Preparation of C_2-Symmetric Bis[2-(diphenylphosphino)ferrocen-1-yl]-methane and Its Use in Rhodium- and Ruthenium-Catalyzed Hydrogenation

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

The two diphosphine ligands (R_p,R_p)- and (S_p,S_p)-bis[2-(diphenylphospino)ferrocenyl]methane, (R_p,R_p)- and (S_p,S_p)-**1**, resp., were prepared in six steps from (*S*)- and (*R*)-ferrocenyl tolyl sulfoxide, respectively (*Scheme*). In the solid state, both the diborane complex (R_p,R_p)-**1**·$(BH_3)_2$ and the palladium dichloride complex [$PdCl_2$((R_p,R_p)-**1**)] were found to adopt C_2-pseudosymmetric structures according to X-ray analyses (*Figs. 2* and *3*). In the Rh- and Ru-catalyzed hydrogenation of selected alkenes and ketones in the presence of the new ligands, enantioselectivities of up to 55% ee were obtained.

1. Introduction. – Homogeneous enantioselective hydrogenation has now developed into a mature synthetic methodology, not only for scientific purposes [1], but also for the production of enantiomerically pure bioactive ingredients and fine chemicals on an industrial scale [2]. Rhodium (Rh) and ruthenium (Ru) complexes of diphosphine ligands are preferentially used for the enantioselective hydrogenation of alkenes and ketones [3]. However, of the innumerable chiral diphosphines that have been investigated, only a few have proven suitable for industrial processes. These include C_2-symmetric ligands like Dipamp [4], Binap [5], or Duphos [6], as well as C_1-symmetric Josiphos [7] ligands. However, despite the huge number of diphosphines that have been tested, particularly in terms of additional industrial applications, ligand development continues intensively.

For a long time, especially since the early development of Diop [8] and Dipamp, ligand design has focused primarily on bidentate and C_2-symmetric diphosphines, which were considered superior to mono- or bidentate C_1-symmetric ligands. This view has changed significantly, especially since C_1-symmetric Josiphos-type derivatives were successfully used as catalyst ligands in industrial hydrogenation processes [7]. Nowadays, complexes of certain monodentate ligands are also known to catalyze hydrogenations with excellent enantioselectivity [9]. In recent years, the successful application of Josiphos-type ligands in enantioselective hydrogenations and other reactions has boosted the further development of C_1- and, to a much lesser extent, of C_2-symmetric ferrocenyl-based diphosphines [10]. In addition, our search for novel classes of ferrocenyl diphosphines has mainly focused on C_1-symmetric ligands with either a homo- or a heteroannulene-bridged ferrocene backbone [11], *e.g.*, Bifep-type biferro-

cenes [12], or derivatives having a ferrocenyl-aryl backbone. Development of the latter system eventually resulted in the Walphos-type ligand family [13].

Recently, in the search for new backbones, we envisaged that ligand development could be extended to additional C_2-symmetric ferrocenyl diphosphines, and we herein report the preparation and structural analysis of (R_p,R_p)- and (S_p,S_p)-bis[2-(diphenylphospino)ferrocen-1-yl)methane (**1**) and discuss the application of these compounds in enantioselective hydrogenation reactions.

2. Results and Discussion. – 2.1. *Synthesis.* In general, chiral C_2-symmetric ferrocene derivatives can be obtained either by hetero-substitution of the ferrocene backbone or by appropriately linking two homochiral C_1-symmetric ferrocene units. Examples of the former system include 1,1′-disubstituted P-stereogenic ferrocenes of type **A** (*Fig. 1*) [14] and Ferriphos-type ligands [15]. The latter type of compounds is represented by Bifep [16], Trap [17], the cyclohexyldiamide-linked bisferrocenyl derivative **B** [18], and the newly synthesized ligand **1** (see *Scheme* below).

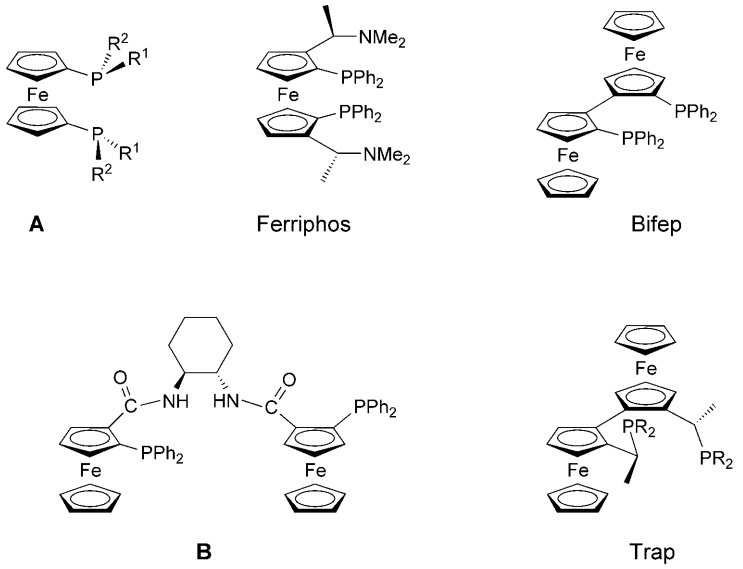
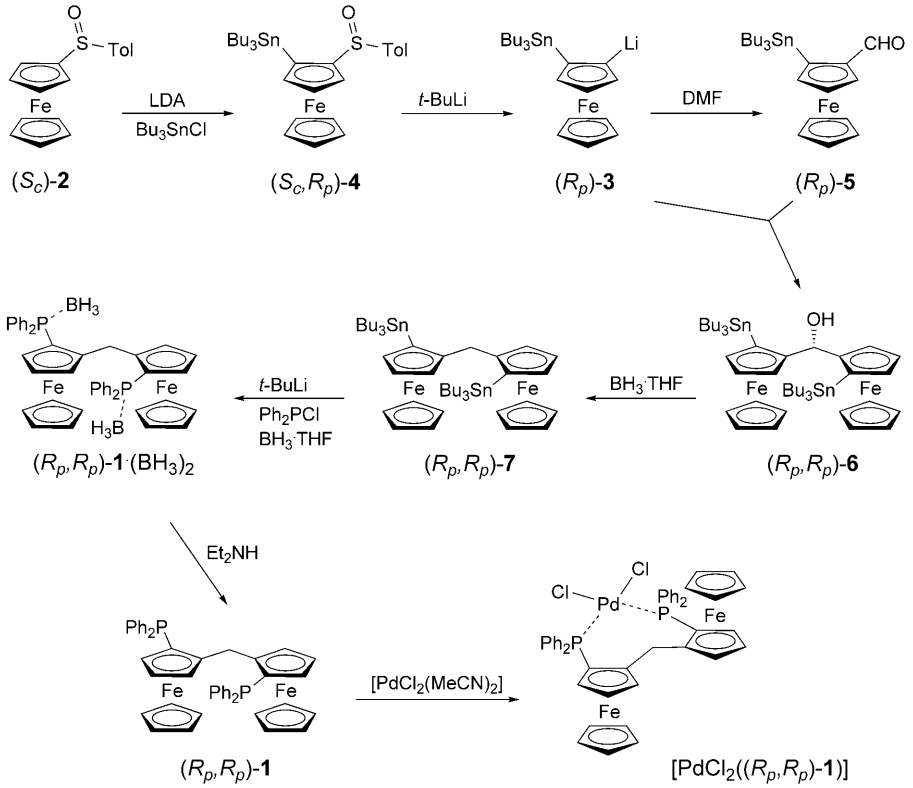


