Phosphorus-Chiral Analogues of 1,1′-Bis(diphenylphosphino)ferrocene: Asymmetric Synthesis and Application in Highly Enantioselective Rhodium-Catalyzed Hydrogenation Reactions

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Five new ferrocene ligands **1a**−**e** (**1** = 1,1′-bis(aryl-phenylphosphino)ferrocene with aryl residues **a** = 1-naphthyl, **b** = 2-naphthyl, **c** = 2-anisyl, **d** = 2-biphenylyl, and **e** = 9-phenanthryl) bearing stereogenic phosphorus atoms have been prepared in enantiomerically pure form via an asymmetric synthesis protocol. The use of (+)- or (−)-ephedrine as the optically active auxiliary during subsequent nucleophilic displacement reactions at borane-protected phosphorus centers gave rise to the title compounds in 41−65% overall yield. The absolute configuration of the ferrocenyldiphosphines was confirmed by crystal structure analysis of **1a**, **1b**, and **1d**. Their efficiency as chiral ligands was demonstrated in rhodium-catalyzed asymmetric hydrogenation reactions of α-(acylamino)cinnamic acid derivatives. While low reactivity or enantiomeric discrimination were observed when employing ligands **1b** and **1d**, the in situ formed catalysts prepared from diphosphines **1a**, **1c**, or **1e** effected complete conversion and enantioselectivities of up to 98.7% ee.

Introduction

Among the chiral ligands that have brought about the success of asymmetric transition metal catalysis, bidentate phosphines have played a dominant role.[1] Landmark discoveries such as BINAP[2] and DIOP[3] promoted the synthesis and application of a vast variety of new, carbon-chiral diphosphines in numerous enantioselective transformations.[4] Considerably less attention, however, has been paid to ligand structures bearing asymmetrically substituted phosphorus donors. Although the use of its most prominent member, Dipamp,[5] in the enantioselective hydrogenation of a L-Dopa precursor had been commercialized in the late 1970's,[6] further developments within the class of phosphorus-chiral ligands suffered from synthetic difficulties and tedious resolution procedures.[7] Only very recently did the elegant approaches involving lithium-sparteine-mediated enantioselective metalation of alkyldimethylphosphine boranes[8] and *tert*-butylphenylphosphine boranes[9] open a practicable access to optically active mono- and diphosphines.

Within our continuous interest in the design and synthesis of "tailor-made" ligand structures for specified applications,[10] we wanted to explore the catalytic behavior of C_2-symmetrical phosphorus-chiral diphosphine ligands bearing three aryl substituents. Upon coordination of such a ligand to a transition metal the stereogenic phosphorus atoms are positioned in utmost proximity of the metal center, giving rise to conformationally rigid complexes. Structural unambiguity as well as pronounced dissymmetric interaction resulting thereof are assumed to improve asymmetric induction in different types of enantioselective reactions.[11]

Since the above-mentioned protocols do not seem to be amenable to the preparation of P-chiral *triaryl*phosphines, we focused our attention on a synthetic procedure describing stepwise stereodefined introduction of different alkyl as well as aryl residues to a phosphorus center. As reported by Jugé et al., this approach avoided an optical resolution procedure and established the first asymmetric synthesis of (R_P)- and (S_P)-anisylmethylphenylphosphine, which were subsequently transformed into enantiopure Dipamp via ipso-coupling.[12] The stereospeci-

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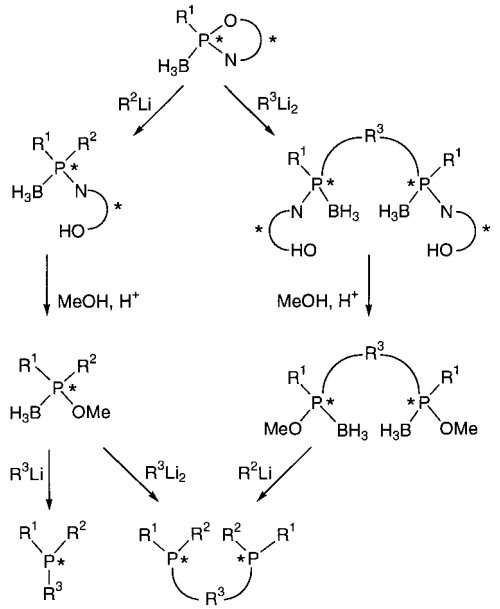
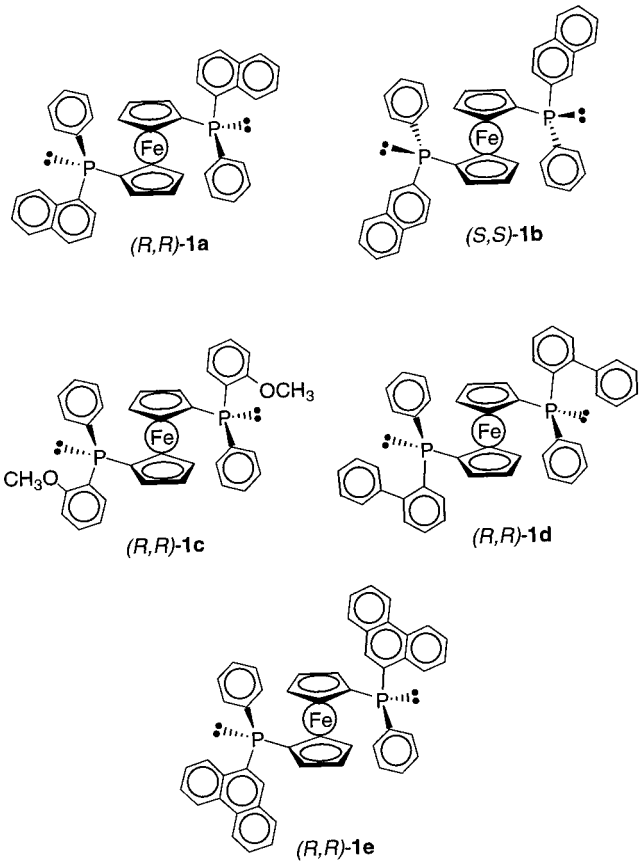


Figure 1. Possible synthetic pathways to (mono)- and (bis)-triarylphosphines utilizing the Jugé−Genêt approach (R = aryl).

ficity of this method is marked by the use of (+)- or (−)-ephedrine as chiral auxiliary and the protection of the phosphorus centers as their borane complexes. Despite the possibilities of steric overcrowding and insufficient chiral discrimination, we envisaged that the stereoselective attachment of three different arylsubstituents to a phosphorus atom should be feasible. Furthermore, we anticipated that nucleophilic attack of a dilithiated aryl species would result in compounds bearing two stereogenic phosphorus moieties (Figure 1).

In this context, we regarded the 1,1′-substituted ferrocene unit to be a suitable chelate backbone. Since dppf (1,1′-bis(diphenylphosphino)ferrocene) is one of the most frequently used phosphorus donors in organometallic chemistry and catalysis,[13] it seemed appealing to create chiral derivatives of this successful ligand. In the following we describe our synthetic efforts based on the mentioned strategy. The intermediate phosphine amide boranes incorporating the ephedrine unit as well as the phosphinite boranes may serve as useful enantiomerically pure organophosphorus building blocks.[14] The subsequent reaction of 1,1′-dilithioferrocene with optically active phosphinites gave rise to the new phosphorus-chiral dppf analogues **1a**−**e**.[15]



Results and Discussion

Ligand Synthesis. The required P-chiral precursor, oxazaphospholidine borane **2**, was readily prepared from bis(diethylamino)phenylphosphine, (+)- or (−)-ephedrine and BH_3·dimethyl sulfide.[12] The stereospecific character of this condensation reaction results in the formation of a single diastereoisomer ((2R_P,4S,5R)-**2** or (2S_P,4R,5S)-**2**, depending on the enantiomer of ephedrine used). Complexation of phosphorus prevented oxidation and contributed to a stereocontrolled course of the subsequent nucleophilic displacement sequence **2** → **4** → **5** → **6** → **1** (Scheme 1).

Treatment of **2** with aryllithium reagents **3a**−**e** at −78 °C afforded the phosphine amide boranes **4a**−**e** in 85−94% yield. In the case of 2-anisyllithium (**3c**), this reaction was proposed to proceed via a cyclic pentacoordinate intermediate followed by stereopermutation with overall retention of configuration at phosphorus. The latter was confirmed by crystal structure analysis,[16] and therefore, we assume that the same holds for structurally related reagents **3a**,**b**,**d**,**e**. Introduction of several dilithioaryl species at this stage of the synthesis was also attempted, but this led to the formation of monosubstituted products or mixtures of diastereomers. (Using 1,1′-dilithioferrocene a mixture of (R_P,R_P)- and (R_P,S_P)-bis(phosphine amide boranes) in a 65:35 ratio was obtained). Considering the mechanism,[16] interference of the increased steric bulk imposed by a neighboring phosphine amide moiety with the second nucleophilic attack or stereorearrangements might account for the observed results.

