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Diastereoselective Cyclopalladation of New Chiral Ferrocenylimines $(-)$-$[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_4C(R){=}NCH_2\text{-}(1S,2R,5S)\text{-}CHCH_2CH_2CHC(CH_3)_2CHCH_2\}]$. Crystal Structures of (S_p)-$[Pd\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2\text{-}(1S,2R,5S)\text{-}CHCH_2CH_2CHC(CH_3)_2CHCH_2)Fe(\eta^5\text{-}C_5H_5)\}(PPh_3)Cl]$ (R = H or Me)

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Summary: Reaction of acylferrocene with (−)-cis-myrtanylamine in benzene gives new chiral ferrocenylimines $(-)$-$[\{\eta^5\text{-}C_5H_4C(R){=}NCH_2R^*\}Fe(\eta^5\text{-}C_5H_5)]$ *[R = H, (−)-**1**, or Me, (−)-**2**; R* = (1S,2R,5S)-*$CHCH_2CH_2CHC(CH_3)_2CHCH_2$*]. Asymmetric cyclopalladation of these imines with sodium tetrachloropalladate(II) in methanol gives the di-μ-chloro-bridged dimers* $(+)$-(S_p,S_p)-$[Pd\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$*. Subsequent treatment of these dimeric complexes with triphenylphosphine, pyridine, and 1,1′-bis(diphenylphosphino)ferrocene (dppf) in acetone yields the corresponding cyclopalladated derivatives* (S_p)-$[Pd\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(PPh_3)Cl]$, $(+)$-(S_p)-$[Pd\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(py)Cl]$, *and* $(+)$-(S_p,S_p)-$[PdCl\{(\eta^5\text{-}C_5H_3C(R){=}NCH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(Ph_2PC_5H_4\text{-}\eta^5)]_2Fe$*, respectively. All compounds have been characterized by NMR, MS, optical rotation, and elemental analysis, and the absolute configuration of two mononuclear complexes,* $(+)$-(S_p)-$[Pd\{(\eta^5\text{-}C_5H_3CH{=}NCH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(PPh_3)Cl]\cdot{}^1/_2C_2H_5OH$ *and* $(-)$-(S_p)-$[Pd\{(\eta^5\text{-}C_5H_3C(CH_3){=}NCH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(PPh_3)Cl]$*, has been determined by single-crystal X-ray analysis.*

Introduction

The synthesis and structural characterization of ortho-palladated complexes containing N-donor ligands has attracted considerable attention.[1,2] Owing to the well-known reactivity of the carbon−palladium bond and planar chirality of 1,2-disubstituted derivatives of ferrocene, the ferrocenylimines $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4C(R){=}NR'\}]$ can be used as precursors of optically active organoiron compounds that are of interest in various fields such as organic synthesis, catalysis, and more recently materials chemistry.[3−5] Enantiopure ferrocenes are mainly obtained by resolution methods. There are no convenient methods for the asymmetric synthesis of ferrocenes with planar chirality. Sokolov *et al.* have developed useful methods to synthesize optically active cyclopalladated derivatives of ferrocene.[6] However, only a few optically active organopalladium compounds with a chiral metalated carbon center have been reported up to now.[2,6] Moreover, it appeared to be difficult to obtain these compounds in enantiomerically pure forms. To our knowledge, the absolute configuration of only one enantiomerically pure 1,2-disubstituted cyclopalladated compound containing the ferrocenyl unit is firmly established,[7] and no crystal structure of an enantiomerically pure 1,2-disubstituted cyclopalladated ferrocenylimine has been reported. On this basis we decided to elucidate whether the use of optically active ferrocenylimines would induce preferentially the activation of one of the two ortho σ(C−H) bonds of the ferrocene moiety. In this paper we present a general method for the preparation of a number of enantiomerically pure ferrocenes.

