

Inorganic Asymmetric Synthesis: Diastereoselective Syntheses of Mono- and Dinuclear Complexes Containing Octahedral, Two-Bladed Propeller, Bis(pyridine-2-aldehyde 2'-pyridylhydrazone)iron(II) Stereocenters

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A C_2 hexadentate diester derived from (5-hydroxymethyl)pyridine-2-aldehyde 2'-pyridylhydrazone (5-HOCH₂PAPHY) and an enantiomerically pure (aS)-spirane dicarboxylic acid diastereoselectively reacts with iron(II) benzenesulfonate in methanol to furnish a 20% diastereomeric excess (de) of a two-bladed propeller, octahedral iron complex in which the *P* configuration of the newly created (\pm) -[Fe(PAPHY)₂]²⁺ stereocenter predominates; when the reaction mixture is heated under reflux for 12 h, however, the excess of the diastereomer having the *P* configuration at iron increases to 80%, as determined by ¹H NMR spectroscopy. The configuration at iron in the major diastereomer of the complex was determined by comparison of the circular dichroism spectrum of the *deprotonated* complex with that of a related complex of known configuration. Repositioning of the hydroxymethyl group of the pyridine-2-aldehyde from the 5- to the 6-position produced a C_2 -spirane ligand that generates a double-stranded diiron(II) helicate in >99% de. Single crystal X-ray structure determinations of the racemates of the protonated and deprotonated helicates revealed that the complexes crystallize diastereoselectively, that is, two ligand strands of aS configuration generate two octahedral iron(II) stereocenters of *P* configuration to give a dinuclear metal helicate of *P* configuration and vice versa for the ligand of aR configuration.

Introduction

The first *inorganic* asymmetric synthesis was reported in 1948.¹ The reaction of (2*R*, 3*R*)-(+)-tartaric acid with [Co(en)₂CO₃]X (en = 1,2-diaminoethane; X = Cl, Br) resulted in unequal amounts of the diastereomers Δ- and Λ-[Co(en)₂{(+)-tartrate}]X (The bridging tartrato complex [(en)₂Co{(+)-tartrate}Co(en)₂]ClO₄ was later isolated from a similar reaction.²), which, when reacted with en gave Λ-(+)-[Co(en)₃]X₃; the reaction of the tartrato-chloride with hydrochloric acid gave Λ-(+)-[Co(en)₂Cl₂]Cl and, when reacted with calcium nitrite, the tartrato-bromide gave Λ-(+)-[Co(en)₂(NO₂)₂]Br. These reactions were claimed by the authors to be “the first examples of asymmetric synthesis in the field of inorganic complex ions.” Subsequent to this pioneering work on inorganic asymmetric synthesis,³ there were reports of the asymmetric synthesis of coordination

complexes by ligand substitution, mostly in cobalt(III) complexes⁴ but also in ruthenium(II) and osmium(II) complexes,⁵ electron transfer,⁶ and the involvement of chiral anions.⁷ There has also been a report of the asymmetric synthesis of Δ-[Co(bpy)₃](NO₃)₃ (bpy = 2,2'-bipyridine) by the silver nitrate oxidation of an equilibrating mixture of cobalt(II) complexes containing boronic acid-substituted bipyridine ligands in the presence of (*R*)-allose.⁸

There is also a long history of work concerning the stereoselective synthesis of chiral octahedral metal complexes by the *diastereoselective coordination* of nonracemic chelat-

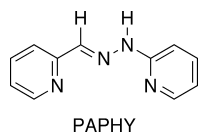
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(3) The syntheses reported in this work (inorganic asymmetric syntheses) are true asymmetric syntheses according to the term “asymmetric synthesis” defined by Marckwald in 1904, Marckwald, W. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1368 (as translated by Morrison and Mosher, H. S. *Asymmetric Organic Reactions*; American Chemical Society: Washington, DC, 1976; pp 4–6) and adopted by Helmchen (Helmchen, G. In *Methods of Organic Chemistry* (Houben-Weyl), Volume E 21a, pp 45–46) as follows: “asymmetric syntheses are those reactions, or sequence of reactions, which produce chiral nonracemic substances from achiral compounds with the intermediate use of nonracemic materials, but excluding a separation operation”.

ing diamines and diamine tetra(acetates).^{9,10} Recent work in this area has involved the synthesis of families of ligands containing pinene-2,2'-bipyridyl groups, the so-called chiraligens,¹² which have been employed with great effect for the diastereoselective synthesis of mononuclear metal complexes,¹³ as well as the self-assembly of helicates and chiral, square-shaped complexes.¹⁴

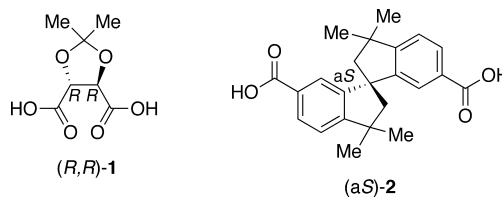


In other work, the diastereoselective synthesis of chiral tetrahedral and octahedral metal helicates has been achieved by the suspension of chelating entities from a chiral auxiliary or scaffold.¹⁵ Thus, a single asymmetric carbon stereocenter embedded in a di- or oligo-2,2'-bipyridyl ligand can facilitate

the self-assembly of double-stranded dinuclear metal helicates with kinetically labile metal ions such as copper(I) and silver(I) that favor tetrahedral coordination;¹⁶ axially chiral atropisomeric or spirocyclic auxiliaries of C_2 symmetry self-assemble chiral bis(2,2'-bipyridine)copper(I) stereocenters,¹⁷ and C_3 macrocyclic scaffolds from which three chelating hydroxamate¹⁸ or catecholato¹⁹ groups are suspended, generate configurationally pure C_3 -octahedral tris(bidentate)metal stereocenters.

We recently reported the first example of an inorganic asymmetric synthesis using the classical organic methodology of chiral auxiliary-directed asymmetric synthesis.²⁰ In this work, a C_2 -hexadentate in which two pyridine-2-aldehyde 2'-pyridylhydrazone (PAPHY)²¹ groups were linked to the (*R,R*)-tartaric acid-derived auxiliary (*R,R*)-**1**, as in (*R,R*)-**3H₂**, was reacted with iron(II) to give an octahedral, two-bladed propeller complex with complete diastereoselectivity, as determined by ¹H NMR spectroscopy and X-ray crystallography. Removal of the auxiliary by hydrolysis of the ester linkages, and deprotonation of the hydrazone-NH groups in the configurationally pure diastereomer of the resulting dipositive complex, afforded the corresponding neutral iron(II)–PAPHY complex with 85% retention of configuration at the iron(II) stereocenter and completed the asymmetric synthesis. The loss of configurational integrity at iron in the saponification step was attributed to racemization brought about by hydrolysis of the deprotonated PAPHY ligands in the product.

We report here our results concerning the diastereoselective synthesis of two-bladed propeller, octahedral mono- and dinuclear iron(II) complexes derived from pyridine-2-aldehyde 2'-pyridylhydrazone derivatives of the spirane dicarboxylic acid (a*S*)-**2**, namely, (a*S*)-**4H₂** and (a*S*)-**5H₂**.



Results and Discussion

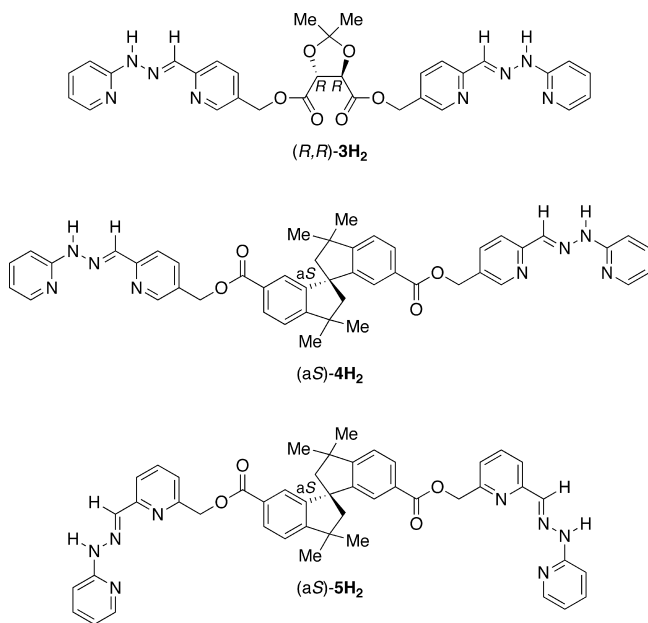
The unsymmetrical tridentate pyridine-2-aldehyde 2'-pyridylhydrazone (PAPHY) is a powerful chelating agent for most first-row, divalent transition metal ions, forming stable two-bladed propeller, octahedral complexes of the type $(\pm)\text{-[Fe(PAPHY)}_2\text{]X}_2$.²¹ We have previously investigated the configurational stability of chiral iron(II) stereocenters in complexes of this type by examining the ¹H NMR spectra of pairs of closely related complexes, where the appearance of resonances in the spectra for the corresponding ligand-crossover complexes indicated intermolecular ligand ex-

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change and loss of configurational integrity at iron.²⁰ On the basis of the ¹H NMR data obtained, it was determined that the half-life for intermolecular ligand exchange between complexes of the type (±)-[Fe(PAPHY)₂]X₂ was about 200 h at 25 °C and for the corresponding deprotonated complexes (±)-[Fe(PAPY)₂] it was considerably longer, a property of the complexes that made them attractive targets for asymmetric synthesis.

The configuration of a chiral cation of the type (±)-[M(PAPHY)₂]²⁺ can be assigned by viewing the molecule as a helix down the principal C₂ axis that bisects the terminal N—M—N angles (Figure 1). The twists of the ligand blades when viewed down this axis (from either direction) give the *actual* twist or helicity of the two-bladed propeller complex; a clockwise twist is assigned the *P* (plus) configuration and the anticlockwise twist the *M* (minus) configuration.¹² The spirocyclic auxiliary (±)-**2** contains a principal C₂ axis and the enantiomers can similarly be assigned a *P* or *M* configuration, although it is usual to assign the descriptors *aR* or *aS* to the enantiomers of spiranes on the basis of the Cahn—Ingold—Prelog (CIP) rules.²² (Note the negative correlation between the descriptors *P* and *aS* and *M* and *aR*, which is general for axially chiral molecules of C₂ symmetry.¹¹) The negative correlation also applies between *P* and *M* and the chirality symbols *A* (anticlockwise) and *C* (clockwise) within the configuration indices for chiral, octahedral bis(tridentate)metal complexes with use of the appropriate IUPAC convention.²³ Because of this discrepancy between the descriptors obtained by the different conventions, we have used here the *helicate descriptors P* and *M* to specify the configurations of axially chiral complexes of the type (±)-[Fe(PAPHY)₂]X₂. These descriptors have the advantage of corresponding to the *actual* twists of the molecules.



