A New Class of Ferrocene-Based 1,2-Bis(phosphanes) Possessing only Planar Chirality

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Dedicated to the memory of Vladimir Prelog

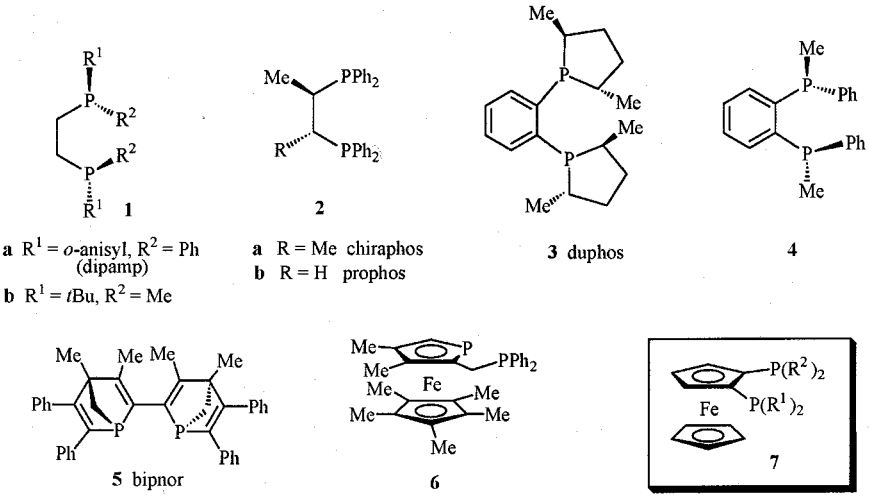
Keywords: Asymmetric catalysis / Chiral sulfoxides / Ferrocene / Hydrogenations / Phosphanes / Planar chirality

Chiral 1,2-bis(phosphanes) **13**, devoid of individual chiral centers, have been prepared in three steps from chiral sulfoxide **10**. Their corresponding rhodium complexes were used as catalysts for asymmetric hydrogenation, giving high *ee* values (≤ 95%) in the reduction of itaconic acid or its ester. A cationic rhodium complex involving coordination of two molecules of **13b** and one molecule of oxygen has been isolated and its crystal structure established.

Introduction

Chiral bis(phosphanes) are of paramount importance in the development of asymmetric catalysis. After the early syntheses of diop in 1971,[1,2] bppfa in 1974,[3] and dipamp (**1a**) in 1975,[4] many other chiral bis(phosphanes) were prepared (for some reviews see refs.[5−7]). Several hundred chiral bis(phosphanes) are presently known. Chirality can only originate from individual centers of chirality (as in diop or in **1**), from axial chirality (as in binap[8]), or from planar chirality.[9−11] Sometimes several sources of chirality are combined within the same molecule, as in bppfa.[3]

1,2-Bis(phosphanes) are excellent transition metal ligands, easily giving a five-membered ring chelate. The first examples of chiral analogs were provided by dipamp (**1a**), chiraphos (**2a**)[12] and prophos (**2b**) (Scheme 1).[13] These compounds accommodate centers of chirality, as do bis(phosphanes) **1b**,[14] **3**,[15] **4**,[16] and **5**.[17] The chirality of 1,2-bis(phosphane) **6**[18] is exclusively of the planar variety. We wish to present the first examples of a class of compounds exemplified by the general formula **7**, where R^1 and R^2 are achiral groups. We will also describe some results given by these new ligands in various asymmetric catalyzed reactions. A preliminary communication has been published.[19]



Scheme 1. Various chiral 1,2-bis(phosphanes)

Asymmetric Synthesis of 1,2-Bis(phosphanes) 13a and 13b

The strategy used to produce enantiopure 1,2-bis(phosphanes) **7,** of predictable absolute configuration, is based on stereochemically controlled reactions involving some chiral ferrocenyl sulfoxides.[19] The main steps leading to bis(phos-