New chiral ferrocenylimines (−)-**1** and (−)-**2** are easily obtained by a condensation reaction between acylferrocene and (−)-(1*S*,2*R*,5*S*)-2-(aminomethyl)-6,6-dimethylbicyclo[3.1.1]heptane, $H_2NCH_2R^*$, commonly known as (−)-*cis*-myrtanylamine. S_p configurational

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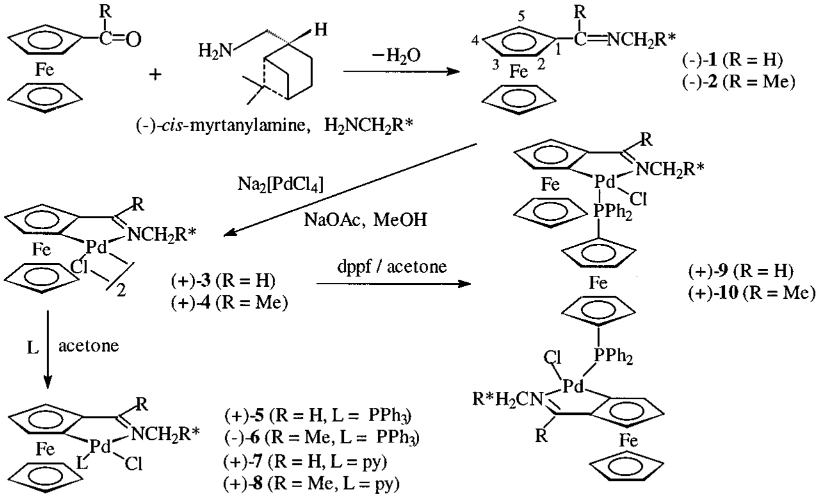
Scheme 1



planar[3,4] chiral derivatives of ferrocene have been synthesized by cyclopalladation of these imines (Scheme 1), and the absolute configurations of (+)-**5** and (−)-**6** have been ascertained by X-ray diffraction studies.

Results and Discussion

Ligand Synthesis. Both optically pure ferrocenylimines were obtained as orange plates in *ca*. 75% yield from the reaction between acylferrocene and (−)-*cis*-myrtanylamine in benzene.[8,9] For these systems the presence of molecular sieves (5 Å) was needed to enforce favorable displacement of the equilibria. Moreover, these ligands were readily decomposed in the purification procedure using column chromatography. ^1H NMR and $^{13}C\{^1H\}$ NMR in $CDCl_3$ of compounds (−)-**1** and (−)-**2** are quite informative about their structures and behaviors in solution (see Experimental Section).

Diastereoselective Cyclopalladation of Ferrocenylimines (−)-1 and (−)-2. Synthesis of Planar Chiral Cyclopalladated Compounds. Asymmetric cyclopalladation of ferrocenylimines with sodium tetrachloropalladate(II) and sodium acetate in methanol gave the diastereoselectively cyclopalladated di-μ-chloro-bridged organometallics (+)-(S_p,S_p)-[$Pd\{(\eta^5\text{-}C_5H_3CR{=}N\text{-}CH_2R^*)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ (+)-**3** and (+)-**4**. Only one diastereoisomer was detected by ^1H NMR {500 MHz} and thin-layer chromatography in every cyclopalladated complex. Addition of triphenylphosphine or pyridine to an acetone suspension of (+)-**3** or (+)-**4** led to cleavage of the di-μ-chloro bridges giving monomeric compounds (+)-(S_p)-$Pd[\{\eta^5\text{-}C_5H_3C(R){=}NCH_2R^*\}Fe(\eta^5\text{-}C_5H_5)(L)Cl]$ (+)-**5**, (−)-**6**, (+)-**7**, or (+)-**8**, respectively. No evidence of cleavage of the Pd−N bond was observed in any of the cases, even when a large excess of triphenylphosphine or pyridine (up to a 4-fold molar ratio) was used. However, when an excess of 1,1′-bis(diphenylphosphino)ferrocene (molar ratio > 2:1) was used, both Pd−N and Pd−C bonds were broken and $PdCl_2$(dppf) was formed. In order to obtain (+)-**9** and (+)-**10**, the reaction between (+)-**3** or (+)-**4** and dppf must be carried out in an exact molar ratio of 1:1 or 1:1.2, respectively, at room temperature.

