Synthesis of Some Ferrocene-Based 1,3-Bis(phosphanes) with Planar Chirality as the Sole Source of Chirality

Gilles Argouarch,[a] Odile Samuel,[a] and Henri B. Kagan*[a]

Dedicated to the memory of Sir Derek Barton

Keywords: Chirality / Ferrocene / Hydrogenation / Phosphanes / Rhodium

Several enantiopure diphosphanes **21** were synthesized in three steps from a common precursor **19**. The cationic rhodium complexes **22** were screened as catalysts for asymmetric hydrogenation of various alkenes. Enantioselectivities up to 95–98% have been observed in some cases. Enantioselectivities are modest in allylic substitution catalyzed by the corresponding palladium complexes.

Introduction

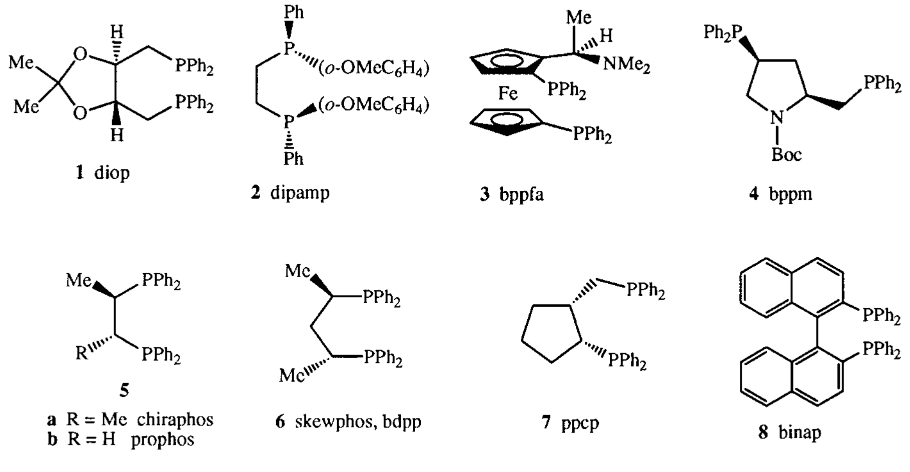
Chiral chelating bis(phosphanes) (Scheme 1) continue to play an important role in the development of asymmetric catalysis.[1] Diop (**1**), prepared in 1971, was the first example of a chiral bis(phosphane) and, by selecting the shortest chain of atoms connecting the two phosphorus atoms, may be considered as a 1,4-bis(phosphane).[6] Dipamp (**2**), described in 1975,[7] is an example of a 1,2-bis(phosphane), as are chiraphos (**5a**)[8] and prophos (**5b**).[9] Binap (**8**) was synthesized in 1980[10] and is a 1,4-bis(phosphane). Bppfa (**3**)[11] is more difficult to classify, but it is not too different from a 1,3-bis(phosphane), if one considers the hypothetical P−C−Fe−C−P fragment.

The true 1,3-bis(phosphane) **6** was synthesized by Bosnich et al. in 1981.[12,13] This ligand, originally named skewphos, is currently known by the name of bdpp. It gives rhodium complexes, which are excellent catalysts for asymmetric hydrogenation. Ppcp (**7**) is another case of a 1,3-bis(phosphane).[14] Quite a few families of chiral 1,3-bis(phosphanes) have now been described.

As discussed above, bppfa (**3**) is an early example of a chelating bis(phosphane) combining central and planar chirality. More recently, extending the synthetic approach of Hayashi et al., Togni et al. investigated a new class of bis(phosphanes), exemplified by **9a** (josiphos).[15] These interesting ligands are also 1,3-bis(phosphanes) involving two types of chirality.

There are very few examples of bis(phosphanes) possessing only planar chirality. Phanephos (**10**) was prepared in 1996 by a team at the Merck company.[16] Compounds **11a** and **11b** (Scheme 2) are excellent ligands in asymmetric catalysis.[17,18] We also recently synthesized the 1,2-bis(phosphane) **12**,[19] while the phosphaferrocene derivative **13** was obtained by Fu and Qiao.[20] The biferrocenylbis(phosphane) Et-TRAP-H (**14**) prepared by Ito et al. is a *trans*-chelating ligand.[21]

In this article, we wish to describe the synthesis and properties of some chiral ferrocene-based 1,3-bis(phosphanes)



Scheme 1

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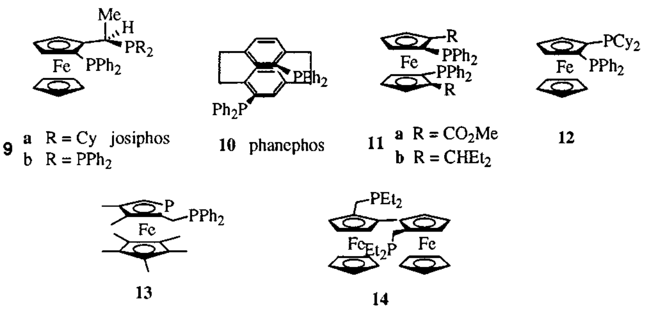
[a] Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, 91405 Orsay, France
Fax: (internat.) + 33-1/69154680
E-mail: kagan@icmo.u-psud.fr

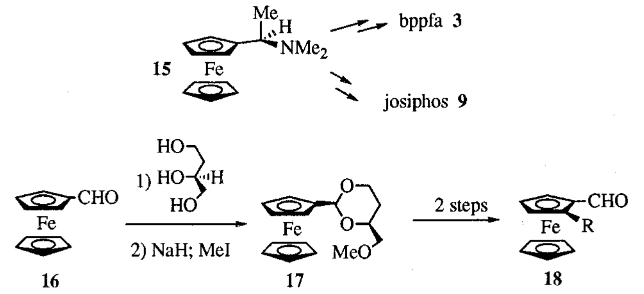


Scheme 2

with planar chirality as their only element of chirality; a situation still quite unusual, as discussed above.

