Synthesis and structure of heteroannular cyclopalladated chiral ferrocenylimines: theoretical interpretation of the cyclopalladated complexes based on density functional calculations†

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The reaction of novel chiral ferrocenylimines (η^5-C_5H_5)Fe(η^5-C_5H_4)–CH(CH_3)–N═CH–2-R (R = furyl (**3**) and pyridyl (**6**)) with Li_2PdCl_4 and anhydrous CH_3COONa in dry MeOH produced heteroannular cyclopalladated {Pd[(η^5-C_5H_4)Fe(η^5-C_5H_4)–CH(CH_3)–N═CH–2-R](μ-Cl)}$_2$ (R = furyl) (**4**) and Pd(N^N) [(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH(CH_3)–N═CH–2-R]$PdCl_2$ (R = pyridyl) (**7**) complexes, respectively. The Pd(μ-Cl)$_2$Pd bridge was cleaved by triphenylphosphine to give monomeric derivative **5**. The structures of the monomeric and dimeric palladium complexes were confirmed by elemental analyses, IR, 1D and 2D NMR spectra, and X-ray diffraction. All the results led to the conclusion that the palladium atom is bound to the unsubstituted ferrocenyl moiety in compounds **4** and **5**, while for compound **7**, the palladium atom is coordinated by two nitrogen atoms. The ^{1}H NMR spectra showed that cyclopalladated complex **4** may exist as two diastereoisomers, with a new axial chirality being induced by the rotation of the two ferrocene rings. To explain these experimental results, detailed DFT computational studies have been carried out.

Introduction

The interest in cyclopalladated complexes derived from N-donor ligands has increased considerably in the past two decades, mainly due to their novel and outstanding applications in areas such as material chemistry,[1] the determination of enantiomeric excesses,[2] asymmetric catalysis[3] and as anti-tumor agents.[4] More recent studies of the cyclopalladation of N-donor ferrocenyl ligands (such as ferrocenylamines, imines, oximes, hydrazones, azines and azo derivatives) revealed a type of *ortho* palladacycle with a σ Pd–$C_{sp^2,\ \mathrm{ferrocene}}$ bond through the activation of *ortho* σ $C_{sp^2,\ \mathrm{ferrocene}}$–H bonds.[5] Moreover, studies have shown that the cyclopalladation of ferrocenylimines [(η^5-C_5H_5)Fe(η^5-C_5H_4)–C(R)═N–R′] (R = H, CH_3 or C_6H_5, and R′ = aryl or benzyl) produced 5-membered rings with a σ Pd–$C_{sp^2,\ \mathrm{ferrocene}}$ bond. The results obtained for [(η_5-C_5H_5)Fe(η^5-C_5H_4)-(CH_2)$_n$–N═C(R)] revealed that this substrate could produce two 5-membered palladacycles: (a) with a σ Pd–$C_{sp^2,\ \mathrm{ferrocene}}$ bond and (b) with a σ Pd–$C_{sp^2,\ \mathrm{phenyl}}$ bond, which would require the activation of the *ortho* σ H–$C_{sp^2,\ \mathrm{ferrocene}}$ and *ortho* σ H–$C_{sp^2,\ \mathrm{phenyl}}$ bonds, by initial coordination to the palladium atom through the N-donor, followed by activation of the appropriate *ortho* C–H bond to produce *ortho* palladacycle species.[6] The cyclopalladation of the 4-ferrocenyl-1,3-oxazoline compound, producing an 'interannular' cyclopalladated compound, has been reported by Moyano *et al.*;[7] they simply performed the optimization of the geometry using the PM3(tm) procedure. Our group has reported the heteroannular cyclopalladated complex [(η^5-C_5H_4)Fe(η^5-C_5H_4)–CH_2–N═CH–C_4H_3S].[8] As part of our work, in this paper, the heteroannular cyclopalladation of chiral ferrocenylimines is reported, and the regioselectivity of the cyclopalladation is studied by DFT computational calculations.

Results and discussion

Synthesis of chiral ferrocene ligands 3 and 6

The chiral amines **2** were synthesized from acetylferrocene with (*R*)- or (*S*)-α-methylbenzylethylamine according to an improved reported method.[9] The reaction was monitored by IR spectroscopy until completely finished. The Schiff bases (*R*)-**1** and (*S*)-**1** were reduced by $NaBH_4$ in dry MeOH, then treated with 5% Pd/C to produce (*R*)- and (*S*)-1-ferrocenylethylamine in 90.3% and 92% yield, respectively (Scheme 1). Chiral Schiff bases **3** and **6** were synthesized by the condensation of (*R*)- and (*S*)-1-ferrocenylethylamine, prepared freshly with furfural and 2-pyridylaldehyde in 82.5% and 79.6% yield, respectively (Scheme 2 and Scheme 3).

