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FULL PAPER

Enantiopure planar chiral monomers and di-μ-bromo-bridged dimers of ferrocenylhydrazones from asymmetric cyclopalladation

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

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong. E-mail: tcwmak@cuhk.edu.hk

Received 3rd August 1998, Accepted 26th August 1998

Planar chiral cyclopalladated ferrocenylhydrozones [PdBr{(η^5-C_5H_3CH=NN(CH_2)$_3$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)}] (−)-(S_p,*R*) and (+)-(R_p,*S*) and di-μ-bromo-bridged dimers [{Pd[(η^5-$C_5H_3C(CH_3)$=NN(CH_2)$_3$CHCH$_2$OCH$_3$)-Fe(η^5-C_5H_5)](μ-Br)}$_2$] *syn*-(−)-(S_p,*R*,*R*,S_p), *syn*-(+)-(R_p,*R*,*R*,R_p), *syn*-(+)-(R_p,*S*,*S*,R_p) and *syn*-(−)-(S_p,*S*,*S*,S_p) have been conveniently synthesized in enantiomerically pure form with a high level of diastereoselectivity and their absolute configurations elucidated by single-crystal X-ray analysis.

Owing to the well known reactivity of the σ(Pd–C) bond,[1] planar chiral cyclopalladated derivatives of ferrocene have found useful applications in organic synthesis, resolution of enantiomers, catalysis, photochemistry, bioinorganic chemistry, and the study of ordered mesophases. Although many cyclopalladated derivatives of ferrocene are known,[2] most of them have been obtained as racemic mixtures due to difficulties in isolating these compounds in enantiomerically pure form,[3] and accordingly their stereochemistries remain unsubstantiated. Several papers[2d,4,5] have reported the synthesis and crystal structures of planar chiral cyclopalladated monomers of ferrocene. However, anion-bridged dimers of such systems exhibit more complex structures and interesting aspects of stereoisomerism.[5] There are six possible diastereomeric di-μ-chloro-bridged dimers of a planar chiral cyclopalladated ferrocenylimine, namely *syn*-(R_p,R_p), *syn*-(S_p,S_p), *anti*-(R_p,S_p), *syn*-(R_p, S_p), *anti*-(S_p,S_p) and *anti*-(R_p,R_p) that differ in regard to planar chiralities, *cis*/*trans* relationship of the pair of co-ordinating nitrogen atoms, or *syn*/*anti* arrangement of the ferrocenyl moieties.[6] Three of these, *syn*-(R_p,R_p), *syn*-(S_p,S_p) and *anti*-(R_p,S_p), were reported in our study,[6] whereas an analog of the *anti*-(R_p,R_p) isomer is also known.[7] Development of a convenient and efficient synthetic procedure for enantiopure ferrocene compounds of this type is important in the advancement of cyclopalladation chemistry.

Previous attempts to carry out cyclopalladation of ferrocenylhydrazones have not been successful.[8] Here we present a simple and highly stereoselective synthesis of enantiopure bromide-ligated monomeric and di-μ-bromo-bridged dimeric planar chiral cyclopalladated derivatives of ferrocenylhydrazones. Their absolute configurations and structural relationship were also elucidated. In comparison with cyclopalladation employing Na_2PdCl_4 and $NaO_2CMe{\cdot}3H_2O$ in our previous studies on the analogous di-μ-chloro-bridged dimers,[5,6] the present synthetic procedure using $Pd(O_2CMe)_2$ and $NaO_2CMe{\cdot}3H_2O$ in MeOH (non-acidic medium) at room temperature results in a superior yield and significantly higher diastereoselectivity.

To investigate 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, we employed the pure chiral ferrocenylhydrazones (−)-(*R*)-**2**, (+)-(*S*)-**2**, (−)-(*R*)-**3** and (+)-(*S*)-**3** from the condensation reaction of ferrocenecarbaldehyde and acetylferrocene, respectively, with (+)-(*R*)- or (−)-(*S*)-1-amino-2-(methoxymethyl)pyrrolidine [(+)-(*R*)-**1** or (−)-(*S*)-**1**], which serves as a chirality marker and facilitates product isolation (Scheme 1).