Chiral Ferrocene-Based 1,3-Bis(phosphanes)

Josiphos (**9a**) and related 1,3-bis(phosphanes) were synthesized by Togni et al. from a common precursor, amine **15** (Scheme 3).[15] This amine has been resolved and studied by Ugi et al., who showed that *n*BuLi promoted a diastereoselective *ortho* deprotonation on the ferrocene system.[22] This approach was used to prepare bppfa (**3**) and most of the subsequent ferrocene-based phosphanes possessing a planar chiral unit.



Scheme 3

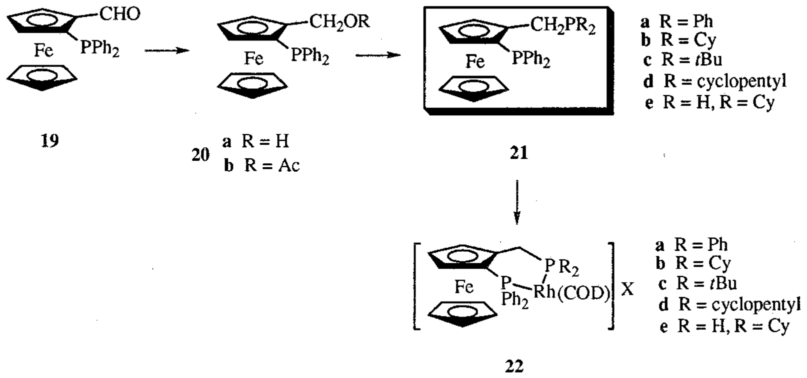
We recently described a new route to ferrocenes with planar chirality. Based on the formation of a chiral acetal **17** from ferrocenecarbaldehyde (**16**),[23,24] this method involves an almost completely diastereoselective *ortho* deprotonation of acetal **17** by *t*BuLi, followed by an electrophilic quenching and an acid-catalyzed hydrolysis. In this manner, many enantiopure *ortho*-substituted aldehydes **18** have been prepared. These compounds are themselves good starting materials for the preparation of more complex molecules. We considered this approach in order to obtain a set of 1,3-bis(phosphanes) possessing only planar chirality as their source of chirality.

We started from phosphanylferrocenecarbaldehyde (*S*)-**19** (100% *ee*), previously obtained in excellent yield from ferrocenecarbaldehyde (**16**).[23,24] This is an air-stable compound, easy to handle. Reduction with sodium tetrahydroborate provided alcohol (*S*)-**20a**, which was transformed into acetate **20b** by treatment with acetic anhydride. The crude compound **20b** was the starting material for the synthesis of 1,3-bis(phosphanes) (*S*)-**21**. We used the procedure given by Hayashi et al. in their synthesis of some ferrocene-based phosphanes,[25] namely heating an acetoxy compound in methanol with an excess of HPR_2. We applied this method on a 3−5-mmol scale, using a 10-fold excess of the phosphane HPR_2. The pure 1,3-bis(phosphanes) **21a**−**21c** could be isolated as crystalline compounds in yields ranging from 30 to 45%. Bis(phosphane) **21d** was an oily material, obtained in 52% yield. Finally, bis(phosphane) **21e**, prepared from **20b** and H_2PCy, was isolated as a mixture of epimers at the phosphorus atom.

Bis(phosphanes) (*S*)-**21a**, (*S*)-**21b** and (*S*)-**21c** have negative specific rotations (−178, −160 and −160, respectively). The *S* configuration is the direct consequence of the synthetic scheme originating from (*S*)-**19** (Scheme 4). Moreover, since initial phosphane (*S*)-**19** is enantiopure, as established by chiral HPLC, we assume that bis(phosphanes) **21** also have *ee* values of 100%. ^{31}P-NMR spectroscopy shows similar signals for the PPh_2 group directly linked to the ferrocene ring (close to $\delta = -23.3$), while the PR_2 signals were at $\delta = -14.8$ (R = Ph), $\delta = -1.8$ (R = Cy) and $\delta = 27$ (R = *t*Bu).

