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Isolation and Structural Characterization of Enantiomerically Pure Planar Chiral Cyclopalladated Derivatives of Ferrocenylimines

Gang Zhao, Qi-Guang Wang, and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Reaction of ferrocenecarboxaldehyde with (+)-(*R*)-1-amino-2-(methoxymethyl)pyrrolidine [(+)-(*R*)-**1]** and (−)-(*S*)-1-amino-2-(methoxymethyl)pyrrolidine [(−)-(*S*)-**1]** in dry benzene gave new chiral ferrocenylimines (−)-(*R*)-$\mathrm{FcCH{=}N\overline{NCH_2CH_2CH_2C}HCH_2OCH_3}$ [(−)-(*R*)-**2**] and (+)-(*S*)-$\mathrm{FcCH{=}N\overline{NCH_2CH_2CH_2C}HCH_2OCH_3}$ [(+)-(*S*)-**2**], respectively. Asymmetric cyclopalladation of (−)-(*R*)-**2** and (+)-(*S*)-**2** with sodium tetrachloropalladate(II) and sodium acetate trihydrate in methanol at room temperature gave a mixture of diasteromeric cyclopalladated products (+)-(S_p,*R*)-$\mathrm{[\overline{PdCl(\eta^5\text{-}C_5H_3CH{=}N}\underline{NCH_2CH_2CH_2C}HCH_2OCH_3)Fe(\eta^5\text{-}C_5H_5)]}$ [(+)-(S_p,*R*)-**3**], (−)-(R_p,*R*)-$\mathrm{[\overline{PdCl(\eta^5\text{-}C_5H_3CH{=}N}\underline{NCH_2CH_2CH_2C}HCH_2OCH_3)Fe(\eta^5\text{-}C_5H_5)]}$ [(−)-(R_p,*R*)-**3**] and (−)-(R_p,*S*)-$\mathrm{[\overline{PdCl(\eta^5\text{-}C_5H_3CH{=}N}\underline{NCH_2CH_2CH_2C}HCH_2OCH_3)Fe(\eta^5\text{-}C_5H_5)]}$ [(−)-(R_p,*S*)-**3**], (+)-(S_p,*S*)-$\mathrm{[\overline{PdCl(\eta^5\text{-}C_5H_3CH{=}N}\underline{NCH_2CH_2CH_2C}HCH_2OCH_3)Fe\ (\eta^5\text{-}C_5H_5)]}$ [(+)-(S_p,*S*)-**3**] in ca. 75% yield with a high level of diastereoselectivity, respectively. The four enantiopure compounds were isolated from the two mixtures through column-layer chromatography. Their relationship was elucidated by NMR, optical rotation, and single-crystal X-ray analysis.

Introduction

Chiral cyclopalladated compounds are of great interest as a consequence of their useful applications in many areas, such as materials chemistry,[1] optical resolution of racemic phosphines and arsines,[2] determination of the optical purity of chiral phosphines and amines,[3] as well as establishment of the absolute configuration of chiral phosphines by NMR spectroscopy and single-crystal X-ray analysis.[4] In addition, some studies on the antitumor activity of such derivatives have also been reported.[5] Recently, chiral cyclopalladated compounds have been employed to promote asymmetric Diels−Alder reaction in the asymmetric synthesis of (P-chiral) As−P and P−P bidentate ligands.[6] Although many cyclopalladated derivatives of ferrocene are known,[1,7,8] most of them have been obtained as racemic mixtures due to the difficulty in isolating these compounds in enantiomerically pure form.[9] Recently, two papers reported optically active cyclopalladated derivatives of

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(1) (a) Togni, A.; Hayashi, T. *Ferrocenes. Homogeneous Catalysis. Organic Synthesis and Materials Science*; VCH: Weinheim, Germany, 1995. (b) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (c) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley & Sons: Chichester, New York, 1995. (d) Baena, M. J.; Buey, J.; Espinet, P.; Kitzerow, H. S.; Heppke, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1201.

(2) (a) Chooi, S. Y. M.; Siah, S.-Y.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812. (b) Gabbitas, N.; Salem, G.; Sterns, M.; Willis, A. C. *J. Chem. Soc. Dalton Trans.* **1993**, 3271. (c) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743. (d) Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Manassero, M. *Tetrahedron: Asymmetry* **1994**, *5*, 511. (e) Tani, K.; Tashiro, H.; Yoshida, M.; Yamagata, T. *J. Organomet. Chem.* **1994**, *469*, 229. (f) Chooi, S. Y. M.; Ranford, J. D.; Leung, P. H.; Mok, K. F. *Tetrahedron: Asymmetry* **1994**, *5*, 1805. (g) Albert, J.; Granell, J.; Sales, M.; Font-Bardía, M.; Solans, X. *Organometallics* **1995**, *14*, 1393.

(3) Chooi, S. Y. M.; Leung, P. H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529.

(4) (a) Bookham, J. L.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1352. (b) Albert, J.; Granell, J.; Muller, G.; Sainz, D.; Font-Bardía, M.; Solans, X. *Tetrahedron: Asymmetry* **1995**, *6*, 325. (c) Siah, S.-Y.; Leung, P.; Mok, K. F.; Drew, M. G. B. *Tetrahedron: Asymmetry* **1996**, *7*, 357. (d) Aw, B.-H.; Selvaratnam, S.; Leung, P.-H.; Rees, N. H.; McFarlane, W. *Tetrahedron: Asymmetry* **1996**, *7*, 1753. (e) López, C.; Bosque, R.; Sainz, D. *Organometallics* **1997**, *16*, 3261.