Results and discussion

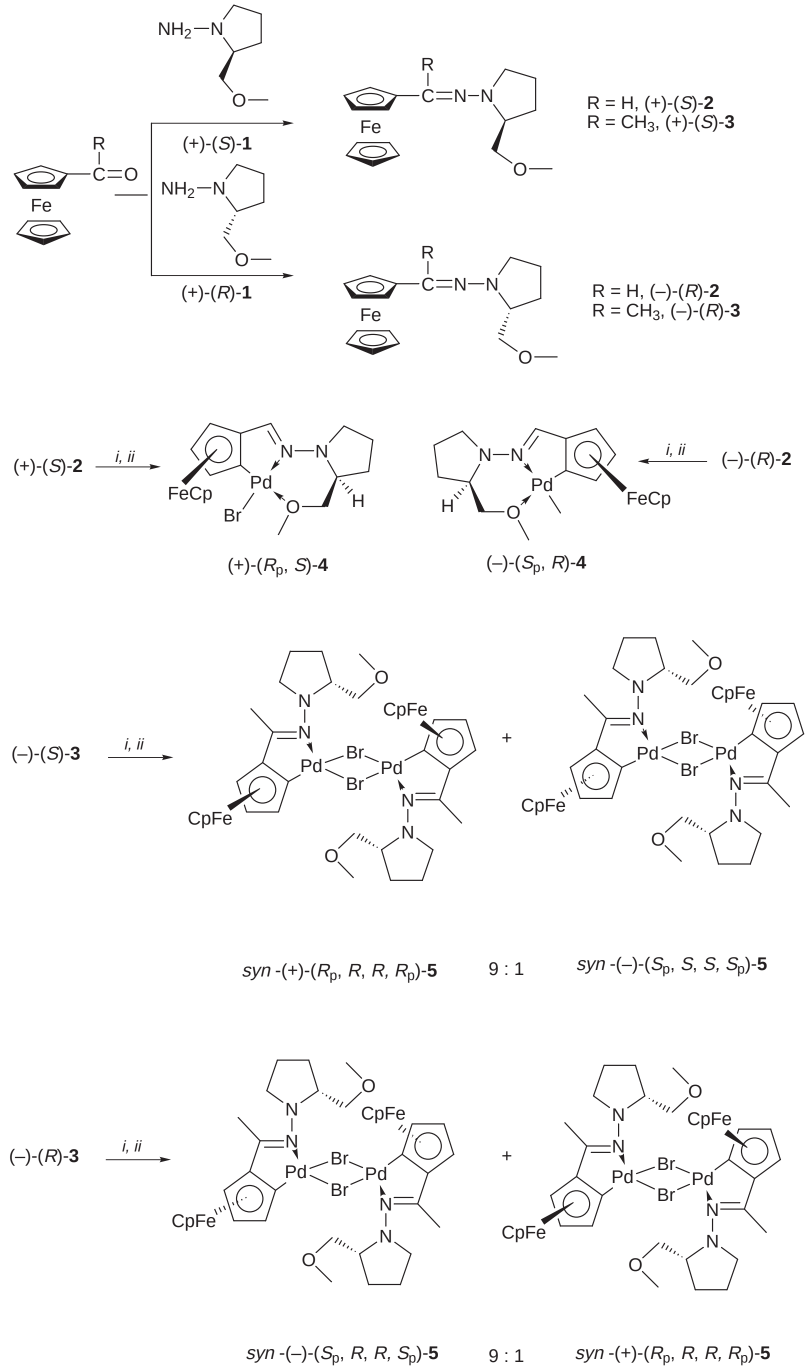
Synthesis of planar chiral cyclopalladated derivatives of ferrocene

Asymmetric cyclopalladation of the ferrocenylimines (−)-(*R*)-**2** and (+)-(*S*)-**2** with $Pd(O_2CMe)_2$ and $NaO_2CMe{\cdot}3H_2O$ in MeOH, followed by treatment with LiBr, gave the corresponding planar chiral cyclopalladated monomers [PdBr{(η^5-C_5H_3CH=NN(CH_2)$_3$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)}] (−)-(S_p,*R*)-**4**, $[\alpha]_D^{20}$ −680.7, and (+)-(R_p,*S*)-**4**, $[\alpha]_D^{20}$ +681.9 deg $cm^3\ g^{-1}\ dm^{-1}$, respectively, in *ca.* 63% yield with a high level of diastereoselectivity. No evidence of the formation of any other isomer was detected by ^1H NMR (300 MHz). The enantiopure compounds were isolated from the two reaction mixtures through column-layer chromatography.

