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Iron(II) Complexes Containing Chiral Unsymmetrical PNP′ Pincer Ligands: Synthesis and Application in Asymmetric Hydrogenations

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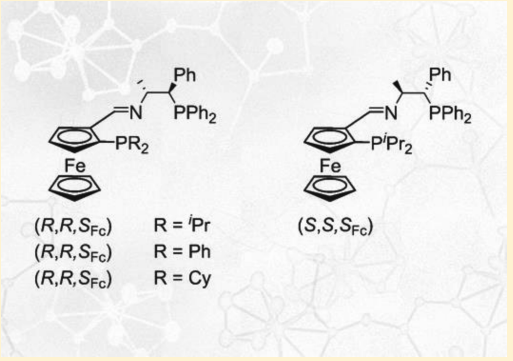
Supporting Information

ABSTRACT: Four new chiral PNP′ pincer ligands with a scaffold consisting of a planar chiral ferrocene and a centro chiral aliphatic unit were synthesized and characterized. Treatment of anhydrous $FeBr_2(THF)_2$ with 1 equiv of the unsymmetrical chiral PNP′ pincer ligands afforded complexes of the general formula [Fe(PNP′)Br_2]. In the solid state these complexes adopt a tetrahedral geometry with the PNP′ ligands coordinated in a κ^2P,N-fashion, as shown by X-ray crystallography. These complexes react with CO in the presence of $NaBH_4$ to yield hydride complexes of the type [Fe(PNP′)(H)(Br)(CO)], which were isolated and tested as catalysts in the asymmetric hydrogenation of ketones. Enantioselectivities of up to 81% ee were obtained.



INTRODUCTION

In recent years, hydrogenation catalysis for the synthesis of enantiopure alcohols and amines in the pharmaceutical, fragrance, and fine chemical industries based on nonplatinum group metals such as iron has attracted significant attention for economic reasons as well as the idea of developing green and environmentally friendly catalysts.[1−9] To date, efficient chiral iron catalysts for the preparation of enantioenriched alcohols and imines have been reported and developed by Gao,[10] Morris,[11] Beller,[12] Gade,[13] and Mezzetti[14] (Chart 1). Very recently, as part of our continuing search for novel iron asymmetric hydrogenation (AH) catalysts, we synthesized PNP diferrocene ligands (Chart 2).[15] These ligands coordinate to iron by forming two six-membered chelate rings (6.6.-ring ligands). It was found that this type of complex is inactive in AH catalysis. Therefore, we modified the system to give a new generation of chiral 6.5.-ring PNP′ ligands by replacing one planar chiral ferrocene by a centro chiral aliphatic unit (Chart 3). The Morris group found that iron complexes with 5.5.-ring PNP′ ligands were active in AH, while those with 6.5.-ring PNP′ ligands obtained by the condensation of *ortho*-diphenylphosphinobenzaldehyde and chiral diphenylphosphino-substituted amines were not.[11] It was also reported that the size of the chelate rings formed on coordination to iron and the flexibility of the PNP pincer ligands, as well as other parameters, have a significant influence on the reaction rate and conversion.[16] Although not privileged with respect to the size of chelate rings, we were curious to ascertain whether our new ferrocenyl-containing 6.5.-ring PNP′ ligands (Chart 2) could be transformed into active catalysts for the asymmetric reduction of ketones. Complexes of the type [Fe(PNP′)(H)-

Chart 1. Examples of Well-Defined Iron-Based Asymmetric Hydrogenation and Transfer Hydrogenation Precatalysts

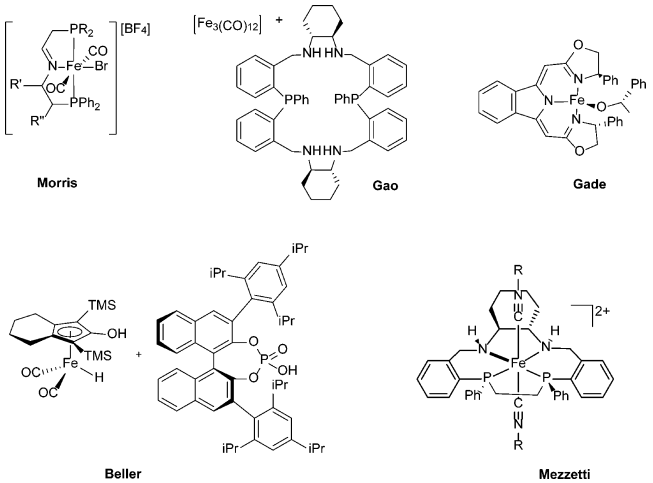


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Chart 2. Structures of Chiral Nonracemic PNP Diferrocene Ligands

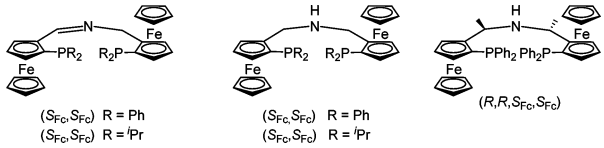
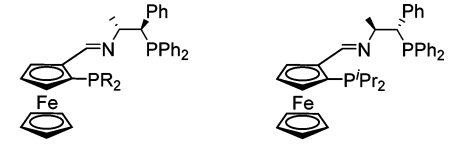


Chart 3. Structures of Chiral Nonracemic Tridentate Ligands with a Scaffold Consisting of a Planar Chiral Ferrocene and a Centro Chiral Aliphatic Unit



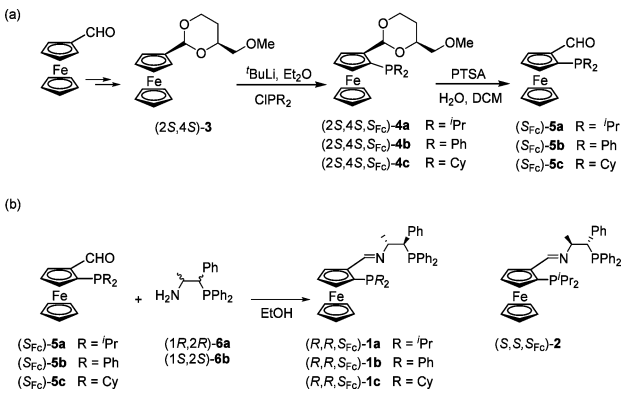
(Br)(CO)] were of particular interest given that achiral [Fe(PNP)(H)(Br)(CO)] complexes with a 5.5.-ring PNP pincer ligand are active hydrogenation catalysts for ketones,[17] aldehydes, and esters.[18]

The study reported here involved the synthesis of chiral PNP′ pincer ligands consisting of a planar chiral ferrocene and a centro chiral aliphatic unit that are connected through an imino nitrogen. It was found that the hydrogenation results were strongly dependent on the relative configuration of the ligands used. For example, when the hydrogenation of acetophenone was carried out with ligand (R,R,S_{Fc})-**1a**, the product 1-phenylethanol with *S* absolute configuration and 81% ee was obtained, while the use of ligand (S,S,S_{Fc})-**2** gave a racemic product. The (R,R,S_{Fc}) configuration clearly matches, while the (S,S,S_{Fc}) configuration is mismatched. Bearing the matching configuration in mind, it seemed interesting to investigate further the influence of substituents of the ferrocene phosphorus on the catalytic behavior. Therefore, (R,R,S_{Fc})-**1b** and (R,R,S_{Fc})-**1c**, which contain ferrocene-bound PPh_2 and PCy_2 units, respectively, were synthesized.