(5) (a) Navarro-Ranninger, C.; López-Solera, C.; Pérez, J. M.; Masaguer, J. M.; Alonso, C. *Appl. Organomet. Chem.* **1993**, *7*, 57. (b) Higgius, J. *J. Inorg. Biochem.* **1993**, *49*, 149.

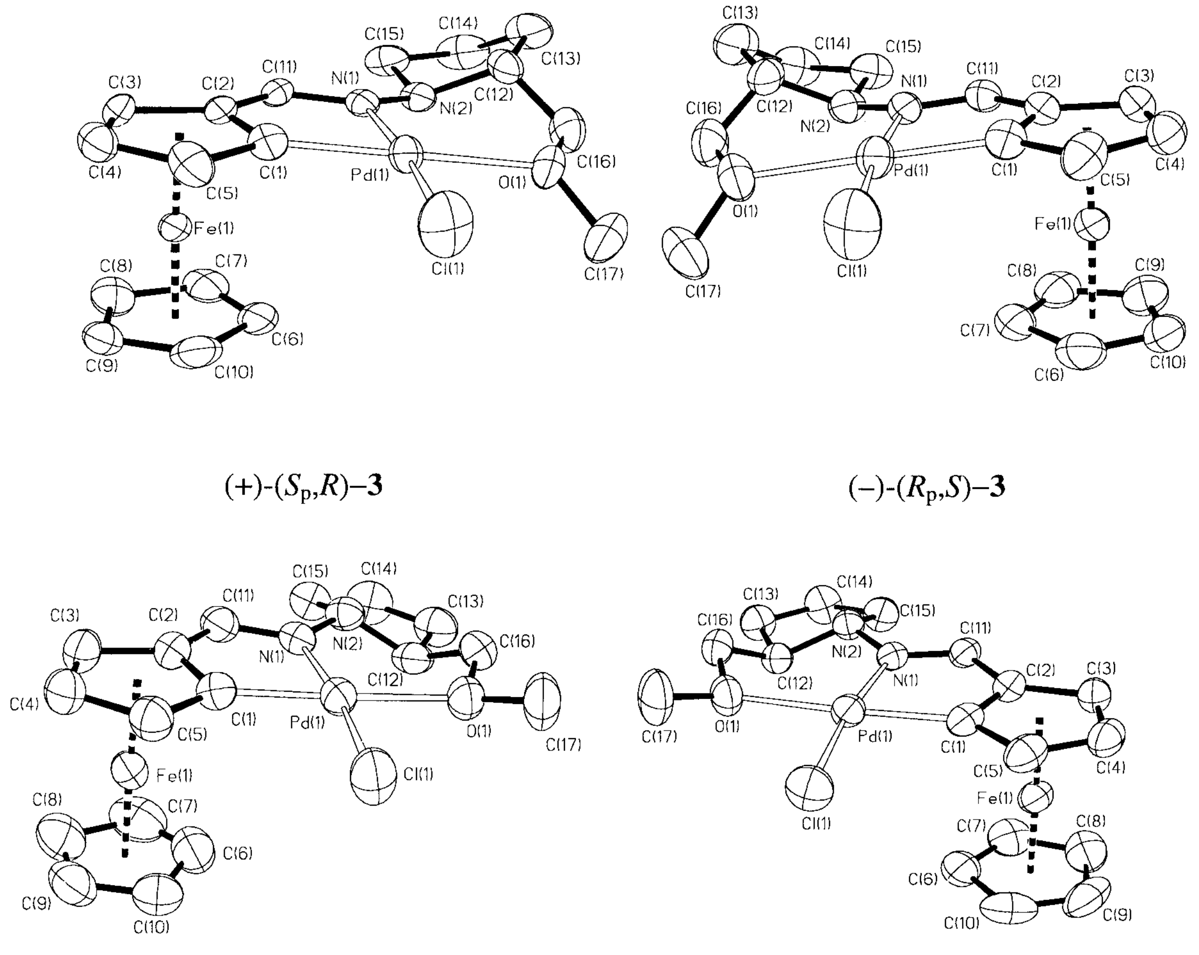
(6) (a) Aw, B.-H.; Leung, P.-H.; White, A. J. P.; Williams, D. J. *Organometallics* **1996**, *15*, 3640. (b) Leung, P. H.; Selvaratnam, S.; Cheng, C. R.; Mok, K. F.; Rees, N. H.; McFarlane, W. *Chem. Commun.* **1997**, 751.

(7) (a) Bosque, R.; López, C.; Sales, J.; Solans, X.; Font-Bardía, M. *J. Chem. Soc., Dalton Trans.* **1994**, 735. (b) Bosque, R.; López, C.; Sales, J.; Solans, X. *J. Organomet. Chem.* **1994**, *483*, 61. (c) Huo, S. Q.; Wu, Y. J.; Du, C. X.; Zhu, Y.; Yuan, H. Z.; Mao, X. A. *J. Organomet. Chem.* **1994**, *483*, 139. (d) Bosque, R.; López, C.; Sales, J.; Tramuns, D.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1995**, 2445. (d) Huo, S. Q.; Wu, Y. J.; Du, C. X.; Zhu, Y.; Yuan, H. Z.; Mao, X. A. *J. Organomet. Chem.* **1994**, *483*, 139. (e) López, C.; Bosque, R.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **1997**, *539*, 99. (f) López, C.; Bosque, R.; Sainz, D.; Solans, X.; Font-Bardía, M. *Organometallics* **1997**, *16*, 3261.