Synthesis of heteroannular cyclopalladated complexes 4 and 5, and complex 7

In order to explore whether the ferrocene derivative's incorporation of the chiral carbon center between the nitrogen

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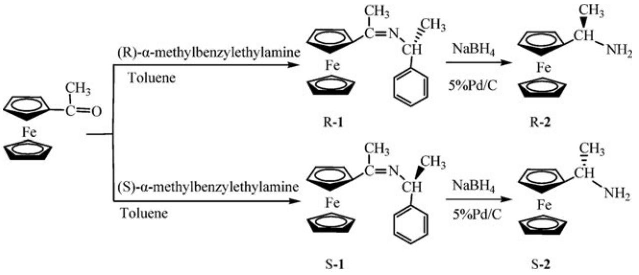
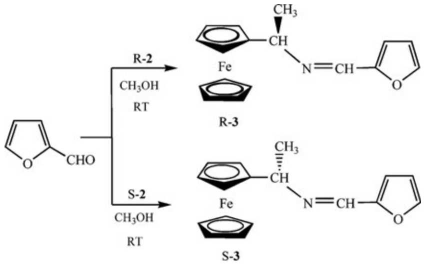
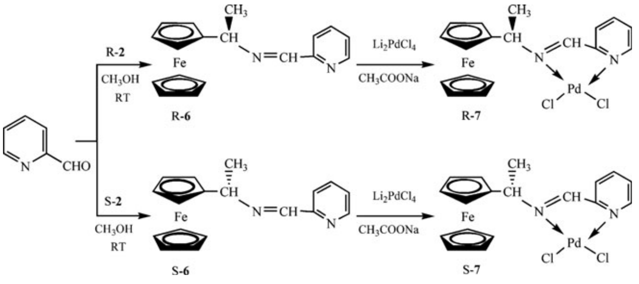


Scheme 1

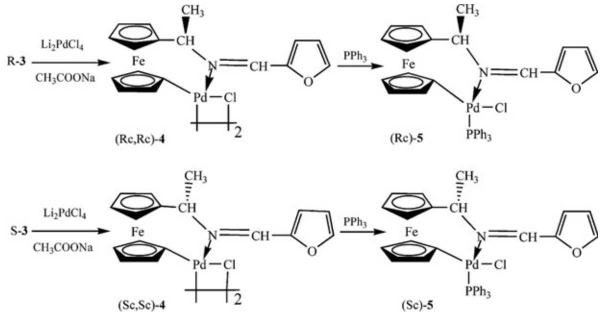


Scheme 2



Scheme 3

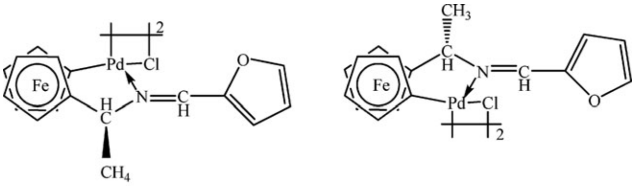
atom and the substituted ferrocene ring could produce cyclopalladated complexes with planar chirality in the ferrocene ring, we studied the cyclopalladation of the novel chiral ferrocenylimines (*R*)- and (*S*)-[(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH(CH_3)–N═CH–2-R] (R = furyl (**3**) and pyridyl (**6**)). Chiral Schiff bases **3** and **6** were reacted with Li_2PdCl_4 in the presence of CH_3COONa in dry MeOH at room temperature to produce dimer "Pd(μ-Cl)$_2$Pd" complexes **4** from Schiff bases **3**, as shown in Scheme 4, while Pd(N^N)-type complexes were produced from Schiff bases **6**, as shown in Scheme 3. Complexes **4** and **7** were purified by chromatography on silica gel plates, recrystallized from CH_2Cl_2–hexane and characterized by elemental analyses, IR, 1D and 2D NMR spectra, and X-ray diffraction.



Scheme 4

The elemental analyses of complexes **4** were consistent with dimer "Pd(μ-Cl)$_2$Pd" complexes, with the palladium atom being bound to a carbon atom of the ferrocene ring, while for complexes **7**, the data was consistent with palladium (N^N) complexes. The infrared spectra of complexes **4** and **7** showed that the palladium atom was coordinated by the imine nitrogen, since the vibration absorption of C═N (1625 cm^{-1} for **4** and 1596 cm^{-1} for **7**) was shifted to a lower wave number compared to that in the free Schiff bases ($\nu_{C=N}$ 1642 cm^{-1} for **3** and $\nu_{C=N}$ 1644 cm^{-1} for **6**). Moreover, for compounds **4**, the absorption bands at 1000 and 1100 cm^{-1}, assigned to the mono-substituted ferrocene derivatives,[10] disappeared, indicating that compounds **4** were bis-substituted ferrocene derivatives. In the ^1H NMR spectra of compounds **4**, the signals were not consistent with 1,2-disubstituted ferrocene derivatives. For example, a singlet at δ 4.14 for (S_c)-**3** was assigned to the unsubstituted ferrocene ring, which was absent for compound (S_c,S_c)-**4**. The ^1H NMR spectra of cyclopalladated compounds **4** showed that the protons in the ferrocenyl moiety were in different magnetic environments, and the signals of the protons could not be assigned unequivocally, which indicates that the σ $C_{sp^2,\ ferrocene}$–H bond in the unsubstituted ferrocene was activated upon the cyclopalladation reaction. It is notable that there are two sets of proton signals in the ratio of 44 : 56 and 43 : 57 for (R_c,R_c)-**4** and (S_c,S_c)-**4**, which might be ascribed to diastereomers **4a** and **4b** (Fig. 1), respectively. Unfortunately, many efforts to isolate **4a** and **4b** from the mixture were unsuccessful. Meanwhile, for compounds **7**, the ^1H NMR spectra showed nine proton signals for the ferrocenyl moiety. Moreover, comparing its ^{13}C NMR and DEPT 135 ^{13}C NMR spectra, only one quaternary carbon signal for the ferrocene ring was observed. These results suggest that palladation did not occur at the ferrocene ring to form a palladacycle, but Pd(N^N)-type complexes instead.