Fig. 1. *Examples of* C_2*-symmetric ferrocenyl diphosphine ligands*

Attempts to build up the diferrocenylmethane backbone in one step from *ortho*-lithiated ferrocenyl tolyl sulfoxide (2-Li-**2**) and ethyl formate failed. A similar observation was recently reported in the literature [19]. As a result, we decided to synthesize the ligand backbone in a stepwise fashion by adopting *Kagan*'s sulfoxide methodology (*Scheme*) [20]. First, 2-lithio-tributylstannylferrocene ((R_p)-**3**) was prepared by reacting (S_c,R_p)-**4**, easily accessible from 4-tolylsulfinylferrocene ((S_c)-**2**), with *t*-BuLi [21]. Trapping of (R_p)-**3** with DMF as the electrophile gave the corresponding aldehyde (R_p)-**5**. In the subsequent step, reaction of (R_p)-**5** with (R_p)-**3** led to the intermediate (R_p,R_p)-**6** in which the final ligand backbone is already preformed. It should be noted that, although

Scheme. *Preparation of the New Ligand* (R_p,R_p)-**1** *and Its Complex* [$PdCl_2$((R_p,R_p)-**1**)]



an alternative preparation of aldehyde **5** has been reported previously [22], in our particular case the synthesis of **5** from **4** is more suitable, given that, in this route, both precursors of **6** (*i.e.*, **3** and **5**) are accessible from a single common intermediate. Reduction of (R_p,R_p)-**6** with BH_3 in THF [23] gave the bis(tributylstannyl) derivative (R_p,R_p)-**7**, which was reacted with *t*-BuLi and chloro(diphenyl)phosphine, and subsequently trapped with BH_3 in THF to afford the diborane complex (R_p,R_p)-**1**·$(BH_3)_2$. Finally, deprotection with Et_2NH led to the target C_2-symmetric diphosphine ligand (R_p,R_p)-**1**. To study the coordination behavior of ligand **1**, its palladium dichloride complex [$PdCl_2$((R_p,R_p)-**1**)] was prepared by reacting (R_p,R_p)-**1** with [$PdCl_2(MeCN)_2$].

2.2. *Structure Elucidation*. The structural integrity of all compounds was assessed by NMR spectroscopy and, in the cases of (R_p,R_p)-**1**·$(BH_3)_2$ and [$PdCl_2$((R_p,R_p)-**1**)], also by single-crystal X-ray-diffraction analyses. Views of the molecular structures are shown in *Figs. 2* and *3* for (R_p,R_p)-**1**·$(BH_3)_2$ and [$PdCl_2$((R_p,R_p)-**1**)], respectively. The NMR results show that, in solution, both ligand **1** and its complex [$PdCl_2$((R_p,R_p)-**1**)] show twofold symmetry. However, in the solid state, they are found in asymmetric environments, but show clear C_2-pseudosymmetry.

The molecular structure of [$PdCl_2$((R_p,R_p)-**1**)] is of particular interest. Both ferrocene units are arranged in a propeller-like fashion that places the Pd-atom and the