(8) (a) López, C.; Bosque, R.; Solans, X.; Font-Bardía, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2527. (b) Zhao, G.; Xue, F.; Zhang, Z. Y.; Mak, T. C. W. *Organometallics* **1997**, *16*, 4023.

(9) Maassarani, F.; Pfeffer, M.; Borgne, G. L.; Jastrzebski, J. T. B. H.; van Koten, G. *Organometallics* **1987**, *6*, 1111.

S0276-7333(98)00203-9 CCC: \$15.00



(+)-(S_p,*R*)–**3**

(–)-(R_p,*S*)–**3**

(+)-(S_p,*S*)–**3**

(–)-(R_p,*R*)–**3**

Figure 1. Perspective views showing the structural relationship between planar chiral ferrocenylimines (+)-(S_p,*R*)-**3**, (−)-(R_p,*S*)-**3**, (+)-(S_p,*S*)-**3**, and (−)-(R_p,*R*)-**3** with a common atom, numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

ferrocene with a planar chiral metalated carbon center, but only one isomer was obtained.[8] Isolation and absolute configuration determination of this kind of compound are very important for understanding the stereochemistry. To our knowledge, this is first example of successful isolation and X-ray structural determination of enantiomerically pure 1,2-disubstituted planar chiral cyclopadallated compounds of ferrocene containing their enantiomers and diastereomers.

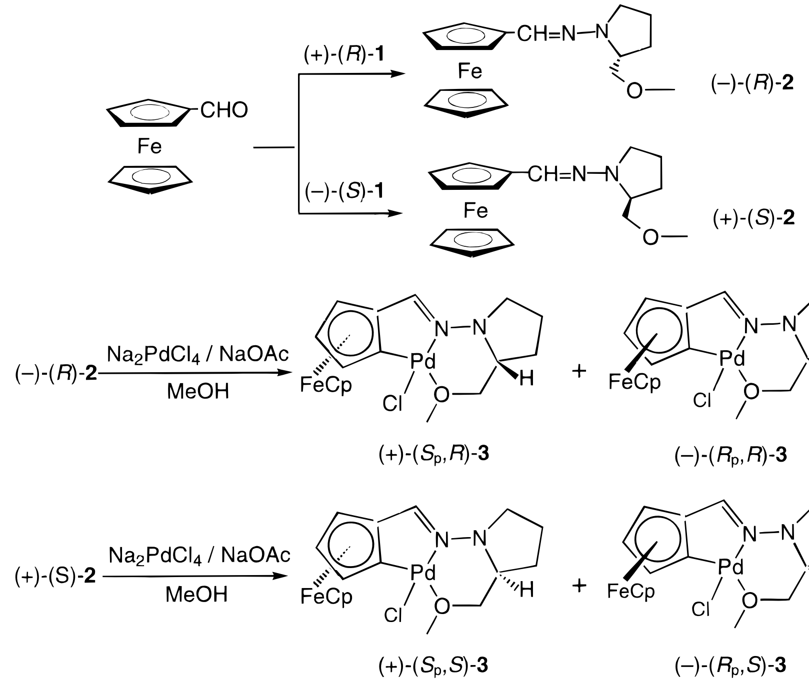
To investigate the asymmetric cyclopalladation of ferrocenes and isolate this kind of compound in enantiomerically pure form, we decided to elucidate whether the presence of a chiral substituent in the cyclopentadienyl ring would preferentially induce the activation of one of the two ortho σ(C−H) bonds of the ferrocene moiety. In this regard, we employed the enantiomerically pure ferrocenylimines (+)-(*S*)-**2**, and (−)-(*R*)-**2**, which were asymmetrically cyclopalladated with sodium tetrachloropalladate(II) and sodium acetate trihydrate in methanol.

Results and Dicussion

Ligand Synthesis. Ferrocenylimines (−)-(*R*)-**2** ($[\alpha]_D^{20}$ = −11.30°; *c* 1.0, $CHCl_3$) and (+)−(*S*)-**2** ($[\alpha]_D^{20}$ = +11.67°; *c* = 1.0, $CHCl_3$) were prepared from ferrocenecarboxaldehyde by condensation with (+)-(*R*)-1-amino-2-(methoxymethyl)pyrrolidine (+)-(*R*)-**1** and (−)-(*S*)-1-amino-2-(methoxymethyl)pyrrolidine (−)-(*S*)-**1** (Aldrich products) in dry benzene. Moreover, these ligands might suffer appreciable decomposition in the purification procedure using column chromatography. ^{1}H NMR and ^{13}C{^{1}H} NMR in $CDCl_3$ of compounds (−)-(*R*)-**2** and (+)-(*S*)-**2** provided useful information about its structure and behavior in solution (see Experimental Section).