Dimer compounds **4** are stable in the air and organic solvents, but undergo a bridge-splitting reaction with triphenylphosphine to produce the monomeric cyclopalladated complexes (R_c)- and (S_c)-Pd{[(η^5-C_5H_4)Fe(η^5-C_5H_4)–CH(CH_3)–N═CH–2-furyl]}ClPPh$_3$ (**5**). The ^1H and ^{13}C NMR spectra (see the Experimental section) were consistent with heteroannular palladacycle compounds. The ^{31}P NMR spectra of compounds **5** exhibited a singlet at δ 32.45 and 32.43 for (R_c)-**5** and (S_c)-**5**, respectively, which is consistent with



4a **4b**

Fig. 1 Diastereomers **4a** and **4b**.

palladacycle compounds having a *trans* arrangement of the triphenylphosphine ligand and imino nitrogen.[11]

Crystal structures of compounds (S_c,S_c)-4 and (R_c)-5

Suitable single crystals of compound (S_c,S_c)-**4** for X-ray diffraction were obtained from a CH_2Cl_2 and MeOH solution. The molecular structure is shown in Fig. 2; selected bond lengths and angles are listed in Table 1.† The structure clearly shows that compound (S_c,S_c)-**4** is a di-nuclear palladium complex, the two halves of the ferrocene being in a *cis* arrangement. The palladium atom is bonded to one carbon atom in the unsubstituted ferrocene ring, the imino nitrogen and two chlorine atoms having a slightly distorted square-planar coordination environment. The "bite" angles for C(1)–Pd(1)–N(1) and C(18)–Pd(2)–N(2) are 88.4 and 87.7°, respectively. The plane Pd(1)Cl(1)Pd(2) forms a dihedral angle of 49.9° with the plane Pd(1)Cl(2)Pd(2). The Pd(1)–N(1) and Pd(2)–N(2) distances are 2.028 and 2.045 Å, respectively, both of which are shorter than the sum of the van der Waals radii of N and Pd (3.180 Å),[12] indicating the presence of intramolecular N→Pd coordination. The Pd(1)–O(1) and Pd(2)–O(2) distances are 3.089 and 4.669 Å, respectively, both of which are longer than the sum of the van der Waals radii of O and Pd (3.040 Å),[12] indicating the absence of intramolecular coordination between the O and Pd atoms. The Pd(1)–Cl(1) and Pd(1)–Cl(2) distances (2.329 and 2.469 Å) (Pd(2)–Cl(2) = 2.311 Å, Pd(2)–Cl(1) = 2.492 Å) are different due to the strong *trans* influence of the imino nitrogen and the carbon atom in the unsubstituted ferrocenyl ring.[13] The two cyclopentadienyl rings are approximately eclipsed, with a deviation from an ideal parallel conformation giving dihedral angles of 7.3 and 8.0° for the two ferrocene units.

The molecular structure of compound R_c-**5** is shown in Fig. 3; selected bond lengths and angles are listed in Table 2. For complex R_c-**5**, the palladium atom is bonded to imino nitrogen atom N(1), carbon atom C(1) in the unsubstituted ferrocene ring, chlorine atom Cl(1) and phosphorus atom P(1) of the triphenylphosphine group, in a slightly distorted square-planar environment. The Pd(1)–N(1) distance (2.120 Å) in (R_c)-**5** is longer than those of the heteroannular cyclopalladated dimer compound (Pd(1)–N(1) = 2.028 Å, Pd(2)–N(2) = 2.045 Å), which may be caused by the high *trans* influence of the triphenylphosphine group.

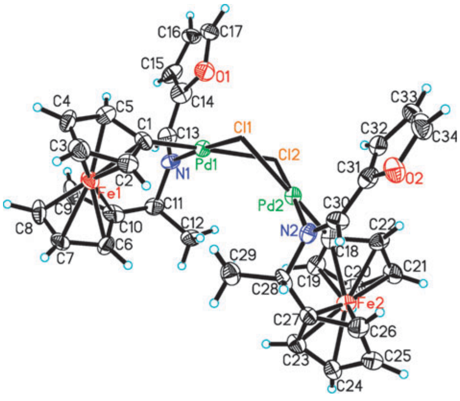


Fig. 2 The molecular structure of compound (S_c,S_c)-**4**.