RESULTS AND DISCUSSION

Synthesis of Ligands (R,R,S_{Fc})-1 and (S,S,S_{Fc})-2. As outlined in Scheme 1, the enantiopure aldehyde (S_{Fc})-**5**, which

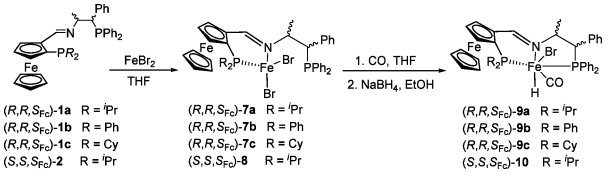
Scheme 1. Synthesis of Chiral Nonracemic Tridentate Ferrocene-Based Ligands



was prepared by applying Kagan's methodology,[19] was condensed with commercially available (1*R*,2*R*)-2-amino-1-phenylpropyldiphenylphosphine ((1*R*,2*R*)-**6a**) or (1*S*,2*S*)-2-amino-1-phenylpropyldiphenylphosphine (1*S*,2*S*)-**6b**) in ethanol to yield the desired ligands (R,R,S_{Fc})-**1** and (S,S,S_{Fc})-**2**, respectively.

Synthesis of Iron Complexes. Treatment of ligands (R,R,S_{Fc})-**1** and (S,S,S_{Fc})-**2** with 0.97 equiv of $FeBr_2(THF)_2$[20] in THF gave the coordinatively unsaturated complexes (R,R,S_{Fc})-**7** and (S,S,S_{Fc})-**8** in quantitative yield (Scheme 2).

Scheme 2. Preparation of the Monohydride Complexes



The molecular structures of (R,R,S_{Fc})-**7a** and (R,R,S_{Fc})-**7c** were determined by X-ray crystallography, and selected bond distances and angles are given in the captions (Figures 1 and

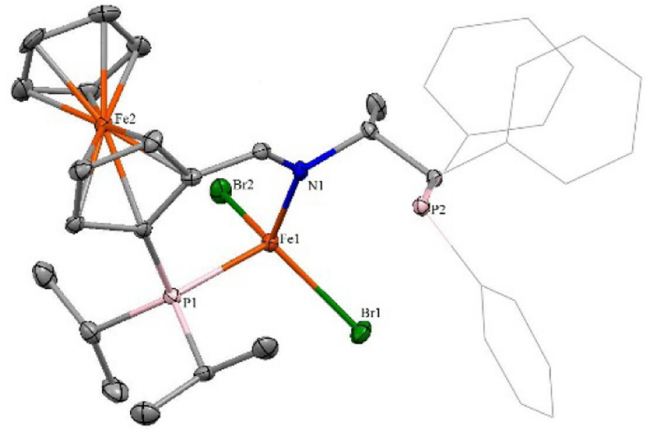


Figure 1. Structural view of (R,R,S_{Fc})-**7a** showing 50% thermal ellipsoids (H atoms and solvent molecules are omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Fe1−Br1 2.3967(6), Fe1−Br2 2.4055(5), Fe1−P1 2.400(1), Fe1−N1 2.125(3), P1−Fe1−Br1 109.56(3), P1−Fe1−N1 94.50(8), Br1−Fe1−N1 112.83(7), Br2−Fe1−P1 107.55(3), Br2−Fe1−N1 118.20(7).

2). Both structures display a distorted tetrahedral geometry around the Fe(II) center, with the PNP′ ligand coordinated in a κ^2P,N-fashion. The Fe−P bond length of around 2.4 Å is comparable with those in other high-spin tetrahedral iron(II) complexes in general[21] and $FeX_2(P-N)$ complexes in particular.[22] The solution magnetic moment of the dibromides (R,R,S_{Fc})-**7** and (S,S,S_{Fc})-**8** was measured and was in the range of 4.9−5.0 μ_B (Evans' method). The values are in good agreement with the effective magnetic moment of HS Fe(II) in the spin-only approximation (4.9 μ_B).

DFT calculations revealed that $[Fe(\kappa^2P,N\text{-PNP}')Br_2]$, (R,R,S_{Fc})-**7a** (denoted as **A**), in agreement with the experimental data, is thermodynamically more stable by 8.3 kcal/mol than the illusive isomer **B**, where the PNP′ ligand is coordinated in a κ^3P,N,P-fashion (Figure 3). Moreover, addition of CO to **B** to form $[Fe(PNP')(Br)_2(CO)]$ (denoted

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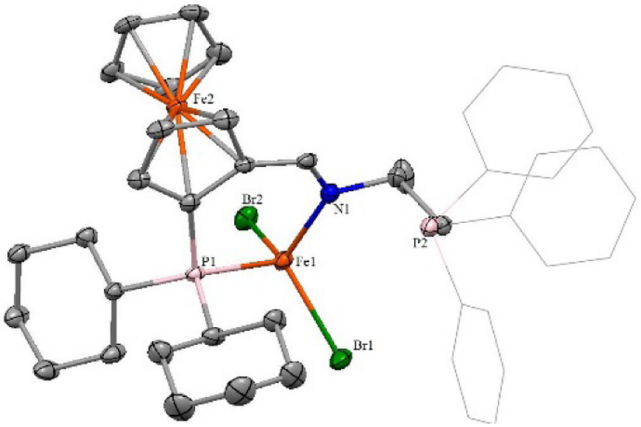


Figure 2. Structural view of (R,R,S_{Fc})-**7c** showing 50% thermal ellipsoids (H atoms and solvent molecules are omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Fe1−Br1 2.409(1), Fe1−Br2 2.405(1), Fe1−P1 2.398(1), Fe1−N1 2.127(4), P1−Fe1−Br1 189.05(4), P1−Fe1−N1 94.2(1), Br1−Fe1−N1 111.1(1), Br2−Fe1−P1 109.41(4), Br2−Fe1−N1 114.4(1).

as **C**) is thermodynamically highly unfavorable and was not observed experimentally.

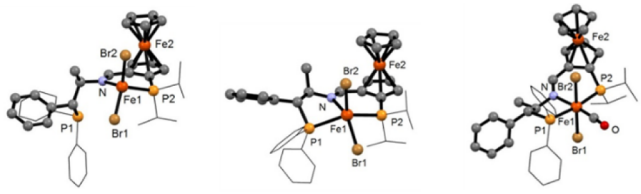


Figure 3. Free energies (enthalpies in parentheses, kcal/mol) of the molecular structures of optimized iron PNP′ complexes (R,R,S_{Fc})-**7a** (denoted as **A**) and **B** featuring κ^2P,N- and κ^3P,N,P-bound PNP′ ligands and complex *trans*-[Fe(PNP′)(CO)Br_2] (**C**) upon addition of CO to **B**.

