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Chiral Macrocyclic N_2P_2 Ligands and Iron(II): A Marriage of Interest

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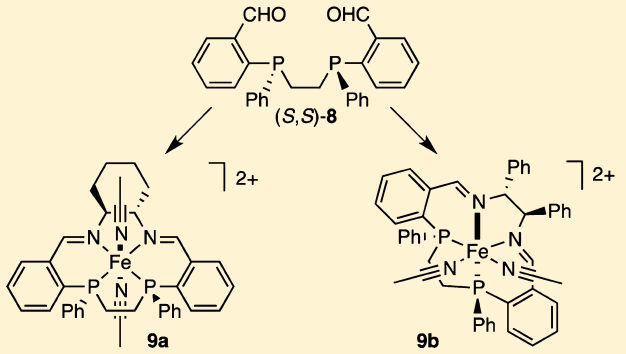
Supporting Information

ABSTRACT: The N_2P_2 macrocyclic ligands (5*S*,8*S*,13*E*,14a-*S*,18a*S*,19*E*)-5,8-diphenyl-5,6,7,8,14a,15,16,17,18,18a-decahydrotribenzo[*b*,*f*,*l*][1,4,8,11]diazadiphosphacyclotetradecine ((1*S*,4*S*,9*S*,10*S*)-**1a**) and (5*E*,7*R*,8*R*,9*E*,15*S*,18*S*)-7,8,15,18-tetraphenyl-7,8,15,16,17,18-hexahydrodibenzo[*f*,*l*][1,4,8,11]diazadiphosphacyclotetradecine ((1*S*,4*S*,9*R*,10*R*)-**1b**) were prepared by condensing the new, enantiomerically pure synthon 2,2′-((1*S*,1′*S*)-ethane-1,2-diylbis(phenylphosphinediyl))-dibenzaldehyde ((*S*,*S*)-**8**), prepared in six steps from (2*R*,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (**3**)), with (1*S*,2*S*)-cyclohexane-1,2-diamine and (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine under high-dilution conditions. The opposite enantiomers of the diamines gave oligomeric products. The stereospecificity of the macrocyclization reaction is explained by conformational analysis based on the X-ray structures of (1*S*,4*S*,9*S*,10*S*)-**1a** and (1*S*,4*S*,9*R*,10*R*)-**1b**. The corresponding diamino macrocycles (1*S*,4*S*,9*S*,10*S*)-**2a** and (1*S*,4*S*,9*R*,10*R*)-**2b** were prepared by reduction of the imine moiety of (1*S*,4*S*,9*S*,10*S*)-**1a** and (1*S*,4*S*,9*R*,10*R*)-**1b**, respectively. Macrocycles (1*S*,4*S*,9*S*,10*S*)-**1a**, (1*S*,4*S*,9*R*,10*R*)-**1b**, and (1*S*,4*S*,9*S*,10*S*)-**2a** react with $[Fe(OH_2)_6](BF_4)_2$ in acetonitrile to give the corresponding stable, diamagnetic bis(acetonitrile) complexes $[Fe(MeCN)_2(\mathbf{1})](BF_4)_2$ (**9a** and **9b**) and $[Fe(MeCN)_2(\mathbf{2a})](BF_4)_2$ (**10a**). Complex **9a** exists as a 3:1 mixture of *trans* and Λ-*cis*-*β* isomers, whereas **9b** and **10a** adopt the Λ-*cis*-*β* configuration exclusively. The bis(acetonitrile) complexes are versatile precursors and were used to prepare the bromocarbonyl analogues $[FeBr(CO)(\mathbf{1})]BPh_4$ (**11a** and **11b**).



INTRODUCTION

Although iron chemistry has experienced a tremendous boost over the past decade, well-defined, bench-stable, preferentially diamagnetic iron(II) (pre)catalysts for enantioselective transformations are still scarce, with systems containing multidentate ligands clearly dominating.[1] Besides the ubiquitous cyclopentadienyl fragment,[2] tetradentate ligands, in particular with the N_4 donor set, are the most prominent ones. However, such N_4 systems are generally achiral and give high-spin complexes.[3] White and co-workers have prepared one of the few chiral examples with a N_4 donor set and used it in C−H oxidation reactions (Chart 1).[4]

Also tetradentate ligands with a N_2P_2 or P_4 donor set are rare, and most of them are achiral. A N_2P_2 iminophosphorane ligand has been used in the transfer hydrogenation of acetophenone,[5] and tripodal PP_3 ligands have been used in the semihydrogenation of alkynes and in the reduction of CO_2, bicarbonate, enals, and nitroarenes, respectively.[6,7] A chiral, but racemic open-chain P_4 ligand and its bis(acetonitrile) Fe(II) complex have recently been prepared, but no catalytic activity has been reported.[8]

Rare examples of the use of chiral PNNP ligands in catalysis with iron(II) are Morris' complexes with ligands **A** and **B** (Chart 2).[9−12] Complex $[Fe(MeCN)_2(\mathbf{A})](BF_4)_2$ hydrogenates acetophenone to 1-phenylethanol with up to 39% ee and TOF as high as 907 h^{-1}.[9] However, the complex is not stable under transfer hydrogenation conditions and decomposes to iron(0) nanoparticles doped with the chiral ligand.[10] Changing the phosphorus-imine bridge from 1,2-phenylene to methylene as in *trans*-$[FeBr(CO)(\mathbf{B})]BPh_4$ increases both the activity (TOF = 2.0 × 10^4 h^{-1}) and the selectivity (81% ee) in the transfer

Chart 1. Selected Well-Characterized Iron(II) Precatalysts

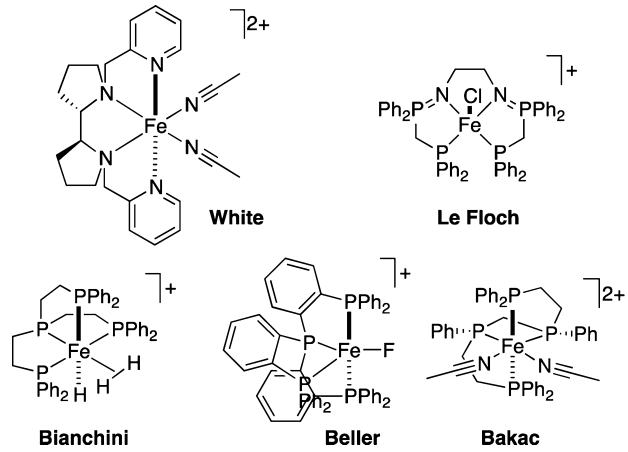


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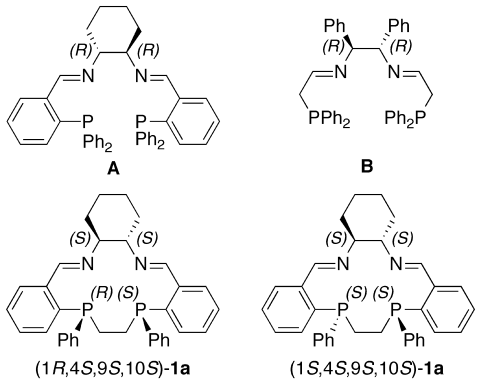
Chart 2. Structural Comparison of Open-Chain PNNP and Macrocyclic N_2P_2 Ligands



hydrogenation of acetophenone.[11] Such second-generation ligands form stable active catalysts that bear a monoreduced amino/enamido ligand.[12]

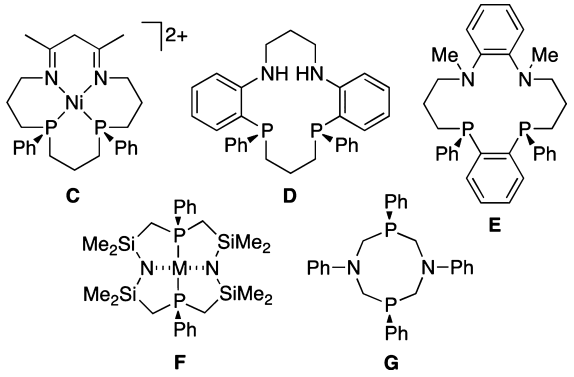
Besides tetradentate ligands, tridentate PNP, PNN, and NNN ligands have been prepared and used in catalysis in combination with iron(II),[13] but only a handful of well-defined, chiral complexes have been prepared[14−18] and used in the asymmetric H_2-hydrogenation (up to 85% ee)[15] and in the asymmetric hydrosilylation of ketones (up to 93% ee).[16−18]

To exploit iron as a cheap, low-toxic metal in catalysis with high turnover numbers and low catalyst loading, robust iron complexes are required.[1] As summarized above, only few chiral iron(II) complexes have been prepared, and besides Morris' systems, most of them are paramagnetic, which complicates their investigation and rational development. Furthermore, their robustness poses a major challenge, such as in the case of the open-chain PNNP complexes with ligand **A** (Chart 2), which decompose under reaction conditions. As the bulkiness of the mutually *cis* PPh_2 groups in $[Fe(MeCN)_2(\mathbf{A})](BF_4)_2$ may account for the instability of the iron catalyst under the reaction conditions,[10] we reasoned that enantiopure macrocyclic N_2P_2 ligands should reduce the steric bulk of the tetradentate N_2P_2 ligand and stabilize the complex by virtue of the macrocyclic effect.[19] The synthesis of such macrocyclic N_2P_2 ligands is challenging, though, because it requires the control of the configuration at phosphorus. In fact, only a few P-containing macrocycles have been prepared,[20] and N_2P_2 macrocycles are even rarer and mostly achiral (Chart 3).[21−26]

The N_2P_2 macrocycles **C** and **D** were prepared by template synthesis with nickel(II),[21,22] whereas **E** was prepared by double alkylation of deprotonated 1,2-bis(phenylphosphino)-benzene under high-dilution conditions.[23] In all cases, only the *meso* isomer of the ligand was obtained. Smaller N_2P_2 macrocycles such as **F** and **G** cannot adopt a *trans* configuration even for 3d transition metals because of the small ring size and hence either give *cis* complexes (**F**)[24] or bind metals in a bidentate way with the phosphine donors (**G**).[25,26] As before, only the *meso* isomers are accessible. Recently, Gao has prepared chiral, non-P-stereogenic N_4P_2 macrocycles and used them in the iron(0)-catalyzed asymmetric H_2-hydrogenation of ketones with excellent enantioselectivity (up to 99% ee).[27]

Our research group has recently reported the first enantiopure, C_1-symmetric, macrocyclic N_2P_2 ligand (1*R*,4*S*,9*S*,10*S*)-**1a** (Chart 2), its diamino analogue, and their ruthenium(II) complexes.[28,29] However, preliminary catalytic tests in the transfer hydrogenation of acetophenone gave low enantioselectivity, which we ascribed to the pseudo-*meso* configuration of the PPh groups, leaving one side of the complex almost unbiased. Therefore, also in view of the successful application of ruthenium(II)/PNNP complexes in enantioselective catalytic reactions such as asymmetric C−C and C−heteroatom bond formation reactions,[30,31] we have pursued an alternative synthetic strategy that gives access to the enantiomerically pure C_2-symmetric diastereoisomer (1*S*,4*S*,9*S*,10*S*)-**1a**, containing two stereogenic phosphorus donors in the *like* configuration as described below.

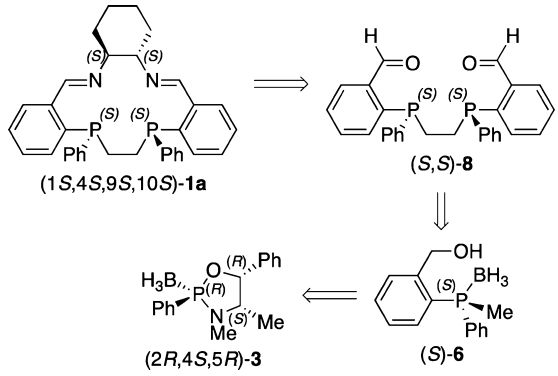
Chart 3. Previously Reported, Achiral N_2P_2 Macrocycles



RESULTS AND DISCUSSION

General Strategy. The retrosynthetic approach shown in Scheme 1 indicates the enantiomerically pure bis-*ortho*-formyl-

Scheme 1. Retrosynthetic Analysis of Macrocycle 1a



substituted diphosphine (*S*,*S*)-**8** as the synthon of choice to prepare C_2-symmetric N_2P_2 macrocycles by condensation with a variety of chiral diamines. As the previous examples of N_2P_2 macrocycles have shown a strong preference for the *meso* form,[21−26,28] it is crucial to control the stereogenic center on phosphorus at an early stage of the synthesis. To this goal, we have adapted Jugé's approach, which is excellently suitable to control the stereochemistry on phosphorus by sequential and selective nucleophilic cleavage of the P−O and P−N bonds of (2*R*,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (**3**) (formed as a single diastereoisomer from $PhP(NEt_2)_2$ and (−)-ephedrine).[32] Starting from **3**, we prepared the enantiomerically enriched intermediate (*S*)-(2-(methyl(phenyl)phosphino)phenyl)methanol borane (*S*)-**6** in three steps. Oxidative coupling, followed by oxidation and

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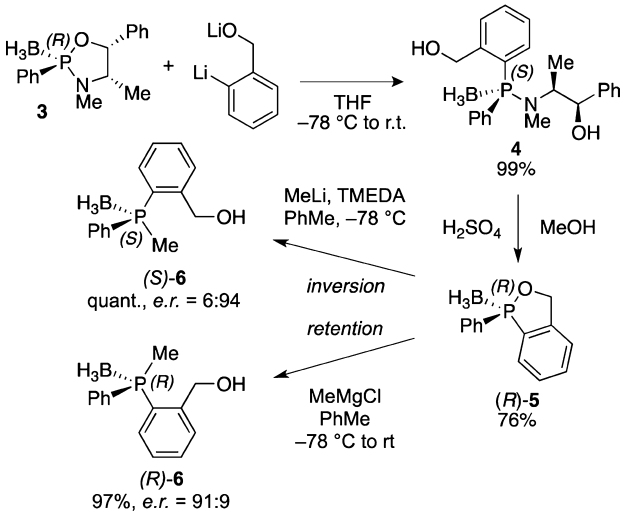
deprotection, gave the bis-*ortho*-formyl-substituted diphosphine (*S*,*S*)-**8** as a single enantiomer as described in detail below.