Table 1 Selected bond lengths (Å) and angles (°) for cyclopalladated complex (S_c,S_c)-**4**

Pd1–C1	1.956(9)	Pd2–C18	1.946(9)
Pd1–N1	2.028(8)	Pd2–N2	2.045(8)
Pd1–Cl1	2.329(2)	Pd2–Cl1	2.492(2)
Pd(1)–Cl2	2.469(2)	Pd2–Cl2	2.311(2)
N1–C13	1.256(13)	N2–C30	1.296(12)
N1–C11	1.523(12)	N2–C28	1.477(11)
Pd1···Pd2	3.1613(11)		
C1–Pd1–N1	88.4(4)	C18–Pd2–N2	87.7(3)
C1–Pd1–Cl1	91.0(3)	C18–Pd2–Cl2	91.5(3)
N1–Pd1–Cl1	175.9(2)	N2–Pd2–Cl2	177.3(2)
C1–Pd1–Cl2	176.7(3)	C18–Pd2–Cl1	177.5(3)
N1–Pd1–Cl2	94.3(2)	N2–Pd2–Cl1	94.7(2)
Cl1–Pd1–Cl2	86.22(9)	Cl2–Pd2–Cl1	86.06(8)
C1–Pd1–Pd2	130.2(3)	C18–Pd2–Pd1	130.9(3)
N1–Pd1–Pd2	126.8(2)	N2–Pd2–Pd1	128.4(2)
Cl1–Pd1–Pd2	51.31(6)	Cl2–Pd2–Pd1	50.79(6)
Cl2–Pd1–Pd2	46.49(5)	Cl1–Pd2–Pd1	46.82(5)
C13–N1–C11	115.7(8)	C30–N2–C28	114.5(8)
C13–N1–Pd1	125.8(7)	C30–N2–Pd2	126.3(6)
C11–N1–Pd1	118.2(6)	C28–N2–Pd2	119.1(6)

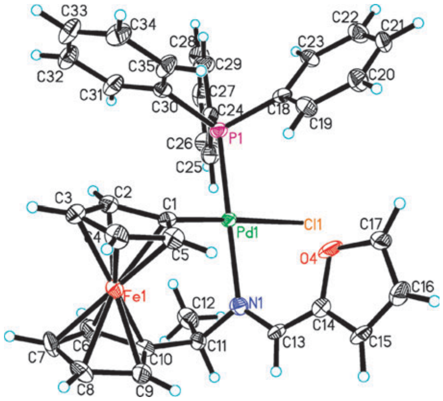


Fig. 3 The molecular structure of compound (R_c)-**5**.

Table 2 Selected bond lengths (Å) and angles (°) for cyclopalladated complex R_c-**5**

Pd1–C1	2.006(6)	C1–Pd1–N1	88.0(2)
Pd1–N1	2.120(5)	C1–Pd1–P1	92.59(18)
Pd1–P1	2.2413(16)	N1–Pd1–P1	179.29(16)
Pd1–Cl1	2.4048(16)	C1–Pd1–Cl1	174.98(19)
N1–C13	1.288(8)	N1–Pd1–Cl1	89.30(14)
N1–C11	1.481(9)	P1–Pd1–Cl1	90.09(6)
		C13–N1–C11	117.0(6)
		C13–N1–Pd1	126.7(5)
		C11–N1–Pd1	116.2(4)

Computational studies on the cyclopalladation of chiral ferrocenylimines

For ligands **3**, the ^1H and ^{13}C NMR spectra showed that the palladium atom was attacked at the unsubstituted ferrocene ring, not the substituted ferrocene ring. In order to explain how, it is possible to activate the type of σ C–H bond in the process of cyclopalladating ferrocenylimines **3**. Quantum calculations based on the density functional theory (DFT) approach have been performed using the GAUSSIAN03 package.[14] The detailed results are shown in Fig. 4.

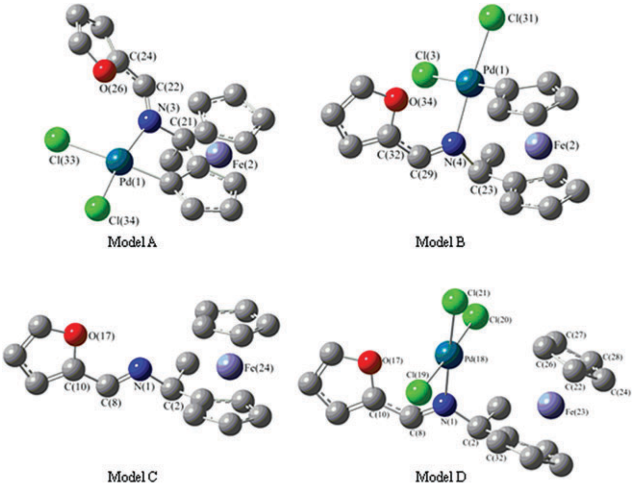
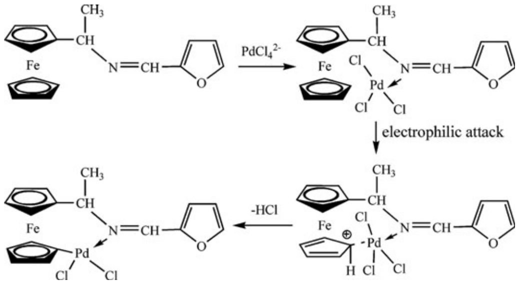


Fig. 4 The optimized structures of models **A**, **B**, **C** and **D**; the hydrogen atoms have been omitted. Model **A**: *ortho*-cyclopalladated complex, **B**: heteroannular cyclopalladated complex, **C**: ligand and **D**: intermediate.