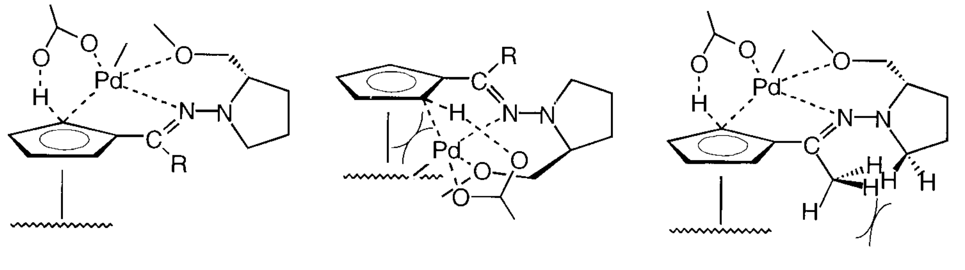
Asymmetric cyclopalladation of the ferrocenylimines (−)-(*R*)-**3** and (+)-(*S*)-**3** in the same manner gave di-μ-bromo-bridged planar chiral cyclopalladated dimers [{Pd[(η^5-$C_5H_3C(CH_3)$=NN(CH_2)$_3$CHCH$_2$OCH$_3$)(Fe(η^5-C_5H_5)]-(μ-Br)}$_2$] *syn*-(−)-(S_p,*R*,*R*,S_p)-**5**, $[\alpha]_D^{20}$ −3506.8, *syn*-(+)-(R_p,*R*,*R*,R_p)-**5**, $[\alpha]_D^{20}$ +2352.9, and *syn*-(+)-(R_p,*S*,*S*,R_p)-**5**, $[\alpha]_D^{20}$ +3510.7, *syn*-(−)-(S_p,*S*,*S*,S_p)-**5**, $[\alpha]_D^{20}$ −2359.3 deg $cm^3\ g^{-1}\ dm^{-1}$, respectively, in *ca.* 70% yield with a high level of diastereoselectivity [product ratio *syn*-(−)-(S_p,*R*,*R*,S_p)-**5**:*syn*-(+)-(R_p,*R*,*R*,R_p)-**5** ≈ *syn*-(+)-(R_p,*S*,*S*,R_p)-**5**:*syn*-(−)-(S_p,*S*,*S*,S_p)-**5** ≈ 9:1].

The results show that ligands (−)-(*R*)-**2** and (+)-(*S*)-**2** lead to higher stereoselectivity than do (−)-(*R*)-**3** and (+)-(*S*)-**3**. Notably, cyclopalladation of (−)-(*R*)-**2** and (+)-(*S*)-**2** gives monomers in which the ether oxygen atom co-ordinates to palladium to form a six membered palladacycle, whereas cyclopalladation of (−)-(*R*)-**3** and (+)-(*S*)-**3** gives bromo-bridged dimers. This different behavior can be explained by the model shown in Fig. 1, assuming prior co-ordination by the methoxymethyl group, a process often encountered in asymmetric synthesis.[9] There is a repulsive interaction between hydrogen atoms at methyl C(12) and ethylene C(16) in the transition state of (−)-(*R*)-**3** and (+)-(*S*)-**3**, thus favouring the formation of dimeric products in their cyclopalladation reaction.

Cyclopalladation is usually carried out in acetic acid, one of the standard solvents. However, a complex reaction mixture is obtained when cyclopalladation of complexes (+)-(*S*)-**2** and



Scheme 1 Synthesis of planar chiral cyclopalladated ferrocenes; (*i*) $Pd(O_2CMe)_2$, NaO_2CMe, MeOH, room temperature (r.t.), 24 h; (*ii*) LiBr, MeOH, r.t., 15 min.



favored

sterically hindered

hydrogen repulsion

Fig. 1 Idealized model of asymmetric cyclopalladation promoted by the methoxymethyl group and destabilization of monomeric cyclopalladated products derived from complexes (−)-(*R*)-**3** and (+)-(*S*)-**3**.

(+)-(*S*)-**3** is conducted in this solvent due to the acid sensitivity of imine, which causes difficulty in purification. We found that cyclopalladation of this kind of imine with $Pd(O_2CMe)_2$ and $NaO_2CMe{\cdot}3H_2O$ in MeOH (non-acidic medium) at room temperature gives planar chiral compounds of ferrocene in good yield with a high level of stereoselectivity. Work-up of the reac-

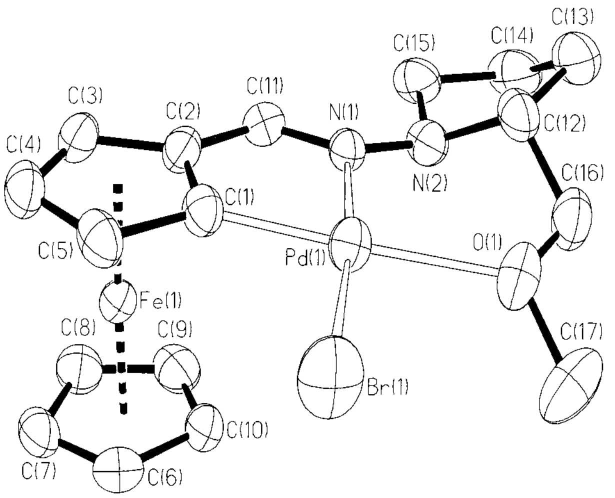


Fig. 2 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-(R_p,S)-**4** with atom-numbering scheme.