Ligand Syntheses. The ligands (aS)-**4H₂** and (aS)-**5H₂** were prepared as indicated in Schemes 1 and 2. Thus, bromination of (±)-**6**²⁴ with *N*-bromosuccinimide furnished the bis(bromo-

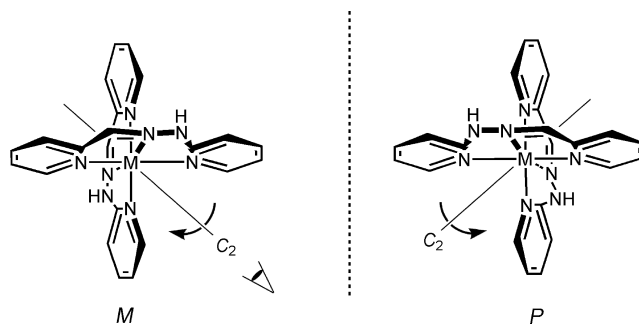


Figure 1. Configurational descriptors for chiral iron stereocenters in (±)-[Fe(PAPHY)₂]X₂.

methyl)spirane (±)-**7**. Hydrolysis of the bromomethyl groups in (±)-**7** with calcium carbonate and subsequent oxidation of the resulting diol (±)-**8** with potassium permanganate gave (±)-**2** in about 80% overall yield from (±)-**6**.

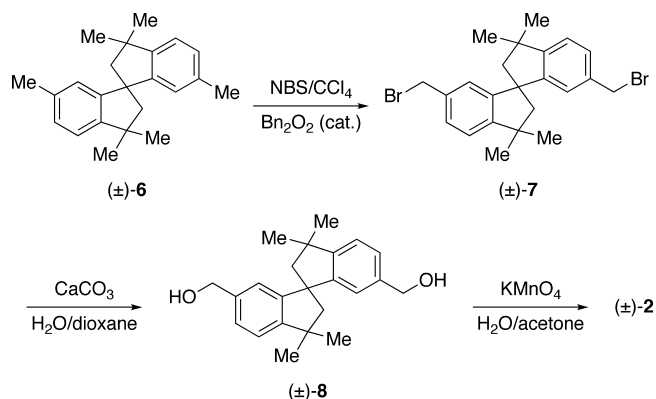
The resolution of (±)-**2** was carried out with (–)-brucine.²⁵ Small modifications to the reported procedure increased the yield of (aS)-**2** from 13% to 22% (of the possible 50%). The enantiomeric purity of the (aS)-**2**, which had $[\alpha]_D^{25} = -94.0$ (*c* 0.20, dioxane), was determined by chiral HPLC of the corresponding methyl ester. Base-line separation of the enantiomers of the racemate was achieved on a Chiralpak AS-H column with use of 5% *i*-propanol–*n*-hexane as eluant. Under similar conditions, the methyl ester of a sample of resolved (aS)-**2** gave a single peak, which indicates an enantiomeric excess (ee) >99%.

The ligands (aS)-**4H₂** and (aS)-**5H₂** were synthesized from (aS)-**2** in parallel with the corresponding racemates, as indicated in Scheme 2 for (aS)-**4H₂**. The optically active ligands were isolated as pale yellow microcrystals having mp 210–212 °C, $[\alpha]_D^{25} = -103.4$ (*c* 1.0, CHCl₃), (aS)-**4H₂**, and mp 201–203 °C, $[\alpha]_D^{25} = -76.8$ (*c* 1.0, CHCl₃), (aS)-**5H₂**.

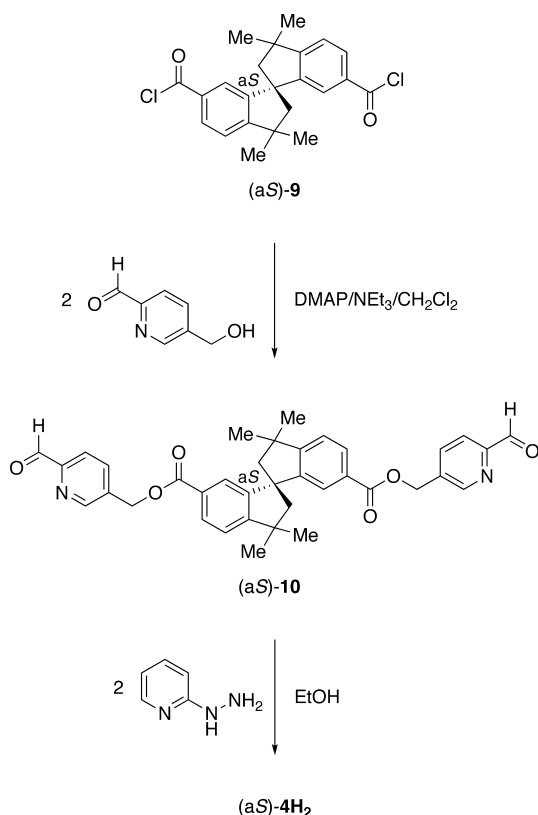
The crystal structure of (aS)-**4H₂**·2.5CHCl₃ was determined to confirm the absolute configuration of the molecule, there being no previously reported crystal structure of (aS)-**2** or a derivative. The *solvate* crystallizes as colorless blocks from chloroform–diethyl ether in the monoclinic space group C2 with one molecule of the spirane ligand and two and one-half chloroform molecules of crystallization in the crystallographic asymmetric unit (Table 1). The structure of (aS)-**4H₂** is shown in Figure 2. The molecules of crystallization are disordered in the lattice. Refinement of the Flack parameter allowed the absolute configuration of (aS)-**4H₂** to be determined and indirectly confirmed the absolute configuration of the dicarboxylic acid (aS)-**2**.

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Scheme 1



Scheme 2



Diastereoselective Syntheses of Iron(II) Complexes of (aS)-4H₂. A solution of hexaaquairon(II) benzenesulfonate in methanol was added to a suspension of an equimolar quantity of (aS)-4H₂ in the same solvent, whereupon the ligand dissolved and the solution turned vibrant red (Scheme 3). After 12 h at room temperature, the solution was heated for 12 h under reflux. The product was isolated from the solution by evaporation of the solvent. The high resolution electrospray mass spectrum (HR ES-MS) of the crude product indicated the exclusive formation of the 1:1 metal-to-ligand complex [Fe{(aS)-4H₂}] (PhSO₃)₂ (*m/z* 839.28 [M - 2PhSO₃ - H]⁺). The complex crystallizes from methanol-diethyl ether as a fine, dark red powder having mp >250 °C and [α]_D²⁵ = -2095 (*c* 0.015, MeOH). The addition of 2 equiv

Table 1. Crystallographic Data and Experimental Parameters for the X-ray Crystal Structure Analysis of (aS)-4H₂·2.5CHCl₃

molec formula	C _{49.5} H _{46.5} Cl _{7.5} N ₈ O ₄
fw, g mol ⁻¹	1083.36
cryst color, habit	colorless, block
cryst size, mm	0.24 × 0.24 × 0.20
space group	C2
cryst syst	monoclinic
<i>a</i> , Å	30.4763(8)
<i>b</i> , Å	16.5010(7)
<i>c</i> , Å	11.2234(4)
β, deg	100.813(2)
<i>V</i> , Å ³	5543.9(3)
<i>Z</i>	4
<i>d</i> _{calc} , g cm ⁻³	1.298
μ, cm ⁻¹	4.31
instrument	Nonius Kappa CCD
radiatn	Mo Kα
no. unique reflcns	8930
no. reflcns obsd	6405 (<i>I</i> > 3.00σ(<i>I</i>))
2θ range, deg	6–50
scan technique	φ and ω scans with CCD
temp, K	200
struct refinement	CRYSTALS ²⁹ /maXus ³⁰
final <i>R</i> , <i>R</i> _w	0.0644, 0.0755

of 10% aqueous sodium hydroxide to an aqueous solution of the complex generated the corresponding dark green–black, neutral, deprotonated complex [Fe{(aS)-4}], which was extracted into dichloromethane. The pure complex was obtained as a dark brown powder by the addition of *n*-hexane to the dichloromethane extract. Yield: >95%; mp >250 °C; [α]_D²⁵ = -612 (*c* 0.009, MeOH). The protonated and deprotonated forms of the complex are air-stable solids.

¹H NMR Spectra. Key regions of the ¹H NMR spectrum of crude (-)-[Fe{(aS)-4H₂}] (PhSO₃)₂ (isolated by evaporation after 12 h stirring of the reaction mixture in methanol at 25 °C) in methanol-*d*₄ at 25 °C are shown in Figure 3. Two singlets, one for each C₂-related pair of diastereotopic methyl groups, and an AB spin system for the spirane-CH₂ protons are expected for each diastereomer of the complex. Figure 3a shows the two sets of spirane-*Me* singlets in the region 1.3–1.5 ppm and the two AB quartets for the spirane-CH₂ groups in the region 1.9–2.5 ppm of the spectrum of the complex, which is consistent with the presence of the diastereomers (*P*_{Fe})- and (*M*_{Fe})-[Fe{(aS)-4H₂}] (PhSO₃)₂ in unequal proportions. The spectrum shown in Figure 3a was recorded for a sample of the complex isolated from a solution of the reactants after 12 h in methanol. Integration of the