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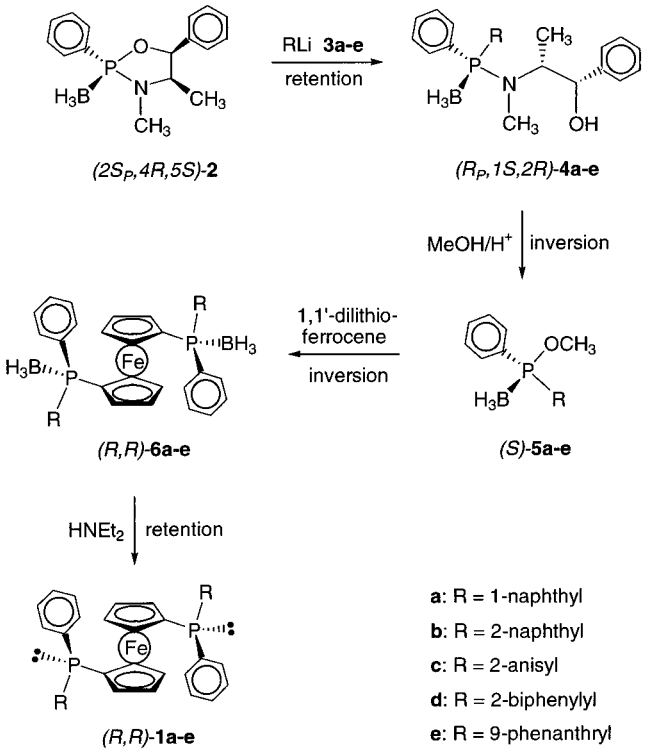
Scheme 1



Compounds **4a**−**e** were subjected to acidic methanolysis from which the methyl phosphinite borane complexes **5a**−**e** were isolated after column chromatography in 66−94% yield. Due to the S_N2-type character of this nucleophilic substitution, inversion of configuration took place at the stereogenic phosphorus atoms.[12,14c] The enantiomeric purity of the products was checked by chiral HPLC and found to be at least 98% ee, which rendered extensive recrystallization procedures unnecessary.

From the viewpoint of stereochemical unambiguity, the subsequent reaction of 1,1′-dilithioferrocene with **5a**−**e** proved to be crucial. To obtain complete configurational inversion at phosphorus, various reaction conditions were applied. We found that addition of a suspension of 1,1′-dilithioferrocene to the phosphinite borane solution at −40 °C, warming to room temperature over a period of 15 h, followed by aqueous workup yielded the desired C_2-symmetrical diphosphine boranes, accompanied by minor amounts (∼10%) of monosubstituted byproduct. Only in the case of phosphinite borane **5d** did we detect small amounts of (*R*,*S*)-*meso*-diphosphine diborane in the crude product (4% with respect to the total yield of diphosphine diborane). Tentatively, we ascribe the incomplete enantiomeric discrimination to the sterically encumbering and flexible nature of the biphenyl moiety. At temperatures above 0 °C, the presence of TMEDA (released from 1,1′-dilithioferrocene·TMEDA complex) caused slow decomplexation of BH_3 from the products in the reaction mixture (up to 30% as judged from ^{31}P NMR). A similar deprotection of the starting phosphinite boranes **5** was not observed and can therefore be excluded as racemization pathway for **6d**. Purification of chiral **6d** was nevertheless easily achieved by column chromatography and subsequent recrystallization.

Summarizing, it turned out that introduction of a bulky diaryl species is best performed as the last substitution step, since stereodiscrimination abilities and reactivity of the different phosphinites seem to surpass that of the oxazaphospholidine borane substrate (vide infra).[17]

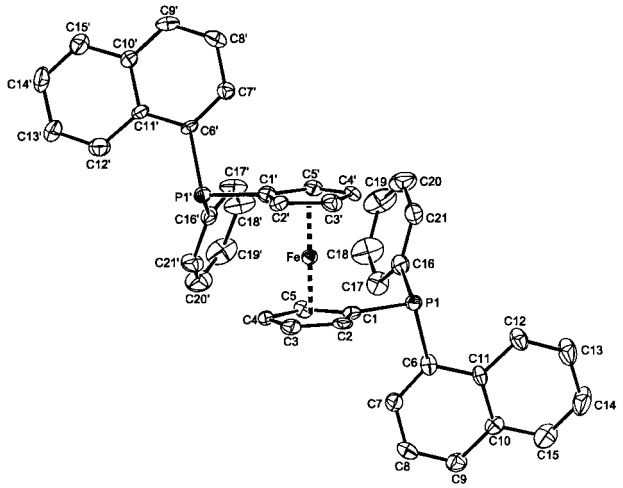


Figure 2. Molecular plot of (*R*,*R*)-**1a**.

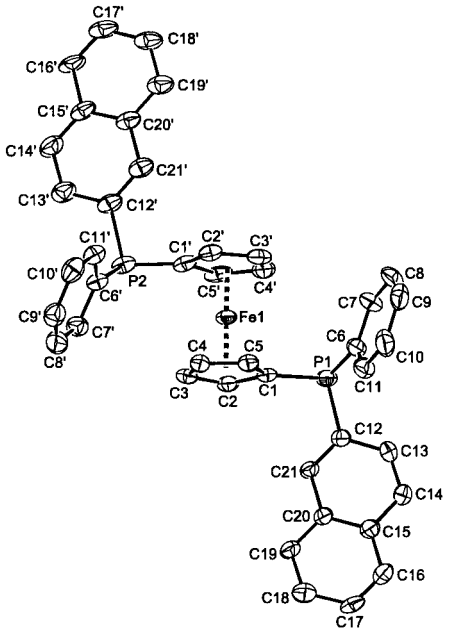


Figure 3. Molecular plot of (*S*,*S*)-**1b**.

Decomplexation of (crude) borane complexes **6a**−**e** was achieved by stirring in diethylamine at 50 °C for several hours, at which point the stereochemical integrity of the phosphorus centers was preserved.[18] After evaporation of solvent and chromatographic purification, the phosphorus-chiral diphosphine ligands **1a**−**e** were obtained in 72−81% yield and enantiomeric excesses of >98% ee.

Crystal Structures and Assignment of Absolute Configuration. Clarification regarding the stereochemical outcome of the dilithioferrocene attack on phosphinites **5** was gained by means of crystal structure determination of ligands **1a**, **1b**, and **1d** (Figures 2−4). As outlined in Scheme 1, the use of (S_P,4*R*,5*S*)-**2** (prepared

(17) These findings are in agreement with previously made observations; see ref 14b.

(18) The deboronation step is reported to proceed without loss of enantiomeric purity: Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. Stirring at reflux temperature for longer reaction times, however, has been observed to cause minor racemization: ref 14c.

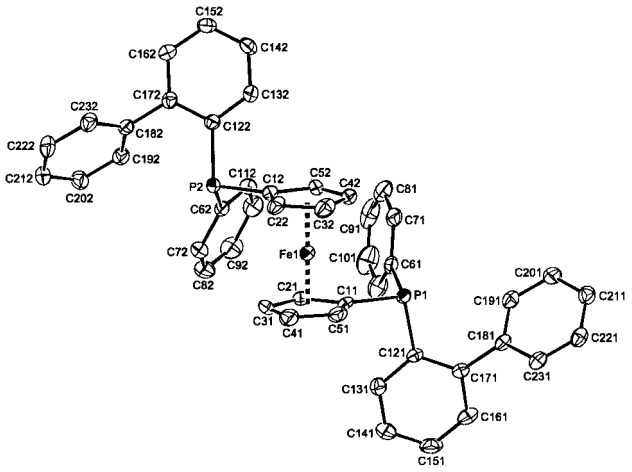


Figure 4. Molecular plot of the first molecule of (*R*,*R*)-**1d**.

from (1*S*,2*R*)-(+)-ephedrine) as starting material should give rise to intermediates (R_P,1*S*,2*R*)-**4** and *(S)*-**5**. If inversion took place during the subsequent nucleophilic substitution, followed by retention of configuration upon decomplexation,[18] (*R*,*R*)-configurated diphosphines should be obtained. The crystal structures of **1a**, **1b** and **1d** were determined in chiral space groups, and their absolute structure was confirmed by refinement of the Flack x parameter.[19] According to our expectations, the ligands **1a** and **1d** showed the (*R*,*R*)-configuration at phosphorus atoms. For diphosphine **1b**, however, the synthesis was started employing (1*R*,2*S*)-(−)-ephedrine as auxiliary. The stereochemistry of the sequence thus became reversed, ending up with the opposite enantiomer of the diphosphine, (*S*,*S*)-**1b**.