Synthesis of Dialdehyde (*S*,*S*)-8. The phosphorus−oxygen bond of **3** was cleaved with lithium (2-(oxidomethyl)-phenyl)lithium (prepared from (2-bromophenyl)methanol and ^{n}BuLi) to give the phosphinamine borane **4** with high diastereoselectivity (dr ≥ 95:5) and *retention* of configuration at phosphorus (Scheme 2).[32] The phosphorus−nitrogen bond

Scheme 2. Synthesis of Intermediates (*R*)- and (*S*)-6

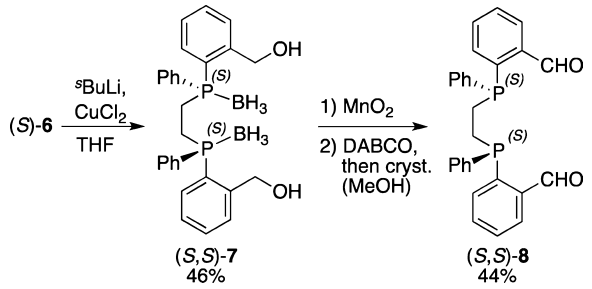


was subsequently cleaved in the presence of sulfuric acid in a *5-exo-tet* fashion to form the cyclic phosphinite borane (*R*)-**5** with the expected *inversion* of configuration (er = 95:5).[32a] Treatment of (*R*)-**5** (er = 95:5) with methyllithium or methylmagnesium chloride in toluene at −78 °C afforded the *retention* product (*R*)-(2-(methyl(phenyl)phosphino)phenyl)-methanol borane, (*R*)-**6** (Scheme 2), and is highly stereoselective (er = 90:10 and 91:9, respectively).

The formation of the *retention* product was unexpected, as acyclic analogues undergo selective cleavage of the P−O bond by S_N2 attack with *inversion* at phosphorus.[32] We attribute the formation of the *retention* product (*R*)-**6** to the coordination of the organometallic species to oxygen, followed by intramolecular *syn* addition/elimination similarly to the opening of **3**. Complete *inversion* was observed in the presence of TMEDA, which probably hinders the formation of the MeLi-substrate adduct and favors an S_N2 reaction (er = 6:94; see also Table S3). An analogous enantiodivergent synthesis of **6** from **3** has been developed independently by Stephan and Mohar, who also found that noncoordinating, apolar solvents are crucial for the stereoselective opening of (*R*)-**5**.[33] The phosphine borane (*S*)-**6** was then oxidatively coupled to build the protected 1,2-diphosphine (*S*,*S*)-**7**,[32a] and the benzylic hydroxy groups were converted to formyl groups by oxidation with MnO_2 in EtOAc (Scheme 3). Due to its low stability, the resulting diformyl phosphine borane was deprotected without purification. Borane removal with DABCO, followed by recrystallization from hot methanol, gave diastereo-[34] and enantiomerically[35] pure (*S*,*S*)-**8** as a yellow, air-stable solid.[36] Overall, the protocol is highly enantioselective, gives access to both enantiomers of dialdehyde **8** in six steps and 15% overall yield, and can be applied on a multigram scale.

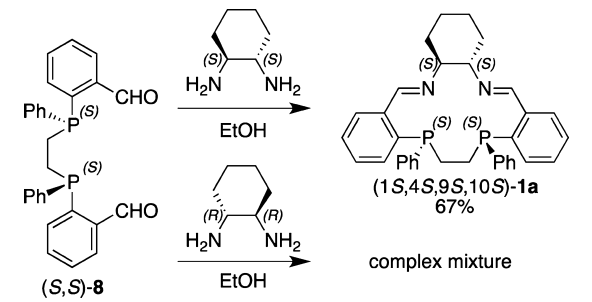
Synthesis of the Macrocyclic Ligands. The condensation of dialdehyde (*S*,*S*)-**8** with chiral diamines was investigated in a

Scheme 3. Synthesis of Diphosphine (*S*,*S*)-8



next step. We first studied the macrocyclization with both enantiomers of (*l*)-cyclohexane-1,2-diamine and (*l*)-1,2-diphenylethane-1,2-diamine under high dilution conditions (0.01 M) in EtOH. The reaction with (1*S*,2*S*)-cyclohexane-1,2-diamine gave a single species in the $^{31}P\{^{1}H\}$ NMR, which crystallized from the solution after concentration. The macrocyclic N_2P_2 ligand (1*S*,4*S*,9*S*,10*S*)-**1a** was isolated in 67% yield by simple filtration as a stable, off-white solid (Scheme 4).[36]

Scheme 4. Reaction of (*S*,*S*)-8 with (*l*)-Cyclohexane-1,2-diamine



No epimerization at phosphorus was observed in the solid state over several months, whereas heating in 1,2-dichloroethane at 100 °C for 24 h gave a 0.20:0.79:0.01 mixture of (S_P,S_P)-**1a**, (S_P,R_P)-**1a**, and (R_P,R_P)-**1a**. This indicates a strong thermodynamic preference for the C_1-symmetric isomers and underlines the difficulties in the preparation of C_2-symmetric N_2P_2 macrocycles such as (1*S*,4*S*,9*S*,10*S*)-**1a** or (1*S*,4*S*,9*R*,10*R*)-**1b** (see below). In contrast, the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution of (*S*,*S*)-**8** with (1*R*,2*R*)-cyclohexane-1,2-diamine shows several signals that are assigned to oligomeric species. Several attempts to isolate and purify these products failed. Similarly, only one enantiomer (in this case the (1*R*,2*R*)-enantiomer) of 1,2-diphenylethane-1,2-diamine formed a macrocycle with (*S*,*S*)-**8**, but the reaction is sluggish, and a catalytic amount of HCl was added to accelerate it (Scheme 5).

As before, the macrocyclic ligand (1*S*,4*S*,9*R*,10*R*)-**1b** precipitated upon concentrating the reaction solution and was isolated by filtration in 69% yield.[36] In the mismatched case with (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine, the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction shows several signals, which were assigned to oligomeric products. Macrocyclization attempts with both enantiomers of (*l*)-1,1′-binaphthyl-2,2′-diamine and (*l*)-1,3-diphenylethane-1,3-diamine, as well as with ethylene diamine and 2,3-dimethylbutane-2,3-diamine, gave no characterizable products.

Conformational Analysis of 1a and 1b. The X-ray structures of (1*S*,4*S*,9*S*,10*S*)-**1a** and (1*S*,4*S*,9*R*,10*R*)-**1b** indicate that both macrocycles adopt conformations in which the allylic

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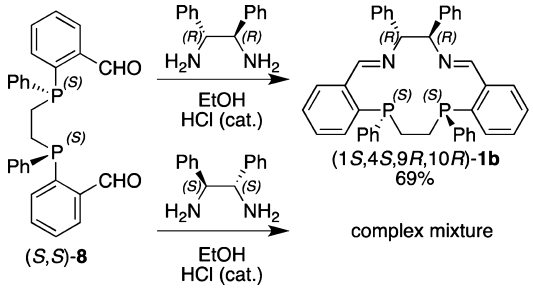
Scheme 5. Reaction of (*S*,*S*)-8 with (*l*)-1,2-Diphenylethane-1,2-diamine



1,3-strain between the imine C−H bonds and the tertiary carbon atoms of the diimino backbone is minimized (Figure 1).[37] The lone pairs of adjacent P and N donors point in

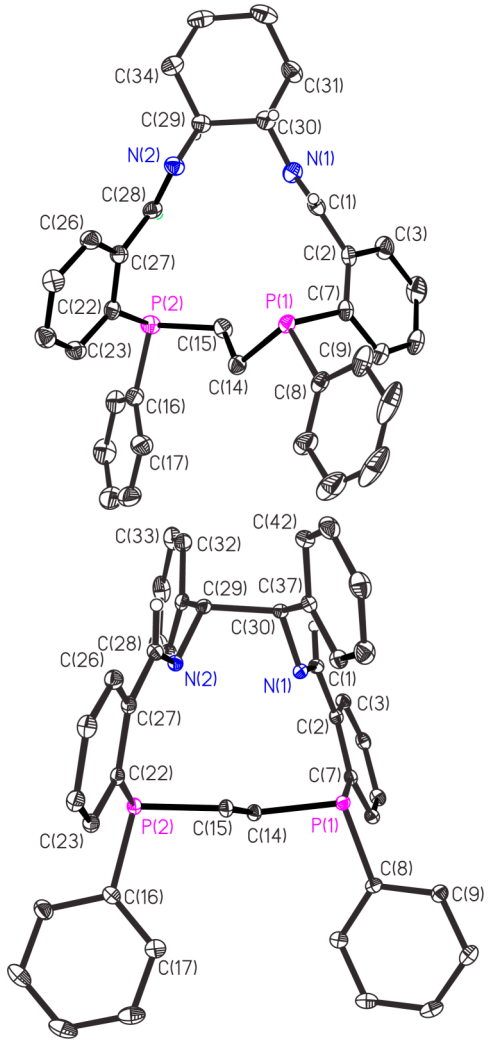
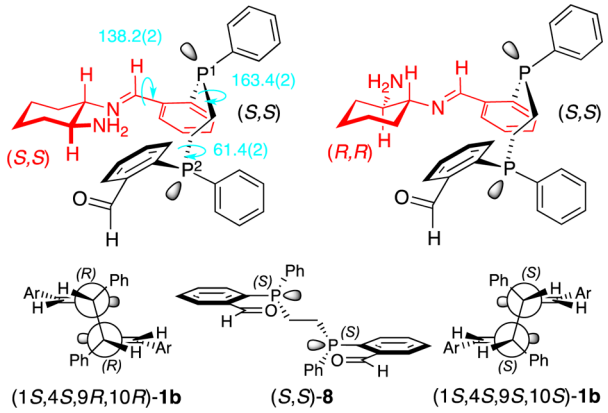


Figure 1. ORTEP drawing of (1*S*,4*S*,9*S*,10*S*)-**1a** (top) and (1*S*,4*S*,9*R*,10*R*)-**1b** (bottom) (with ellipsoids at 30% probability).

opposite directions of the macrocycle (1*S*,4*S*,9*S*,10*S*)-**1a**, as indicated by the N(1)−C(1)−C(2)−C(7) and N(2)−C(28)−C(27)−C(22) torsion angles (−138.2(2)° and −158.0(2)°, respectively). Assuming that the conformational preferences observed for macrocycle (1*S*,4*S*,9*S*,19*S*)-**1a** also apply for the intermediate in which the first imine bond has already formed (Chart 4, top), it is apparent that the most stable conformer of the (S_P,S_P)/(S_C,S_C)-diastereoisomer is stereochemically pre-

Chart 4. Conformational Analysis of 1a (before Ring Closure, Top) and of 1b (Bottom)

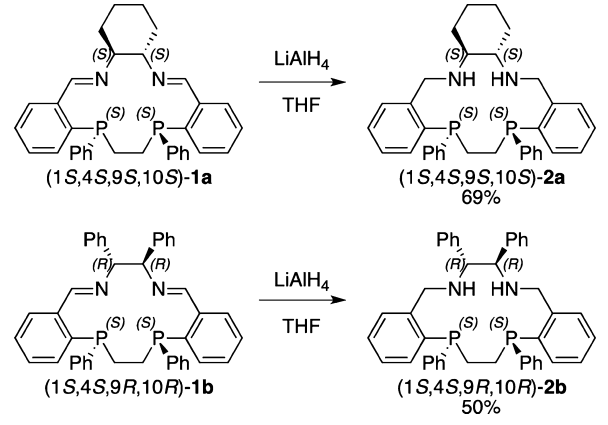


pared for the second condensation step and thus for macrocyclization, whereas the most stable conformer of the (S_P,S_P)/(R_C,R_C)-diastereoisomer needs to rearrange to a less stable structure to cyclize since the free amine is pointing away from the aldehyde.

For (1*S*,4*S*,9*R*,10*R*)-**1b**, the analysis is carried out on the macrocycle, and not the macrocyclization step, because the use of HCl as catalyst yields the thermodynamic product. The allylic 1,3-strain between the imine C−H bond and the tertiary carbon centers of the diimino backbone carrying mutually *trans* phenyl groups enforces a conformation of dialdehyde (*S*,*S*)-**8** that can accommodate only the (1*R*,2*R*)-enantiomer of 1,2-diphenylethane-1,2-diamine in the macrocycle (Chart 4, bottom).

Reduction to Diamino Macrocycles. As in some cases the diamino analogues of PNNP ligands have been more successfully employed in asymmetric catalysis,[38] we also investigated the reduction of the imine moieties using different hydride sources (Scheme 6). The imine reduction turned out to be delicate, as reduction with $NaBH_4$ in EtOH at elevated temperatures led to epimerization at phosphorus.[39] The reaction with $LiAlH_4$ in THF gave the diamino analogues (1*S*,4*S*,9*S*,10*S*)-**2a** and (1*S*,4*S*,9*R*,10*R*)-**2b** as off-white solids in modest yield. Therefore, the reactions were run on a small

Scheme 6. Synthesis of the Diamino Macrocycles (1*S*,4*S*,9*S*,10*S*)-2a and (1*S*,4*S*,9*R*,10*R*)-2b



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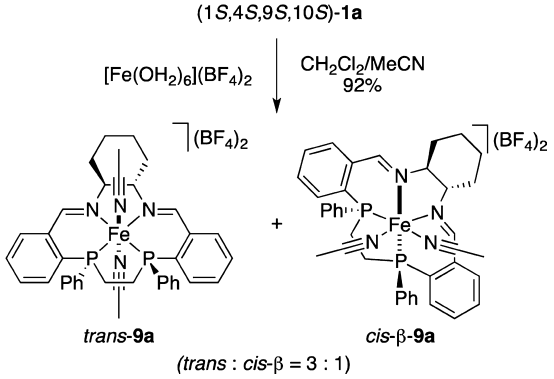
scale, and (1*S*,4*S*,9*S*,10*S*)-**2a** and (1*S*,4*S*,9*R*,10*R*)-**2b** were not purified further. We were not able to obtain X-ray-quality crystals of the diamino ligands for comparison with **1a**, **1b**, and the C_1-symmetric analogue (1*R*,4*S*,9*S*,10*S*)-**2a**.[28]

Bis(acetonitrile) Complex [Fe(MeCN)$_2$(1a)](BF$_4$)$_2$ (9a). The cyclohexane-based macrocycle (1*S*,4*S*,9*S*,10*S*)-**1a** reacts with $[Fe(OH_2)_6](BF_4)_2$ in CH_2Cl_2/MeCN at room temperature to give the diamagnetic dicationic complex [Fe(MeCN)$_2$((1*S*,4*S*,9*S*,10*S*)-**1a**)](BF$_4$)$_2$ (**9a**), whose formation is indicated by an immediate color change to dark red. Complex **9a** exists in solution as a ca. 3:1 mixture of *trans* and *cis*-*β* isomers (Scheme 7), as indicated by the $^{31}P\{^1H\}$ spectrum of the reaction solution, which shows a singlet for the *trans* isomer at *δ* 93.4 (s) (78%).