In order to obtain iron hydride complexes as potential catalysts for the asymmetric hydrogenation of ketones and imines, [Fe(PNP′)$(Br)_2$] ((R,R,S_{Fc})-**7a−c** and (S_{Fc},S,S)-**8**) complexes were exposed to CO (ca. 1 bar) and were subsequently treated with various hydride reagents such as Na[$HBEt_3$], $NaBH_4$, and $LiAlH_4$. However, in all cases except for $NaBH_4$ decomposition was observed and the main product was the reduced free ligand. The synthesis of the complexes [Fe(PNP′)(H)(Br)(CO)] ((R,R,S_{Fc})-**9** and (S,S,S_{Fc})-**10**) was accomplished using $NaBH_4$ to give 58−71% isolated yields. This reaction may proceed via the intermediacy of carbonyl complexes, which are presumably cationic bis-carbonyl complexes [Fe(PNP′)(Br)$(CO)_2$]$^+$ that, in principle, can be isolated. However, it was observed that the CO ligands are labile and the compounds slowly lose CO. This behavior was also observed in the case of Taddol-based Fe(II) PNP pincer complexes[23] and PNP biferrocene complexes.[15] Therefore, these compounds were directly used without prior isolation. All of the hydride complexes are air-sensitive both in the solid state and in solution. The ^{1}H NMR spectrum of (R,R,S_{Fc})-**9a** confirmed the presence of two hydride species in a ca. 4:1 ratio, the proton signals of which appeared at −17.7 ppm as a well-resolved triplet with a $^2J_{HP}$ coupling constant of 45 Hz and at −20.4 ppm as a dd with $^2J_{HP}$ coupling constants of 50 and 60 Hz. The observed chemical shift indicates that the hydride ligand is positioned *trans* to the bromide.[24] The structures of the two possible isomers (**D** and **E**) were calculated and are depicted in Figure 4. It was found that one is more stable by 5

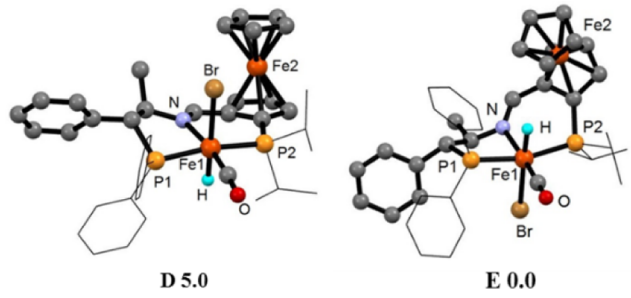


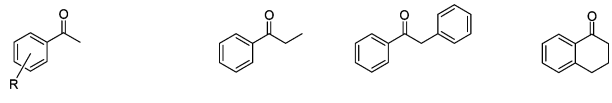
Figure 4. Free energies (kcal/mol) for the optimized structures of the two (R,R,S_{Fc}) stereoisomers of [Fe(PNP′)(CO)(H)Br] (**D** and **E**) (PNP′ = (R,R,S_{Fc})-**1a**) with the hydride *trans* to the bromide ligand.

kcal/mol, which is consistent with the experimental findings. These isomers could not be separated, and all attempts to crystallize them failed. In the $^{13}C\{^1H\}$ NMR spectrum the most noticeable resonance is the low-field signal of the carbonyl carbon observed as a triplet at 223.5 ppm (J_{CP} = 22.9 Hz). The $^{31}P\{^1H\}$ NMR spectra contained two doublets centered at 77.6 and 85.7 ppm with a $^2J_{PP}$ coupling constant of 151 Hz for the major isomer and two dd's centered at 93.1 and 108.1 ppm with a $^2J_{PP}$ of 117 Hz and a residual coupling to the hydride $^2J_{HP}$ of 37 Hz for the minor isomer. In the IR spectrum the strong bands for the CO stretching frequencies appeared at 1962 and 1947 cm^{-1}. Interestingly, in the case of (S,S,S_{Fc})-**10** four different isomers were observed, as indicated by four different hydride resonances in the range −7.9 to −4.4 ppm. The chemical shifts suggest that the hydrides are *trans* to the CO and imine ligand, respectively.[24] These isomers could not be unequivocally identified or isolated, and they were not investigated further.

The chemical shifts, coupling constants, and HRMS data that support the tentative structures of the iron hydride species (R,R,S_{Fc})-**9a−c** and (S,S,S_{Fc})-**10** are provided in the Experimental Section.

Catalytic Reactions. The catalytic activity of all of the hydride complexes was investigated in the asymmetric hydrogenation of 10 ketones (Chart 4). All reactions were carried out in single experiments. For hydrogenations a steel autoclave was used. In an effort to ensure consistency and reproducibility, all reactions were carried out at least twice. The reaction conditions for hydrogenations (HY) were first optimized with acetophenone with respect to the amount of base, solvents, pressure, the substrate-to-catalyst ratio (S/C),

Chart 4. Ketones Used as Substrates in Catalytic Hydrogenations



R =	H	ACP
	2-F	2-F-ACP
	2-Cl	2-Cl-ACP
	4-Cl	4-Cl-ACP
	4-CF_3	4-CF_3-ACP
	4-OMe	4-MeO-ACP
	4-Me	4-Me-ACP

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the reaction temperature and time (Table S1, see Supporting Information). On the basis of this optimization procedure, all screening reactions were carried out at room temperature (rt) with an S/C/base ratio of 100:1:4 in 2-propanol as solvent for 2−16 h and at a hydrogen pressure of 20 bar. The results are listed in Table 1. The *in situ* generated catalyst derived from

Table 1. HY Results Obtained with Complexes (R,R,S_{Fc})-9a−c and (S,S,S_{Fc})-10[a]

