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Insertion reaction between planar chiral cyclopalladated derivatives of ferrocene and diphenylacetylene

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Abstract

The reaction between diphenylacetylene and the planar chiral halogeno-bridged cyclopalladated compounds of ferrocene, $[Pd\{(\eta^5\text{-}C_5H_3C(CH_3){=}NNCH_2CH_2CH_2CHCH_2OCH_3)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}X)]_2$ [X = Cl: *syn*-(−)-(S_p,*R*,*R*,S_p)-**1**, *syn*-(−)-(R_p,*R*,*R*,R_p)-**1**, *syn*-(+)-(R_p,*S*,*S*,R_p)-**1** and *syn*-(−)-(S_p,*S*,*S*,S_p)-**1**; X = Br: *syn*-(−)-(S_p,*R*,*R*,S_p)-**2**, *syn*-(−)-(R_p,*R*,*R*,R_p)-**2**, *syn*-(+)-(R_p,*S*,*S*,R_p)-**2** and *syn*-(−)-(S_p,*S*,*S*,S_p)-**2**], afforded monomeric products in which one or two alkynes had been inserted into the Pd–C bond. Mono-insertion of alkyne occurred when reacting these compounds with stoichiometric amounts of diphenylacetylene, whereas bi-insertion was achieved with excess diphenylacetylene. The structures of mono-insertion compounds $[PdX(\eta^5\text{-}C_5H_3(PhC{=}CPh)C(CH_3){=}NNCH_2CH_2CH_2CHCH_2OCH_3)Fe(\eta^5\text{-}C_5H_5)]$ [X = Cl: (−)-(S_p,*S*)-**3**; X = Br: (−)-(S_p,*S*)-**4**] and bi-insertion compounds $[PdX(\eta^5\text{-}C_5H_3\{\eta^3\text{-}(PhC{=}C(Ph){-}(Ph)C{=}CPh)\}C(CH_3){=}N\ NCH_2CH_2CH_2CHCH_2OCH_3)Fe(\eta^5\text{-}C_5H_5)]$ [X = Cl: (−)-(S_p,*R*)-**5**, (+)-(R_p,*S*)-**5**; X = Br: (−)-(S_p,*R*)-**6**, (+)-(R_p,*R*)-**6**] have been determined by single-crystal X-ray analysis.

Keywords: Ferrocene; Planar chirality; Insertion reaction; Diphenylacetylene

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1. Introduction

It is well known that insertion of alkynes into Pd–C_{sp^3} and Pd–C_{sp^2} bonds of intramolecular co-ordination systems gives products involving the incorporation of one, two or three alkyne units into the Pd–C bond [1]. Several papers have reported various insertion derivatives of ferrocene, but all of them were obtained as racemic mixtures [2]. Only a few optically active cyclopalladated compounds containing the ferrocenyl moiety have been synthesized [3]. Recently, the authors reported the bi-insertion products of planar chiral cyclopalladated ferrocenes with alkynes and established their absolute configurations by single-crystal X-ray analysis [4]. However, no mono-insertion derivative of ferrocene has been reported so far.

In this study, mono-insertion and bi-insertion products were obtained from the reaction of optically active di-μ-chloro- and di-μ-bromo-bridged cyclopalladated dimers of ferrocenylhydrazones with diphenylacetylene and structurally characterized by single-crystal X-ray analysis.

2. Results and discussion

2.1. Insertion of diphenylacetylene into planar chiral cyclopalladated compounds

The synthesis and isolation of planar chiral cyclopalladated ferrocenyl compounds *syn*-(−)-(S_p,*R*,*R*,S_p)-**1**, *syn*-(+)-(R_p,*S*,*S*,R_p)-**1**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**1**, *syn*-(−)-(S_p,*R*,*R*,S_p)-**2**, *syn*-(−)-(R_p,*R*,*R*,R_p)-**2**, *syn*-(+)-(R_p,*S*,*S*,R_p)-**2** and *syn*-(−)-(S_p,*S*,*S*,S_p)-**2** were described in previous papers [3,4]. The mono-insertion complexes

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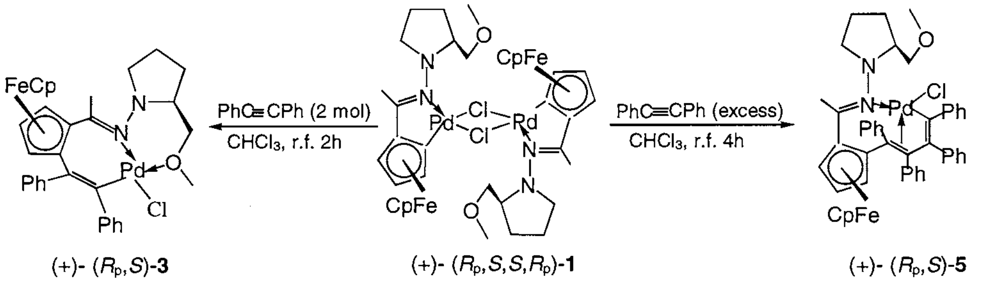

