Diastereoselective Ortho-Metalation of Stereogenic Ferrocenylphosphine Oxides. Asymmetric Synthesis of the First Enantiopure Phosphorus-Chiral 2,2′-Bis(diarylphosphino)-1,1′-biferrocenyls

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Two novel phosphorus-chiral ligands, 2,2′-bis(arylphenylphosphino)-1,1′-biferrocenyls **1a** (aryl = 1-naphthyl) and **1b** (aryl = 2-biphenylyl), have been prepared in enantiopure form by stereoselective multistep synthesis. While asymmetry on phosphorus was established via nucleophilic substitution reactions at borane-protected phosphorus centers, ortho-iodination of the derived optically pure ferrocenylphosphine oxides served as the key step for the introduction of planar chirality. Utilizing biphenylylphenylphosphinoxyferrocene, **5b**, the latter reaction was found to proceed in a highly diastereoselective manner, resulting in a product distribution of 97:3. The absolute configuration of the predominantly formed diastereomer was confirmed by crystal structure analysis of the Ullmann-coupled bis-(arylphenylphosphinoxy)biferrocenyl **6b** (aryl = biphenylyl). Reduction of dioxides **6a** (aryl = 1-naphthyl) and **6b** gave rise to the enantiopure C_2-symmetrical title compounds comprising four adjacent stereocenters. The coordination behavior of **1a** was investigated by a crystal structure determination of its Pt(II) dichloride complex **8a** and compared with the structure of complex **8c**, bearing the related 1,1′-bis(1-naphthylphenylphosphino)ferrocene ligand **1c**.

Introduction

During recent years the development of new efficient transition metal-catalyzed reactions and asymmetric variants thereof resulted in a growing demand for novel, highly active, and selective donor ligands. While chiral synthons such as atropisomeric biphenyls, binaphthyls, and their derivatives[1] or planar chiral ferrocenyl moieties[2] have been successfully incorporated in a vast variety of different ligand structures, other related asymmetric building blocks, for instance biferrocenyls, gained little attention. Although rotational barriers around the bond linking the two cyclopentadienyl rings in binaphthyl-analogous 2,2′-functionalized biferrocenyl compounds are usually too low to promote axial chirality,[3] the combination of two planar chiral elements renders these structures attractive as C_2-symmetrical auxiliaries. The synthesis of enantiopure derivatives is not straightforward, however, which might account for the rather limited number of biferrocenyl-based ligands reported to date.[4] A practicable and stereoselective access to the 2,2′-substituted biferrocenyl skeleton was previously used by Ito and co-workers in the course of their synthesis of trans-coordinating 2,2′-bis[1-(diaryl-

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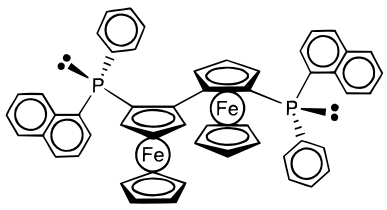
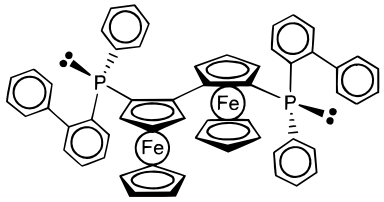
or dialkylphosphino)ethyl]-1,1′-biferrocenyls (TRAP ligands).[4a,c,d] The key features of that reaction sequence are the diastereoselective ortho-iodination of optically pure *N,N*-dimethyl-1-ferrocenylethylamine, followed by stereospecific replacement of the amine moiety by phosphine oxides, herewith determining centro-chirality as well as metallocene chirality before the subsequent establishment of the biferrocenyl backbone via Ullmann-type coupling.

Within our current research directed toward the synthesis and application of novel ligands incorporating stereogenic phosphorus moieties, we wanted to explore the catalytic properties of biferrocenyl-based aryldiphosphine structures. In addition, we became interested in the stereodifferentiating potential of optically active ferrocenylphosphine oxides. During recent years, several new methods for the generation of planar chiral enantioenriched ferrocene derivatives were disclosed,[5] among which the lithium−sparteine-mediated ortho-metalation of diisopropylamidoferrocene was considered especially useful.[6] Concerning dissymmetric ortho-directing groups, various oxazoline,[7] sulfoxide,[8] and acetal moieties[9] were previously found to give the desired 1,2-substituted derivatives with the same or even higher selectivities than that stated for the well-known Ugi-amine (92% de).[10] In contrast, stereoselective ortho-metalation effected by optically pure ferrocenylphosphine oxides has not been reported to date. In this paper we describe the results of a study on the diastereoselective ortho-magnesiation of two different diarylphosphinoxyferrocenes. The thus obtained *ortho*-iodoferrocenylphosphine oxides were employed in the asymmetric synthesis of the first P-chiral enantiopure biferrocenyldiphosphine ligands **1a** and **1b**.

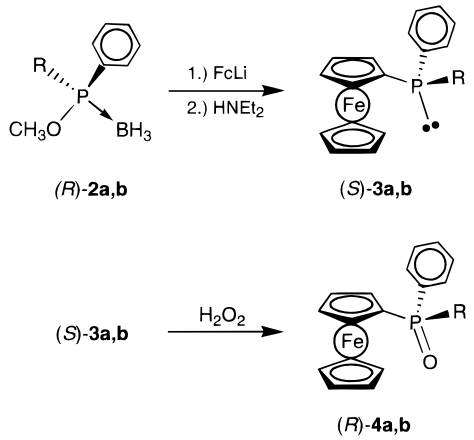


(S_P,R_m,R_m,S_P)-**1a**



(S_P,R_m,R_m,S_P)-**1b**

Scheme 1



a: R = 1-naphthyl, **b**: R = 2-biphenylyl

Results and Discussion

Diastereoselective Ortho-Metalation of Enantiopure Ferrocenylphosphine Oxides. As a part of our ongoing project concerned with the development and exploration of new asymmetrically substituted phosphorus donors, we recently prepared a series of P-chiral 1,1′-bis(diphenylphosphino)ferrocene (dppf) analogues.[11] Expanding a synthetic pathway described by Jugé et al.,[12] we succeeded in the stereoselective coupling of different methyl arylphenylphosphinite boranes with dilithioferrocene. After decomplexation of the bis(borane) adducts using diethylamine, five novel enantiopure ferrocenyldiphosphine ligands were obtained.

In a similar manner, this methodology was applied to the synthesis of the desired P-chiral ferrocenylphosphine oxides. Monolithioferrocene, prepared according to Kagan's protocol,[13] was made to react with 1 equiv of (*R*)- or (*S*)-phosphinite borane **2a**,**b**, after deprotection yielding configurationally inversed ferrocenylmonophosphines **3a**,**b**. These were stereoselectively oxidized in the presence of H_2O_2, giving the optically pure phosphine oxides **4a**,**b** (Scheme 1).

On extrapolating our findings during the synthesis of the related diphosphines, where nucleophilic attack of dilithioferrocene proceeded with high degrees of stereoselectivity,[12] we expected a similar outcome for the analogous monosubstitution step. The enantiomeric purity of the monophosphine oxides was checked by applying the chiral NMR solvating reagent (*S*)-*N*-(3,5-dinitrobenzoyl)-1-phenylethylamine.[14] Within the NMR integration errors of ±2%, indeed, no traces of the other

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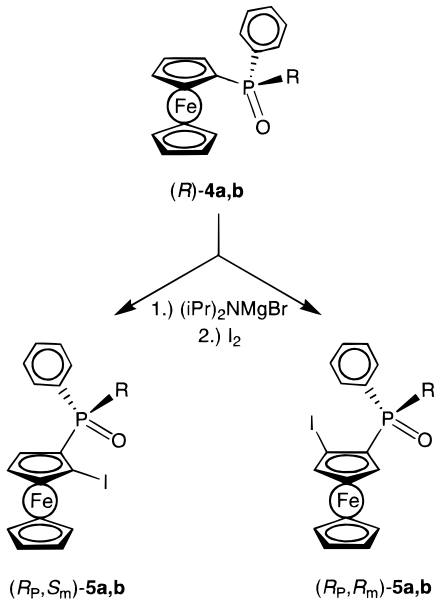
Scheme 2



a: R = 1-naphthyl, **b**: R = 2-biphenylyl

enantiomer were detected in recrystallized samples of phosphine oxides **4a**,**b**, respectively.

Preliminary ortho-lithiation experiments were carried out using phosphine oxide **4a** and *n*-butyllithium as metalating agent. Quenching reactions with D_2O, I_2, or 1,2-diiodoethane yielded only small quantities (10−20%) of regioisomeric product mixtures, indicating unspecific and ineffective lithiation behavior. Variation of reaction temperature (−78 °C, 0 °C, room temperature), reagent (*tert*-BuLi), and solvent (diethyl ether, THF, and mixtures thereof) gave no improvement. These findings contrasted with the reports of successful ortho-lithiation reactions on (substituted) benzenes, directed by related bis(dimethylamino)phosphinoxy,[15] diphenylphosphinoxy,[16] and, especially, di-*tert*-butylphosphinoxy[17] groups. Considering the longer P═O···ortho-H distance in the five-membered ferrocene skeleton, nonselective deprotonation might be due to insufficient lithium−oxygen orbital overlap, suggesting that the use of a different metal might improve selectivity. To this aim, employment of diisopropylamidomagnesium bromide[18] was attempted, and this reagent proved to effect quantitative ortho-magnesiation of **4a** after 3 h at room temperature. Subsequent quenching of the reaction with iodine/THF solution at −30 °C afforded a mixture of the two ortho iodo products in good yields (Scheme 2). After column chromatographic separation the ratio of diastereomers was found to be 75:25, which was in agreement with NMR measurements of the crude product mixture.

