# 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).

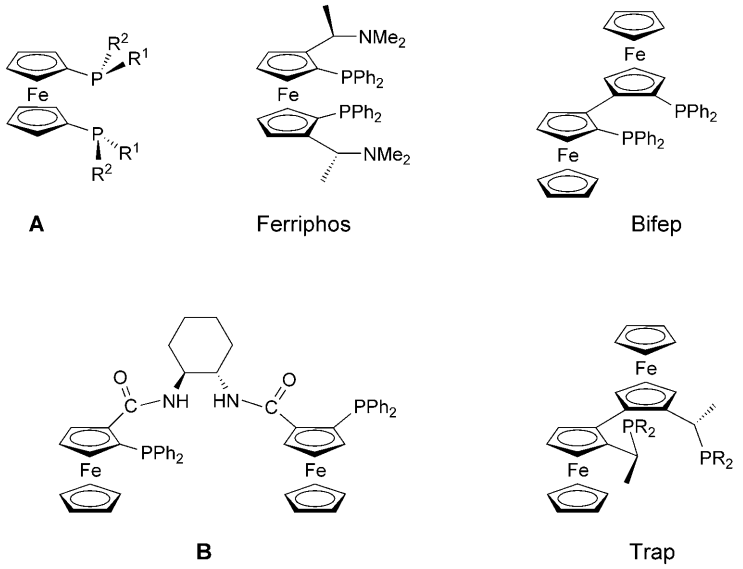
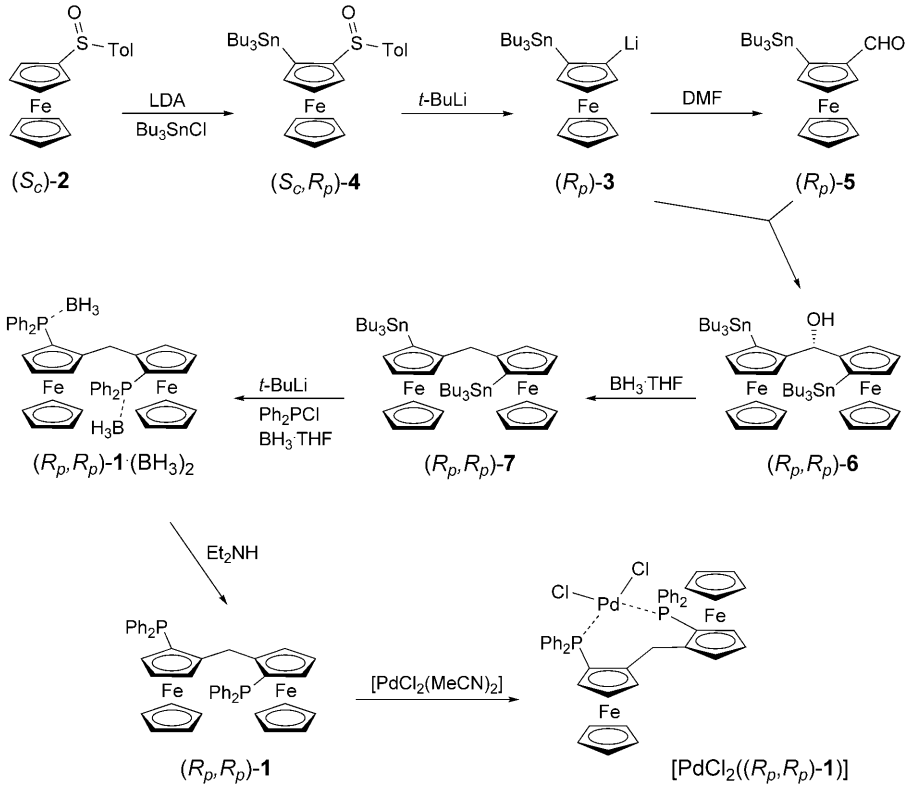



Fig. 1. *Examples of* $C_2$*-symmetric ferrocenyl diphosphine ligands*

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

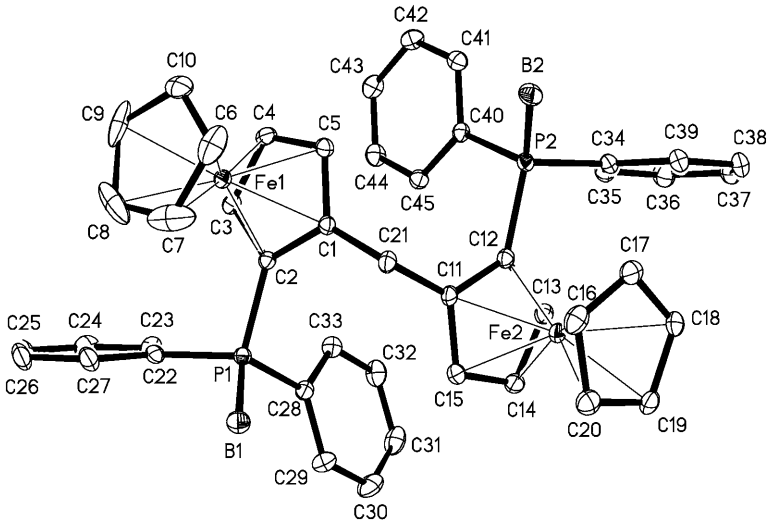



Fig. 2. *X-Ray crystal structure of* $(R_p,R_p)$-**1**·*$(BH_3)_2$*. Ellipsoids are shown at the 40% level; H-atoms have been omitted for clarity. Selected distances [Å] and angles [°]: $(Fe-C_{Cp})_{aver}$, 2.046(1); P(1)–C(2), 1.798(1); P(1)–C(22), 1.816(1); P(1)–C(28), 1.818(1); P(1)–B(1), 1.929(1); 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 $\pi$-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**