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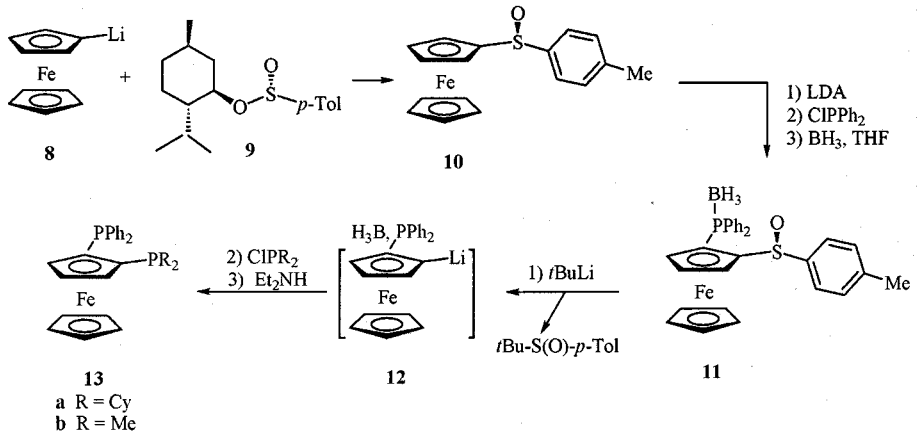


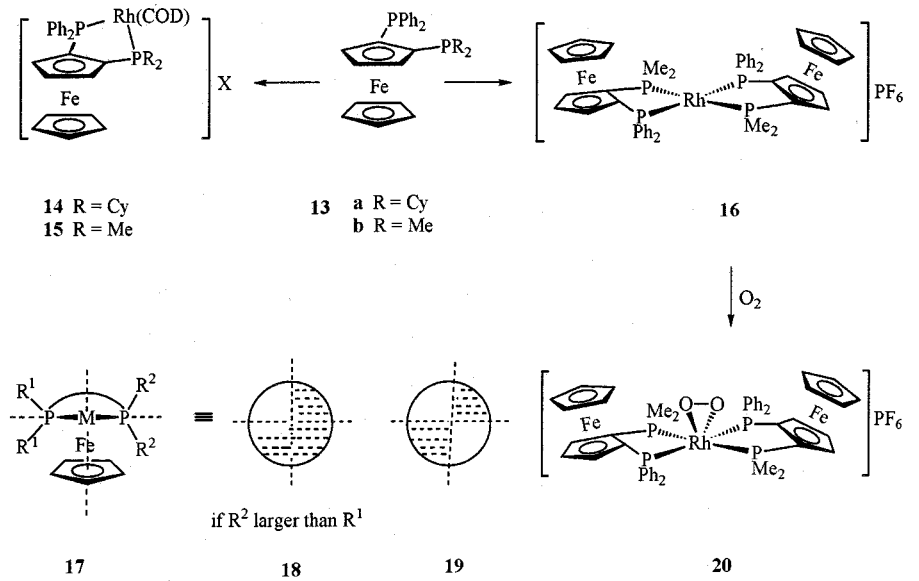
Scheme 2. Synthetic scheme for preparation of bis(phosphanes) **13**

phanes) **13** (which are a sub-class of general formula **7**) are described in Scheme 2.

Monolithioferrocene (**8**) was prepared first, as previously described.[19,20] It was subjected to an Andersen reaction[21] involving (S_S,1*R*)-menthyl *p*-tolylsulfinate (**9**). Under the correct conditions, this reaction gives a clean inversion of configuration at the sulfur atom, and in this way ferrocenyl *p*-tolyl (*S*)-sulfoxide (**10**) could be obtained in 47% yield and 99% *ee*.[19] Diastereoselective *ortho*-lithiation was achieved using LDA at −78 °C (*n*BuLi was unsuccessful for this purpose).[19,22] Electrophilic quenching by $ClPPh_2$ at the same temperature gave, after borane protection of the phosphorus atom, the sulfoxide **11** (> 98% *de*) in 57% yield.[19] This compound is a key intermediate for the in situ generation of the chiral lithioferrocene **12**, which is subsequently trapped by $ClPR_2$. We have found that *t*BuLi is capable of attacking the sulfur atom in various *ortho*-substituted ferrocenyl *p*-tolyl sulfoxides, including **11**.[19] The result is a substitution reaction, giving *tert*-butyl *p*-tolyl sulfoxide and **12**. In view of the mechanism of the reaction, one can assign the absolute configuration of the bis(phosphanes) as depicted in **13**. This has been confirmed in the case of R = Me (vide infra) by X-ray crystallography. This method allowed us to prepare crystalline bis(phosphane) (*R*)-**13a** ($[\alpha]_D$ = +327) in 33% yield (based on the converted portion of **11**, the unchanged **11** being recovered). Deprotection of the borane intermediate (a mixture of the two *P*-substituted monoboranes of **13a**) was accomplished by the Imamoto method, using reflux in diethylamine.[23] The low yield arises from the incomplete quenching of lithio compound **12** by $ClPCy_2$, giving after workup a borane adduct of ferrocenyldiphenylphosphane. The conversion (87%) of lithio intermediate **12** is more satisfactory when quenched with $ClPMe_2$,. A similar workup gave crystalline bis(phosphane) (*R*)-**13b** in 35% yield (based on the converted **11**).