When biphenylylphenylphosphinoxyferrocene **4b** was subjected to the above-mentioned protocol, diastereo-

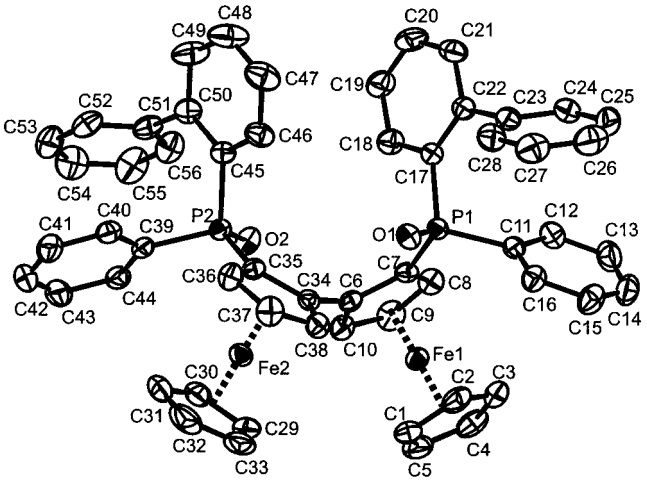


Figure 1. Displacement ellipsoid plot of (R_P,R_m,R_m,R_P)-**6b**, drawn at the 50% probability level.

differentiation proved to be considerably higher, with the two isomers being formed in a 97:3 ratio. Change of solvent (Et_2O) or reaction temperature (magnesiation at −40 °C) affected neither the yield nor the stereoselectivity. The thus obtained diastereomeric excess of 94% de ranks among the highest values for induction of planar chirality reported to date and constitutes the first example of an efficient, stereoselective phosphine oxide-functionalized directing metalation group on ferrocene.

Synthesis of Enantiopure 1,1′-Biferrocenyl-2,2′-diphosphines. Optically pure *ortho*-iodoferrocenylphosphine oxides, obtained stereoselectively (**5b**) or by column chromatographic separation (**5a**), were subjected to Ullmann coupling at 130 °C using activated copper powder (Scheme 3). After 2 days the desired biferrocenyldiphosphine dioxides were isolated, together with some amounts of starting material, thus making the yields in products range from 58% (**6a**) to 70% (**6b**).

To determine the relative configuration of the predominantly formed ortho-iodination product **5b**, a crystal structure analysis of the derived Ullmann-coupled biferrocenyl diphosphine dioxide **6b** was performed. Having employed (*R*)-methyl phosphinite borane **2b** as electrophile in the reaction with monolithioferrocene, (*S*)-configurated phosphine **3b** and, subsequently, phosphine oxide (*R*)-**4b** were expected to be formed (vide supra). Since (partial) racemization of planar chiral compounds is rather unlikely to occur under Ullmann conditions, conservation of metallocene chirality can be assumed. As depicted in Figure 1, the crystals of enantiopure **6b** possess the (R_P,R_m,R_m,R_P) configuration at the four stereogenic elements. Consequently, the (R_P)-configurated phosphine oxide gave rise to the (R_m)-magnesiated intermediate and, finally, lead to the (S_m)-iodo product. Considering the schematic model structures displayed below, the preferred site of metalation corresponds to a conformation in which the bulky biphenyl group occupies a position above the ferrocene moiety in order to minimize steric interactions with the unsubstituted cyclopentadienyl ring (Scheme 4). This sort of mechanistic rationale has also been invoked for other stereodiscriminating directing ortho-metalation groups on ferrocene,[19] including the structurally similar ferrocenyl-*tert*-butylsulfoxide.[8] In our case, it is further sub-

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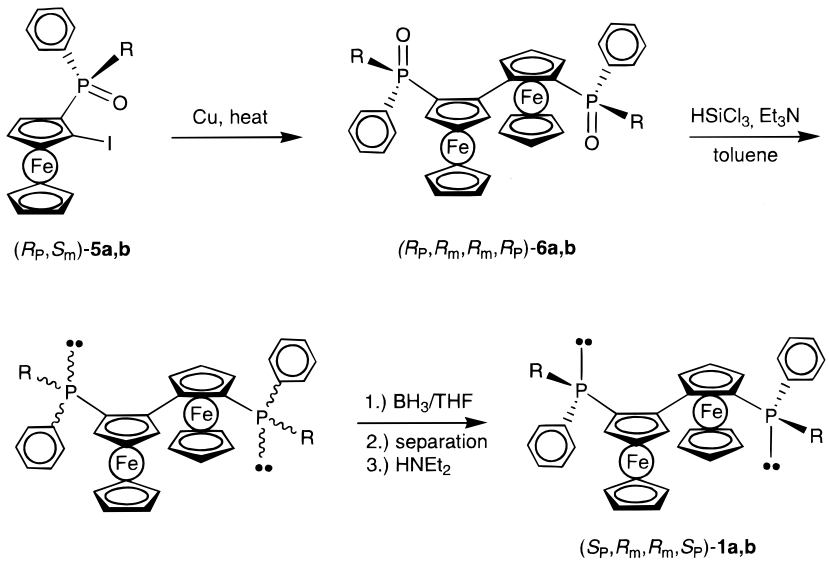
Scheme 3

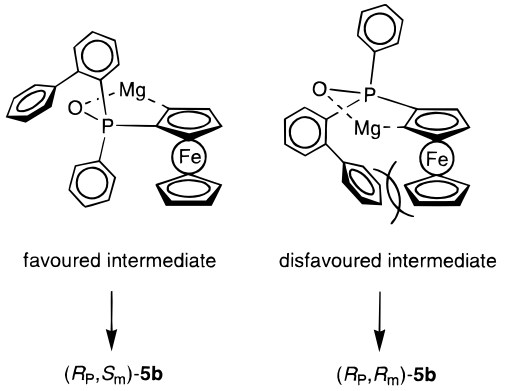


(R_P,S_m)-**5a,b** (R_P,R_m,R_m,R_P)-**6a,b**

(S_P,R_m,R_m,S_P)-**1a,b**

a: R = 1-naphthyl, **b**: R = 2-biphenylyl

Scheme 4



stantiated by the lower diastereomeric ratio obtained for phosphine oxide **4a**, which seems less prone to exhibit intramolecular repulsive interaction, due to its smaller degree of sterical encumbrance.

Diphosphine dioxide **6b** was found to crystallize as a dichloromethane solvate in the chiral space group $P2_12_12_1$ with four biferrocenyl molecules in the unit cell. The absolute configuration was determined via anomalous dispersion; the Flack parameter $x = 0.019(12)$ indicated enantiomeric integrity.[20] The biferrocenyl molecule is approximately C_2 symmetrical in the crystal (Figure 1). In view of the considerable conformational freedom of this compound, this finding seems surprising, but may in part result from favorable intramolecular $\pi\cdots\pi$ interactions between the inner phenyl rings of the two biphenyl groups (e.g., C18···C46 = 3.45 Å) and between the terminal phenyl rings of the biphenyl units and the P-bonded phenyl rings (e.g., C11···C23 = 3.14 Å, C39···C51 = 3.09 Å). The torsional angle of the biferrocenyl moiety is Fe1−C6−C34−Fe2 = −69.9(3)°. The biphenyl groups adopt the usual twisted conformations, with plane angles of 69.4(2)° and 67.0(2)°. Their orientations relative to ferrocene are defined by the dihedral angles Fe1−C7−P1−C17 = 160.3(2)°, C7−P1−C17−C18 = 21.7(3)°, Fe2−C35−P2−C45 = 158.4(2)°, and C35−P2−C45−C46 = 15.0(3)°.

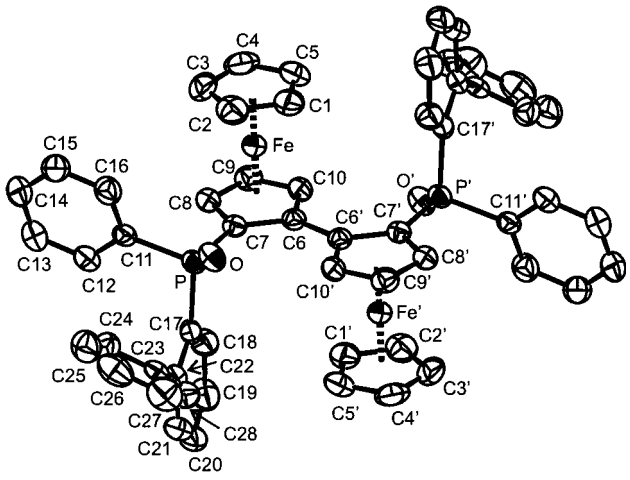


Figure 2. Displacement ellipsoid plot of (R_P,R_m,S_m,S_P)-**6b**, drawn at the 50% probability level (symmetry operation ′: $1-x, -y, 1-z$).

If racemic or nonenantiopure *ortho*-iodophosphinoxyferrocene **5** was employed in the Ullmann reaction, not only homocoupling of identically configurated isomers but also heterodimerization between the two enantiomers with opposite configuration took place. For starting material (±)-**5a**, the presumably formed (R_m,S_m)-configurated meso products were unstable and could not be isolated. In contrast, using racemic 1-iodo-2-biphenylylphenylphosphinoxyferrocene **5b**, we were able to obtain the meso product (R_P,R_m,S_m,S_P)-**6b**. Formation of the C_i-symmetrical isomer seemed, indeed, to be preferred for steric reasons, resulting in a meso:rac product distribution of 2.3:1. The crystal structure of the *meso*-diphosphine dioxide is shown in Figure 2.