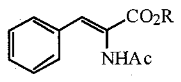
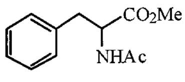
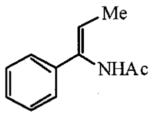
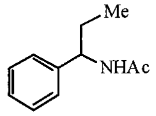
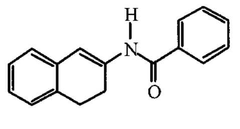
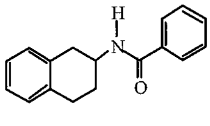
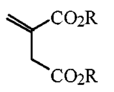
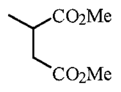
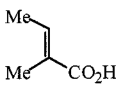
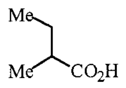
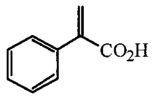
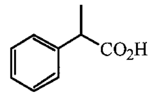
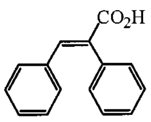
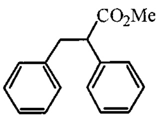
Asymmetric Catalysis

Bis(phosphanes) **21** were used as ligands in rhodium complexes of general formula [Rh(COD)**21**]X (where X = BF_4 or PF_6) or [RhCl(COD)**21**]. The cationic complexes for hydrogenation were prepared in situ, by adding the calcu-



Scheme 4

Table 1. Unsaturated substrates which were hydrogenated in the presence of chiral catalysts

Substrate	Product	Ref.	Analysis
 **23** R = H **24** R = Me	 **32**	[26]	HPLC 0.8 mL/min., λ = 254 nm hexane/*i*PrOH 9/1 (*R*)-**32**: t_1 = 12.2 min. (*S*)-**32**: t_2 = 16.2 min.
 **25**	 **33**	[27]	HPLC 1.0 mL/min., λ = 254 nm hexane/*i*PrOH 95/5 (*R*)-**33**: t_1 = 17.5 min. (*S*)-**33**: t_2 = 22.3 min.
 **26**	 **34**	[a]	HPLC 1.0 mL/min., λ = 254 nm hexane/*i*PrOH 9/1 t_1 = 17.8 min. t_2 = 22.6 min.
 **27** R = H **28** R = Me	 **35**	[b]	HPLC 0.8 mL/min., λ = 215 nm hexane/*i*PrOH 98/2 (*R*)-**35**: t_1 = 8.6 min. (*S*)-**35**: t_2 = 15.4 min.
 **29**	 **36**	[b]	GC isotherm: 100°C (*R*)-**36**: t_1 = 30.0 min. (*S*)-**36**: t_2 = 31.4 min.
 **30**	 **37**	[28]	Polarimetry $[\alpha]_D$ = +72 (c = 1.60, $CHCl_3$) 100% *ee* (*S*)-**37**
 **31**	 **38**	[29]	HPLC 0.5 mL/min., λ = 254 nm hexane/*i*PrOH 99/1 (*R*)-**38**: t_1 = 13.2 min. (*S*)-**38**: t_2 = 15.0 min.

[a] See Experimental Section. – [b] Commercially available compounds.

lated amount of bis(phosphane) **21** to $[Rh(COD)_2]BF_4$. The chlororhodium complexes were generated in situ by addition of bis(phosphane) **21** to $[RhCl(COD)]_2$. Cationic complexes of **21b** and **21d** were also isolated (see Experimental Section). These complexes (1 mol-%) efficiently catalyzed the hydrogenation of various types of C=C double bonds. The various unsaturated substrates which were studied are listed in Table 1.

Bis(phosphane) **21a**, with two PPh_2 moieties, gave moderate enantioselectivities in the reduction of *N*-acetyldehydrophenylalanine or enamide **25** (77–65% *ee*). Very poor enantioselectivities were observed in the hydrogenation of itaconic acid (**27**) or its dimethyl ester **28**. At the opposite extreme, bis(phosphane) **21b**, bearing a CH_2PCy_2 group, is an excellent ligand for reduction of itaconic acid or its dimethyl ester (93% *ee* and 98% *ee*, respectively; Entries 8, 9, Table 2). It also gave 94% *ee* in the reduction of enamide **25** (Entry 6, Table 2). All these hydrogenations were carried out under 1 atm of hydrogen. In contrast, bis(phosphane) **21b** provided poor enantioselectivities in hydrogenations of *N*-acetyldehydrophenylalanine and its methyl ester.

The catalyst made from bis(phosphane) **21d** [bearing the $CH_2P(cyclopentyl)_2$ group] was very active and enantioselective for the hydrogenation of itaconic acid and dimethyl

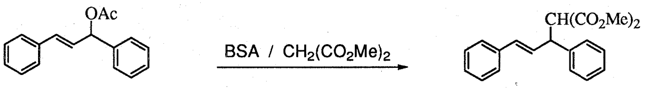
Table 2. Asymmetric hydrogenation catalyzed by rhodium complexes **22**

Entry	Bis(phosphane)[a][b]	Substrate[c]	H_2 pressure [atm]	Yield (%)	*ee* (%)[d]	Configuration[e]
1	**21a**	**23**	5	86	77	*S*
2	**21a**	**24**	1	97	65	*S*
3	**21a**	**25**	20	99	65	*R*
4	**21a**	**26**	20	95	26	*S*
5	**21b**	**23**	1	98	34	*S*
6	**21b**	**25**	1	98	94	*R*
7	**21b**	**26**	5	93	36	
8	**21b**	**27**	1	92	93	*S*
9	**21b**	**28**	1	94	98	S
10	**21b**	**30**	1	87	81	*R*
11	**21c**	**26**	5	93	30	
12	**21c**	**31**	5	98	42	*S*
13	**21d**	**30**	1	90	83	*R*
14	**21d**	**27**	1	98	88	*S*
15	**21d**	**28**	1	95	92	*S*
16	**21d**	**25**	10	95	82	*S*