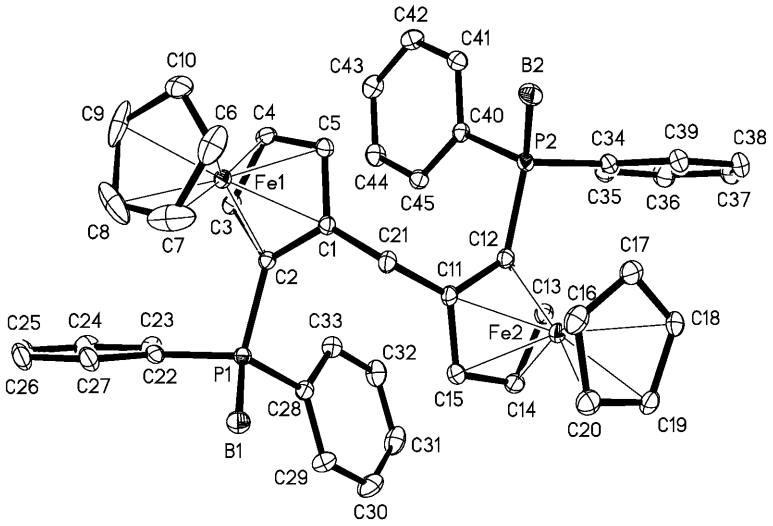


Fig. 2. *X-Ray crystal structure of* (R_p,R_p)-**1**·*$(BH_3)_2$*. Ellipsoids are shown at the 40% level; H-atoms have been omitted for clarity. Selected distances [Å] and angles [°]: $(Fe-C_{Cp})_{aver}$, 2.046(1); P(1)–C(2), 1.798(1); P(1)–C(22), 1.816(1); P(1)–C(28), 1.818(1); P(1)–B(1), 1.929(1); P(2)–C(12), 1.800(1); P(2)–C(34), 1.820(1); P(2)–B(2), 1.939(1); C(21)–C(1), 1.510(2); C(21)–C(11), 1.512(2); C(1)–C(21)–C(11), 112.0(1); B(1)–P(1)–C(2)–C(1), 42.8(1); B(2)–P(2)–C(12)–C(11), 43.2(1); P(1)–C(2)–C(1)–C(21), 1.1(2); P(2)–C(12)–C(11)–C(21), 2.5(2); C(2)–C(1)–C(21)–C(11), 80.0(1); C(12)–C(11)–C(21)–C(1), 72.2(1).

methylene carbon C(21) on a line that almost dissects the bond angles Cl(1)–Pd–Cl(2), P(1)–Pd–P(2), and C(1)–C(21)–C(11) (*Fig. 3*). In a perfect C_2-symmetric arrangement, this line would be the C_2 symmetry axis.

An additional striking feature of the molecular structure of $[PdCl_2((R_p,R_p)$-**1**$)]$ is that each of the substituted ferrocenyl cyclopentadienyl (Cp) rings is oriented nearly parallel to one of the phenyl (Ph) rings (*e.g.*, the Cp ring made of C(1) to C(5) is parallel to the Ph ring consisting of C(34) to C(39), *etc.*) and shows pronounced π-stacking interactions with very short C···C contacts (*e.g.*, C(1)···C(34) = 3.134, C(5)···C(35) = 3.160, C(11)···C(22) = 3.115, and C(13)···C(27) = 3.193 Å). This stacking interaction certainly contributes a great deal to the stability of the observed C_2-symmetric conformer. This phenomenon is also present in (R_p,R_p)-**1**·$(BH_3)_2$, albeit to a lesser extent (only one C···C contact <3.20 Å).

However, although one might expect a C_2-symmetric or higher-symmetric diphosphine ligand to form a palladium dichloride complex adopting the same symmetry as the free ligand, this is not necessarily the case. For example, in the solid state, the molecular structure of $[PdCl_2$(Binap)$]$ [24] and also of the related Rh norbornadiene (NBD) complex $[Rh$(Binap)(NBD)$]ClO_4$ [25] have C_2 pseudosymmetry. In contrast, the palladium dichloride complex of bis[2-(diphenylphosphino)phenyl]methane, $[PdCl_2($**8**$)]$ [26], with a maximum ligand and complex symmetry of C_{2v}, adopts an asymmetric conformation (*Fig. 4,a*). In solution, average C_2 and C_s symmetry is observed for $[PdCl_2$(Binap)$]$ and $[PdCl_2($**8**$)]$, respectively. Since the ligand backbones of **1** and **8**

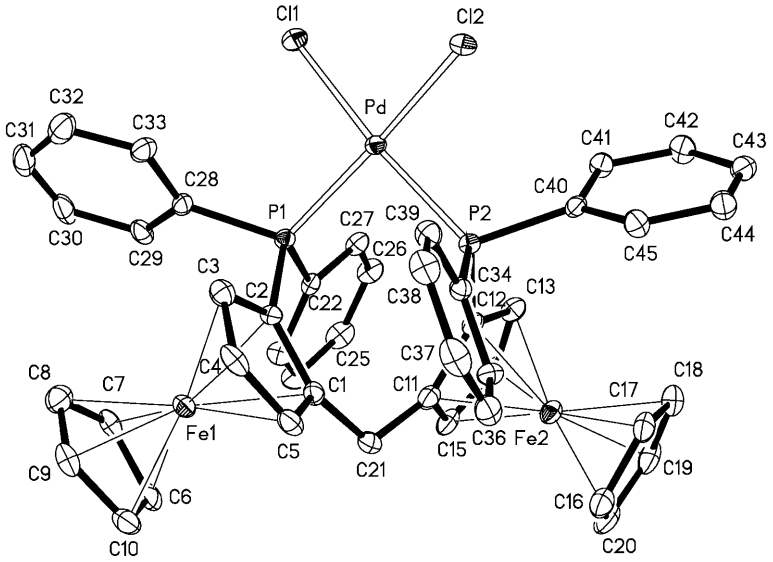


Fig. 3. *X-Ray crystal structure of [PdCl$_2$((*R$_p$,R$_p$*)-***1***)]·CHCl$_3$*. Ellipsoids are shown at the 40% level; H-atoms have been omitted for clarity. Selected distances ([Å] and angles [°]: Pd–P(1), 2.277(1); Pd–P(2), 2.278(1); Pd–Cl(1), 2.352(1); Pd–Cl(2), 2.362(1); (Fe–C$_{Cp}$)$_{aver}$, 2.048(4); P(1)–C(2), 1.798(4); P(1)–C(22), 1.813(4); P(1)–C(28), 1.838(4); P(2)–C(12), 1.812(4); P(2)–C(34), 1.810(4); P(2)–C(40), 1.814(4); C(21)–C(1), 1.503(5); C(21)–C(11), 1.499(6); C(1)–C(21)–C(11), 117.9(3); Pd–P(1)–C(2)–C(1), −90.3(4); Pd–P(2)–C(12)–C(11), −87.8(4); P(1)–C(2)–C(1)–C(21), −15.2(6); P(2)–C(12)–C(11)–C(21), −7.5(7); C(2)–C(1)–C(21)–C(11), 40.8(6); C(12)–C(11)–C(21)–C(1), 31.6(7).