Compound *meso*-**6b** crystallizes in the centrosymmetric space group $P\bar{1}$ with the inversion center located on

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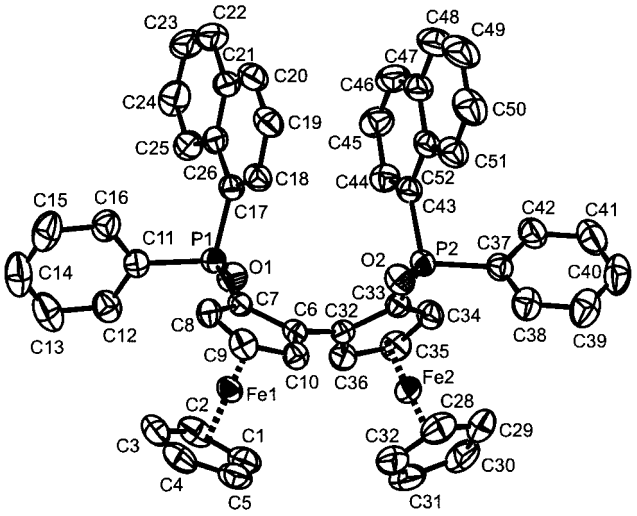

Figure 3. Displacement ellipsoid plot of (R_P,R_m,R_m,R_P)-**6a**, drawn at the 50% probability level.

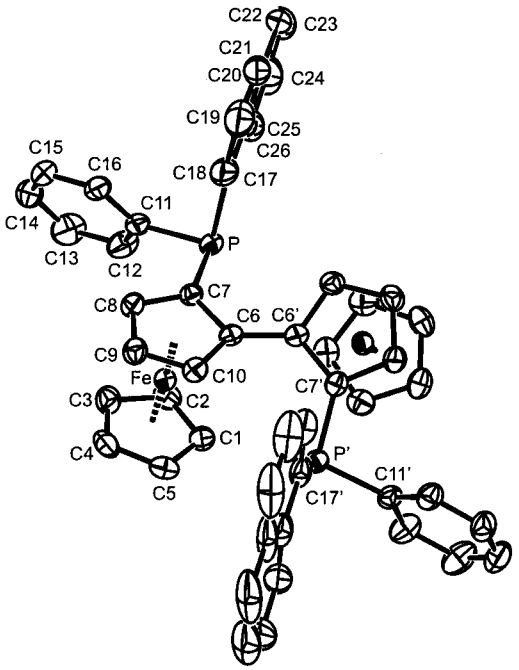

Figure 4. Displacement ellipsoid plot of (S_P,R_m,R_m,S_P)-**1a**, drawn at the 50% probability level (symmetry operation ′: 1−*x*, *y*, 1.5−*z*).

the midpoint of the ferrocenyl−ferrocenyl bond (C_i symmetry). The inversion center implies that the Cp planes of the ferrocene units are coplanar and that Fe−C6−C6′−Fe′ = 180°. In contrast to ortho-substituted biphenyls, no steric interactions of ortho protons are detected in the biferrocenyl entity, rendering the coplanar arrangement not unfavorable. The orientations of the biphenyl goups differ with dihedral angles of Fe1−C7−P1−C17 = 177.1(2)° and C7−P1−C17−C18 = −16.8(4)° from (R_P,R_m,R_m,R_P)-**6b** and do not permit the intramolecular $\pi\cdots\pi$ interactions mentioned above. The biphenyl substituents adopt a typical angle of 65.1(2)°.

For reasons of comparison, and in order to define the relative metallocene configuration of the ortho-iodo product formed in excess, we also performed a crystal structure analysis on a racemic sample of 1-naphthyl-substituted biferrocenyldiphosphine dioxide **6a** (Figure 3). The observed (R_P,R_m,R_m,R_P) configuration of the four stereocenters is in agreement with the stereochemical model discussed above, assuming the 1-naphthyl substituent displays the larger steric bulk with respect to the phenyl group.

Dioxide *rac*-**6a** was found to crystallize in the centrosymmetric space group $P2_1/c$ with four molecules in the unit cell. The molecules display approximately C_2 symmetry in the crystal. The biferrocenyl unit shows a twist angle of Fe1−C6−C32−Fe2 = −67.7(2)°, similar to (R_P,R_m,R_m,R_P)-**6b**. The orientations of the naphthyl groups relative to ferrocene are defined by dihedral angles of Fe1−C7−P1−C17 = 171.4(1)°, C7−P1−C17−C18 = −2.6(2)°, Fe2−C33−P2−C43 = 170.5(1)°, and C33−P2−C43−C44 = −0.2(2)°. This conformation results in an almost parallel arrangement of the naphthyl groups with a distance between them of about 3.3 Å, indicating favorable intramolecular $\pi\cdots\pi$ interactions.

With enantiopure biferrocenyl derivatives **6a** and **6b** in hand, the reduction of the phosphine oxides remained to be accomplished. Mild reducing agents, however, such as polymethylhydrosiloxane/Ti(O-^{i}Pr)$_4$,[21] left the starting material unchanged, as did the combination $HSiCl_3$/benzene/triethylamine. Only when rather harsh reaction conditions were applied, namely, $HSiCl_3$/toluene/triethylamine at 130 °C for 72 h, were the sterically hindered dioxides completely reduced to the corresponding diphosphines **1a** and **1b**. As a consequence of the prolonged treatment, partial epimerization of the stereogenic phosphorus centers was observed, resulting in a mixture of stereoisomers. For diphosphine **1a**, the product average composition was found to be 60% of the desired (S_P,R_m,R_m,S_P)-configurated isomer, 35% of the monoepimerized C_1-symmetrical (R_P,R_m,R_m,S_P)-diastereomer, and 5% of the doubly isomerized (R_P,R_m,R_m,R_P)-product. In the case of diphosphine **1b**, the extent of epimerization was somewhat smaller, resulting in a 65:30:5 distribution of diastereomers, configurated as mentioned above. Isolation and purification of the C_2-symmetrical (S_P,R_m,R_m,S_P)-products was achieved by column chromatographic separation of their bis(borane) adducts.[22] Finally, stereospecific deprotection of the borane complexes using diethylamine[23] or trifluoromethanesulfonic acid/KOH[24] gave rise to enantiomerically pure P-chiral biferrocenyldiphosphines **1a** and **1b**, respectively.

Crystals of ligand (±)-**1a**, prepared in an analogous manner from racemic starting material, were grown from CH_2Cl_2/hexane and found to crystallize in the centrosymmetric space group *Pbcn* (Figure 4). The molecules exhibit an exact, crystallographic C_2 symmetry. In the solid state, channels in the direction of the *c*-axis are present, which are filled with disordered solvent molecules. The twist angle of the biferrocenyl unit is, with Fe−C6−C6′−Fe′ = 37.6(4)°, distinctly smaller than in the previously discussed compounds.

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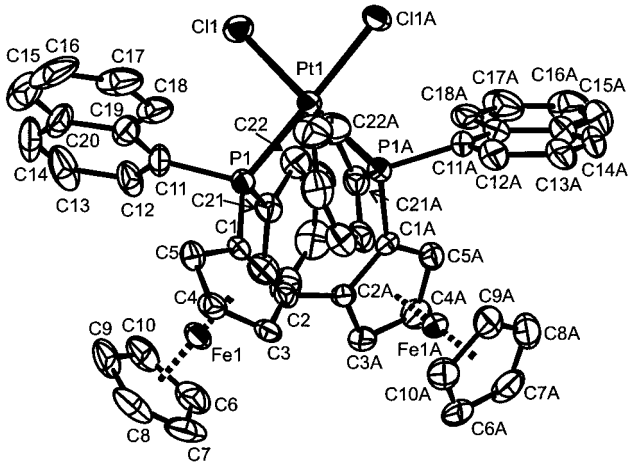


Figure 5. Displacement ellipsoid plot of [(S_P,R_m,R_m,S_P)-**1a**]$PtCl_2$, **8a**, drawn at the 50% probability level.

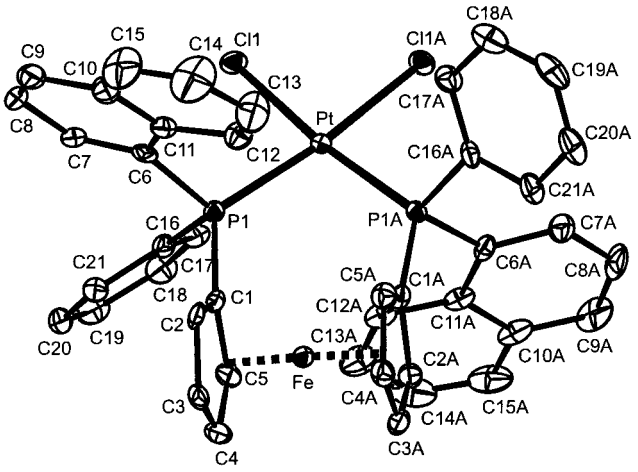
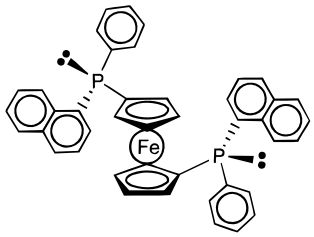


Figure 6. Displacement ellipsoid plot of [(S_P,S_P)-**1c**]$PtCl_2$, **8c**, drawn at the 50% probability level.

