorophosphate 13. Diphosphine ( $S_p, S_p$ )-1 (50 mg, 0.068 mmol) and AgPF<sub>6</sub> (17.1 mg, 0.068 mmol) were added to a solution of [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (20.7 mg, 0.034 mmol) in THF (30 mL) and the mixture was heated under reflux for 3 h. The resulting suspension was concentrated to dryness under reduced pressure and the solid residue was treated twice with EtOH (10 mL each). The orange-yellow solution was filtered through Celite and after removal of the solvent under reduced pressure  $[RuCl(p-cymene)((S_p,S_p)-1)]PF_6$  (68 mg, 87%, soluble in acetone) was obtained as an orange solid.

Found: C 55.86, H 4.47. C<sub>54</sub>H<sub>50</sub>ClF<sub>6</sub>Fe<sub>2</sub>P<sub>3</sub>Ru requires C 56.2, H 4.38%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K) δ 0.78 (3 H, s, H15), 1.31 (3 H, d,  $J_{H-H} = 6.9$ , H13), 1.4 (3 H, d,  $J_{H-H} = 7.1$ , H14), 2.92 (1 H, spt,  $J_{H-H} = 7.0$ , H12), 3.48 (1 H, m, Cp–H3), 3.63 (5 H, s, Cp'''-H), 3.91 (5 H, s, Cp'-H); 4.13 (1 H, m, Cp-H3"), 4.46 (1 H, t,  $J_{H-H} = 2.3$ , Cp–H4), 4.53 (1 H, t,  $J_{H-H} = 2.7$ , Cp–H4"), 5.25 (1 H, d, J<sub>H-H</sub> = 6.3, H8), 5.30 (1 H, m, Cp–H5), 5.34 (1 H, m, Cp-H5"), 5.96 (2 H, br s, H10 + H11), 6.18 (1 H, m, H7), 6.78 (2 H, br t, Ph–H), 7.13 (2 H, t,  $J_{H-H} = 7.1$ , Ph–H), 7.34 (2 H, t,  $J_{\text{H-H}} = 7.3$ , Ph–H), 7.52 (2 H, t,  $J_{\text{H-H}} = 6.9$ , Ph–H), 7.68 (8 H, m, Ph-H), 8.08 (2 H, br t, Ph-H), 8.54 (2 H, br s, Ph-H). Assignment of signal sets Cp-H/C1-5, Cp'-H/C (ferrocene unit 1) and Cp-H/C1"-5", Cp"'-H/C (ferrocene unit 2) interchangeable. Some of the signals are broad.  ${}^{13}C{}^{1}H$  NMR (100.6 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K) δ 13.4 (1 C, s, C15), 20.3 (1 C, s, C13), 21.9 (1 C, s, C14), 32.0 (1 C, s, C12), 68.3 (1 C, d, J = 8.3, Cp-C4), 70.1 (1 C, d, J = 5.9, Cp-C4"), 71.4 (5 C, s, Cp'-C), 72.4 (5 C, s, Cp"-C), 75.2 (1 C, d, J = 7.9, Cp–C3), 76.0 (1 C, d, J = 7.6, Cp–C5"), 76.8 (1 C, d, J = 4.3, Cp–C3"), 77.0 (1 C, s, Cp–C1"), 77.3 (1 C, s, Cp–C1), 77.4 (1 C, d, J = 9.2, Cp–C5), 77.8 (1 C, s, C6), 88.0 (1 C, d, J = 12.7, Cp-C2''), 88.3 (1 C, d, J = 10.4, C10), 89.5(1 C, d, J = 10.3, C8), 90.0 (1 C, d, J = 15.9, Cp–C2), 96.7 (1 C, d, J = 2.7, C7), 97.2 (1 C, s, C9), 102.6 (1 C, d, J = 4.2, C11), 127.8 (2 C, d, J = 10.7, Ph-C-meta), 128.0 (2 C, d, J = 9.5, Ph-C-meta), 128.0 (2 C, d, J = 10.3, Ph–C-meta), 128.2 (2 C, d, J = 10.3, Ph–C-meta), 130.0 (1 C, d, J = 2.5, Ph–C-para), 131.4 (1 C, d, J = 2.6, Ph-C-para), 131.6 (2 C, pseudo t, Ph-C-para), 133.1 (1 C, dd, J = 52.3, J = 2.5, Ph-C-ipso), 133.1 (2 C, d, J = 9.3)Ph–C-ortho), 135.3 (2 C, d, J = 10.8, Ph–C-ortho), 136.2 (1 C, dd, J = 51.3, J = 2.6, Ph–C-ipso), 136.7 (4 C, br m, Ph–C-ortho), 138.3 (1 C, dd, J = 50.3, J = 2.2, Ph-C-ipso), 140.0 (1 C, d, J = 51.6)Ph-C-*ipso*). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K) δ -143.2 (spt,  $J_{\rm FP} = 707.5$ ,  $PF_6^-$ ), 27.8 (d,  $J_{\rm PP} = 58.2$ ), 33.2 (d,  $J_{\rm PP} =$ 58.2). <sup>19</sup>F NMR (376.3 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  -73.0 (d,  $J_{\rm FP} = 707.5, \rm PF_6^{-}$ ). IR (KBr, cm<sup>-1</sup>): 1488.1, 1443.2, 1321.8, 1137.4,  $1091.3, 840.4 (PF_6), 707.25, 562.9, 496.9, 376. MS (FAB+) m/z =$  $1009 [M - (PF_6)]^+, 875 [M - (PF_6) - (C_{10}H_{14})]^+.$ 