are structurally related to each other (**8** can be obtained from **1** by replacing the ferrocenyl units by aryl rings), we envisaged that, like [PdCl$_2$(**8**)], complex [PdCl$_2$(**1**)] could adopt C_1-symmetric conformers. We, therefore, carried out simple force-field calculations (for details see *Exper. Part*) and found that [PdCl$_2$(**1**)] can, indeed, adopt not only a C_2-symmetric conformer (very similar to that found in the solid state), but two homomeric C_1-symmetric conformers also seem to be accessible [27]. In principle, both C_1-symmetric conformers are interchangeable by rotation of the ferrocenyl units about the ferrocenyl–CH$_2$ bonds. Therefore, the observed twofold symmetry of [PdCl$_2$(**1**)] in solution could arise either from a C_2- and/or from two interchanging C_1-symmetric conformers (*Fig. 4*,*b*). Since low-temperature ^{1}H- and ^{31}P{^{1}H}-NMR studies did not show evidence for any exchange phenomena, neither possibility can be excluded (see *Exper. Part*).

Although unexpected, superposition of the molecular structures of complex [PdCl$_2$((*R$_p$*,*R$_p$*)-**1**)], which forms an eight-membered chelate ring system, and complexes [PdCl$_2$((*S*)-Binap)] or [Rh((*S*)-(Binap))(NBD)]ClO$_4$ (with seven-membered chelate rings) shows surprising similarities. The arrangement of the substituted Cp rings is almost identical to that of the naphthyl groups of Binap, placing the P-atoms and, in particular, the attached Ph rings and the transition metal in comparable positions.

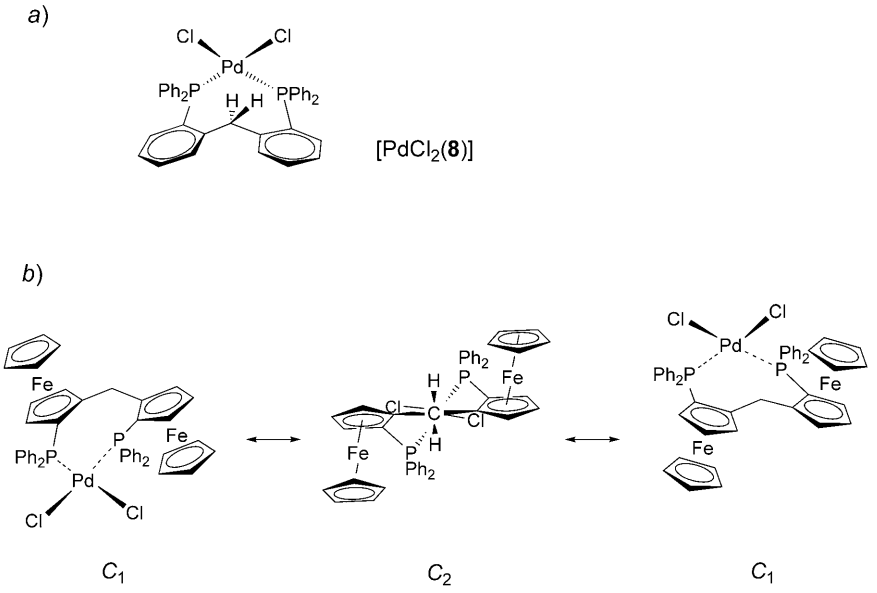
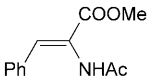


Fig. 4. a) *Schematic representation of the molecular structure of [PdCl$_2$(**8**)] in the solid state.* b) *Calculated Structures of* C_1*- and* C_2*-symmetric conformers of [PdCl$_2$(**1**)]*

2.3. *Catalysis.* The catalytic behavior of ligand (S_p,S_p)-**1** was assessed by screening it in catalytic hydrogenations of the olefins and ketones **9**–**14**. All catalyst precursors were formed *in situ* using an appropriate Rh or Ru source (*Table*). Each hydrogenation reaction gave quantitative or nearly quantitative conversion (*Table*, *Entry 6*), except when methyl 2-oxo-2-phenylacetate (**13**) was used as the substrate. However, the products were formed with only low-to-moderate enantioselectivities. For example, regardless of the Rh source used, hydrogenation of methyl α-(acetamido)cinnamate (**9**) afforded *N*-acetylphenylalanine methyl ester in 55% enantiomeric purity (*Entries 1* and *2*), and ethyl (*Z*)-3-(acetamido)but-2-enoate (**10**) gave the corresponding butanoate in an enantiomeric excess (ee) of 53% (*Entry 3*). Unfortunately, hydrogenation of the other olefins tested gave products in only very poor enantiomeric purities (17 and 8% ee for **11** (*Entry 4*) and **12** (*Entry 5*), resp.). Similar low ee values were obtained for the Rh- and Ru-mediated hydrogenation of the α- and β-oxo esters **13** and **14** (6 and 15% ee, resp.; *Entries 6* and *7*).