Asymmetric Catalysis

As their source of chirality, bis(phosphanes) **13a** and **13b** have only the planar variety. The dissymmetry of these unusual compounds and related molecules of general formula



Scheme 3. Rhodium complexes deriving from bis(phosphanes) **13**

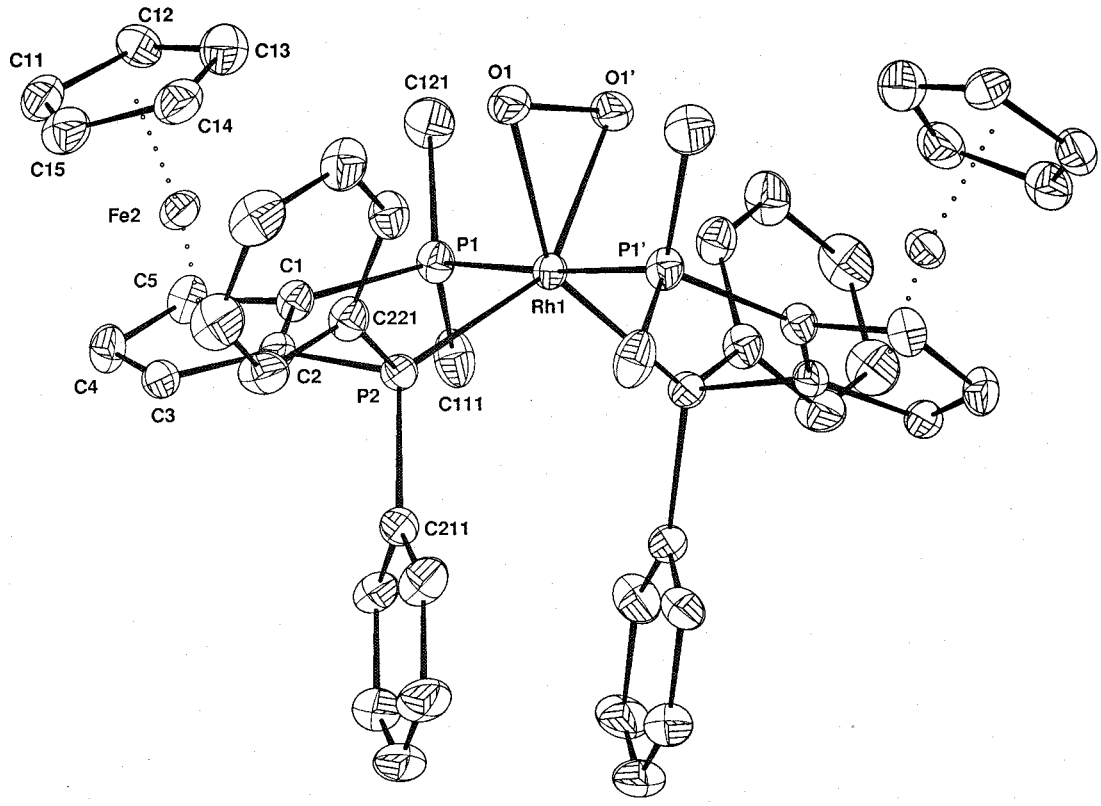


Figure 1. Molecular view of complex **20** showing the atom numbering scheme; ellipsoids represent 30% probability; hydrogen atoms are omitted