As for ligand **3**, the energy of model **B** was lower about 4.2 kJ mol^{-1} than that of model **A**. From these optimized geometries, torsion angle C(32)–C(29)–N(4)–C(23) in model **B** (heteroannular cyclopalladated complex) (178.8°) is close to that of C(10)–C(8)–N(1)–C(2) in ligand **C** (−179.6°), while torsion angle C(24)–C(22)–N(3)–C(21) in model **A** [−169.6]° is twisted from the ideal co-plane between the imino and furyl rings, which may explain why model **B** is more stable. To further explain the experimental result of the heteroannular cyclopalladation of ligand **3**, model **D**, $\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}CH(CH_3)\text{–}N{=}CH\text{–}2\text{-}R]Cl_3\}^-$ (R = furyl) (where the palladium is bound to the imino nitrogen), was optimized. The net charges on the carbon atoms that are inclined to undertake the metallation process are listed in Table 3. The values of the net charges on the carbon atoms in the unsubstituted ferrocene ring are higher than that on the *ortho* position carbon atom in the substituted ferrocene ring, which means that the σ C–H bond in the unsubstituted ferrocene ring is more easily activated after coordination of the palladium atom to the imino nitrogen.

Possible mechanism

According to the literature,[15] the cyclopalladation reaction of ferrocenylimines includes two steps: (1) coordination of the palladium atom to the imino nitrogen and (2) electrophilic attack of the palladium atom at the carbon atom. Once the N → Pd coordination bond is formed, the orientated σ C–H bonds could then be activated. The coordinated Pd(II) center is attacked at the carbon atom, either in the substituted or unsubstituted ferrocene ring, which results in either the *ortho* palladacycle (model **A**; models **A**, **B**, **C** and **D** are shown in Fig. 4) or the heteroannular palladacycle (model **B**), respectively. The proposed mechanism is shown in Scheme 5.



Scheme 5 Proposed mechanism of the cyclopalladation of ferrocenylimine.

Model **D** (where the palladium is bound to the imino nitrogen) was optimized according the literature.[16] From the optimized geometry, the values of the net charges on the carbon atoms involved in the cyclometallation process in the unsubstituted ferrocene ring are higher than those in the substituted ferrocene ring (Table 3). This indicates that the σ C–H bond in the unsubstituted ferrocene ring is more easily activated, which may therefore be responsible for the formation of the heteroannular cyclopalladated compound (model **B**), consistent with our experimental results.

Conclusion

Novel heteroannular palladacycle complexes **4** and **5** were obtained from ligands **3** $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}CH(CH_3)\text{–}N{=}CH\text{–}2\text{-furyl}]$. NMR spectra and X-ray diffraction showed clearly that the palladium was bound to the carbon atom of the unsubstituted ferrocene ring, while coordinated palladium (N^N)-type complexes were formed from ligands **6** $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}CH(CH_3)\text{–}N{=}CH\text{–}2\text{-pyridyl}]$. Quantum calculations based on DFT gave reasonable agreement with the experimental results. The applications of these chiral compounds in organic synthesis are currently under study in our laboratory.

Experimental

General

Melting points were measured on an X_4-1 microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. 1D and 2D NMR spectra were recorded on a Bruker DPX 400 spectrometer, using $CDCl_3$ as the solvent and TMS as the internal reference standard. All *J* values were measured in Hz. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. Optical rotations were determined at 589 Å on a Perkin-Elmer 341 polarimeter at 20 °C. All solvents were dried according to the standard methods. (*R*)- and (*S*)-α-methylbenzylamine, and $PdCl_2$, were purchased from Acros and were used without purification.

Table 3 The net charge on the carbon atoms around the palladium atom; the atom numbering refers to model **D** in Fig. 4

Atom:	C(26)	C(27)	C(28)	C(24)	C(22)	C_{ortho}(32)
Electronic charge:	−0.030	−0.016	−0.105	−0.086	−0.092	−0.002

Syntheses

Compounds (*R*)-(−)-3 and (*S*)-(+)-3. (*R*)-α-Ferrocenylethylamine (2 mmol, 0.458 g) and furfural (2 mmol, 0.192 g) were dissolved in dry MeOH and stirred for 2 h at room temperature, and then evaporated to dryness. The residue was purified by chromatography on a silica gel plate, developed by the elute (petroleum : CH_2Cl_2 = 1 : 1), to give (*R*)-(−)-**3** as an orange oil. Yield: 82.5%. $[\alpha]_D^{20}$ = −153.7 (*c* 1.29 in benzene). IR (KBr pellet): 1739, 1723, 1640, 1482, 1365, 1105 and 820 cm^{-1}. ^{1}H NMR (*δ*/ppm): 1.59 (d, 3H, *J* = 6.4 Hz, C*H*$_3$), 4.38 (m, 1H, CH_3C*H*), 4.14 (s, 5H, unsubstituted Cp-H), 4.16, 4.29 (s, 4H, substituted Cp-*H*), 6.47, 6.76, 7.51 (s, 3H, furyl-*H*) and 8.05 (s, 1H, N=C*H*). ^{13}C NMR (*δ*/ppm): 22.2(*C*H$_3$), 65.2 (CH_3CH), 66.3, 67.3, 67.6, 67.8, 91.1 (substituted Cp-*C*), 69.1 (unsubstituted Cp-*C*), 112.1, 113.3, 143.2, 147.1 (furyl-*C*) and 152.3 (N=*C*H).