The orientations of the naphthyl groups relative to ferrocene, Fe−C7−P−C17 = 177.1(1)° and C7−P−C17−C18 = 1.7(2)°, however, compare well with those of *rac*-**6a**. The structure is devoid of intramolecular $\pi\cdots\pi$ interactions. The phosphino groups occupy trans positions with respect to each other, resulting in a P···P′ distance of 5.995(3) Å.

Crystal Structures of [2,2′-Bis(1-naphthylphenylphosphino)-1,1′-biferrocenyl]$PtCl_2$ and [1,1′-Bis(1-naphthylphenylphosphino)ferrocene]-$PtCl_2$. With regard to their unique structure and intended application in catalysis, we were intrigued to investigate the complexation behavior of the new P-chiral biferrocenyldiphosphines. In contrast to the TRAP ligands, which, due to their intrinsic conformational flexibility and large natural bite angles,[25] were found to form trans-coordinated nine-membered-ring square-planar Pd(II) and Rh(I) complexes,[5c] we expected the formation of cis-fashioned seven-membered chelates. Yet, the question arose, what influence might the biferrocenyl moiety have on complex ring strain, phosphorus−metal−phosphorus bite angle, and structural features in general? Such data seemed especially interesting when compared to those of a platinum dichloride complex of the related ferrocene-based ligand **1c**,[11] which is depicted below.



(S_P,S_P)-**1c**

Because ligands **1a** and **1c** bear identical substitution patterns on the chiral phosphorus donors, their electronic properties were assumed to be similar, whereas major differences in their platinum complex structures were expected to arise from backbone constitution. Platinum complexes **8a**,**c** were prepared by reaction of bis(benzonitrile)dichloroplatinum(II) with the respective ligands (S_P,R_m,R_m,S_P)-**1a** and (S_P,S_P)-**1c**. The crystal structures are depicted in Figures 5 and 6; comparative interatomic distances and angles are summarized in Table 1.

Interestingly, the platinum and phosphorus geometries observed for **8a** and **8c** display few similarities. Complex **8c**, bearing the (S_P,S_P)-configurated diphosphine, crystallizes in the chiral space group $P2_12_12_1$, and a determination of the Flack *x* parameter[20] confirmed the absolute configuration. The C_2 symmetry of the complex is only approximately fulfilled in the solid state. The large deflection from the ideal 90 ° phosphorus−platinum−phosphorus angle of an undistorted square-planar cis-coordinated complex may be rationalized by simple modeling considerations. Assuming an ideal

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in Complexes 8a,c

	8a	**8c**
P1−Pt	2.2558(14)	2.2555(13)
P1A-Pt	2.2415(16)	2.2521(14)
Pt−Cl1	2.3726(16)	2.3487(13)
Pt−Cl1A	2.3660(14)	2.3552(11)
P1−C1	1.824(6)	1.807(5)
P1A−C1A	1.816(6)	1.807(5)
P1···P1A	3.243(2)	3.5269(19)
P1−Pt−P1A	92.30(5)	102.97(5)
Cl1−Pt−Cl1A	88.87(6)	88.28(5)
Pt−P1−C1	116.59(19)	123.96(17)
Pt−P1A−C1A	115.06(19)	123.80(17)
Pt−P1−C11	116.0(2)	
Pt−P1A−C11A	117.85(19)	
Pt−P1−C6		111.82(15)
Pt−P1A−C6A		111.23(18)
Pt−P1−C21	105.4(2)	
Pt−P1A−C21A	106.0(2)	
Pt−P1−C16		111.46(17)
Pt−P1A−C16A		111.82(18)
Pt−P1−C1−C2	−72.8(6)	103.6(5)
Pt−P1A−C1A−C2A	−74.4(5)	102.2(5)
Pt−P1−C11−C12	129.19(17)	
Pt−P1A−C11A−C12A	135.3(2)	
Pt−P1−C6−C7		116.1(4)
Pt−P1A−C6A−C7A		121.9(4)
Pt−P1−C21−C22	−30.6(5)	
Pt−P1A−C21A−C22A	−34.7(6)	
Pt−P1−C16−C17		6.9(5)
Pt−P1A−C16A−C17A		4.0(5)

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platinum−phosphorus distance of 2.29 Å (mean value of 5404 bond lengths extracted from the Cambridge Structural Database[26]), the optimum P1···P1A distance attainable by any bidentate ligand is 3.24 Å. This value is similar to the Cp···Cp distance in ferrocene, 3.26 Å. Rotation of the cyclopentadienyl rings of a 1,1′-ferrocenyldiphosphine against each other results in enlargement of the P1···P1A distance of up to 6.8 Å (trans-arrangement of the phosphine moieties). In an eclipsed conformation of the latter, the platinum geometry is prevailingly undistorted, whereas the Pt−P1−C1 angles of about 135° are unfavorably high, herewith strongly deviating from the ideal value of 114−115°.[26] Thus, for complex **8c**, distortion of the platinum geometry toward a wider P1−Pt−P1A angle and/or the phosphorus geometries toward smaller Pt−P1−C1 angles was expected. The crystal structure, indeed, revealed a highly strained system with a bite angle of 102.97(5)° as well as Pt−P1−C1 and Pt−P1A−C1A angles of 124.0(2)° and 123.8(2)°, respectively. This compromise between the distortion of the platinum and phosphorus geometries is achieved by a small rotation of the cyclopentadienyl rings toward a staggered arrangement (torsion angle P1−C1−C1A−P1A = 5.3(3)°) and a distortion at the atoms C1 and C1A (C2−C1−P1 and C2A−C1A−P1A angles: 129.4(4)° and 127.7(4)°), both together resulting in a P1···P1A distance of 3.527(2) Å. Similar values for that distance were found in the platinum(II) dichloride complex of dppf[27] and its palladium(II) analogue,[28] which exhibit bite angles of 99.3(1)° and 99.07(5)°, respectively. Yet, in these cases distortion is mainly due to a truly staggered conformation of the cyclopentadienyl rings. For compound **8c**, release of steric strain via such an arrangement might be impeded by the bulkiness of the 1-naphthyl substituents, herewith enforcing the widest bite angle reported for comparable dppf-type complexes so far.

In complex **8a**, representing the first crystallographically characterized example of ligation by a 2,2′-diphosphino-1,1′-biferrocenyl, the P1···P1A distance may be tuned by rotation around the C−C bond linking the two ferrocenyl groups. Consequently, the accessible distances range between 2.0 and 6.0 Å, allowing for easy accommodation of the optimum value of 3.24 Å, calculated for a square-planar cis-chelated platinum complex (vide supra). Additionally, the Pt−P1−C1 angle was assumed to be less strained in comparison to complex **8c**. The actual structure of **8a** was found to be in good agreement with these expectations; neither the platinum nor the phosphorus geometries are severely distorted. The space group of complex **8a** was identified as $P2_12_12_1$, and, again, determination of the Flack *x* parameter confirmed the absolute configuration. The C_2 symmetry of compound **8a** is not completely met in the crystal. The naphthyl groups occupy pseudoequatorial positions with respect to the P1−Pt−P1A plane, whereas the phenyl rings are oriented in an axial fashion. The P1−Pt−P1A bite angle is 92.30(5)°, and Pt−P and Pt−Cl bond lengths are within the typical range observed for related complexes.[29] Due to the similarity of the backbone skeletons, these features compare well with the structural data reported for a Binap palladium(II) dichloride complex.[30] The almost in-plane arrangement of Pt, P1, P1A, Cl1, and Cl1A atoms with an angle sum of 359.9(9)° around platinum suggested, however, the steric repulsion between the chlorine atoms and equatorial phosphine substituents in **8a** to be less pronounced than in the mentioned Binap derivative (angle sum: 367.3(2)°).

The dissimilar modeling of the platinum coordination sphere by the two diphosphines was also evidenced by the solution structures of the respective complexes **8a** and **8c**. The ^{31}P-resonance signals for the free ligands were found at chemical shift values of $\delta = -30.60$ ppm (**1a**) and $\delta = -30.39$ ppm (**1c**).[11b] Upon complexation, however, the coordination chemical shift $\Delta\delta^{31}$ observed for **8c** of 43.88 ppm to $\delta = +13.49$ ppm was larger than the shift value for **8a** ($\delta = -6.21$ ppm; $\Delta\delta = 24.39$ ppm). These findings reflect the stronger bending[32] of phosphine metal bonds in five-membered platinum(II) ring chelates as compared to their seven-membered analogues, since the occurrence of endo- and exocyclic metal−phosphorus−carbon angles close to the tetrahedral value will result in a deshielding contribution to the isotropic shift tensor (Table 1).[33]

Steric effects imposed by the phenyl and naphthyl substituents on chiral phosphorus appeared less pronounced; only for complex **8c** was broadening of signals due to hindered rotation around phosphorus carbon bonds observed to a small extent. At room temperature, the signals at $\delta = 8.61$ ppm and $\delta = 8.41$ ppm, assigned to the protons in positions 2 and 8 of the naphthyl moieties by 2D NMR experiments, showed slight broadening. Cooling the sample resulted in gradual broadening of all signals; however, no defined decoalescence could be reached at the lowest available temperature of 163 K.[34]

Conclusions

Utilizing a multistep approach, we succeeded in the stereoselective synthesis of the first enantiopure P-chiral 2,2′-bis(diarylphosphino)-1,1′-biferrocenyls. An asymmetrically substituted phosphorus moiety, introduced by stereoselective nucleophilic attack of monolithioferrocene on optically pure methyl phosphinite boranes, served as a key structural motif of the sequence. Subsequently, chirality on phosphorus allowed for separation of the derived *ortho*-iodoferrocenylphosphine oxides. Depending on the nature of residues at the phosphorus atom, the ortho-iodination reaction was found to proceed stereoselectively (up to 94% de under optimized reaction conditions). This represents the first

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(34) An analogous NMR investigation of complex **8a** was prevented due to its insufficient solubility at lower temperatures.

example of a P-chiral phosphinoxy substituent effecting a highly diastereoselective ortho-metalation on ferrocene. The stereospecific reduction of (bulky) chiral biferrocenyldiphosphine dioxides, however, remained troublesome. Nevertheless, metallocene chirality was not affected during reduction and permitted the separation of partially epimerized products. The C_2-symmetrical structure of the first enantiopure biferrocenyl ligand **1a** comprising four adjacent stereocenters was substantiated by a crystal structure analysis, showing a trans arrangement of the phosphine moieties.