Scheme 1. Preparation of insertion compounds $(+)$-($R_{\rm p}$,S)-**3** and $(+)$-($R_{\rm p}$,S)-**5**; the other compounds are obtained under the same conditions. Compounds **2**, **4** and **6** are bromo analogs of **1**, **3** and **5**, respectively.

were obtained by the reaction of optically active planar chiral halogeno-bridged cyclopalladated derivatives of ferrocene with stoichiometric amounts of diphenylacetylene (1:2) under reflux for a shorter time. Bi-insertion complexes were prepared in a similar manner, but excess diphenylacetylene and a longer reflux time were required (Scheme 1).

2.2. Characterization

Chemical shifts for the unsubstituted cyclopentadienyl protons of mono-insertion compounds $(-)$-($S_{\rm p}$,S)-**3** and $(-)$-($S_{\rm p}$,S)-**4** are 4.15 and 4.25 ppm, respectively. The signals due to substituted cyclopentadienyl protons are 4.33, 4.45, 4.72 for $(-)$-($S_{\rm p}$,S)-**3** and 4.35, 4.45, 4.73 for $(-)$-($S_{\rm p}$,S)-**4**. The ^{1}H-NMR spectra in $CDCl_3$ of the enantiomers, $(-)$-($S_{\rm p}$,R)-**5** and $(+)$-($R_{\rm p}$,S)-**5**, are similar: chemical shifts are 4.33 ppm for the unsubstituted cyclopentadienyl protons and 4.26, 4.46, 4.50 ppm for the substituted cyclopentadienyl protons. However, the ^{1}H-NMR spectra of diastereomers, $(-)$-($S_{\rm p}$,R)-**6** and $(+)$-($R_{\rm p}$,R)-**6**, are obviously quite different. The signals due to unsubstituted cyclopentadienyl protons are 4.34 ppm for $(-)$-($S_{\rm p}$,R)-**6** and 4.25 ppm for $(+)$-($R_{\rm p}$,R)-**6**. Chemical shifts for the unsubstituted cyclopentadienyl protons of $(-)$-($S_{\rm p}$,R)-**6** and $(+)$-($R_{\rm p}$,R)-**6** are 4.25, 4.44, 4.50 and 4.22, 4.34, 4.56 ppm, respectively.

2.3. Crystal and molecular structures of $(-)$-(S_p,S)-3 · CH_2Cl_2 and $(-)$-(S_p,S)-4

Single-crystal X-ray analysis has established the absolute planar chirality of the ferrocenyl moiety based on the $(-)$-(S)-1-amino-2-(methoxymethyl)pyrrolidine marker in $(-)$-($S_{\rm p}$,S)-**3** · CH_2Cl_2 and $(-)$-($S_{\rm p}$,S)-**4**. In either crystal structure, the asymmetric unit contains two independent, nearly alike molecules (designated A and B) each containing six- and seven-membered palladacyclic rings sharing a common edge; only molecule A is shown in Fig. 1. The six-membered ring is in a boat form and the seven-membered ring takes an envelope-like configuration with the palladium atom out of the plane defined by the atoms N(1), C(11), C(19) and C(20) by 1.06 Å for $(-)$-($S_{\rm p}$,S)-**3** · CH_2Cl_2 and 1.11 Å. for $(-)$-($S_{\rm p}$,S)-**4**. The palladium atom is bound to halogen X(1), imino nitrogen atom N(1), ethylenic carbon atom C(20) and ether oxygen atom O(1) in a distorted square-planar co-ordination environment. The deviations (in Å) from the least-squares plane defined by the five atoms Pd(1), X(1), O(1), N(1), C(20) are (-0.012, -0.082, 0.097, -0.105, 0.102) for $(-)$-($S_{\rm p}$,S)-**3** · CH_2Cl_2 and (-0.010, 0.127, -0.139, 0.173, -0.151) for $(-)$-($S_{\rm p}$,S)-**4**. In the compound, the Pd–N bond lengths [2.042(2) Å for molecule A, 2.051(2) Å for molecule B in $(-)$-($S_{\rm p}$,S)-**3** · CH_2Cl_2; 2.047(4) Å for molecule A, 2.024(4) Å for molecule B in $(-)$-($S_{\rm p}$,S)-**4**] are significantly shorter than those reported for related five-membered metallacycles with a σ(Pd–$C_{\rm sp^2,\ ferrocene}$) bond (2.08 Å) [3]. In the molecular structure, the two cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle: 2.2° for $(-)$-($S_{\rm p}$,S)-**3** · CH_2Cl_2, 3.5° $(-)$-($S_{\rm p}$,S)-**4**].