Scheme 7. Synthesis of [Fe(MeCN)$_2$((1*S*,4*S*,9*S*,10*S*)-1a)](BF$_4$)$_2$ (9a)



An additional AB system (*δ* 96.8 (d, $^2J_{P,P'}$ = 41.3 Hz), 88.9 (d, $^2J_{P,P'}$ = 41.3 Hz), 22%) is assigned to the minor *cis*-*β* isomer. It should be noted that, of two possible *cis*-*β* isomers (Δ-*cis*-*β* and Λ-*cis*-*β*), only the Λ-*cis*-*β* isomer can be formed due to the (S_P,S_P)-configuration of the phosphorus stereocenters. The $^{31}P\{^1H\}$ NMR signals of **9a** are significantly shifted to lower field as compared to Morris' iron(II) PNNP complexes [Fe(MeCN)$_2$(**A**)](BF$_4$)$_2$ (*δ* 53.4 (s))[9a] and [Fe(MeCN)$_2$(**B**)](BPh$_4$)$_2$ (*δ* 72.6 (s)),[11b] which we attribute to the Δ_R contribution of the five-membered chelate ring between the two phosphines.[40]

Crystallization of the isomer mixture from MeCN/Et_2O gave pure *trans*-**9a**. Upon dissolving the crystals of the pure *trans* isomer in CD_2Cl_2, the room-temperature $^{31}P\{^1H\}$ NMR spectrum of the solution showed that a mixture of *trans* and *cis*-*β* isomers is formed with the same 3:1 ratio obtained in the synthesis described above. A $^{31}P-^{31}P$ EXSY experiment in CD_2Cl_2 showed no cross-peaks between the two isomers. After adding MeCN-d_3, the ^1H NMR signals of coordinated acetonitrile disappeared, and free acetonitrile was observed. We conclude that the observed isomers are in equilibrium with each other and that ligand exchange is slow on the NMR time scale.

The X-ray structure of *trans*-**9a**(SbF$_6$)$_2$ shows that the macrocyclic ligand (1*S*,4*S*,9*S*,10*S*)-**1a** is large enough to accommodate a low-spin iron(II) ion in the *trans* configuration (Figure 2).[41] The coordination to low-spin iron(II) forces the P···N distances to shrink from 4.531(2) and 5.057(2) Å in the free macrocycle (1*S*,4*S*,9*S*,10*S*)-**1a** to 4.123(6) and 4.118(5) Å in *trans*-**9a**(SbF$_6$)$_2$ (Table 1). Upon coordination, the macrocycle slightly flattens, as indicated by the torsion angles (Table S6), and adopts the typical "stepped" conformation observed for open-chain PNNP complexes.[9a,11a] The two acetonitrile ligands complete a slightly distorted octahedral coordination sphere. The Fe–P and Fe–N bond distances involved in the macrocyclic complex *trans*-**9a**(SbF$_6$)$_2$ are significantly shorter than in the related open-chain complex [Fe(MeCN)$_2$(**A**)](BF$_4$)$_2$ (Table 1),[9a] which indicates that the compression exerted by the macrocycle is significant.

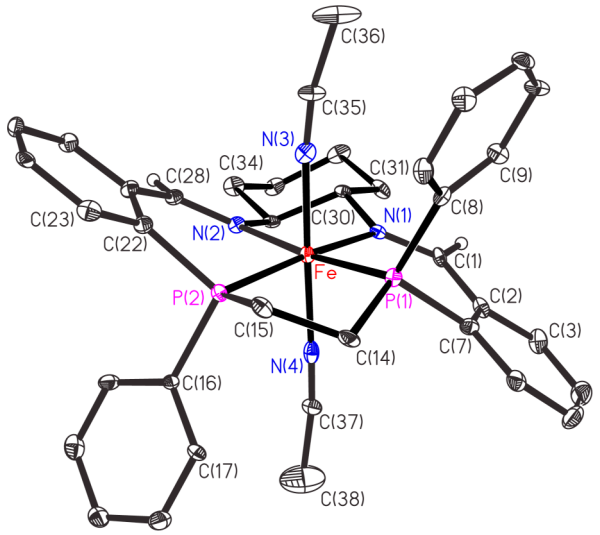
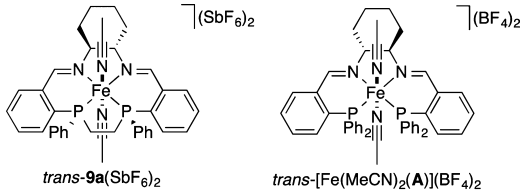


Figure 2. ORTEP drawing of the complex cation of *trans*-**9a**(SbF$_6$)$_2$ (with ellipsoids at 30% probability).

Table 1. Selected Bond Distances (Å) and Angles (deg) in *trans*-9a(SbF$_6$)$_2$ and *trans*-[Fe(MeCN)$_2$(A)](BF$_4$)$_2$[9a]



Fe–P(1)	2.1740(19)	2.276(2)
Fe–P(2)	2.1621(18)	2.272(2)
Fe–N(1)	1.963(5)	2.007(6)
Fe–N(2)	1.955(5)	2.010(6)
Fe–N(3)	1.909(6)	1.915(7)
Fe–N(4)	1.913(7)	1.904(4)
N(1)–Fe–N(3)	91.7(2)	91.4(3)
N(1)–Fe–N(4)	86.9(2)	85.4(3)
N(2)–Fe–N(3)	86.4(2)	86.2(3)
N(2)–Fe–N(4)	94.0(2)	90.9(3)

Bis(acetonitrile) Complex [Fe(MeCN)$_2$(1b)](BF$_4$)$_2$ (9b). The reaction of (1*S*,4*S*,9*R*,10*R*)-**1b** with $[Fe(OH_2)_6](BF_4)_2$ in CH_2Cl_2/MeCN at room temperature is accompanied by an immediate color change to dark red and gives the diamagnetic, dicationic complex [Fe(MeCN)$_2$((1*S*,4*S*,9*R*,10*R*)-**1b**)](BF$_4$)$_2$ (**9b**) (Scheme 8). Complex **9b** exists exclusively as the *cis*-*β* isomer, as indicated by the AB system in the $^{31}P\{^1H\}$ NMR spectrum (*δ* 103.7 (d, $^2J_{P,P'}$ = 36.5 Hz), 91.4 (d, $^2J_{P,P'}$ = 36.5 Hz)). The chemical shift values suggest that one of the phosphines is *trans* to an imine and the other one *trans* to an

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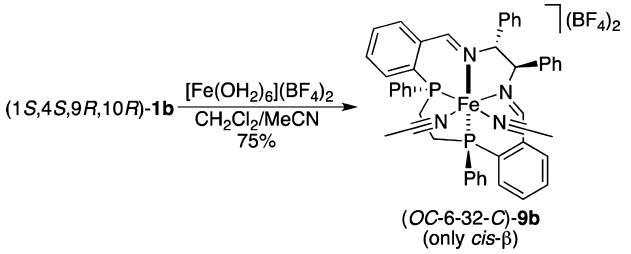
Scheme 8. Synthesis of [Fe(MeCN)$_2$((1*S*,4*S*,9*R*,10*R*)-1b)](BF$_4$)$_2$ (9b)

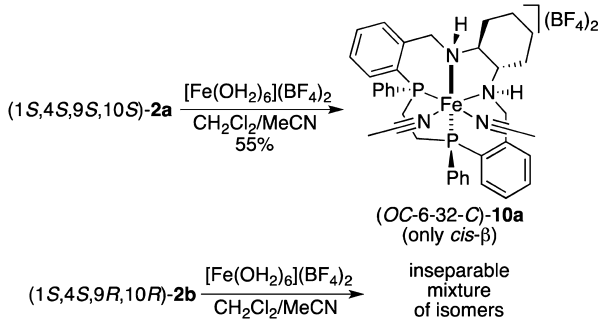


acetonitrile ligand. Again, the $^{31}P\{^1H\}$ NMR signals for **9b** are significantly shifted to lower field compared to analogous open-chain Fe(II)/PNNP complexes.[40] Attempts to grow X-ray-quality crystals of **9b** were unsuccessful.

At difference with macrocycle (1*S*,4*S*,9*S*,10*S*)-**1a**, which forms either *trans* or *cis*-*β* complexes, the 1,2-diphenylethylene-based ligand (1*S*,4*S*,9*R*,10*R*)-**1b** adopts the *cis*-*β* configuration in all complexes prepared so far (*vide infra*). In fact, the *trans* configuration of **9b** would cause strong nonbonded interactions of the acetonitrile ligands with the PPh_2 and with the axial phenyl groups of the diamine backbone. Such interactions are responsible for the slight angular distortions of *trans*-**9a**$(SbF_6)_2$ (Table 1) and would be more severe in the *trans* configuration of **9b** because of the pseudo-axial phenyl groups of the diamine backbone.

Bis(acetonitrile) Complexes [Fe(MeCN)$_2$(2)](BF$_4$)$_2$ (10). The reaction of the diamino ligand (1*S*,4*S*,9*S*,10*S*)-**2a** with $[Fe(OH_2)_6](BF_4)_2$ in CH_2Cl_2/MeCN gives the bis-(acetonitrile) complex [Fe(MeCN)$_2$((1*S*,4*S*,9*S*,10*S*)-**2a**)]-(BF$_4$)$_2$ (**10a**) as an orange solid in 55% yield after recrystallization from MeCN/Et_2O (Scheme 9). The complex-

Scheme 9. Synthesis of [Fe(MeCN)$_2$((1*S*,4*S*,9*S*,10*S*)-2a)](BF$_4$)$_2$ (10a)



ation of (1*S*,4*S*,9*S*,10*S*)-**2a** is much slower than with the diimino analogue (1*S*,4*S*,9*S*,10*S*)-**1a** and requires 2 days at 50 °C for completion, which can be attributed to the additional degrees of freedom caused by the reduction of the imine moiety.

Due to the two new stereocenters on the nitrogen atoms, five isomers (three *trans* and two Λ-*cis*-*β* isomers) are possible.[9c] Nevertheless, complex **10a** is formed as a single species, which is formulated as a *cis*-*β* isomer on the basis of its $^{31}P\{^1H\}$ NMR AB system (*δ* 103.3 (d, $^2J_{P,P'}$ = 19.6 Hz), 92.4 (d, $^2J_{P,P'}$ = 19.6 Hz)). The difference in chemical shift indicates that one phosphine is *trans* to acetonitrile and one is *trans* to amine. In contrast, (1*S*,4*S*,9*R*,10*R*)-**2b** reacts with $[Fe(OH_2)_6](BF_4)_2$ in MeCN at 50 °C for 2 days to give a complex mixture of products that we tentatively formulate as three isomers of [Fe(MeCN)$_2$((1*S*,4*S*,9*R*,10*R*)-**2b**)](BF$_4$)$_2$ (**10b**) (isomer A: *δ* 94.9 (d, $^2J_{P,P'}$ = 25.5 Hz), 92.2 (d, $^2J_{P,P'}$ = 25.5 Hz), 29%; isomer B: *δ* 94.2 (s), 42%; isomer C: *δ* 93.3 (d, $^2J_{P,P'}$ = 23.4 Hz), 78.5 (d, $^2J_{P,P'}$ = 23.4 Hz), 30%). As all attempts to obtain a single isomer by recrystallization failed, the complex was only characterized in CD_2Cl_2 solution by $^{31}P\{^1H\}$ NMR spectroscopy.

An X-ray analysis of crystals of **10a** (obtained from MeCN/Et_2O) confirmed the *cis*-*β* configuration (Figure 3). The

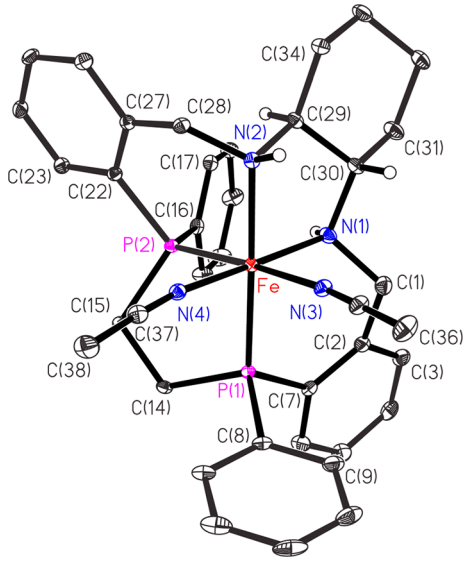


Figure 3. ORTEP drawing of the complex cation of **10a** (with ellipsoids at 30% probability).

absolute configuration of both nitrogen stereocenters was unambiguously assigned as R_N. Two acetonitrile ligands complete the octahedral coordination sphere, in which the largest deviations from the ideal octahedral geometry are observed for N(1)−Fe−N(2), P(1)−Fe−P(2), and N(1)−Fe−P(1) (85.26(8)°, 85.32(2)°, and 94.93(9)°, respectively). Interestingly, the P(1)−Fe−N(2) angle (178.38(6)°) is close to the ideal value, which shows that the ring size of the diamino macrocycle (1*S*,4*S*,9*S*,10*S*)-**2a** is not the reason for the preference of the *cis*-*β* configuration. In fact, for small N_2P_2 macrocycles (i.e., **F**), which favor the *cis*-*β* configuration, the angle between the *trans* ligands of the macrocycle and the metal is considerably reduced from the ideal value of 180°.[24] We assume that the change from sp^2 nitrogen in the diimino ligand (1*S*,4*S*,9*S*,10*S*)-**1a** to the sp^3 nitrogen in the diamino ligand (1*S*,4*S*,9*S*,10*S*)-**2a** increases the flexibility of the macrocycle and favors its bent *cis*-*β* configuration.