Diastereoselective Cyclopalladation of Ferrocenylimines (−)-(*R*)-2 and (+)-(*S*)-2. Synthesis and Isolation of Planar Chiral Cyclopalladated Compounds. Asymmetric cyclopalladation of (−)-(*R*)-**2** with sodium tetrachloropalladate(II) and sodium acetate trihydrate in methanol at room temperature gave a mixture of diasteromeric cyclopalladated products (+)−(S_p,*R*)-**3** ($[\alpha]_D^{20}$ = +3461°; *c* = 1.0, $CHCl_3$) and (−)-(R_p,*R*)-**3** ($[\alpha]_D^{20}$ = −2885°; *c* = 1.0, $CHCl_3$) in 70−77% yield with a high level of diastereoselectivity [(−)-(R_p,*R*)-**3**:(+)−(S_p,*R*)-**3** = 15:85]. Asymmetric cyclopalladation of (+)−(*S*)-**2** under the same conditions likewise furnished a pair of diastereomers (−)-(R_p,*S*)-**3** ($[\alpha]_D^{20}$ = −3458°; *c* = 1.0, $CHCl_3$) and (+)-(S_p,*S*)-**3** ($[\alpha]_D^{20}$ =

Scheme 1



+2888°; $c = 1.0$, $CHCl_3$) in 78% yield with a high level of diastereoselectivity [(+)-(S_p,S)-**3**:(−)-(R_p,S)-**3** = 15:85]. The four enantiopure compounds were isolated from the two mixtures through column-layer chromatography [2.5 × 20 cm SiO_2 column, $CHCl_3$:n-hexane (9:1) as the eluent]. Their relationship was elucidated by ^1H NMR, $^{13}C\{^1H\}$ NMR, thin-layer chromatography, and single-crystal X-ray analysis. It is noted that the ^1H NMR spectra in $CDCl_3$ of the enantiomers are similar but obviously quite different from those of their diastereomers. Chemical shifts for substituted cyclopentadienyl protons of enantiomeric (+)-(S_p,R)-**3** and (−)-(R_p,S)-**3** are 4.80, 4.28 and 4.17 ppm, respectively, but those of (−)-(R_p,R)-**3** and (+)-(S_p,S)-**3** are 4.85, 4.23 and 4.19 ppm, respectively. Moreover, the signals due to unsubstituted cyclopentadienyl protons of (+)-(S_p,R)-**3** and (−)-(R_p,S)-**3** shifted downfield by 0.14 ppm at 4.22 ppm and those in (−)-(R_p,R)-**3** and (+)-(S_p,S)-**3** shifted downfield by 0.27 ppm at 4.35 ppm.

Crystal and Molecular Structures of (+)-(S_p,R)-3, (−)-(R_p,S)-3, (−)-(R_p,R)-3·$^1/_4CH_2Cl_2$·$^1/_4H_2O$ and (+)-(S_p,S)-3·$^1/_4CH_2Cl_2$·$^1/_4H_2O$. X-ray analysis confirmed that the desired compounds had indeed been obtained (Figure 1) and established the absolute configuration of the planar chiralities of the four ferrocenyl moieties. The compounds (+)-(S_p,R)-**3** and (−)-(R_p,S)-**3** constitute a pair of enantiomers, as do the pair (−)-(R_p,R)-**3** and (+)−(S_p,S)-**3**. However, the pair (+)-(S_p,R)-**3** and (+)-(S_p,S)-**3** and the pair (−)-(R_p,R)-**3** and (−)-(R_p,S)-**3** are diastereomers. The six-membered ring in each of the four compounds is in a distorted chair form, and all of the substituents are equatorial. The palladium atom in the metallacycle is bound to a chloride and an oxygen atom, with the latter cis to the imino nitrogen atom, which is unusual for palladocyclic compounds, thus leading to a slightly distorted square-planar coordination environment around it. The deviations (in Å) from the least-squares plane defined by the atoms Pd(1), Cl(1), O(1), N(1), and C(1) are Pd, −0.036; Cl, −0.009; O, 0.026; N, −0.014; C, 0.032) for (+)-(S_p,R)-**3**, Pd, −0.036; Cl, −0.010; O, 0.028; N, −0.016; C, 0.034 for (−)-(R_p,S)-**3**, Pd, 0.019; Cl, −0.019; O, 0.009; N, −0.022; C, 0.012 for (−)-(R_p,R)-**3** and Pd, 0.021; Cl, −0.011; O, 0.007; N, −0.023; C, 0.018 for (+)-(S_p,S)-**3**. In all four structures the two cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle = 3.1° for (+)-(S_p,R)-**3**, 3.1° for (−)-(R_p,S)-**3**, 1.6° for (−)-(R_p,R)-**3**, and 1.8° for (+)−(S_p,S)-**3**], 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 4.3° for (+)−(S_p,R)-**3**, 4.9° for (−)-(R_p,S)-**3**, 1.0° for (−)-(R_p,R)-**3**, and 0.8° for (+)−(S_p,S)-**3**. The diastereoselectivity of the ortho-palladation reaction can be explained by the model shown in Figure 2, assuming prior coordination by the methoxymethyl group, a process often encountered in asymmetric synthesis.[10−12]

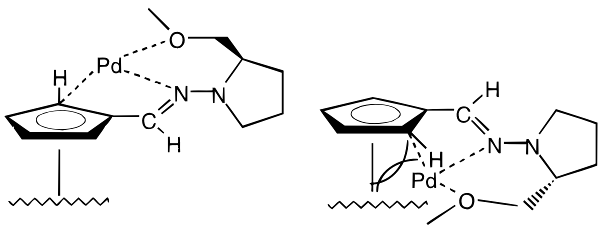


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Figure 2. Model accounting for the stereoselectivity of ortho-palladation of ferrocenylimines.