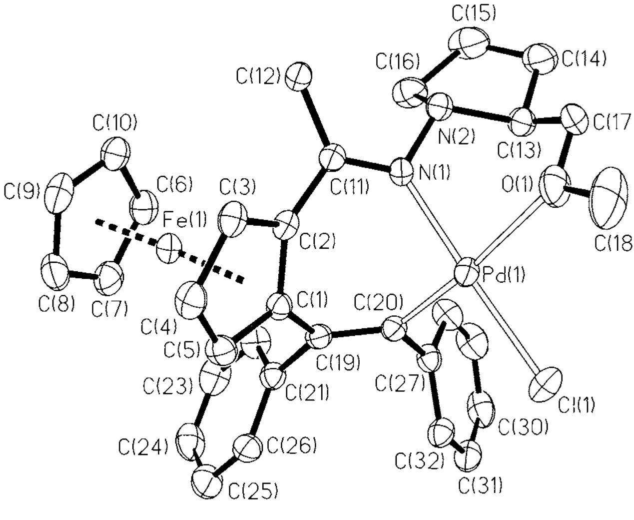

Fig. 1. Molecular structure (30% thermal ellipsoids) and absolute configuration of $(-)$-($S_{\rm p}$,S)-**3** in $(-)$-($S_{\rm p}$,S)-**3** · CH_2Cl_2 with atom numbering scheme. Molecule $(-)$-($S_{\rm p}$,S)-**4** has the same structure except that the chloride ligand Cl(1) is replaced by a bromide atom.

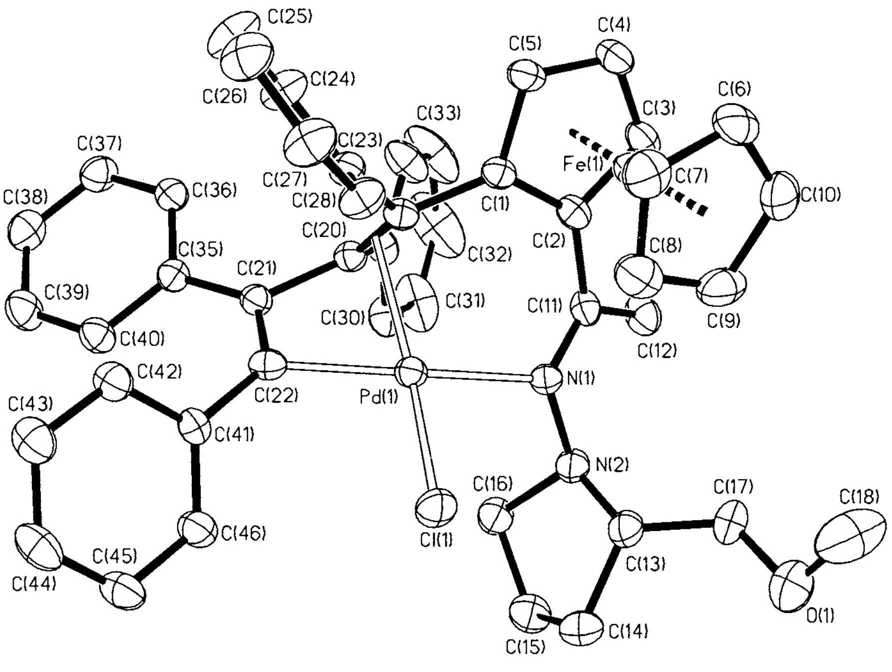

Fig. 2. Molecular structure (30% thermal ellipsoids) and absolute configuration of (+)-(R_p,S)-5 with atom numbering scheme.

*2.4. Crystal and molecular structures of (−)-(S_p,R)-**5**, (+)-(R_p,S)-**5** and (−)-(S_p,R)-**6***

The crystal structures of enantiomers (−)-(S_p,R)-**5** and (+)-(R_p,S)-**5**, plus their bromo analog (−)-(S_p,R)-**6**, have been determined by X-ray analysis. A perspective drawing of the representative molecular structure of (−)-(S_p,R)-**5**, including atom labeling scheme, is presented in Fig. 2. Selected bond lengths and bond angles are presented in Table 2. In each compound the palladium atom is effectively square planar, being bound to a halogen atom, the imino nitrogen atom, terminal carbon atom C(15) of the η^3-butadienyl fragment, and the mid-point of the C(12)=C(13) bond (hereafter referred to as Y) (Fig. 2 and Table 2). The Pd–N bond lengths [2.201(3) Å for (−)-(S_p,R)-**5**, 2.204(3) Å for (+)-(R_p,S)-**5** and 2.212(2) Å for (−)-(S_p,R)-**6**] are clearly longer than those reported for related five-membered metallacycles with σ(Pd–$C_{sp^2,\ ferrocene}$) bond (2.08 Å) [3].