Similarly to the diimino analogue *trans*-**9a**$(SbF_6)_2$, the Fe−P and Fe−N bond distances to the macrocycle in **10a** are significantly shorter than in a related open-chain diamino complex (Table 2).[9c] The acetonitrile ligand *trans* to phosphorus is less tightly bound to iron (Fe−N(3), 1.962(2) Å) than the one *trans* to the amine (Fe−N(4), 1.927(2) Å). Also, the Fe−amine bond length *trans* to acetonitrile is shorter (Fe−N(1), 2.020(2) Å) than the one *trans* to phosphorus (Fe−N(2), 2.039(2) Å). Both findings reflect the higher *trans* influence of phosphorus as compared to nitrogen.

Bromocarbonyl Complex [FeBr(CO)(1a)]BPh$_4$ (11a). When treated with KBr (2 equiv) in acetone under a CO

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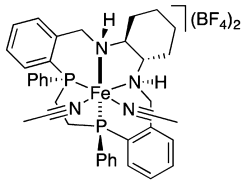
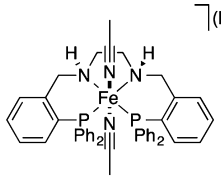
Table 2. Coordination Bond Distances in 10a and *trans*-[Fe(MeCN)$_2$(P(NH)(NH)P)](BF$_4$)$_2$[9c]



cis-β-**10a**(BF$_4$)$_2$

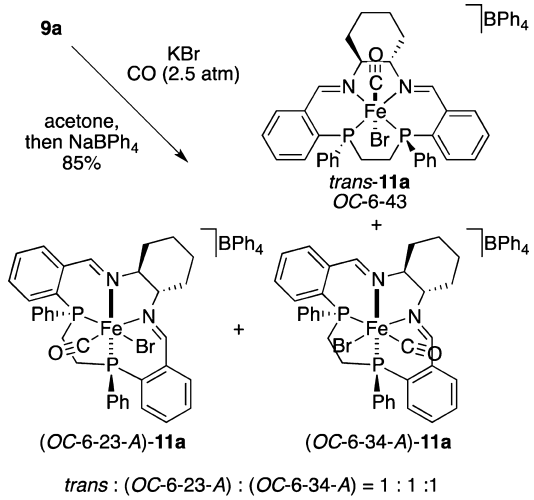


trans-[Fe(MeCN)$_2$(P(NH)(NH)P)](BF$_4$)$_2$

Fe–P(1)	2.1837(2)	2.3379(14)
Fe–P(2)	2.1724(6)	2.3221(15)
Fe–N(1)	2.020(2)	2.068(4)
Fe–N(2)	2.039(2)	2.087(3)
Fe–N(3)	1.962(2)	1.916(4)
Fe–N(4)	1.927(2)	1.890(4)

atmosphere at room temperature, the bis(acetonitrile) complex **9a** gives the bromocarbonyl derivative [FeBr(CO)((1*S*,4*S*,9*S*,10*S*)-**1a**)]$^+$, which was isolated as the tetraphenylborate salt [FeBr(CO)((1*S*,4*S*,9*S*,10*S*)-**1a**)]BPh$_4$ (**11a**) (Scheme 10). The ^{31}P{^{1}H} NMR spectrum of **11a** indicates

Scheme 10. Synthesis of [FeBr(CO)((1*S*,4*S*,9*S*,10*S*)-1a)]BPh$_4$ (11a)



the presence of three species in a ca. 1:1:1 ratio, which are formulated as the *trans* isomer (AB pattern; δ 89.7 (d, $^2J_{P,P'}$ = 46.9 Hz), 86.0 (d, $^2J_{P,P'}$ = 46.9 Hz); 42%) and two Λ-*cis*-β isomers. The two AX patterns are assigned to (*OC*-6–23-*A*)-**11a** (δ 96.7 (d, $^2J_{P,P'}$ = 37.4 Hz, P *trans* to Br), 91.2 (d, $^2J_{P,P'}$ = 37.4 Hz, P *trans* to imine); 30%) and to (*OC*-6–34-*A*)-**11a** (δ 84.8 (d, $^2J_{P,P'}$ = 31.7 Hz, P *trans* to imine), 76.3 (d, $^2J_{P,P'}$ = 31.7 Hz, P *trans* to CO); 28%) on the basis of the *trans* influence of the *trans* ligand.[42]

The SbF_6^- salt of one of the *cis*-β isomers of **11a** was crystallized and structurally characterized as (*OC*-6–34-*A*)-**11a**SbF$_6$ (CO *trans* to phosphorus, Br *trans* to imine, Figure 4).[41] As in **10a**, the coordination bond distances reflect the different *trans* influence of the ligands. The Fe–N(2) bond *trans* to phosphorus is longer than Fe–N(1) *trans* to bromide (2.010(5) vs 1.928(5) Å, respectively). Also, the Fe–P(1) bond *trans* to imine is significantly shorter than the Fe–P(2) bond *trans* to carbonyl (2.1708(17) vs 2.2413(16) Å, respectively).

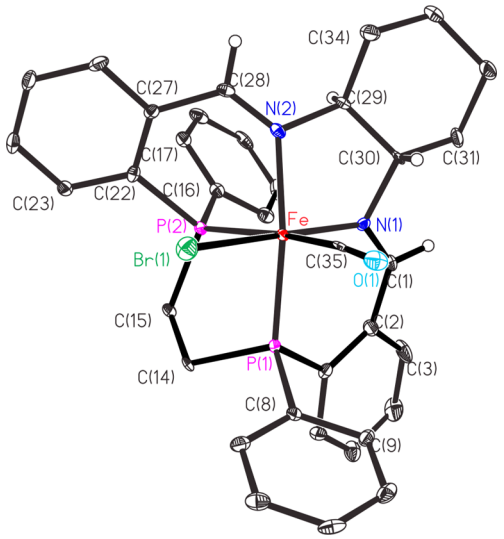


Figure 4. ORTEP drawing of the complex cation of (*OC*-6–34-*A*)-**11a**SbF$_6$ (with ellipsoids at 30% probability). Selected bond lengths (Å): Fe–N(1) 1.928(5), Fe–N(2) 2.010(5), Fe–P(1) 2.1708(17), Fe–P(2) 2.2413(16), Fe–Br(1) 2.437(1), Fe–C(35) 1.832(6), C(35)–O(1) 1.135(8).

This is in agreement with the ^{31}P{^{1}H} NMR spectrum, where P(2) resonates at higher field compared to P(1) (δ 76.3 vs 84.8, respectively).

The Fe–C(35) bond length (1.832(6) Å) is at the upper limit of the range observed for related complexes, which we attribute to the *trans* influence of the P(2) phosphine, whereas the C(35)–O(1) bond distance (1.135(8) Å) is unexceptional for Br/CO or MeCN/CO Fe(II) complexes (1.115(5)–1.165(8) Å).[9b,11b,f,h] The largest deviation from the ideal octahedral geometry involves the N(1)–Fe–P(2) angle, which opens up to 102.70(15)°, possibly due to the strain of the *cis*-β configuration. Hence, the C(35)–Fe–Br angle is compressed to 80.5(2)°. The N(2)–Fe–P(1) angle of 165.48(15)° is far off the ideal value of 180°, which suggests that the ring size of the rigid diimino ligand (1*S*,4*S*,9*S*,10*S*)-**1a** is at the lower end of the range required to accommodate the *trans* structure. In fact, small macrocycles (such as ligand **F** in Chart 3) favor the *cis*-β configuration.[24]

However, macrocycle (1*S*,4*S*,9*S*,10*S*)-**1a** must possess a certain degree of flexibility since both configurations (*trans* and *cis*-β) are accessible. The comparison of the geometry of ligand (1*S*,4*S*,9*S*,10*S*)-**1a** in *trans*-**9a**(SbF$_6$)$_2$ and (*OC*-6–34-*A*)-**11a**SbF$_6$ shows that only a few torsion angles change drastically (more than 15°; see Table 3). The distortions are localized in the C(29)–N(2)–C(28)–C(27) pivot around the imine and in the ethylene bridge between P(1) and P(2). Together, a ring-flip of the P(1)–Fe–P(2) chelate ring and a rotation around the N(2)–C(29) bond allow for the configuration change from *trans* to *cis*-β and explain the flexibility of (1*S*,4*S*,9*S*,10*S*)-**1a** (Figure 5).

Bromocarbonyl Complex [FeBr(CO)(1b)]BPh$_4$ (11b). The reaction of **9b** with KBr (2 equiv) under CO gives a single isomer, as judged by ^{31}P{^{1}H} NMR spectroscopy (δ 92.4 (d, $^2J_{P,P'}$ = 43.8 Hz), 91.2 (d, $^2J_{P,P'}$ = 43.8 Hz)), which was isolated as the tetraphenylborate salt [FeBr(CO)((1*S*,4*S*,9*R*,10*R*)-**1b**)]BPh$_4$ (**11b**). On the basis of the large difference in the $^2J_{P,C}$ coupling of the phosphines to CO in the ^{13}C{^{1}H} NMR spectrum (δ 212.7 (dd, $^2J_{P,C}$ = 58.9, 18.3 Hz)), the complex was

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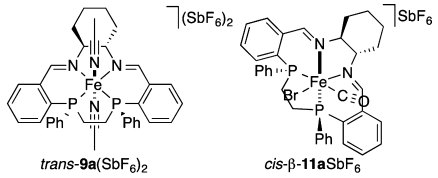
Table 3. Selected Torsion Angles of *trans*-9a$(SbF_6)_2$ and (*OC*-6-34-*A*)-11aSbF_6



C(29)–N(2)–C(28)–C(27)	−174.6(6)	155.1(5)
C(28)–N(2)–C(29)–C(30)	127.9(6)	178.7(5)
P(1)–C(14)–C(15)–P(2)	46.7(6)	−38.0(5)
C(14)–P(1)–C(7)–C(2)	151.4(6)	126.9(5)
C(15)–P(2)–C(22)–C(27)	155.7(5)	163.5(4)

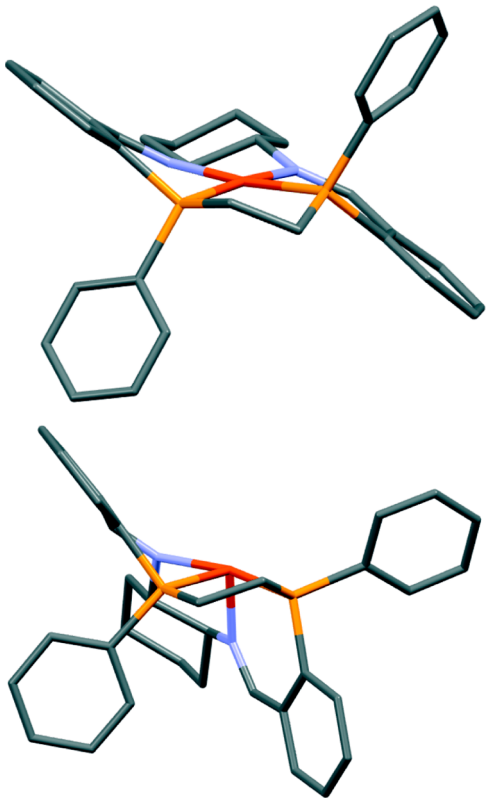
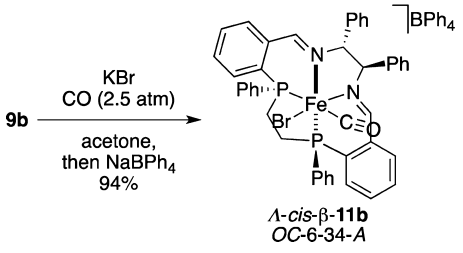


Figure 5. Comparison of ligand (1*S*,4*S*,9*S*,10*S*)-**1a** in the *trans* configuration (*trans*-**9a**$(SbF_6)_2$, top) and the *cis*-*β* configuration ((*OC*-6−34-*A*)-**11a**SbF_6, bottom).

formulated as the *cis*-*β* isomer with CO *trans* to phosphorus and Br *trans* to imine (*OC*-6−34-*A*, Scheme 11). Both, the other Λ-*cis*-*β* and the *trans* isomer should have similar coupling

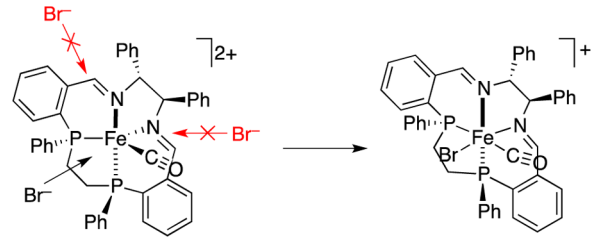
Scheme 11. Synthesis of [FeBr(CO)((1*S*,4*S*,9*R*,10*R*)-1b)]BPh_4 (11b)



constants (due to the two phosphines being *cis* to CO), resulting in a pseudo-triplet in the $^{13}C\{^1H\}$ NMR spectrum. Unfortunately, all attempts to obtain crystals of **11b** suitable for X-ray analysis failed.