3. Conclusions. – The C_2-symmetric bis[2-(diphenylphosphino)ferrocenyl]methane ligands (R_p,R_p)- and (S_p,S_p)-**1** were synthesized in six steps from (*S*)- and (*R*)-ferrocenyl tolyl sulfoxide, respectively. In the solid state, the complex [PdCl$_2$((R_p,R_p)-**1**)] adopts a C_2-pseudosymmetric conformation, with the chiral pocket being surprisingly similar to those of the Binap complexes [PdCl$_2$((*S*)-Binap)] and [Rh((*S*)-(Binap))(NBD)]ClO$_4$. However, when diphosphine **1** was used as the ligand in Rh- and Ru-catalyzed hydrogenations of olefins and ketones, only low-to-moderate enantioselectivities were obtained. Based on the X-ray crystal structure of [PdCl$_2$(**8**)] (**8** = bis[2-(diphenylphos-



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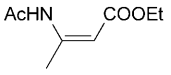

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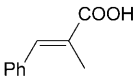

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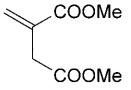

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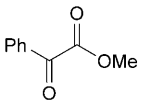

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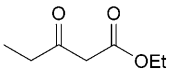

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Table. *Rhodium- and Ruthenium-Catalyzed Hydrogenations of Alkenes and Ketones in the Presence of the New Ligand* (S_p,S_p)-**1**

Entry	Substrate	Catalyst precursor	Additive	Condition[a])	p (H_2) [bar]	T [h]	Conv. [%]	ee [%]	Config.
1	**9**	$[Rh(NBD)_2]BF_4$	–	*A*	1	1	100	55[b])	(*R*)
2	**9**	[Rh(COD)(acac)]	$HBF_4 \cdot Et_2O$	*A*	1	1	100	55[b])	(*R*)
3	**10**	$[Rh(NBD)_2]BF_4$	CF_3CH_2OH	*B*	1	1	99	53[c])	(*R*)
4	**11**	$[Rh(NBD)_2]BF_4$	–	*A*	5	20	100	17[d])	(*R*)
5	**12**	$[Rh(NBD)_2]BF_4$	–	*A*	1	1	100	8[e])	(*R*)
6	**13**	$[Rh(NBD)Cl]_2$	–	*C*	80	20	18	6[f])	(*R*)
7	**14**	$[RuI_2(p\text{-cymene})]_2$	HCl	*D*	80	19	100	15[g])	(*R*)

[a]) *A*: MeOH (10 ml); substrate/catalyst (S/C): 200:1, 25°. *B*: EtOH (10 ml), S/C 100:1, 25°. *C*: Toluene (10 ml), S/C 200:1, 25°. *D*: EtOH (10 ml), S/C 200:1, 25°. [b]) Determined by GC (*Chirasil-L-Val*, 170°, isothermal). [c]) By GC (*Lipodex E*, 130°, isothermal). [d]) By HPLC (*Chiralcel OB*, hexane/i-PrOH 98:2, 0.1 ml/min) of Me ester. [e]) By GC (*Lipodex E*, 80°, isothermal). [f]) By HPLC (*Chiralcel OJ*, hexane/i-PrOH 90:10, 1.0 ml/min). [g]) By GC (*Lipodex E*, 80°, isothermal) of TFA derivative.

phino)phenyl]methane) and corroborated by simple force-field calculations on [$PdCl_2$(**1**)], we assume that, unlike in the case of Binap in solution, transition-metal complexes of ligand **1** are much more flexible and are not only able to adopt C_2- but also C_1-symmetric conformations, an observation that could well be responsible for the low enantioselectivities observed.

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Experimental Part

General. All manipulations were carried out under Ar atmosphere using standard *Schlenk* techniques. Solvents were distilled from the appropriate drying agents, and degassed before use. Chromatographic separations were performed under gravity, either on silica gel (40–62 μm; *Merck*) or on alumina (activity II–III, 63–200 μm; *Merck*). Petroleum ether (PE) with a boiling range of 55–65° was used for column chromatography (CC). *(S_c)-(4-Methylphenyl)sulfinylferrocene* ((S_c)-**2**) and *2-[(4-methylphenyl)-sulfinyl]-1-(tributylstannyl)ferrocene* ((S_c,R_p)-**4**) were prepared according to [21]. Melting points (m.p.) were determined on a *Kofler* melting-point apparatus; uncorrected. Optical rotations were measured on a *Perkin Elmer 241* polarimeter. NMR Spectra were recorded on a *Bruker DPX-400* spectrometer

in $CDCl_3$; chemical shifts δ in ppm rel. to $CHCl_3$ (^{1}H: 7.26 ppm), $CDCl_3$ (^{13}C{^{1}H}: 77.0 ppm), or 85% H_3PO_4 (^{31}P{^{1}H}: 0 ppm); coupling constants J in Hz; in the ^{13}C-NMR spectra, the J values refer to ^{13}C,^{31}P couplings. Abbreviations: br., *s*, *d*, *t*, and *q* refer to broad, *singlet*, *doublet*, *triplet*, and *quartet*, resp., and C_q (^{13}C-NMR) stands for quaternary C-atom; for arbitrary atom numbering, see *Fig. 2*. Low-temp. NMR spectra of [$PdCl_2$(**1**)] were recorded on a *Bruker Avance-300* spectrometer in CD_2Cl_2 in a temp. range of -80 to $+25°$. Mass spectra were recorded on a *Finnigan MAT-8230* apparatus (EI) or on *Finnigan MAT-900S* (FD); in *m*/*z*. Elemental analyses were performed by the Mikroanalytisches Laboratorium der Fakultät für Chemie der Universität Wien.

2-(Tributylstannyl)ferrocene-1-carbaldehyde ((R_p)-**5**). To a degassed soln. of (S_c,R_p)-**4** (9 g, 14.6 mmol) in THF (80 ml) at $-78°$ under Ar gas was added dropwise 1.7M *t*-BuLi in pentane (9.46 ml, 16.09 mmol) *via* syringe. The soln. was stirred at $-78°$ for 5 min. Then, DMF (3.41 ml, 43.89 mmol) was added, and the soln. was stirred for an additional 2 h at $-78°$. Then, the reaction was quenched with H_2O (20 ml). The product was extracted with Et_2O, the org. phase was washed with H_2O and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by CC (*Alox 90*; PE/Et_2O 9:1) to afford (R_p)-**5** (6.42 g) in 87% yield. The spectroscopic and physical data were identical with those reported in [22]. Red oil. ^{1}H-NMR (400 MHz): 0.91 (*t*, J=7.3, 3 Me); 1.01–1.15 (*m*, 3 CH_2); 1.30–1.42 (*m*, 3 CH_2); 1.47–1.62 (*m*, 3 CH_2); 4.22 (*s*, 5 H of Cp′); 4.45–4.51 (*m*, 1 H of Cp); 4.74 (*t*, J=2.4, 1 H of Cp); 4.90–4.94 (*m*, 1 H of Cp); 9.94 (*s*, HCO).