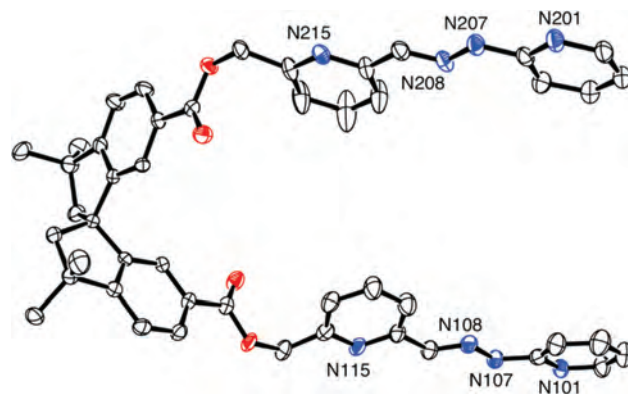
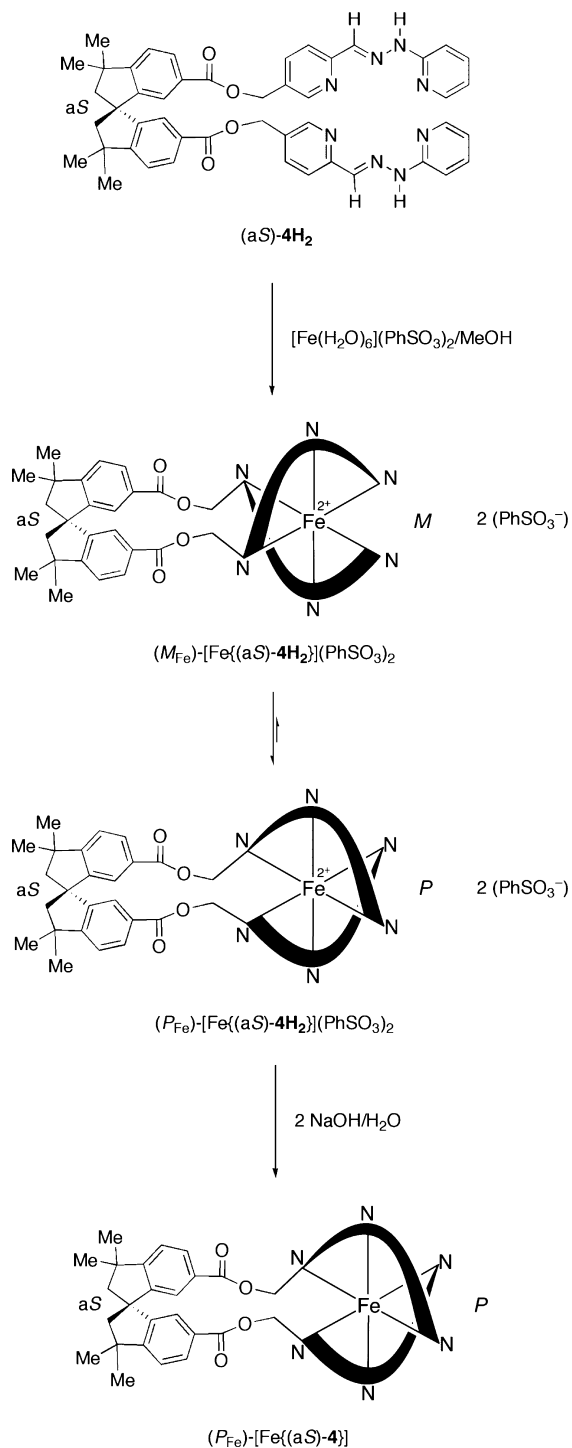


Figure 2. Structure of (aS)-4H₂ (thermal ellipsoids contain 30% probability levels).

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Scheme 3



resonances in the spectrum gave about 20% de of one diastereomer. A variety of experimental conditions were investigated in an attempt to improve the diastereoselectivity of the reaction. High dilution syntheses at room temperature and changing the anion and solvent employed did not increase the diastereoselectivity of the reaction. When the reaction mixture was heated for 12 h under reflux, however, there was a significant increase in the concentration of the major diastereomer, as indicated in the spectrum shown in Figure 3b. Integration of the two sets of resonances in this spectrum gave about 80% de for the major diastereomer.

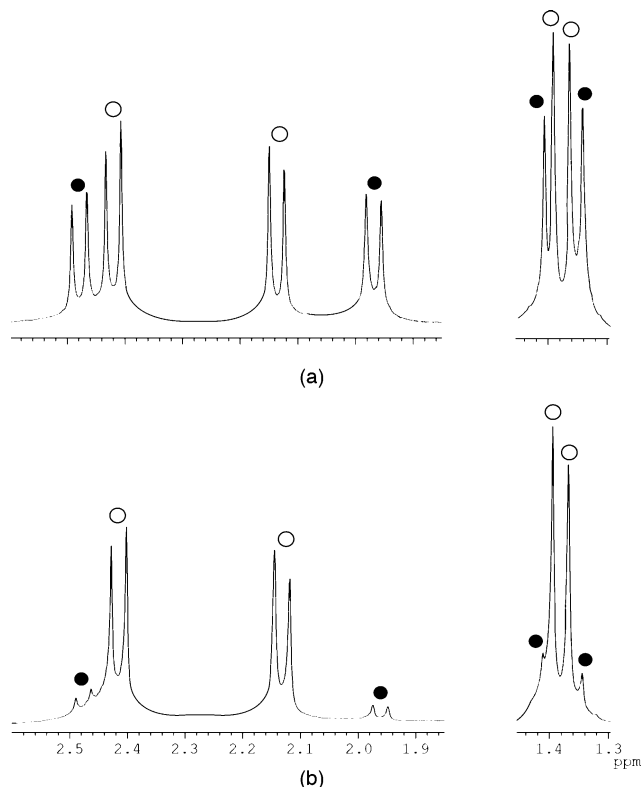


Figure 3. 1H NMR spectra (500 MHz, CD_3OD , 25 $^\circ C$): (a) crude (—) $[Fe\{(aS)\text{-}4H_2\}](PhSO_3)_2$ isolated after reaction had proceeded for 12 h in methanol at 25 $^\circ C$; (b) after 12 h heating of reaction mixture in methanol under reflux ($\circ = (P_{Fe})$, $\bullet = (M_{Fe})$).

Further heating of a solution of the 90:10 mixture under reflux in methanol (or ethanol, *i*-propanol, or *n*-butanol) did not improve this ratio, which established the major diastereomer as the kinetically and thermodynamically preferred product (Scheme 3). Deprotonation of the complex having about 80% de gave neutral (—) $[Fe\{(aS)\text{-}4\}]$ of similar de. The neutral complex was stable on an alumina column, but the diastereomers could not be separated with use of the usual eluents. Attempted fractional crystallizations of the mixtures of the protonated and deprotonated complexes were also unsuccessful.

Circular Dichroism Spectra. Circular dichroism (CD) spectroscopy was used to establish the configuration of the iron stereocenter in the major diastereomer of the neutral complex (—) $[Fe\{(aS)\text{-}4\}]$ by comparison with the spectrum of $(P_{Fe})\text{-}(+)\text{-}[Fe\{(R,R)\text{-}3\}]$, for which the crystal structure of the protonated complex $(P_{Fe})\text{-}(+)\text{-}[Fe\{(R,R)\text{-}3H_2\}]\text{-}(PhSO_3)_2 \cdot 2CH_3OH \cdot 3H_2O$ has been determined.²⁰ The CD spectra of the two neutral complexes in methanol at 18 $^\circ C$ are shown in Figure 4. Both complexes show strong Cotton effects between 350–600 nm and 200–300 nm. The similarity of the spectra in the metal-to-ligand charge transfer (MLCT) excitation regions for the two complexes is consistent with the *P* configuration at the metal stereocenter in the major diastereomer of (—) $[Fe\{(aS)\text{-}4\}]$. The free ligands show no absorptions in the MLCT excitation region.

Diastereoselective Syntheses of Diiron(II) Complexes of (aS)-5H₂. The iron(II) complex of enantiomerically pure (aS)-5H₂ was prepared by the addition of a methanol solution

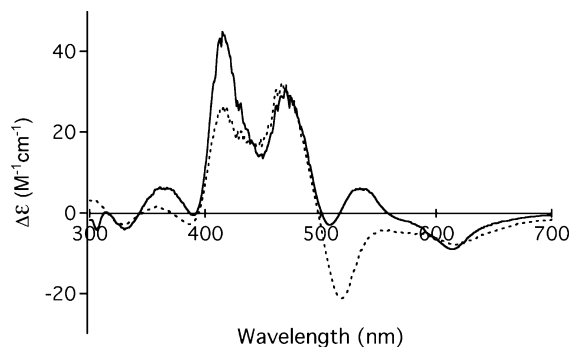


Figure 4. CD spectra of (–)-[Fe₂{(aS)-4}] (solid line) and (P_{Fe})-(+)-[Fe₂{(R,R)-3}] of established configuration (dashed line) in methanol at 18 °C.

of hexaaquairon(II) benzenesulfonate to a suspension of an equimolar quantity of the ligand in the same solvent (Scheme 4). Upon the addition of the iron salt, the reaction mixture turned deep red. The solution was stirred for 12 h at room temperature and the product was then isolated by evaporation of the solvent. The analytical data and the HR ES-MS of the crude product indicated the exclusive formation of the 2:2 metal-to-ligand complex [Fe₂{(aS)-5H₂}]₂(PhSO₃)₄ (*m/z* 839.77 ([M – 4PhSO₃ – 2H]²⁺), which had [α]_D²⁵ = –2000 (*c* 0.0168, MeOH). Treatment of the complex in ethanol with 4 equiv of a 10% aq sodium hydroxide led to the quantitative precipitation of the dark green-brown, deprotonated, organic soluble complex [Fe₂{(aS)-5}]₂, which had [α]_D²⁵ = +2228 and [α]_D³⁶ = +3079 (*c* 0.016, MeOH). The corresponding racemate was similarly prepared from (±)-5H₂, crystallizing as deep red plates of the 2-dichloromethane solvate from dichloromethane.