tion mixture is generally more effective and convenient. In comparison with cyclopalladation using Na_2PdCl_4 and $NaO_2CMe{\cdot}3H_2O$,[5,6] the present reaction condition leads to significantly higher diastereoselectivity. Moreover, the new procedure can readily be applied to the preparation of related planar chiral anion-bridged dimers such as the chloro-, iodo-, acetato- and nitrito-bridged derivatives.[10]

Characterization

Chemical shifts (^1H NMR spectra in $CDCl_3$) for substituted cyclopentadienyl protons of enantiomeric complexes (−)-(S_p,R)-**4** and (+)-(R_p,S)-**4** are δ 5.07, 4.32 and 4.22. Moreover, the signals due to unsubstituted cyclopentadienyl protons of (−)-(S_p,R)-**4** and (+)-(R_p,S)-**4** shifted downfield by 0.34 ppm at δ 4.43. Chemical shifts for substituted cyclopentadienyl protons of enantiomeric *syn*-(−)-(S_p,R,R,S_p)-**5** and *syn*-(+)-(R_p,S,S,R_p)-**5** are δ 4.83, 4.34 and 4.24, respectively, but those of *syn*-(+)-(R_p,R,R,R_p)-**5** and *syn*-(−)-(S_p,S,S,S_p)-**5** are δ 4.87, 4.34 and 4.25, respectively. Moreover, the signals due to unsubstituted cyclopentadienyl protons of *syn*-(−)-(S_p,R,R,S_p)-**5** and *syn*-(+)-(R_p,S,S,R_p)-**5** shifted downfield by 0.26 ppm at δ 4.34 and those in *syn*-(+)-(R_p,R,R,R_p)-**5** and *syn*-(−)-(S_p,S,S,S_p)-**5** shifted downfield by 0.15 ppm at δ 4.13. In all spectra of cyclopalladated compounds, H^3 and H^5 shifted upfield and H^4 downfield for *syn*-(+)-(R_p,S,S,R_p)-**5** and *syn*-(−)-(S_p,S,S,S_p)-**5**.

The ^{13}C-{^1H} NMR spectra of 'free' ligands and their cyclopalladated complexes differ in regard to the splitting of the resonance due to the C^3, C^4 pair of carbon atoms since the formation of the metallacycle causes a decrease in the symmetry of the substituted cyclopentadienyl ring.

Crystal structure of compounds (−)-(S_p,R)-4 and (+)-(R_p,S)-4

X-Ray analysis confirmed that the desired enantiomeric compounds had indeed been obtained and established the absolute configuration of the planar chiralities of the ferrocenyl moieties (Fig. 2). The six-membered ring in each enantiomer is in a distorted chair form, and all of the substituents are equatorial. The palladium atom in the metallacycle is bound to a bromide 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 co-ordination environment around it. The deviations (in Å) from the least-squares plane defined by the atoms Pd(1), Br(1), O(1), N(1) and C(1) are 0.038, 0.002, −0.022, 0.006 and −0.025 for (−)-(S_p,R)-**4** and −0.038, −0.004, 0.023, −0.009 and 0.028 for (+)-(R_p,S)-**4**. The cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle: 3.8° for (−)-(S_p,R)-**4** and 4.1° for (+)-(R_p,S)-**4**], 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 3.0° for (−)-(S_p,R)-**4** and 3.3° for (+)-(R_p,S)-**4**.

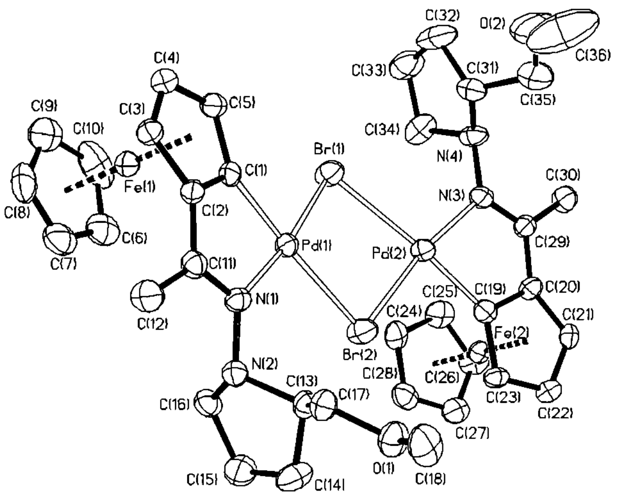


Fig. 3 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex *syn*-(+)-(R_p,R,R,R_p)-**5** with atom-numbering scheme.