(R_p,R_p*)-Bis[(2-(tributylstannyl)ferrocen-1-yl]methanol* (R_p,R_p)-**6**. To a degassed soln. of (S_c,R_p)-**4** (7.85 g, 12.76 mmol) in THF (80 ml) at $-78°$ under Ar gas was added dropwise 1.7M *t*-BuLi in pentane (8.26 ml, 14.04 mmol) *via* syringe, and the soln. was stirred at $-78°$ for 5 min. A degassed soln. of (R_p)-**5** (6.42 g, 12.76 mmol) in THF (5 ml) was added, and the mixture was stirred for another 2 h at $-78°$. Then, the mixture was allowed to reach r.t., and the reaction was quenched with H_2O (20 ml). The product was extracted with Et_2O, the org. phase was washed with H_2O and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by CC (*Alox 90*; PE/Et_2O 100:1) to afford (R_p,R_p)-**6** (9.94 g) in 80% yield. Due to its rather low stability, the compound was immediately used in the next step. Orange oil. ^{1}H-NMR (400 MHz): 0.85–0.98 (*m*, 6 Me); 1.00–1.14 (*m*, 6 CH_2); 1.32–1.45 (*m*, 6 CH_2); 1.49–1.66 (*m*, 6 CH_2); 2.28 (*d*, J=2.4, OH); 3.93–3.96 (*m*, 1 H of Cp); 3.97–4.00 (*m*, 1 H of Cp); 4.12 (*s*, 5 H of Cp′); 4.15–4.17 (*m*, 1 H of Cp); 4.18 (*s*, 5 H of Cp′); 4.22 (*t*, J=2.3, 1 H of Cp); 4.28 (*t*, J=2.4, 1 H of Cp); 4.32–4.36 (*m*, 1 H of Cp); 5.08 (*d*, J=2.4, 1 CH). ^{13}C{^{1}H}-NMR (100.6 MHz): 10.92 (CH_2); 11.59 (CH_2); 13.72 (Me); 13.77 (Me); 27.53 (CH_2); 27.62 (CH_2); 29.34 (CH_2); 29.47 (CH_2); 66.92 (C_q of Cp); 67.82 (CH); 68.26 (Cp′); 68.59 (Cp′); 69.40 (CH); 69.51 (C_q of Cp); 69.66 (CH); 70.13 (CH); 70.75 (CH); 74.19 (CH); 74.24 (CH); 97.44 (C_q of Cp); 102.21 (C_q of Cp). FD-MS: 978.0 (M^+).

(R_p,R_p*)-Bis[2-(tributylstannyl)ferrocen-1-yl]methane* ((R_p,R_p)-**7**). To a degassed soln. of (R_p,R_p)-**6** (5 g, 5.11 mmol) in THF (40 ml) was added dropwise 1M BH_3 in THF (40.88 ml, 40.88 mmol). The mixture was heated at reflux for 7 h, until the starting material was consumed according to TLC analysis (alumina; PE). The mixture was cooled to 0°, quenched by addition of H_2O, extracted with Et_2O, washed with H_2O and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by CC (*Alox 90*; PE/Et_2O 100:1) to afford (R_p,R_p)-**7** (3.82 g) in 78% yield. Orange oil. $[\alpha]_\lambda^{20}$ (λ in nm): -17.4 (589), -20.0 (578), -36.9 (546) (c=0.88, $CHCl_3$). ^{1}H-NMR (400.1 MHz): 0.97 (*t*, J=7.33, 6 Me); 1.05–1.24 (*m*, 6 CH_2); 1.37–1.48 (*m*, 6 CH_2), 1.55–1.70 (*m*, 6 CH_2); 3.38 (*s*, 1 CH_2); 3.83 (*dd*, J=2.3, 1.3, 2 H of Cp, exchangeable); 4.06 (*s*, 2×5 H of Cp′); 4.13–4.16 (*m*, 2 H of Cp, exchangeable); 4.17 (*t*, J=2.3, 2 H of Cp). ^{13}C{^{1}H}-NMR (100.6 MHz): 10.85 (CH_2); 13.72 (Me); 27.57 (CH_2); 29.40 (CH_2); 33.38 (CH_2); 68.60 (Cp′); 69.57 (C_q of Cp); 70.34 (C(4) of Cp); 70.38 (C(5) of Cp); 73.82 (C(3) of Cp); 94.75 (C_q of Cp). FD-MS: 962 (M^+).

(μ-{(R_p,R_p*)-Bis[2-(diphenylphosphino)ferrocen-1-yl]methane*-P,P*})hexahydrodiboron* ((R_p,R_p)-**1**·$(BH_3)_2$). To a degassed soln. of (R_p,R_p)-**7** (2.5 g, 2.6 mmol) in THF (20 ml) at 0° under Ar gas was added dropwise 1.6M BuLi (in hexane; 3.41 ml, 5.46 mmol) *via* syringe. The soln. was stirred at this. temp. for 10 min, and Ph_2PCl (1.4 ml, 7.8 mmol) was added. The mixture was stirred for a further 30 min at 0°, and then allowed to reach r.t. Stirring was continued, until all starting material was consumed (TLC control (alumina; PE/Et_2O 10:1)). Then, 1M BH_3 in THF (20.8 ml, 20.8 mmol) was added, and the mixture was stirred for a further 16 h at r.t. The mixture was quenched with sat. aq. $NaHCO_3$ soln.,