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(10) Meyers, A. I.; Lutomski, K. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 213.

(11) Enders, D. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol, 3, p 275.

(12) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835.

(13) (a) Tanner, J.; Krause, K. *Rigaku J.* **1994**, *11*, 4; **1990**, *7*, 28. (b) Krause, K.; Phillips, G. N., Jr. *J. Appl. Crystallogr.* **1992**, *25*, 146. (C) Sato, M.; Yamamoto, M.; Katsube, Y.; Tanaka, N.; Higashi, T. *J. Appl. Crystallogr.* **1992**, *25*, 348.

Table 1. Crystal Data

	(+)-(S_p,R)-**3**	(−)-(R_p,S)-**3**	(−)-(R_p,R)-$\mathbf{3}^1/_4CH_2Cl_2\cdot{}^1/_4H_2O$	(+)-(S_p,S)-$\mathbf{3}\cdot{}^1/_4CH_2Cl_2\cdot{}^1/_4H_2O$
Crystal Parameters				
formula	$C_{17}H_{21}ClFeN_2OPd$	$C_{17}H_{21}ClFeN_2OPd$	$C_{17.25}H_{21.50}Cl_{1.50}FeN_2O_{1.25}Pd$	$C_{17.25}H_{21.50}Cl_{1.50}FeN_2O_{1.25}Pd$
fw	467.1	467.1	492.3	492.3
shape (color)	blocks (red)	blocks (red)	blocks (red)	blocks (red)
size, mm	0.15 × 0.20 × 0.25	0.15 × 0.25 × 0.25	0.20 × 0.10 × 0.15	0.15 × 0.20 × 0.25
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_1$
a, Å	8.060(2)	8.067(2)	11.108(2)	11.108(2)
b, Å	13.920(3)	13.941(3)	16.363(3)	16.403(3)
c, Å	15.769(3)	15.774(3)	11.962(2)	11.969(2)
β, deg			117.52(3)	117.65(3)
V, Å^3	1769(1)	1774(1)	1928.2(6)	1931.8(6)
Z	4	4	4	4
F(000)	936	936	986	986
D(calcd), g cm^{-3}	1.753	1.749	1.696	1.693
μ(Mo Kα), mm^{-1}	1.991	1.986	1.900	1.896
Data Collection				
scan type	36 oscillation photos	34 oscillation photos	60 oscillation photos	60 oscillationphotos
2θ range, deg	$3 < 2\theta < 55$	$3 < 2\theta < 55$	$3 < 2\theta < 55$	$3 < 2\theta < 55$
no. of rflns colld	5994	6027	6537	6532
no. of indep rflns	3232 (R_{int} = 3.10%)	3256 (R_{int} = 2.92%)	6537 (R_{int} = 0.00%)	6530 (R_{int} = 0.00%)
Refinement				
R$_1$[a]	0.0321	0.0271	0.0355	0.0448
wR$_2$[b]	0.0778	0.0721	0.1054	0.1271
weighting scheme[c]	a = 0.0382, b = 0.8479	a = 0.0382, b = 0.3019	a = 0.0791, b = 0.1813	a = 0.0942, b = 0.5457
no. of params refined	210	210	452	452
S (GOF)[d]	1.118	1.062	1.079	1.052
Flack parameter	0.50(2)	0.61(3)	0.40(2)	0.45(3)
max, mean Δ	−0.128, 0.003	0.001, 0.000	−0.221, 0.008	−0.017, 0.003
$\Delta\rho_{max}$, e Å^{-3}	0.351, −0.551	0.0387, −0.366	0.594, −0.577	0.645,−0.721

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [d] GOF = $S = \{[\sum w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Experimental Section

General Methods. ^1H and $^{13}C\{^1H\}$ NMR were recorded on a Bruker DPX 300 instrument using $CDCl_3$ (99.8%) as the solvent. Optical rotations were measured in $CHCl_3$ in a 1-dm cell at 20 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by MEDAC Ltd. of the Department of Chemistry at Brunel University. Melting points were determined on a Regeltrafo F. Thermogeräte 7950 instrument. Ferrocenecarboxaldehyde, sodium tetrachloropalladate(II), 5 Å molecular sieves, (+)-(R)-**1**, and (−)-(S)-**1** were products of Aldrich and used as received.