The N(1)–C(11) bond length [1.298 Å for (−)-(S_p,R)-**5**, 1.292(4) Å for (+)-(R_p,S)-**5** and 1.272(3) Å for (−)-(S_p,R)-**6**] is shorter than those (1.32 Å) reported for related five-membered metallacycles [3]. The two cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle: 4.4° for (−)-(S_p,R)-**5**, 4.2° for (+)-(R_p,S)-**5**, 4.3° for (−)-(S_p,R)-**6**].

*2.5. Crystal and molecular structure of (+)-(R_p,R)-**6** · 0.5CH_3OH · 0.5H_2O*

Compound (+)-(R_p,R)-**6** is a diastereomer of compound (−)-(S_p,R)-**6** with the opposite planar chirality (see Fig. 3 and Table 2).

3. Experimental

3.1. Physical measurements

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

3.2. Synthesis of the compounds

Compounds *syn*-(−)-(S_p,R,R,S_p)-**1**, *syn*-(+)-(R_p,S,S,R_p)-**1**, *syn*-(−)-(S_p,S,S,S_p)-**1**, *syn*-(−)-(S_p,R,R,S_p)-**2**, *syn*-(−)-(R_p,R,R,R_p)-**2**, *syn*-(+)-(R_p,S,S,R_p)-**2** and *syn*-(−)-(S_p,S,S,S_p)-**2** were prepared by published proceduces [3,4]. All other reagents were obtained from commercial sources and used as-received.

*3.3. Preparation of [PdX(η^5-C_5H_3(PhC=CPh)C(CH_3)=N NCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)] [(S_p,S)-(−)-**3** and (−)-(S_p,S)-**4**]*

Syn-(−)-(S_p,S,S,S_p)-**1** [or *syn*-(−)-(S_p,S,S,S_p)-**2**] (0.25 mmol) was dissolved in 30 ml of $CHCl_3$ and then

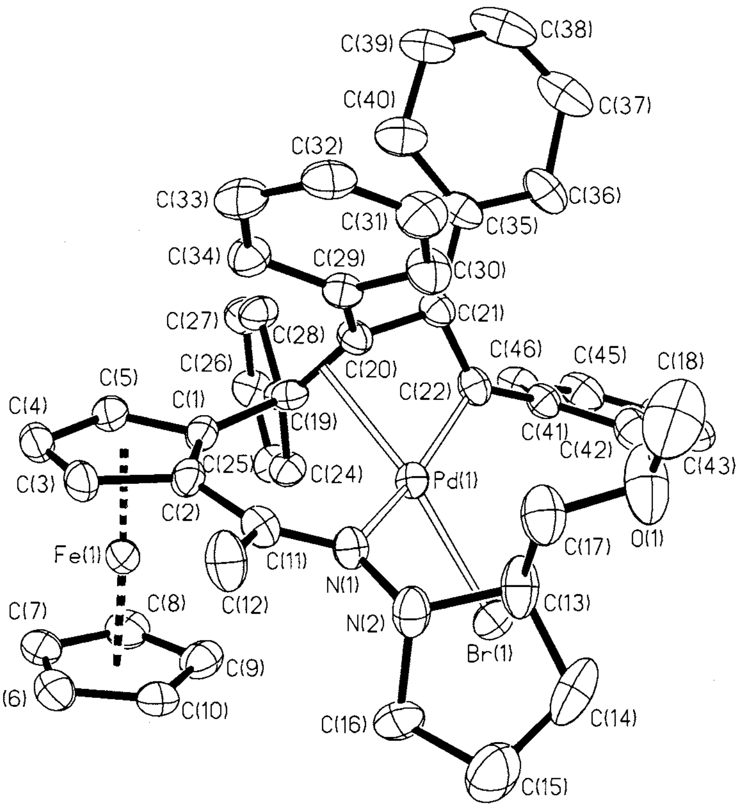

Fig. 3. Molecular structure (30% thermal ellipsoids) and absolute configuration of (+)-(R_p,R)-**6** in (+)-(R_p,R)-**6** · 0.5CH_3OH · 0.5H_2O with atom numbering scheme.

PhC$\equiv$CPh (0.089 g, 0.5 mmol) was added. The mixture was refluxed for 2 h, allowed to evaporate to ca. 5 ml, and isolated via column chromatography (silica-60, chloroform as eluent). The red solid was subsequently recrystallized as red needles from dichloromethane and *n*-hexane.