Iodo-{ $(S_p, S_p)$ -[2,2"-bis(diphenylphosphino-κ*P*)-1,1"-biferrocene]-(η<sup>6</sup>-*p*-cymene)} ruthenium(1) hexafluorophosphate 14. Complex 14 was prepared as described for 13.  $(S_p, S_p)$ -1 (50 mg, 0.068 mmol); AgPF<sub>6</sub> (17.1 mg, 0.068 mmol); [RuI<sub>2</sub>(*p*-cymene)]<sub>2</sub> (33 mg, 0.034 mmol) in THF (35 mL). Product [RuI(*p*-cymene)( $(S_p, S_p)$ -1)]PF<sub>6</sub> (71 mg, 83%, soluble in acetone) was obtained as a deep-red solid.

Found: C 52.4, H 4.2.  $C_{34}H_{50}F_6Fe_2IP_3Ru$  requires: C 52.1, H 4%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  0.55 (3 H, s, H15), 1.40 (3 H, d,  $J_{H-H} = 7.0$ , H14), 1.44 (3 H, d,  $J_{H-H} = 7.0$ , H13), 3.15 (1 H, m, Cp–H3), 3.62 (5 H, s, Cp<sup>'''</sup>–H), 3.63 (1 H, spt,  $J_{H-H} = 7.0$ , H12), 3.98 (5 H, s, Cp'–H), 4.31 (1 H, m, Cp–3''), 4.38 (1 H, td,  $J_{H-H} = 2.6$ ,  $J_{H-P} = 1.1$ , Cp–H4), 4.6 (1 H, t,  $J_{H-H} = 2.6$ , Cp–H4''), 5.30 (1 H, m, Cp–H5), 5.38 (1 H, m, Cp–H5''), 5.59 (1 H, dd,  $J_{H-H} = 6.4$ ,  $J_{H-P} = 1.4$ , H8), 5.77 (2 H, br t, H11), 6.1 (2 H, br dd,  $J_{H-H} = 6.4$ ,  $J_{H-P} = 1.4$ , H10), 6.34 (1 H,  $J_{H-H} = 4.9$ , br t, H7), 6.55 (2 H, br s, Ph–H), 6.95 (2 H, m, Ph–H), 7.22 (2 H, br td, Ph–H), 7.6