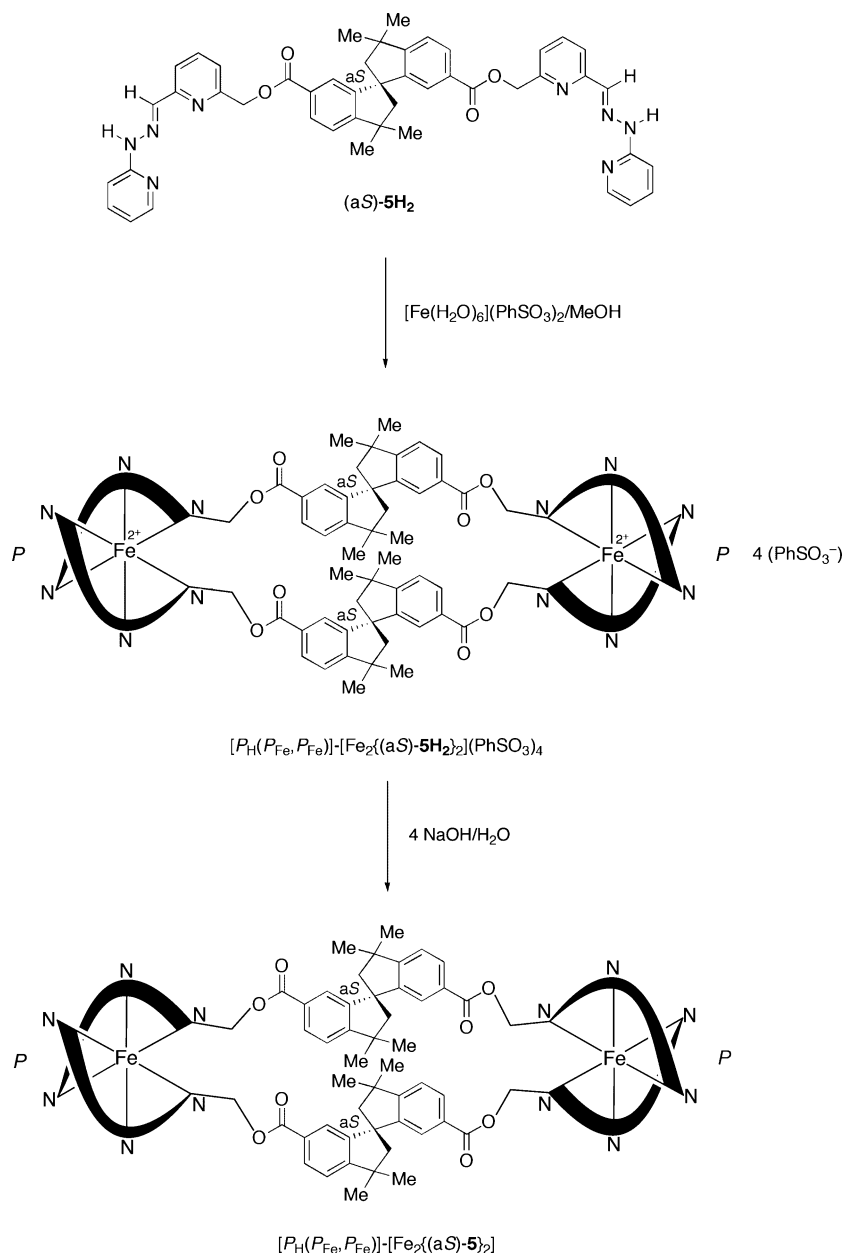
¹H NMR Spectra. The room-temperature ¹H NMR spectrum of (–)-[Fe₂{(aS)-5H₂}]₂(PhSO₃)₄ in methanol-*d*₄ at 25 °C consists of a series of broad resonances in the range 0–35 ppm. At 0 °C, however, most of the resonances in the spectrum are sharp, as expected for a diamagnetic iron(II) complex. The protons for the four diastereotopic pairs of methyl groups in the dihedral cation of C₂ symmetry appear as four singlets between 1 and 2 ppm in the spectrum and, downfield of these, there are two doublets and a virtual triplet (overlapping doublets) for the four pairs of diastereotopic *methylene* protons of the two 5-membered spirane rings. Between 4.6 and 5.6 ppm, the spectrum of the complex consists of three broad singlets for three of the four pairs of diastereotopic β-picoly-CH₂ protons—the fourth β-picoly-CH₂ resonance is obscured by the HOD peak at 5.2 ppm.

The ¹H NMR spectrum of (+)-[Fe₂{(aS)-5}]₂ in dichloromethane-*d*₂ at 25 °C is sharp, which is consistent with a single diastereomer (*de* >99%) of D₂ symmetry containing low-spin, diamagnetic iron(II). In solution, the neutral helicate has effective D₂ symmetry compared to the C₂ symmetry of the protonated complex. At 25 °C, one resonance at 9.19 ppm is observed for the four azomethine-*H* protons in the helicate. At –90 °C, however, this singlet is split into two broad singlets, which is consistent with a structure of C₂ symmetry. The C₂ structure of the cation is found in the solid state (see below).

Crystal and Molecular Structures of Diiron(II) Complexes. Dark red needles of (–)-[Fe₂{(aS)-5H₂}]₂(PhSO₃)₄ were grown by the slow diffusion of diethyl ether into a concentrated methanol solution of the crude complex. The complex crystallized in a C-centered orthorhombic cell having dimensions 35 × 55 × 49 Å³ (*V* = 95721 Å³) and contained eight independent Fe₂(5H₂)₂ units, but the crystals rapidly lost solvent. Because of this difficulty and the size and complexity of the cell, the analysis of the *optically active* complex was not completed. Dark red plates of the *racemate* (±)-[Fe₂(5H₂)₂](PhSO₃)₄·C₂H₅OH·5.65CH₃OH·H₂O crystallized following the slow diffusion of diethyl ether into a concentrated solution of the crude racemate in 95% aqueous ethanol–methanol. Large, dark green-black plates of the *deprotonated* complex (±)-[Fe₂(5)]₂·2CH₂Cl₂ were grown by the concentration of a dichloromethane solution of the crude complex. Crystallographic data and experimental details for the two complexes are given in Table 2. Interatomic bond lengths and angles around the chiral iron stereocenters in the complexes are given in Table 3 following the numbering scheme shown in Figure 5.

The complex (±)-[Fe₂(5H₂)₂](PhSO₃)₄·C₂H₅OH·5.65CH₃OH·H₂O crystallizes as a racemic compound in the triclinic space group *P* $\bar{1}$ with two diiron(II) cations of opposite configurations and associated anions and molecules of crystallization in the unit cell (Figure 6). Half of the anions and the molecules of crystallization are disordered. The final *R* factor of 0.093 for the structure refinement suggested some limitations in the modeling of the disorder, but the structure of the cation is unambiguously determined. In the structure, two ligands of aS configuration chelate two octahedral iron stereocenters of *P* configuration to give a double-stranded, diiron helicate of *P* configuration; the enantiomeric helicate of *M* configuration completes the centrosymmetrical unit. When viewed down the *c* axis, the molecules pack in columns in which the configurations of the helicates alternate. The C₂ axis of each helicate ion passes through the quaternary carbon atoms of the two auxiliary groups; the two ligand strands in each enantiomer twist around the metal–metal axis in the same direction to generate a double-stranded, dinuclear helicate having the same overall configuration. Thus, two ligand strands of aS configuration generate two octahedral iron stereocenters of *P* configuration, which in turn generate a double-stranded helix of *P* configuration (*P_H*); two ligand strands of aR configuration generate the enantiomeric helicate of *M* configuration (*M_H*). The two ligand strands in each helicate ion wrap around each other so that the *gem*-dimethyl groups of the auxiliary groups are situated away from the center of the molecule. The coordination geometry around the metal atoms in the helicate ions is distorted octahedral, the Fe···Fe distance being 11.38 Å. The four terminal Fe–N distances in the cations average 1.988 Å, and the central Fe–N bonds average 1.886 Å. These distances are typical for bis(tridentate)iron(II) complexes of this type.²⁶ The Fe–N distances to the pyridine-*N* atoms bearing the ester linkages average 2.071 Å.

Scheme 4



The deprotonated complex $(\pm)\text{-}[\text{Fe}_2(\mathbf{5})_2] \cdot 2\text{CH}_2\text{Cl}_2$ crystallizes as a racemic compound in the monoclinic space group $C2/c$ with one half of one enantiomer of the racemate and one dichloromethane molecule of crystallization comprising the crystallographic asymmetric unit. The dichloromethane molecule is disordered. The cation possesses a crystallographically imposed 2-fold axis passing through the quaternary carbon atoms of the chiral auxiliary group of each ligand strand (Figure 7). When viewed down the c axis, the helicate molecules pack in columns in which the configurations of the iron stereocenters alternate. The coordination geometry around each iron atom in the helicate molecule is distorted octahedral, the bond distances and angles in each case being comparable to those in the helicate cations of the protonated

complex, including the lengthening of the Fe–N bonds to the substituted pyridine rings. As for the protonated complex, the aS ligand generates chiral iron stereocenters of P configuration and the aR ligand centers of M configuration, the configuration of the overall helicate in each case corresponding to the metal configurations. The $\text{Fe} \cdots \text{Fe}$ distance of 13.26 Å in the neutral complex, however, is 1.88 Å longer than the corresponding distance in the charged complex.

Circular Dichroism Spectra. The CD spectrum of $(+)\text{-}[\text{Fe}_2((aS)\text{-}5)_2] \cdot 2\text{CH}_2\text{Cl}_2$ in methanol at 18 °C is very similar to that of $(P_{\text{Fe}})\text{-}(-)\text{-}[\text{Fe}\{(aS)\text{-}4\}]$ under similar conditions (Figure 8). In the visible region, $\Delta\epsilon$ reaches a highest magnitude of about 30 and 40 $\text{M}^{-1} \text{cm}^{-1}$ for the diiron complex; these peaks are associated with the absorption maxima of the MLCT transitions in the complex. Absorptions at shorter wavelengths

(26) *International Tables for Crystallography, Volume C: Mathematical, Physical and Chemical Tables.*; Kluwer Academic Publishers: Dordrecht, Netherlands, 1992.

Table 2. Crystallographic Data and Experimental Parameters for the X-ray Crystal Structure Analysis of $[(P_H)-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(5H_2)_2](PhSO_3)_4 \cdot C_2H_5OH \cdot 5.65CH_3OH \cdot H_2O$ and $[(P_H)-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(5)_2] \cdot 2CH_2Cl_2$

molec formula	$C_{125.65}H_{138.60}Fe_2N_{16}O_{27.65}S_4$	$C_{96}H_{88}Cl_4Fe_2N_{16}O_8$
fw, g mol ⁻¹	2555.2	1847.36
cryst color, habit	red, plate	black, plate
cryst size, mm	$0.42 \times 0.18 \times 0.13$	$0.40 \times 0.30 \times 0.12$
space group	$P\bar{1}$	$C2/c$
cryst syst	triclinic	monoclinic
a, Å	16.8888(3)	33.7536(6)
b, Å	18.8087(3)	15.3817(3)
c, Å	20.6913(3)	18.0814(3)
α, deg	94.4353(11)	
β, deg	94.9183(10)	111.6070(11)
γ, deg	105.3598(9)	
V, Å ³	6280.29(7)	8728.0(3)
Z	2	4
d_{calc} , g cm ⁻³	1.351	1.406
μ , cm ⁻¹	3.77	5.24
instrument	Enraf-Nonius Kappa CCD	Enraf-Nonius Kappa CCD
radiatn	Mo Kα	Mo Kα
no. unique reflcns	22240	7675
no. reflcns obsd	12142 ($I > 3.00\sigma(I)$)	5021 ($I > 3.00\sigma(I)$)
2θ range, deg	4–50	6–50
scan technique	φ and ω scans with CCD	φ and ω scans with CCD
temp, K	150	200
struct refinement	CRYSTALS ²⁹	CRYSTALS ²⁹
final R, R _w	0.0928, 0.1030	0.0368, 0.0435

corresponding to the chiral auxiliary are also present in the spectrum.