Preparation of (−)-(*R*)-FcCH=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$ [(−)-(*R*)-2] and (+)-(*S*)-FcCH=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$ [(+)-(*S*)-2]. Ferrocenecarboxaldehyde (1.6 g, 7.7 mmol), (+)-(R)-1-amino-2-(methoxymethyl)pyrrolidine [(+)-(R)-**1**], or (−)-(S)-1-amino-2-(methoxy-methyl)pyrrolidine [(−)-(S)-**1**] (1.0 g, 7.7 mmol) was 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 6 h and carefully filtered. The filtrate was reduced to dryness and then washed with n-hexane. Yield: 1.88 g (75%) and 1.83 g (73%), respectively. Characterization data for (−)-(R)-**2**: mp 75−76 °C; $[\alpha]_D^{20}$ −11.30° (c = 1.0, $CHCl_3$); ^1H NMR (selected data) δ 4.13 (s, C_5H_5), 4.22 (s, C_5H_4), 4.42 (d, C_5H_4, J = 9.6 Hz), 7.04 (s, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 69.2 [C^2, C^5 (C_5H_4)], 69.6 (C_5H_5), 75.3 [C^3, C^4 C_5H_4)], 134.4 (N=C). Anal. Calcd for $C_{17}H_{22}N_2OFe$: C, 62.58; H, 6.75; N, 8.59. Found: C, 62.83; H, 7.04; N, 8.60. For (+)-(S)-**2**: mp 75−76 °C; $[\alpha]_D^{20}$ = +11.67° (c 1.0, $CHCl_3$); ^1H NMR (selected data) δ 4.15 (s, C_5H_5), 4.25 (s, C_5H_4), 4.44 (d, C_5H_4, J = 9.6 Hz), 7.05 (s, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 69.3 [C^2, C^5 (C_5H_4)], 69.7 (C_5H_5), 75.4 [C^3, C^4 C_5H_4)], 134.5 (N=C). Anal. Calcd for $C_{17}H_{22}N_2OFe$: C, 62.58; H, 6.75; N, 8.59. Found: C, 62.98; H, 7.05; N, 8.56.

Preparation of (+)-(S_p,*R*)-[PdCl(η^5-C$_5$H$_3$CH=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$)Fe(η^5-C$_5$H$_5$)] [(+)-(S_p,*R*)-3] and (−)-(R_p,*R*)-[PdCl(η^5-C$_5$H$_3$CH=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$) Fe(η^5-C$_5$H$_5$)] [(−)-(R_p,*R*)-3]. The imine (−)-(R)-**2** or (+)-(S)-**2** (0.35 g, 1.0 mmol) was added to a methanolic (30 mL) solution containing Na_2PdCl_4 (0.30 g, 1.0 mmol) and $NaOAc\cdot3H_2O$ (0.14 g, 1.0 mmol). The resulting mixture was stirred at room temperature for 24 h. The mixture was eluted through a silica 60 column with 10:1 chloroform/n-hexane. Concentration of the eluted solution of two successive red bands produced (+)-(S_p,R)-**3** and (−)-(R_p,R)-**3** in that order, which were recrystallized from dichloromethane/n-hexane (1:3) as red plates [product ratio 85:15, total yield 0.33 g (70.7%)]. Characterization data for (+)-(S_p,R)-**3**: mp > 200 °C (dec); $[\alpha]_D^{20}$ = +3461° (c 1.0, $CHCl_3$); ^1H NMR (selected data) δ 4.17 (s, C_5H_3), 4.22 (s, C_5H_5), 4.28 (s, C_5H_3), 4.80 (s, C_5H_3), 7.16 (s, CH=N); $^{13}C\{^1H\}$ NMR (selected data): δ 67.2 [C^4 (C_5H_3)], 71.4 (C_5H_5), 74.3 [C^3 (C_5H_3)], 79.5 [C^5 (C_5H_3)], 95.5 [C^1 (C_5H_3)], 148.6 (C=N). Anal. Calcd for $C_{17}H_{21}ClFeN_2OPd$: C, 43.68; H, 4.50; N, 6.00. Found: C, 43.49; H, 4.63; N, 6.05. For (−)-(R_p,R)-**3**: mp > 200 °C (dec); $[\alpha]_D^{20}$ = −2885° (c 1.0, $CHCl_3$); ^1H NMR (selected data) δ 4.19 (s, C_5H_3), 4.23 (s, C_5H_3), 4.35 (s, C_5H_5), 4.85 (s, C_5H_3), 7.10 (s, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 67.0 [C^4 (C_5H_3)], 71.4 (C_5H_5), 74.4 [C^3 (C_5H_3)], 79.2 [C^5 (C_5H_3)], 86.9 [C^1 (C_5H_3)], 148.0 (C=N). Anal. Calcd for $C_{17}H_{21}ClFeN_2OPd$: C, 43.68; H, 4.50; N, 6.00. Found: C, 43.41; H, 4.66; N, 6.07.

Preparation of (−)-(R_p,*S*)-[PdCl(η^5-C$_5$H$_3$CH=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$)Fe(η^5-C$_5$H$_5$)] [(−)-(R_p,*S*)-3] and (+)-(S_p,*S*)-[PdCl(η^5-C$_5$H$_3$CH=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$)Fe-