extracted with Et_2O, washed with H_2O and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by CC (*Alox 90*; PE/Et_2O/Et_3N 10:4:0.1) to afford (R_p,R_p)-**1** (0.64 g) in 32% yield. Yellow solid. M.p. > 243° (dec.). $[\alpha]_\lambda^{20}$ (λ in nm): +129.0 (589), +128.4 (578), +103.2 (546) (c = 0.98, $CHCl_3$). ^{1}H-NMR (400.1 MHz): 1.24–2.18 (very br. *s*, 2 BH_3); 3.42–3.46 (*m*, 2 H of Cp); 3.71 (*t*, J = 2.5, 2 H of Cp); 3.90–3.93 (*m*, 2 H of Cp); 4.13 (*s*, 2×5 H of Cp′); 4.14 (*s*, 1 CH_2); 7.31–7.38 (*m*, 4 H of Ph); 7.39–7.52 (*m*, 12 H of Ph); 7.60–7.72 (*m*, 4 H of Ph). ^{13}C{^{1}H}-NMR (100.6 MHz): 26.93 (CH_2); 67.42 (*d*, J = 65.0, C_q of Cp); 69.54 (*d*, J = 6.1, C(4) of Cp); 70.49 (Cp′); 72.37 (*d*, J = 3.8, C(3) of Cp); 74.27 (*d*, J = 7.6, C(5) of Cp); 92.86 (*d*, J = 15.7, C_q of Cp); 128.08, 128.15, 128.18, 128.25 (2*d*, 4 *m*-C of Ph); 130.68 (*d*, J = 2.3, 2 *p*-C of Ph); 130.85 (*d*, J = 2.3, 2 *p*-C of Ph); 131.29, 131.48, 132.04 (4 *ipso*-C of Ph); 132.99 (*d*, J = 9.2, 2 *o*-C of Ph); 133.32 (*d*, J = 9.2, 2 *o*-C of Ph). ^{31}P{^{1}H}-NMR (162.0 MHz): 15.68 (br. *s*). EI-MS (270°): 780 (1, M^+), 766 (9, $[M-BH_3]^+$), 752 (100, $[M-2\,BH_3]^+$), 566 (96), 500 (18), 445 (16).

(R_p,R_p*)-Bis[2-(diphenylphosphino)ferrocen-1-yl]methane* ((R_p,R_p)-**1**). A soln. of (R_p,R_p)-**1**·$(BH_3)_2$ (1.14 g, 1.46 mmol) in freshly distilled Et_2NH (20 ml) was stirred for 4 h at r.t., until the starting material was consumed (TLC). The solvent was removed under reduced pressure, and the residue was purified by CC (*Alox 90*; PE/Et_2O/Et_3N 70:30:3) to afford (R_p,R_p)-**1** (1.07 g) in 98% yield. Yellow solid. M.p. 154–158°. $[\alpha]_\lambda^{20}$ (λ in nm): +267.7 (589), +278.4 (578), +318.8 (546) (c = 0.96, $CHCl_3$). ^{1}H-NMR (400.1 MHz): 3.46–3.52 (*m*, 2 H of Cp, exchangeable); 3.70 (*t*, J = 2.4, 2 H of Cp); 3.88 (*s*, 2×5 H of Cp′); 3.90 (*s*, 1 CH_2); 3.92–3.95 (*m*, 2 H of Cp, exchangeable); 7.03–7.12 (*m*, 4 H of Ph); 7.16–7.23 (*m*, 6 H of Ph); 7.32–7.40 (*m*, 6 H of Ph); 7.49–7.59 (*m*, 4 H of Ph). ^{13}C{^{1}H}-NMR (100.6 MHz): 28.83 (*t*, J = 9.1, CH_2); 68.59 (C(4) of Cp); 69.53 (Cp′); 70.48 (*d*, J = 3.8, C(3) of Cp); 73.03 (*t*, J = 4.6, C(5) of Cp); 74.38 (*d*, J = 6.1, C_q of Cp); 93.55 (*d*, J = 27.1, C_q of Cp); 127.60 (2 *p*-C of Ph); 127.69 (*d*, J = 6.1, 4 *m*-C of Ph); 127.99 (*d*, J = 8.4, 4 *m*-C of Ph); 128.98 (2 *p*-C of Ph); 132.64 (*d*, J = 17.59, *o*-C of Ph); 135.19 (*d*, J = 20.6, *o*-C of Ph); 137.68 (*d*, J = 6.9, 2 *ipso*-C of Ph); 140.10 (*d*, J = 8.4, 2 *ipso*-C of Ph). ^{31}P{^{1}H}-NMR (162.0 MHz): −22.55 (*s*). EI-MS (230°): 752 (67, M^+), 566 (100), 500 (12), 424 (13). Anal. calc. for $C_{45}H_{38}Fe_2P_2$: C 71.83, H 5.09, P 8.23, found: C 71.95, H 5.44, P 8.06.