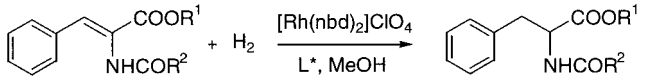
The molecular plots of these structures are shown in Figures 2−4. The crystals of **1d** consist of two crystallographically independent molecules, which mainly differ in the torsion angles within the biphenyl groups and in the torsion angles along the P−$C_{biphenyl}$ bonds. The geometries at the phosphorus atoms are quite similar in all structures with CPC angle sums of 301.8−307.6° and distances P−C_{phenyl} = 1.821(9)−1.843(4) Å, P−$C_{ferrocenyl}$ = 1.797(6)−1.820(3) Å, P−$C_{naphthyl}$ = 1.823(5)−1.842(7) Å, and P−$C_{biphenyl}$ = 1.845(3)−1.851(4) Å. The conformations of the ferrocenyl groups in structure **1a** and both molecules of **1d** are rather similar with C1−Centr.−Centr.′−C1′ torsion angles of 123.1(3)−128.6(2)°; in structure **1b** this torsion angle is 158.5(3)°. There is no obvious intramolecular reason for this conformation change so that we assume crystal packing effects as a cause.

Determination of Enantiomeric Excess. After conducting reactions **5** → **6** no signals originating from the meso-(*R*,*S*)-forms of the diphosphine diboranes could be detected in the NMR spectra of the crude products (with exception of compound **6d**, vide supra), which seems to support a highly stereoselective course of the nucleophilic substitution. Nevertheless, experimental evidence concerning the enantiomeric purity of the ligands was sought and prompted us to perform chiral HPLC measurements. Sufficient enantioseparation, however, could only be obtained for the diborane complex **6c**, in which the methoxy functionalization is believed to facilitate interaction with the column material (Chiralcel OD, *n*-hexane/2-propanol/acetic acid = 97:2.8:0.2 or Chiralcel OJ, heptane/ethanol = 85:15).

An alternative method, which proved to be faster and more general, was the use of chiral NMR shift reagents, especially *N*-(3,5-dinitrobenzoyl)-1-phenylethylamine. While it was originally developed by Kagan et al. for the determination of enantiomeric purity of sulfoxides,[20a] this reagent also efficiently interacts with (racemic) phosphine oxide functionalities, giving rise to well-resolved signals of (diastereomeric) complexes.[20b]

Oxidation of ligands **1a**−**e** by H_2O_2 in acetone yielded configurationally unchanged diphosphine dioxides **7a**−**e**.[21] Upon addition of 2 equiv of (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-1-phenylethylamine to racemic or enantiomerically enriched samples of **7a**−**e**, splitting of signals of the ferrocenylprotons occurred that allowed easy determination of enantiomeric purity by integration (error ±2%). In the corresponding ^{31}P NMR spectrum, a significant downfield shift was observed upon complexation of the phosphine oxide moiety with the shift reagent. Complete separation of signals, however, could only be obtained after addition of 3 equiv of Kagan's reagent and performing measurements at low temperature (233 K). On the contrary, in samples of diphosphine dioxides **7a**−**e**, prepared from ligands **1a**−**e** by stereospecific oxidation, we could not detect any trace of the second enantiomer within the error range of NMR integration.

Asymmetric Hydrogenation Reactions. The catalytic performance of the new ligands was readily explored in enantioselective rhodium-catalyzed hydrogenation reactions.[22] Cinnamic acid derivatives **8a**−**c** were hydrogenated at 2 bar of initial H_2 pressure in the presence of catalysts formed in situ from $[Rh(nbd)_2]ClO_4$ and the respective ligand (eq 1).



8a-c **9a-c**

Equation 1: **8a**, **9a**: R^1 = H; R^2 = Me
8b, **9b**: R^1 = H; R^2 = Ph
8c, **9c**: R^1 = Me; R^2 = Me

With the exception of the catalyst containing ligand **1d**, all reactions proceeded smoothly and were completed within 2−6 h; the results are summarized in Table 1.

The disappointing performance of diphosphine **1b** might be explained by its structural properties. Bearing

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Table 1. Enantioselectivities in Hydrogenation Reactions Using in Situ Formed [Rh(1a−e)]ClO_4 Catalysts

entry[a]	substrate	ligand L*	% ee (abs config)[b]
1	**8a**	(*S*,*S*)-**1a**	98.2 (*R*)
2	**8a**	(*S*,*S*)-**1b**	21.0 (*S*)
3	**8a**	(*R*,*R*)-**1c**	95.4 (*S*)
4	**8a**	(*R*,*R*)-**1d**	*c*
5	**8a**	(*R*,*R*)-**1e**	98.5 (*S*)
6	**8b**	(*S*,*S*)-**1a**	94.8 (*R*)
7	**8b**	(*S*,*S*)-**1b**	11.0 (*S*)
8	**8b**	(*R*,*R*)-**1c**	92.0 (*S*)
9	**8b**	(*R*,*R*)-**1e**	95.5 (*S*)
10	**8c**	(*R*,*R*)-**1a**	97.3 (*S*)
11	**8c**	(*S*,*S*,-**1b**	7.6 (*S*)
12	**8c**	(*R*,*R*)-**1c**	95.1 (*S*)
13	**8c**	(*R*,*R*)-**1e**	98.7 (*S*)

[a] Reactions were conducted at 25 °C using 0.01 mmol of [Rh(nbd)$_2$]ClO_4, 0.011 mmol of ligand, 1 mmol of substrate in 14 mL of methanol under an initial H_2 pressure of 2 bar. [b] Determination of ee values was performed by chiral GC analysis (Chirasil-Val) after conversion of **9a** and **9b** into the corresponding methyl esters. Assignments of absolute configurations were made by comparing signs of optical rotations with those of authentic samples. [c] Conversion was found to be <10%; increasing the H_2 pressure to 20 bar did not give a significant improvement.

substituents only in the meta position of the aryl moiety, the steric environment of the active [Rh−**1b**] complex resembles the one created by the achiral dppf chelate. Modeling of the outer coordination sphere of the catalyst by the far-reaching 2-naphthyl substituent not only has a deleterious effect on enantiodiscrimination but also causes inversion of the chirality of the product.

The low reactivity of catalyst systems incorporating ligand **1d**, however, was not anticipated. Tentatively, we assume that intramolecular coordination[23] of one of the *o*-phenyl groups of the biphenyl moieties prevents effective substrate complexation.[24]

On the contrary, the performance of ligands **1a**, **1c**, and **1e** and the obtained enantioselectivities as high as 98.7% correspond well to results reported for other phosphorus-chiral ligands such as Dipamp[5b] or the recently introduced tetramethylsilanebis(1-naphthylphenylphosphine)[14c] (96% and 97.7% ee, respectively, for the hydrogenation of **8c**). The absolute configuration of the hydrogenation products being opposite to that of the diphosphine is also in agreement with observations made employing the two latter mentioned ligands. Apparently, in the case of the methyl (α-acetamido)cinnamate substrate, a change in the backbone structure from ethylene or carbosilane bridges to the less flexible ferrocene influences reactivity and enantiomeric discrimination only to a small extent. In hydrogenation reactions of free acids, high enantioselectivities are retained, contrasting the results observed for Dipamp in analogous experiments.[5b] By using ligands **1a**, **1c**, and **1e**, reduction of α-benzamidocinnamic acid **8b** afforded the N-benzoylphenylalanine product in up to 95.5% ee, and the acetamido derivative **8a** was hydrogenated with comparatively high or even higher ee values as obtained for **8c**.

For all three substrates tested, the highest asymmetric inductions were achieved using the bulky 9-phenanthryl-substituted ligand **1e**, followed closely by the structurally related 1-naphthyl analogue **1a**. Creation of very rigid complex species displaying larger bite angles[10a] and thus allowing more effective shielding of diagonal quadrants by the sterically demanding aryl groups might account for the observed results.[25] Employment of catalysts incorporating the smaller anisyl-functionalized ligand **1c** gave rise to slightly lower ee values in comparison to **1a** and **1e**. To what extent this behavior can be ascribed to steric effects only remains unclear.[26] Action of the methoxy group as a hemilabile intramolecular oxygen donor has been observed previously in alkylhydride catalytic intermediates,[27] but the influence of such a coordination on the enantioselectivity-determining step is still a matter of debate. Our results as well as the ones obtained by Imamoto et al.[8b] suggest, however, that, on providing a suitable backbone framework, marked steric differences between the alkyl or aryl residues on phosphorus are more important with respect to stereodifferentiation than possible cooperative effects attributed to the methoxy functionalization.