(*S*)-(+)-**3** was prepared as above. (*S*)-α-Ferrocenylethylamine was used as starting material instead of (*R*)-α-ferrocenylethylamine. Orange oil. Yield: 79.6% (0.488 g). $[\alpha]_D^{20}$ = +150.2 (*c* 1.27 in benzene). IR (KBr pellet): 1739, 1723, 1642, 1482, 1365, 1106 and 818 cm^{-1}. ^{1}H NMR (*δ*/ppm): 1.60 (d, 3H, *J* = 6.4 Hz, C*H*$_3$), 4.39 (m, 1H, CH_3C*H*), 4.14 (s, 5H, unsubstituted Cp-H), 4.16, 4.20 (s, 4H, substituted Cp-*H*), 6.48, 6.81, 7.53 (s, 3H, furyl-*H*) and 8.04 (s, 1H, N=C*H*). ^{13}C NMR (*δ*/ppm): 22.8(*C*H$_3$), 64.8 (CH_3CH), 66.3, 67.4, 67.5, 67.8, 91.9 (substituted Cp-*C*), 68.5 (unsubstituted Cp-*C*), 111.5, 113.9, 144.6, 147.5 (furyl-*C*) and 151.7 (N=*C*H).

Compounds (R_c,R_c)-4 and (S_c,S_c)-4. Chiral Schiff bases (*R*)-**3** or (*S*)-**3** (1 mmol, 0.307 g), Li_2PdCl_4 (10 mL, 0.1 mol L^{-1}) and NaOAc (1 mmol, 82 mg) were dissolved in dry MeOH and stirred for 24 h at room temperature. Pure compounds (R_c,R_c)-**4** and (S_c,S_c)-**4** were easily separated by chromatography on a silica gel plate developed using $CHCl_3$: CH_3COOEt 22 : 1 and recrystallized from CH_2Cl_2–MeOH.

For (R_c,R_c)-**4**: yield: 30.6%. m.p. 200–202 °C. $[\alpha]_D^{20}$ = +165.2 (*c* 0.09 in CH_2Cl_2). IR (KBr pellet): 1708, 1625, 1471, 1366, 1108, 1021, 870 and 496 cm^{-1}. ^{1}H NMR (*δ*/ppm): 2.13, 2.38 (d, 6H, *J* = 6.24 Hz, 2C*H*$_3$), 3.77, 3.78 (m, 2H, 2CH_3C*H*), 3.82–4.50 (m, 16H, Cp-*H*), 6.77, 6.83, 7.77, 7.79, 9.52, 9.68 (6H, furyl-*H*), 8.08 and 8.14 (s, 2H, N=C*H*). ^{13}C NMR (*δ*/ppm): 21.4(*C*H$_3$), 65.1, 65.4 (CH_3CH), 66.2, 66.8, 67.8, 69.0, 69.6, 71.1, 71.3, 73.3, 73.7, 87.1, 89.6, 91.2 (Cp-*C*), 113.1, 118.7, 146.9, 150.9 and 151.3 (furyl-*C*). Anal. calc. for $C_{51}H_{48}Cl_3Fe_3N_3O_3Pd_3\cdot CH_3OH\cdot CH_2Cl_2$: C, 43.57; H, 3.40; N, 2.88. Found: C, 43.75; H, 3.45; N, 2.92%.

For (S_c,S_c)-**4**: yield: 25.5% (0.228 g). m.p. 200–201 °C. $[\alpha]_D^{20}$ = −167.2 (*c* 0.09 in CH_2Cl_2). IR (KBr pellet): 1708, 1625, 1471, 1341, 1108, 1021, 870 and 496 cm^{-1}. ^{1}H NMR (*δ*/ppm): 2.12, 2.37 (d, 6H, *J* = 6.2 Hz, 2C*H*$_3$), 3.77, 3.79 (m, 2H, 2CH_3C*H*), 3.82–4.50 (m, 16H, Cp-*H*), 6.76, 6.83, 7.77, 7.79, 9.52, 9.68 (6H, furyl-*H*), 8.07 and 8.13 (s, 2H, N=C*H*). ^{13}C NMR ppm (*δ*/ppm): 21.4 (*C*H$_3$), 65.1, 65.3 (CH_3CH), 66.3, 66.8, 67.9, 69.3, 69.5, 71.1, 71.3, 73.3, 73.7, 87.1, 89.6, 91.2 (Cp-*C*), 113.1, 118.7, 146.9, 150.9 and 151.3 (furyl-*C*). Anal. calc. for $C_{102}H_{96}Cl_6Fe_6N_6O_6Pd_6\cdot 2CH_2Cl_2\cdot 2H_2O$: C, 43.12; H, 3.59; N, 2.90. Found: C, 43.43; H, 3.48; N, 2.87%.

Compounds (R_c)-5 and (S_c)-5. Triphenylphosphine (1.5 mmol, 0.393 mg) was added to a CH_2Cl_2 suspension (10 mL) of compounds (R_c,R_c)-**4** or (S_c,S_c)-**4** (0.1 mmol, 90 mg), respectively. The mixture was stirred at room temperature for 2 h and then filtered. The filtrate was evaporated to dryness under reduced pressure. Compounds (R_c)-**5** and (S_c)-**5** were purified by chromatography on a silica gel plate developed using $CHCl_3$: CH_3COOEt 18 : 1 as the eluent and recrystallized from CH_2Cl_2–hexane.