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

(+)-(S_p,R)-**3**		(−)-(R_p,S)-**3**		(−)-(R_p,R)-**3**		(+)-(S_p,S)-**3**	
Pd(1)−C(1)	1.945(3)	Pd(1)−C(1)	1.946(4)	Pd(1)−C(1)	1.941(4)	Pd(1)−C(1)	1.947(5)
Pd(1)−N(1)	2.035(2)	Pd(1)−N(1)	2.039(3)	Pd(1)−N(1)	2.039(3)	Pd(1)−N(1)	2.060(4)
Pd(1)−O(1)	2.227(3)	Pd(1)−O(1)	2.227(3)	Pd(1)−O(1)	2.230(3)	Pd(1)−O(1)	2.192(4)
Pd(1)−Cl(1)	2.289(1)	Pd(1)−Cl(1)	2.290(1)	Pd(1)−Cl(1)	2.290(1)	Pd(1)−Cl(1)	2.290(2)
O(1)−C(16)	1.421(5)	O(1)−C(16)	1.427(6)	O(1)−C(16)	1.420(6)	O(1)−C(16)	1.426(6)
O(1)−C(17)	1.429(5)	O(1)−C(17)	1.436(6)	O(1)−C(17)	1.419(6)	O(1)−C(17)	1.440(8)
N(1)−C(11)	1.302(4)	N(1)−C(11)	1.303(5)	N(1)−C(11)	1.300(5)	N(1)−C(11)	1.335(7)
N(1)−N(2)	1.375(3)	N(1)−N(2)	1.383(4)	N(1)−N(2)	1.383(4)	N(1)−N(2)	1.373(5)
N(2)−C(12)	1.472(5)	N(2)−C(12)	1.476(5)	N(2)−C(12)	1.466(6)	N(2)−C(12)	1.453(7)
N(2)−C(15)	1.466(5)	N(2)−C(15)	1.460(6)	N(2)−C(15)	1.466(6)	N(2)−C(15)	1.456(7)
C(12)−C(13)	1.537(6)	C(12)−C(13)	1.541(7)	C(12)−C(13)	1.547(7)	C(12)−C(13)	1.565(7)
C(13)−C(14)	1.517(8)	C(13)−C(14)	1.510(1)	C(13)−C(14)	1.500(1)	C(13)−C(14)	1.500(1)
C(14)−C(15)	1.511(6)	C(14)−C(15)	1.518(7)	C(14)−C(15)	1.509(7)	C(14)−C(15)	1.492(9)
C(2)−Pd(1)−N(1)	81.1(1)	C(2)−Pd(1)−N(1)	81.1(1)	C(1)−Pd(1)−N(1)	81.1(1)	C(1)−Pd(1)−N(1)	81.2(2)
C(2)−Pd(1)−O(1)	171.2(1)	C(2)−Pd(1)−O(1)	171.2(1)	C(1)−Pd(1)−O(1)	171.4(1)	C(1)−Pd(1)−O(1)	174.3(2)
N(1)−Pd(1)−O(1)	90.8(1)	N(1)−Pd(1)−O(1)	90.9(1)	N(1)−Pd(1)−O(1)	91.0(1)	N(1)−Pd(1)−O(1)	93.2(2)
C(2)−Pd(1)−Cl(1)	93.1(1)	C(2)−Pd(1)−Cl(1)	93.0(1)	C(2)−Pd(1)−Cl(1)	93.0(1)	C(1)−Pd(1)−Cl(1)	92.1(1)
N(1)−Pd(1)−Cl(1)	174.1(1)	N(1)−Pd(1)−Cl(1)	174.0(1)	N(1)−Pd(1)−Cl(1)	174.0(1)	N(1)−Pd(1)−Cl(1)	173.1(1)
O(1)−Pd(1)−Cl(1)	94.9(1)	O(1)−Pd(1)−Cl(1)	94.9(1)	O(1)−Pd(1)−Cl(1)	94.8(1)	O(1)−Pd(1)−Cl(1)	93.5(1)
C(16)−O(1)−C(17)	112.3(3)	C(16)−O(1)−C(17)	112.0(4)	C(16)−O(1)−C(17)	112.4(4)	C(16)−O(1)−C(17)	111.6(5)
C(16)−O(1)−Pd(1)	122.6(2)	C(16)−O(1)−Pd(1)	122.8(3)	C(16)−O(1)−Pd(1)	122.5(3)	C(16)−O(1)−Pd(1)	117.2(3)
C(17)−O(1)−Pd(1)	120.5(2)	C(17)−O(1)−Pd(1)	120.4(3)	C(17)−O(1)−Pd(1)	120.5(3)	C(17)−O(1)−Pd(1)	120.8(3)
C(11)−N(1)−N(2)	122.3(3)	C(11)−N(1)−N(2)	122.1(3)	C(11)−N(1)−N(2)	122.4(3)	C(11)−N(1)−N(2)	120.8(4)
C(11)−N(1)−Pd(1)	115.9(2)	C(11)−N(1)−Pd(1)	116.0(2)	C(11)−N(1)−Pd(1)	116.1(2)	C(11)−N(1)−Pd(1)	114.9(3)
N(2)−N(1)−Pd(1)	120.5(3)	N(2)−N(1)−Pd(1)	120.7(2)	N(2)−N(1)−Pd(1)	120.2(2)	N(2)−N(1)−Pd(1)	124.1(3)
N(1)−N(2)−C(12)	117.4(3)	N(1)−N(2)−C(12)	113.2(3)	N(1)−N(2)−C(12)	113.5(3)	N(1)−N(2)−C(12)	115.0(4)
N(1)−N(2)−C(15)	113.6(3)	N(1)−N(2)−C(15)	117.2(3)	N(1)−N(2)−C(15)	116.8(3)	N(1)−N(2)−C(15)	117.3(4)
C(12)−N(2)−C(15)	109.4(3)	C(12)−N(2)−C(15)	109.8(3)	C(12)−N(2)−C(15)	110.0(3)	C(12)−N(2)−C(15)	109.3(4)
N(1)−C(11)−C(1)	113.5(3)	N(1)−C(11)−C(1)	113.4(3)	N(1)−C(11)−C(2)	113.2(3)	N(1)−C(11)−C(2)	113.8(4)
N(2)−C(12)−C(13)	103.7(3)	N(2)−C(12)−C(13)	103.6(4)	N(2)−C(12)−C(13)	102.9(4)	N(2)−C(12)−C(13)	101.2(5)
C(14)−C(13)−C(12)	103.0(4)	C(14)−C(13)−C(12)	105.5(4)	C(14)−C(13)−C(12)	106.3(4)	C(14)−C(13)−C(12)	105.4(6)
C(13)−C(14)−C(15)	106.0(3)	C(13)−C(14)−C(15)	103.9(4)	C(13)−C(14)−C(15)	103.7(4)	C(13)−C(14)−C(15)	107.2(5)