Summarizing, regarding the excellent enantioselectivities of up to 98.7% ee obtained in asymmetric hydrogenations of α-acylamino cinnamic acid derivatives, we feel that a promising new class of C_2-symmetrical phosphorus-chiral ligands has been disclosed. Having a range of diphosphines with differing steric and electronic properties available, tuning of ligand structures becomes possible and we expect further successful applications in other types of hydrogenation reactions.

Conclusions

We have developed a versatile and efficient route for the preparation of optically active (bis)triarylphosphines bearing a ferrocene moiety. The synthetic pathway is characterized by its tolerance toward bulky aryl substituents as well as excellent enantio- and diastereoselectivity. The possibility and necessity of steric tuning was demonstrated by the synthesis of five phosphorus-chiral ferrocenyldiphosphines **1a**−**e** and their application in rhodium-catalyzed asymmetric hydrogenation reactions.

Ligands **1a** and **1e**, creating sterically pretentious rigid complexes, or ligand **1c**, offering the possibility of hemilabile or secondary interaction by means of the methoxy functionalization, have been identified as valuable tools for the reduction of cinnamic acid derivatives. The structural similarity with the well-known Dipamp is also mirrored in catalysis results, giving ee values of up to 98.7% for *N*-acylphenylalanine products. The disappointing performance of ligands **1b** and **1d** is assumed to originate from a too low or too high a degree of steric interaction, respectively, with the substrate during hydrogenation reactions.

Extension of this investigation toward electronic variations of ligand structures and exploration of ligand performance in other asymmetric transformations is currently under progress and will be reported in due course.

Experimental Section

General Procedures. Melting points are uncorrected. NMR spectra were recorded on 250, 300, and 400 MHz instruments; $CDCl_3$ was used as solvent if not mentioned

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otherwise. Assignments of ^{13}C-carbon multiplicities were made by means of spin-echo-Fourier transform (SEFT) and two-dimensional (^{1}H,^{13}C-COSY) experiments. Phosphorus−carbon coupling constants (J_{CP}) were identified by comparison of ^{13}C spectra measured at different magnetic field strengths. Phosphorus−boron coupling constants (J_{PB}) were determined between the central peaks of the nonbinomial quartets. Optical rotations were measured in a thermostated polarimeter with l = 1 dm. Mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer; 3-nitrobenzyl alcohol was used as matrix for FAB-MS. Elemental analyses were obtained using an Elementar Vario EL apparatus. Chiral GC separations were conducted with a Chirasil-L-Val capillary column (0.25 mm × 25 m). Chiral HPLC analyses were carried out using a Daicel Chiralcel-OD column (0.46 × 25 cm).

Materials. If not otherwise stated, reactions were performed under argon atmosphere using standard Schlenk techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl, CH_2Cl_2 and acetonitrile were distilled from CaH_2, and toluene and methanol were distilled from sodium wire under nitrogen. Except for the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Diethylamine was distilled from KOH under argon. 2-Bromoanisole and 1-bromonaphthalene were distilled prior to use. 1,1′-dilithioferrocene was synthesized following a procedure given by Bishop et al.[28] (2S_P,4R,5S)-(−)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine borane **2** and its enantiomer were prepared according to the method of Jugé et al.[12]

Synthesis of Phosphinamides 4a−e (Typical Procedure). A degassed 0.5 M solution of the aryl bromide RBr (with R = 1-naphthyl, 2-naphthyl, 2-methoxyphenyl, 2-biphenylyl, or 9-phenanthryl) (11.5 mmol) in diethyl ether was cooled to −78 °C and *n*-butyllithium (12 mmol) was added via syringe. The reaction mixture was kept at this temperature for 2 h and then warmed to −20 °C to ensure complete lithiation. The resulting aryllithium suspension **3** was added slowly via Teflon cannula to a precooled (−78 °C) 1 M solution of oxazaphospholidine borane **2** (10 mmol) in THF. The reaction mixture was warmed to room temperature over a period of 15 h and then quenched with water. Solvent was evaporated, and the residue was extracted with CH_2Cl_2, washed with water, and dried ($MgSO_4$). After removal of the solvent in vacuo, the crude product was subjected to column chromatography (SiO_2, toluene/ethyl acetate = 95:5) to give diastereomerically pure amides **4** as white, slightly air-sensitive crystals.

(S_P,1R,2S)-(+)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(1-naphthyl)-*P*-(phenyl)phosphinamide borane, 4a. Yield: 94%. Mp: 113 °C. ^{1}H NMR (400.13 MHz): δ 0.72−2.00 (br, m, 3H); 1.32 (d, 3H, J = 7.0 Hz); 1.83 (d, 1H, J = 4.0 Hz); 2.66 (d, 3H, J_{HP} = 7.5 Hz); 4.47 (m, 1H); 5.00 (br, t, 1H, J = 4.0 Hz); 7.22−7.54 (m, 12H); 7.56−7.63 (m, 2H); 7.85 (br, d, 1H, J = 8.0 Hz); 7.94 (br, d, 1H, J = 8.0 Hz); 8.23 (br, d, 1H, J = 8.5 Hz) ppm.^{13}C NMR (100.58 MHz): δ 11.55 (d, CH_3, J_{CP} = 3.8 Hz); 31.48 (d, CH_3, J_{CP} = 3.1 Hz); 58.13 (d, CH, J_{CP} = 9.9 Hz); 79.18 (d, CH, J_{CP} = 2.9 Hz); 124.62 (d, CH, J_{CP} = 10.7 Hz); 126.05 (CH); 126.22 (CH); 126.32 (CH); 127.10 (d, C, J_{CP} = 61.2 Hz); 127.27 (d, CH, J_{CP} = 6.1 Hz); 127.50 (CH); 128.36 (CH); 128.49 (d, CH, J_{CP} = 9.9 Hz); 128.85 (d, CH, J_{CP} = 1.4 Hz); 130.89 (d, CH, J_{CP} = 2.3 Hz); 132.22 (d, CH, J_{CP} = 9.9 Hz); 132.38 (d, CH, J_{CP} = 2.3 Hz); 132.38 (d, C, J_{CP} = 62.0 Hz); 132.74 (d, CH, J_{CP} = 7.6 Hz); 133.39 (d, C, J_{CP} = 11.1 Hz); 134.06 (d, C, J_{CP} = 8.4 Hz); 142.54 (C) ppm. ^{31}P NMR (121.50 MHz): δ 71.42 (br, q, J_{PB} = 75 Hz) ppm. $[\alpha]^{20}_D$ = +97.8 (c = 0.680; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{26}H_{27}NOP$ ([MH]$^+$ − BH_3) 400.1830, obsd 400.1827. Anal. Calcd for $C_{26}H_{29}BNOP$: C, 75.55; H, 7.08; N, 3.39. Found: C, 75.74; H, 7.15; N, 3.26.

(S_P,1R,2S)-(+)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(2-naphthyl)-*P*-(phenyl)phosphinamide borane, 4b. Yield: 89%. Mp: 133 °C. ^{1}H NMR (400.13 MHz): δ 0.69−1.77 (br, m, 3H); 1.27 (d, 3H, J = 6.7 Hz); 1.87 (s, 1H); 2.52 (d, 3H, J_{HP} = 7.8 Hz); 4.35 (m, 1H); 4.84 (d, 1H, J = 6.3 Hz); 7.17−7.63 (m, 13H), 7.81−7.89 (m, 3H); 8.09 (br, d 1H, J = 12.2 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 13.48 (d, CH_3, J_{CP} = 1.1 Hz); 30.57 (d, CH_3, J_{CP} = 3.8 Hz); 58.18 (d, CH, J_{CP} = 10.3 Hz); 78.74 (d, CH, J_{CP} = 5.8 Hz); 126.71 (d, CH, J_{CP} = 3.3 Hz); 126.72 (CH); 127.61 (CH); 127.73 (d, CH, J_{CP} = 1.8 Hz); 127.73 (CH); 127.88 (d, CH, J_{CP} = 3.8 Hz); 128.08 (d, CH, J_{CP} = 9.9 Hz); 128.29 (d, C, J_{CP} = 60.3 Hz); 128.34 (d, CH, J_{CP} = 10.4 Hz); 128.55 (CH); 128.78 (CH); 130.65 (d, C, J_{CP} = 68.1 Hz); 130.71 (d, CH, J_{CP} = 2.2 Hz); 132.05 (d, CH, J_{CP} = 9.9 Hz); 132.60 (d, C, J_{CP} = 11.4 Hz); 133.84 (d, CH, J_{CP} = 9.9 Hz); 134.31 (d, C, J_{CP} = 1.9 Hz); 142.45 (C) ppm. ^{31}P NMR (121.50 MHz): δ 71.40 (br, q, J_{PB} = 82 Hz) ppm. $[\alpha]^{20}_D$ = +61.1 (c = 0.524; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{26}H_{27}NOP$ ([MH]$^+$ − BH_3) 400.1830, obsd 400.1827. Anal. Calcd for $C_{26}H_{29}BNOP$: C, 75.55; H, 7.08; N, 3.39. Found: C, 75.68; H, 7.01; N, 3.32.