Crystal structures of compounds *syn*-(+)-(R_p,R,R,R_p)-5·$2C_6H_6$ and *syn*-(−)-(S_p,S,S,S_p)-5·$2C_6H_6$

X-Ray analysis has established the absolute planar chiralities of the ferrocenyl moieties based on the (+)-(R)-**1** or (−)-(S)-**1** marker in the enantiomers *syn*-(+)-(R_p,R,R,R_p)-**5**·$2C_6H_6$ (Fig. 3) and *syn*-(−)-(S_p,S,S,S_p)-**5**·$2C_6H_6$. The pair of co-ordinating N atoms bear a *trans* relationship, and each palladium atom in the metallacycle is in a slightly distorted square-planar co-ordination environment. With reference to the mean plane of the Pd and Br atoms, the pair of ferrocenyl groups take a *syn* arrangement. Accordingly the Pd_2Br_2 ring is slightly folded [the angle between the two planes defined by the atoms Pd(1), Br(1), Br(2) and Pd(2), Br(1), Br(2) is 22.0° for *syn*-(+)-(R_p,R,R,R_p)-**5** and 21.9° for *syn*-(−)-(S_p,S,S,S_p)-**5**]. The two five-membered palladocycles are nearly coplanar [tilt angle: 20.0° for *syn*-(+)-(R_p,R,R,R_p)-**5** and 20.1° for *syn*-(−)-(S_p,S,S,S_p)-**5**]. The cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle: 1.4° for *syn*-(+)-(R_p,R,R,R_p)-**5** and 1.1° for *syn*-(−)-(S_p,S,S,S_p)-**5**], 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 4.7° for *syn*-(+)-(R_p,R,R,R_p)-**5** and 4.9° for *syn*-(−)-(S_p,S,S,S_p)-**5**.

Crystal structure of compound *syn*-(−)-(S_p,R,R,S_p)-5

As shown in Fig. 4, two ferrocenyl units of S_p configuration are bridged by two bromo ligands in *syn*-(−)-(S_p,R,R,S_p)-**5**. Unlike its diastereomers *syn*-(+)-(R_p,R,R,R_p)-**5** and *syn*-(−)-(S_p,S,S,S_p)-**5**, the Pd_2Br_2 ring is markedly folded [the angle between the two planes defined by the atoms Pd(1), Br(1), Br(2) and Pd(2), Br(1), Br(2) is 52.1°]. Each palladium atom in the metallacycle is in a slightly distorted square-planar co-ordination environment. The two five-membered palladocycles exhibit a non-planar, open-book shape (fold angle: 123.3°). The pair of cyclopentadienyl rings are each planar and nearly parallel to each other (tilt angle: 1.7°), and the two rings involved in the bicyclic system formed by fusion of the palladocycle with the ferrocenyl C_5H_3 moiety are virtually coplanar, the relevant dihedral angle being 0.2°.

Experimental

General methods

Proton and ^{13}C-{^1H} NMR were recorded on a Bruker DPX

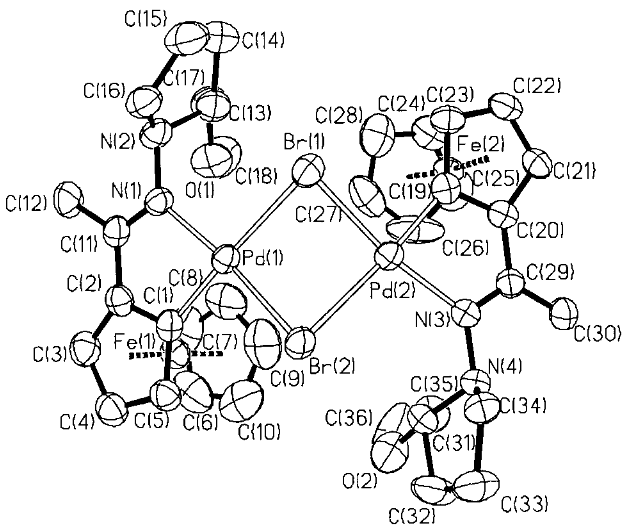


Fig. 4 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex *syn*-(−)-(S_p,*R*,*R*,S_p)-**5** with atom-numbering scheme.