entry	complex	substrate[b]	time	% conv	% ee	abs config
1	(R,R,S_{Fc})-**9a**	ACP	2 h	96	81	*S*
2	(R,R,S_{Fc})-**9b**	ACP	2 h	93	74	*S*
3	(R,R,S_{Fc})-**9c**	ACP	2 h	96	79	*S*
4	(S,S,S_{Fc})-**10**	ACP	2 h	92		
5	(R,R,S_{Fc})-**9a**	2-Cl-ACP	16 h	62	61	*S*
6	(R,R,S_{Fc})-**9b**	2-Cl-ACP	16 h	60	56	*S*
7	(R,R,S_{Fc})-**9c**	2-Cl-ACP	16 h	61	61	*S*
8	(S,S,S_{Fc})-**10**	2-Cl-ACP	16 h	60		
9	(R,R,S_{Fc})-**9a**	4-Cl-ACP	2 h	92	79	*S*
10	(R,R,S_{Fc})-**9b**	4-Cl-ACP	2 h	91	72	*S*
11	(R,R,S_{Fc})-**9c**	4-Cl-ACP	2 h	94	78	*S*
12	(S,S,S_{Fc})-**10**	4-Cl-ACP	2 h	90		
13	(R,R,S_{Fc})-**9a**	2-F-ACP	16 h	64	65	*S*
14	(R,R,S_{Fc})-**9b**	2-F-ACP	16 h	62	60	*S*
15	(R,R,S_{Fc})-**9c**	2-F-ACP	16 h	62	64	*S*
16	(R,R,S_{Fc})-**9a**	4-CF_3-ACP	2 h	92	66	*S*
17	(R,R,S_{Fc})-**9b**	4-CF_3-ACP	2 h	91	59	*S*
18	(R,R,S_{Fc})-**9c**	4-CF_3-ACP	2 h	92	65	*S*
19	(R,R,S_{Fc})-**9a**	4-MeO-ACP	2 h	95	80	*S*
20	(R,R,S_{Fc})-**9b**	4-MeO-ACP	2 h	93	73	*S*
21	(R,R,S_{Fc})-**9c**	4-MeO-ACP	2 h	95	78	*S*
22	(R,R,S_{Fc})-**9a**	4-Me-ACP	2 h	96	80	*S*
23	(R,R,S_{Fc})-**9b**	4-Me-ACP	2 h	91	73	*S*
24	(R,R,S_{Fc})-**9c**	4-Me-ACP	2 h	96	79	*S*
25	(R,R,S_{Fc})-**9a**	PEK	16 h	89	68	*S*
26	(R,R,S_{Fc})-**9b**	PEK	16 h	80	63	*S*
27	(R,R,S_{Fc})-**9c**	PEK	16 h	88	67	*S*
28	(R,R,S_{Fc})-**9a**	PBK	16 h	88	70	*S*
29	(R,R,S_{Fc})-**9b**	PBK	16 h	82	66	*S*
30	(R,R,S_{Fc})-**9c**	PBK	16 h	86	69	*S*
31	(R,R,S_{Fc})-**9a**	TETN	16 h	48	26	*S*
32	(R,R,S_{Fc})-**9b**	TETN	16 h	43	20	*S*
33	(R,R,S_{Fc})-**9c**	TETN	16 h	47	25	*S*

[a]Substrate: 1 mmol, catalyst: 0.01 mmol, KO^{t}Bu: 0.04 mmol, 20 bar H_2, reaction time: 2−16 h. [b]ACP, 2-F-ACP, 2-Cl-ACP, 4-CF_3-ACP, 4-MeO-ACP, 4-Me-ACP, PEK, and TETN determined by GC on a Beta Dex 110 (30 m) column, and PBK determined by HPLC on a Chiraldex OD-H column.

(R,R,S_{Fc})-**9a** as the catalyst precursor in hydrogenation of acetophenone resulted in lower selectivity and conversion (90% conv and 72% ee).

In order to study the influence of steric and electronic effects, 2- and 4-substituted acetophenones (2-F-ACP, 2-Cl-ACP, 4-CF_3-ACP, 4-MeO-ACP, and 4-Me-ACP) together with additional phenyl alkyl ketones (phenyl ethyl ketone (PEK) and phenyl benzyl ketone (PBK)) were tested. Furthermore, a bicyclic system (1-tetralone (TETN)) was used. Since (S_{Fc},*S*,*S*)-**10** was not selective in the hydrogenations of ACP, 2-Cl-ACP, and 4-Cl-ACP, it was not tested for the other substrates. The best results were obtained with complexes (R,R,S_{Fc})-**9a** and (R,R,S_{Fc})-**9c** together with substrates acetophenone and *para*-substituted acetophenones; in these cases alcohols with ee values of approximately 80% were produced in nearly quantitative yield. The influence of *para*-substituents was found to be small. Only the strongly electron-withdrawing substituents CF_3 caused a drop in enantioselectivity (Table 1, entries 16−18). The system was also found to catalyze the reduction of PEK and PBK to near completion with moderate selectivity. In the case of TETN inferior conversion and selectivity were observed. The absolute configuration of all products was determined to be *S*. Curiously the same *S* configuration alcohols are obtained using a Morris catalyst with R = Cy, R′ = Me, and R″ = Ph in the *S*,*S* configuration of the ligand (Chart 1).[11a] The ferrocenyl group must play a strong role in this reversal of enantioselection.

CONCLUSION

Iron complexes of the type [Fe(PNP′)(H)(Br)(CO)] (**9a−c** and **10**) with four tridentate PNP′ ligands (**1a−c** and **2**), all of which consist of a planar chiral ferrocene and a centro chiral aliphatic unit, were synthesized and characterized. The newly synthesized monohydride iron precatalysts (R,R,S_{Fc})-**9a−c** and (S,S,S_{Fc})-**10** were tested in the asymmetric hydrogenation of 10 ketones under mild basic condition (rt and 20 bar). Complexes (R,R,S_{Fc})-**9a** and (R,R,S_{Fc})-**9c** performed best and delivered products with high conversion and with ee values of up to 81%. Interestingly, it was found that (S,S,S_{Fc})-**10** as a diastereomer of (R,R,S_{Fc})-**9a** did not show any selectivity at all, and this is an isomer with mismatched chiral units.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an argon atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox and dry solvents. Solvents were either purchased as extra dry solvents from Acros or dried according to standard procedures under argon and distilled prior to use. Tetrahydrofuran (THF) was dried over sodium/benzophenone, dichloromethane (DCM) over P_2O_5, diethyl ether (Et_2O) over $LiAlH_4$, ethanol (EtOH) over magnesium alkoxide, and pentane over calcium hydride. Column chromatography was performed on silica gel (Merck, 40−63 μm) or on aluminum oxide (Merck, aluminum oxide 90). Petroleum ether (PE, boiling range 60−80 °C), ethyl acetate (EA), and triethylamine (TEA) were used as eluents.

NMR spectra were recorded on Bruker DRX-400 or Bruker DRX-600 spectrometers in $CDCl_3$, CD_2Cl_2, or THF-d_8. The following abbreviations are used for peak assignments: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Coupling constants in ^{13}C NMR are due to $^{31}P-^{13}C$ coupling. Atom-numbering scheme for NMR assignment is depicted in Figure 5. High-resolution mass spectra were recorded on a Bruker ESI-Qq aoTOF MS spectrometer. Melting points were measured on a Kofler or a Boif X-4 melting point apparatus.

Synthesis. *(R,R,S$_{Fc}$)-1a.* A mixture of (S_{Fc})-**5a** (258.5 mg, 0.78 mmol) and (1*R*,2*R*)-**6a** (250.0 mg, 0.78 mmol) in ethanol (10 mL) was heated under reflux for 90 min. The mixture was cooled to rt and stirred overnight. The solvent was removed in vacuo, and the title compound as an orange solid was used in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$): δ 0.64 (t, J = 7.7 Hz, 3H,

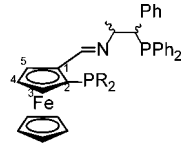

Figure 5. Atom-numbering scheme for NMR assignment.