(S_P,1R,2S)-(+)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(2-methoxyphenyl)-*P*-(phenyl)phosphinamide borane, 4c. Yield: 93%. Mp: 115 °C. ^{1}H NMR (400.13 MHz): δ 0.51−1.73 (br, m, 3H); 1.22 (d, 3H, J = 6.7 Hz); 2.03 (d, 1H, J = 4.1 Hz); 2.54 (d, 3H, J_{HP} = 8.0 Hz); 3.56 (s, 3H); 4.33 (m, 1H); 4.87 (d, 1H, J = 5.6 Hz); 6.90 (br, dd, 1H, J = 4.1, 8.3 Hz); 7.01 (m, 1H); 7.17−7.40 (m, 8H); 7.42−7.51 (m, 3H); 7.58 (ddd, 1H, J = 1.7, 7.6, 12.7 Hz) ppm. ^{13}C NMR (100.61 MHz): δ 12.50 (br, CH_3); 30.90 (d, CH_3, J_{CP} = 3.8 Hz); 55.00 (CH_3); 58.06 (d, CH, J_{CP} = 10.7 Hz); 78.77 (d, CH, J_{CP} = 5.5 Hz); 111.51 (d, CH, J_{CP} = 4.6 Hz); 118.60 (d, C, J_{CP} = 57.2 Hz); 120.78 (d, CH, J_{CP} = 10.6 Hz); 126.52 (CH); 127.51 (CH); 127.87 (d, CH, J_{CP} = 10.7 Hz); 128.28 (CH); 129.85 (d, CH, J_{CP} = 2.2 Hz); 130.84 (d, CH, J_{CP} = 10.4 Hz); 132.23 (d, C, J_{CP} = 71.1 Hz); 133.20 (d, CH, J_{CP} = 1.6 Hz); 134.90 (d, CH, J_{CP} = 10.8 Hz); 142.56 (C); 161.06 (d, C, J_{CP} = 2.5 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 69.18 (br, q, J_{PB} = 71 Hz) ppm. $[\alpha]^{20}_D$ = +38.1 (c = 0.360; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{23}H_{30}BNO_2P$ ([MH]$^+$) 394.2107, obsd 394.2112. Anal. Calcd for $C_{23}H_{29}BNO_2P$: C, 70.24; H, 7.44; N, 3.56. Found: C, 70.04; H, 7.22; N, 3.48.

(S_P,1R,2S)-(+)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(2-biphenylyl)-*P*-(phenyl)phosphinamide borane, 4d. Yield: 85%. Mp: 100−101 °C. ^{1}H NMR (400.13 MHz): δ 0.55−1.65 (br, m, 3H); 0.71 (d, 3H, J = 6.9 Hz); 2.38 (s, 1H); 2.59 (d, 3H, J_{HP} = 7.2 Hz); 3.97 (m, 1H); 4.88 (d, 1H, J = 2.8 Hz); 7.16−7.52 (m, 17H); 7.67−7.75 (m, 2H) ppm. ^{13}C NMR (100.58 MHz): δ 9.87 (d, CH_3, J_{CP} = 6.9 Hz); 31.72 (d, CH_3, J_{CP} = 3.8 Hz); 58.04 (d, CH, J_{CP} = 10.7 Hz); 78.78 (CH); 125.62 (CH); 126.75 (d, CH, J_{CP} = 9.9 Hz); 127.11 (CH); 127.32 (d, CH; J_{CP} = 4.6 Hz); 127.34 (CH); 128.10 (CH); 128.10 (d, CH, J_{CP} = 9.9 Hz); 128.81 (d, C, J_{CP} = 66.6 Hz); 129.64 (CH); 130.46 (d, CH, J_{CP} = 2.3 Hz); 130.51 (d, CH, J_{CP} = 2.3 Hz); 132.18 (d, CH, J_{CP} = 9.9 Hz); 132.67 (d, CH, J_{CP} = 8.4 Hz); 133.39 (d, C, J_{CP} = 58.1 Hz); 134.08 (d, CH, J_{CP} = 9.9 Hz); 141.35 (d, C, J_{CP} = 3.1 Hz); 142.47 (C); 147.37 (d, C, J_{CP} = 9.9 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 70.95 (br, q, J_{PB} = 64 Hz) ppm. $[\alpha]^{20}_D$ = +64.9 (c = 0.297; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{28}H_{29}NOP$ ([MH]$^+$ − BH_3) 426.1987, obsd 426.1958. Anal. Calcd for $C_{28}H_{31}BNOP$: C, 76.54; H, 7.12; N, 3.19. Found: C, 76.80; H, 7.22; N, 3.06.

(R_P,1S,2R)-(−)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(9-phenanthryl)-*P*-(phenyl)phosphinamide borane, 4e. Yield: 86%. Mp: 135 °C. ^{1}H NMR (400.13 MHz): δ 0.83−2.01 (br, m, 3H); 1.36 (d, 3H, J = 6.9 Hz); 2.36 (s, 1H), 2.70 (d, 3H, J_{HP} = 7.4 Hz); 4.54 (m, 1H); 5.06 (d, 1H, J = 3.9 Hz); 7.13−7.86 (m, 16H); 8.37 (d, 1H, J = 8.3 Hz); 8.67 (d, 1H, J = 8.3 Hz); 8.72 (d, 1H, J = 8.4 Hz) ppm. ^{13}C NMR (100.58 MHz): δ 11.48 (d, CH_3, J_{CP} = 4.2 Hz); 31.47 (d, CH_3, J_{CP} = 3.2 Hz); 58.11 (d, CH, J_{CP} = 10.4 Hz); 79.13 (d, CH, J_{CP} = 2.3 Hz); 122.51 (CH); 122.97 (CH); 125.99 (d, C, J_{CP} = 60.3 Hz); 126.00 (CH); 126.33 (CH); 126.91 (CH); 127.43 (CH); 128.19 (d, CH, J_{CP} = 7.2 Hz); 128.29 (CH); 128.41 (d, CH, J_{CP} = 24.4 Hz); 128.52 (d, CH, J_{CP} = 16.6 Hz); 128.97 (CH); 129.56 (CH); 130.19 (d, C, J_{CP} = 11.0 Hz); 130.79 (d, C, J_{CP} = 7.4 Hz); 130.83 (d, C, J_{CP} = 11.3 Hz); 130.94 (d, CH, J_{CP} = 1.9 Hz); 131.75 (d, C, J_{CP} = 1.8 Hz); 132.18 (d, C, J_{CP} = 62.4 Hz); 132.29 (d, CH,

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J_{CP} = 10.0 Hz); 135.52 (d, CH, J_{CP} = 7.2 Hz); 142.28 (C) ppm. ^{31}P NMR (121.50 MHz): δ 72.50 (br, q, J_{PB} = 50 Hz) ppm. $[\alpha]^{20}_D = -101.0$ (c = 0.243; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{30}H_{29}NOP$ ($[MH]^+ - BH_3$) 450.1987, obsd 450.1971. Anal. Calcd for $C_{30}H_{31}BNOP$: C, 77.76; H, 6.75; N, 3.02. Found: C, 77.40; H, 6.98; N, 2.78.

Synthesis of Phosphinite Boranes 5a−e (Typical Procedure). The phosphinamide borane **4** (11.5 mmol) was dissolved in 100 mL of methanol, degassed, and cooled in an ice bath. Concentrated sulfuric acid (11.5 mmol) was added dropwise, and the solution was stirred for 20 h at room temperature. After removal of solvent, the residue was purified by column chromatography (SiO_2; hexane/ethyl acetate = 95:5). Phosphinites **5a−e** were obtained as white crystalline products that proved to be largely air-stable. The enantiomeric composition was determined by chiral HPLC and found to be >98% ee. Eventually, recrystallization from hexane yielded enantiopure products.