The kinetic *cis*-*β* isomer (*OC*-6−34-*A*), which features mutually *trans* CO and phosphine ligands, is energetically unfavorable over the thermodynamic *cis*-*β* isomer with CO *trans* to imine and bromide *trans* to phosphorus. We explain the stereoselectivity by assuming that **11b** is formed with the intermediacy of [Fe(CO)(MeCN)((1*S*,4*S*,9*R*,10*R*)-**1b**)]$^{2+}$,[43] which then undergoes acetonitrile dissociation to give the 16-electron fragment [Fe(CO)((1*S*,4*S*,9*R*,10*R*)-**1b**)]$^{2+}$ (Scheme 12). We suggest that the latter five-coordinate species adopts a

Scheme 12. Stereochemistry of the Formation of 11b



distorted trigonal-bipyramidal structure with the *π*-accepting carbonyl ligand in the equatorial position because of the tendency of the (1*S*,4*S*,9*R*,10*R*)-**1b** macrocycle to adopt a *cis*-*β* configuration as discussed above. The two phenyl substituents of the diimino backbone, which are expected to be in a *trans* conformation, disfavor two out of three possible directions of bromide attack along the trigonal plane (in red in Scheme 12). In particular, they block the attack between phosphine and imine, which would result in a *trans*-complex, and also in between imine and CO, which would give the other Λ-*cis*-*β* isomer (bromide *trans* to phosphorus, CO *trans* to imine).

The attack along the sterically least congested direction (in between CO and phosphine) is consistent with the observed formation of the Λ-*cis*-*β* isomer with bromide *trans* to imine and CO *trans* to phosphorus. In contrast, in the sterically less demanding cyclohexane analogue (1*S*,4*S*,9*S*,10*S*)-**1a**, bromide can attack from all three directions, which explains the formation of a mixture of isomers for **11a**.

■ CONCLUSION AND OUTLOOK

The first enantiomerically pure C_2-symmetric, P-stereogenic, macrocyclic N_2P_2 ligands (1*S*,4*S*,9*S*,10*S*)-**1a** and (1*S*,4*S*,9*R*,10*R*)-**1b** were prepared by a straightforward, enantiodivergent synthesis, and their X-ray structures gave insight into the stereospecificity of the macrocyclization step. The marriage of interest between macrocyclic N_2P_2 ligands and iron(II) produces complexes that are monomeric, stable, and diamagnetic and that can be used as fully characterized catalyst precursors. We are currently exploring the potential of these complexes in the asymmetric hydrogenation of ketones. Depending on the diamine moiety and on the ancilliary ligands, the Fe(II) complexes adopt either *trans* and/or Λ-*cis*-*β* structures, which allows for rational design of the catalytic site. As the formation of the *cis*-*β* isomers partially follows from the relatively small size of the macrocycles, we are also preparing larger analogues that are expected to favor the exclusive formation of *trans* complexes.

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EXPERIMENTAL SECTION

General Procedures. Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques or in a glovebox under argon or purified nitrogen. All solvents were distilled from an appropriate drying agent under argon prior to use (CH_2Cl_2, CD_2Cl_2, MeOH, and MeCN from CaH_2; Et_2O, hexane, and THF from Na/benzophenone; toluene and EtOH from Na). ^1H and ^{13}C positive chemical shifts in ppm are downfield from tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra are referenced to external 85% H_3PO_4. For most complexes and for some ligands, $^{13}C\{^{31}P,^1H\}$ spectra were measured with ^{31}P (and ^1H) decoupling to improve the S/N ratio. Mass spectra were measured by the MS service of the Laboratory of Organic Chemistry (ETH Zürich). Elemental analyses were carried out by the Laboratory of Microelemental Analysis (ETH Zürich). (1*R*,2*R*)-1,2-Diphenylethylene-1,2-diamine and (1*S*,2*S*)-1,2-diphenylethylene-1,2-diamine were prepared by a literature procedure.[44] The preparation of *N*,*N*,*N*′,*N*′-tetraethyl-1-phenylphosphinediamine and (2*R*,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (**3**) is described in the Supporting Information. All commercially available materials were used as received.

(1*R*,2*S*)-2-(((*S*)-(2-(Hydroxymethyl)phenyl)(phenyl)-phosphino)(methyl)amino)-1-phenylpropan-1-ol Borane, 4. *n*-Butyllithium (545 mL, 1.6 M in hexanes, 871 mmol, 2.58 equiv) was added to a solution of 2-bromobenzyl alcohol (82.3 g, 440 mmol, 1.30 equiv) in tetrahydrofuran (1.3 L) at −78 °C over 0.5 h, and the solution was stirred at room temperature for 1 h. A THF solution (0.3 L) of **3** (96.5 g, 338 mmol) was added at −78 °C, and the mixture was warmed to room temperature over 6 h. Water (0.3 L) was added, and the organic phase was removed under reduced pressure. Saturated aqueous KH_2PO_4 solution (0.5 L) and aqueous 1 M HCl solution (0.5 L) were added, and the aqueous phase was extracted four times with dichloromethane (4 × 0.5 L). The combined organic phases were washed with saturated aqueous NaCl solution (1 L), dried over Na_2SO_4, and filtered, and hexane (1 L) was added. Dichloromethane was removed under reduced pressure to precipitate the product, which was crystallized overnight at −20 °C. The white solid was filtered off, dried at high vacuum, and used without further purification. Yield: 132 g (99%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.68−7.62 (m, 1H, Ar−*H*), 7.61−7.23 (m, 13H, Ar−*H*), 4.95 (dd, $^3J_{H,H'}$ = 4.0, 3.6 Hz, 1H, OC*H*), 4.69 (dd, $^2J_{H,H'}$ = 13.2 Hz, $^3J_{H,H'}$ = 6.7 Hz, 1H, OC*H*H), 4.61 (dd, $^2J_{H,H'}$ = 13.2 Hz, $^3J_{H,H'}$ = 6.9 Hz, 1H, OC*H*H), 4.30 (dqd, $^3J_{P,H}$ = 10.8 Hz, $^3J_{H,H'}$ = 6.9, 4.0 Hz, 1H, NC*H*), 2.67 (d, $^3J_{P,H}$ = 7.6 Hz, 3H, NCH_3), 2.46 (dd, $^3J_{H,H'}$ = 6.9, 6.7 Hz, 1H, CH_2OH), 1.98 (d, $^3J_{H,H'}$ = 3.6 Hz, 1H, CHO*H*), 1.27 (d, $^3J_{H,H'}$ = 6.9 Hz, 3H, CHCH_3), 1.87−0.42 (br m, 3H, BH_3). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 68.4 (br d, $^1J_{P,B}$ = 86 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 144.9 (d, $J_{P,C}$ = 12.5 Hz, arom.), 142.5 (arom.), 132.8 (d, $J_{P,C}$ = 6.8 Hz, arom.), 132.2 (d, $^1J_{P,C}$ = 73.6 Hz, arom.), 131.8 (d, $J_{P,C}$ = 10.2 Hz, arom.), 131.7 (arom.), 131.11 (arom.), 131.07 (d, $J_{P,C}$ = 11.7 Hz, arom.), 128.7 (d, $J_{P,C}$ = 10.2 Hz, arom.), 128.5 (d, $^1J_{P,C}$ = 61.2 Hz, arom.), 128.4 (arom.), 127.6 (arom.), 127.5 (d, $J_{P,C}$ = 8.8 Hz, arom.), 126.1 (arom.), 79.0 (d, $^3J_{P,C}$ = 2.6 Hz, OCH), 62.7 (d, $^3J_{P,C}$ = 4.9 Hz, OCH_2), 58.2 (d, $^2J_{P,C}$ = 9.6 Hz, NCH_3), 31.6 (d, $^2J_{P,C}$ = 2.9 Hz, NCH), 11.8 (d, $^3J_{P,C}$ = 4.2 Hz, $CHCH_3$). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −35.6 (*m*). Melting point: 120.5 °C. IR (liquid film, cm^{-1}): 3402 (O−H), 3060 (C−H), 2921 (C−H), 2386 (B−H), 2245, 1436, 1175, 1070, 1022, 1001, 951, 907. HRMS (ESI): calcd for $C_{23}H_{29}BNNaO_2P$ *m*/*z* 416.1925, found *m*/*z* 416.1926 $[M + Na]^+$. Anal. Calcd for $C_{23}H_{29}BNO_2P$: C, 70.24; H, 7.43; N, 3.56. Found: C, 69.99; H, 7.33; N, 3.60. R_f (EtOAc:hex = 3:7): 0.28.

(*R*)-1-Phenyl-1,3-dihydrobenzo[*c*][1,2]oxaphosphole-1-borane, (*R*)-5. Sulfuric acid (17.6 mL, 316 mmol, 0.95 equiv) was added to a solution of **4** (131 g, 333 mmol) in methanol (1.3 L) at 0 °C and warmed to room temperature overnight. The solution was concentrated to 0.3 L under reduced pressure and ethyl acetate (1.5 L) was added. The precipitated salts were filtered off, and the solvent was removed under reduced pressure. Flash column chromatography on silica gel (EtOAc:hex = 1:9) afforded the product as a colorless oil that solidified upon standing. Yield: 57.6 g (76%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.68−7.55 (m, 4H, Ar−*H*), 7.54−7.46 (m, 2H, Ar−*H*), 7.45−7.38 (m, 3H, Ar−*H*), 5.62−5.48 (m, 2H, CH_2), 1.90−0.30 (br m, 3H, BH_3). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 125.1 (br m). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 142.8 (d, $^2J_{P,C}$ = 12.1 Hz, arom.), 132.8 (d, $^1J_{P,C}$ = 47.6 Hz, arom.), 132.5 (d, $^4J_{P,C}$ = 2.3 Hz, arom.), 132.0 (d, $^4J_{P,C}$ = 2.4 Hz, arom.), 131.1 (d, $^2J_{P,C}$ = 11.9 Hz, arom.), 131.6 (d, $^1J_{P,C}$ = 59.0 Hz, arom.), 129.2 (d, $^3J_{P,C}$ = 9.9 Hz, arom.), 128.8 (d, $^3J_{P,C}$ = 10.1 Hz, arom.), 128.5 (d, $^2J_{P,C}$ = 13.6 Hz, arom.), 121.7 (d, $^3J_{P,C}$ = 8.6 Hz, arom.), 76.1 (d, $^2J_{P,C}$ = 9.5 Hz, CH_2). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −39.0 (m). Melting point: 97.5 °C. IR (liquid film, cm^{-1}): 3058 (C−H), 2938 (C−H), 2878 (C−H), 2375 (B−H), 2236, 1452, 1436, 1160, 1141, 1111, 1056, 982 (P−O−C). HRMS (ESI): calcd for $C_{13}H_{14}BNaOP$ *m*/*z* 251.0770, found *m*/*z* 251.0770 $[M + Na]^+$. Anal. Calcd for $C_{13}H_{14}BOP$: C, 68.47; H, 6.19. Found: C, 68.37; H, 6.14. HPLC: Chiralpak IC-3 (hexane/*i*-PrOH, 90:10, flow rate 1.0 mL/min, λ = 230 nm), retention times t_R(minor) = 8.2 min, t_R(major) = 9.6 min; 90% ee. $[\alpha]^{20}_D$: −20.3 (*c* 1.0, CH_2Cl_2). R_f (EtOAc:hex = 3:7): 0.52.

(*S*)-(2-(Methyl(phenyl)phosphino)phenyl)methanol Borane, (*S*)-6. The optimization of the nucleophilic opening of (*R*)-**5** is described in the Supporting Information. (*R*)-**5** (22.8 g, 100 mmol, 90% ee) in toluene (0.25 L) was added to a solution of methyllithium (156 mL, 1.6 M in Et_2O, 250 mmol, 2.5 equiv) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (45.0 mL, 300 mmol, 3.0 equiv) in toluene (1.1 L) at −78 °C over 5 h. After 1 h, 2-propanol (50 mL) and 1.5 M aqueous HCl solution (1.0 L) were added, and the aqueous phase was extracted twice with toluene (2 × 0.4 L). The combined organic phases were washed with saturated aqueous NaCl solution (0.5 L) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash column chromatography on silica gel (EtOAc:hex = 2:8) afforded the product as a clear oil. Yield: 23.7 g (97%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.68−7.39 (m, 9H, Ar−*H*), 4.71 (d, $^2J_{H,H'}$ = 13.3 Hz, 1H, OC*H*H), 4.40 (d, $^2J_{H,H'}$ = 13.3 Hz, 1H, OC*H*H), 2.17 (br s, 1H, O*H*), 1.89 (d, $^2J_{P,H}$ = 9.9 Hz, 3H, CH_3), 1.75−0.40 (br m, 3H, BH_3). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 8.4 (br m). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.0 (d, $^2J_{P,C}$ = 10.1 Hz, arom.), 132.1 (d, $^4J_{P,C}$ = 2.3 Hz, arom.), 131.9 (d, $^3J_{P,C}$ = 6.9 Hz, arom.), 131.6 (d, $^2J_{P,C}$ = 9.7 Hz, arom.), 131.4 (d, $^4J_{P,C}$ = 2.5 Hz, arom.), 131.3 (d, $^1J_{P,C}$ = 55.6 Hz, arom.), 130.7 (d, $^3J_{P,C}$ = 8.5 Hz, arom.), 129.1 (d, $^2J_{P,C}$ = 10.1 Hz, arom.), 128.0 (d, $^3J_{P,C}$ = 8.7 Hz, arom.), 127.6 (d, $^1J_{P,C}$ = 52.9 Hz, arom.), 62.9 (d, $^3J_{P,C}$ = 6.6 Hz, OCH_2), 13.6 (d, $^1J_{P,C}$ = 41.5 Hz, PCH_3). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −35.8 (m). IR (liquid film, cm^{-1}): 3444 (O−H), 3058 (C−H), 2922 (C−H), 2379 (B−H), 1437, 1418, 1133, 1035, 1000, 893. HRMS (ESI): calcd for $C_{14}H_{18}BNaOP$ *m*/*z* 267.1083, found *m*/*z* 267.1086 $[M + Na]^+$. HPLC: Chiralpak IC-3 (hexane/*i*-PrOH, 90:10, flow rate 1.0 mL/min, λ = 230 nm), retention times t_R(minor) = 14.6 min, t_R(major) = 18.2 min; 87% ee. $[\alpha]^{20}_D$: +19.1 (*c* 1.0, CH_2Cl_2). R_f (EtOAc:hex = 3:7): 0.34.