Microanalysis indicated that (+)-**3** and (+)-**4** were dimeric cyclopalladated complexes, whereas ^1H NMR in $CDCl_3$ showed that the two singlets (in the range δ 4.18−4.66) due to the pairs H^2, H^5 and H^3, H^4 of the ferrocenylimines split into three signals (H^3, H^4, H^5), and the H^3 signal was shifted upfield upon cyclopalladation, thus indicating that the palladium atom causes a decrease in the ring current of the substituted pentagonal ring of the ferrocenyl moiety.[10] One of the most relevant differences observed in the $^{13}C\{^1H\}$ NMR spectra of free (−)-**1** and (−)-**2** and in those of their cyclopalladated complexes is the splitting of the resonance due to the C^3, C^4 pair of carbon atoms, since the formation of the metallacycle involves a decrease in symmetry of the substituted cyclopentadienyl ring. The resonance of the imino C atom is observed at 161.2 ppm for (−)-**1**. The signal of the metalated carbon atom exhibits a low intensity due to the nuclear Overhauser effect, but this was not observed in all of the complexes.[11] $^{31}P\{^1H\}$ NMR spectra of (+)-**5** and (−)-**6** are in agreement with a *trans* relationship between the phosphine ligands and the nitrogen donor atoms.[12]

The cyclopalladation reactions of the ferrocenylimines reported here (Scheme 1) have very high stereoselectivity as well as good yields, and compounds (+)-**5** and (−)-**6** are the first examples of S_p configurational planar chiral 1,2-disubstituted cyclopalladated derivatives of ferrocene that have been structurally characterized.

Crystal and Molecular Structures of (+)-5·$^1/_2C_2H_5OH$ and (−)-6. X-ray analysis has confirmed that both compounds have the same absolute configuration at each of the four chiral centers: S_p for planar chirality of the ferrocenyl moiety at C(13), *S* at C(1) and C(5), and *R* at C(2) as expected from the synthetic route (Scheme 1). The palladium atom in the metallacycle is bound to a chloride and a PPh_3 ligand, with the latter *trans* to the imino nitrogen atom, thus leading to a slightly distorted square-planar coordination environment around it (Figure 1). The Pd−ligand bond lengths (Table 2) are similar to those found in five-membered palladocyclic compounds containing organic imines. The bond angles (Table 2) between adjacent atoms in the coordination sphere of the palladium atom lie in the

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Table 1. Crystal Data

	(+)-**5**·$^1/_2C_2H_5OH$	(−)-**6**
	Crystal Parameters	
formula	$C_{39}H_{41}NPClFePd \cdot {}^1/_2C_2H_5OH$	$C_{40}H_{43}NPClFePd$
fw	775.4	766.4
shape (color)	plate (red)	prism (red)
size, mm	0.05 × 0.20 × 0.55	0.20 × 0.30 × 0.38
cryst syst	monoclinic	orthorhombic
space group	$C2$ (No. 5)	$P2_12_12_1$ (No. 19)
a, Å	18.292(1)	10.311(1)
b, Å	9.162(1)	14.128(1)
c, Å	23.128(1)	23.794(2)
β, deg	104.40(1)	
V, Å^3	3754.3(5)	3466.2 (5)
Z	4	4
F(000)	1596	1576
D(calcd), g cm^{-3}	1.372	1.469
μ(Mo Kα), mm^{-1}	1.008	1.090
	Data Collection	
scan type	80 oscillation photos	24 oscillation photos
2θ range, deg	$3 < 2\theta < 55$	$3 < 2\theta < 55$
rflns collected	5257	12340
indep rflns	5241 ($R_{int} = 15.55\%$)	6860 ($R_{int} = 6.07\%$)
obsd rflns ($F > 4\sigma(F)$)	3472 ($h,\pm k,\pm l$)	5958 ($\pm h,k,\pm l$)
	Refinement	
R_1[a]	0.0478	0.0500
wR_2[b]	0.1571	0.1160
weighting scheme[c]	$a = 0.1160$, $b = 4.92$	$a = 0.0488$, $b = 2.93$
no. of params refined	355	407
S (GOF)[d]	1.092	1.49
max, mean Δ/α	0.005, 0.000	0.001, 0.000
$\Delta\rho_{max}$, e Å^{-3}	0.595, −0.768	0.397, −0.967