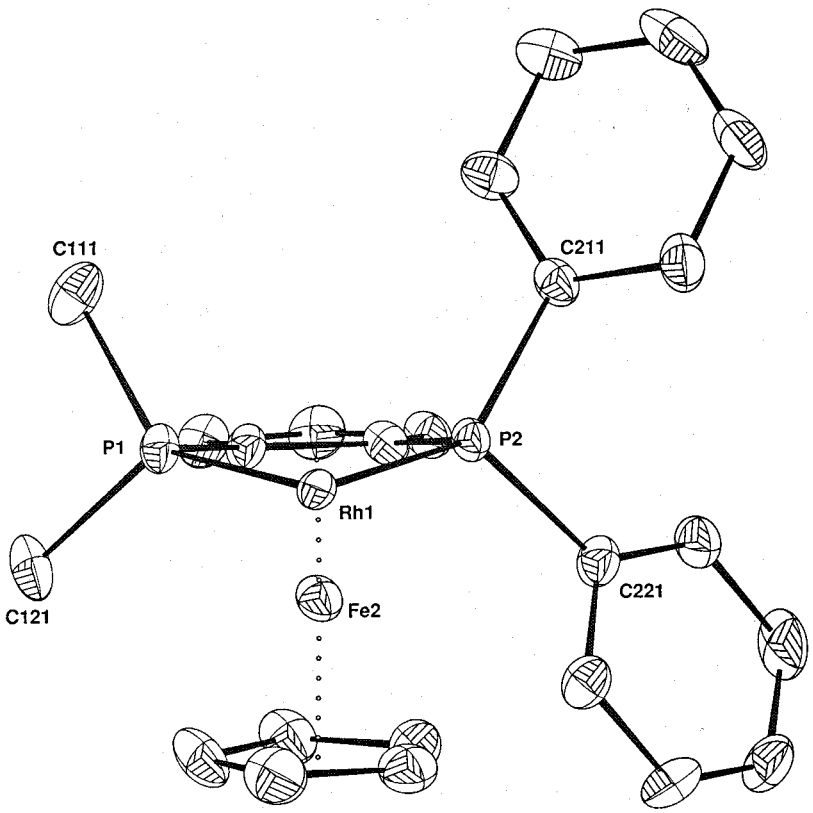
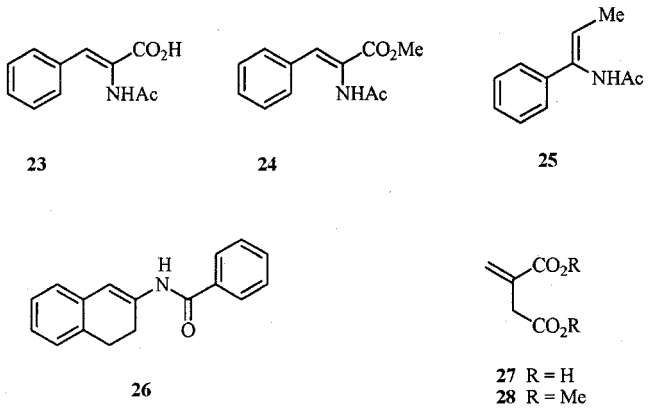


Figure 2. Perspective view along the chelating Rh−phosphanes plane of complex **20**; O atoms have been omitted



Scheme 4

7 is purely a function of the nature of the achiral R^1 and R^2 groups bound to the phosphorus atom. If one considers the chelation plane P−M−P, where M is a transition metal center, one may draw the projection **17** (Scheme 3). A quadrant picture **18** can be described, considering the unsubstituted Cp ring as hindering the bottom part of the space. With these assumptions, one quadrant remains unhindered. This situation is very different from the quadrant rule (**19**) given by Knowles et al. for the C_2-symmetric bis(phosphanes), where two quadrants are available to accommodate the bulky groups of the substrate.[24] This rule has been widely used; for binap[25] or duphos,[16] for example. Because of this unique situation, we have investigated the coordination chemistry of rhodium complexes of bis(phosphanes) **13a** and **13b**.