***(S)*-(+)-Methyl (1-Naphthyl)phenylphosphinite Borane, 5a.** Yield: 84%. Enantiomeric purity: >99.5% ee. HPLC: Chiralcel OD, heptane/2-propanol = 99.5:0.5, t_R [(*R*)-**5a**] = 20.9 min, t_R [(*S*)-**5a**] = 22.3 min. Mp: 82−83 °C. ^{1}H NMR (400.14 MHz): δ 0.49−1.76 (br, m, 3H); 3.74 (d, 3H, J_{HP} = 12.2 Hz); 7.32−7.50 (m, 5H); 7.52−7.68 (m, 3H); 7.86 (br, d, 1H, J = 8.1 Hz); 8.03 (br, d, 1H, J = 8.3 Hz); 8.11 (br, d, 1H, J = 8.5 Hz); 8.25 (ddd, 1H, J = 0.9, 7.2, 15.0 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 53.98 (d, CH_3, J_{CP} = 1.9 Hz); 124.73 (d, CH, J_{CP} = 13.7 Hz); 126.30 (CH); 126.32 (d, CH, J_{CP} = 5.1 Hz); 126.57 (d, C, J_{CP} = 55.1 Hz); 127.10 (CH); 128.57 (d, CH, J_{CP} = 10.6 Hz); 129.06 (d, CH, J_{CP} = 0.9 Hz); 130.87 (d, CH, J_{CP} = 11.1 Hz); 131.58 (d, CH, J_{CP} = 2.2 Hz); 132.20 (d, C, J_{CP} = 67.5 Hz); 132.63 (d, C, J_{CP} = 5.1 Hz); 133.71 (d, CH, J_{CP} = 2.4 Hz); 133.74 (d, C, J_{CP} = 6.8 Hz); 135.24 (d, CH, J_{CP} = 17.2 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 111.50 (br, q, J_{PB} = 81 Hz) ppm. $[\alpha]^{20}_D = +14.9$ (c = 0.808, CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{17}H_{16}OP$ ($[MH]^+ - BH_3$) 267.0939, obsd 267.0945. Anal. Calcd for $C_{17}H_{18}BOP$: C, 72.89; H, 6.48. Found: C, 73.11; H, 6.48.

***(R)*-(+)-Methyl (2-Naphthyl)phenylphosphinite Borane, 5b.** Yield: 94%. Enantiomeric purity: >99.5% ee. HPLC: Chiralcel OD, hexane/2-propanol = 99.5:0.5, t_R [(*R*)-**5b**] = 17.6 min, t_R [(*S*)-**5b**] = 19.2 min. Mp: 85−86 °C. ^{1}H NMR (400.14 MHz): δ 0.53−1.68 (br, m, 3H); 3.77 (d, 3H, J_{HP} = 12.1 Hz); 7.42−7.60 (m, 5H); 7.66 (dt, 1H, J = 1.5, 8.7 Hz); 7.73−7.79 (m, 2H); 7.83−7.93 (m, 3H); 8.36 (br, d, 1H, J = 12.7 Hz) ppm. ^{13}C NMR (100.58 MHz): δ 54.12 (d, CH_3, J_{CP} = 1.8 Hz); 125.92 (d, CH, J_{CP} = 9.7 Hz); 126.94 (CH); 127.82 (CH); 128.25 (CH); 128.55 (d, CH, J_{CP} = 9.8 Hz); 128.67 (d, CH, J_{CP} = 10.5 Hz); 128.69 (d, C, J_{CP} = 63.0 Hz); 128.92 (CH); 131.26 (d, CH, J_{CP} = 11.3 Hz); 131.76 (d, C, J_{CP} = 64.7 Hz); 131.90 (d, CH, J_{CP} = 2.3 Hz); 132.52 (d, C, J_{CP} = 12.3 Hz); 133.42 (d, CH, J_{CP} = 13.3 Hz); 134.74 (d, C, J_{CP} = 2.1 Hz) ppm. ^{31}P NMR (161.98 MHz): δ 108.84 (br, q, J_{PB} = 68 Hz) ppm. $[\alpha]^{20}_D = +44.9$ (c = 1.29; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{17}H_{16}OP$ ($[MH]^+ - BH_3$) 267.0939, obsd 267.0951. Anal. Calcd for $C_{17}H_{18}BOP$: C, 72.89; H, 6.48. Found: C, 72.80; H, 6.49.

***(S)*-(+)-Methyl (2-Methoxyphenyl)phenylphosphinite Borane, 5c.** Yield: 85%. Enantiomeric purity: 99.3% ee. HPLC: Chiralcel OD, hexane/2-propanol = 99.5:0.5, t_R [(*R*)-**5c**] = 20.7 min, t_R [(*S*)-**5c**] = 21.8 min. Oil. ^{1}H NMR (400.14 MHz): δ 0.61−1.60 (br, m, 3H); 3.58 (s, 3H); 3.71 (d, 3H, J_{HP} = 12.1 Hz); 6.84 (dd, 1H, J = 4.3, 8.3 Hz); 7.06 (dt, 1H, J = 1.8, 7.4 Hz); 7.36−7.50 (m, 4H); 7.69−7.84 (m, 3H) ppm. ^{13}C NMR (100.61 MHz): δ 53.80 (d, CH_3, J_{CP} = 3.6 Hz); 55.45 (CH_3), 111.65 (d, CH, J_{CP} = 4.9 Hz); 119.16 (d, C, J_{CP} = 61.6 Hz); 120.75 (d, CH, J_{CP} = 11.0 Hz); 128.07 (d, CH, J_{CP} = 10.8 Hz); 131.01 (d, CH, J_{CP} = 11.5 Hz); 131.29 (d, CH, J_{CP} = 2.1 Hz); 131.97 (d, C, J_{CP} = 65.8 Hz); 133.80 (d, CH, J_{CP} = 11.1 Hz); 134.16 (br, CH); 160.95 (d, C, J_{CP} = 3.1 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 106.96 (br, q, J_{PB} = 80 Hz) ppm. $[\alpha]^{20}_D = +26.2$ (c = 0.565; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{14}H_{19}BO_2P$ ($[MH^+]$) 261.1216, obsd 261.1206. Anal. Calcd for $C_{14}H_{18}BO_2P$: C, 64.65; H, 6.98. Found: C, 64.45; H, 6.91.

***(S)*-(+)-Methyl (2-Biphenylyl)phenylphosphinite Borane, 5d.** Yield: 87%. Enantiomeric purity: 98.1% ee. HPLC: Chiralcel OD, hexane/2-propanol = 99.5:0.5, t_R [(*S*)-**5c**] = 13.0 min, t_R [(*R*)-**5c**] = 14.5 min. Recrystallization from hexane yielded enantiopure product. Mp: 120 °C. ^{1}H NMR (400.14 MHz): δ 0.32−1.50 (br, m, 3H); 3.57 (d, 3H, J_{HP} = 10.6 Hz); 6.89−6.94 (m, 2H); 7.08−7.14 (m, 2H); 7.18−7.26 (m, 4H); 7.29−7.39 (m, 3H); 7.47−7.57 (m, 2H); 8.06 (ddd, 1H, J = 1.6, 7.5, 12.6 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 53.43 (d, CH_3, J_{CP} = 1.1 Hz); 126.84 (d, CH, J_{CP} = 11.3 Hz); 126.97 (CH); 127.00 (d, CH, J_{CP} = 5.1 Hz); 127.86 (d, CH, J_{CP} = 10.8 Hz); 129.37 (CH); 130.04 (d, C, J_{CP} = 59.9 Hz); 130.72 (d, CH, J_{CP} = 11.4 Hz); 130.88 (d, CH, J_{CP} = 2.3 Hz); 131.32 (d, CH, J_{CP} = 2.0 Hz); 131.47 (d, CH, J_{CP} = 7.7 Hz); 132.08 (d, C, J_{CP} = 64.8 Hz); 133.32 (d, CH, J_{CP} = 14.9 Hz); 140.17 (d, C; J_{CP} = 3.2 Hz); 146.47 (d, C, J_{CP} = 7.4 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 109.78 (br, q, J_{PB} = 83 Hz) ppm. $[\alpha]^{20}_D = +17.4$ (c = 0.945, CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{19}H_{18}OP$ ($[MH]^+ - BH_3$) 293.1095, obsd 293.1114. Anal. Calcd for $C_{19}H_{20}BOP$: C, 74.54; H, 6.59. Found: C, 74.50; H 6.60.