Compound (−)-(S_p,S)-**3**. Yield: 0.23 g, 71.4%. $[\alpha]_D$ −64.0 (*c* 1.0, $CHCl_3$); selected ^{1}H-NMR: δ 2.35 (s, 3H, H_3CC=N), 3.21 (m, 5H, OCH_2, OCH_3), 4.33 [t, $J = 6.0$ Hz, 1H, H^3 (C_5H_3)], 4.15 (s, 5H, C_5H_5), 4.45 [d, $J = 1.5$ Hz, 1H, H^5 (C_5H_3)], 4.72 [s, 1H, H^4 (C_5H_3)], 6.45–7.49 (m, 10H, aromatic); selected $^{13}C\{^1H\}$-NMR data: δ 24.3 (N=C*Me*), 70.2 [C^3 (C_5H_3)], 70.4 [C^5 (C_5H_3)], 64.9 [C^4 (C_5H_3)], 73.0 (C_5H_5), 97.3 [C^1 (C_5H_3)], 125.8, 126.9, 127.3, 128.0, 128.3, 129.1, 132.3 (Ph and =C), 182.2 (C=N). Anal. calc. for $C_{32}H_{33}ClFeN_2Pd$: C, 59.72; H, 5.13; N, 4.35. Found: C, 59.68; H, 5.45; N, 4.61.

Compound (−)-(S_p,S)-**4**. Yield: 0.28 g, 81.4%. $[\alpha]_D$ −49.5 (*c* 1.0, $CHCl_3$); selected ^{1}H-NMR: δ 2.35 (s, 3H, H_3CC=N), 3.23 (m, 5H, OCH_2, OCH_3), 4.34 [t, $J = 6.0$ Hz, 1H, H^3 (C_5H_3)], 4.15 (s, 5H, C_5H_5), 4.46 [d, $J = 1.5$ Hz, 1H, H^5 (C_5H_3)], 4.72 [s, 1H, H^4 (C_5H_3)], 6.47–7.51 (m, 10H, aromatic); selected $^{13}C\{^1H\}$-NMR data: δ 24.1 (N=C*Me*), 70.1 [C^3 (C_5H_3)], 70.4 [C^5 (C_5H_3)], 64.7 [C^4 (C_5H_3)], 73.2 (C_5H_5), 97.3 [C^1 (C_5H_3)], 125.8, 126.8, 127.2, 127.9, 128.2, 129.0, 132.3 (Ph and =C), 182.3 (C=N); Anal. calc. for $C_{32}H_{33}BrFeN_2Pd$: C, 55.88; H, 4.84; N, 4.07. Found: C, 55.54; H, 4.71; N, 4.26.

*3.4. Preparation of [PdX(η^5-C_5H_3\{η^3-(PhC=C(Ph)−(Ph)C=CPh)\}C(CH_3)=NNCH$_2$CH$_2$CH$_2$CHCH$_2$OCH$_3$)Fe(η^5-C_5H_5)] [(−)-(S_p,R)-**5**, (+)-(R_p,S)-**5**, (−)-(S_p,R)-**6** and (+)-(R_p,R)-**6**]*

Syn-(−)-(S_p,R,R,S_p)-**1** [similarly *syn*-(+)-(R_p,S,S,R_p)-**1**, *syn*-(−)-(S_p,R,R,S_p)-**2** or *syn*-(−)-(R_p,R,R,R_p)-**2**] (0.25 mmol) was dissolved in 30 ml of $CHCl_3$ and then PhC$\equiv$CPh (0.267 g, 1.5 mmol) was added. The mixture was refluxed for 6 h, allowed to evaporate to ca. 5 ml, and isolated via column chromatography (silica-60, chloroform as eluent). The red solid was subsequently recrystallized as red needles from THF/MeOH.

Compound (−)-(S_p,R)-**5**. Yield: 0.30 g, 71.6%. $[\alpha]_D$ −157.6 (*c* 1.0, $CHCl_3$); selected ^{1}H-NMR data: δ 2.49 (s, 3H, H_3CC=N), 3.22 (m, 5H, OCH_2, OCH_3), 4.26 [t, $J = 2.4$ Hz, 1H, H^3 (C_5H_3)], 4.33 (s, 5H, C_5Hd_5), 4.46 [d, $J = 1.5$ Hz, 1H, H^5 (C_5H_3)], 4.50 [d, $J = 2.7$ Hz, 1H, H^4 (C_5H_3)], 6.55–7.49 (m, 20H, aromatic); selected $^{13}C\{^1H\}$-NMR data: δ 19.7 (N=C*Me*), 70.3 [C^3 (C_5H_3)],