Conclusion

Enantiomerically pure (aS)-**4H₂** reacts with iron(II) benzenesulfonate in methanol to furnish the two-bladed propeller, octahedral complex $(P_{Fe})-(\pm)-[Fe\{(aS)-4H_2\}](PhSO_3)_2$ in about 20% de as the kinetic product, but the de increases to 80% when the reaction mixture is heated for 12 h under reflux, as indicated by ¹H NMR spectroscopy and a comparison of the CD spectrum of a methanol solution of the product with that of a solution of a closely related complex of known configuration. Repositioning of the ester linkages in the pyridine 2-alimine groups of the ligand from the 5-position in (aS)-**4H₂** to the 6-position in (aS)-**5H₂** results in a double-stranded, diiron(II) helicate in >99% de, as determined by ¹H NMR spectroscopy. The configurations of the octahedral metal stereocenters in the enantiomerically pure helicate were inferred from the crystal structure of the corresponding racemate, which crystallizes as a racemic compound in which two aS ligands generate two octahedral iron stereocenters of P configuration in a diiron helicate of P configuration (P_H) and vice versa for the aR ligand in the centrosymmetrical unit cells of the crystals.

Experimental Section

General Methods. Reactions involving air-sensitive compounds were performed under a positive pressure of nitrogen using Schlenk techniques. Dry, degassed solvents were obtained by distillation over appropriate drying agents. Routine NMR spectra were measured in the solvents specified at 298 K on Varian Inova spectrometers operating at 300 or 500 MHz (¹H) and 75 MHz or 125 (¹³C{¹H}). Chemical shifts (δ) are reported in ppm relative to the internal TMS for ¹H NMR spectra recorded in chloroform-d,

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Cation of $[P_H-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(5H_2)_2](PhSO_3)_4 \cdot C_2H_5OH \cdot 5.65CH_3OH \cdot H_2O$ and $[(P_H)-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(5)_2] \cdot 2CH_2Cl_2$

	$(\pm)-[Fe_2(5H_2)_2](PhSO_3)_4$	$(\pm)-[Fe_2(5)_2]^a$
Fe1–N101	1.997(5)	1.960(2)
Fe1–N108	1.890(5)	1.888(2)
Fe1–N115	2.071(5)	2.067(2)
Fe1–N301	1.992(5)	1.969(2)
Fe1–N308	1.886(5)	1.884(2)
Fe1–N315	2.075(5)	2.058(2)
Fe2–N201	1.989(6)	
Fe2–N208	1.883(6)	
Fe2–N215	2.069(5)	
Fe2–N401	1.975(5)	
Fe2–N408	1.884(6)	
Fe2–N415	2.068(5)	
N101–Fe1–N108	80.5(2)	79.54(8)
N101–Fe1–N115	159.9(2)	160.32(8)
N101–Fe1–N301	91.6(2)	89.51(8)
N101–Fe1–N308	93.7(2)	93.94(8)
N101–Fe1–N315	89.7(2)	91.47(7)
N108–Fe1–N115	79.5(2)	80.95(8)
N108–Fe1–N301	90.7(2)	91.03(8)
N108–Fe1–N308	169.5(2)	168.71(9)
N108–Fe1–N315	109.4(2)	107.88(8)
N115–Fe1–N301	90.8(2)	93.38(7)
N115–Fe1–N308	106.4(2)	105.73(8)
N115–Fe1–N315	94.9(2)	92.08(7)
N301–Fe1–N308	80.7(2)	79.63(9)
N301–Fe1–N315	159.8(2)	160.93(8)
N308–Fe1–N315	79.1(2)	81.31(8)
N201–Fe2–N208	80.5(3)	
N201–Fe2–N215	160.8(3)	
N201–Fe2–N401	89.3(2)	
N201–Fe2–N408	93.8(3)	
N201–Fe2–N415	89.1(2)	
N208–Fe2–N215	80.4(2)	
N208–Fe2–N401	93.7(2)	
N208–Fe2–N408	172.3(2)	
N208–Fe2–N415	104.9(2)	
N215–Fe2–N401	90.2(2)	
N215–Fe2–N408	105.0(2)	
N215–Fe2–N415	97.5(2)	
N401–Fe2–N408	80.9(2)	
N401–Fe2–N415	160.8(2)	
N408–Fe2–N415	80.1(2)	

^a The complex contains a crystallographically imposed 2-fold axis.

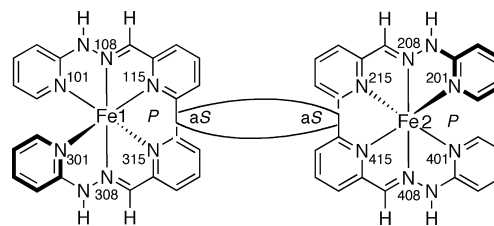


Figure 5. Atom labeling scheme for selected atoms of $[P_H-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(5H_2)_2](PhSO_3)_4 \cdot C_2H_5OH \cdot 5.65CH_3OH \cdot H_2O$ and $[(P_H)-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(5)_2] \cdot 2CH_2Cl_2$.

or relative to the residual solvent peak for other solvents. Melting points were determined with use of a Reichert hot-stage melting point apparatus. Optical rotations were measured on the specified solutions at 18 °C with a Perkin-Elmer Model 241 spectropolarimeter. Specific rotations are within ± 0.05 deg cm² g⁻¹. The rotations of the metal complexes were measured on solutions in 1 or 5 cm cells at 18 °C with use of a Jobin Yvon Model CD6 spectrophotometer operating in the ORD mode. CD measurements were recorded in methanol on the same instrument. Elemental analyses were performed and mass spectra measured by staff within

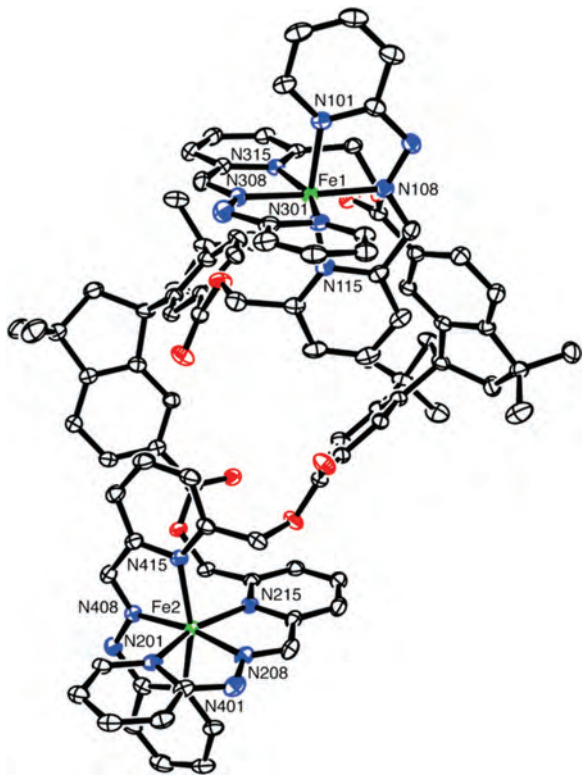


Figure 6. Structure of $[P_H-(P_{Fe},P_{Fe})]$ enantiomer of $(\pm)\text{-}[\text{Fe}_2(\mathbf{5H}_2)_2]\cdot(\text{PhSO}_3)_4\cdot\text{C}_2\text{H}_5\text{OH}\cdot 5.65\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$ (thermal ellipsoids contain 30% probability levels).

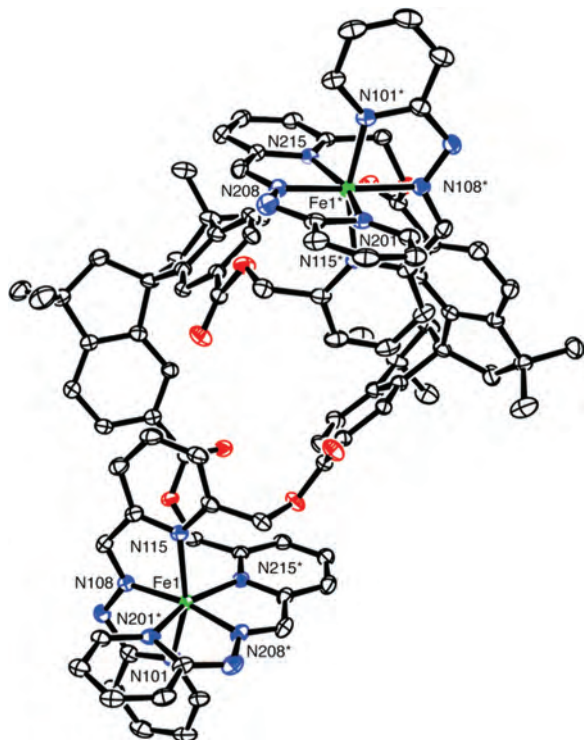


Figure 7. Structure of $[P_H-(P_{Fe},P_{Fe})]$ enantiomer of $(\pm)\text{-}[\text{Fe}_2(\mathbf{5})_2]\cdot 2\text{CH}_2\text{Cl}_2$ (thermal ellipsoids contain 30% probability levels).

the Research School of Chemistry. 4-Methyl-4-*p*-tolyl-2-pentanone²⁴ and hexaaquairon(II) benzenesulfonate²⁷ were prepared by the literature methods.