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum(wF_o^2)^2]\}^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (a \times P)^2 + b \times P$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$. [d] GOF $\equiv S = \{[\sum w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)

	(+)-**5**·$^1/_2C_2H_5OH$	(−)-**6**
Pd(1)−C(13)	2.013(7)	2.000(5)
Pd(1)−N(1)	2.153(6)	2.147(4)
Pd(1)−P(1)	2.236(2)	2.250(1)
Pd(1)−Cl(1)	2.383(2)	2.372(2)
C(10)−N(1)	1.48(1)	1.467(7)
N(1)−C(11)	1.30(1)	1.294(7)
C(11)−C(40)		1.516(8)
C(13)−Pd(1)−N(1)	80.8(3)	80.5(2)
C(13)−Pd(1)−P(1)	91.3(2)	93.0(2)
N(1)−Pd(1)−Cl(1)	93.4(2)	93.8(1)
P(1)−Pd(1)−Cl(1)	94.93(7)	92.40(6)
C(10)−N(1)−Pd(1)	129.0(5)	125.5(4)
C(11)−N(1)−C(10)	118.8(6)	121.0(4)
C(11)−N(1)−Pd(1)	112.0(5)	113.5(4)
C(12)−C(11)−C(40)		119.0(6)

range 81.0(1)−95.0(1)° for (+)-**5**·$^1/_2C_2H_5OH$ and 80.8(2)−93.7(1)° for (−)-**6**. In both structures, the two cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle: 3.7° for (+)-**5**·$^1/_2C_2H_5OH$ and 4.0° for (−)-**6**], and the two rings involved in the bicyclic system formed by fusion of the palladocycle with the ferrocenyl C_5H_3 moiety are approximately coplanar, the relevant dihedral angle being 9.7° for (+)-**5**·$^1/_2C_2H_5OH$ and 6.1° for (−)-**6**.

Experimental Section

General Methods. ^1H NMR spectra were recorded at on a Bruker WM 250 using $CDCl_3$ (99.8%) and $SiMe_4$ as solvent and internal standard. $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX 500 using $CDCl_3$ (99.8%) as solvent and $SiMe_4$ and H_3PO_4 (85%) as internal standards, respectively. Optical rotations were measured in chloroform solution within a 1-dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Mass spectra were recorded on a Hewlett Packard 5989B mass spectrometer. Melting points were determined on a Regeltrafo F. Thermogeräte 7950 instrument. Elemental analyses were performed by MEDAC Ltd of the Department of Chemistry at Brunel University. Ferrocenecarboxaldehyde, acetylferrocene, and sodium tetrachloropalladate(II) were obtained from Strem Chemicals, Inc. (−)-*cis*-Myrtanylamine and 5 Å molecular sieves were purchased from Aldrich. All were used as received. Benzene was dried over sodium metal and boiled under reflux in a nitrogen atmosphere until it gave a blue coloration with Ph_2CO, and then it was distilled.