Table 1
Crystal data of selected compounds

	$(-)$-(S_p,S)-**3** · CH_2Cl_2	$(-)$-(S_p,S)-**4**	$(-)$-(S_p,R)-**5**	$(+)$-(R_p,R)-**6** · $0.5CH_3OH \cdot 0.5H_2O$
Formula	$C_{33}H_{35}Cl_3N_2OFePd$	$C_{32}H_{33}BrN_2OFePd$	$C_{46}H_{43}ClN_2OFePd$	$C_{46.5}H_{46}BrN_2O_2FePd$
Formula weight	744.2	703.8	837.5	904.0
Shape (color)	Prism (orange)	Prism (orange)	Prism (orange)	Prism (orange)
Size (mm^3)	0.4 × 0.35 × 0.30	0.4 × 0.10 × 0.10	0.35 × 0.20 × 0.15	0.40 × 0.05 × 0.05
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	17.041(3)	17.014(3)	13.477(3)	10.461(2)
b (Å)	18.653(4)	18.632(3)	16.025(3)	20.591(4)
c (Å)	20.570(4)	20.098(3)	17.875(4)	20.634(4)
V (Å^3)	6539(2)	6371(2)	3860(1)	4445(2)
Z	8	8	4	4
F(000)	3024	2832	1720	1836
$D_{calc.}$ (g cm^{-3})	1.512	1.467	1.441	1.351
μ(Mo–K$_\alpha$) (mm^{-1})	1.267	2.299	0.949	1.666
Scan type	60 oscillation photos	60 oscillation photos	45 oscillation photos	60 oscillation photos
2θ range (°)	$3<2\theta<55$	$3<2\theta<55$	$3<2\theta<55$	$3<2\theta<55$
Reflections collected	22 011	13 880	13 250	13 561
Independent reflections	11 959 ($R_{int}=3.88\%$)	8563 ($R_{int}=6.40\%$)	7087 ($R_{int}=2.64\%$)	7625 ($R_{int}=5.39\%$)
R_1[a]	0.0409	0.0875	0.0360	0.0636
wR_2[b]	0.1352	0.2052	0.0937	0.1526
Flack parameters	0.41(1)	0.57(1)	0.59(2)	0.40(1)
Weighting scheme[c]	$a=0.0436$, $b=0.2484$	$a=0.1081$, $b=0.0000$	$a=0.1188$, $b=1.2471$	$a=0.0909$, $b=0.2911$
No. parameters refine	741	687	471	498
S(GOF)[d]	1.055	1.126	1.054	1.124
Max, mean Δ	0.009, 0.000	0.030, 0.001	0.000, 0.000	0.029, 0.001
$\Delta\rho_{max}$ (eÅ^{-3})	1.143, −0.409	0.731, −0.583	0.340, −0.382	0.705, −0.358

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

70.7 [C^5 (C_5H_3)], 69.7 [C^4 (C_5H_3)], 72.7 (C_5H_5), 109.5 [C^1 (C_5H_3)], 125.6, 126.7, 128.0, 128.3, 129.2, 132.3, 134.3, 136.6, 139.9 (Ph and =C), 181.3 (C=N). Anal. calc. for $C_{46}H_{43}ClFeN_2Pd$: C, 65.96; H, 5.18; N, 3.35. Found: C, 65.84; H, 4.96; N, 3.59.

Compound $(+)$-(R_p,S)-**5**. Yield: 0.27 g, 64.4%. $[\alpha]_D$ $+158.9$ (c 1.0, $CHCl_3$); selected ^{1}H-NMR data: δ 2.48 (s, 3H, H_3CC=N), 3.23 (m, 5H, OCH_2, OCH_3), 4.24 [t, $J=2.6$ Hz, 1H, H^3 (C_5H_3)], 4.33 (s, 5H, C_5H_5), 4.45 [d, $J=1.5$ Hz, 1H, H^5 (C_5H_3)], 4.50 [d, $J=2.7$ Hz, 1H, H^5 (C_5H_3)], 6.49–7.47 (m, 20H, aromatic); selected $^{13}C\{^1H\}$-NMR data: δ 19.7 (N=C*Me*), 70.2 [C^3 (C_5H_3)], 70.6 [C^5 (C_5H_3)], 69.7 [C^4 (C_5H_3)], 72.9 (C_5H_5), 109.5 [C^1 (C_5H_3)], 125.7, 126.8, 128.0, 128.4, 129.1, 132.3, 134.3, 136.6, 139.9 (Ph and =C), 181.3 (C=N). Anal. calc. for $C_{46}H_{43}ClFeN_2Pd$: C, 65.96; H, 5.18; N, 3.35. Found: C, 65.89; H, 4.99; N, 3.54.