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$CH(CH_3)(CH_3)^A$), 0.82−0.92 (m, 3H, $CH(CH_3)(CH_3)^A$), 1.09−1.22 (m, 6H, $CH(CH_3)^B(CH_3)$ + $CHCH_3$), 1.48 (dd, J = 7.0 Hz, J = 15.8 Hz, 3H, $CH(CH_3)(CH_3)^B$), 1.68−1.76 (m, 1H, $CH(CH_3)_2^A$), 2.14−2.22 (m, 1H, $CH(CH_3)_2^B$), 3.69−3.84 (m, 2H, $CHCH_3$ + CHPh), 3.93−3.99 (m, 1H, H3/H5), 4.05 (s, 5H, Cp′), 4.20−4.25 (m, 1H, H4), 4.31−4.35 (m, 1H, H3/H5), 6.88−7.87 (15H, Ph), 8.63 (bs, 1H, CHN). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 17.9 (d, $^2J_{CP}$ = 1.5 Hz, $CH(CH_3)(CH_3)^A$), 19.9 (d, $^2J_{CP}$ = 12.9 Hz, $CH(CH_3)(CH_3)^B$), 20.8 (d, $^2J_{CP}$ = 17.2 Hz, $CH(CH_3)(CH_3)^A$), 22.0−22.4 (3C, $CH(CH_3)(CH_3)^B$ + $CH(CH_3)_2{}^B$ + $CHCH_3$), 25.4 (d, $^1J_{CP}$ = 13.4 Hz, $CH(CH_3)_2{}^A$), 52.3 (bs, CHPh), 68.2 (bs, C3/C5), 70.4 (5C, Cp′), 70.7 (bs, $CHCH_3$), 71.4 (bs, C3/C5), 71.9 (C4), 79.1 (bs, C1/C2), 85.3 (bs, C1/C2), 125.3−140.3 (18C, Ph), 160.7 (bs, CHN). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −7.24, −2.70. HR-MS (ESI, MeOH/MeCN): m/z $[M + H]^+$ calcd 632.2298 for $C_{38}H_{44}FeNP_2$; found 632.2293.

*(R,R,S$_{Fc}$)-**1b***. Starting from (S_{Fc})-**5b** (311.8 mg, 0.78 mmol) and (1*R*,2*R*)-**6a** (250.0 mg, 0.78 mmol) and following the procedure for (*R*,*R*,S_{Fc})-**1a**, the desired product was obtained as an orange solid. ^1H NMR (600 MHz, CD_2Cl_2): δ 0.96 (d, $^3J_{HH}$ = 6.3 Hz, 3H, $CHCH_3$), 3.63−3.84 (m, 3H, $CHCH_3$ + CHPh + H3), 4.03 (s, 5H, Cp′), 4.31−4.33 (m, 1H, H5), 4.34 (t, $^4J_{HP}$ = 2.5 Hz, 1H, H4), 6.94−7.81 (25H, Ph), 8.41 (d, $^4J_{HP}$ = 2.3 Hz, 1H, CH═N). $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2): δ 22.3 (d, $^3J_{CP}$ = 6.9 Hz, $CHCH_3$), 52.4 (d, $^1J_{CP}$ = 15.1 Hz, CHPh), 70.2 (d, $^3J_{CP}$ = 2.2 Hz, C5), 71.1 (5C, Cp′), 71.5 (d, $^2J_{CP}$ = 21.0 Hz, $CHCH_3$), 72.3 (C4), 73.9 (d, $^2J_{CP}$ = 4.1 Hz, C3), 78.9 (d, $^2J_{CP}$ = 11.9 Hz, C1), 86.9 (d, $^1J_{CP}$ = 17.5 Hz, C2), 126.3−140.9 (30C, Ph), 159.4 (d, $^3J_{CP}$ = 10.8 Hz, CH═N). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ −22.6, −5.6. HR-MS (ESI, MeOH/MeCN): m/z $[M + H]^+$ calcd 700.1985 for $C_{44}H_{40}FeNP_2$; found 700.1980.

*(R,R,S$_{Fc}$)-**1c***. Starting from (S_{Fc})-**5c** (321.3 mg, 0.78 mmol) and (1*R*,2*R*)-**6a** (250.0 mg, 0.78 mmol) and following the procedure for (*R*,*R*,S_{Fc})-**1a**, the desired product was obtained as an orange solid. ^1H NMR (600 MHz, CD_2Cl_2): δ 0.88−2.15 (m, 25H, $CHCH_3$ + Cy), 3.82−3.94 (m, 2H, $CHCH_3$ + CHPh), 4.08 (s, 5H, Cp′), 4.24−4.26 (m, 1H, H3/5), 4.27−4.29 (m, 1H, H3/5), 4.37 (t, $^4J_{HP}$ = 2.5 Hz, 1H, H4), 6.98−7.85 (15H, Ph), 8.57 (d, $^4J_{HP}$ = 3.2 Hz, 1H, CH═N). $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2): δ 21.9 (d, $^3J_{CP}$ = 7.9 Hz, $CHCH_3$), 25.8−35.6 (12C, Cy), 52.3 (d, $^1J_{CP}$ = 15.5 Hz, CHPh), 70.4 (bs, C3/C5), 70.5 (5C, Cp′), 71.0 (d, $^2J_{CP}$ = 24.2 Hz, $CHCH_3$), 71.6 (C4), 71.7 (bs, C3/C5), 79.6 (d, $^1J_{CP}$ = 24.7 Hz, C2), 86.3 (d, $^2J_{CP}$ = 15.7 Hz, C1), 125.6−140.8 (18C, Ph), 160.6 (d, $^3J_{CP}$ = 12.1 Hz, CH═N). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ −16.4, −4.7. HR-MS (ESI, MeOH/MeCN): m/z $[M + H]^+$ calcd 712.2924 for $C_{44}H_{52}FeNP_2$; found 712.2921.