[a] The rhodium catalyst (1 mol-%) was [Rh(COD)**21**]BF4, except Entry 1 {[RhCl(COD)**21**]} and Entries 13−16 {[Rh(COD)**21**]PF6}. − [b] Reactions were performed in methanol, except Entry 9 (THF). [Substrate] = 2×10^{-1} M. − [c] Enantioselectivities lower than 30% (and yield over 90%) were obtained in the following experiments (ligand/substrate): **21a/27** or **28**; **21b/24** or **29**; **21e/23**, **24**, **27−29**; **21d/23** or **24**; **21e/24** or **28**. Hydrogen pressure: 1 atm, except for **21a/31** (20 atm), **21b/29** (5 atm), **21c/29** (5 atm); for **21a/31** (20 atm): no reaction. − [d] Measured by HPLC. − [e] Not established for Entries 7 and 11.

itaconate (88% *ee* and 92% *ee*, respectively, *S* configuration; Entries 14, 15, Table 2), while the enantioselectivity was poor in the hydrogenation of *N*-acetyldehydrophenylalanine (**23**) and its methyl ester **24**. There are strong parallels in the behavior of bis(phosphanes) **21b** and **21d**, although the latter generated a catalyst of higher activity. Bis(phosphanes) **21c** and **21e** (as a mixture of diastereomers) were checked in asymmetric hydrogenation. The catalytic activities were good but the *ee* values were low.

Rhodium complexes involving bis(phosphanes) **21** are excellent hydrogenation catalysts for many unsaturated substrates listed in Table 1. Moreover, enantiomeric excesses close to or higher than 90% have been achieved (Entries 6, 8, 9, 14, and 15, Table 2), indicating that, in ferrocene-based bis(phosphanes), planar chirality alone may be a powerful stereodirecting factor for enantioselective hydrogenation. It is interesting to compare some of our results with asymmetric hydrogenation induced by (josiphos)rhodium complexes.[15] Josiphos (**9a**) gave good enantioselectivities for hydrogenation of dehydroamino acids and their esters (96% *ee* in the hydrogenation of **24**), and was excellent in the reduction of dimethyl itaconate (98% *ee* in *S* configuration). The planar chirality should hence be of major importance, since bis(phosphane) **21b**, with exclusively planar chirality, also gave an asymmetric induction of 98% *ee* (*S* configuration) for reduction of dimethyl itaconate. When the PCy_2 group in josiphos (**9a**) was replaced with PPh_2, the corresponding [bis(phosphane)]rhodium complex was less enantioselective for asymmetric hydrogenation, as we observed when going from **21b** to **21a**. Togni et al. discovered for the josiphos family that a good combination of groups is a PPh_2 moiety placed on the ferrocene ring and a basic phosphorus group [P(alkyl)$_2$] on the asymmetric carbon atom of the side chain.[15] The same rule stands for the family of chiral bis(phosphanes) **21** that we synthesized.



39 **40**

Scheme 5

Allylic alkylation of racemic **39** by dimethyl malonate (Scheme 5) also allows us to compare our results with those obtained with ligands **9** (93% and 81% *ee*, respectively for **9a** and **9b**, *S* configuration).[15] Bis(phosphanes) **21a**, **21b**, and **21c** gave 12, 62 and 83% *ee*, respectively, in the *S* configuration. Thus, results are comparable for **21c** and **9b**, both ligands possessing the P*t*Bu$_2$ group on the side chain, indicating that the planar chirality is also of major importance in allylic alkylation with this type of ferrocene-based bis(phosphanes).

Conclusion

We have prepared very simple enantiopure ferrocene-based bis(phosphanes) **21**, possessing planar chirality as their sole source of chirality. Screening of the catalytic properties of the corresponding rhodium complexes has been performed for the hydrogenation of a selected set of C=C double bonds. Excellent catalytic activities allowed operation at atmospheric pressure, with 1 mol-% of catalyst. In some cases, *ee* values of up to 95−98% were observed. The simplicity of the synthetic scheme (starting compound phosphanylferrocenecarbaldehyde **19** is easily available[24]), or its modification, should permit the preparation of many types of enantiopure bis(phosphanes) possessing only planar chirality. We are presently investigating the catalytic properties of ruthenium and iridium complexes with bis(phosphanes) **21** as ligands.

Experimental Section

General: ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded at 250 MHz, 63 MHz, and 101 MHz, respectively, with a Bruker AM 250 instrument. Chemical shifts are denoted in ppm (δ) relative to TMS (^{1}H and ^{13}C) or external H_3PO_4 (^{31}P). Coupling constants are reported in Hz. − Optical rotations: Perkin−Elmer 241 polarimeter (589 nm, 20 °C). Concentrations (*c*) are reported in g/100 mL. − Elemental analyses were performed by the "Service de microanalyse du CNRS" at Gif sur Yvette. − Mass spectra (MS) were determined with a GC/MS Ribermag R 10−10 instrument. Chemical ionisation (CI) was carried out using NH_3 as the reactant gas; electronic impact (EI) was performed at 70 eV. − High Resolution Mass Spectra (HRMS) were performed using a GC/MS Finningan-MAT-95-S. − Analytical HPLC was performed with an HPLC machine equipped with a Spectra Series P100 pump and a Spectra Series UV100 detector. The chiral stationary phase was a Daicel Chiralcel OD-H column. − Analytical GC was performed with a GC machine equipped with a Fison EL 980 detector. The chiral stationary phase was a Chiraldex B-PM column (β-cyclodextrin, Permethyl, 50 m and 0.25 mm). − All reactions were carried out under argon in oven-dried glassware using standard vacuum lines techniques. − All commercial reagents were used as received. Preparation of alcohol **20a**, see ref.[24] Description of **39** and **40**, see ref.[15]. Absolute configuration of planar chirality was named according to the Schlögl nomenclature (ref.[30]).