(8 H, m, Ph-H), 7.75 (2 H, m, Ph-H), 8.4 (2 H, br s, Ph-H), 8.52 (2 H, br s, Ph-H). Assignment of signal sets Cp-H/C1-5, Cp'-H/C (ferrocene unit 1) and Cp-H/C1"-5", Cp""-H/C (ferrocene unit 2) interchangeable. Some of the signals are broad.  ${}^{13}C{}^{1}H{}$ NMR (100.6 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K): δ 12.7 (1 C, s, C15), 20.6 (1 C, s, C13), 23.2 (1 C, s, C14), 33.4 (1 C, s, C12), 67.9 (1 C, d, J = 9.2, Cp–C4), 70.3 (1 C, d, *J* = 6.3, Cp–C4"), 71.2 (5 C, s, Cp'–C), 72.8 (5 C, s, Cp<sup>'''</sup>-C), 74.2 (1 C, d, J = 7.8, Cp-C3), 76.4 (1 C, d, J = 8, Cp–C5"), 77.7 (1 C, dd, J = 40.6, J = 0.8, Cp–C1"), 78.4 (1 C, d, J = 8.8, Cp–C5), 78.8 (1 C, d, J = 4.2, Cp–C3"), 85.4 (1 C, dd, J = 54.0, J = 1.0, Cp–C1), 87.4 (1 C, d, J = 10.1, C10), 89.0 (1 C, dd, J = 11.6, J = 1.1, Cp–C2"), 89.4 (1 C, d, J = 9.7, C8), 90.4 (1 C, d, J = 16.2, Cp-C2), 96.5 (1 C, d, J = 2.9, C7), 99.6 (1 C, s, C6), 100.7 (1 C, s, C9), 103.4 (1 C, d, J = 3.8, C11), 127.4 (2 C, d, J = 10.5, Ph–C-meta), 127.7 (2 C, d, J = 9.6, Ph–C-meta), 128.2 (2 C, d, J = 10.3, Ph–C-meta), 128.2 (2 C, d, J = 9.9, Ph-C-meta), 129.5 (1 C, d, J = 2.5, Ph-C-para), 131.4 (1 C, d, J = 2.7, Ph-C-para), 131.5 (1 C, d, J = 2.6, Ph-C-para),132.1 (1 C, d, J = 2.5, Ph–C-para), 132.4 (2 C, br m, Ph–C-ortho), 133.2 (2 C, d, J = 8.8, Ph–C-ortho), 133.3 (1 C, dd, J = 51.7, J = 3.0, Ph–C-*ipso*), 134.1 (1 C, dd, J = 50.8, J = 3.0, Ph–C-*ipso*), 135.2 (2 C, br m, Ph–C-ortho), 138.1 (1 C, dd, J = 52.1, J = 2.5, Ph-C-*ipso*), 138.6 (2 C, br m, Ph-C-*ortho*), 142.3 (1 C, d, J =50.2, Ph–C-ipso). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  -143.2 (spt,  $J_{\rm FP} = 707.6$ ,  $PF_6^{-}$ ), 27.5 (d,  $J_{\rm PP} = 53.8$ ), 29.3 (d,  $J_{\rm PP} = 53.8$ ). <sup>19</sup>F NMR (376.3 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  -73.0 (d,  $J_{\rm FP} = 707.6$ ,  $\rm PF_6^{-}$ ). IR (cm<sup>-1</sup>): 1482, 1436, 1409, 1092, 840.6  $(PF_6)$ , 747.8, 701, 557  $(PF_6)$ , 523, 491, 475, 447. MS (FAB+) $m/z = 1101 [M - (PF_6)]^+, 967 [M - (PF_6) - (C_{10}H_{14})]^+.$ 

**Chloro-**{( $S_p$ , $S_p$ )-[2,2"-bis(diphenylphosphino-κ*P*)-1,1"-biferrocene]-(η<sup>6</sup>-benzene)} ruthenium(1) hexafluorophosphate 15. Complex 15 was prepared as described for 13. ( $S_p$ , $S_p$ )-1 (50 mg, 0.068 mmol); AgPF<sub>6</sub> (17.1 mg, 0.068 mmol); [RuCl<sub>2</sub>-(C<sub>6</sub>H<sub>6</sub>)]<sub>2</sub> (17 mg, 0.034 mmol) in THF (30 mL). Product [RuCl-(C<sub>6</sub>H<sub>6</sub>)(( $S_p$ , $S_p$ )-1)]PF<sub>6</sub> (65 mg, 84%, soluble in acetone) was obtained as a red solid.