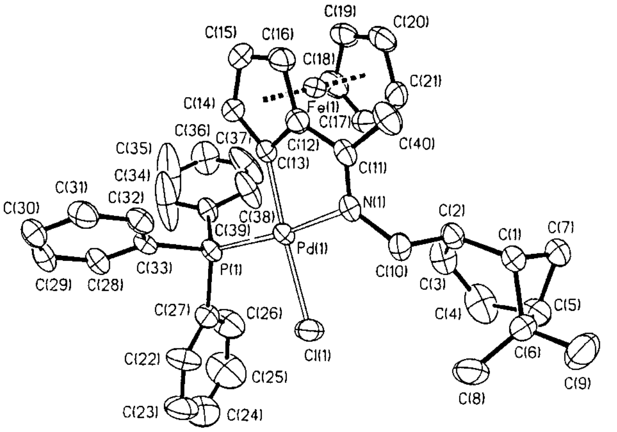

Figure 1. ORTEP drawing (30% thermal ellipsoids) of (−)-**6** and atom-numbering scheme. Molecule (+)-**5** has the same structure except that the methyl group C(40) is replaced by a hydrogen atom.

Preparation of (−)-(η^5-$C_5H_4CR{=}NCH_2R^*$)Fe(η^5-C_5H_5) [R = H, (−)-1, or Me, (−)-2]. Acylferrocene (10 mmol) and (−)-*cis*-myrtanylamine (1.53 g, 10 mmol) were dissolved in dry benzene (100 mL). The flask containing the reaction mixture was connected to a condenser equipped with a Dean−Stark apparatus. The red solution was refluxed over an oil bath for about 6 h and then transferred into a Schlenk tube, into which 5 Å molecular sieves (3.0 g) were introduced. The mixture was further refluxed for 5−6 h and carefully filtered, and the filtrate was reduced to dryness. Addition of *n*-hexane to the oily material and cooling at −20 °C produced yellow plate-like crystals. Yield: 2.48 g (71%) and 2.80 g (77%), respectively. Characterization data for (−)-**1**: mp 98−99 °C; $[\alpha]_D$ −9.6° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.47 (m, 2H, NCH_2), 4.18 (s, 5H, C_5H_5), 4.35 [s, 2H, H^3, H^4 (C_5H_4)], 4.63 [s, 2H, H^2, H^5 (C_5H_4)], 8.09 (s, 1H, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 69.0 (NCH_2), 69.7 (C_5H_5), 70.3 [C^2, C^5 (C_5H_4)], 70.9 [C^3, C^4 (C_5H_4)], 161.2 (C=N); MS *m/z* 349 (M^+). Anal. Calcd for $C_{21}H_{27}NFe$: C, 72.14; H, 7.73; N, 3.99. Found: C, 72.21; H, 7.79; N, 4.01. (−)-**2**: mp 69−70 °C; $[\alpha]_D$ −39.1° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.48 (m, 3H, $H_3CC{=}N$), 3.37 (m, 2H, NCH_2), 4.21 (s, 5H, C_5H_5), 4.51 [s, 2H, H^3, H^4 (C_5H_4)], 4.66 [s, 2H, H^2, H^5 (C_5H_4)]; $^{13}C\{^1H\}$ NMR (selected data) δ 17.0 (N=C*Me*), 58.4 (NCH_2), 68.4 (C_5H_5), 69.8 [C^2, C^5 (C_5H_4)], 70.7 [C^3, C^4 (C_5H_4)]; MS *m/z* 363 (M^+). Anal. Calcd for $C_{22}H_{29}NFe$: C, 72.73; H, 8.04; N, 3.85. Found: C, 72.49; H, 8.00; N, 3.77.