For (R_c)-**5**: yield: 82.5%. m.p. 205 °C (dec.). $[\alpha]_D^{20}$ = +373.2 (*c* 0.10 in CH_2Cl_2). IR (KBr pellet): 1637, 1479, 1435, 1096, 1020, 724 and 494 cm^{-1}. ^{1}H NMR (*δ*/ppm): 2.18 (d, 3H, *J* = 5.9 Hz, C*H*$_3$), 3.81 (m, 1H, CH_3C*H*), 3.32, 3.58, 3.72, 3.86, 3.89, 3.99, 4.01, 4.25 (s, 8H, Cp-*H*), 7.26–7.61 (m, 15H, PPh_3-*H*), 6.61m, 7.68d, 8.11d, (3H, furyl-*H*) and 8.18 (1H, N=C*H*). ^{13}C NMR (*δ*/ppm): 20.9 (*C*H$_3$), 65.7 (CH_3C*H*), 66.3, 66.9, 68.3, 69.5, 69.8, 73.0, 75.0, 87.9, 98.5 (Cp-*C*), 119.0 (N=*C*H), 112.6, 131.1, 146.3, 149.2 (furyl-*C*), 127.8, 127.9, 130.0, 131.6, 134.7 and 134.8 (PPh_3-*C*). Anal. calc. for $C_{35}H_{31}ClFeNOPPd$: C, 59.15; H, 4.37; N, 1.97. Found: C, 59.34; H, 4.35; N, 1.90%.

For (S_c)-**5**: yield: 79.8% (0.113 g). m.p. 205 °C (dec.). $[\alpha]_D^{20}$ = −375.9 (*c* 0.10 in CH_2Cl_2). IR (KBr pellet): 1640, 1479, 1435, 1096, 1017, 724 and 494 cm^{-1}. ^{1}H NMR (*δ*/ppm): 2.16 (d, 3H, *J* = 5.9 Hz, C*H*$_3$), 3.80 (m, 1H, CH_3C*H*), 3.30, 3.57, 3.72, 3.86, 3.89, 3.97, 4.03, 4.28 (s, 8H, Cp-*H*), 7.26–7.61 (m, 15H, PPh_3-*H*), 6.61m, 7.68d, 8.11d (3H, furyl-*H*) and 8.18 (1H, N=C*H*). ^{13}C NMR (*δ*/ppm): 20.9 (*C*H$_3$), 64.6 (CH_3CH), 66.3, 66.9, 68.2, 69.2, 69.6, 73.0, 74.9, 87.9, 98.3 (Cp-*C*), 118.9 (N=CH), 112.6, 131.1, 146.3, 149.2 (furyl-*C*), 127.8, 127.9, 130.0, 131.6, 134.7 and 134.8 (PPh_3-*C*). Anal. calc. for $C_{35}H_{31}FeClNOPPd$: C, 59.15; H, 4.37; N, 1.97. Found: C, 59.38; H, 4.34; N, 1.88%.

Compounds (*R*)-6 and (*S*)-6. (*R*)-α-Ferrocenylethylamine (2 mmol, 0.458 g) and 2-pyridylaldehyde (2 mmol, 0.214 g) were dissolved in dry MeOH and stirred for 2 h at room temperature, before being evaporated to dryness. The residue was purified by chromatography on a silica gel plate developed by the elute (petroleum : CH_2Cl_2 1 : 1) to give the compound (*R*)-(+)-**6** as an orange-red oil. Yield: 78.9% (0.501 g). $[\alpha]_D^{20}$ = −218.2 (*c* 1.26 in benzene). IR (KBr pellet): 1715, 1644, 1586, 1462, 1110, 997 and 817 cm^{-1}. ^{1}H NMR (*δ*/ppm): 1.56 (d, 3H, *J* = 6.4 Hz, C*H*$_3$), 4.44 (m, 1H, CH_3C*H*), 4.14 (s, 5H, unsubstituted Cp-*H*), 4.18, 4.20, 4.22 (s, 4H, substituted Cp-*H*), 7.32m, 7.77m, 8.07d, 8.63d (4H, pyridyl-*H*) and 8.40 (s, 1H, N=C*H*).

(S)-(+)-**6** was prepared as above, but with (*S*)-α-ferrocenylethylamine used as the starting material instead of (*R*)-α-ferrocenylethylamine. Orange-red oil. Yield: 81.6% (0.518 g). $[\alpha]_D^{20}$ = +220.2 (*c* 1.27 in benzene). IR (KBr pellet): 1714, 1644, 1586, 1467, 1107, 997 and 817 cm^{-1}. ^{1}H NMR (*δ*/ppm): 1.56 (d, 3H, *J* = 6.5 Hz, C*H*$_3$), 4.44 (m, 1H, CH_3C*H*), 4.13 (s, 5H, unsubstituted Cp-*H*), 4.17, 4.18, 4.20 (4H, substituted Cp-*H*), 7.32m, 7.77m, 8.08d, 8.64d (4H, pyridyl-*H*) and 8.40 (s, 1H, N=C*H*).