The coordination behavior of diphosphine **1a** was investigated by means of a crystal structure determination of its platinum(II) dichloride complex. The cis-chelated compound exhibits a P−Pt−P bite angle of 92.30(5)°, in agreement with less distorted phosphorus and platinum geometries than observed for a structurally similar Binap palladium(II) compound and the corresponding complex of the C_2-symmetrical ferrocene-based ligand **1c** (bite angle: 102.97(5)°). As to what extent these solid-state structural features may influence efficient encumbering of the metal center by the bulky 1-naphthyl substituents is unclear. Yet, the higher flexibility of ligand **1a** might still allow for selective shielding of reagent trajectories, although the latter is more commonly associated with the presence of ligands enforcing large bite angles.[35] Application of the new chiral auxiliaries in several catalytic transformations is currently in progress, and we intend to report on results and comparison with related ferrocene-based P-chiral diphosphines[11b] in due course.

Experimental Section

General Comments. If not otherwise stated, reactions were carried out under an atmosphere of argon 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 from sodium wire under nitrogen. 1D and 2D ($^1H-^1H$ COSY) NMR spectra were recorded on 250, 300, and 400 MHz instruments; $CDCl_3$ was used as solvent, if not further specified. Phosphorus−carbon coupling constants (J_{CP}) were identified by comparison of *J*-modulated ^{13}C spectra measured at different magnetic field strengths. Elemental analyses were obtained using an Elementar Vario EL apparatus. Mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. Melting points are uncorrected. Optical rotations were measured in a thermostated polarimeter with $l = 1$ dm. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Diethylamine was distilled from KOH under argon. (*R*)-(−)-Methyl (1-naphthyl)phenylphosphinite borane (**2a**) and (*R*)-(−)-methyl (2-biphenylyl)phenylphosphinite borane (**2b**) were prepared as previously described.[11] Diisopropylamidomagnesium bromide was synthesized according to a literature protocol.[18]

Synthesis of Ferrocenylphosphines 3 (Typical Procedure). Ferrocene (75 mmol) was dissolved in 70 mL of THF and degassed by three freeze−pump−thaw cycles. After cooling to 0 °C, *tert*-BuLi (60 mmol of a 1.7 M solution in pentane) was added dropwise via syringe, and the reaction was kept stirring for 15 min. A degassed solution of the respective phosphinite borane **2** (30 mmol) in 60 mL of THF was cooled to −40 °C, and the monolithioferrocene suspension was slowly added via Teflon cannula. The reaction mixture was allowed to warm to ambient temperature over a period of 12 h and then quenched with H_2O. THF was evaporated, and the residue was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over $MgSO_4$, and filtrated, and the solvent was evaporated. For deboronation, the residue was dissolved in 50 mL of degassed diethylamine and stirred overnight at room temperature. After removal of solvent, the crude product was purified by column chromatography (SiO_2; hexane/CH_2Cl_2 = 4:1) to remove excess ferrocene and small quantities (<3%) of diphosphine byproduct. The desired ferrocenylmonophosphines were obtained as orange-yellow solids, which were recrystallized from CH_2Cl_2/hexane.

(*S*)-(+)-1-Naphthylphenylphosphinoferrocene, 3a. Yield: 66%. Mp: 172 °C. ^1H NMR (400.13 MHz): δ 3.88 (m, 1H); 4.08 (s, 5H); 4.29 (m, 1H); 4.37 (m, 1H); 4.42 (m, 1H); 7.19 (m, 1H); 7.27−7.50 (m, 8H); 7.77−7.82 (m, 2H); 8.42 (m, 1H) ppm. ^{13}C NMR (100.62 MHz): δ 69.16 (5CH, d, $J_{CP} = 0.9$ Hz); 70.55 (d, CH, $J_{CP} = 1.5$ Hz); 71.15 (d, CH, $J_{CP} = 6.1$ Hz); 72.26 (d, CH, $J_{CP} = 3.1$ Hz); 74.08 (d, CH, $J_{CP} = 26.0$ Hz); 75.64 (d, C, $J_{CP} = 4.6$ Hz); 125.28 (d, CH, $J_{CP} = 1.4$ Hz); 125.75 (d, CH, $J_{CP} = 1.4$ Hz); 125.96 (d, CH, $J_{CP} = 2.3$ Hz); 126.05 (d, CH, $J_{CP} = 26.0$ Hz); 128.15 (d, CH, $J_{CP} = 7.6$ Hz); 128.51 (d, CH, $J_{CP} = 1.5$ Hz); 128.74 (CH); 129.06 (CH); 131.53 (d, CH, $J_{CP} = 1.4$ Hz); 133.35 (d, C, $J_{CP} = 3.8$ Hz); 133.93 (d, CH, $J_{CP} = 19.9$ Hz); 134.78 (d, C, $J_{CP} = 20.6$ Hz); 136.91 (d, C, $J_{CP} = 14.5$ Hz); 137.42 (d, C, $J_{CP} = 7.6$ Hz) ppm. ^{31}P NMR (161.98 MHz): δ −24.66 (s) ppm. $[\alpha]_D^{20} = +127.8$ (*c* 0.51; CH_2Cl_2). HRMS (EI$^+$): *m/z* calcd 420.0730; obsd 420.0728. Anal. Calcd for $C_{26}H_{21}FeP$: C, 74.31; H, 5.04. Found: C, 74.14; H, 5.20.

(*S*)-(+)-2-Biphenylylphenylphosphinoferrocene, 3b. Yield: 66%. Mp: 102−104 °C. ^1H NMR (400.13 MHz): δ 3.80 (m, 1H); 3.94 (s, 5H); 4.27 (m, 1H), 4.31 (m, 1H); 4.37 (m, 1H); 7.05−7.08 (m, 2H); 7.11−7.15 (m, 2H); 7.16−7.33 (m, 10H) ppm. ^{13}C NMR (100.62 MHz): δ 68.99 (5CH); 70.49 (CH); 71.01 (d, CH, $J_{CP} = 6.9$ Hz); 71.83 (CH); 74.71 (d, CH, $J_{CP} = 30.6$ Hz); 76.50 (d, C, $J_{CP} = 7.6$ Hz); 126.84 (CH); 127.51 (2CH); 127.76 (d, CH, $J_{CP} = 7.6$ Hz); 128.02 (CH); 128.43 (d, CH, $J_{CP} = 0.9$ Hz); 129.60 (d, CH, $J_{CP} = 3.8$ Hz); 129.76 (d, CH, $J_{CP} = 3.8$ Hz); 132.75 (CH); 134.27 (d, CH, $J_{CP} = 20.6$ Hz); 138.20 (d, C, $J_{CP} = 8.4$ Hz); 138.93 (d, C, $J_{CP} = 14.5$ Hz); 141.73 (d, C, $J_{CP} = 5.4$ Hz); 146.72 (d, C, $J_{CP} = 24.5$ Hz) ppm. ^{31}P NMR (161.98 MHz): δ −21.36 (s) ppm. $[\alpha]_D^{20} = +71.7$ (*c* 0.45; CH_2Cl_2). HRMS (EI$^+$): *m/z* calcd 446.0887; obsd 446.0875. Anal. Calcd for $C_{28}H_{23}FeP$: C, 75.35; H, 5.19. Found: C, 75.36; H, 5.47.

Synthesis of Ferrocenylphosphine Oxides 4 (Typical Procedure). The respective phosphinoferrocene **3** (20 mmol) was suspended in 200 mL of acetone and cooled on an ice bath. H_2O_2 (8.3 mL of a 30% solution in H_2O) was added dropwise, and the reaction mixture was stirred for 30 min while warming to room temperature. Then it was quenched with saturated $Na_2S_2O_3$ solution, followed by extraction with CH_2Cl_2. The combined organic phases were washed with H_2O, dried over $MgSO_4$, and filtrated, and the solvent was removed in vacuo. The crude product was purified by filtration over a short column of alumina, using 4:1 ethyl acetate/hexane as eluent.