Preparation of (+)-(S_p,S_p)-[Pd{(η^5-$C_5H_3CR{=}NCH_2R^*$)Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ [R = H, (+)-3, or Me, (+)-4]. Imine (−)-**1** or (−)-**2** (2.0 mmol) was added to a methanolic (30 mL) solution containing $Na_2[PdCl_4]$ (0.60 g, 2.0 mmol) and sodium acetate trihydrate (0.27 g, 2.0 mmol). The resulting mixture was stirred at room temperature for 24 h, and the wine-red precipitate was collected by vacuum filtration and air-dried. The product was extracted into chloroform and isolated as a red solid *via* column chromatography (silica 60 using 10:1 chloroform/*n*-hexane as eluent). The red solid was subsequently recrystallized as orange needles from dichloromethane by addition of *n*-hexane. Yield: 0.72 g (73%) and 0.81 g (80%), respectively. Characterization data for (+)-**3**: mp >220 °C (dec); $[\alpha]_D$ +244.6° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.40 (m, 4H, NCH_2), 4.29 [s, 2H, H^3 (C_5H_3)], 4.38 (s, 10H, C_5H_5), 4.76 [m, 4H, H^4, H^5 (C_5H_3)], 7.75 (s, 2H, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 65.5 (NCH_2), 72.5 [$C^4(C_5H_3)$], 72.8 [$C^5(C_5H_3)$], 73.0 [$C^3(C_5H_3)$], 73.3 (C_5H_5), 129.0 (CPd). Anal. Calcd for $C_{42}H_{52}N_2Cl_2Fe_2Pd_2$: C, 51.46; H, 5.35; N, 2.86. Found: C, 51.46; H, 5.36; N, 2.69. (+)-**4**: mp >220 °C (dec); $[\alpha]_D$ +160.0° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.39 (m, 6H, H_3CC=N), 3.40 (m, 4H, NCH_2), 4.21 [s, 2H, H^3 (C_5H_3)], 4.30 (s, 10H, C_5H_5), 4.70 [m, 4H, H^4, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ NMR (selected data) δ 17.0 (N=C*Me*), 59.0 (NCH_2), 67.7 (C_5H_3), 72.6 (C_5H_5). Anal. Calcd for $C_{44}H_{56}N_2Cl_2Fe_2Pd_2$: C, 52.41; H, 5.60; N, 2.78. Found: C, 52.63; H, 5.70; N, 2.71.

Preparation of (S_p)-[Pd{(η^5-C_5H_3CR=NCH_2R^*)Fe(η^5-C_5H_5)}(PPh_3)Cl] [R = H, (+)-5, or Me, (−)-6]. Triphenylphosphine (0.105 g, 0.4 mmol) was added to an acetone suspension (15 mL) containing the dimeric complex (+)-**3** or (+)-**4** (0.1 mmol). The resulting mixture was refluxed for 30 min. During this period the starting material dissolved gradually. After cooling to room temperature, the solution was filtered and the filtrate concentrated to dryness under vacuum. Addition of diethyl ether to the residue resulted in precipitation of the desired compound, which was recrystallized as orange plates from THF/EtOH (4:1). Yield: 0.086 g (57%) and 0.11 g (69%), respectively. Characterization data for (+)-**5**·$^1/_2$EtOH: mp 206 °C (dec); $[\alpha]_D$ +29.4° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.47 (m, 2H, NCH_2), 3.84 [s, 1H, H^3 (C_5H_3)], 3.88 (s, 5H, C_5H_5), 4.37 [s, 2H, H^3 (C_5H_3)], 7.26−7.44 (m, 15H, Ph), 7.75 (s, 1H, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 59.2 (NCH_2), 64.5 [$C^4(C_5H_3)$], 68.7 [C^3, $C^5(C_5H_3)$], 72.0 (C_5H_5)]; 128.7, 131.0, 132.3, 135.6 (PPh_3); $^{31}P\{^1H\}$ NMR δ 49.7. Anal. Calcd for $C_{40}H_{44}NO_{0.5}PClFePd$: C, 61.93; H, 5.68; N, 1.80. Found: C, 61.63; H, 5.89; N, 1.78. (−)-**6**: mp 216 °C (dec); $[\alpha]_D$ −291.2° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.65 (m, 3H, H_3CC=N), 3.19 (m, 2H, NCH_2), 3.50 [s, 1H, H^3 (C_5H_3)], 3.77 (s, 5H, C_5H_5), 4.27 [m, 2H, H^4, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ NMR (selected data) δ 16.2 (N=C*Me*), 56.9 (NCH_2), 66.7 [$C^4(C_5H_3)$], 68.2 [$C^5(C_5H_3)$], 70.6 [$C^3(C_5H_3)$], 70.8 (C_5H_5); 128.5, 130.9, 132.7, 135.6 (PPh_3); $^{31}P\{^1H\}$ NMR δ 49.5. Anal. Calcd for $C_{40}H_{43}NPClFePd$: C, 62.68; H, 5.65; N, 1.83. Found: C, 63.06; H, 5.65; N, 1.80.