Found: C 54.24, H 4.03. C<sub>50</sub>H<sub>42</sub>ClF<sub>6</sub>Fe<sub>2</sub>P<sub>3</sub>Ru requires: C 54.67, H 3.86. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K) δ 3.73 (1 H, m, Cp-H3), 3.79 (5 H, s, Cp'''-H), 3.89 (5 H, s, Cp'), 4.0 (1 H, m, Cp-H3"), 4.52 (1 H, t,  $J_{H-H} = 2.6$ , Cp–H4"), 4.55 (1 H, t,  $J_{H-H} = 2.4$ , Cp-H4), 5.35 (1 H, m, Cp-H5), 5.39 (1 H, m, Cp-H5"), 5.79 (6 H, s, C<sub>6</sub>H<sub>6</sub>), 6.92 (2 H, m, Ph-H), 7.19 (2 H, m, Ph-H), 7.39 (4 H, m, Ph-H), 7.62 (10 H, m, Ph-H), 8.47 (2 H, br s, Ph-H). Assignment of signal sets Cp-H/C1-5, Cp'-H/C (ferrocene unit 1) and Cp-H/ C1"-5", Cp"'-H/C (ferrocene unit 2) interchangeable, some of the signals are broad.  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR (100.6 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  68.9 (1C, d, J = 8.1, CH–Cp), 70.3 (1C, d, J = 6.6, CH-Cp), 71.8 (5C, s, CH-Cp), 72.6 (5C, s, CH-Cp), 74.8 (1C, d, J = 41.4, CH–Cp), 75.7 (1C, d, J = 4.4, CH–Cp), 76.3 (1C, d, J = 7.9, CH–Cp), 76.4 (1C, d, J = 7.0, CH–Cp), 76.6 (1C, d, J = 8.7, CH-Cp), 76.9 (1C, d, J = 43.5, CH-Cp), 87.1 (1C, d, J = 11.6, CH–Cp), 89.7 (1C, d, J = 15.4, CH–Cp), 97.4 (6C, s,  $C_6H_6$ ), 128.1 (4C, d, J = 10.5, Ph–C-meta), 128.2 (2C, d, J =10.4, Ph–*C*-meta), 128.4 (2C, d, *J* = 10.0, Ph–*C*-meta), 130.2 (2C, d, J = 2.3, Ph-C-para), 131.2 (4C, pt, Ph-C-para), 131.5 (2C, d, J = 2.4, Ph-*C*-para), 132.0 (4C, d, J = 9.1, Ph-*C*-ortho), 133.7 (1C, d, *J* = 55.4, Ph–*C*-*ipso*), 135.1 (2C, br m, Ph–*C*-*ortho*), 135.8 (2C, br m, Ph-*C*-ortho), 138.6 (1C, d, *J* = 51.2, Ph-*C*-ipso), 139.8

(1C, d, J = 53.5, Ph–*C-ipso*), 140.9 (1C, d, J = 54.2, Ph–*C-ipso*). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  –143.2 (spt,  $J_{\rm FP} = 707.7$ , PF<sub>6</sub><sup>-</sup>), 28.1 (d,  $J_{\rm PP} = 63.6$ ); 33.1 (d,  $J_{\rm PP} = 63.6$ ). <sup>19</sup>F NMR (376.308 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  –73.0 (d,  $J_{\rm FP} = 707.7$ , PF<sub>6</sub><sup>-</sup>) IR (KBr, cm<sup>-1</sup>): 3431, 3088, 3052, 1705, 1480, 1439, 1306, 1142, 1004, 840 (PF<sub>6</sub><sup>-</sup>), 748, 702, 559 (PF<sub>6</sub><sup>-</sup>), 492, 381. MS (FAB+)  $m/z = 953 [M - (PF_6^-)]^+$ , 875 [M - (PF<sub>6</sub><sup>-</sup>) - (C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup>.

**Iodo-**{( $S_p$ , $S_p$ )-[2,2"-bis(diphenylphosphino- $\kappa P$ )-1,1"-biferrocene]-(η<sup>6</sup>-*p*-cymene)} ruthenium(1) iodide 16. Diphosphine ( $S_p$ , $S_p$ )-1 (142 mg, 0.192 mmol) was added to a solution of [RuI<sub>2</sub>(*p*-cymene)]<sub>2</sub> (94 mg, 0.096 mmol) in a 4 : 1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and MeOH (5 mL). The resulting mixture was heated under reflux with stirring for 3 h. After cooling the flask to r.t., the solvent was removed under reduced pressure. The remaining solid was washed with pentane (3 × 15 mL), filtered off and dried. Product [RuI(*p*-cymene)(( $S_p$ , $S_p$ )-1)]I (201 mg, 85%, soluble in acetone) was obtained as a red solid.