$(\pm)\text{-}3,3,3',6,6'\text{-Hexamethyl-1,1'\text{-spirobi-indane}}$ ($(\pm)\text{-}6$). This compound was prepared with modifications to the literature

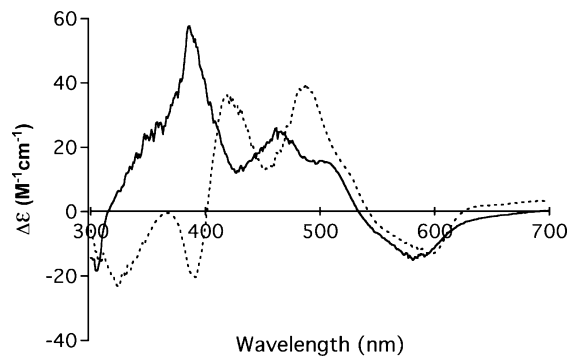


Figure 8. CD spectra of $[P_H-(P_{Fe},P_{Fe})]\text{-}(\pm)\text{-}[\text{Fe}_2\{(\text{aS})\text{-}5\text{H}_2\}_2](\text{PhSO}_3)_4$ (solid line) and $[P_H-(P_{Fe},P_{Fe})]\text{-}(\pm)\text{-}[\text{Fe}_2\{(\text{aS})\text{-}5\}_2]$ of established configuration (dashed line) in methanol at 18 °C.

procedure.²⁸ 4-Methyl-4-*p*-tolyl-2-pentanone (51.41 g, 0.27 mol) was heated under reflux overnight in sulfuric acid (18 M, 600 mL). The cooled reaction mixture was extracted with diethyl ether (3 × 200 mL), and the extract was washed with saturated aq sodium bicarbonate and dried (MgSO_4). The ether fraction was concentrated to about 50 mL, whereupon the product separated as a colorless solid that was filtered off and washed with ice-cold ethanol. The mother liquor and ethanol washings were combined, the solvent removed, and the remaining oil fractionally distilled to furnish a viscous, yellow oil (bp 120–150 °C/0.5 mmHg) that yielded a second batch of the product when it was dissolved in hot ethanol and the solution allowed to cool. Yield: 18.61 g (46%); mp = 128 °C [lit.¹⁸ 137–138 °C]. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 1.34 (s, 6 H, CH_3), 1.40 (s, 6 H, CH_3), 2.26 (s, 6 H, CH_3) (doublet obscured by singlet at 2.26, 2 H, CH_2), 2.33 (d, 2 H, $^2J_{\text{HH}} = 13.1$ Hz, CH_2), 6.64 (s, 2 H, ArH), 7.08 (m, 4 H, ArH).

$(\pm)\text{-}3,3,3',6,6'\text{-bis(bromomethyl)-1,1'\text{-spirobi-indane}}$ ($(\pm)\text{-}7$). Benzoyl peroxide (0.06 g, cat.) was added to a suspension of $(\pm)\text{-}6$ (6.00 g, 0.020 mol) and *N*-bromosuccinimide (7.52 g, 0.042 mmol) in carbon tetrachloride (90 mL). The solution was heated under reflux for 1 h. The precipitate of succinimide was filtered off from the hot solution and the filter cake was washed with hot carbon tetrachloride (20 mL). The filtrates were combined, and the carbon tetrachloride was removed under reduced pressure to yield the colorless product. Yield: 7.65 g (85%); mp = 173 °C. Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{Br}_2$: C, 59.8; H, 5.7. Found: C, 59.9; H, 5.9. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 1.36 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 2.25 (d, 2 H, $^2J_{\text{HH}} = 13.2$ Hz, CHH), 2.38 (d, 2 H, $^2J_{\text{HH}} = 13.1$ Hz, CHH), 4.45 (s, 4 H, CH_2Br), 6.82 (s, 2 H, ArH), 7.19 (d, 2 H, $^3J_{\text{HH}} = 7.8$ Hz, ArH), 7.30 (t, 2 H, $^3J_{\text{HH}} = 7.9$ Hz, ArH). EI-MS: $m/z = 461.0$ (31, $[\text{M} + \text{H}]^+$), 459.0 amu (100, $[\text{M} - \text{H}]^+$).

$(\pm)\text{-}3,3,3',6,6'\text{-bis(hydroxymethyl)-1,1'\text{-spirobi-indane}}$ ($(\pm)\text{-}8$). Calcium carbonate (16.54 g, 0.17 mol) and water (90 mL) were combined and heated to reflux. To this boiling solution was added $(\pm)\text{-}7$ (7.60 g, 0.017 mol) in dioxane (140 mL); the reaction mixture was heated overnight under reflux. The reaction mixture was cooled to room temperature, and the dioxane/water were removed under reduced pressure. The residue was dissolved in dichloromethane (150 mL), and 2 M hydrochloric acid was added

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(29) Watkin, D. T.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, U.K., 1996.

(30) Mackay, S.; Gilmore, C. J.; Edwards, C.; Stewart, N.; Shankland, K. *maxus Computer Program for the Solution and Refinement of Crystal Structures*; Nonius, Delft, The Netherlands, MacScience, Japan, and University of Glasgow, Glasgow, Scotland, 1999.

(ca. 80 mL), which clarified the organic layer. The organic layer was separated, washed with saturated sodium bicarbonate (150 mL), and dried (MgSO₄). The solvent was removed to furnish the colorless product. Yield: 4.82 g (87%); mp = 188–190 °C. Anal. Calcd for C₂₃H₂₈O₂: C, 82.1; H, 8.4. Found: C, 81.7; H, 8.7. ¹H NMR (CDCl₃, 300 MHz): δ 1.36 (s, 6 H, CH₃), 1.42 (s, 6 H, CH₃), 2.27 (d, 2 H, ²J_{HH} = 13.1 Hz, CHH), 2.38 (d, 2 H, ²J_{HH} = 13.1 Hz, CHH), 4.59 (s, 4 H, CH₂OH), 6.81 (s, 2H, ArH), 7.20 (d, 2 H, ³J_{HH} = 7.7 Hz, ArH), 7.26 (d, 2 H, ³J_{HH} = 8.7 Hz, ArH). EI-MS: *m/z* = 336.2 (90, [M]⁺), 321.1 amu (100, [M - CH₃]⁺).

(±)-**3,3,3',3'-Tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylic acid ((±)-2)**. A hot solution of potassium permanganate (14.50 g, 0.094 mol) in a mixture of water (30 mL) and acetone (210 mL) was added dropwise to a boiling mixture of (±)-**8** (4.51 g, 0.013 mol) in acetone (80 mL) over 30 min. The reaction mixture was heated under reflux for 4.5 h during which time the color changed from purple to brown. The manganese(IV) oxide and residual potassium permanganate were filtered off from the hot solution through a bed of celite. The filter cake was stirred in ethanol and refiltered. The solvent was removed from the combined filtrates to leave a brown solid that was dissolved in water and diethyl ether added (in a separating funnel). To this mixture was added aq sodium hydroxide (2M, 20 mL). The aqueous layer was separated, cooled to ice-temperature, and acidified with aq hydrochloric acid (2M). The colorless precipitate was left to settle overnight. The solid was filtered off, washed with dilute hydrochloric acid and diethyl ether, and dried under vacuum to give the title compound as a colorless solid. Yield: 5.27 g (95%); mp = >250 °C. [lit.²⁸ >250 °C]. ¹H NMR (acetone-*d*₆, 300 MHz): δ 1.41 (s, 6 H, CH₃), 1.49 (s, 6 H, CH₃), 2.33 (d, 2 H, ²J_{HH} = 13.1 Hz, CHH), 2.51 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH), 7.41 (s, 2 H, ArH), 7.42 (d, 2 H, ³J_{HH} = 7.1 Hz, ArH), 7.96 (d, 2 H, ³J_{HH} = 7.9 Hz, ArH).

(-)-**Dibrucinium (-)-3,3,3',3'-tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylate**. The diacid (±)-**2** was resolved using (-)-brucine with modifications to the literature procedure.²⁵ A mixture of the diacid (6.00 g, 0.016 mol) and (-)-brucine (13 g, 0.033 mol) was heated in ethanol (75 mL) under reflux for 2 h. The hot solution was filtered through a paper, and the flask containing the filtrate was returned to the hot oil bath, which was then allowed to cool slowly. A colorless precipitate separated overnight. The mother liquor was decanted off, and the solid was washed with diethyl ether containing 5% ethanol, followed by diethyl ether. The solid was recrystallized six times from boiling ethanol (250 mL) to constant rotation. Yield: 4.14 g (22%); [lit.²⁵ 13%]; [α]_D²⁵ = -100.8 (c 0.32, CHCl₃), [lit.²⁵ [α]_D = -91.6 (c 0.32, CHCl₃)].

(aS)-(-)-**3,3,3',3'-Tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylic Acid ((aS)-2)**. The (-)-dibrucinium salt (4.00 g, 3.44 mmol) was stirred in hydrochloric acid (6M, 30 mL) at 50 °C for 1 h. The solution was cooled, and the colorless acid was filtered off, washed with water, and dried overnight in a desiccator (KOH, concd H₂SO₄). Yield: 1.25 g (21%), [lit.²⁵ 13%]; [α]_D²⁵ = -94.0 (c 0.20, dioxane) [lit.²⁵ [α]_D = -94.2 (c 0.24, dioxane)].

(±)-**Dimethyl 3,3,3',3'-tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylate**. A solution of (±)-**2** (0.10 g, 0.27 mmol) and thionyl chloride (10 mL) containing two drops of pyridine was stirred for 2 h under nitrogen. The excess thionyl chloride was distilled off under reduced pressure, and methanol (20 mL) was added to the colorless residue at 0 °C. The mixture was heated under reflux for 30 min, and the solvent was removed under reduced pressure. The colorless solid that remained was recrystallized from hot *n*-hexane to furnish colorless crystals of the pure ester. Yield: 0.10 g (94%); mp = 168–170 °C. ¹H NMR (acetone-*d*₆, 300 MHz): δ 1.37 (s, 6 H, CH₃), 1.49 (s, 6 H, CH₃), 2.27 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH),

2.40 (d, 2 H, ²J_{HH} = 13.1 Hz, CHH), 3.83 (s, 6 H, OCH₃), 7.26 (d, 2 H, ³J_{HH} = 7.7 Hz, ArH), 7.43 (s, 2 H, ArH), 7.95 (d, 2 H, ³J_{HH} = 8.3 Hz, ArH).

(aS)-(-)-**Dimethyl 3,3,3',3'-tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylate**. This compound was prepared from (aS)-**2** in an identical manner to that used for the *racemate*. Yield: 94%; mp = 172–174 °C [lit.²⁵ 170.5–171 °C]. [α]_D²⁵ = -125 (c 0.25, *n*-heptane) [lit.²⁵ [α]_D²⁵ = -124 (c 0.23, *n*-heptane)]. ¹H NMR (acetone-*d*₆, 300 MHz): δ 1.40 (s, 6 H, CH₃), 1.47 (s, 6 H, CH₃), 2.30 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH), 2.50 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH), 3.78 (s, 6 H, OCH₃), 7.43 (d, 2 H, ³J_{HH} = 8.0 Hz, ArH), 7.94 (d, 2 H, ³J_{HH} = 8.0 Hz, ArH), 7.94 (s, 2 H, ³J_{HH} = 8.0 Hz, ArH).