General Procedure for the Preparation of the Bis(phosphanes): (*S*)-2-(Diphenylphosphanyl)-1-(hydroxymethyl)ferrocene (**20a**) was placed under argon in a dry flask equipped with a reflux condenser and degassed acetic anhydride (10 mL) was added. The solution was heated at 80 °C for 2 h and then cooled to room temp. before addition of toluene (5 mL). Removal of the solvents under vacuum was performed overnight to give crude acetate **20b** as an orange solid. Methanol (30 mL) and an excess of nucleophile were injected to this acetate under argon and the solution was refluxed for 12 h. After cooling to room temp. and concentration under vacuum for 3 h, a dark oil was obtained. The crude product was purified by chromatography on alumina (200 g). The excess of nucleophile was first removed by using hexane (1 L) as the eluent, and elution of the bis(phosphane) was then performed using toluene.

(*S*)-1-(Diphenylphosphanyl)-2-[(diphenylphosphanyl)methyl]ferrocene (21a): General procedure with (*S*)-**20a** (1.2 g, 3.0 mmol) and $HPPh_2$ (5.3 g, 28.7 mmol). A yellow solid (630 mg, 1.1 mmol, 37%) was obtained. − M.p. 92 °C. − $[\alpha]_{589}^{20} = -178$ (c = 1.0, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 3.35 (s, 2 H, CH_2), 3.75 (s, 1 H, Cp subst.), 3.96 (s, 5 H, Cp), 4.06 (s, 1 H, Cp subst.), 4.13 (m, 1 H, Cp subst.), 7.19−7.43 (m, 18 H, Ph), 7.50−7.62 (m, 2 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 28.8 (dd, J_{PC} = 15.5 and 10.6 Hz, 1 C, CH_2), 68.9 (1 C, Cp subst.), 69.8 (5 C, Cp), 70.5 (d, J_{PC} = 3.6 Hz, 1 C, Cp subst.), 71.7 (dd, J_{PC} = 7.3 and 3.8 Hz, 1 C, Cp subst.), 75.6 (dd, J_{PC} = 6.5 and 3.7 Hz, 1 C, Cp subst.), 90.4 (dd, J_{PC} = 26.9 and 16.7 Hz, 1 C, Cp subst.), 127.7 (d, J_{PC} = 15.4 Hz, 2 C, Ph), 127.9 (2 C, Ph), 128.0 (2 C, Ph), 128.1 (1 C, Ph), 128.2 (2 C, Ph), 128.3 (1 C, Ph), 128.8 (d, J_{PC} = 18.4 Hz, 2 C, Ph), 132.0 (d, J_{PC} = 18 Hz, 2 C, Ph), 132.3 (d, J_{PC} = 17.4 Hz, 2 C, Ph), 133.4 (d, J_{PC} = 19.7 Hz, 2 C, Ph), 135.0 (d, J_{PC} = 21.3 Hz, 2 C, Ph), 137.8 (d, J_{PC} = 8.4 Hz, 1 C, Ph), 138.8 (d, J_{PC} = 16.2 Hz, 1 C, Ph), 139.1 (d, J_{PC} = 16.5 Hz, 1 C, Ph), 139.9 (d, J_{PC} = 9.1 Hz, 1 C, Ph). − ^{31}P NMR ($CDCl_3$): δ = −23.35 (d, J_{PP} = 8 Hz, 1 P, $FcPPh_2$), −14.83 (d, J_{PP} = 8 Hz, 1 P, CH_2PPh_2). − MS (IE); m/z (%): 570 (9) [M + 2], 569 (36) [M + 1], 568 (71) [M], 491 (17) [M − Ph], 383 (100) [M − PPh_2], 306 (23) [M − PPh_2−Ph], 226 (12) [FeCpPPh], 121 (10) [FeCp]. − $C_{35}H_{30}FeP_2$ (568.4): calcd. C 73.95, H 5.32, P 10.90, Fe 9.83; found C 74.18, H 5.22, P 10.87, Fe 9.65. − HRMS: calcd. 568.1172; found 568.1172.

(*S*)-1-[(Dicyclohexylphosphanyl)methyl]-2-(diphenylphosphanyl)ferrocene (21b): General procedure with (*S*)-**20a** (2 g, 5.0 mmol) and $HPCy_2$ (10 g, 50.4 mmol). After crystallization from ethanol, 1.3 g (2.2 mmol, 45%) of a yellow solid was obtained. − M.p. 115 °C. − $[\alpha]_{589}^{20} = -160$ (c = 1.0, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 1.00−1.76 (m, 22 H, Cy), 2.58 (dd, J_{AB} = 15.5 Hz, J_{PH} = 2.2 Hz, 1 H, CH_2), 2.68 (dd, J_{AB} = 15.5 Hz, J_{PH} = 2.3 Hz, 1 H, CH_2), 3.69 (s, 1 H, Cp subst.), 3.94 (s, 5 H, Cp), 4.19 (m, 1 H, Cp subst.), 4.52 (s, 1 H, Cp subst.), 7.14−7.23 (m, 5 H, Ph), 7.34−7.37 (m, 3 H, Ph), 7.50−7.57 (m, 2 H, Ph). − ^{31}P NMR ($CDCl_3$): δ = −23.41 (d, J_{PP} = 4.5 Hz, 1 P, P−Ph), −1.81 (d, J_{PP} = 4.5 Hz, 1 P, P−Cy). − MS (EI); m/z (%): 580 (4) [M], 497 (100) [M − Cy], 414 (6) [M − 2×Cy], 121 (7) [FeCp], 83 (11) [Cy], 56 (20) [Fe]. − $C_{35}H_{42}FeP_2$ (580.5): calcd. C 72.41, H 7.30, P 10.67; found C 72.11, H 7.21, P 10.71. − HRMS: calcd. 580.2111; found 580.2111.