Found: C 52.6, H 4.2. C<sub>54</sub>H<sub>50</sub>Fe<sub>2</sub>I<sub>2</sub>P<sub>2</sub>Ru requires: C 52.84, H 4.11. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K) δ 0.54 (3 H, s, H15), 1.40 (3 H, d, J = 7.0, H14), 1.43 (3 H, d, J = 7.0, H13), 3.14 (1 H, m, Cp–H3), 3.61 (5 H, s, Cp<sup>111</sup>–H), 3.63 (1 H, spt, J = 7.0, H12), 3.97 (5 H, s, Cp'-H), 4.30 (1 H, m, Cp-H3"), 4.37  $(1 \text{ H}, \text{td}, J_{\text{H-H}} = 2.6, J_{\text{H-P}} = 1.0, \text{Cp-H4}), 4.59 (1 \text{ H}, \text{t}, J_{\text{H-H}} = 2.7)$ Cp-H4"), 5.29 (1 H, m, Cp-H5), 5.36 (1 H, m, Cp-H5"), 5.56 (1 H, dd,  $J_{H-H} = 6.3$ ,  $J_{H-P} = 1.5$ , H8), 5.76 (2 H, m, H11), 6.07 (2 H, dd,  $J_{\text{H-H}} = 6.6$ ,  $J_{\text{H-P}} = 1.4$ , H10), 6.35 (1 H, t,  $J_{\text{H-H}} = 5.6$ , H7), 6.53 (2 H, br s, Ph), 6.97 (2 H, m, Ph), 7.22 (2 H, m, Ph), 7.60 (8 H, m, Ph), 7.74 (2 H, m, Ph), 8.36 (2 H, br s, Ph), 8.59 (2 H, br s, Ph). Assignment of signal sets Cp-H/C1-5, Cp'-H/C (ferrocene unit 1) and Cp-H/C1"-5", Cp""-H/C (ferrocene unit 2) interchangeable. Some of the signals are broad.  ${}^{13}C{}^{1}H$  NMR (100.6 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K) δ 12.9 (1 C, s, C15), 20.8 (1 C, s, C13), 23.4 (1 C, s, C14), 33.5 (1 C, s, C12), 67.9 (1 C, d, J = 9.2, Cp–C4), 70.3 (1 C, d, J = 6.2, Cp–C4"), 71.2 (5 C, s, Cp'–C), 72.8 (5 C, s, Cp<sup>'''</sup>–C), 74.2 (1 C, d, J = 7.6, Cp–C3), 76.4 (1 C, d, J = 8.5, Cp–5"), 77.7 (1 C, d, J = 40.8, Cp–C1"), 78.4 (1 C, d, J = 9.1, Cp–C5), 78.9 (1 C, d, J = 3.8, Cp–C3"), 85.4 (1 C, d, J = 54.2, Cp–C1), 87.3 (1 C, d, J = 10.4, C10), 89.0 (1 C, d, J = 11.3, Cp-C2"), 89.4 (1 C, d, J = 9.8, C8), 90.4 (1 C, d, J = 16.1, Cp–C2), 96.5 (1 C, d, J = 1.8, C7), 99.6 (1 C, s, C6), 100.6 (1 C, s, C9), 103.4 (1 C, d, J = 3.8, C11), 127.3 (2 C, d, J = 10.3, Ph–C-*meta*), 127.6 (2 C, d, J = 9.6, Ph–C-*meta*), 128.2 (2 C, d, J = 10.5, Ph–C-meta), 128.2 (2 C, d, J = 10.2, Ph–C-meta), 129.5 (1 C, d, J = 1.8, Ph–C-para), 131.3 (1 C, d, J = 2.6, Ph–C-para), 131.5 (1 C, d, J = 2.6, Ph-C-para), 132.0 (1 C, d, J = 2.3, Ph-C-para),132.4 (2 C, br m, Ph–C-*ortho*), 133.1 (2 C, d, *J* = 9.2, Ph–C-*ortho*), 133.3 (1 C, dd, J = 51.7, J = 3.0, Ph-C-ipso), 134.1 (1 C, dd, J = 50.8, J = 3.0, Ph-C-ipso), 135.2 (2 C, br m, Ph-C-ortho), 138.0 (1 C, dd, J = 52.1, J = 2.5, Ph-C-ipso), 138.6 (2 C, br m, Ph–C-*ortho*), 142.2 (1 C, d, J = 49.9, Ph–C-*ipso*). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 295 K)  $\delta$  27.56 (d,  $J_{PP}$  = 53.9), 29.37 (d,  $J_{PP} = 53.9$ ). IR (cm<sup>-1</sup>): 1481.3, 1434.1, 1089.8, 828.2, 701.0, 491.7. MS (FAB+)  $m/z = 1101 [M - (I^{-})]^{+}, 974 [M - 2 \cdot (I^{-})]^{+}, 967$  $[M - (I^{-}) - (C_{10}H_{14})]^{+}$ .