*(S,S,S$_{Fc}$)-**2***. Starting from (S_{Fc})-**5a** (258.5 mg, 0.78 mmol) and (1*S*,2*S*)-**6a** (250.0 mg, 0.78 mmol) and following the procedure for (*R*,*R*,S_{Fc})-**1a**, the desired product was obtained as an orange solid. ^1H NMR (400 MHz, $CDCl_3$): δ 0.72 (dd, J = 7.1 Hz, J = 7.5 Hz, 3H, $CH(CH_3)(CH_3)^A$), 0.93 (dd, J = 7.1 Hz, J = 7.5 Hz, 3H, $CH(CH_3)(CH_3)^A$), 1.18−1.24 (6H, $CHCH_3$ + $CH(CH_3)(CH_3)^B$), 1.44 (dd, J = 7.1 Hz, J = 8.6 Hz, 3H, $CH(CH_3)(CH_3)^B$), 1.66−1.86 (m, 1H, $CH(CH_3)_2{}^A$), 2.11−2.26 (m, 1H, $CH(CH_3)_2{}^B$), 3.74−3.86 (m, 1H, $CHCH_3$), 3.88−3.95 (m, 1H, CHPh), 4.00 (s, 5H, Cp′), 4.17−4.21 (m, 1H, H3), 4.36−4.40 (m, 1H, H4), 4.71−4.75 (m, 1H, H5), 6.89−7.71 (15H, Ph), 8.34 (d, $^4J_{HP}$ = 2.6 Hz, 1H, CHN). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 17.4 (bs, $CHCH_3$), 18.6 (d, $^2J_{CP}$ = 4.2 Hz, $CH(CH_3)(CH_3)^A$), 20.0 (d, $^2J_{CP}$ = 12.3 Hz, $CH(CH_3)(CH_3)^B$), 20.7 (d, $^2J_{CP}$ = 4.2 Hz, $CH(CH_3)(CH_3)^A$), 22.1−22.6 (2C, $CH(CH_3)(CH_3)^B$ + $CH(CH_3)(CH_3)^B$), 25.7 (d, $^1J_{CP}$ = 13.0 Hz, $CH(CH_3)_2{}^A$), 51.8 (d, $^1J_{CP}$ = 14.7 Hz, CHPh), 68.4 ($CHCH_3$), 68.6 (C5), 70.2 (5C, Cp′), 70.5 (C4), 71.2 (d, $^2J_{CP}$ = 4.2 Hz, C3), 78.7 (d, $^1J_{CP}$ = 23.0 Hz, C2), 84.6 (d, $^2J_{CP}$ = 14.5 Hz, C1), 124.4−141.1 (18C, Ph), 158.5 (d, $^3J_{CP}$ = 11.4 Hz, CHN). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −6.36, −3.94. HR-MS (ESI, MeOH/MeCN): m/z $[M + H]^+$ calcd 632.2298 for $C_{38}H_{44}FeNP_2$; found 632.2293.

*(2S,4S,S$_{Fc}$)-**4c***. To a degassed solution of (2*S*,4*S*)-**3** (7.6 g, 24.1 mmol) in diethyl ether (100 mL) was added dropwise a solution of ^{t}BuLi (16.9 mL, 1.6 M, 26.5 mmol) at −78 °C. The reaction mixture was stirred for 20 min at −78 °C and for an additional 90 min at rt. The resulting orange suspension was cooled to −78 °C, and neat chlorodicyclohexylphosphine (6.7 g, 28.9 mmol) was added. The reaction mixture was stirred for an additional 30 min at −78 °C and for 16 h at rt. The reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ (30 mL), and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine (3 × 20 mL) and dried over $MgSO_4$. Column chromatography on silica gel using PE/EA = 5:1 as eluent gave the desired product as a red oil (10.6 g, 20.7 mmol, 86% yield). This compound can be used in the next step without further purification. ^1H NMR (600 MHz, $CDCl_3$): δ 0.96−2.46 (m, 24H, CH_2 + Cy), 3.28−3.33 (m, 4H, OCH_3 + MeO-CHH), 3.41−3.46 (m, 1H, MeO-CHH), 3.93−4.00 (m, 2H, CH + CHHO), 4.04−4.07 (m, 1H, H3), 4.13 (s, 5H, Cp′), 4.24−4.30 (m, 2H, H4 + CHHO), 4.57−4.60 (m, 1H, H5), 5.57 (d, $^4J_{HP}$ = 2.8 Hz, 1H, CH). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): δ 26.1−36.2 (13C, CH_2 + Cy), 59.2 (OCH_3), 66.9 (OCH_2), 68.1 (d, J = 3.0 Hz, C5), 68.9 (C4), 69.9 (d, $^2J_{CP}$ = 3.7 Hz, C3), 70.0 (5C, Cp′), 75.5 (MeO-CH_2), 75.6 (CH), 77.2 (d, $^1J_{CP}$ = 19.9 Hz, C2), 90.4 (d, $^2J_{CP}$ = 18.9 Hz, C1), 99.6 (d, $^3J_{CP}$ = 11.7 Hz, CH). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ −12.4. HR-MS (ESI, MeOH/MeCN): m/z $[M + H]^+$ calcd 513.2221 for $C_{28}H_{42}FeO_3P$; found 513.2219.

*(S$_{Fc}$)-**5c***. To a degassed solution of (2*S*,4*S*,S_{Fc})-**4c** (5.0 g, 9.8 mmol) in DCM (60 mL) was added a solution of *para*-toluenesulfonic acid monohydrate (PTSA) (1.99 g, 10.4 mmol) in degassed water (30 mL). The reaction mixture was stirred at rt overnight. After adding water (50 mL), the aqueous phase was extracted with DCM (3 × 20 mL); the organic layers were combined, washed with water and brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure. Column chromatography on silica gel using PE/EA = 5:1 as eluent gave the desired product as an orange semisolid (2.96 g, 7.2 mmol, 74% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 0.74−2.49 (m, 22H, Cy), 4.23 (s, 5H, Cp′), 4.46−4.49 (m, 1H, H5), 4.73 (t, J = 2.5 Hz, 1H, H4), 5.02−5.05(m, 1H, H3), 10.23 (d, $^4J_{HP}$ = 3.8 Hz, CHO). $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): δ 24.7−36.1 (12C, Cy), 68.9 (bs, C3), 70.9 (5C, Cp′), 73.3 (C4), 74.3 (d, $^3J_{CP}$ = 5.3 Hz, C5), 81.6 (d, $^1J_{CP}$ = 28.8 Hz, C2), 83.5 (d, $^2J_{CP}$ = 11.9 Hz, C1), 193.4 (d, $^3J_{CP}$ = 13.4 Hz, CHO). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ −16.6. HR-MS (ESI, MeOH/MeCN): m/z $[M + H]^+$ calcd 411.1540 for $C_{23}H_{32}FeOP$; found 411.1532.

*(R,R,S$_{Fc}$)-**7a***. $FeBr_2(THF)_2$, free of iron(III), was prepared by stirring $FeBr_2$ (115.5 mg, 0.537 mmol) and excess Fe powder (89.0 mg, 1.61 mmol) in THF (10 mL) under argon until it turned colorless. The suspension was filtered through a frit, and a solution of (*R*,*R*,S_{Fc})-**1a** (0.35 g, 0.55 mmol) in THF (10 mL) was slowly added to it. The immediately formed red suspension was stirred overnight. The solvent was removed under vacuum, and the remaining solid was dissolved in CH_2Cl_2 (5 mL) and filtered through a short pad of Celite. The solution was concentrated to 1 mL, and the product was precipitated by addition of *n*-pentane (40 mL). The precipitate was separated from the supernatant solution, washed with *n*-pentane (3 × 10 mL), and dried under vacuum to afford a red-orange powder (0.43 g, 0.50 mmol, 94% yield). Single crystals suitable for X-ray structure determination were grown from CH_2Cl_2/ACN/Et_2O by slow evaporation of the solvent. Mp > 170 °C (dec). HR-MS (ESI, MeOH/MeCN): m/z $[M - Br]^+$ calcd 766.0753 for $C_{38}H_{43}BrFe_2NP_2$; found 766.0746. μ_{eff} = 5.0 μ_B (CD_2Cl_2, Evans' method).