***(S)*-(−)-Methyl (9-Phenanthryl)phenylphosphinite Borane, 5e.** Yield: 64%. Enantiomeric purity: >99.5% ee. HPLC: Chiralcel OD, hexane/2-propanol = 98:2, t_R [(*R*)-**5e**] = 26.1 min, t_R [(*S*)-**5e**] = 29.6 min. Mp: 140 °C. ^{1}H NMR (400.13 MHz): δ 0.60−1.75 (br, m, 3H); 3.81 (d, 3H, J_{HP} = 12.2 Hz); 7.34−7.49 (m, 4H); 7.61 (ddd, 1H, J = 1.1, 7.1, 8.2 Hz); 7.65−7.71 (m, 3H); 7.78 (ddd, 1H, J = 1.3, 7.0, 8.3 Hz); 8.05 (dd, 1H, J = 1.0, 7.7 Hz); 8.14 (br, d, 1H, J = 8.3 Hz); 8.62−8.75 (m, 3H) ppm. ^{13}C NMR (100.58 MHz): δ 54.04 (d, CH_3, J_{CP} = 1.9 Hz); 122.58 (CH); 123.22 (CH); 125.20 (d, C, J_{CP} = 53.3 Hz); 126.95 (d, CH, J_{CP} = 7.4 Hz); 127.26 (CH); 127.34 (d, CH, J_{CP} = 4.7 Hz); 128.61 (d, CH, J_{CP} = 10.6 Hz); 129.35 (CH); 129.91 (d, C, J_{CP} = 4.3 Hz); 130.04 (d, C, J_{CP} = 14.6 Hz); 130.22 (CH); 130.68 (d, C, J_{CP} = 6.7 Hz); 130.69 (CH); 130.80 (CH); 131.55 (d, CH, J_{CP} = 2.2 Hz); 132.10 (d, C, J_{CP} = 68.5 Hz); 132.32 (d, C, J_{CP} = 1.9 Hz); 138.91 (d, CH, J_{CP} = 18.1 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 111.53 (br, q, J_{PB} = 84 Hz) ppm. $[\alpha]^{20}_D = -78.1$ (c = 0.702, CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{21}H_{18}OP$ ($[MH]^+ - BH_3$) 317.1095, obsd 317.1081. Anal. Calcd for $C_{21}H_{20}BOP$: C, 76.39; H, 6.11. Found: C, 76.53; H, 6.12.

Synthesis of Ferrocenyldiphosphines 1a−e (Typical Procedure). The respective phosphinite **5** (10 mmol) was dissolved in 10 mL of THF, degassed, and cooled to −40 °C. A suspension of 1,1′-dilithioferrocene (5 mmol) in 40 mL of diethyl ether and 5 mL of THF was cooled and slowly added to the phosphinite solution via Teflon cannula. The reaction mixture was allowed to reach room temperature over a period of 15 h and was then quenched with water. After evaporation of solvent, the residue was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), and concentrated. The crude borane complex **6** was suspended in 50 mL of diethylamine, degassed, and stirred at 50 °C for 5 h. After treatment, the solvent was evacuated and the product diphosphine was purified by column chromatography (SiO_2; hexane/CH_2Cl_2 = 3:1 for **1a−d**; hexane/CH_2Cl_2 = 2:1 for **1e**). Minor amounts of monophosphine byproduct were eluted first, followed by diphosphines **1a−e**, which were obtained as yellow to orange crystals. Recrystallization from CH_2Cl_2/hexane afforded analytically pure products.

***(R,R)*-(−)-1,1′-Bis(1-naphthylphenylphosphino)ferrocene, 1a.** Yield: 74%. Mp: 176 °C. ^{1}H NMR (400.13 MHz): δ 3.70 (m, 2H); 4.25 (m, 2H); 4.32 (m, 2H); 4.36 (m, 2H); 7.11−7.16 (m, 2H); 7.19−7.28 (m, 6H); 7.30−7.43 (m, 10H); 7.75−7.81 (m, 4H); 8.33−8.37 (m, 2H) ppm. ^{13}C NMR (100.61 MHz): δ 72.47 (br, CH); 72.95 (d, CH, J_{CP} = 6.9 Hz); 73.06 (d, CH, J_{CP} = 3.0 Hz); 75.25 (d, CH, J_{CP} = 25.9 Hz); 76.50 (d, C, J_{CP} = 5.3 Hz); 125.22 (d, CH, J_{CP} = 1.5 Hz); 125.73 (br, CH); 125.94 (d, CH, J_{CP} = 2.3 Hz); 126.02 (d, CH, J_{CP} = 25.9 Hz); 128.13 (d, CH, J_{CP} = 7.6 Hz); 128.50 (br, CH); 128.81 (CH); 129.09 (CH); 131.41 (br, CH); 133.33 (d, C, J_{CP} = 4.6 Hz); 133.83 (d, CH, J_{CP} = 20.6 Hz); 134.71 (d, C, J_{CP} = 21.4 Hz); 136.68 (d, C, J_{CP} = 14.5 Hz); 137.10 (d, C, J_{CP} = 8.4 Hz) ppm. ^{31}P NMR (161.98 MHz): δ −30.39 (s) ppm. $[\alpha]^{20}_D = -197.2$ (c = 0.251; $CHCl_3$). HRMS (EI$^+$): m/z calcd for $C_{42}H_{32}FeP_2$

654.1329, obsd 654.1342. Anal. Calcd for $C_{42}H_{32}FeP_2$: C, 77.07; H, 4.93. Found: C, 76.98; H, 5.02.

(*S*,*S*)-(−)-1,1′-Bis(2-naphthylphenylphosphino)ferrocene, 1b. Yield: 78%. Mp: 87 °C. ^{1}H NMR (400.13 MHz): δ 4.04 (m, 4H); 4.28 (m, 4H); 7.23−7.35 (m, 12H); 7.41−7.49 (m, 4H); 7.63 (br, d, 2H, J = 8.4 Hz); 7.70−7.83 (m, 6H) ppm. ^{13}C NMR (100.61 MHz): δ 72.51 (m, 2CH); 73.77 (d, CH, J_{CP} = 3.0 Hz); 73.91 (d, CH, J_{CP} = 3.8 Hz); 76.58 (d, C, J_{CP} = 7.6 Hz); 126.16 (CH); 126.49 (CH); 127.49 (d, CH, J_{CP} = 6.1 Hz); 127.67 (CH); 128.04 (CH); 128.15 (d, CH, J_{CP} = 6.9 Hz); 128.53 (CH); 129.81 (d, CH, J_{CP} = 16.0 Hz); 133.00 (d, C, J_{CP} = 8.4 Hz); 133.20 (C); 133.44 (d, CH, J_{CP} = 19.0 Hz); 133.64 (d, CH, J_{CP} = 23.0 Hz); 136.27 (d, C, J_{CP} = 9.9 Hz); 138.70 (d, C, J_{CP} = 9.9 Hz) ppm. ^{31}P NMR (161.98 MHz): δ −17.77 (s) ppm. $[\alpha]^{20}_D$ = −15.3 (c = 0.261; $CHCl_3$). HRMS (EI$^+$): m/z calcd for $C_{42}H_{32}FeP_2$ 654.1329, obsd 654.1298. Anal. Calcd for $C_{42}H_{32}FeP_2$: C, 77.07; H, 4.93. Found: C, 76.91; H, 5.30.

(*R*,*R*)-(−)-1,1′-Bis[(2-methoxyphenyl)phenylphosphino]ferrocene, 1c. Yield: 73%. Mp: 153 °C. ^{1}H NMR (400.13 MHz): δ 3.57 (m, 2H); 3.65 (s, 6H); 4.21 (m, 2H); 4.26 (m, 2H); 4.37 (m, 2H); 6.77 (dd, 2H, J = 4.8, 8.3 Hz); 6.80−6.83 (m, 4H); 7.20−7.28 (m, 8H); 7.31−7.36 (m, 4H) ppm. ^{13}C NMR (100.61 MHz): δ 55.58 (CH_3); 72.48 (br, CH); 72.68 (d, CH, J_{CP} = 3.1 Hz); 72.84 (br, d, CH, J_{CP} = 6.9 Hz); 75.00 (d, CH, J_{CP} = 26.0 Hz); 76.39 (d, C, J_{CP} = 6.1 Hz); 110.23 (CH); 120.67 (CH); 127.81 (d, CH, J_{CP} = 7.6 Hz); 127.97 (d, C, J_{CP} = 12.2 Hz); 128.46 (CH); 129.93 (CH); 133.50 (CH); 133.54 (d, CH, J_{CP} = 19.9 Hz); 137.67 (d, C, J_{CP} = 8.4 Hz); 160.67 (d, C, J_{CP} = 15.3 Hz) ppm. ^{31}P NMR (121.50 MHz): δ −29.19 (s) ppm. $[\alpha]^{20}_D$ = −198.9 (c = 0.272; $CHCl_3$). HRMS (EI$^+$): m/z calcd for $C_{36}H_{32}FeO_2P_2$ 614.1227, obsd 614.1239. Anal. Calcd for $C_{36}H_{32}FeO_2P_2$: C, 70.37; H, 5.25. Found: C, 70.63; H, 5.60.