#### Standard procedure for hydrogenation reactions

The substrate (2.53 mmol) and the catalyst were dissolved separately in the appropriate solvent (5 mL) under argon (total

volume: 10 mL) and the catalyst solution was stirred for 15 min. For *in situ* reactions the metal source (1 equiv.) and the appropriate amount of ligand (1.05, 2.1 or 2.2 equiv., for details see below) were dissolved in the same solvent like the substrate and the resulting solution was stirred for 15 min. Both the catalyst and the substrate solutions were transferred through a steel capillary into a 180 mL thermostated glass reactor or a 50 mL stainless steel autoclave. The inert gas was then replaced by hydrogen (three cycles) and the pressure was set. After completion of the reaction, the conversion was determined by gas chromatography and the product was recovered quantitatively after filtering the reaction solution through a plug of silica. The enantiomeric purity of the product was determined either by gas chromatography or by HPLC.

The following reaction conditions and methods for e.e. determination were applied:

MAC: 2.53 mmol (0.25 mol  $L^{-1}$ ) MAC; [Rh(NBD)<sub>2</sub>][BF<sub>4</sub>] + 1.05 equiv. ligand; s/c = 200; solvent: MeOH (10 mL); p(H<sub>2</sub>): 1 bar; 25 °C; reaction time: 16 h; e.e.: GC, Chirasil-L-Val, 170 °C, isotherm.

MCA: 2.53 mmol (0.25 mol L<sup>-1</sup>) MCA;  $[Rh(NBD)_2][BF_4] + 1.05$  equiv. ligand; s/c = 200; solvent: MeOH (10 mL); p(H<sub>2</sub>): 5 bar; 25 °C; reaction time: 15 h; e.e.: as methyl ester; HPLC; Chiralcel OB, hexane–iPrOH: 98 : 2, 0.1 mL min<sup>-1</sup>.

PCA: 2.53 mmol (0.25 mol L<sup>-1</sup>) PCA;  $[Rh(NBD)_2][BF_4] + 1.05$  equiv. ligand; s/c = 200; solvent: MeOH (10 mL);  $p(H_2)$ : 80 bar; 25 °C; reaction time: 14.5 h; e.e.: as methyl ester; HPLC; Chiralcel OD-H, hexane–iPrOH: 97 : 3, 0.3 mL min<sup>-1</sup>.

DMI: 2.53 mmol  $(0.25 \text{ mol } L^{-1})$  DMI; [Rh(NBD)<sub>2</sub>][BF<sub>4</sub>] + 1.05 equiv. ligand; s/c = 200; solvent: MeOH (10 mL); p(H<sub>2</sub>): 1 bar; 25 °C; reaction time: 1 h; e.e.: GC, Lipodex E, 100 °C, isotherm.

EAA: 6.45 mmol (0.43 mol L<sup>-1</sup>) EAA;  $[RuI_2(p\text{-cymene})]_2 + 2.2$  equiv. ligand; s/c = 1000; solvent: EtOH (15 mL); additive: 1 N HCl (aq.): 60  $\mu$ L; p(H<sub>2</sub>): 80 bar; 80 °C; reaction time: 19–21 h; e.e.: as trifluoroacetate derivative; GC, Lipodex E, 80 °C, isotherm.