*(R,R,S$_{Fc}$)-**7b***. Starting from (*R*,*R*,S_{Fc})-**1b** (0.40 g, 0.57 mmol) and $FeBr_2$ (119.6 mg, 0.55 mmol) and following the procedure for (*R*,*R*,S_{Fc})-**7a** the desired product was obtained as a red-orange powder (0.47 g, 0.51 mmol, 92% yield). Mp > 170 °C (dec). HR-MS (ESI, MeOH/MeCN): m/z $[M - Br]^+$ calcd 834.0440 for $C_{44}H_{39}BrFe_2NP_2$; found 834.0429. μ_{eff} = 4.9 μ_B (CD_2Cl_2, Evans' method).

*(R,R,S$_{Fc}$)-**7c***. Starting from (*R*,*R*,S_{Fc})-**1c** (0.30 g, 0.42 mmol) and $FeBr_2$ (88.2 mg, 0.41 mmol) and following the procedure for (*R*,*R*,S_{Fc})-**7a**, the desired product was obtained as a red-orange powder (0.36 g, 0.39 mmol, 94% yield). Single crystals suitable for X-ray structure determination were grown from DCM/ACN/Et_2O by slow

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evaporation of the solvent. Mp > 170 °C (dec). HR-MS (ESI, MeOH/MeCN): m/z [M − Br]$^+$ calcd 846.1379 for $C_{44}H_{51}BrFe_2NP_2$; found 846.1368. μ_{eff} = 4.9 μ_B (CD_2Cl_2, Evans' method).

*(S,S,S$_{Fc}$)-**8***. Starting from (*S,S,S*$_{Fc}$)-**2** (0.30 g, 0.47 mmol) and $FeBr_2$ (99.4 mg, 0.46 mmol) and following the procedure for (*R,R,S*$_{Fc}$)-**7a**, the desired product was obtained as a red-orange powder (0.36 g, 0.43 mmol, 93% yield). Mp > 170 °C (dec). HR-MS (ESI, MeOH/MeCN): m/z [M − Br]$^+$ calcd 766.0753 for $C_{38}H_{43}BrFe_2NP_2$; found 766.0746. μ_{eff} = 5.0 μ_B (CD_2Cl_2, Evans' method).

*(R,R,S$_{Fc}$)-**9a***. A solution of (*R,R,S*$_{Fc}$)-**7a** (0.20 g, 0.24 mmol) in THF (10 mL) in a Schlenk flask was exposed to an atmosphere of CO (1 bar) for 3 h. The mixture was transferred to a glovebox, and EtOH (5 mL) and subsequently $NaBH_4$ (7.98 mg, 0.21 mmol) were added in one portion at rt. Gas evolution was observed, and the color of the solution changed immediately from red to dark brown-green. After stirring for 1 h the solution was filtered and the solvent was removed under reduced pressure. The dark residue was taken up in THF (1 mL), and the product was precipitated by addition of pentane (20 mL). The precipitate was separated from the supernatant solution, washed with *n*-pentane (3 × 10 mL), and dried under vacuum to afford a dark green powder (133.5 mg, 0.17 mmol, 71% yield). Mp > 170 °C (dec). Major isomer: ^{1}H NMR (600 MHz, THF-d_8): δ −17.7 (t, $^2J_{HP}$ = 44.7 Hz, 1H, Fe-*H*), 0.76 (d, *J* = 6.0 Hz, $CHCH_3$), 0.84−0.92 (m, 3H, $CH(CH_3)(CH_3)$), 0.98−1.05 (m, 3H, $CH(CH_3)(CH_3)$), 1.21−1.34 (m, 6H, $CH(CH_3)_2$), 1.48−1.62 (m, 1H, $CH(CH_3)_2$), 2.01−2.10 (m, 1H, $CH(CH_3)_2$), 3.57−3.70 (m, 2H, $CHCH_3$ + *CH*Ph), 3.89−3.92 (m, 1H, Cp), 4.00 (s, 5H, Cp′), 4.16−4.21 (m, 1H, Cp), 4.30−4.33 (m, 1H, Cp), 6.78−7.64 (15H, Ph), 8.16 (bs, 1H, CHN). ^{13}C{^{1}H} NMR (150.9 MHz, THF-d_8): δ 19.4 (7C, $CHCH_3$ + $CH(CH_3)_2$ + $CH(CH_3)_2$), 57.4 (dd, *J* = 5.5 Hz, *J* = 15.0 Hz, *C*HPh), 60.0 (dd, *J* = 5.6 Hz, *J* = 16.0 Hz, $CHCH_3$), 70.2 (Cp), 70.6 (5C, Cp′), 70.9 (Cp), 71.4 (Cp), 126.7−138.9 (18C, Ph), 176.8 (bs, CHN), 223.5 (t, $^2J_{CP}$ = 22.9 Hz, CO), C1 and C2 not observed. ^{31}P{^{1}H} NMR (243 MHz, THF-d_8): δ 77.6 (d, $^2J_{PP}$ = 151.0 Hz), 85.7 (d, $^2J_{PP}$ = 151.0 Hz). Minor isomers: ^{1}H NMR (600 MHz, THF-d_8): δ −20.42 (dd, *J* = 50.0 Hz, *J* = 60.4 Hz). ^{31}P{^{1}H} NMR (243 MHz, THF-d_8): δ 93.1 (dd, *J* = 37.2 Hz, *J* = 117.0 Hz), 108.1 (dd, *J* = 37.2 Hz, *J* = 117.0 Hz). IR (ATR, cm^{-1}): 1962 (ν_{CO}) (major isomer), 1947 (ν_{CO}) (minor isomer). HR-MS (ESI, MeOH/MeCN): m/z [M − Br − CO]$^+$ calcd 688.1648 for $C_{38}H_{44}Fe_2NP_2$; found 688.1632.

*(R,R,S$_{Fc}$)-**9b***. Starting from (*R,R,S*$_{Fc}$)-**7b** (0.20 g, 0.22 mmol) and following the procedure for (*S*$_{Fc}$,*R,R*)-**9a** the desired product was obtained as a yellow-green powder (126.5 mg, 0.146 mmol, 67% yield). Mp > 170 °C (dec). ^{1}H NMR (600 MHz, THF-d_8): δ −20.21 (dd, *J* = 55.3 Hz, *J* = 67.2 Hz, 1H, Fe-*H*), −19.66 (t, $^2J_{HP}$ = 63.3 Hz, 1H, Fe-*H*), − 6.39 (t, $^2J_{HP}$ = 47.1 Hz, 1H, Fe-*H*). ^{31}P{^{1}H} NMR (243 MHz, THF-d_8): δ 48.9 (d, $^2J_{PP}$ = 97.0 Hz), 64.1 (d, $^2J_{PP}$ = 104.8 Hz), 77.6 (d, $^2J_{PP}$ = 150.8 Hz), 85.7 (d, $^2J_{PP}$ = 150.8 Hz), 90.3 (d, $^2J_{PP}$ = 104.8 Hz), 96.0 (d, $^2J_{PP}$ = 97.0 Hz). IR (ATR, cm^{-1}): 1908 (ν_{CO}), 1942 (ν_{CO}), 2007 (ν_{CO}). HR-MS (ESI, MeOH/MeCN): m/z [M − Br − CO]$^+$ calcd 756.1335 for $C_{44}H_{40}Fe_2NP_2$; found 756.1326.