Compound $(-)$-(S_p,R)-**6**. Yield: 0.30 g, 68.0%. $[\alpha]_D$ -58.8 (c 1.0, $CHCl_3$); selected ^{1}H-NMR data: δ 2.47 (s, 3H, H_3CC=N), 3.20 (m, 5H, OCH_2, OCH_3), 4.25 [t, $J=3.9$ Hz, 1H, H^3 (C_5H_3)], 4.34 (s, 5H, C_5H_5), 4.44 [d, $J=1.5$ Hz, 1H, H^5 (C_5H_3)], 4.50 [d, $J=2.4$ Hz, 1H, H^4 (C_5H_3)], 6.46–7.51 (m, 20H, aromatic); selected $^{13}C\{^1H\}$-NMR data: δ 19.9 (N=C*Me*), 71.4 [C^3 (C_5H_3)], 72.8 [C^5 (C_5H_3)], 70.4 [C^4 (C_5H_3)], 75.4 (C_5H_5), 109.5 [C^1 (C_5H_3)], 125.8, 126.7, 128.0, 128.4, 129.0, 132.3, 134.2, 136.6, 141.3 (Ph and =C), 181.5 (C=N). Anal. calc. for $C_{46}H_{43}BrFeN_2Pd$: C, 62.64; H, 4.91; N, 3.18. Found: C, 62.39; H, 4.76; N, 3.28.

Compound $(+)$-(R_p,R)-**6**. Yield: 0.26 g, 59.0%. $[\alpha]_D$ $+339.3$ (c 1.0, $CHCl_3$); selected ^{1}H-NMR data: δ 2.61(s, 3H, H_3CC=N), 3.33 (m, 5H, OCH_2, OCH_3), 4.22 [t, $J=1.5$ Hz, 1H, H^3 (C_5H_3)], 4.25 (s, 5H, C_5H_5), 4.34 [d, $J=2.7$ Hz, 1H, H^5 (C_5H_3)], 4.56 [d, $J=4.5$ Hz, 1H, H^4 (C_5H_3)], 6.45–7.56 (m, 20H, aromatic); selected $^{13}C\{^1H\}$-NMR data: δ 18.6 (N=C*Me*), 71.4 [C^3 (C_5H_3)], 71.9 [C^5 (C_5H_3)], 64.6 [C^4 (C_5H_3)], 73.2 (C_5H_5), 88.6 [C^1 (C_5H_3)], 125.6, 127.0, 128.0, 128.4, 129.2, 131.9, 134.2, 136.3, 140.1 (Ph and =C), 176.8 (C=N). Anal. calc. for $C_{46}H_{43}BrFeN_2Pd$: C, 62.64; H, 4.91; N, 3.18. Found: C, 62.69; H, 4.86; N, 3.09.

3.5. Crystallographic studies

A summary of the crystallographic data of $(-)$-(S_p,S)-**3** · CH_2Cl_2, $(-)$-(S_p,S)-**4**, $(-)$-(S_p,R)-**5**, $(+)$-(R_p,S)-**5**, $(-)$-(S_p,R)-**6**, and $(+)$-(R_p,R)-**6** · $0.5CH_3OH \cdot 0.5H_2O$ measured on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer is shown in Table 1. Intensity data were collected at 294 K using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å)

Table 2
Selected bond lengths (Å) and bond angles (°) of three selected compounds[a]