(*R*)-(+)-1-Naphthylphenylphosphinoxyferrocene, 4a. Yield: 98%. Mp: 152 °C. ^1H NMR (400.13 MHz): δ 4.08 (m, 1H); 4.22 (s, 5H); 4.44 (m, 1H); 4.54 (m, 1H); 4.69 (m, 1H); 7.34−7.50 (m, 6H); 7.55 (ddd, 1H, $J = 1.0, 7.0, 16.0$ Hz); 7.71−7.76 (m, 2H); 7.81 (d, 1H, $J = 8.0$ Hz); 7.93 (d, 1H, $J = 8.0$ Hz); 8.55 (d, 1H, $J = 8.6$ Hz) ppm. ^{13}C NMR (100.62 MHz): δ 69.75 (5CH); 71.31 (d, CH, $J_{CP} = 10.7$ Hz); 71.92 (d, CH, $J_{CP} = 10.7$ Hz); 72.28 (d, CH, $J_{CP} = 11.5$ Hz); 72.83 (d, CH, $J_{CP} = 13.8$ Hz); 73.60 (d, C, $J_{CP} = 120.1$ Hz); 124.08 (d, CH, $J_{CP} = 14.5$ Hz); 126.17 (CH); 126.90 (CH); 127.40 (d, CH, $J_{CP} = 5.4$ Hz); 128.21 (d, CH, $J_{CP} = 12.2$ Hz); 128.56 (d, CH, $J_{CP} = 1.4$ Hz); 130.86 (d, C, $J_{CP} = 103.9$ Hz); 131.06 (d, CH, $J_{CP} = 10.7$ Hz); 131.40 (d, CH, $J_{CP} = 2.3$ Hz); 132.72 (d, CH, $J_{CP} = 4.0$

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Hz); 133.18 (C), 133.24 (d, CH, J_{CP} = 10.7 Hz); 133.75 (d, C, J_{CP} = 9.2 Hz); 134.49 (d, C, J_{CP} = 104.8 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 32.29 (s) ppm. $[\alpha]_D^{20}$ = +110.3 (*c* 0.23; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd 436.0679; obsd 436.0681. Anal. Calcd for $C_{26}H_{21}FeOP$: C, 71.58; H, 4.85. Found: C, 71.28; H, 5.16.

(*R*)-(+)-2-Biphenylylphenylphosphinoxyferrocene, 4b. Yield: 98%. Mp: 169−170 °C. ^{1}H NMR (400.13 MHz): δ 3.92 (m, 1H); 3.97 (s, 5H); 4.35 (m, 1H); 4.49 (m, 1H); 4.79 (m, 1H); 7.01−7.12 (m, 5H); 7.16−7.27 (m, 4H); 7.31−7.45 (m, 5H) ppm. ^{13}C NMR (100.62 MHz): δ 69.53 (5CH); 71.37 (d, CH, J_{CP} = 9.9 Hz); 71.52 (d, CH, J_{CP} = 1.5 Hz); 71.64 (d, CH, J_{CP} = 1.5 Hz); 72.86 (d, CH, J_{CP} = 9.9 Hz); 73.24 (d, C, J_{CP} = 119.3 Hz); 126.18 (d, CH, J_{CP} = 12.2 Hz); 126.83 (CH); 126.92 (CH); 127.51 (d, CH, J_{CP} = 12.2 Hz); 130.13 (CH); 130.43 (d, CH, J_{CP} = 9.9 Hz); 130.56 (d, CH, J_{CP} = 2.3 Hz); 131.08 (d, CH, J_{CP} = 3.0 Hz); 131.41 (d, CH, J_{CP} = 9.9 Hz); 133.34 (d, CH, J_{CP} = 12.2 Hz); 133.65 (d, C, J_{CP} = 14.5 Hz); 134.70 (d, C, J_{CP} = 10.7 Hz); 140.40 (d, C, J_{CP} = 4.6 Hz); 146.95 (d, C, J_{CP} = 9.2 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 30.52 (s) ppm. $[\alpha]_D^{20}$ = +106.4 (*c* 0.64; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd 462.0836; obsd 462.0832. Anal. Calcd for $C_{28}H_{23}FeOP$: C, 72.75; H, 5.01. Found: C, 72.87; H, 5.11.

Synthesis of *ortho*-Iodoferrocenylphosphine Oxides 5 (Typical Procedure). Phosphine oxide **4a** or **4b** (15 mmol) was dissolved in 180 mL of THF, degassed, and cooled to 0 °C. Diisopropylamidomagnesium bromide (60 mmol) was added slowly via syringe, and the reaction mixture was allowed to reach room temperature. After 3 h, the solution was cooled to −30 °C, and a degassed iodine solution (45 mmol of I_2 in 60 mL of THF) was added via a cannula. After warming to ambient temperature overnight, the reaction mixture was quenched with H_2O and THF was evaporated. The residue was extracted with CH_2Cl_2, and the combined organic layers were washed with saturated sodium bisulfite solution and water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (SiO_2; 5:1CH_2Cl_2/ethyl acetate), upon which the predominantly formed diastereomers of **5a** and **5b**, respectively, were eluted first, followed by a second diastereomer and starting material.

(R_P,S_m)-(+)-1-Iodo-2-(1-naphthylphenylphosphinoxy)-ferrocene, 5a (Main Product). Yield: 62%. Mp: 196−197 °C. ^{1}H NMR (400.13 MHz): δ 3.77 (m, 1H); 4.37 (m, 1H); 4.41 (s, 5H); 4.83 (m, 1H); 7.36−7.52 (m, 7H); 7.70−7.77 (m, 2H); 7.83 (d, br, 1H, *J* = 8.0 Hz); 7.96 (d, br, 1H, *J* = 7.5 Hz); 8.66 (d, br, 1H, *J* = 8.0 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 41.79 (d, C, J_{CP} = 10.1 Hz); 71.76 (d, CH, J_{CP} = 9.9 Hz); 72.82 (5CH); 74.60 (d, CH, J_{CP} = 15.3 Hz); 75.92 (d, C, J_{CP} = 120.0 Hz); 80.00 (d, CH, J_{CP} = 8.4 Hz); 124.07 (d, CH, J_{CP} = 13.8 Hz); 126.25 (CH); 127.10 (CH); 127.65 (d, CH, J_{CP} = 5.4 Hz); 128.15 (d, CH, J_{CP} = 11.5 Hz); 128.52 (d, CH, J_{CP} = 1.6 Hz); 129.19 (d, C, J_{CP} = 105.7 Hz); 131.46 (d, CH, J_{CP} = 9.9 Hz); 131.57 (d, CH, J_{CP} = 3.1 Hz); 132.84 (d, CH, J_{CP} = 3.1 Hz); 133.35 (d, CH, J_{CP} = 10.7 Hz); 133.55 (d, C, J_{CP} = 8.4 Hz); 133.72 (d, C, J_{CP} = 105.5 Hz); 133.91 (d, C, J_{CP} = 9.2 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 32.07 (s) ppm. $[\alpha]_D^{20}$ = +49.6 (*c* 0.52; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd 561.9646; obsd 561.9652. Anal. Calcd for $C_{26}H_{20}FeIOP$: C, 55.55; H, 3.59. Found: C, 55.28; H, 3.52.

(R_P,S_m)-(+)-1-Iodo-2-(2-biphenylylphenylphosphinoxy)-ferrocene, 5b. Yield: 86%. Mp: 160 °C (dec). ^{1}H NMR (400.13 MHz): δ 3.75 (m, 1H); 4.15 (s, 5H); 4.29 (m, 1H); 4.78 (m, 1H); 6.98−7.11 (m, 5H); 7.18−7.26 (m, 3H); 7.29−7.36 (m, 4H); 7.42−7.52 (m, 2H) ppm. ^{13}C NMR (100.62 MHz): δ 42.36 (d, C, J_{CP} = 9.9 Hz); 72.05 (d, CH, J_{CP} = 9.9 Hz); 72.66 (5CH); 73.57 (d, CH, J_{CP} = 14.5 Hz); 74.72 (d, C, J_{CP} = 118.6 Hz); 79.89 (d, CH, J_{CP} = 9.2 Hz); 126.37 (d, CH, J_{CP} = 12.2 Hz); 126.80 (CH); 126.84 (CH); 127.48 (d, CH, J_{CP} = 12.2 Hz); 130.32 (CH); 130.78 (d, CH, J_{CP} = 2.3 Hz); 131.01 (d, CH, J_{CP} = 9.9 Hz); 131.23 (d, CH, J_{CP} = 2.3 Hz); 131.64 (d, CH, J_{CP} = 9.9 Hz), 132.87 (d, C, J_{CP} = 105.5 Hz); 133.58 (d, C, J_{CP} = 107.9 Hz); 133.77 (d, CH, J_{CP} = 11.5 Hz); 140.23 (d, C, J_{CP} = 3.8 Hz); 147.18 (d, C, J_{CP} = 9.2 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 29.41 (s) ppm. $[\alpha]_D^{20}$ = +33.8 (*c* 0.32; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd 587.9802; obsd 587.9814. Anal. Calcd for $C_{28}H_{22}FeIOP$: C, 57.18; H, 3.77. Found: C, 57.17; H, 3.93.

Synthesis of Bis(diarylphosphinoxy)biferrocenyls 6 (Typical Procedure). In a Schlenk tube, *ortho*-iodophosphine oxide **5** (2 mmol) was dissolved in CH_2Cl_2, and copper powder (10 mmol, activated with HCl/I_2[36] was added under stirring. The solvent was evaporated and the residue was heated to 135 °C for 48 h. After this treatment, the caked product was agitated with CH_2Cl_2, filtrated, and concentrated. Column chromatography (SiO_2; 4:1 CH_2Cl_2/ethyl acetate for **6a**; 5:3:2 CH_2Cl_2/hexane/ethyl acetate for **6b**) eluted unreacted starting material or meso-configurated (by)product first, followed by the desired diphosphine dioxides **6a** or **6b**.