Preparation of (+)-(S_p)-[Pd{(η^5-C_5H_3CR=NCH_2R^*)Fe(η^5-C_5H_5)}(py)Cl] [R = H, (+)-7, or Me, (+)-8]. Orange needles of (+)-**7** or (+)-**8** were prepared according to the procedure described above for (+)-**5** and (−)-**6** using pyridine in place of triphenylphosphine as starting material. Yield: 0.068 g (60%) and 0.078 g (67%), respectively. Characterization data for (+)-**7**: mp 167−168 °C; $[\alpha]_D$ +76.2° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.40 (m, 2H, NCH_2), 3.86 [s, 1H, H^3 (C_5H_3)], 4.25 (C_5H_5), 4.47 [s, 1H, H^4 (C_5H_3)], 4.66 [s, 1H, H^5 (C_5H_3)], 7.75 (s, 1H, CH=N), 7.34, 7.77, 8.90 (3m, 5H, py); $^{13}C\{^1H\}$ NMR (selected data) δ 66.4 (NCH_2), 68.7 [$C^4(C_5H_3)$], 70.5 [C^3, $C^5(C_5H_3)$], 73.1 (C_5H_5); 125.4, 138.3, 153.8, 154.3 (py). Anal. Calcd for $C_{26}H_{31}N_2ClFePd$: C, 54.86; H, 5.49; N, 4.92. Found: C, 55.01; H, 5.60; N, 4.88. (+)-**8**: mp >220 °C (dec); $[\alpha]_D$ +93.5° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.18 (s, 3H, H_3CC=N), 3.78 (m, 2H, NCH_2), 3.86 [s, 1H, H^3 (C_5H_3)], 4.25 [s, 5H, (C_5H_5)], 4.47 [s, 1H, H^4 (C_5H_3)], 4.66 [s, 1H, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ NMR (selected data) δ 16.4 (N=C*Me*), 58.8 (NCH_2), 66.9 [$C^4(C_5H_3)$], 67.3 [$C^5(C_5H_3)$], 70.6 [$C^3(C_5H_3)$], 72.5 (C_5H_5); 125.4, 138.3, 154.3 (py). Anal. Calcd for $C_{27}H_{33}N_2ClFePd$: C, 55.60; H, 5.70; N, 4.80. Found: C, 55.71; H, 5.77; N, 4.78.