(aS)-(-)-**3,3,3',3'-Tetramethyl-bis-1,1'-spirobi-indane-6,6'-diacid Chloride ((aS)-9)**. The diacid (aS)-**2** (0.610 g, 1.67 mmol) was suspended in thionyl chloride (30 mL). Five drops of dry pyridine were added to the mixture, which was then stirred for 2 h (during which time the solid dissolved). The solution was evaporated to dryness to afford the crude product as a pale yellow solid. This material was used for the next step without further purification. Yield: 0.72 g (99%). ¹H NMR (CDCl₃, 300 MHz): δ 1.38 (s, 6 H, CH₃), 1.46 (s, 6 H, CH₃), 2.28 (d, 2 H, ²J_{HH} = 13.3 Hz, CHH), 2.44 (d, 2 H, ²J_{HH} = 13.3 Hz, CHH), 7.35 (d, 2 H, ³J_{HH} = 8.1 Hz, ArH), 7.46 (s, 2 H, ArH), 8.07 (d, 2 H, ³J_{HH} = 8.2 Hz, ArH).

(aS)-(-)-**Bis(5-methylpyridine-2-carboxaldehyde) 3,3,3',3'-Tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylate ((aS)-10)**. This compound was obtained as a colorless solid from the reaction between (aS)-**9** and 5-(hydroxymethyl)pyridine-2-aldehyde (*R*_f 0.29 in 1:1.5 v/v ethyl acetate-*n*-hexane on silica) following the method described in ref 20. Yield: 73%; mp = 59–62 °C; [α]_D²⁵ = -127.2 (c 0.617, CHCl₃). Anal. Calcd for C₃₇H₃₄N₂O₆: C, 73.6; H, 5.7; N, 4.7. Found: C, 73.5; H, 5.8; N, 4.4. ¹H NMR (CDCl₃, 300 MHz): δ 1.38 (s, 6 H, CH₃), 1.45 (s, 6 H, CH₃), 2.30 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH), 2.43 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH), 5.39 (d, 2 H, ²J_{HH} = 13.4 Hz, CH₂), 5.45 (d, 2 H, ²J_{HH} = 13.3 Hz, CH₂), 7.29 (d, 2 H, ³J_{HH} = 8.0 Hz, ArH), 7.49 (s, 2 H, ArH), 7.90–8.00 (m, 6 H, pyH and ArH), 8.83 (s, 2 H, pyH), 10.08 (s, 2 H, CHO). EI-MS: *m/z* = 602.2 (62, [M]⁺), 574.2 amu (88, [M - CHO]⁺).

(aS)-(-)-**Bis(6-methylpyridine-2-carboxaldehyde) 3,3,3',3'-Tetramethyl-bis-1,1'-spirobi-indane-6,6'-dicarboxylate ((aS)-11)**. This compound was obtained as a colorless solid from the reaction between (aS)-**9** and 6-(hydroxymethyl)pyridine-2-aldehyde (*R*_f 0.36 in 1:2.5 v/v ethyl acetate-*n*-hexane on silica) following the method described in ref 20. Yield: 72%; mp = 65 °C; [α]_D²⁵ = -113.1 (c 1.0, CHCl₃). Anal. Calcd for C₃₇H₃₄N₂O₆: C, 73.6; H, 5.7; N, 4.7. Found: C, 73.6; H, 5.8; N, 4.4. ¹H NMR (CDCl₃, 300 MHz): δ 1.40 (s, 6 H, CH₃), 1.47 (s, 6 H, CH₃), 2.33 (d, 2 H, ²J_{HH} = 13.2 Hz, CHH), 2.45 (d, 2 H, ²J_{HH} = 13.3 Hz, CHH), 5.50 (d, 2 H, ²J_{HH} = 13.9 Hz, CHH), 5.57 (d, 2 H, ²J_{HH} = 13.9 Hz, CHH), 7.31 (d, 2 H, ³J_{HH} = 7.9 Hz, ArH), 7.56 (s, 2 H, ArH), 7.64 (d, 2 H, ³J_{HH} = 6.3 Hz, pyH), 7.89–7.91 (m, 4 H, pyH), 8.05 (d, 2 H, ³J_{HH} = 6.4 Hz, ArH), 10.07 (s, 2 H, CHO). EI-MS: *m/z* = 602.2 (55, [M]⁺), 545.2 amu (50, [M - 2(CH=O)]⁺).

(aS)-(-)-**Bis(5-methylpyridine-2-carboxaldehyde 2'-pyridylhydrazone) 3,3,3',3'-Tetramethyl-bis-1,1'-spiroindane-6,6'-dicarboxylate ((aS)-4H₂)**. This compound was obtained as a pale yellow solid from the reaction between (aS)-**10** and pyridine-2-hydrazine. Thus, the aldehyde (aS)-**10** (3.62 g, 6 mmol) was added to a solution of pyridine-2-hydrazine (1.53 g, 14 mmol) in ethanol (100 mL), and the solution was heated under reflux for 30 min; the pure product separated as yellow crystals from the cooled solution over 12–15 h and was filtered off, washed with diethyl ether, and dried in vacuo (3.77 g). Yield: 80%; mp = 210–212

°C; $[\alpha]_D^{25} = -103.4$ (*c* 1.0, CHCl₃). Anal. Calcd for C₄₇H₄₄N₈O₄: C, 71.9; H, 5.7; N, 14.3. Found: C, 71.6; H, 5.8; N, 14.0. ¹H NMR (CDCl₃, 500 MHz): δ 1.28 (s, 6 H, CH₃), 1.36 (s, 6 H, CH₃), 2.20 (d, 2 H, ²J_{HH} = 13.5 Hz, CHH), 2.32 (d, 2 H, ²J_{HH} = 13.0 Hz, CHH), 5.20 (d, 2 H, ²J_{HH} = 12.5 Hz, CH₂), 5.26 (d, 2 H, ²J_{HH} = 12.5 Hz, CH₂), 6.73 (t, 2 H, ³J_{HH} = 5.0 Hz, pyH), 7.18 (d, 2 H, ³J_{HH} = 8.5 Hz, pyH), 7.33 (d, 2 H, ³J_{HH} = 8.5 Hz, ArH), 7.40 (s, 2 H, ArH), 7.53–7.56 (m, 4 H, pyH), 7.65 (d, 2 H, ³J_{HH} = 6.0 Hz, pyH), 7.85 (s, 2 H, CH = N), 7.89 (d, 2 H, ³J_{HH} = 8.5 Hz, ArH), 8.10 (d, 2 H, ³J_{HH} = 7.0 Hz, pyH), 8.52 (s, 2 H, pyH-6). ESI-MS: *m/z* 784.9 amu (35, [M]⁺). Crystals of (aS)-**4H₂**·2.5CHCl₃ suitable for X-ray crystallography separated from a concentrated solution of (aS)-**4H₂** in chloroform following dilution with diethyl ether.

(±)-Bis(5-methylpyridine-2-carboxaldehyde 2'-pyridylhydrazone) **3,3,3',3'-Tetramethyl-bis-1,1'-spiroindane-6,6'-dicarboxylate** ((±)-**4H₂**). Yield: 80%; mp = 237–240 °C. ¹H NMR and ESI-MS: identical to those for (aS)-**4H₂**.

(aS)-(-)-Bis(6-methylpyridine-2-carboxaldehyde 2'-pyridylhydrazone) **3,3,3',3'-Tetramethyl-bis-1,1'-spiroindane-6,6'-dicarboxylate** ((aS)-**5H₂**). This compound was obtained as a pale yellow solid from the reaction between (aS)-**11** and pyridine-2-hydrazine following the method described in ref 20. Yield: 96%; mp = 200–203 °C; $[\alpha]_D^{25} = -76.8$ (*c* 1.0, CHCl₃). Anal. Calcd for C₄₇H₄₄N₈O₄: C, 71.9; H, 5.7; N, 14.3. Found: C, 72.2; H, 5.5; N, 14.4. ¹H NMR (CDCl₃, 500 MHz): δ 1.40 (s, 6 H, CH₃), 1.47 (s, 6 H, CH₃), 2.34 (d, 2 H, ²J_{HH} = 13.5 Hz, CHH), 2.44 (d, 2 H, ²J_{HH} = 13.0 Hz, CHH), 5.42 (d, 2 H, ²J_{HH} = 13.5 Hz, CHH), 5.49 (d, 2 H, ²J_{HH} = 13.5 Hz, CHH), 6.82 (t, 2 H, ³J_{HH} = 5.0 Hz, pyH), 7.27 (d, 2 H, ³J_{HH} = 7.5 Hz, pyH), 7.30 (d, 2 H, ³J_{HH} = 7.5 Hz, ArH), 7.55 (s, 2 H, ArH), 7.60–7.68 (m, 6 H, pyH), 7.88 (s, 2 H, CH=N), 7.92 (d, 2 H, ³J_{HH} = 7.47 Hz, pyH), 8.08 (d, 2 H, ³J_{HH} = 8.0 Hz, pyH), 8.22 (d, 2 H, ³J_{HH} = 4.0 Hz, ArH), 10.2 (s, 2 H, NH). ESI-MS: *m/z* = 784.9 amu (30, [M]⁺).

(±)-Bis(6-methylpyridine-2-carboxaldehyde 2'-pyridylhydrazone) **3,3,3',3'-Tetramethyl-bis-1,1'-spiroindane-6,6'-dicarboxylate**, ((±)-**5H₂**). Yield: 96%; mp 235–237 °C. ¹H NMR and ESI-MS: identical to those for (aS)-**5H₂**.

(P_{Fe})-(-)-[Fe((aS)-**4H₂**)](PhSO₃)₂. (Hexaaqua)iron(II) benzenesulfonate (0.24 g, 0.50 mmol) was dissolved in methanol (80 mL), and the solution was added over 1 h to a suspension of (aS)-**4H₂** (0.40 g, 0.50 mmol) in the same solvent (200 mL). The solution was heated under reflux for 12 h, and then it was filtered and the solvent removed from the filtrate under reduced pressure to yield the crude product as a red solid. Yield: 0.56 (95%); mp > 250 °C; $[\alpha]_D^{25} = -2095$ (*c* 0.015, MeOH), $[\alpha]_D^{25} = +2924$ (*c* 0.015, MeOH). Anal. Calcd for C₅₉H₅₄FeN₈O₁₂S₂: C, 60.8; H, 4.5; N, 9.7. Found: C, 61.3; H, 4.7; N, 9.7. ¹H NMR (CD₃OD, 500 MHz): δ 1.37 (s, 6 H, CH₃), 1.40 (s, 6 H, CH₃), 2.14 (d, 2 H, ²J_{HH} = 13.5 Hz, CHH), 2.43 (d, 2 H, ²J_{HH} = 13.5 Hz, CHH), 4.85 (d, 2 H, ²J_{HH} = 11.5 Hz, CHH), 5.10 (d, 2 H, ²J_{HH} = 12.0 Hz, CHH), 6.77 (t, 2 H, ³J_{HH} = 6.0 Hz, pyH), 6.85 (s, 2 H, pyH), 7.05 (d, 2 H, ³J_{HH} = 8.0 Hz, pyH), 7.31 (d, 2 H, ³J_{HH} = 7.5 Hz, ArH), 7.39–7.43 (m, 6 H, C₆H₅SO₃⁻), 7.55–7.61 (m, 4 H, pyH and ArH), 7.78–7.80 (m, 4 H, C₆H₅SO₃⁻), 7.88 (d, 2 H, ³J_{HH} = 6.0 Hz, ArH), 9.56 (s, 2 H, CH=N). HR ESI-MS: *m/z* = 839.2734 (calcd 839.2757) amu ([M - 2PhSO₃ - H]⁺).