(*S*)-1-[(Di-*tert*-butylphosphanyl)methyl]-2-(diphenylphosphanyl)ferrocene (21c): General procedure with (*S*)-**20a** (1.8 g, 4.5 mmol) and $HPtBu_2$ (5 g, 34.2 mmol). An orange solid (710 mg, 1.3 mmol, 30%) was obtained. − M.p. 94 °C. − $[\alpha]_{589}^{20} = -160$ (c = 1.0, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 0.89 (d, J_{HH} = 10.9 Hz, 9 H, *t*Bu), 1.19 (d, J_{HH} = 10.9 Hz, 9 H, *t*Bu), 2.60 (dd, J_{AB} = 16.3 Hz, J_{PH} = 4.9 Hz, 1 H, CH_2), 2.81 (d, J_{AB} = 16.3 Hz, 1 H, CH_2), 3.75 (s, 1 H, Cp subst.), 3.98 (s, 5 H, Cp), 4.20 (m, 1 H, Cp subst.), 4.75 (s, 1 H, Cp subst.), 7.22−7.26 (m, 5 H, Ph), 7.35−7.38 (m, 3 H, Ph), 7.55−7.62 (m, 2 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 20.4 (dd, J_{PC} = 23.1 and 9.6 Hz, 1 C, CH_2), 29.5 [d, J_{PC} = 9 Hz, 3 C, $C(CH_3)_3$], 29.8 [d, J_{PC} = 9.3 Hz, 3 C, $C(CH_3)_3$], 31.1 [d, J_{PC} = 12.5 Hz, 1 C, $C(CH_3)_3$], 31.6 [d, J_{PC} = 14.6 Hz, 1 C, $C(CH_3)_3$], 68.1 (1 C, Cp subst.), 69.6 (5 C, Cp), 70.4 (d, J_{PC} = 3.4 Hz, 1 C, Cp subst.), 72.7 (dd, J_{PC} = 13.7 and 4.1 Hz, 1 C, Cp subst.), 75.5 (d, J_{PC} = 9.6 Hz, 1 C, Cp subst.), 93.7 (dd, J_{PC} = 25 and 21 Hz, 1 C, Cp subst.), 127.7 (2 C, Ph), 127.8 (2 C, Ph), 128.0 (1 C, Ph), 128.8 (1 C, Ph), 132.6 (d, J_{PC} = 18.1 Hz, 2 C, Ph), 134.8 (d, J_{PC} = 20.8 Hz, 2 C, Ph), 137.7 (d, J_{PC} = 8.9 Hz, 1 C, Ph), 139.2 (d, J_{PC} = 9.6 Hz, 1 C, Ph). − ^{31}P NMR ($CDCl_3$): δ = −23.31 (s, 1 P, P−Ph), 26.99 (s, 1 P, P-*t*Bu). − MS (EI); m/z (%): 528 (1) [M], 471 (100) [M − Bu], 414 (14) [M − 2×Bu], 57 (10) [Bu], 56 (6) [Fe]. − $C_{31}H_{38}FeP_2$ (528.5): calcd. C 70.46, H 7.25, P 11.72; found C 69.87, H 7.18, P 10.57. − HRMS: calcd. 528.1798; found 528.1798.

(*S*)-1-[(Dicyclopentylphosphanyl)methyl]-2-(diphenylphosphanyl)ferrocene (21d): General procedure with (*S*)-**20a** (1.6 g, 4.0 mmol) and HP(cyclopentyl)$_2$ (5 g, 29.4 mmol). A red oil (1.1 g, 2 mmol, 52%) was obtained. − ^{1}H NMR ($CDCl_3$): δ = 1.30−1.82 (m, 18 H, 2×cyclopentyl), 2.76 (s, 2 H, CH_2), 3.77 (s, 1 H, Cp subst.), 3.95 (s, 5 H, Cp), 4.24 (m, 1 H, Cp subst.), 4.58 (s, 1 H, Cp subst.), 7.21−7.25 (m, 5 H, Ph), 7.36−7.38 (m, 3 H, Ph), 7.53−7.62 (m, 2 H, Ph). − ^{31}P NMR ($CDCl_3$): δ = −23.81 (s, 1 P, P−Ph), −3.10 (s, 1 P, P-cyclopentyl). − MS (CI); m/z (%): 570 (2) [M + NH_4], 553 (100) [M + H], 552 (8) [M], 483 (19) [M − cyclopentyl]. − HRMS: calcd. 552.1798; found 552.1798.