(R_P,R_m,R_m,R_P)-(−)-2,2′-Bis(1-naphthylphenylphosphinoxy)-1,1′-biferrocenyl, 6a. Yield: 58%. Mp: 230 °C (dec). ^{1}H NMR (400.13 MHz): δ 3.85 (m, 2H), 4.19 (s, 10H); 4.53 (m, 2H); 5.37 (m, 2H); 5.83 (dt, 2H, *J* = 2.5, 7.8 Hz); 6.85 (dd, 2H, *J* = 7.0, 16.1 Hz); 7.18−7.26 (m, 4H); 7.31−7.41 (m, 8H); 7.56−7.63 (m, 6H); 8.42 (d, 2H, *J* = 8.6 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 70.47 (5CH); 70.51 (d, CH, J_{CP} = 11.1 Hz); 72.75 (d, C, J_{CP} = 119.3 Hz); 72.77 (d, CH, J_{CP} = 13.8 Hz); 81.11 (d, CH, J_{CP} = 9.2 Hz); 88.17 (d, C, J_{CP} = 9.2 Hz); 123.74 (d, CH, J_{CP} = 14.5 Hz); 125.70 (CH); 126.43 (CH); 127.56 (d, CH, J_{CP} = 6.1 Hz); 127.94 (d, CH, J_{CP} = 11.5 Hz); 128.00 (d, CH, J_{CP} = 1.3 Hz); 130.03 (d, C, J_{CP} = 104.8 Hz); 130.94 (d, CH, J_{CP} = 11.8 Hz); 130.96 (d, CH, J_{CP} = 3.8 Hz); 131.70 (d, CH, J_{CP} = 2.3 Hz); 132.75 (d, C, J_{CP} = 8.4 Hz); 133.20 (d, C, J_{CP} = 9.2 Hz); 133.86 (d, CH, J_{CP} = 11.5 Hz); 136.01 (d, C, J_{CP} = 104.0 Hz) ppm. ^{31}P NMR (161.98 MHz): δ 32.64 (s) ppm. $[\alpha]_D^{20}$ = −295.4 (*c* 0.54; CH_2Cl_2). MS (FD): *m*/*z* obsd 870.3 (M^+). Anal. Calcd for $C_{52}H_{40}Fe_2O_2P_2$: C, 71.75; H, 4.63. Found: C, 71.97; H, 4.99.

(R_P,R_m,R_m,R_P)-(−)-2,2′-Bis(2-biphenylylphenylphosphinoxy)-1,1′-biferrocenyl, 6b. Yield: 70%. Mp: 175−177 °C (dec). ^{1}H NMR (400.13 MHz): δ 3.92 (m, 2H); 3.96 (s, 10H); 4.53 (m, 2H); 5.18 (m, 2H); 6.51 (m, 2H); 6.93 (m, 4H); 6.98−7.02 (m, 6H); 7.10−7.19 (m, 8H); 7.24−7.31 (m, 8H) ppm. ^{13}C NMR (100.62 MHz): δ 70.13 (5CH); 70.62 (d, CH, J_{CP} = 10.7 Hz); 71.81 (d, CH, J_{CP} = 13.8 Hz); 73.98 (d, C, J_{CP} = 119.3 Hz); 80.82 (d, CH, J_{CP} = 9.2 Hz); 89.12 (d, C, J_{CP} = 9.2 Hz); 125.72 (d, CH, J_{CP} = 12.2 Hz); 126.53 (CH); 126.91 (CH); 127.28 (d, CH, J_{CP} = 11.7 Hz);130.27 (d, CH, J_{CP} = 11.5 Hz); 130.28 (d, CH, J_{CP} = 8.4 Hz); 130.33 (CH); 130.56 (d, CH, J_{CP} = 2.8 Hz); 130.58 (d, CH, J_{CP} = 9.2 Hz); 133.55 (d, C, J_{CP} = 103.3 Hz); 135.53 (d, C, J_{CP} = 105.6 Hz); 136.02 (d, CH, J_{CP} = 12.2 Hz); 140.71 (d, C, J_{CP} = 4.6 Hz); 146.38 (d, C, J_{CP} = 9.2 Hz) ppm. ^{31}P NMR (161.98 MHz): δ 31.88 (s) ppm. $[\alpha]_D^{20}$ = −134.6 (*c* 0.69; CH_2Cl_2). HRMS (FAB^+): *m*/*z* calcd for $C_{56}H_{45}Fe_2O_2P_2$ (MH^+): 923.1594; obsd 923.1573. Anal. Calcd for $C_{56}H_{44}Fe_2O_2P_2$: C, 72.90; H, 4.81. Found: C, 72.51; H, 4.99.

Synthesis of Bis(diarylphosphino)biferrocenyls 1 (Typical Procedure). In a glass tube, diphosphine dioxide **6a** or **6b** (0.6 mmol) was suspended in 9 mL of toluene. Trichlorosilane (30 mmol) and triethylamine (45 mmol) were added consecutively, and the tube was sealed under vacuum. Then it was placed into an autoclave and heated at 140 °C for 72 h. After cooling in liquid nitrogen, the tube was opened and the reaction mixture was treated with 15 N NaOH solution. The crude product was extracted with CH_2Cl_2; the combined organic layers were washed with H_2O, dried, and filtered, and the solvent was evaporated. The residue was dissolved in 15 mL of THF, and BH_3·THF (1 mL, 1M in THF) was added via syringe. Complexation was followed by TLC, and after completion, THF was removed in vacuo. The residual diphosphine diborane was chromatographed over SiO_2, using 1:1 CH_2Cl_2/

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Table 2. Details of Crystal Structure Determinations for Compounds 6b, *meso*-6b, and 6a

	6b	***meso*-6b**	**6a**
formula	$C_{56}H_{44}Fe_2O_2P_2 \cdot 2CH_2Cl_2$[a]	$C_{56}H_{44}Fe_2O_2P_2$	$C_{52}H_{40}Fe_2O_2P_2$
fw	1092.40	922.55	870.48
diffractometer	Bruker SMART	Bruker SMART	Bruker SMART
wavelength (Å)	0.71073	0.71073	0.71073
temperature (K)	213(2)	296(2)	299(2)
cryst syst	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a (Å)	9.620(4)	8.289(4)	14.861(3)
b (Å)	12.430(5)	9.607(5)	16.076(4)
c (Å)	43.31(2)	14.485(7)	17.451(5)
α (deg)	90	108.55(1)	90
β (deg)	90	90.84(1)	90.170(10)
γ (deg)	90	96.99(1)	90
V (Å^3)	5179(4)	1083.7(9)	4169.1(18)
Z	4	1	4
density (g cm^{-3})	1.401	1.414	1.387
μ (mm^{-1})	0.871	0.788	0.814
crystal size (mm^3)	0.70 × 0.65 × 0.45	0.22 × 0.10 × 0.07	0.70 × 0.14 × 0.14
abs corr	SADABS	XABS2	SADABS
transmission	0.63−0.75	0.78−1.37	0.75−0.96
extinction coeff	0.00047(9)		0.00025(8)
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.64	0.59	0.59
R1 ($I > 2\sigma(I)$)	0.0414	0.0499	0.0312
wR2 ($I > 2\sigma(I)$)	0.0846	0.0906	0.0684
R1 (all data)	0.0434	0.0889	0.0468
wR2 (all data)	0.0854	0.1077	0.0771
GooF	1.185	1.092	1.058
Flack x	0.019(12)		

[a] Structure **6b** contains partly disordered CH_2Cl_2 molecules. Solvent content idealized in chemical formula, formula weight, density, and absorption coefficient.

Table 3. Details of Crystal Structure Determinations for Compounds 1a, 8c, and 8a

	1a	**8c**	**8a**
formula	$C_{52}H_{40}Fe_2P_2 \cdot 2CH_2Cl_2$ [a]	$C_{42}H_{32}Cl_2FeP_2Pt \cdot CH_2Cl_2$	$C_{52}H_{40}Cl_2Fe_2P_2Pt$[b]
fw	1004.30	1005.38	1104.47[b]
diffractometer	Bruker SMART	Enraf-Nonius CAD4T	Nonius KappaCCD
wavelength (Å)	0.71073	0.71073	0.71073
temperature (K)	213(2)	150(2)	150(2)
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	*Pbcn*	$P2_12_12_1$	$P2_12_12_1$
a (Å)	16.392(8)	11.6781(12)	11.8381(3)
b (Å)	17.161(8)	17.166(2)	19.7931(5)
c (Å)	16.522(8)	18.737(2)	20.8439(5)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V (Å^3)	4648(4)	3756.1(7)	4884.0(2)
Z	4	4	4
density (g cm^{-3})	1.435	1.778	1.502[a]
μ (mm^{-1})	0.960	4.509	3.651[a]
cryst size (mm^3)	0.30 × 0.20 × 0.20	0.41 × 0.20 × 0.18	0.45 × 0.45 × 0.10
abs corr	SADABS	DELABS	MULABS
transmission	0.69−0.86	0.47−0.83	0.53−0.70
extinction coeff	0.00049(8)		
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.64	0.65	0.65
R1 ($I > 2\sigma(I)$)	0.0363	0.0320	0.0413
wR2 ($I > 2\sigma(I)$)	0.0813	0.0598	0.1031
R1 (all data)	0.0429	0.0406	0.0476
wR2 (all data)	0.0847	0.0623	0.1063
GooF	1.121	1.026	1.041
Flack x		−0.017(5)	−0.020(5)

[a] Structure **1a** contains partly disordered CH_2Cl_2 molecules. Solvent content idealized in chemical formula, formula weight, density, and absorption coefficient. [b] Structure **8a** contains disordered CH_2Cl_2 molecules. Their contribution to the calculated structure factors was calculated with the routine CALC SQUEEZE of the program PLATON (339 electrons/unit cell).[39] The solvent is not included in formula weight, density, and absorption coefficient.

hexane as eluent. The desired C_2-symmetrical product was eluted first, followed by unseparated isomerized byproducts.