(((1*S*,1′*S*)-Ethane-1,2-diylbis(phenylphosphinediyl))bis(2,1-phenylene))dimethanol Diborane, (*S*,*S*)-7. *sec*-Butyllithium (36.0 mL, 1.3 M in cyclohexane/hexane (92:8), 46.8 mmol, 2.1 equiv) was added at 0 °C over 15 min to (*S*)-**6** (5.44 g, 22.3 mmol, 87% ee) in THF (110 mL) and stirred for 1 h. Copper(II) chloride (3.40 g, 24.5 mmol, 1.1 equiv) was added to the vigorously stirred solution at −78 °C, and the mixture was warmed overnight to room temperature. Water (50 mL) was added and THF was removed under reduced pressure. Aqueous 2 M HCl solution (50 mL) was added, and the aqueous phase was extracted five times with dichloromethane (5 × 50 mL). The combined organic phases were washed with saturated aqueous NaCl solution (100 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash column chromatography on silica gel (EtOAc:hex = 4:6) afforded the product as a white solid. Yield: 2.51 g (46%). NMR signals for the (*R*,*S*)-diastereoisomer are overlapping with those of the *like*-product. ^1H NMR (300 MHz, $CDCl_3$): δ 7.63−7.34 (m, 18H, Ar−*H*), 4.65 (d, $^2J_{H,H'}$ = 13.2 Hz, 2H, OC*H*H), 4.36 (d, $^2J_{H,H'}$ = 13.2 Hz, 2H, OC*H*H), 2.70−2.50 (m, 2H, PC*H*H), 2.36−2.09 (m, 4H, PC*H*H + O*H*), 1.85−0.30 (br m, 6H, BH_3). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 16.5 (br s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 145.2 (m, arom.), 132.7 (m,

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arom.), 132.4 (br s, arom.), 132.0 (m, arom.), 131.8 (br s, arom.), 131.1 (m, arom.), 129.3 (m, arom.), 128.8 (d, $^1J_{P,C}$ = 55.0 Hz, arom.), 128.2 (m, arom.), 125.8 (d, $^1J_{P,C}$ = 51.9 Hz, arom.), 63.0 (m, OCH_2), 20.3 (d, $^1J_{P,C}$ = 38.1 Hz, PCH_2). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ −37.5 (m). Melting point: 98.5 °C. IR (liquid film, cm^{-1}): 3387 (O−H), 3059 (C−H), 2380 (B−H), 2245 (B−H), 1437, 1107, 1059. HRMS (ESI): calcd for $C_{28}H_{38}B_2NO_2P_2$ m/z 504.2568, found m/z 504.2567 $[M + NH_4]^+$. Anal. Calcd for $C_{28}H_{34}B_2O_2P_2$: C, 69.18; H, 7.05. Found: C, 68.57; H, 8.07. Samples from different experiments gave similar results. HPLC: Chiralpak IC-3 (hexane/*i*-PrOH, 80:20, flow rate 1.0 mL/min, λ = 230 nm), retention times t_R((*R*,*R*)-7, minor) = 8.6 min, t_R((*R*,*S*)-7) = 9.6 min, t_R((*S*,*S*)-7, major) = 12.7 min; 97% ee, dr = 1:18. R_f (EtOAc:hex = 3:7): 0.09.

2,2′-((1*S*,1′*S*)-Ethane-1,2-diylbis(phenylphosphinediyl))-dibenzaldehyde Diborane, (*S*,*S*)-8·2BH$_3$. Activated manganese-(IV) oxide (207 g, 2.15 mol, 75 equiv) was added portionwise to (*S*,*S*)-7 (13.9 g, 28.6 mmol) in ethyl acetate (700 mL), and the mixture was stirred at room temperature in the dark for 4 h. The solution was filtered, and the residue washed with ethyl acetate (1 L). Careful removal of the solvent under reduced pressure afforded the product as an off-white solid, which was used directly without purification in the next step due to the low stability of the product. Yield: 10.3 g (74%). ^1H NMR (300 MHz, $CDCl_3$): δ 10.11 (s, 2H, O=C*H*), 8.12−7.86 (m, 4H, Ar−*H*), 7.81−7.66 (m, 4H, Ar−*H*), 7.63−7.28 (m, 10H, Ar−*H*), 2.86−2.58 (m, 2H, PC*H*H), 2.57−2.33 (m, 2H, PC*H*H), 1.90−0.30 (br m, 6H, BH_3). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 20.8 (br s). IR (liquid film, cm^{-1}): 3058 (C−H), 2920 (C−H), 2851 (C−H), 2383 (B−H), 1696 (C=O), 1436, 1198, 1107, 1058. R_f(EtOAc:hex = 3:7): 0.31.

2,2′-((1*S*,1′*S*)-Ethane-1,2-diylbis(phenylphosphinediyl))-dibenzaldehyde, (*S*,*S*)-8. 1,4-Diazabicyclo[2.2.2]octane (6.98 g, 62.2 mmol, 3.0 equiv) was added at 0 °C to (*S*,*S*)-**8**·2BH$_3$ (10.3 g, 20.7 mmol) in toluene (250 mL) and warmed to room temperature overnight. The solvent was removed under reduced pressure. Flash column chromatography on silica gel (EtOAc:hex = 2:8) and recrystallization from hot methanol afforded the product as a yellow solid. Yield: 5.64 g (60%). ^1H NMR (300 MHz, CD_2Cl_2): 10.54 (t, $^4J_{P,H}$ = 2.7 Hz, 2H, O=C*H*), 7.92−7.85 (m, 2H, Ar−*H*), 7.55−7.44 (m, 4H, Ar−*H*), 7.37−7.25 (m, 12H, Ar−*H*), 2.28−2.01 (m, 4H, PC*H*H). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2): δ −22.0 (s, (*S*,*S*)-**8**), −22.2 (s, (*R*,*S*)-**8**), dr > 99:1. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 192.2 (t, $^3J_{P,C}$ = 10.0 Hz, O=CH), 142.2 (m, arom.), 138.9 (m, arom.), 137.0 (m, arom.), 133.8 (arom.), 133.4 (m, arom.), 132.0 (arom.), 131.1 (m, arom.), 129.4 (arom.), 129.3 (arom.), 129.0 (m, arom.), 23.8 (d, $^1J_{P,C}$ = 3.9 Hz, PCH_2). Melting point: 129.5 °C. IR (liquid film, cm^{-1}): 3052 (C−H), 2918 (C−H), 2823, 2742, 1693 (C=O), 1584, 1482, 1433, 1198. HRMS (ESI): calcd for $C_{28}H_{25}O_2P_2$ m/z 455.1324, found m/z 455.1324 $[M + H]^+$. Anal. Calcd for $C_{28}H_{24}O_2P_2$: C, 74.00; H, 5.32; P, 13.63. Found: C, 73.81; H, 5.11; P, 13.51. HPLC: no sufficient separation achieved with standard columns. $[\alpha]^{20}_D$: +35.9 (*c* 1.0, CH_2Cl_2). R_f(EtOAc:hex = 3:7) = 0.45. For the determination of the enantiomeric purity, the product was converted to (((1*S*,1′*S*)-ethane-1,2-diylbis(phenylphosphinediyl))bis-(2,1-phenylene))dimethanol diborane, (*S*,*S*)-7. Sodium borohydride (8.2 mg, 0.22 mmol, 5.0 equiv) was added to (*S*,*S*)-**8** (19.8 mg, 43.6 μmol) in THF (1 mL) at 0 °C. After 1 h, borane dimethyl sulfide complex (21 μL, 0.22 mol, 5.0 equiv) was added, and the solution was stirred overnight at room temperature. Saturated aqueous NH_4Cl solution (20 mL) was added, and the aqueous phase was extracted three times with EtOAc (2 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl solution (30 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Flash column chromatography on silica gel (EtOAc:hex = 1:2) afforded the product as a white solid. Yield: 19.3 mg (91%). Analytical data are in agreement with the above data for (*S*,*S*)-7. HPLC: Chiralpak IC-3 (hexane/*i*-PrOH, 80:20, flow rate 1.0 mL/min, λ = 230 nm), retention times t_R((*R*,*R*)-7, minor) = 7.8 min, t_R((*R*,*S*)-7) = 9.7 min, t_R((*S*,*S*)-7, major) = 13.1 min; >99% ee, dr = 33:1. The presence of the (*R*,*S*)-isomer is attributed to racemization during the reduction.

(5*S*,8*S*,13*E*,14a*S*,18a*S*,19*E*)-5,8-Diphenyl-5,6,7,8,14a,15,16,17,18,18a-decahydrotribenzo[*b*,*f*,*l*][1,4,8,11]-diazadiphosphacyclotetradecine, (1*S*,4*S*,9*S*,10*S*)-1a. Diphosphine (*S*,*S*)-**8** (600 mg, 1.32 mmol) and (1*S*,2*S*)-cyclohexane-1,2-diamine (151 mg, 1.32 mmol, 1.0 equiv) were dissolved in ethanol (130 mL), and the solution was stirred for 48 h at room temperature. The solution was concentrated to 5 mL under reduced pressure, and the resulting white solid was filtered off and washed with ice-cold ethanol (10 mL). Yield: 470 mg (67%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.95 (s, 2H, N=C*H*), 7.78−7.72 (m, 2H, Ar−*H*), 7.44−7.24 (m, 16H, Ar−*H*), 3.51−3.39 (m, 2H, N−C*H*), 2.27−2.10 (m, 2H PC*H*H), 1.98−1.78 (m, 8H, PC*H*H + C*H*H), 1.57−1.45 (m, 2H, C*H*H). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2): δ −27.2 (s). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 161.3 (t, $^3J_{P,C}$ = 11.5 Hz, N=CH), 144.3 (m, arom.), 139.4 (m, arom.), 136.9 (m, arom.), 133.1 (arom.), 132.1 (m, arom.), 130.0 (arom.), 129.8 (arom.), 128.9 (m, arom.), 128.35 (m, arom.), 128.34 (arom.), 73.2 (N−CH), 33.5 ($NCHCH_2$), 25.0 ($NCHCH_2CH_2$), 22.0 (m, PCH_2). Melting point: 175.0 °C. IR (liquid film, cm^{-1}): 3052 (C−H), 2927 (C−H), 2855, 1636 (C=N), 1585, 1481, 1448, 1432, 1079. HRMS (ESI): calcd for $C_{34}H_{35}N_2P_2$ m/z 533.2270, found m/z 533.2269 $[M + H]^+$. Anal. Calcd for $C_{34}H_{34}N_2P_2$: C, 76.67; H, 6.43; N, 5.26; P, 11.63. Found: C, 76.45; H, 6.33; N, 5.11; P, 11.60.

(5*E*,7*R*,8*R*,9*E*,15*S*,18*S*)-7,8,15,18-Tetraphenyl-7,8,15,16,17,18-hexahydrodibenzo[*f*,*l*][1,4,8,11]-diazadiphosphacyclotetradecine, (1*S*,4*S*,9*R*,10*R*)-1b. Diphosphine (*S*,*S*)-**8** (500 mg, 1.10 mmol), (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (234 mg, 1.10 mmol, 1.0 equiv), and HCl (28 μL, 2 M in Et_2O, 56 μmol, 0.05 equiv) were dissolved in ethanol (110 mL), and the solution was stirred at room temperature for 40 h. The solution was concentrated to 20 mL under reduced pressure, and the resulting white solid was filtered off and washed with ice-cold ethanol (10 mL). Yield: 478 mg (69%). This material was used for complexation without purification. Analytically pure samples were obtained by recrystallization from dichloromethane/ethanol. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.17 (s, 2H, N=C*H*), 7.67 (d, $^2J_{H,H'}$ = 7.5 Hz, 4H, Ar−*H*), 7.56−7.49 (m, 4H, Ar−*H*), 7.47−7.10 (m, 18H, Ar−*H*), 7.02−6.95 (m, 2H, Ar−*H*), 4.97 (s, 2H, N−C*H*), 2.74−2.58 (m, 2H, PC*H*H), 2.39−2.24 (m, 2H, PC*H*H). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2): δ −9.2 (s). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 163.3 (N=CH), 141.9 (arom.), 140.8 (m, arom.), 138.8 (m, arom.), 138.4 (m, arom.), 134.2 (m, arom.), 133.7 (m, arom.), 133.5 (arom.), 130.0 (m, arom.), 129.2 (m, arom.), 129.0 (arom.), 128.8 (m, arom.), 128.6 (arom.), 128.5 (arom.), 127.5 (arom.), 85.0 (N−CH), 26.2 (m, PCH_2). Melting point: 205.0 °C (dec). IR (liquid film, cm^{-1}): 3046 (C−H), 2905 (C−H), 2842, 1631 (C=N), 1463, 1449, 1390, 1028. HRMS (MALDI): calcd for $C_{42}H_{37}N_2P_2$ m/z 631.2426, found m/z 631.2425 $[M + H]^+$. The crystals obtained by recrystallization contained CH_2Cl_2, which was not fully removed under high vacuum (ca. 0.77 equiv), as indicated by the integration of a one-pulse ^1H NMR spectrum in $CDCl_3$ (Figure S31). Anal. Calcd for $C_{42}H_{36}N_2P_2$·0.77(CH_2Cl_2): C, 73.84; H, 5.44; N, 4.03. Found: C, 73.53; H, 5.36; N, 3.81.