300 instrument using $CDCl_3$ (99.8%) as 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. Ferrocenecarbaldehyde, acetylferrocene, (+)-(*R*)- or (−)-(*S*)-1-amino-2-(methoxymethyl)pyrrolidine, palladium(II) acetate, and 5 Å molecular sieves were products of Aldrich and used as received. Compounds (+)-(*S*)-**2**, (−)-(*R*)-**2**, (+)-(*S*)-**3** and (−)-(*R*)-**3** were prepared by published methods.[5,6]

Preparations

(−)-(S_p,*R*)- and (+)-(R_p,*S*)-[PdBr{(η^5-C_5H_3CH=NN(CH_2)$_3$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)}] 4. The hydrazone (−)-(*R*)-**2** or (+)-(*S*)-**2** (0.33 g, 1.0 mmol) was added to a methanolic (30 mL) solution containing $Pd(O_2CMe)_2$ (0.22 g, 1.0 mmol) and $NaO_2CMe{\cdot}3H_2O$ (0.14 g, 1.0 mmol), and stirred at room temperature for 24 h. A solution of LiBr in 10 cm³ of methanol was added to the reaction mixture, and the red suspension stirred at room temperature for 15 min. The resulting reaction mixture was dried under high vacuum. The product was extracted into chloroform and isolated as a red solid *via* column chromatography (silica 60 and chloroform as eluent). The solid was subsequently recrystallized from dichloromethane by addition of *n*-hexane as red plates, yield 0.34 g (66%) for (−)-(S_p,*R*)-**4** and 0.31 g (61%) for (+)-(R_p,*S*)-**4**. Characterization data for (−)-(S_p,*R*)-**4**: $[\alpha]_D^{20}$ −680.7 deg cm³ g^{-1} dm^{-1} (*c* 1.0 in $CHCl_3$); ^{1}H NMR (selected data) δ 4.22 (s, C_5H_3), 4.32 (s, C_5H_3), 4.42 (s, C_5H_5), 5.07 (s, C_5H_3), 7.00 (s, CH=N); ^{13}C-{^{1}H} NMR (selected data) δ 68.3 [C^4 (C_5H_3)], 70.9 (C_5H_5), 72.6 [C^3 (C_5H_3)], 79.3 [C^5 (C_5H_3)], 95.9 [C^1 (C_5H_3)] and 148.8 (C=N) (Found: C, 39.86; H, 4.08, N, 5.53. Calc. for $C_{17}H_{21}BrFeN_2OPd$: C, 39.91; H, 4.14; N, 5.48%). For (+)-(R_p,*S*)-**4**: $[\alpha]_D^{20}$ +681.9 deg cm³ g^{-1} dm^{-1} (*c* 1.0 in $CHCl_3$); ^{1}H NMR (selected data) δ 4.24 (s, C_5H_3), 4.33 (s, C_5H_3), 4.43 (s, C_5H_5), 5.08 (s, C_5H_3) and 6.99 (s, CH=N); ^{13}C-{^{1}H} NMR (selected data) δ 68.3 [C^4 (C_5H_3)], 70.9 (C_5H_5), 72.4 [C^3 (C_5H_3)], 79.5 [C^5 (C_5H_3)], 95.9 [C^1 (C_5H_3)] and 148.7 (C=N) (Found: C, 39.99; H, 4.16; N, 5.39%).

***syn*-(−)-(S_p,*R*,*R*,S_p)- and *syn*-(+)-(R_p,*R*,*R*,R_p)-[{Pd[(η^5-$C_5H_3C(CH_3)$=NN(CH_2)$_3$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)]-(μ-Br)}$_2$] 5.** The above procedure was repeated using hydrazone (−)-(*R*)-**3** (0.34 g, 1.0 mmol). The product was eluted through a column of SiO_2 with chloroform. Concentration of the eluted solution of two successive red bands produced complexes *syn*-(−)-(S_p,*R*,*R*,S_p)-**5** and *syn*-(+)-(R_p,*R*,*R*,R_p)-**5** in that order, which were recrystallized from dichloromethane–*n*-hexane (1 : 3) as red plates [product ratio 9 : 1, total yield 0.38 g (72%)]. Characterization data for *syn*-(−)-(S_p,*R*,*R*,S_p)-**5**: $[\alpha]_D^{20}$ −3506.8 deg cm³ g^{-1} dm^{-1} (*c* 1.0 in $CHCl_3$); ^{1}H NMR (selected data) δ 3.34 (s, 6 H, H_3CC=N), 4.24 [d, *J* = 6.0, 2 H, H^3 (C_5H_3)], 4.34 [s, 12 H, C_5H_5 + H^5 (C_5H_3)] and 4.83 [t, *J* = 1.8 Hz, 2 H, H^4 (C_5H_3)]; ^{13}C-{^{1}H} NMR (selected data) δ 86.4 [C^5 (C_5H_3)], 76.1 [C^3 (C_5H_3)], 68.6 [C^4 (C_5H_3)], 71.6 (C_5H_5), 102.6 [C^1 (C_5H_3)] and 187.9 (C=N) (Found: C, 41.50; H, 4.45; N, 5.55. Calc. for $C_{18}H_{23}BrFeN_2OPd$: C, 41.13; H, 4.41; N, 5.33%). For *syn*-(+)-(R_p,*R*,*R*,R_p)-**5**: $[\alpha]_D^{20}$ +2352.9 deg cm³ g^{-1} dm^{-1} (*c* 1.0 in $CHCl_3$); ^{1}H NMR (selected data) δ 3.20 (s, 6 H, H_3CC=N), 4.25 [t, *J* = 2.7, 2 H, H^3 (C_5H_3)], 4.19 (s, 10 H, C_5H_5), 4.87 [s, 2 H, H^5 (C_5H_3)] and 4.34 [s, *J* = 2.7 Hz, 2 H, H^4 (C_5H_3)]; ^{13}C-{^{1}H} (selected data) δ 71.9 [C^5 (C_5H_3)], 69.0 [C^3 (C_5H_3)], 66.6 [C^4 (C_5H_3)], 74.7 (C_5H_5), 100.7 [C^1 (C_5H_3)] and 187.1 (C=N) (Found: C, 41.48; H, 4.20; N, 5.07%).