Dichloro(μ-{(R_p,R_p*)-bis[2-(diphenylphosphino)ferrocen-1-yl]methane-P,P})palladium(II)* ([$PdCl_2$-((R_p,R_p)-**1**)]. A degassed soln. of (R_p,R_p)-**1** (75 mg, 0.1 mmol) in benzene (2 ml) was added to a suspension of [$PdCl_2(MeCN)_2$] (24 mg, 0.094 mmol) in benzene (2 ml) through a *Teflon* tube. The mixture was stirred for 18 h at r.t., and the resulting precipitate was filtered off and washed with both benzene (2×2 ml) and Et_2O (3×3 ml) to afford the title compound (81 mg) in 87% yield. Red solid. M.p. > 215° (dec.). $[\alpha]_D^{20} = -838$ (c = 0.06, $CHCl_3$). ^{1}H-NMR (400.1 MHz): 3.64–3.67 (*m*, 2 H of Cp); 3.68–3.71 (*m*, 2 H of Cp); 3.77 (*s*, 2×5 H of Cp′); 3.91 (*s*, 1 CH_2); 3.96–4.01 (*m*, 2 H of Cp); 7.27–7.33 (*m*, 4 *m*-H of Ph^1); 7.33–7.40 (*m*, 2 *p*-H of Ph^1); 7.41–7.49 (*m*, 4 *m*-H of Ph^2); 7.50–7.56 (*m*, 2 *p*-H of Ph^2); 7.56–7.66 (*m*, 4 *o*-H of Ph^1); 8.51–8.62 (*m*, 4 *o*-H of Ph^2); the Ph^2 H-atoms are stacking to the Cp ring. ^{13}C{^{1}H}-NMR (100.6 MHz): 31.96 (CH_2); 69.83 (br. *s*, C(4) of Cp); 70.66 (Cp′); 73.08 (*d*, J = 16.1, C(3) of Cp); 75.03 (br. *s*, C(5) of Cp); 126.61 (*d*, J = 12.2, 4 *m*-C of Ph^1); 128.42 (*d*, J = 11.5, 4 *m*-C of Ph^2); 130.34 (2 *p*-C of Ph); 131.81 (2 *p*-C of Ph); 134.36 (*d*, J = 11.8, *o*-C of Ph^1); 135.90 (*d*, J = 13.0, *o*-C of Ph^2); the C_q- and *ipso*-C-atoms of the Ph rings were not observed. ^{31}P{^{1}H}-NMR (162.0 MHz): 31.60 (*s*).

X-Ray Crystal-Structure Determination[1]*) of (*R_p,R_p*)-***1***·(BH₃)₂ and [PdCl₂((*R_p,R_p*)-***1***)]·CHCl₃.* Crystals of (R_p,R_p)-**1**·$(BH_3)_2$ were obtained by layering a CH_2Cl_2 soln. with Et_2O, and crystals of [$PdCl_2$((R_p,R_p)-**1**)]·$CHCl_3$ were obtained by evaporation of a $CHCl_3$ soln. of the target compound. X-ray data were collected on a *Bruker Smart CCD* area-detector diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å), with 0.3° ω-scan frames covering the complete spheres of the reciprocal space. After frame data integration with the SAINT program [28], corrections were applied for absorption, $\lambda/2$ effects, and crystal decay using the SADABS program [28]. The structures were solved by direct

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[1]) CCDC 299604-299606 contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from the *Cambridge Crystallographic Data Centre* at www.ccdc.cam.ac.uk/data_request/cif. Note that the data includes the room-temperature structure of [$PdCl_2$((R_p,R_p)-**1**)]·CH_3NO_2, a nitromethane solvate that is isostructural with [$PdCl_2$((R_p,R_p)-**1**)]·$CHCl_3$.

methods using the program SHELXS97 [29]. Structure refinement on F^2 was carried out with the program SHELXL97 [29]. All non-H-atoms were refined anisotropically. H-Atoms were inserted in idealized positions, and were refined riding with the atoms to which they are bonded. Views of the molecular structures are shown in *Figs. 2* and *3*, and selected geometric data are given in the figure legends.

Crystal data for (R_p,R_p)-**1**·$(BH_3)_2$. Formula, $C_{45}H_{44}B_2Fe_2P_2$; M_r 780.06; $T=100(2)$ K; orthorhombic, space group $P2_12_12_1$ (No. 19); $a=12.2672(14)$, $b=13.9364(16)$, $c=22.063(3)$ Å; $V=3771.8(8)$ Å^3; $Z=4$; $\mu=0.89$ mm^{-1}. Of 55,054 reflections collected ($\theta_{max}=30°$), 10,961 were independent; final R indices: $R_1=0.0209$ (all data), $wR_2=0.0529$ (all data); *Flack* absolute structure parameter = −0.008(5).

Crystal data for [$PdCl_2$((R_p,R_p)-**1**)]·$CHCl_3$. Formula, $C_{46}H_{39}Cl_5Fe_2P_2Pd$, M_r 1049.06; $T=100(2)$ K; tetragonal, space group $P4_32_12$ (No. 96); $a=14.2830(12)$, $c=40.512(4)$ Å; $V=8264.7(12)$ Å^3; $Z=8$; $\mu=1.56$ mm^{-1}. Of 109,989 reflections collected ($\theta_{max}=28.3°$), 10,160 were independent; final R indices: $R_1=0.0449$ (all data), $wR_2=0.0903$ (all data); *Flack* absolute structure parameter = −0.011(18).

Standard Procedure for Hydrogenation Reactions. The substrate (2.53 mmol) and the catalyst (formed *in situ*, for details see *Table*) were dissolved separately in 5 ml of the solvent under Ar gas (total volume: 10 ml). The catalyst soln. was stirred for 15 min. Both the catalyst and the substrate soln. were then transferred through a steel capillary either into a 180-ml thermostated glass reactor or into a 50-ml stainless-steel autoclave. The inert gas was then replaced by H_2 (three cycles), and the pressure was set. After completion of the reaction (1–20 h according to GC analysis), the product was isolated quantitatively after filtration through a plug of SiO_2 to remove the catalyst. The enantiomeric purity of the product was determined either by GC or HPLC (see *Table*).

Force-Field Calculations. Computer modeling was carried out with the program PCMODEL (vers. 8.50.0) [27] and *Allinger*'s MMX force field. The minimization 'Steepest Descent' followed by *Newton–Raphson* were applied in each case. A square-planar Pd coordination sphere was predefined. All conformers of [$PdCl_2$(**1**)] were minimized in two different ways: by including PI calculations as well as by using a predefined atom type (atom type 40) for all aromatic C-atoms. With both methods, the C_1-symmetric conformer was calculated to be more stable than the C_2-symmetric one (3.2 (PI) *vs.* 4.9 kcal/mol, resp.).

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