When trying to prepare a crystalline rhodium complex **15**, we were able to isolate crystals of the unexpected complex **20**. This cationic complex involves the binding of two molecules of bis(phosphane) **13b** and one molecule of oxygen coordinated in an η^2 mode. Presumably, traces of molecular oxygen present during the crystallization assays attacked the cationic complex **16** produced during the formation of **15** {from **13b** and [Rh(COD)(acac)] (1:1 mixture), followed by addition of NH_4PF_6}. It is known that the cationic complex $[(dppe)_2Rh]PF_6$ can give rise to $[(dppe)_2RhO_2]PF_6$, its crystal structure showing an η^2 coordination of O_2 above the equatorial plane of the four phosphorus atoms.[26] In complex **20**, a similar coordination occurs, with the O−O bond measuring 1.412 Å (against 1.418 Å when dppe is the ligand). The molecular view of the complex **20** is shown in Figure 1. The whole molecule (cation + anion) system is made up of two asymmetric units, the rhodium center and the phosphorus atom of the PF_6 being located on two fold axes. In this complex, rhodium(III) is formally an 18-electron species. The two basic PMe_2 moieties are *trans* to each other. The absolute configuration of each ferrocene moiety is *R*, as expected from the synthetic scheme. A partial representation of one of the two bis(phosphanes) in Figure 2 clearly shows that the empty space is at the top (*anti* to the bottom Cp ring). The Rh−P distances [2.354(1) Å for $(Me_2)P$ and 2.333(1) Å for $(Ph_2)P$] are roughly the same and compare well with a related complex, within experimental error.[26] ^{31}P-NMR spectra of complex **20** in chloroform have been studied, revealing the expected dissymmetry of the molecule. The doublets of doublets that should be obtained for complex **15** become two pairs of doublets of doublets in complex **20**.

A preliminary screening of the catalytic properties of rhodium complexes **14** and **15** as catalysts for asymmetric hydrogenation has been performed. The main results concerning compounds **23**−**28** (Scheme 4) are listed in Table 1.

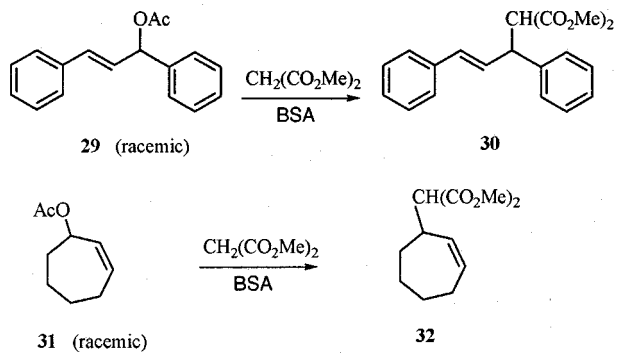
Table 1. Asymmetric hydrogenation of various types of C=C double bonds catalyzed by rhodium complexes of bis(phosphanes) **13a** or **13b**

Entry	Ligand[a][b]	Substrate	Yield (%)	*ee* (%)[c]	Configuration
1	**13a**	**23**	95	23	*S*
2	**13a**	**24**	96	36	*S*
3	**13a**	**25**	86	82	*S*
4	**13a**	**26**	96	29	*S*
5	**13a**	**27**	> 98	82	*R*
6	**13a**	**28**	92	40	*R*
7	**13b**	**23**	92	16	*S*
8	**13b**	**24**	93	0	
9	**13b**	**25**	> 98	82	*S*
10	**13b**	**27**	92	60	*R*
11	**13b**	**28**	94	95	*R*

[a] Complexes prepared in situ by mixing 1.3 mol-% of **13a** or **13b** and 1 mol-% of $[Rh(COD)_2]BF_4$, except for Entries 2, 5 and 6 {0.5 mol-% of $[RhCl(COD)]_2$}. − [b] Reactions performed in methanol, under 1 atm hydrogen (except Entry 4: 10 atm H_2) at room temp. (except Entry 10: 40 °C). [Substrate] = 2×10^{-1} M. − [c] Measured by chiral hplc (Daicel Chiralcel OD-H). All the acids were analyzed as their methyl esters.