*(R,R,S$_{Fc}$)-**9c***. Starting from (*R,R,S*$_{Fc}$)-**7c** (0.20 g, 0.22 mmol) and following the procedure for (*S*$_{Fc}$,*R,R*)-**9a** the desired product was obtained as a yellow-green powder (109.6 mg, 0.125 mmol, 58% yield). Mp > 170 °C (dec).

^{1}H NMR (600 MHz, THF-d_8): δ −20.60 (dd, *J* = 50.4 Hz, *J* = 65.4 Hz, 1H, Fe-*H*), −6.01 (t, $^2J_{HP}$ = 46.0 Hz, 1H, Fe-*H*). ^{13}C{^{1}H} NMR (150.9 MHz, THF-d_8): δ 223.9 (bs, CO). ^{31}P{^{1}H} NMR (243 MHz, THF-d_8): 32.5 (d, $^2J_{PP}$ = 89.8 Hz), 40.8 (d, $^2J_{PP}$ = 78.6 Hz), 77.4 (d, $^2J_{PP}$ = 149.7 Hz), 84.9 (d, $^2J_{PP}$ = 149.7 Hz). IR (ATR, cm^{-1}): 1914 (ν_{CO}), 1953 (ν_{CO}). HR-MS (ESI, MeOH/MeCN): m/z [M − Br − CO]$^+$ calcd 768.2274 for $C_{44}H_{52}Fe_2NP_2$; found 768.2265.

*(S,S,S$_{Fc}$)-**10***. Starting from (*S,S,S*$_{Fc}$)-**8** (0.20 g, 0.22 mmol) and following the procedure for (*R,R,S*$_{Fc}$)-**9a** the desired product was obtained as a yellow-green powder (122.2 mg, 0.15 mmol, 65% yield). Mp > 170 °C (dec). ^{1}H NMR (600 MHz, THF-d_8): δ −17.8 (t, $^2J_{HP}$ = 53.0 Hz, 1H, Fe-*H*), −7.5 (t, $^2J_{HP}$ = 58.9 Hz, 1H, Fe-*H*), −7.0 (t, $^2J_{HP}$ = 57.6 Hz, 1H, Fe-*H*), − 4.8 (t, $^2J_{HP}$ = 37.1 Hz, 1H, Fe-*H*). ^{31}P{^{1}H} NMR (243 MHz, THF-d_8): δ 57.4 (d, $^2J_{PP}$ = 75.1 Hz), 64.2 (d, $^2J_{PP}$ = 95.5 Hz), 65.0 (d, $^2J_{PP}$ = 75.1 Hz), 66.4 (d, $^2J_{PP}$ = 95.5 Hz), 66.9 (d, $^2J_{PP}$ = 96.0 Hz), 80.6 (d, $^2J_{PP}$ = 96.0 Hz), 91.8 (d, $^2J_{PP}$ = 77.2 Hz), 92.3 (d, $^2J_{PP}$ = 77.2 Hz), 94.1 (d, $^2J_{PP}$ = 96.7 Hz), 104.9 (d, $^2J_{PP}$ = 96.7 Hz). IR (ATR, cm^{-1}): 1926 (ν_{CO}), 1951 (ν_{CO}), 1988 (ν_{CO}), 2007 (ν_{CO}). HR-MS (ESI, MeOH/MeCN): m/z [M − Br]$^+$ calcd 716.1597 for $C_{39}H_{44}Fe_2NP_2O$; found 716.1586.

General Procedure for the Asymmetric Hydrogenation of Ketones. To a solution of the substrate (1 mmol) dissolved under argon in degassed 2-propanol (2.5 mL) was added the appropriate catalyst (1 mol %) dissolved in degassed 2-propanol (2.5 mL). KO^{t}Bu (4 mol %) was added, and the reaction mixture was transferred through a stainless steel capillary into a steel autoclave. The argon gas was then replaced by hydrogen gas (3−5 cycles), and the pressure was set. All hydrogenations were carried out under hydrogen gas at a pressure of 20 bar. After completion of the reaction, diethyl ether (10 mL) was added and the reaction was quenched by the addition of an aqueous solution of H_3PO_4 (20%). The organic phase was separated, washed with brine, dried over $MgSO_4$, and filtered through a plug of aluminum oxide. Conversions and ee values for the product were determined by GC or HPLC[25] (for details see the Supporting Information).

Computational Details. All calculations were performed using the Gaussian 09 software package[26] on the Phoenix Linux Cluster of the Vienna University of Technology. The optimized geometries were obtained with the B3LYP functional[27] without symmetry constraints. That functional includes a mixture of Hartree−Fock[28] exchange with DFT[29] exchange−correlation, given by Becke's three-parameter functional with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms. The basis set used for the geometry optimizations consisted of the Stuttgart/Dresden ECP (SDD) basis set[30] to describe the electrons of iron and a standard 6-31G** basis set[31] for all other atoms. Frequency calculations were performed and confirmed all optimized structures as minima (zero imaginary frequency modes). The free energy values presented were obtained at 298.15 K and 1 atm by using zero-point energy and thermal energy corrections based on structural and vibration frequency data.

Crystal Structure Determination. X-ray diffraction data for (*R,R,S*$_{Fc}$)-**7a** and (*R,R,S*$_{Fc}$)-**7c** [CCDC entries: 1484270 (*R,R,S*$_{Fc}$)-**7a**) and 1499346 ((*R,R,S*$_{Fc}$)-**7c**)] were collected at *T* = 100 K in a dry stream of nitrogen on a Bruker KAPPA APEX II ((*R,R,S*$_{Fc}$)-**7a**) diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) and fine-sliced φ- and ω-scans and a Bruker D8 Venture ((*R,R,S*$_{Fc}$)-**7c**) diffractometer with multilayer monochromators, a Cu K/a INCOATEC micro focus sealed tube, and Kryoflex II cooling device. Data were reduced to intensity values with SAINT, and an absorption correction was applied with the multiscan approach implemented in SADABS.[32] The structures were solved by direct methods implemented in SHELXS.[33] The structures were refined using SHELXL[34] against F^2. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. The H atoms of the borane unit were located in difference Fourier maps and freely refined. Molecular graphics were generated with the programs MERCURY[35] and OLEX2.[36] Crystal data and experimental details are given in Table S2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00711.

Full experimental descriptions and spectroscopic data are given for all newly synthesized ligands and complexes as well as detailed hydrogenation data; NMR spectra, crystallographic data, and atomic coordinates for DFT-optimized structures (PDF)

X-ray crystallographic data (CIF)

Optimized Cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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