Preparation of (+)-(S_p,S_p)-[PdCl{(η^5-$C_5H_3C(R)$=N-CH_2R^*)Fe(η^5-C_5H_5)}($Ph_2PC_5H_4$-η^5)]$_2$Fe [R = H, (+)-9, or Me, (+)-10]. An acetone solution (5 mL) of 1,1′-bis(diphenylphosphino)ferrocene [0.055 g, 0.1 mmol for (+)-**3** or 0.066 g, 0.12 mmol for (+)-**4**] was added dropwise to an acetone suspension (5 mL) containing the dimeric complex (+)-**3** or (+)-**4** (0.1 mmol). The resulting mixture was stirred at room temperature for 3 h. After the red suspension became clear upon stirring, the solution was filtered and the filtrate concentrated to dryness under vacuum. Addition of diethyl ether to the residue resulted in precipitation of the desired compound, which was recrystallized as orange plates from CH_2Cl_2/*n*-hexane (3:1). Yield: 0.087 g (57%) and 0.11 g (69%), respectively. Characterization data for (+)-**9**·$^1/_2CH_2Cl_2$: mp 195−196 °C (dec); $[\alpha]_D$ +146.5° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.33−3.45 (m, 4H, NCH_2), 3.69 (s, 4H, C_5H_3), 3.94 (s, 10H, C_5H_5), 4.12−4.53 (m, 6H, C_5H_3 + C_5H_4), 4.85−4.95 (m, 4H, C_5H_4), 7.29−7.55 (m, 24H, Ph), 7.84 (s, 2H, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 59.0 (NCH_2), 65.3 (C_5H_3), 70.7 (C_5H_4), 72.8 (C_5H_5); 128.2, 131.0, 132.0, 135.6 (PPh_2); $^{31}P\{^1H\}$ NMR δ 39.7. Anal. Calcd for $C_{76.5}H_{81}N_2P_2Cl_3Fe_3Pd_2$: C, 58.19; H, 5.13; N, 1.77. Found: C, 58.06; H, 5.23; N, 1.73. (+)-**10**: mp 189−191 °C (dec); $[\alpha]_D$ +76.2° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.86−2.99 (m, 6H, H_3CC=N), 3.47 (m, 4H, NCH_2), 3.50 (s, 4H, C_5H_3), 4.05 (s, 10H, C_5H_5), 4.20−4.39 (s, 6H, C_5H_3 + C_5H_4), 4.90−5.16 (m, 4H, C_5H_4), 7.39−7.57 (m, 24H, Ph); $^{13}C\{^1H\}$ NMR (selected data) δ 16.2 (N=C*Me*), 56.4 (NCH_2), 70.7 (C_5H_3, C_5H_4), 71.1 (C_5H_5); 128.2, 128.6, 134.7, (PPh_2); $^{31}P\{^1H\}$ NMR δ 39.4. Anal. Calcd for $C_{78}H_{84}N_2P_2Cl_2Fe_3Pd_2$: C, 59.94; H, 5.42; N, 1.79. Found: C, 60.61; H, 5.51; N, 1.89.

Crystallographic Studies. Red crystals of (+)-**5**·$^1/_2C_2H_5OH$ (plate) and (−)-**6** (prism) were grown in a 3:1 mixture of THF and ethanol, and selected specimens were mounted on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer. Crystallographic data are summarized in Table 1. Intensity data were collected at 294 K using graphite-monochromatized Mo Kα radiation (λ = 0.7103 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min}$ = 3°, $2\theta_{max}$ = 55°, 36 5° oscillation frames in the range 0−180°, exposure 8 min/frame).[13] A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program.[14] The crystal structures were determined by the direct method, which yielded the positions of all non-hydrogen atoms, which were refined anisotropically. The ethanol solvate molecule in (+)-**5**·$^1/_2C_2H_5OH$ is located in a general position with half site occupancy for its component atoms. Hydrogen atoms were all generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. All computations were performed on an IBM compatible 486 PC with the Siemens SHELXTL/PC version 5.03 program package.[15] Refinement of weighted *R*-index wR_2 was based on F^2 for all reflections except for *n* with very negative F^2 or flagged for potential systematic errors. A conventional *R*-factor R_1 based on observed *F* greater than $4\sigma(F_o)$ is also calculated for comparison. The final R_1 and wR_2 indices, the number of parameters refined for each structure, largest and mean Δ/σ, and largest difference peaks are presented in Table 1. Table 2 gives selected bond distances and angles.

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Supporting Information Available: Tables of final atomic coordinates, all bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for (+)-**5**·$^1/_2C_2H_5OH$ and (−)-**6** (16 pages). Ordering information is given on any current masthead page.

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