(η^5-C_5H_5)] [(+)-(S_p,S)-3]. Enantiopure compounds of (-)-(R_p,S)-**3** or (+)-(S_p,S)-**3** were prepared according to the procedure described above using (+)-(S)-**2** as the starting material [product ratio (−)-(R_p,S)-**3**:(+)-(S_p,S)-**3** = 85:15, total yield 0.36 g (76.6%)]. Characterization data for (−)-(R_p,S)-**3**: mp > 200 °C (dec); $[\alpha]_D^{20} = -3458°$ (c 1.0, $CHCl_3$); ^1H NMR (selected data) δ 4.17 (s, C_5H_3), 4.22 (s, C_5H_5), 4.28 (s, C_5H_3), 4.80 (s, C_5H_3), 7.16 (s, CH═N); $^{13}C\{^1H\}$ NMR (selected data) δ 67.3 [C^4 (C_5H_3)], 71.5 (C_5H_5), 74.4 [C^3 (C_5H_3)], 79.5 [C^5 (C_5H_3)], 95.5 [C^1 (C_5H_3)], 148.7 (C═N). Anal. Calcd for $C_{17}H_{21}ClFeN_2OPd$: C, 43.68; H, 4.50; N, 6.00. Found: C, 43.44; H, 4.64; N, 6.05. For (+)−(S_p,S)-**3**: mp > 200 °C (dec); $[\alpha]_D^{20} = +2888°$ (c = 1.0, $CHCl_3$); ^1H NMR (selected data) δ 4.19 (s, C_5H_3), 4.23 (s, C_5H_3), 4.35 (s, C_5H_5), 4.85 (s, C_5H_3), 7.10 (s, CH═N); $^{13}C\{^1H\}$ NMR (selected data) δ 67.0 [C^4 (C_5H_3)], 71.4 (C_5H_5), 74.4 [C^3 (C_5H_3)], 79.2 [C^5 (C_5H_3)], 86.9 [C^1 (C_5H_3)], 148.1 (C═N). Anal. Calcd for $C_{17}H_{21}ClFeN_2OPd$: C, 43.68; H, 4.50; N, 6.00. Found: C, 43.35; H, 4.62; N, 6.01.

Crystallographic Studies. Crystallographic data of (+)−(S_p,R)-**3**, (−)-(R_p,S)-**3**, (−)-(R_p,R)-**3**$\cdot{}^1/_4CH_2Cl_2\cdot{}^1/_4H_2O$ and (+)-(S_p,S)-**3**$\cdot{}^1/_4CH_2Cl_2\cdot{}^1/_4H_2O$ measured on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer are summarized in Table 1. Intensity data were collected at 294 K using graphite-monochromatized Mo Ka radiation (λ = 0.710 73 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 for (+)-(S_p,R)-**3**, 34 5° frames for (−)-(R_p,S)-**3**, 60 3° frames for (−)-(R_p,R)-**3**$\cdot{}^1/_4CH_2Cl_2\cdot{}^1/_4H_2O$ and 60 3° for (+)-(S_p,S)-**3**$\cdot{}^1/_4CH_2Cl_2\cdot{}^1/_4H_2O$ in the range of 0−180°, exposure 8 min per 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 of all four compounds were solved with the Patterson superposition method, and subsequent difference Fourier syntheses were employed to locate the remaining non-hydrogen atoms which did not show up in the initial structure. All of the non-hydrogen atoms were refined anisotropically. 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 of the H atoms were held stationary and included in structure factor calculations in the final stages of full-matrix least-squares refinement on F^2. The determination of the absolute configuration was based on the known (+)-(R)-1-amino-2-(methoxymethyl)pyrrolidine or (−)-(S)-1-amino-2-(methoxymethyl)-pyrrolidine moiety. Computation was performed on an IBM-compatible 486 PC with the SHELXTL-PC program package.[15] The final R1 and wR2 indices and other refinement parameters are presented in Table 1, and 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 the four compounds (18 pages). Ordering information is given on any current masthead page.

OM980203K

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[14] Higashi, T. *ABSCOR−An Empirical Absorption Correction Based on Fourier Coefficient Fitting*; Rigaku Corp.: Tokyo, 1995.

[15] (a) *SHELXL/PC Version 5.0 Reference Manual*; Siemens Energy & Automation Inc.: Madison, WI, 1996. (b) Sheldrick, G. M. in *Computational Crystallography 6*; Flack, H. D., Ed.; Párkányi, L.; Simon, K. IUCr and O. U. P: Oxford, 1993; pp 111−112.