EBA (ethyl benzoylacetate): 6.54 mmol (0.43 mol L<sup>-1</sup>) EBA; [RuI<sub>2</sub>(*p*-cymene)]<sub>2</sub> + 2.2 equiv. ligand; s/c = 1000; solvent: EtOH (15 mL); additive: 1 N HCl (aq.): 60  $\mu$ L; p(H<sub>2</sub>): 80 bar; 80 °C; reaction time: 16–21 h; e.e.: HPLC, Chiralcel OD-H, hexane–iPrOH: 99 : 1, 0.8 mL min<sup>-1</sup>.

ACA (acetylacetone): 6.45 mmol (0.43 mol L<sup>-1</sup>) ACA;  $[RuI_2(p-cymene)]_2 + 2.2$  equiv. ligand; s/c = 1000; solvent: EtOH (10 mL); additive: 1 N HCl (aq.): 60  $\mu$ L;  $p(H_2)$ : 80 bar; 80 °C; reaction time: 18–20 h; e.e.: as bis(trifluoroacetate) derivative; GC, Lipodex E, 80 °C, isotherm.

EPY (ethyl pyruvate): 2.53 mmol (0.25 mol  $L^{-1}$ ) EPY; [RhCl(NBD)<sub>2</sub>]<sub>2</sub> + 2.1 equiv. ligand; s/c = 100; solvent: toluene (10 mL); p(H<sub>2</sub>): 40 bar; 25 °C; reaction time: 16 h; e.e.: GC, Lipodex E, 80 °C, isotherm.

MEAI: 12.8 mmol (1.3 mol L<sup>-1</sup>) MEAI; [IrCl(COD)]<sub>2</sub>; + 2.1 equiv. ligand; s/c = 1000; solvent: toluene (10 mL); additives: tetrabutylammonium iodide (2 equiv./Ir), CF<sub>3</sub>COOH (30  $\mu$ L); p(H<sub>2</sub>): 80 bar; 25 °C; reaction time: 15.5 h; e.e.: HPLC, Chiralcel OD-H, hexane–iPrOH: 99.5 : 0.5; 1.0 mL min<sup>-1</sup>.

#### X-Ray structure determination

Crystals of  $(S_p, S_p)$ -1,  $(S_p, S_p)$ -[PdCl<sub>2</sub>(1)] (10),  $(S_p, S_p)$ -[PdCl<sub>2</sub>(4)] (11), and  $(S_p, S_p)$ -[RuCl(C<sub>6</sub>H<sub>6</sub>)(1)]PF<sub>6</sub> (15) were obtained by slow

diffusion of Et<sub>2</sub>O (1, 11), EtOH (10), or hexane (15) into solutions of the corresponding complex in CH<sub>2</sub>Cl<sub>2</sub> (11), CHCl<sub>3</sub> (1, 10), or acetone (15). Compound  $(S_p, S_p)$ -1 crystallized unsolvated. Complex 10 formed an ordered solvate with two CHCl<sub>3</sub> and one H<sub>2</sub>O per bifep moiety. Complexes 11 and 15 crystallized in the form of disordered solvates with unknown solvent content. X-ray data were collected on Bruker Smart CCD area detector diffractometers using graphite-monochromated Mo Ka radiation  $(\lambda = 0.71073 \text{ Å})$  and  $\varphi$ - and  $\omega$ -scan frames covering complete spheres of the reciprocal space. Corrections for absorption,  $\lambda/2$ effects, and crystal decay were applied.11 The structures were solved by direct methods and refined on  $F^2$  with the program suite SHELX-97.12 Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. For complexes 11 and 15 the disordered solvent was subjected to the SQUEEZE procedure in the PLATON program prior to final refinement.<sup>13</sup> In the case of complex 15 only a tiny crystal of weak scattering power was available; data collection was therefore restricted to  $\theta = 23^{\circ}$  and 5- and 6-membered rings were refined as idealized rigid groups. Crystal data and experimental details are given in Table 1. Selected geometric data are presented in Table 2. Further details are given in the ESI.†

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