[(*S*,*S*$_P$) and (*S*,*R*$_P$)]-1-[(Dicyclohexylphosphanyl)methyl]-2-(diphenylphosphanyl)ferrocene (21e): General procedure with (*S*)-**20a** (1.4 g, 3.5 mmol) and H_2PCy (10 g, 86.0 mmol). After a second chromatographic purification (SiO_2, hexane/ethyl acetate, 9:1) and crystallization from ethanol, 630 mg (1.3 mmol, 36%) of a yellow solid was obtained. − M.p. 68−70 °C. − $[\alpha]_{589}^{20} = -220$ (c = 1.13, $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 1.00−1.80 (m, 11 H, Cy), 2.20−3.10 (m, 3 H, CH_2−PH), 3.72 (d, 1 H, Cp subst.), 3.95 (d, 5 H, Cp), 4.23 (d, 1 H, Cp subst.), 4.39 (s, 1 H, Cp subst.), 7.17−7.24 (m, 5 H, Ph), 7.34−7.36 (m, 3 H, Ph), 7.50−7.56 (m, 2 H, Ph). − ^{31}P NMR ($CDCl_3$): Diastereomer 1: δ = −43.80 (d, J_{PH} = 202.5 Hz, 1 P, PHCy), −23.95 (s, 1 P, P−Ph); Diastereomer 2: δ = −44.21 (d, J_{PH} = 201.4 Hz, 1 P, PHCy), −23.95 (s, 1 P, P−Ph). − MS (EI); m/z (%): 499 (1) [M + 1], 498 (2) [M], 497 (2) [M − H], 415 (100) [M − Cy], 414 (38) [M − H−Cy], 121 (6) [FeCp]. − $C_{29}H_{32}FeP_2$ (498.4): calcd. C 69.89, H 6.48, P 12.43; found C 69.76, H 6.42, P 12.69. − HRMS: calcd. 498.1328; found 498.1329.

(Cycloocta-1,5-diene){(*S*)-1-[(dicyclopentylphosphanyl)methyl]-2-(diphenylphosphanyl)ferrocene}rhodium(I) Hexafluorophosphate (22d): A dry Schlenk tube was charged with (*S*)-**21d** (190 mg, 0.34 mmol), [Rh(COD)(acac)] (105 mg, 0.34 mmol) and NH_4PF_6 (200 mg, 1.2 mmol) under argon, before adding CH_2Cl_2 (5 mL) and water (3 mL). This mixture was stirred at room temp. for 2 h and then the water was removed. The organic phase was washed with water and then concentrated under vacuum. The crude product was purified twice by stirring in 6 mL of refluxing benzene (in which it was insoluble) to give 250 mg (0.27 mmol, 80%) of a red powder. − M.p. 178 °C. − $[\alpha]_{589}^{20} = +15$ (c = 0.39, $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 1.23−2.50 (m, 28 H, CH_2+2 × cyclopentyl + COD), 3.07 (m, 1 H, COD), 3.41 (s, 1 H, COD), 3.65 (s, 5 H, Cp), 4.25 (s, 1 H, Cp subst.), 4.32 (s, 1 H, Cp subst.), 4.36 (s, 1 H, COD), 4.71 (s, 1 H, Cp subst.), 5.09 (s, 1 H, COD), 7.24−7.43 (m, 5 H, Ph), 7.69−7.75 (m, 3 H, Ph), 8.27−8.34 (m, 2 H, Ph). − ^{31}P NMR ($CDCl_3$): δ = −143.78 (m, J_{PF} = 711 Hz, 1 P, PF_6), 19.16 (dd, J_{PP} = 32.8 Hz, J_{PRh} = 144.6 Hz, 1 P, P−Ph), 46.09 (dd, J_{PP} = 32.8 Hz, J_{PRh} = 144 Hz, 1 P, P-cyclopentyl). − $C_{41}H_{50}F_6FeP_3Rh$ (908.5): calcd. C 54.20, H 5.55; found C 54.84, H 5.68.

(Cycloocta-1,5-diene){(*S*)-1-[(Dicyclohexylphosphanyl)methyl]-2-(diphenylphosphanyl)ferrocene}rhodium(I) Hexafluorophosphate (22b): Prepared as for **22d**; crystallized from ethanol, red crystals (85%). − M.p. 250 °C (decomp.). − $[\alpha]_{589}^{20} = -5$ (c = 2.0, $CHCl_3$). − ^1H NMR ($CDCl_3$): δ = 1.23−2.50 (m, 32 H, CH_2 + Cy + COD), 3.12 (m, 1 H, COD), 3.30 (s, 1 H, COD), 3.65 (s, 5 H, Cp), 4.20 (s, 1 H, Cp subst.), 4.33 (s, 1 H, Cp subst.), 4.35 (s, 1 H, COD), 4.75 (s, 1 H, Cp subst.), 5.15 (s, 1 H, COD), 7.02−7.70 (m, 8 H, Ph), 8.20−8.40 (m, 2 H, Ph). − ^{31}P NMR ($CDCl_3$): δ = −143.76 (m, J_{PF} = 711 Hz, 1 P, PF_6), 19.12 (dd, J_{PP} = 33.1 Hz, J_{PRh} = 142.5 Hz, 1 P, P−Ph), 44.20 (dd, J_{PP} = 33.1 Hz, J_{PRh} = 142.5 Hz, 1 P, P−Cy). − HRMS: calcd. for $C_{43}H_{54}FeP_2Rh^+$ 791.2098; found 791.2099.