$(-)$-(S_p,S)-**3** · CH_2Cl_2		$(-)$-(S_p,R)-**5**		$(+)$-(R_p,R)-**6** · $0.5CH_3OH$ · $0.5H_2O$	
Molecule A					
Pd(1)–C(20)	1.957(2)	Pd(1)–C(22)	1.989(4)	Pd(1)–C(22)	2.005(2)
Pd(1)–N(1)	2.042(2)	Pd(1)–C(20)	2.163(4)	Pd(1)–C(20)	2.167(2)
Pd(1)–O(1)	2.239(2)	Pd(1)–C(19)	2.175(3)	Pd(1)–C(19)	2.190(2)
Pd(1)–Cl(1)	2.316(1)	Pd(1)–N(1)	2.201(3)	Pd(1)–N(1)	2.199(2)
N(1)–C(11)	1.300(2)	Pd(1)–Cl(1)	2.344(1)	Pd(1)–Br(1)	2.468(1)
C(19)–C(20)	1.352(3)	N(1)–C(11)	1.298(5)	N(1)–C(11)	1.316(3)
C(20)–Pd(1)–N(1)	91.5(1)	C(2)–C(11)	1.471(5)	C(2)–C(11)	1.488(3)
C(20)–Pd(1)–O(1)	171.0(1)	C(1)–C(19)	1.482(5)	C(1)–C(19)	1.517(3)
N(1)–Pd(1)–O(1)	82.2(1)	C(19)–C(20)	1.421(5)	C(19)–C(20)	1.401(3)
C(20)–Pd(1)–Cl(1)	93.5(1)	C(20)–C(21)	1.500(5)	C(20)–C(21)	1.511(3)
N(1)–Pd(1)–Cl(1)	173.5(1)	C(21)–C(22)	1.341(5)	C(21)–C(22)	1.301(3)
O(1)–Pd(1)–Cl(1)	93.2(1)	Pd(1)–Y	2.050	Pd(1)–Y	2.063
C(1)–C(2)–C(11)	130.0(2)	C(22)–Pd(1)–C(20)	66.5(1)	C(22)–Pd(1)–C(20)	65.8(1)
N(1)–C(11)–C(2)	119.1(2)	C(22)–Pd(1)–C(19)	83.5(1)	C(22)–Pd(1)–C(19)	81.8(1)
C(20)–C(19)–C(1)	122.5(2)	C(20)–Pd(1)–C(19)	38.2(1)	C(20)–Pd(1)–C(19)	37.5(1)
C(19)–C(20)–Pd(1)	122.8(1)	C(20)–Pd(1)–N(1)	97.9(1)	C(20)–Pd(1)–N(1)	99.0(1)
Molecule B		C(19)–Pd(1)–N(1)	95.6(1)	C(19)–Pd(1)–N(1)	95.7(1)
Pd(1′)–C(20′)	1.957(2)	C(22)–Pd(1)–Cl(1)	97.8(1)	C(22)–Pd(1)–Br(1)	98.1(1)
Pd(1′)–N(1′)	2.051(2)	N(1)–Pd(1)–Cl(1)	98.1(1)	N(1)–Pd(1)–Br(1)	98.0(1)
Pd(1′)–O(1′)	2.257(2)	C(22)–Pd(1)–C(21)	31.3(1)	C(22)–Pd(1)–C(21)	30.2(1)
Pd(1′)–Cl(1′)	2.309(1)	C(20)–Pd(1)–C(21)	35.9(1)	C(20)–Pd(1)–C(21)	36.2(1)
N(1′)–C(11′)	1.274(2)	C(19)–Pd(1)–C(21)	62.9(1)	C(19)–Pd(1)–C(21)	61.5(1)
C(19′)–C(20′)	1.337(2)	N(1)–Pd(1)–C(21)	128.3(1)	N(1)–Pd(1)–C(21)	131.0(1)
C(20′)–Pd(1′)–N(1′)	90.9(1)	Cl(1)–Pd(1)–C(21)	128.8(1)	Br(1)–Pd(1)–C(21)	128.2(1)
C(20′)–Pd(1′)–O(1′)	170.4(1)	C(1)–C(2)–C(11)	129.3(3)	C(1)–C(2)–C(11)	130.6(2)
N(1′)–Pd(1′)–O(1′)	82.7(1)	C(2)–C(1)–C(19)	130.3(3)	C(2)–C(1)–C(19)	130.3(2)
C(20′)–Pd(1′)–Cl(1′)	93.2(1)	N(1)–C(11)–C(2)	119.3(3)	N(1)–C(11)–C(2)	118.8(2)
N(1′)–Pd(1′)–Cl(1′)	173.2(1)	C(20)–C(19)–C(2)	120.3(3)	C(20)–C(19)–C(1)	120.9(2)
O(1′)–Pd(1′)–Cl(1′)	93.9(1)	C(19)–C(20)–C(21)	116.8(3)	C(19)–C(20)–C(21)	114.2(2)
C(1′)–C(2′)–C(11′)	128.4(2)	C(22)–C(21)–C(20)	106.6(3)	C(22)–C(21)–C(20)	107.4(2)
N(1′)–C(11′)–C(2′)	119.3(2)	C(22)–Pd(1)–Y	74.3	C(22)–Pd(1)–Y	73.0
C(20′)–C(19′)–C(1′)	121.2(2)	N(1)–Pd(1)–Y	97.1	N(1)–Pd(1)–Y	97.8
C(19′)–C(20′)–Pd(1′)	121.6(1)				

[a] The mid-point of the C(12)=C(13) bond is referred to as Y.

from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{\min} = 3°$, $2\theta_{\max} = 55°$, 3°–4° oscillation frames in the range 0°–180°, exposure 8 min per frame) [5]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program [6]. The crystal structures of all three compounds were solved with the Patterson superposition method, and subsequent difference Fourier syntheses were employed to located the remaining non-hydrogen atoms that do not show up in the initial structure. All 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 the H atoms were held stationary and included in the structure factor calculation in the final stages of full-matrix least-squares refinement on F^2. The computation was performed on an IBM-compatible 486 PC with the SHELXTL-PC program package [7]. Although the Flack parameter [8] failed to give a clear indication of the absolute structure in the X-ray analysis, the known chiralities of (+)-(*R*)- and (−)-(*S*)-1-amino-2-(methoxymethyl)pyrrolidine as starting synthetic materials ensured the correct assignment of the absolute configurations of all stereomers. The final R_1 and wR_2 indices and other refinement parameters are presented in Table 1, and Table 2 gives selected bond distances and angles.

The atomic parameters for the four crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 102704, 102705, 102706 and 102707).

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