(P_{Fe})-(-)-[Fe((aS)-**4**)](PhSO₃)₂. Complex (P_{Fe})-(-)-[Fe((aS)-**4H₂**)](PhSO₃)₂ (0.020 g, 0.017 mmol) was suspended in water (5 mL) and 10% aq sodium hydroxide solution (0.014 mL, 0.034 mmol) was added. Dichloromethane (5 mL) was added, and the mixture was stirred for 30 min. The organic layer was separated, dried (MgSO₄), and the solvent removed from the filtrate to yield the title compound as a green-brown solid. Yield: 0.014 g (95%); mp > 250 °C; $[\alpha]_D^{25}$

= -612 (*c* 0.009, MeOH), $[\alpha]_D^{25} = +2826$ (*c* 0.009, MeOH). Anal. Calcd for C₄₇H₄₂FeN₈O₄: C, 67.3; H, 5.1; N, 13.4. Found: C, 67.5; H, 4.7; N, 13.5. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.36 (s, 6 H, CH₃), 1.37 (s, 6 H, CH₃), 2.19 (d, 2 H, ²J_{HH} = 13.0 Hz, CHH), 2.37 (d, 2 H, ²J_{HH} = 13.0 Hz, CHH), 4.70 (d, 2 H, ²J_{HH} = 12.0 Hz, CHH), 4.84 (d, 2 H, ²J_{HH} = 11.5 Hz, CHH), 6.11 (t, 2 H, ³J_{HH} = 6.5 Hz, pyH), 6.65 (d, 2 H, ³J_{HH} = 8.5 Hz, pyH), 6.91–6.92 (m, 4 H, pyH), 6.99–7.03 (m, 4 H, pyH), 7.08 (d, 2 H, ³J_{HH} = 5.5 Hz, pyH), 7.19 (d, 2 H, ³J_{HH} = 8.5 Hz, pyH), 7.24 (d, 2 H, ³J_{HH} = 8.0 Hz, ArH), 7.23 (s, 2 H, ArH), 7.80 (d, 2 H, ³J_{HH} = 7.5 Hz, pyH), 8.99 (s, 2 H, CH=N). HR ESI-MS: *m/z* = 839.2743 (calcd 839.2757) amu ([M + H]⁺).

[P_H(P_{Fe}P_{Fe})](-)-[Fe₂((aS)-**5H₂**)](PhSO₃)₄. This compound was prepared by the addition of (aS)-**5** in *i*-propanol to a solution of (hexaaqua)iron(II) benzenesulfonate in the same solvent; the pure complex crystallized as fine red needles from an ethanol–water–diethyl ether solution. Yield: 96%; mp > 250 °C; $[\alpha]_D^{25} = -2000$ (*c* 0.0168, MeOH), $[\alpha]_D^{25} = +2714$ (*c* 0.0168, MeOH). Anal. Calcd for C₁₁₈H₁₀₈Fe₂N₁₆O₂₀S₄: C, 61.4; H, 4.7; N, 9.7. Found: C, 59.7; H, 5.2; N, 9.4. ¹H NMR (CD₃OD, 273 K, 500 MHz): δ 1.21 (s, 6 H, CH₃), 1.23 (s, 6 H, CH₃), 1.40 (s, 6 H, CH₃), 1.61 (s, 6 H, CH₃), 1.80 (d, 2 H, ²J_{HH} = 12.5 Hz, CHH), 2.32 (d, 2 H, ²J_{HH} = 11.0 Hz, CHH), 2.34 (d, 2 H, ²J_{HH} = 11.5 Hz, CHH), 2.49 (d, 2 H, ²J_{HH} = 12.5 Hz, CHH), 4.73 (br s, 2 H, CH₂), 4.87 (br s, 2 H, CH₂), 5.06 (br s, 2 H, CH₂), 6.13 (d, 2 H, ³J_{HH} = 6.0 Hz, pyH), 6.33 (br s, 2 H, pyH), 6.68 (t, 2 H, ³J_{HH} = 6.5 Hz, pyH), 7.13 (br s, 4 H, ArH), 7.20–7.23 (br m), 7.38–7.43 (m, 16 H, pyH and C₆H₅SO₃⁻), 7.50 (d, 2 H, ³J_{HH} = 8.0 Hz, pyH), 7.85 (d, 8 H, ³J_{HH} = 8.0 Hz, C₆H₅SO₃⁻), 8.08–8.09 (br m, 4 H, pyH), 8.47–8.79 (br m, 6 H, pyH and ArH), 10.59 (br s, 4 H, pyH), 14.72 (br s, 4 H, pyH). HR ESI-MS: *m/z* 839.7747 (calcd 839.7771) amu ([M - 4PhSO₃ - 2H]²⁺).

[P_H(P_{Fe}P_{Fe})]/[M_H(M_{Fe}M_{Fe})]-(±)-[Fe₂(**5H₂**)](PhSO₃)₄. This compound was prepared by an identical procedure to that used for the (-) enantiomer of the complex and crystallized as large red needles from methanol–diethyl ether. Yield: 88%; mp > 250 °C. Anal. Calcd for C₁₁₈H₁₀₈Fe₂N₁₆O₂₀S₄: C, 61.4; H, 4.7; N, 9.7. Found: C, 59.2; H, 5.0; N, 9.2. ¹H NMR and HR ESI-MS: identical to those of the pure (-) enantiomer. The crystal of [P_H(P_{Fe}P_{Fe})]/[M_H(M_{Fe}M_{Fe})]-(±)-[Fe₂(**5H₂**)](PhSO₃)₄·C₂H₅OH·5.65CH₃OH·H₂O for the crystal structure determination was obtained from an ethanol–methanol solution (wet) of the complex by dilution with diethyl ether.

[P_H(P_{Fe}P_{Fe})]-(+)-[Fe₂((aS)-**5**)](PhSO₃)₄. The protonated complex (-)-[Fe₂((aS)-**5**)](PhSO₃)₄ (0.023 g, 0.020 mmol) was suspended in water (5 mL), and 10% aq sodium hydroxide solution (0.016 mL, 0.040 mmol) was added. Dichloromethane (5 mL) was added, and the mixture was stirred for 30 min. The organic layer was separated, dried (MgSO₄), and solvent removed to yield the title compound as a dark green-brown solid. Yield: 0.016 g, 95%; mp > 250 °C; $[\alpha]_D^{25} = +2228$ (*c* 0.016, MeOH), $[\alpha]_D^{25} = +3079$ (*c* 0.016, MeOH). Anal. Calcd for C₉₄H₈₈Fe₂N₁₆O₈: C, 67.1; H, 5.1; N, 13.3. Found: C, 67.2; H, 4.6; N, 13.1. ¹H NMR (CD₂Cl₂, 500 MHz): δ 1.31 (s, 12 H, CH₃), 1.43 (s, 12 H, CH₃), 2.11 (d, 4 H, ²J_{HH} = 12.0 Hz, CHH), 2.38 (d, 4 H, ²J_{HH} = 13.5 Hz, CHH), 4.63 (d, 4 H, ²J_{HH} = 11.0 Hz, CHH), 5.74 (d, 4 H, ²J_{HH} = 11.0 Hz, CHH), 6.00 (t, 4 H, ³J_{HH} = 5.5 Hz, pyH), 6.40–6.42 (br m, 18 H, pyH), 6.61 (d, 4 H, ³J_{HH} = 8.0 Hz, pyH), 6.67 (d, 4 H, ³J_{HH} = 4.5 Hz, pyH and ArH), 6.71 (br s, 8 H, pyH and ArH), 6.77 (br s, 8 H, pyH), 6.91 (t, 4 H, ³J_{HH} = 7.0 Hz, pyH), 6.98 (br s, 4 H, pyH and ArH), 9.19 (s, 4 H, CH=N). HR ESI-MS: *m/z* 839.7790 (calcd 839.7771) amu ([M + 2H]²⁺).

$[P_H-(P_{Fe},P_{Fe})]/[(M_{Fe}-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(\mathbf{5})_2]$. The compound was prepared in an identical procedure to that used for the (+) enantiomer of the complex. Yield: 97%; mp >250 °C. Anal. Calcd for $C_{94}H_{88}Fe_2N_{16}O_8$: C, 67.1; H, 5.1; N, 13.3. Found: C, 67.0; H, 4.9; N, 13.0. 1H NMR spectrum and HR ESI-MS: identical to those of pure (+) enantiomer. This material crystallized as dark green-black blocks of the *2-dichloromethane solvate* from dichloromethane.

Crystal Structures. Crystal data and experimental parameters for (aS)- $4H_2 \cdot 2.5CHCl_3$ are given in Table 1. The absolute configuration of the molecule was established by refinement of the Flack

parameter, final value -0.10 (11). Crystal data and experimental parameters for $[(P_H)-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2((aS)-5H_2)_2](PhSO_3)_4 \cdot C_2H_5OH \cdot 5.65CH_3OH \cdot H_2O$ and $[(P_H)-(P_{Fe},P_{Fe})]/[(M_H)-(M_{Fe},M_{Fe})]-(\pm)-[Fe_2(\mathbf{5})_2] \cdot 2CH_2Cl_2$ are given in Table 2.

Supporting Information Available: Additional crystallographic data in CIF format and 1H NMR spectra of $[P_H-(P_{Fe},P_{Fe})]-(-)-[Fe_2((aS)-5H_2)_2](PhSO_3)_4$ and $[P_H-(P_{Fe},P_{Fe})]-(+)-[Fe_2((aS)-5)_2]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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