(*R*,*R*)-(−)-1,1′-Bis(2-biphenylylphenylphosphino)ferrocene, 1d. Separation of *meso*-(*R*,*S*)-diphosphine diborane was achieved by column chromatography (SiO_2; hexane/CH_2Cl_2 = 3:2), followed by recrystallization of the (*R*,*R*)-diphosphine diborane complex from CH_2Cl_2/hexane. The thus-obtained product was subjected to decomplexation as described above. Yield: 81%. Mp: 160 °C. ^{1}H NMR (400.13 MHz): δ 3.43 (m, 2H); 4.01 (m, 2H); 4.28 (m, 4H); 7.03−7.10 (m, 6H); 7.15−7.38 (m, 22H) ppm. ^{13}C NMR (100.61 MHz): δ 72.27 (d, CH, J_{CP} = 1.4 Hz); 72.50 (d, CH, J_{CP} = 1.8 Hz); 72.89 (dd, CH, J_{CP} = 1.8, 7.2 Hz); 75.84 (d, CH, J_{CP} = 32.2 Hz); 76.95 (d, C, J_{CP} = 8.5 Hz); 126.80 (d, CH, J_{CP} = 1.5 Hz); 127.49 (2CH); 127.71 (d, CH, J_{CP} = 8.3 Hz); 127.97 (CH); 128.45 (br, CH); 129.54 (d, CH, J_{CP} = 3.8 Hz); 129.75 (d, CH, J_{CP} = 3.8 Hz); 132.51 (br, CH); 134.16 (d, CH, J_{CP} = 20.7 Hz); 137.71 (d, C, J_{CP} = 7.8 Hz); 138.77 (d, C, J_{CP} = 14.7 Hz); 141.66 (d, C, J_{CP} = 5.1 Hz); 146.60 (d, C, J_{CP} = 24.3 Hz) ppm. ^{31}P NMR (121.50 MHz): δ −22.52 (s) ppm. $[\alpha]^{20}_D$ = −208.9 (c = 0.257; $CHCl_3$). HRMS (EI$^+$): m/z calcd for $C_{46}H_{36}FeP_2$ 706.1642, obsd 706.1639. Anal. Calcd for $C_{46}H_{36}FeP_2$: C, 78.19; H, 5.14. Found: C, 77.95; H, 5.15.

(*R*,*R*)-(−)-1,1′-Bis(9-phenanthrylphenylphosphino)ferrocene, 1e. Yield: 72%. Mp: 252−253 °C dec. ^{1}H NMR (400.13 MHz): δ 3.67 (m, 2H); 4.32 (m, 2H); 4.46 (m, 4H); 7.17−7.30 (m, 6H); 7.37 (d, 2H, J = 5.0 Hz); 7.40−7.69 (m, 14H); 8.33 (ddd, 2H, J = 1.0, 4.5, 8.0 Hz); 8.59−8.66 (m, 4H) ppm.^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 72.99 (CH); 73.15 (CH); 73.39 (d, CH, J_{CP} = 8.0 Hz); 76.36 (d, C, J_{CP} = 5.6 Hz); 76.45 (d, CH, J_{CP} = 30.8 Hz); 122.73 (CH); 123.26 (CH); 126.67 (d, CH, J_{CP} = 3.0 Hz); 126.71 (CH); 126.99 (d, CH, J_{CP} = 26.2 Hz); 127.00 (CH); 127.35 (CH); 128.54 (d, CH, J_{CP} = 7.9 Hz); 129.05 (CH); 129.47 (CH); 130.40 (d, C, J_{CP} = 4.1 Hz); 130.83 (C); 131.60 (d, CH, J_{CP} = 2.1 Hz); 132.92 (CH); 133.15 (C); 134.44 (d, CH, J_{CP} = 20.7 Hz); 136.18 (d, C, J_{CP} = 15.4 Hz); 136.69 (d, C, J_{CP} = 7.5 Hz) ppm. ^{31}P NMR (121.50 MHz, $CDCl_3$: δ −24.24 (s) ppm. $[\alpha]^{20}_D$ = −349.3 (c = 0.152, $CHCl_3$). HRMS (EI$^+$): m/z calcd for $C_{50}H_{36}FeP_2$ 754.1642, obsd 754.1628. Anal. Calcd for $C_{50}H_{36}FeP_2$: C, 79.58; H, 4.81. Found: C, 79.18; H, 4.86.

Experimental Details for Crystal Structure Determination. Intensity data were collected at T = 150 K on a Enraf-Nonius CAD4T diffractometer with rotating anode and Mo Kα radiation (λ = 0.710 73 Å) up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.649 Å^{-1}. The structures were solved with the program DIRDIF-97[29] and refined by a full-matrix least-squares refinement against F^2 with the program SHELXL-97.[30] For confirmation of the absolute structure the Flack x parameter was included in the refinement.[19] Hydrogen atoms were introduced in calculated positions and refined as rigid groups. Structure graphics and checking for higher symmetry were performed with the program PLATON.[31]

(*R*,*R*)-(−)-1,1′-Bis(1-naphthylphenylphosphino)ferrocene, 1a: $C_{42}H_{32}FeP_2$, M_r = 654.47, orthorhombic, $P2_12_12_1$ (No. 19), a = 9.4685(19) Å, b = 13.6848(19) Å, c = 24.721(4) Å, V = 3203.2(9) Å^3, Z = 4, ρ_{calcd} = 1.357 g/cm^3. Red-brown plate, 0.45 × 0.32 × 0.18 mm^3. Absorption correction with DE-LABS (PLATON, 0.77−0.90 transmission). 4612 measured reflections, 4476 unique reflections, 407 parameters. R1(F) [$I > 2\sigma I$] = 0.0665, wR2(F^2) [all data] = 0.2008.

(*S*,*S*)-(−)-1,1′-Bis(2-naphthylphenylphosphino)ferrocene, 1b: $C_{42}H_{32}FeP_2 \cdot CH_2Cl_2$, M_r = 739.45, monoclinic, $P2_1$ (No. 4), a = 8.8921(5) Å, b = 21.0173(12) Å, c = 9.6078(12) Å, β = 90.724(4)°, V = 1795.4(3) Å^3, Z = 2, ρ_{calcd} = 1.368 g/cm^3. Orange block, 0.5 × 0.5 × 0.5 mm^3. No absorption correction considered necessary. The electron density contribution of the disordered solvent molecules was added to the calculated F^2 values via back-Fourier transformation. This calculation was performed with the routine CALC SQEEZE as implemented in the PLATON package. The diffuse electron density corresponds to one crystallographic independent CH_2Cl_2 molecule. 4719 measured reflections, 4209 unique reflections, 407 parameters. R1(F) [$I > 2\sigma I$] = 0.0473, wR2(F^2) [all data] = 0.1250.

(*R*,*R*)-(−)-1,1′-Bis(2-biphenylylphenylphosphino)ferrocene, 1d: $C_{46}H_{36}FeP_2$, M_r = 706.54, monoclinic, $P2_1$ (No. 4), a = 9.2755(8) Å, b = 14.0054(11) Å, c = 27.6627(13) Å, β = 96.275(6)°, V = 3572.1(4) Å^3, Z = 4, ρ_{calcd} = 1.314 g/cm^3. Orange block, 0.5 × 0.5 × 0.5 mm^3. No absorption correction considered necessary. 10102 measured reflections, 8491 unique reflections, 884 parameters. R1(F) [$I > 2\sigma I$] = 0.0362, wR2(F^2) [all data] = 0.0825.

Asymmetric Hydrogenation Reactions (Typical Procedure). A solution of $[Rh(nbd)_2]ClO_4$ (0.01 mmol) and ligand (0.011 mmol) in 10 mL of absolute methanol was degassed by three freeze−thaw cycles and stirred for 30 min at room temperature. It was then transferred via cannula in a 70 mL glass autoclave, followed by a degassed solution of substrate (1 mmol) in 4 mL of methanol. The argon atmosphere was replaced by hydrogen, initial pressure was set to 2.0 bar, and the reaction mixture was stirred for 6 h at 25 °C. Conversion was checked by NMR measurement of the crude product. Compound **9c** was filtered over a plug of silica to remove the catalyst, while products **9a** and **9b** were subjected to extractive workup and subsequently transformed into their methylesters.[32] Enantiomeric purities were determined by chiral GC (Chiralsil-L-Val, isothermal, T = 150 °C for *N*-acetylphenylalanine methylester, t_R (*R*) = 13.0 min, t_R (*S*) = 14.8 min; T = 180 °C for *N*-benzoylphenylalanine methylester, t_R (*R*) = 28.2 min, t_R (*S*) = 30.3 min).

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Supporting Information Available: Crystal structure refinement data for compounds **1a**, **1b**, and **1d** including atomic coordinates, isotropic and anisotropic displacement parameters, and a complete listing of bond angles and bond lengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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