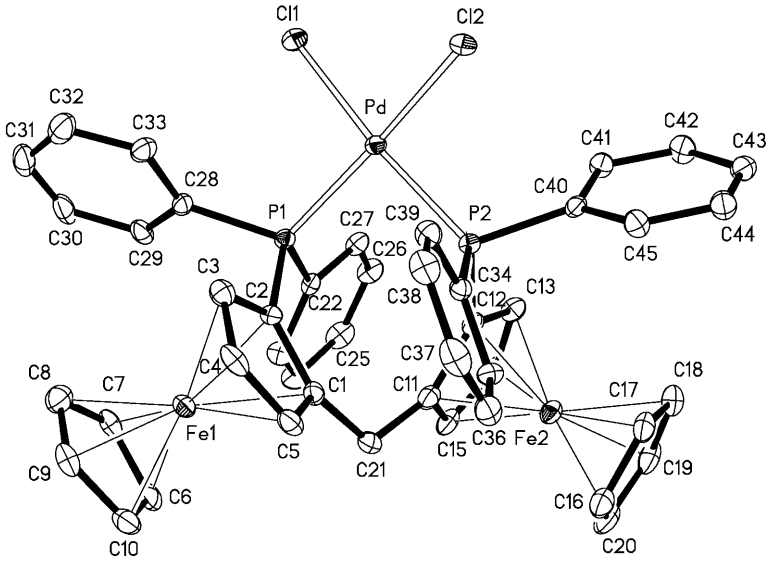



Fig. 3. *X-Ray crystal structure of [PdCl$_2$((*R$_p$,R$_p$*)-***1***)]·CHCl$_3$*. Ellipsoids are shown at the 40% level; H-atoms have been omitted for clarity. Selected distances ([Å] and angles [°]: Pd–P(1), 2.277(1); Pd–P(2), 2.278(1); Pd–Cl(1), 2.352(1); Pd–Cl(2), 2.362(1); (Fe–C$_{Cp}$)$_{aver}$, 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.

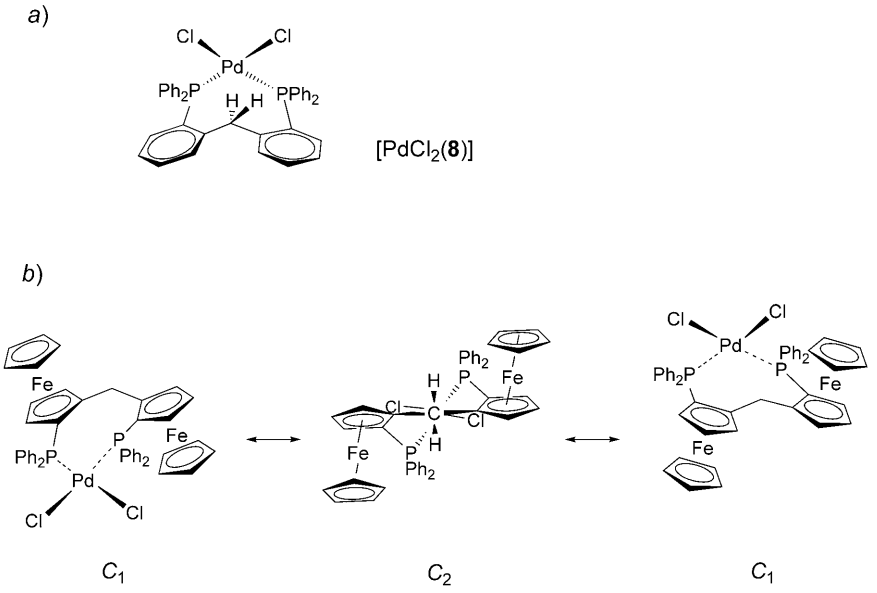
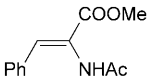


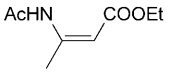

Fig. 4. a) *Schematic representation of the molecular structure of [PdCl$_2$(**8**)] in the solid state.* b) *Calculated Structures of* $C_1$*- and* $C_2$*-symmetric conformers of [PdCl$_2$(**1**)]*

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 $\alpha$-(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 $\alpha$- and $\beta$-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-




**9**

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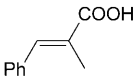


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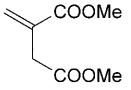


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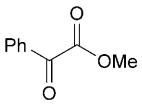


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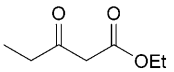


**14**

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.

This work was supported by *Solvias AG* (Basel) and by the *Österreichischer Akademischer Austauschdienst*.

## 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 $\delta$ 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. $[\alpha]_\lambda^{20}$ ($\lambda$ 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.). $[\alpha]_\lambda^{20}$ ($\lambda$ 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°. $[\alpha]_\lambda^{20}$ ($\lambda$ 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 Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å), with 0.3° $\omega$-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**$\cdot(BH_3)_2$. 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**$)]\cdot CHCl_3$. 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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*Received March 29, 2006*