(5*S*,8*S*,14a*S*,18a*S*)-5,8-Diphenyl-5,6,7,8,13,14,14a,15,16,17,18,18a,19,20-tetradecahydrotribenzo[*b*,*f*,*l*][1,4,8,11]diazadiphosphacyclotetradecine, (1*S*,4*S*,9*S*,10*S*)-2a. (1*S*,4*S*,9*S*,10*S*)-**1a** (175 mg, 329 μmol) was added to a solution of lithium aluminum hydride (125 mg, 3.29 mmol, 10 equiv) in THF (3.3 mL), and the mixture was stirred overnight at room temperature. EtOAc (1 mL) was added followed, after 1 h, by a 1:1 mixture of sodium sulfate/Celite (1 g) and water (1 mL). After 2 h, the mixture was filtered with THF (50 mL) through a 1:1 pad of sodium sulfate/Celite, and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane (4 mL) and filtered, and hexane (15 mL) was added. The solution was concentrated to 2 mL under reduced pressure, and the resulting white solid was filtered off and washed with ice-cold hexane (4 mL). The compound was used in the next step without further purification (95% purity by integration of the $^{31}P\{^1H\}$ NMR spectrum). Yield: 121 mg (69%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.47 (ddd, $^3J_{P,H}$ = 8.9 Hz, $^3J_{H,H'}$ = 7.2 Hz, $^4J_{H,H'}$ = 1.9 Hz, 4H, Ar−*H*), 7.39 (ddd, $^3J_{P,H}$ = 7.4 Hz,

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$^{3}J_{H,H'}$ = 7.4 Hz, $^{4}J_{H,H'}$ = 1.5 Hz, 2H, Ar−*H*), 7.34−7.27 (m, 2H, Ar−*H*), 7.24−7.18 (m, 6H, Ar−H), 7.15−7.08 (m, 4H, Ar−H), 4.12 (d, $^{2}J_{H,H'}$ = 10.5 Hz, 2H, NC*H*H), 3.93 (d, $^{2}J_{H,H'}$ = 10.5 Hz, 2H, NC*H*H), 3.27−2.92 (br s, 2H, NH), 2.69−2.58 (m, 2H, NC*H*), 2.57−2.49 (m, 2H, PC*H*H), 2.36−2.24 (m, 4H, PC*H*H + NCHC*H*H), 1.85−1.76 (m, 2H, NCHC*H*H), 1.37−1.29 (m, 4H, NCHCH$_2$C*H*H). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ −30.9 (s). ^{13}C{^{31}P,^{1}H} NMR (126 MHz, CD_2Cl_2): δ 146.8 (arom.), 141.2 (arom.), 136.1 (arom.), 133.5 (arom.), 131.8 (arom.), 131.4 (arom.), 130.0 (arom.), 128.8 (arom.), 128.2 (arom.), 128.1 (arom.), 63.0 (NCH$_2$), 52.4 (NCH), 32.7 (PCH$_2$), 25.9 (CH$_2$), 24.5 (CH$_2$). Melting point: 169 °C. IR (liquid film, cm^{-1}): 3249 (N−H), 3052 (C−H), 2927 (C−H), 2853, 1461, 1433, 1265. HRMS (ESI): calcd for $C_{34}H_{39}N_2P_2$ *m*/*z* 537.2583, found *m*/*z* 537.2590 [M + H]$^{+}$.

(7*R*,8*R*,15*S*,18*S*)-7,8,15,18-Tetraphenyl-5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[*f*,*l*][1,4,8,11]diazadiphosphacyclotetradecine, (1*S*,4*S*,9*R*,10*R*)-2b. (1*S*,4*S*,9*R*,10*R*)-**1b** (90.0 mg, 143 μmol) was added to lithium aluminum hydride (1.8 mL, 2.4 M in THF, 4.3 mmol, 30 equiv), and the mixture was stirred for 2 days at 45 °C. THF (5 mL) and EtOAc (1 mL) were added followed, after 1 h, by a 1:1 mixture of sodium sulfate/Celite (1.5 g) and water (1 mL). After 2 h, the mixture was filtered with THF (50 mL) through a 1:1 pad of sodium sulfate/Celite, and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane (4 mL) and filtered, and hexane (15 mL) was added. The solution was concentrated to 2 mL under reduced pressure, and the resulting white solid was filtered off and washed with ice-cold hexane (4 mL). The compound was used in the next step without further purification. Yield: 45.6 mg (50%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.44−6.97 (m, 28H, arom.), 4.34 (d, $^{2}J_{H,H'}$ = 12.9 Hz, 2H, NC*H*H), 3.69 (s, 2H, NC*H*), 3.31 (d, $^{2}J_{H,H'}$ = 12.9 Hz, 2H, NC*H*H), 2.69−2.59 (m, 4H, PC*H*H), 2.51−2.22 (br s, 2H, N*H*). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ −20.5 (s). ^{13}C{^{31}P,^{1}H} NMR (126 MHz, CD_2Cl_2): δ 146.1 (arom.), 141.9 (arom.), 140.3 (arom.), 139.2 (arom.), 135.5 (arom.), 132.4 (arom.), 131.1 (arom.), 129.3 (arom.), 129.2 (arom.), 129.0 (arom.), 128.43 (arom.), 128.38 (arom.), 128.0 (arom.), 127.3 (arom.), 67.8 (NCH$_2$), 50.4 (NCH), 26.6 (PCH$_2$). Melting point: 145 °C (dec). IR (liquid film, cm^{-1}): 3316 (N−H), 3054 (C−H), 3026 (C−H), 2922 (C−H), 2849, 1453, 1433, 1130. HRMS (ESI): calcd for $C_{42}H_{41}N_2P_2$ *m*/*z* 635.2739, found *m*/*z* 635.2737 [M + H]$^{+}$.

[Fe(MeCN)$_2$((1*S*,4*S*,9*S*,10*S*)-1a)](BF$_4$)$_2$, 9a. A solution of [Fe(OH$_2$)$_6$](BF$_4$)$_2$ (218 mg, 626 μmol) in acetonitrile (16.7 mL) was added dropwise to a solution of (1*S*,4*S*,9*S*,10*S*)-**1a** (350 mg, 657 μmol, 1.05 equiv) in dichloromethane (8.3 mL). After stirring for 2.5 h at room temperature, the solvent was removed under reduced pressure. Recrystallization from acetonitrile/diethyl ether afforded the product as a crystalline orange solid. The product exists as a 3.5:1 mixture of *trans* and Λ-*cis*-β isomers. Yield: 486 mg (92%). ^{1}H NMR (700 MHz, CD_2Cl_2): δ 9.33−9.28 (m, 1H (minor), N=C*H*), 9.18 (d, $^{4}J_{P,H}$ = 3.7 Hz, 2H (major), N=C*H*), 8.52 (br s, 1H (minor), N=C*H*), 8.12−7.63 (m, 10H (major) + 6H (minor), Ar−*H*), 7.52−7.45 (m, 4H (minor), Ar−*H*), 7.42−7.26 (m, 8H (major) + 4H (minor), Ar−*H*), 7.14 (td, *J* = 7.9, 2.3 Hz, 2H (minor), Ar−*H*), 6.31−6.22 (m, 2H (minor), Ar−*H*), 4.27−4.20 (m, 1H (minor), N−C*H*), 4.06 (m, 2H (major), PC*H*H), 3.91−3.80 (m, 2H (major), N−C*H*), 3.61−3.28 (m, 2H (minor), PC*H*H), 3.14−3.08 (m, 1H (minor), N−C*H*), 2.90 (d, *J* = 4.5 Hz, 2H (major) + 1H (minor), NCHC*H*H (major) + PC*H*H (minor)), 2.69−2.50 (m, 2H (major) + 1H (minor), PC*H*H), 2.35−2.12 (m, 4H (major) + 2H (minor), NCHC*H*H (major) + NCHCH$_2$C*H*H (major) + C*H*H (minor)), 2.09−1.99 (m, 2H (minor), C*H*H), 1.96−1.92 (m, 1H (minor), C*H*H), 1.88 (s, 3H (minor), NC*H*$_3$), 1.84−1.80 (m, 1H (minor), C*H*H), 1.77 (s, 3H (minor), NC*H*$_3$), 1.71−1.60 (m, 2H (major), NCHCH$_2$C*H*H), 1.59−1.53 (m, 1H (minor), C*H*H), 1.39−1.21 (m, 1H (minor), C*H*H), 1.05 (s, 6H (major), NC*H*$_3$). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ 96.8 (d, $^{2}J_{P,P'}$ = 41.3 Hz, minor), 93.4 (s, major), 88.9 (d, $^{2}J_{P,P'}$ = 41.3 Hz, minor). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2): δ 172.6 (m, N=CH, minor), 170.3 (m, N=CH, minor), 169.8 (N=CH, major), 138.9 (m, arom., major), 138.6 (m, arom., major), 134.2 (arom., major), 133.3 (m, arom., major), 133.1 (arom., major), 131.5 (m, arom., major), 131.3 (arom., major), 131.2 (arom., major), 130.7 (m, arom., major), 130.3 (m, arom., major), 127.9 (m, CH_3CN, minor), 125.3 (m, CH_3CN, major), 121.4 (m, CH_3CN, minor), 76.6 (N−CH, minor), 73.0 (N−CH, major), 72.4 (N−CH, minor), 31.1 (NCHCH$_2$, minor), 30.4 (NCHCH$_2$, major), 30.1 (NCHCH$_2$, minor), 27.1 (m, PCH$_2$, minor), 25.7 (NCHCH$_2$CH$_2$, minor), 24.9 (NCHCH$_2$CH$_2$, minor), 24.7 (NCHCH$_2$CH$_2$, major), 24.4 (m, PCH$_2$, major), 21.3 (m, PCH$_2$, minor), 4.1 (*C*H$_3$CN, minor), 4.0 (*C*H$_3$CN, minor), 3.2 (*C*H$_3$CN, major). Signals of aromatic carbon atoms of the minor isomer are not resolved. IR (KBr, cm^{-1}): 3056 (C−H), 2993 (C−H), 2929 (C−H), 2862, 2295 (MeCN), 2280 (MeCN), 2250 (MeCN), 1624 (C=N), 1484, 1435, 1417, 1310. HRMS (MALDI): calcd for $C_{34}H_{34}FFeN_2P_2$ *m*/*z* 607.1531, found *m*/*z* 607.1524 [FeF((1*S*,4*S*,9*S*,10*S*)-**1a**)]$^{+}$. Anal. Calcd for $C_{38}H_{40}N_4B_2F_8FeP_2$: C, 54.07; H, 4.78; N, 6.64. Found: C, 53.91; H, 4.83; N, 6.72.

[Fe(MeCN)$_2$((1*S*,4*S*,9*R*,10*R*)-1b)](BF$_4$)$_2$, 9b. A solution of [Fe(OH$_2$)$_6$](BF$_4$)$_2$ (78.8 mg, 227 μmol) in acetonitrile (6.0 mL) was added dropwise to a solution of (1*S*,4*S*,9*R*,10*R*)-**1b** (150 mg, 238 μmol, 1.05 equiv) in dichloromethane (3.0 mL), and the mixture was stirred for 2.5 h at room temperature. The solvent was removed under reduced pressure. Recrystallization from acetonitrile/diethyl ether afforded the product as a crystalline red solid. The product exists only as the Λ-*cis*-β isomer. Yield: 160 mg (75%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.50−8.32 (m, 1H, N=C*H*), 8.19 (br s, 1H, N=C*H*), 8.08−7.23 (m, 23H, Ar−*H*), 6.81 (dd, *J* = 6.5, 3.0 Hz, 2H, Ar−*H*), 6.60−6.49 (m, 3H, Ar−*H*), 6.35 (d, $^{3}J_{H,H'}$ = 12.5 Hz, 1H, N−C*H*), 3.79−3.46 (m, 2H, PC*H*H), 3.38−3.26 (m, 1H, PC*H*H), 3.30 (d, $^{3}J_{H,H'}$ = 12.5 Hz, 1H, N−C*H*), 2.22−2.08 (m, 1H, PC*H*H), 2.15 (s, 3H, NC*H*$_3$), 1.75 (s, 3H, NC*H*$_3$). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ 103.7 (d, $^{2}J_{P,P'}$ = 36.5 Hz), 91.4 (d, $^{2}J_{P,P'}$ = 36.5 Hz). ^{13}C{^{31}P,^{1}H} NMR (126 MHz, CD_2Cl_2): 175.0 (N=CH), 170.8 (N=CH), 139.2 (arom.), 138.7 (arom.), 138.2 (arom.), 137.5 (arom.), 135.8 (arom.), 135.5 (arom.), 134.90 (arom.), 134.86 (arom.), 134.6 (arom.), 134.2 (arom.), 133.5 (arom.), 133.2 (arom.), 132.5 (arom.), 132.2 (arom.), 132.1 (arom.), 131.8 (arom.), 131.7 (arom.), 131.3 (arom.), 130.94 (arom.), 130.86 (arom.), 130.6 (arom.), 130.5 (arom.), 130.2 (arom.), 130.02 (arom.), 130.00 (arom.), 129.98 (arom.), 129.4 (arom.), 128.6 (arom.), 126.9 (*C*H$_3$CN), 119.9 (*C*H$_3$CN), 84.3 (N−CH), 78.7 (N−CH), 28.6 (PCH$_2$), 22.5 (PCH$_2$), 4.4 (*C*H$_3$CN), 4.1 (*C*H$_3$CN). IR (KBr, cm^{-1}): 3059 (C−H), 2932 (C−H), 2317 (MeCN), 2283 (MeCN), 2250 (MeCN), 1620 (C=N), 1603 (C=N), 1562, 1484, 1435, 1416, 1305. HRMS (MALDI): calcd for $C_{42}H_{36}FFeN_2P_2$ *m*/*z* 705.1682, found *m*/*z* 705.1686 [FeF(((1*S*,4*S*,9*R*,10*R*)**1b**)]$^{+}$. Anal. Calcd for $C_{46}H_{42}N_4B_2F_8FeP_2$: C, 58.64; H, 4.49; N, 5.95. Found: C, 57.86; H, 4.60; N, 5.41. Samples from different experiments gave similar results.