***syn*-(+)-(R_p,*S*,*S*,R_p)- and *syn*-(−)-(S_p,*S*,*S*,S_p)-[{Pd[(η^5-$C_5H_3C(CH_3)$=NN(CH_2)$_3$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)]-(μ-Br)}$_2$] 5.** Red plates of *syn*-(+)-(R_p,*S*,*S*,R_p)-**5** and *syn*-(S_p,*S*,*S*,S_p)-**5** were prepared according to the procedure described above using hydrazone (+)-(*S*)-**3** as starting material. Product ratio 9 : 1 [*syn*-(+)-(R_p,*S*,*S*,R_p)-**5** : *syn*-(−)-(S_p,*S*,*S*,S_p)-**5**], total yield 0.36 g (69%)]. Characterization data for *syn*-(+)-(R_p,*S*,*S*,R_p)-**5**: $[\alpha]_D^{20}$ +3510.7 deg cm³ g^{-1} dm^{-1} (*c* 1.0 in $CHCl_3$); ^{1}H NMR (selected data) δ 3.34 (s, 6 H, H_3CC=N), 4.24 [d, *J* = 6.0, 2 H, H^3 (C_5H_3)], 4.34 [s, 12 H, C_5H_5 + H^5 (C_5H_3)] and 4.83 [t, *J* = 1.8 Hz, 2 H, H^4 (C_5H_3)]; ^{13}C-{^{1}H} NMR (selected data) δ 86.6 [C^5 (C_5H_3)], 76.2 [C^3 (C_5H_3)], 68.8 [C^4 (C_5H_3)], 71.6 (C_5H_5), 102.9 [C^1 (C_5H_3)] and 187.5 (C=N) (Found: C, 41.32; H, 4.17; N, 5.60%). For *syn*-(−)-(S_p,*S*,*S*,S_p)-**5**: $[\alpha]_D^{20}$ −2359.3 deg cm³ g^{-1} dm^{-1} (*c* 1.0 in $CHCl_3$); ^{1}H NMR (selected data) δ 3.26 (s, 6 H, H_3CC=N), 4.25 [s, 2 H, H^3 (C_5H_3)], 4.13 (s, 10 H, C_5H_5), 4.34 [s, 2 H, H^5 (C_5H_3)] and 4.87 [s, *J* = 3.0 Hz, 2 H, H^4 (C_5H_3)]; ^{13}C-{^{1}H} NMR (selected data) δ 71.0 [C^5 (C_5H_3)], 68.8 [C^3 (C_5H_3)], 66.4 [C^4 (C_5H_3)], 73.0 (C_5H_5), 97.5 [C^1 (C_5H_3)] and 185.8 (C=N) (Found: C, 41.24; H, 4.15; N, 5.18%).

Crystallographic studies

Crystallographic data of complexes (−)-(S_p,*R*)-**4**, (+)-(R_p,*S*)-**4**, *syn*-(−)-(S_p,*R*,*R*,S_p)-**5**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**5**·$2C_6H_6$ and *syn*-(+)-(R_p,*R*,*R*,R_p)-**5**·$2C_6H_6$ measured on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer are summarized in Table 1. Intensities 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°, 2–5° oscillation frames in the range of 0–180°, exposure 8 min per frame).[11] A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program.[12]

The crystal structures of all four compounds were solved with the Patterson superposition method, and Fourier-difference syntheses. All the non-hydrogen atoms were refined anisotropically. The benzene solvate molecules in *syn*-(+)-(R_p,*R*,*R*,R_p)-**5**·$2C_6H_6$ and *syn*-(−)-(S_p,*S*,*S*,S_p)-**5**·$2C_6H_6$ are located in a general position with full site occupancy for their 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. Full-matrix least-squares refinement on F^2 was performed on an IBM-compatible 486 PC with the SHELXTL PC program package.[13] Although the Flack *x* parameter[14] failed to give a clear indication of the absolute structure in the X-ray analysis, the known chiralities of (+)-(*R*)-**1** and (−)-(*S*)-**1** as starting synthetic materials ensured the correct assignment of the absolute configurations of all three