Hydrogenation Procedure Using a Complex Prepared In Situ: The substrate (2 mmol) was placed under hydrogen. The preformed catalyst solution {1 mol-% of $[Rh(COD)_2]BF_4$ or 0.5 mol-% of $[RhCl(COD)]_2$ and 1.3 mol-% of bis(phosphane) **21** in 10 mL of methanol} was added to the substrate and the mixture was stirred under hydrogen until 1 equiv. of H_2 had been consumed. The solvent was evaporated and the enantiomeric excesses were measured by HPLC (carboxylic acids were analyzed as their methyl esters, after methylation by $MeOH/SOCl_2$), GC or polarimetry.

Hydrogenation Procedure Using an Isolated Complex: The substrate (2 mmol) and the cationic complex **22** (1 mol-%) were placed under hydrogen. After addition of methanol (10 mL), stirring was continued until 1 equiv. of H_2 had been consumed. The solvent was evaporated and the enantiomeric excesses were measured by HPLC (carboxylic acids were analyzed as their methyl esters, after methylation by $MeOH/SOCl_2$), GC or polarimetry.

Allylic Alkylation Procedure: To the reaction mixture containing $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.0064 mmol) and bis(phosphane) **21** (0.0128 mmol) in THF (4 mL) under argon, were added successively the racemic acetate **39** (1.28 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (2.56 mmol) and dimethyl malonate (2.56 mmol), and potassium acetate (6 mg, 0.06 mmol). The mixture was stirred for 2 d; then the solvent was evaporated and the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate, 4:1). The enantiomeric excesses were measured by HPLC, column Daicel Chiralcel OD−H, 0.5 mL/min, λ = 254 nm, hexane/*i*PrOH (99:1). (*R*)-**40**: t_1 = 19.7 min; (*S*)-**40**: t_2 = 21.1 min.

3-Benzamido-1,2-dihydronaphthalene (26): A Dean−Stark apparatus was charged with β-tetralone (14.62 g, 0.1 mol), benzamide (24.22 g, 0.2 mol), Amberlyst 15 (10 g) and toluene (120 mL). The mixture was stirred at 120 °C for 1 d and, after cooling to 60 °C, filtered through paper. After addition of a solution of $NaHCO_3$, the organic phase was separated, washed twice with water and the solvent was evaporated. Crude product was purified by chromatography on alumina with a mixture of dichloromethane/cyclohexane (4:1) as the eluent. The brown solid obtained (18.10 g) was then recrystallized from 250 mL of hot toluene to give 13.7 g (54.9 mmol, 55%) of pure enamide. − M.p. 121 °C. − ^1H NMR ($CDCl_3$): δ = 2.55 (t, J_{HH} = 7.7 Hz, 2 H, CH_2), 2.93 (t, J_{HH} = 7.7 Hz, 2 H, CH_2), 7.07−7.80 (m, 11 H, Ph + CH + NH). − ^{13}C NMR ($CDCl_3$): δ = 27.6 (1 C, CH_2), 27.9 (1 C, CH_2), 112.0 (1 C, CH), 125.9 (1 C, Ph), 126.1 (1 C, Ph), 126.6 (1 C, Ph), 126.8 (2 C, Ph), 127.0 (1 C, Ph), 128.7 (2 C, Ph), 131.7 (1 C, Ph), 132.7 (1 C, C−NH), 134.5 (1 C, Ph), 134.8 (1 C, Ph), 135.0 (1 C, Ph), 165.8 (1 C, CO). − MS (IE); m/z (%): 249 (3) [M], 105 (8) $[C_7H_5O]$, 77 (5) [Ph], 43 (100) [CO−NH]. − $C_{17}H_{15}NO$ (249.3): calcd. C 81.90, H 6.07, N 5.62; found C 81.57, H 6.77, N 5.64.

2-Benzamidotetrahydronaphthalene (34): M.p. 138−140 °C. − ^1H NMR ($CDCl_3$): δ = 1.88 (m, 1 H, CH_2), 2.14 (m, 1 H, CH_2), 2.75 (dd, J_{AB} = 16.3 Hz, J_{HH} = 8.3 Hz, 1 H, CH_2), 2.91 (m, 2 H, CH_2), 3.21 (dd, J_{AB} = 16.3 Hz, J_{HH} = 5.1 Hz, 1 H, CH_2), 4.47 (m, 1 H, CH), 6.24 (s, 1 H, NH), 7.04−7.13 (m, 4 H, Ph), 7.35−7.49 (m, 3 H, Ph), 7.71−7.75 (m, 2 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 27.2 (1 C, CH_2), 28.6 (1 C, CH_2), 35.5 (1 C, CH_2), 45.6 (1 C, CH), 125.8 (1 C, Ph), 126.0 (1 C, Ph), 126.8 (2 C, Ph), 128.3 (2 C, Ph), 128.7 (1 C, Ph), 129.3 (1 C, Ph), 131.2 (1 C, Ph), 134.0 (1 C, Ph), 134.6 (1 C, Ph), 135.3 (1 C, Ph), 167.0 (1 C, CO). − MS (IE); m/z (%) = 251 (3) [M], 105 (56) $[C_7H_5O]$, 91 (14) [Trop.], 77 (100) [Ph], 43 (15) [CO−NH]. − HRMS: calcd. 251.1346; found 251.1346.

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