The rhodium complexes of bis(phosphanes) **13a** and **13b** make excellent hydrogenation catalysts. Typically, the reactions could be run at 1 atm pressure of hydrogen, using 1 mol-% of catalyst. Significant enantioselectivities have been observed. For example, enamide **25** was hydrogenated to the corresponding amide (*S* configuration and 82% *ee*) with either **13a** or **13b** as the catalyst ligand (Entries 3 and 9, Table 1). Dehydrophenylalanine (**23**) and its methyl ester **24** gave low enantioselectivities (Entries 1, 2, 7, and 8). Itaconic acid (**27**) gave 82% *ee* in the hydrogenation catalyzed by a rhodium/**13a** complex (Entry 5), while dimethyl itaconate (**28**) was reduced in 95% *ee* in the presence of the rhodium/**13b** catalyst (Entry 11). As expected, the "more dissymmetric" bis(phosphane) **13b** (on the basis of steric comparisons with **13a**, as indicated in **17** and **18**) provided the highest enantioselectivity (95% *ee*).

The ability of bis(phosphanes) **13a** and **13b** to provide chiral palladium catalysts for allylic alkylation was briefly checked on allylic acetates **29** and **31** (Scheme 5). The action of dimethyl malonate anion gave products **30** and **32** with moderate enantioselectivities (lower than 45% *ee*, see Experimental Section). These reactions, performed at room temperature, were carried out with 1 mol-% of catalyst, and in almost quantitative yields.



Scheme 5

Conclusion

We report the asymmetric synthesis of a new family of chelating 1,2-bis(phosphanes), possessing planar chirality as the sole element of their chirality. Two representative bis(phosphanes) (**13a** and **13b**), with both steric and electronic dissymmetry, have been studied. The crystal structure of **20** clearly shows the bidentate character of this new class of chiral 1,2-bis(phosphanes), and firmly confirms the assigned absolute configuration. The first results obtained for asymmetric hydrogenation of C=C double bonds are promising; enantioselectivities of up to 95% *ee* have been achieved in the reduction of dimethyl itaconate using **13b** as the chiral ligand. We are currently studying the scope of bis(phosphanes) **13** in asymmetric hydrogenation and adjusting the "sulfoxide route" for the asymmetric synthesis of a wide range of 1,2-bis(phosphanes) **7**.

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 and electronic impact (EI) was performed at 70 eV. − High Resolution Mass Spectra (HRMS) were obtained with a GC/MS Finnigan-MAT-95-S. − Analytical HPLC data were recorded 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. − All reactions were carried out under argon in oven-dried glassware using standard vacuum lines techniques. − All commercial reagents were used as received. Absolute configuration of planar chirality was named according to the Schlögl nomenclature (ref.[27]). Preparation of **10**, **11** and **13a**, see ref.[19]

Hydrogenation Procedure: The substrate (2 or 3 mmol) was placed under hydrogen. The preformed catalytic solution (1 mol-% of $[Rh(COD)_2]BF_4$ and 1.3 mol-% of chiral ligand in 10 mL of methanol) was added to the substrate (2×10^{-1} M) and the mixture was stirred under 1 atm H_2, until 1 equiv. of H_2 had been consumed. The solvent was evaporated and the enantiomeric excesses were measured by HPLC (column Daicel Chiralcel OD-H). (Acids were first methylated using $MeOH/SOCl_2$.)

Allylic Alkylation Procedure: To the reaction mixture containing $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.0064 mmol) and bis(phosphane) (0.0128 mmol) in THF (4 mL) under argon, were added successively: the racemic acetates **29** or **31** (1.28 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (2.56 mmol), dimethyl malonate (2.56 mmol), and potassium acetate (6 mg, 0.06 mmol). The reaction mixture was stirred for 2 d, the solvent was evaporated and the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate, 4:1), and then dried. The enantiomeric excesses of product **30** were measured by HPLC (Daicel Chiralcel OD-H), 0.5 mL/min., hexane/*i*PrOH (99:1). (*R*)-**30:** t_1= 19.7 min.; (*S*)-30: t_2= 21.1 min.