Table 1 Crystal data

	(+)-(R_p,S)-**4**	*syn*-(−)-(S_p,R,R,S_p)-**5**	*syn*-(+)-(R_p,R,R,R_p)-**5**·2C_6H_6
Formula	$C_{17}H_{21}BrFeN_2OPd$	$C_{36}H_{46}Br_2Fe_2N_4O_2Pd_2$	$C_{48}H_{58}Br_2Fe_2N_4O_2Pd_2$
M	511.5	1051.1	1207.3
Shape (color)	Prism (red)	Prism (red)	Prism (red)
Size/mm	0.35 × 0.25 × 0.15	0.30 × 0.35 × 0.50	0.20 × 0.01 × 0.30
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a/Å	8.296(2)	12.872(1)	10.654(2)
b/Å	13.865(3)	11.296(1)	13.156(3)
c/Å	15.585(3)	13.337(1)	34.577(7)
β/°		96.37(1)	
V/Å^3	1793(1)	1927(1)	4847(2)
Z	4	2	4
F(000)	1008	1040	2416
D_c/g cm^{-3}	1.895	1.811	1.655
μ(Mo-Kα)/mm^{-1}	4.045	3.766	3.007
Reflections collected	6054	6579	14539
Independent reflections (R_{int})	3291 (0.0465)	6458 (0.0609)	8380 (0.0870)
R1	0.0377	0.0553	0.0615
wR2	0.0899	0.1571	0.1387

Table 2 Selected bond lengths (Å) and angles (°) of complexes (+)-(R_p,S)-**4**, *syn*-(−)-(S_p,R,R,S_p)-**5** and *syn*-(+)-(R_p,R,R,R_p)-**5**·2C_6H_6

(+)-(R_p,S)-**4**		*syn*-(−)-(S_p,R,R,S_p)-**5**		*syn*-(+)-($R_p$$R$,$R$,$R_p$)-**5**·2$C_6H_6$	
Pd(1)–C(1)	1.937(2)	Pd(1)–C(1)	1.955(3)	Pd(1)–C(1)	1.951(4)
Pd(1)–N(1)	2.055(2)	Pd(1)–N(1)	2.104(3)	Pd(1)–N(1)	2.097(3)
Pd(1)–O(1)	2.228(2)	Pd(1)–Br(2)	2.465(1)	Pd(1)–Br(1)	2.455(1)
Pd(1)–Br(1)	2.417(1)	Pd(1)–Br(1)	2.582(1)	Pd(1)–Br(2)	2.579(1)
N(1)–C(11)	1.288(3)	N(1)–C(11)	1.292(4)	N(1)–C(11)	1.322(5)
C(2)–C(11)	1.429(3)	C(2)–C(11)	1.451(5)	C(2)–C(11)	1.443(6)
		C(20)–C(29)	1.437(5)	C(20)–C(29)	1.424(6)
C(1)–Pd(1)–N(1)	81.3(1)	C(1)–Pd(1)–N(1)	79.6(1)	C(1)–Pd(1)–N(1)	80.0(2)
C(1)–Pd(1)–O(1)	171.2(1)	C(1)–Pd(1)–Br(2)	93.0(1)	C(1)–Pd(1)–Br(1)	91.8(1)
N(1)–Pd(1)–O(1)	90.6(1)	Br(2)–Pd(1)–Br(1)	84.7(1)	Br(1)–Pd(1)–Br(2)	86.0(1)
C(1)–Pd(1)–Br(1)	92.2(1)	Pd(2)–Br(1)–Pd(1)	83.6(1)	Pd(1)–Br(1)–Pd(2)	91.4(1)
N(1)–Pd(1)–Br(1)	173.4(1)	Pd(1)–Br(2)–Pd(2)	82.7(1)	Pd(2)–Br(2)–Pd(1)	92.5(1)
O(1)–Pd(1)–Br(1)	95.8(1)	C(1)–C(2)–C(11)	116.6(3)	C(1)–C(2)–C(11)	118.2(4)
C(11)–C(2)–C(1)	115.9(2)	N(1)–C(11)–C(2)	113.3(3)	N(1)–C(11)–C(2)	111.6(4)
N(1)–C(11)–C(2)	114.4(2)				

diastereomers. The final R1 and wR2 indices and other refinement parameters are presented in Table 1, and Table 2 gives selected bond distances and angles.

CCDC reference number 186/1134.

See http://www.rsc.org/suppdata/dt/1998/3785/ for crystallographic files in .cif format.

Acknowledgements

This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 4022/98P.

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Paper 8/06052E