[Fe(MeCN)$_2$((1*S*,4*S*,9*S*,10*S*)-2a)](BF$_4$)$_2$, 10a. A solution of [Fe(OH$_2$)$_6$](BF$_4$)$_2$ (34.0 mg, 98 μmol) in acetonitrile (2.6 mL) was added dropwise to a solution of (1*S*,4*S*,9*S*,10*S*)-**2a** (55.0 mg, 102 μmol, 1.05 equiv) in dichloromethane (1.3 mL). After stirring for 2 d at 50 °C, the solution was filtered. Layering with diethyl ether afforded the product as a crystalline orange solid. The product exists as a single Λ-*cis*-β isomer. Yield: 45.0 mg (55%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.96 (t, *J* = 8.2 Hz, 1H, Ar−*H*), 7.76 (t, *J* = 7.5 Hz, 1H, Ar−*H*), 7.69−7.43 (m, 8H, Ar−*H*), 7.39−7.23 (m, 3H, Ar−*H*), 7.13 (dd, *J* = 7.6, 4.4 Hz, 1H, Ar−*H*), 7.00 (t, *J* = 6.7 Hz, 2H, Ar−*H*), 6.28 (t, *J* = 8.8 Hz, 2H, Ar−*H*), 6.09 (br d, $^{3}J_{H,H'}$ = 12.2 Hz, 1H, N*H*), 4.78 (d, $^{2}J_{H,H'}$ = 17.3 Hz, 1H, NC*H*H), 4.60 (d, $^{2}J_{H,H'}$ = 17.3 Hz, 1H, NC*H*H), 3.75−3.63 (m, 1H, NC*H*H), 3.54 (d, $^{2}J_{H,H'}$ = 17.6 Hz, 1H, NC*H*H), 3.53−3.31 (m, 2H, PC*H*H), 3.14−2.93 (m, 2H, PC*H*H), 2.66 (br d, $^{3}J_{H,H'}$ = 11.2 Hz, 1H, N*H*), 2.32−2.05 (m, 2H, C*H*H), 2.14 (s, 3H, NC*H*$_3$), 2.11 (s, 3H, NC*H*$_3$), 1.89−1.77 (m, 2H, NC*H* + C*H*H), 1.66−1.49 (m, 2H, NC*H* + C*H*H), 1.31−1.11 (m, 1H, C*H*H), 0.95−0.77 (m, 1H, C*H*H), 0.00 to −0.12 (m, 1H, C*H*H), −0.12 to −0.28 (m, 1H, C*H*H). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ 103.3 (d, $^{2}J_{P,P'}$ = 19.6 Hz), 92.4 (d, $^{2}J_{P,P'}$ = 19.6 Hz). ^{13}C{^{31}P,^{1}H} NMR (126 MHz, CD_2Cl_2): δ 142.5 (arom.), 141.9 (arom.), 136.5 (arom), 133.5 (arom.) 133.43 (arom.), 133.36 (arom.), 132.9 (arom.), 132.4 (arom.), 132.0 (arom.), 131.8 (arom.), 131.7 (arom.), 131.6 (arom.), 131.33 (arom.),

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131.29 (arom.), 130.5 (arom.), 130.2 (arom.), 129.9 (arom.), 129.8 (arom.), 129.5 (arom.), 128.9 (arom.), 127.4 (CH_3CN), 124.0 (CH_3CN), 66.0 (NCH_2), 65.4 (NCH_2), 53.5 (NCH), 50.2 (NCH), 31.3 (PCH_2), 30.2 (PCH_2), 27.4 ($NCHCH_2$), 27.2 ($NCHCH_2$), 25.0 ($NCHCH_2CH_2$), 24.7 ($NCHCH_2CH_2$), 5.1 (CH_3CN), 4.3 (CH_3CN). IR (liquid film, cm^{-1}): 3251 (N−H), 3236 (N−H), 3058 (C−H), 2938 (C−H), 1481, 1436, 1263. IR (KBr, cm^{-1}): 2170 (MeCN). HRMS (MALDI): calcd for $C_{34}H_{38}FFeN_2P_2$ m/z 611.1839, found m/z 611.1840 [FeF((1*S*,4*S*,9*S*,10*S*)-**2a**)]$^+$. Anal. Calcd for $C_{38}H_{44}B_2F_8FeN_4P_2$: C, 53.81; H, 5.23; N, 6.61. Found: C, 53.92; H, 5.13; N, 6.52.

[FeBr(CO)((1*S*,4*S*,9*S*,10*S*)-1a)]BPh$_4$, 11a. A solution of **9a** (455.5 mg, 540 μmol) and potassium bromide (128 mg, 1.08 mmol, 2.00 equiv) in acetone (13.8 mL) was stirred for 2 d under a CO atmosphere (2.5 bar). The solvent was removed under reduced pressure. The crude was dissolved in MeOH and filtered. Sodium tetraphenylborate (185 mg, 0.540 μmol, 1.00 equiv) in MeOH was added, and the orange precipitate was collected by filtration and washed with diethyl ether. The product exists as a ca. 0.42:0.30:0.28 mixture of the *trans* and the two Λ-*cis*-β isomers. Yield: 463.2 mg (85%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.04−8.96 (m, 2H, N=C*H*), 8.83−8.70 (m, 4H, N=C*H*), 7.97−6.81 (m, 105H, arom.), 6.31−6.15 (m, 7H, arom.), 6.07−5.56 (m, 2H, arom.), 4.30−4.14 (m, 3H, N−C*H*), 3.86−2.47 (m, 14H, N−C*H* + C*H*H), 2.37−1.72 (m, 15H, C*H*H), 1.56−1.09 (m, 8H, C*H*H), 0.99−0.84 (m, 2H, C*H*H). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ 96.7 (d, $^2J_{P,P'}$ = 37.4 Hz, *OC*-6−23-*A*, P *trans* to Br), 91.2 (d, $^2J_{P,P'}$ = 37.4 Hz, *OC*-6−23-*A*, P *trans* to imine), 89.7 (d, $^2J_{P,P'}$ = 46.9 Hz, *OC*-6−43), 86.0 (d, $^2J_{P,P'}$ = 46.9 Hz, *OC*-6−43), 84.8 (d, $^2J_{P,P'}$ = 31.7 Hz, *OC*-6−34-*A*, P *trans* to imine), 76.3 (d, $^2J_{P,P'}$ = 31.7 Hz, *OC*-6−34-*A*, P *trans* to CO). ^{13}C{^{31}P,^{1}H} NMR (126 MHz, CD_2Cl_2): due to the low solubility of **11a** in common solvents and the three C_1-symmetric isomers, no ^{13}C spectrum with sufficient S/N ratio could be obtained. ^{11}B{^{1}H} NMR (96 MHz, CD_2Cl_2): δ −6.6 (br s, BPh_4^-). IR (KBr, cm^{-1}): 3056 (C−H), 2983 (C−H), 2935 (C−H), 2859, 1974 (CO), 1610 (C=N), 1580 (C=N), 1561 (C=N), 1480, 1435, 1302, 1267, 1136, 1099, 1031, 999. HRMS (MALDI): calcd for $C_{36}H_{34}BrFeN_2OP_2$ m/z 695.0674, found m/z 695.0672 [FeBr(CO)((1*S*,4*S*,9*S*,10*S*)-**1a**)]$^+$. Anal. Calcd for $C_{59}H_{54}BBrFeN_2OP_2$: C, 69.78; H, 5.36; N, 2.76. Found: C, 68.54; H, 5.24; N, 2.80. A possible explanation for the low carbon content is combustion problems due to tetraphenylborate.[45]

[FeBr(CO)(1*S*,4*S*,9*R*,10*R*)-1b)]BPh$_4$ (11b). A solution of **9b** (100.0 mg, 106 μmol) and potassium bromide (25.3 mg, 212 μmol, 2.00 equiv) in acetone (5.3 mL) was stirred for 4 d under a CO atmosphere (2.5 bar). The solvent was removed under reduced pressure. The crude was dissolved in MeOH and filtered. Sodium tetraphenylborate (36.3 mg, 106 μmol, 1.00 equiv) in MeOH was added, and the orange precipitate was collected by filtration and washed with diethyl ether. Only one Λ-*cis*-β isomer was observed. Yield: 111.0 mg (94%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.37−8.31 (m, 1H, N=C*H*), 7.88 (br s, 1H, N=C*H*), 7.84−7.63 (m, 5H, Ar−*H*), 7.58−7.39 (m, 8H, Ar−H), 7.37−7.23 (m, 15H, Ar−H), 7.17−7.11 (m, 2H, Ar−*H*), 7.01−6.90 (m, 10H, Ar−*H*), 6.85−6.77 (m, 5H, Ar−*H*), 6.74 (dd, *J* = 6.1, 2.9 Hz, 1H, Ar−*H*), 6.53 (t, *J* = 8.7 Hz, 2H, Ar−*H*), 6.27 (d, $^3J_{H,H'}$ = 11.4 Hz, 1H, N−C*H*), 3.61−3.47 (m, 1H, PC*H*H), 3.38 (d, $^3J_{H,H'}$ = 11.4 Hz, 1H, N−C*H*), 3.34−3.14 (m, 1H, PC*H*H), 3.03−2.67 (m, 1H, PC*H*H), 2.56−2.38 (m, 1H, PC*H*H). ^{31}P{^{1}H} NMR (122 MHz, CD_2Cl_2): δ 92.4 (d, $^2J_{P,P'}$ = 43.8 Hz), 91.2 (d, $^2J_{P,P'}$ = 43.8 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 212.7 (dd, $^2J_{P,C}$ = 58.9, 18.3 Hz, CO), 173.7 (d, $^3J_{P,C}$ = 2.9 Hz, N=CH), 171.5 (d, $^3J_{P,C}$ = 6.9 Hz, N=C*H*), 164.6 (dd, $^1J_{B,C}$ = 98.6, 49.4 Hz, BC), 139.0 (d, $J_{P,C}$ = 11.7 Hz, arom.), 138.0 (d, $J_{P,C}$ = 13.3 Hz, arom.), 137.9 (d, $J_{P,C}$ = 5.9 Hz, arom.), 136.5 (BPh_4), 136.3 (arom.), 135.5 (m, arom.), 134.1 (d, $J_{P,C}$ = 7.4 Hz, arom.), 134.0 (arom.), 133.6 (m, arom.), 133.5 (m, arom.), 133.2 (d, $J_{P,C}$ = 5.9 Hz, arom.), 132.9 (arom.), 132.7 (d, $J_{P,C}$ = 8.8 Hz, arom.), 132.4 (d, $J_{P,C}$ = 9.5 Hz, arom.), 132.3 (arom.), 131.7 (arom.), 131.5 (d, $J_{P,C}$ = 9.8 Hz, arom.), 131.3 (m, arom.), 131.1 (d, $J_{P,C}$ = 12.9 Hz, arom.), 131.0 (arom.), 130.8 (m, arom.), 130.3 (arom.), 129.8 (m, arom.), 129.7 (arom.), 129.3 (arom.), 129.2 (arom.), 127.3 (arom.), 126.2 (m, BPh_4), 124.4 (d, $^1J_{P,C}$ = 47.7 Hz, arom.), 122.3 (BPh_4), 121.7 (d, $^1J_{P,C}$ = 32.0 Hz, arom.), 84.6 (N−CH), 84.1 (N−CH), 32.0 (dd, $^1J_{P,C}$ = 36.7 Hz, $^2J_{P,C}$ = 15.6 Hz, PCH_2), 20.4 (dd, $^1J_{P,C}$ = 29.2 Hz, $^2J_{P,C}$ = 11.4 Hz, PCH_2). IR (KBr, cm^{-1}): 3157 (C−H), 3052 (C−H), 2997 (C−H), 2981 (C−H), 1988 (CO), 1617 (C=N), 1579 (C=N), 1478, 1434, 1426, 1402, 1304, 1265, 1137, 1099, 1066, 1030, 998. HRMS (MALDI): calcd for $C_{42}H_{36}BrFeN_2P_2$ m/z 765.0883, found m/z 765.0885 [FeBr((1*S*,4*S*,9*R*,10*R*)-**1b**)]$^+$. Anal. Calcd for $C_{67}H_{56}BBrFeN_2OP_2$: C, 72.26; H, 5.07; N, 2.52. Found: C, 69.34; H, 4.92; N, 2.40. A possible explanation for the low carbon content is combustion problems due to tetraphenylborate.[45]

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, product characterization data, X-ray structures, and ^{1}H, ^{31}P, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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(35) The enantiomeric purity of (*S*,*S*)-**8** was determined after reduction with $NaBH_4$ and protection with $BH_3{\cdot}SMe_2$, yielding (*S*,*S*)-**7** with >99% ee (see also Experimental Section).
(36) No oxidation or epimerization was observed in the solid state over several months.
(37) Crystals of the diimino ligands (1*S*,4*S*,9*S*,10*S*)-**1a** and (1*S*,4*S*,9*R*,10*R*)-**1b** suitable for X-ray analysis were obtained by slow diffusion from CH_2Cl_2/EtOH and $CDCl_3$/hexane, respectively.
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(41) Crystals of (*OC*-6−33)-$[Fe(MeCN)_2$((1*S*,4*S*,9*S*,10*S*)-**1a**$)]$ $(SbF_6)_2$ (*trans*-**9a**$(SbF_6)_2$) and (*OC*-6−34-*A*)-[FeBr(CO)-((1*S*,4*S*,9*S*,10*S*)-**1a**)]SbF_6 (*cis*-*β*-**11a**SbF_6, CO *trans* to P) were obtained by treating a 1:1:1 mixture of isomers of [FeBr(CO)-

((1*S*,4*S*,9*S*,10*S*)-**1a**)]BPh_4 (**11a**) with Et_3OSbF_6 (1.0 equiv) in CD_2Cl_2 at room temperature. After stirring overnight, two of the three isomers (presumably (*OC*-6−43)-**11a** (*trans*-**11a**) and (*OC*-6−23-*A*)-**11a** (*cis*-*β*-**11a**, Br *trans* to P)) had disappeared. Addition of MeCN (20 equiv) and layering with Et_2O gave red crystals of (*OC*-6−33)-[$Fe(MeCN)_2$-((1*S*,4*S*,9*S*,10*S*)-**1a**)]$(SbF_6)_2$ (*trans*-**9a**$(SbF_6)_2$) and orange crystals of (*OC*-6−34-*A*)-[FeBr(CO)((1*S*,4*S*,9*S*,10*S*)-**1a**)]SbF_6 (*cis*-*β*-**11a**SbF_6, CO *trans* to P). Loss of CO in the presence of excess MeCN has previously been observed; see ref 9b.

(42) For the stereochemical notation of coordination compounds, see: *Nomenclature of Inorganic Chemistry: IUPAC Recommendations 2005*; Conelly, N. G.; Hartshorn, R. M.; Damhus, T.; Hutton, A. T., Eds.; RSC Publishing: Cambridge, 2005; pp 174−199.

(43) We assume that the reaction in Scheme 11 proceeds via intermediate $[Fe(CO)(MeCN)(\mathbf{1b})]^{2+}$ based on the observation that $[Fe(MeCN)_2(\mathbf{1b})]^{2+}$ does not react with KBr unless in the presence of CO; see also refs 11a and 11c.

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