Results with 13a: 29 gave (*R*)-**30** (34% *ee*), **31** gave (*R*)-**32** (17% *ee*).

Results with 13b: 29 gave (*S*)-**30** (47% *ee*), **31** gave (*S*)-**32** (32% *ee*).

(*R*)-1-(Dimethylphosphanyl)-2-(diphenylphosphanyl)ferrocene (13b): Compound **11** (0.94 g, 1.8 mmol) was treated with *t*BuLi (1.25 M; 2.16 mmol) in dry ether (40 mL) at −78 °C for 1 h, before quenching with chlorodimethylphosphane (1 g, 10.4 mmol) and stirring at this temperature for 1 h. The yellow reaction mixture was slowly hydrolyzed with 20 mL of a 2 M NaOH solution and extracted with ether. After standard workup, the crude product was subjected to flash chromatography on silica gel (hexane/ethyl acetate, 1:1), giving two fractions. The second fraction contained recovered starting material (120 mg, 87% conversion). The first fraction contained a mixture of the two *P*-substituted monoboranes of **13b**, which was deprotected by refluxing in dry diethylamine (10 mL) under argon overnight. The solution was concentrated and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 15:1). The resulting solid was recrystallized from absolute alcohol (20 mL) and gave 240 mg (0.56 mmol) of pure bis(phosphane) **13b**. Yield: 31%. − $C_{24}H_{24}FeP_2$ (430.3). − M.p. 130 °C. − $[\alpha]_D$ = +155 (*c* = 0.51, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 0.70 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 3.87 (s, 1 H, Cp subst.), 4.09 (s, 5 H, Cp), 4.40 (m, 1 H, Cp subst.), 4.44 (s, 1 H, Cp subst.), 7.18−7.22 (m, 5 H, Ph), 7.33−7.36 (m, 3 H, Ph), 7.50−7.55 (m, 2 H, Ph). − ^{31}P NMR ($CDCl_3$): δ = −60.18 (d, J_{PP} = 86 Hz, 1 P, P−Me), −23.51 (d, J_{PP} = 86 Hz, 1 P, P−Ph). − MS (EI); *m*/*z* (%) = 432 (6) [M + 2], 431 (34) [M + 1], 430 (100) [M], 415 (17) [M − Me], 353 (23) [M − Ph], 201 (12) [PCpPPh], 170 (19) [CpPPh], 121 (23) [FeCp], 56 (21) [Fe]. − HRMS: calcd. 430.0702; found 430.0703.

Preparation of 20: A dry Schlenk tube was charged with (*S*)-**13b** (110 mg, 0.25 mmol), [Rh(COD)(acac)] (77.5 mg, 0.25 mmol) and NH_4PF_6 (100 mg, 0.6 mmol) under argon, before addition of CH_2Cl_2 (5 mL) and water (3 mL). The mixture was stirred at room temperature for 2 h and then the water was removed. The organic phase was washed with water and concentrated under vacuum. The crude product was recrystallized from ethanol to give dark red crystals. − $[\alpha]_D$ = +130 (*c* = 0.2, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 1.30 (s, 6 H, CH_3), 1.40 (s, 6 H, CH_3), 3.90 (s, 2 H, Cp subst.), 4.10 (s, 10 H, Cp), 4.75 (s, 2 H, Cp subst.), 4.81 (s, 2 H, Cp subst.), 6.50−7.70 (m, 20 H, Ph). − ^{31}P NMR ($CDCl_3$): δ = −143.79 (m, J_{PP} = 711 Hz, 1 P, PF_6), 16.54 (dd, J_{PP} = 25.5 Hz, J_{PRh} = 90 Hz, 1 P, P−Me), 16.92 (dd, J_{PP} = 25.5 Hz, J_{PRh} = 90 Hz, 1 P, P−Me), 43.9 (dd, J_{PP} = 25.5 Hz, J_{PRh} = 131 Hz, 1 P, P−Ph), 44.3 (dd, J_{PP} = 25.5 Hz, J_{PRh} = 131 Hz, 1 P, P−Ph). − HRMS: calcd. for $C_{48}H_{48}RhO_2Fe_2P_4^+$ 995.0355; found 995.0353.