(S_P,R_m,R_m,S_P)-(−)-2,2′-Bis(1-naphthylphenylphosphino)-1,1′-biferrocenyl, 1a. Deprotection was performed by stirring the diborane complex of **1a** in degassed Et_2NH (15 mL) at room temperature. After 5 h, TLC showed complete conversion. The reaction mixture was concentrated, and the crude diphosphine was chromatographed (SiO_2, 1:1 CH_2Cl_2/hexane), to afford the enantiopure ligand as orange crystals. Yield: 40%. Mp: 236−238 °C (dec). ^{1}H NMR (400.13 MHz; CD_2Cl_2): δ 3.90 (m, 2H); 4.12 (s, 10H); 4.52 (dt, 2H, J = 0.6, 2.6 Hz); 5.01 (m, 2H); 5.88 (m, 2H); 6.41 (m, 2H); 7.10 (d, br, 2H, J = 8.2 Hz); 7.22−7.36 (m, 10H); 7.43−7.48 (m, 4H); 7.65 (dd, br, 2H, J = 0.6, 8.0 Hz); 8.03 (ddd, br, 2H, J = 1.0, 3.5, 8.6 Hz) ppm. ^{13}C NMR

(100.62 MHz; CD_2Cl_2): δ 70.10 (CH); 70.14 (5CH); 72.22 (d, CH, J_{CP} = 4.6 Hz); 77.00 (d, CH, J_{CP} = 11.5 Hz); 77.93 (d, C, J_{CP} = 9.2 Hz); 91.05 (dd, C, J_{CP} = 2.2, 29.1 Hz); 124.66 (CH); 125.02 (CH); 125.10 (d, CH, J_{CP} = 2.3 Hz); 126.15 (d, CH, J_{CP} = 24.5 Hz); 127.94 (CH); 127.98 (d, CH, J_{CP} = 7.9 Hz); 128.17 (d, CH, J_{CP} = 1.4 Hz); 128.84 (CH); 130.87 (CH); 133.03 (d, C, J_{CP} = 3.8 Hz); 133.61 (d, C, J_{CP} = 19.9 Hz); 134.69 (d, CH, J_{CP} = 21.4 Hz); 135.79 (d, C, J_{CP} = 13.8 Hz); 138.13 (d, C, J_{CP} = 7.7 Hz) ppm. ^{31}P NMR (161.98 MHz; CD_2Cl_2): δ −30.60 (s) ppm. $[\alpha]_D^{20} = -175.7$ (*c* 0.44; CH_2Cl_2). MS (FD): *m/z* obsd 838.5 (M^+). Anal. Calcd. for $C_{52}H_{40}Fe_2P_2$: C, 74.48; H, 4.81. Found: C, 74.20; H, 4.92.

(S_P,R_m,R_m,S_P)-(+)-2,2′-Bis(2-biphenylylphenylphosphino)-1,1′-biferrocenyl, 1b. Since in the case of **1b**·$(BH_3)_2$ the decomplexation procedure with Et_2NH resulted in up to 15% epimerization of chiral phosphorus, an acidic deprotection method was employed, which proved to proceed without any observable degree of isomerization. A solution of the diborane complex (1 mmol) in 8 mL of toluene was degassed and cooled in an ice bath, and trifluoromethanesulfonic acid (5 mmol) was added slowly via syringe. After 30 min, stirring was continued at room temperature until TLC indicated complete protonation. The solvent was removed, and the residue was treated with a solution of 10 mmol of KOH in 3 mL of degassed 10:1 EtOH/H_2O. The suspension was stirred for 30 min at ambient temperature, after which degassed Et_2O (7 mL) was added. The upper layer was transferred in a second Schlenk tube by Teflon cannula, and this extraction was repeated twice. The combined ether layers were dried over Na_2SO_4, concentrated, and subjected to column chromatography (alumina; 1:1 CH_2Cl_2/hexane). Evaporation of the eluent left enantiopure ligand **1b** as yellow powder. Yield: 44%. Mp: 150−151 °C. ^{1}H NMR (400.13 MHz): δ 3.90 (m, 2H); 3.99 (s, 10H); 4.37 (m, 2H); 4.58 (m, 2H); 6.75 (m, 2H); 6.83 (m, 2H); 7.00−7.04 (m, 8H); 7.16−7.29 (m, 16H) ppm. ^{13}C NMR (100.62 MHz): δ 69.28 (CH); 70.57 (d, 5CH, J_{CP} = 1.5 Hz); 71.96 (d, CH, J_{CP} = 4.6 Hz); 76.71 (dd, CH, J_{CP} = 4.6, 8.4 Hz); 77.28 (d, C, J_{CP} = 15.0 Hz); 91.10 (dd, C, J_{CP} = 2.0, 28.5 Hz); 126.56 (d, CH, J_{CP} = 3.1 Hz); 127.33 (CH); 127.38 (d, CH, J_{CP} = 10.7 Hz); 127.46 (CH); 127.49 (d, CH, J_{CP} = 8.4 Hz); 128.29 (CH); 129.19 (d, CH, J_{CP} = 3.8 Hz); 129.54 (d, CH, J_{CP} = 3.8 Hz); 132.52 (CH); 134.95 (d, CH, J_{CP} = 22.2 Hz); 138.77 (d, C, J_{CP} = 10.7 Hz); 138.80 (d, C, J_{CP} = 17.6 Hz); 142.08 (d, C, J_{CP} = 4.6 Hz); 145.77 (d, C, J_{CP} = 23.7 Hz) ppm. ^{31}P NMR (161.98 MHz): δ −28.36 (s) ppm. $[\alpha]_D^{20}$ = +6.3 (*c* 0.25; CH_2Cl_2). HRMS (FAB^+): *m/z* calcd for $C_{56}H_{45}Fe_2P_2$ (MH^+): 891.1695; obsd 891.1686. Anal. Calcd for $C_{56}H_{44}Fe_2P_2$: C, 75.52; H, 4.98. Found: C, 75.37; H, 5.36.

Synthesis of Platinum Complexes 8 (Typical Procedure). Bis(benzonitrile)dichloroplatinum(II) (0.1 mmol) was dissolved in 15 mL of degassed benzene and heated to 70 °C. A solution of diphosphine **1** (0.11 mmol) in 10 mL of benzene was slowly added via a Teflon cannula, and the resulting mixture was kept at reflux temperature for 1 h. Upon cooling and, eventually, concentrating, a red precipitate formed, which was filtrated, washed with hexane, and dried under vacuum. Recrystallization from CH_2Cl_2/hexane gave crystals suitable for crystal structure determination.

[(S_P,R_m,R_m,S_P)-2,2′-Bis(1-naphthylphenylphosphino)-1,1′-biferrocenyl]dichloroplatinum(II), 8a. Yield: 63%. ^{1}H NMR (400.13 MHz; CD_2Cl_2): δ 3.31 (m, 2H); 4.02 (s, 10H); 4.15 (m, 2H); 4.99 (m, 2H); 7.18−8.00 (m, 18H); 8.70 (dd, 4H, *J* = 0.9; 2.0 Hz); 8.84 (d, 2H, *J* = 2.2 Hz) ppm. ^{31}P NMR (161.98 MHz; CD_2Cl_2): δ −6.21 (t, J_{PPt} = 1758 Hz) ppm. Anal. Calcd for $C_{52}H_{40}Cl_2Fe_2P_2Pt$: C, 56.55; H, 3.65. Found: C, 56.34; H, 3.82.

[(S_P,S_P)-(1,1′)-Bis(1-naphthylphenylphosphino)ferrocene]dichloroplatinum(II), 8c. Yield: 72%. ^{1}H NMR (400.13 MHz; CD_2Cl_2): δ 4.19 (m, 4H, fc); 4.32 (m, 2H, fc); 4.53 (m, 2H, fc); 7.28 (ddd, 2H, *J* = 1.2; 6.8; 8.3 Hz, naphthyl-H7); 7.37−7.43 (m, 4H, phenyl-H3,5); 7.47−7.58 (m, 6H, phenyl-H4, naphthyl-H3, naphthyl-H6); 7.90 (m, 4H, phenyl-H2,6); 7.96 (d, 2H, *J* = 8.3 Hz, naphthyl-H5); 8.09 (d, 2H, *J* = 8.2 Hz, naphthyl-H4); 8.41 (d, br, 2H, *J* = 8.4 Hz, naphthyl-H8); 8.61 (dd, br, 2H, *J* = 7.6; 16.7 Hz, naphthyl-H2) ppm. ^{31}P NMR (161.98 MHz; CD_2Cl_2): δ 13.49 (t, J_{PPt} = 1926 Hz) ppm. Anal. Calcd for $C_{42}H_{32}Cl_2FeP_2Pt$: C, 54.80; H, 3.50. Found: C, 54.44; H, 3.56.

Crystal Structure Determinations. Structures **6b**, *meso*-**6b**, **6a**, and **1a** were solved using direct methods (SHELXS-97).[37] Structures **8a** and **8c** were solved with Patterson methods (DIRDIF-97).[38] All structures were refined with SHELXL-97 against F^2 of all reflections. Further details of the structure determinations are included in Tables2 and 3.

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Supporting Information Available: NMR and MS data of the minor isomer of **5a** and *meso*-**6b**, crystal structure refinement data for compounds **6a**, **6b**, *meso*-**6b**, **1a**, **8a**, and **8c**, including atomic coordinates, isotropic and anisotropic displacement parameters, and a complete listing of bond angles and bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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