Compounds (*S*)-7 and (*R*)-7. Compounds (*R*)-**6** or (*S*)-**6** (1 mmol, 0.318 g), Li_2PdCl_4 (10 mL, 0.1 mol L^{-1}) and NaOAc

Table 4 Crystallographic data for compounds (S_c,S_c)-**4** and R_c-**5**

	(S_c,S_c)-**4**	R_c-**5**
Formula	$C_{104}H_{104}Cl_{10}Fe_6N_6O_8Pd_6$	$C_{35}H_{31}ClFeNOPPd$
M_w	2893.93	710.28
Crystal size/mm^3	0.20 × 0.18 × 0.17	0.20 × 0.18 × 0.18
Crystal colour	Red	Red
Crystal system	Monoclinic	Orthorhombic
Space group	C_2	$P2_12_12_1$
a/Å	19.839(4)	11.550(2)
b/Å	14.322(3)	13.138(3)
c/Å	19.416(4)	20.046(4)
α/°	90.00	90.00
β/°	99.75	90.00
γ/°	90.00	90.00
V/Å^3	5437.0(19)	3042.0(10)
Z	2	4
ρ/g cm^{-3}	1.768	1.551
μ/mm^{-1}	2.042	1.238
Transmission	0.6854–0.7099	0.7899–0.8079
Measured reflections	8119	5834
Unique reflections	6789	5025
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Parameters/restraints	641/1	371/0
Flack parameters	0.08(3)	0.02(3)
$R1$/w$R2$ (all reflections)	0.0629/0.1089	0.0671/0.1069
$R1$/w$R2$ (observed reflections)	0.0525/0.1070	0.0524/0.1040

(1 mmol, 82 mg) were dissolved in dry MeOH and stirred for 24 h at room temperature. Compounds (R)-**7** and (S)-**7** were easily purified by filtration and recrystallization from CH_2Cl_2.

For (R)-**7**: yield: 90.2% (0.445 g). m.p. 215–216 °C. $[\alpha]_D^{20}$ = −230.2 (c 0.12 in CH_2Cl_2). IR (KBr pellet): 1596, 1450, 1367, 1238, 1100 and 829 cm^{-1}. ^{1}H NMR (δ/ppm): 1.84 (d, 3H, J = 6.4 Hz, CH_3), 4.25 (s, 5H, unsubstituted Cp-H) , 4.25, 4.32, 4.36 (s, 4H, substituted Cp-H), 5.70 (m, 1H, CHCH$_3$), 7.69 (s, 1H, N=CH), 7.55m, 7.61m, 8.05d and 9.35d (4H, pyridyl-H). ^{13}C NMR (δ/ppm): 20.7(CH$_3$), 60.3 (CH$_3$$C$H), 67.2, 68.3, 68.8, 69.0, 69.2, 87.2 (Cp-C), 128.3, 128.6, 141.3, 150.1, 156.3 (pyridyl-C) and 168.8 (N=CH). Anal. calc. for $C_{18}H_{18}Cl_2FeN_2Pd$: C, 43.64; H, 3.64; N, 5.65. Found: C, 43.85; H, 3.60; N, 5.43%.

For (S)-**7**, Yield: 91.3% (0.450 g). m.p. 215–216 °C, $[\alpha]_D^{20}$ = +241.2 (c 0.12 in CH_2Cl_2). IR (KBr pellet): 1596, 1450, 1369, 1235, 1100 and 829 cm^{-1}. ^{1}H NMR (δ/ppm): 1.83 (d, 3H, J = 5.5 Hz, CH_3), 4.24 (s, 5H, unsubstituted Cp-H), 4.24, 4.31, 4.35 (s, 4H, substituted Cp-H), 5.70 (m, 1H, CHCH$_3$), 7.71 (s, 1H, N=CH), 7.58m, 7.63m, 8.03d and 9.33d (4H, pyridyl-H). ^{13}C NMR (δ/ppm): 20.7(CH$_3$), 60.2 (CH$_3$$C$H), 67.2, 68.3, 68.8, 69.0, 69.1, 87.2 (Cp-C), 128.6, 128.7, 141.3, 150.1, 156.3 (pyridyl-C) and 168.8 (N=CH). Anal. calc. for $C_{18}H_{18}FeCl_2N_2Pd$: C, 43.64; H, 3.64; N, 5.65. Found: C, 43.55; H, 3.55; N, 5.60%.

Crystal structure determination

Crystallographic summary data for compounds (S_c,S_c)-**4** and R_c-**5** are given in Table 4, and bond lengths and angles in Table 1 and Table 2. All measurements were made on a RAXIS-IV imagine plate area detector with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods, expanded using Fourier techniques and refined by full matrix least-squares methods. All calculations were performed using the SHELXL-97 crystallographic software package.[17] It was not possible to locate the H atoms of the disordered partial occupancy water molecules in the difference maps and so no allowance was made for these atoms in the final refinement cycles of (S_c,S_c-**4**). The water molecules lie in three positions, and two of them lie on two-fold axes. Their occupancies were 0.3 and 0.3 by free variable quantity refinement, respectively.†

Computational details

The structures of the ligands and palladated complexes were first fully optimized at the B3LYP level of theory using the GenEcp basis set. The 6-31G(d, p) basis set was employed for the C, H, O, N and Cl atoms. The effective pseudopotential basis set Lanl2dz was used for the Fe and Pd atoms, considering the electrons localized around their large nucleus. The model systems chosen for the computational studies were {[(η^5-C_5H_4)Fe(η^5-C_5H_4)–CH(CH$_3$)–N=CH–2-R]}PdCl$_2$ (R = furyl), where the triphenylphosphine was replaced by one chlorine atom.

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