X-ray Crystallographic Study: Data for **20** were collected with a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. The structure was solved by direct methods (SIR92[28]) and refined by least-squares procedures on F_{obs}. All H atoms attached to carbon atoms were introduced by calculation in their idealized positions [d(C−H)= 0.96 Å] and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon atoms to which they are attached. The unsubstituted cyclopentadienyl ring is disordered over two positions. Both disordered rings were severely constrained to chemically reasonable dimensions. Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Absolute configuration was confirmed by the refinement of Flack's enantiopole parameter[29] and careful examination of the sensitive reflections. The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\sigma(F_o)\}^2]^2$, where $w' = 1/\Sigma_1{}^n A_r T_r(x)$ with 3 coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$, and where x was $F_c/F_c(\max)$.[30] Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $Rw = \Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, having values listed in Table 2. The calculations were carried out with the CRYSTALS program[31] running on a PC. Molecular views were produced with the help of CAMERON.[32] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127534. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road Cambridge CB2 IE2, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Selected bond lengths [Å] and bond angles [°] of **20** with esds in parentheses

Rh(1)−P(1)	2.354(1)	P(1)−C(121)	1.800(6)
Rh(1)−P(2)	2.333(1)	P(2)−C(2)	1.814(5)
Rh(1)−O(1)	2.040(4)	P(2)−C(211)	1.832(5)
P(1)−C(1)	1.786(4)	P(2)−C(221)	1.831(5)
P(1)−C(111)	1.821(6)	O(1)−O(1)′[a]	1.412(7)
P(1)−Rh(1)−P(1)′[a]	176.63(8)	O(1)−Rh(1)−O(1)′[a]	40.5(2)
P(1)−Rh(1)−P(2)	85.84(4)	Rh(1)−P(1)−C(1)	106.20(16)
P(1)−Rh(1)−P(2)′[a]	96.04(4)	Rh(1)−P(1)−C(111)	122.0(2)
P(2)−Rh(1)−P(2)′[a]	112.48(6)	Rh(1)−P(1)−C(121)	115.1(2)
P(1)−Rh(1)−O(1)	86.89(12)	Rh(1)−P(2)−C(2)	106.51(15)
P(1)−Rh(1)−O(1)′[a]	89.95(12)	Rh(1)−P(2)−C(211)	122.84(16)
P(2)−Rh(1)−O(1)	103.5(1)	Rh(1)−P(2)−C(221)	115.59(18)
P(2)−Rh(1)−O(1)′	144.0(1)	Rh(1)−O(1)−O(1)′[a]	69.8(1)

[a] Symmetry transformation used to generate equivalent atoms: ′: $-x + 2$, y, $-z + 2$.

Table 2. Crystal data of **20**

	20
Crystal parameters	
Empirical formula	$C_{48}H_{48}F_6Fe_2O_2P_5Rh$
Molecular mass	1140.36
Shape (color)	box (orange)
Size [mm]	0.20 × 0.20 × 0.10
Crystal system	monoclinic
Space group	*I*2
a [Å]	11.126(1)
b [Å]	11.832(2)
c [Å]	17.844(2)
β [°]	96.44(2)
V [Å^3]	2333.8(5)
Z	2
F(000)	785
$\rho_{calcd.}$ [g.cm^{-3}]	1.622
μ (Mo-K_α) [cm^{-1}]	11.88
Data collection	
Diffractometer	Stoe IPDS
Radiation	Mo-K_α (λ = 0.71073)
Temperature [K]	293(2)
Detector distance [mm]	70
Scan mode	(oscillation)
range [°]	0.0 < < 250.8
incr. [°]	2.2
Exposure time [min]	6
2θ range [°]	4.1 < 2θ < 52.4
No. of rflns collected	11663
No. of unique rflns	4613
Merging factor R_{int}	0.0440
Reflections used [$I > 2\sigma(I)$]	3619
Refinement	
R	0.0352
R_w	0.0428
Weighting scheme	Chebyshev
Coefficient Ar	2.69; 0.302; 2.31
$(\Delta/\sigma)_{max}$	0.025
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.971/0.941
GOF	0.952
Variable parameters	338

Acknowledgments

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