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Abnormal cyclopalladation of Schiff bases made of metallocenyl aldehydes and α-ferrocenylethylamine: Unexpected formation of the heteroannular 3-atomic bridge

Ludmila L. Troitskaya, Zoya A. Starikova, Tatiana V. Demeshchik, Svetlana T. Ovseenko, Evgenii V. Vorontsov, Viatcheslav I. Sokolov *

''Nesmeyanov'' Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russian Federation

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Abstract

Cyclopalladation of the Schiff bases of general formula McCH=N–CH(Me)Fc (Mc=Fc, Ru) (**1a**,**b**) with a chiral centre leads to the mixtures of three products, two of which (**2** and **3**) are planar chiral diastereomers formed from homoannular substitution into the aldehyde fragment. The third product **4** is a result of the unusual heteroannular palladation of the amine fragment in starting aldimine. This *ansa*-structure **4** having 3-atomic C–N–Pd bridge is without precedent in metallocenes. The molecular structures of all organopalladium compounds obtained have been proved using X-ray analysis of single crystals.

Keywords: Cyclopalladation; Ferrocenes; Ruthenocenes; Schiff bases; Aldimines; X-ray analysis; *ansa*-Compounds; Heteroannular bridged ferrocene; NMR spectroscopy

1. Introduction

Recently many publications have appeared devoted to organometallic derivatives of Schiff bases (aldimines and ketimines) in ferrocenyl series [1–6]. Synthetic approaches have been elaborated such as direct mercuration [1,2], cyclopalladation [3,4], cycloplatination [5] as well as transmetalation [6]. Azomethines derived from α-carbonyl derivatives of ferrocene and primary amines, mostly arylamines, served as models for cyclopalladation, and regioselectivity of the reaction was demonstrated since palladium atom enters into position 2 of the cyclopentadienyl ring of metallocene exclusively, in spite of the presence of aryl group which might form stable five- or six-membered chelated palladacycle. The only case when cyclopalladation followed two pathways had been reported [7] for the Schiff base prepared from benzaldehyde and ferrocenylmethylamine.

In the course of cyclopalladation of monosubstituted metallocenes the planar chirality arises, and much attention was paid to their preparation in optically active form. Different approaches were used such as classical one, through diastereomers [8], or diastereoselective synthesis starting with optically active ferrocenyl azomethines [9,10].

2. Results and discussion

In this paper, cyclopalladation of Schiff bases of general formula McCH=NCH(Me)Fc (**1a**,**b**), where Mc = Fc (**a**), Rc (**b**) has been investigated. Characteristic feature of these models is metallocenyl nature of both

* Corresponding author. Tel.: +7 095 1359211; fax: +7 095 1355085.
E-mail address: sokol@ineos.ac.ru (V.I. Sokolov).

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fragments, carbonyl and amine parts of the molecule. These azomethines are derivatives of α-ferrocenylethylamine which had been classical substrate of cyclopalladation in the form of *N*,*N*-dimethyl derivative [11]. Taking these facts into account, it was natural to expect that reaction might occur into substituted Cp rings of both aldehyde and amine fragments. These two pathways lead to the formation of chiral plane and, correspondingly, to diastereomeric organopalladiums since the chiral center is maintained. It is worth to note that aldimine composed of ferrocenylaldehyde and α-cyclohexylethylamine showed 100% diastereoselectivity on cyclopalladation [10].

The model compounds chosen permit to compare the tendencies to form five-membered palladacycles including either simple C–N or double C=N bond of the triad HC–N=C into the new ring and thus to determine the regioselectivity of the reaction.

The starting aldimines **1a**,**b** have been prepared by mixing of equimolar quantities of metallocenyl aldehydes and freshly obtained α-ferrocenylethylamine [12] without solvent with subsequent keeping in desiccator over P_2O_5 during seven days. Cyclopalladation was performed following the procedure [13] that afforded dimeric organopalladium products hardly soluble in organic solvents. If there is no regio- and diastereoselectivity, monomeric product should be a mixture of four diastereoisomers whereas for dimers the number of isomers will be more. Therefore, dimers were immediately converted into the monomeric triphenylphosphine complexes. Three organopalladiums **2**–**4a**,**b** were obtained, separated, and identified in each case.

IR spectra contained two characteristic bands of C=N bonds and three signals of phosphorus and Me groups in ^{31}P and ^{1}H NMR spectra correspondingly that evidenced for the presence of three isomers **2**–**4a**,**b** in the ratios 2.5:1.6:1 (**a**) and 2:1:1 (**b**). Isomers **2**–**4a** have been separated by thin-layer chromatography on SiO_2 (eluent $CHCl_3$), and individual **2**–**4b** have been obtained using stepwise crystallization from methanol but separation by TLC is also possible. Patterns of ^{1}H NMR spectra suggest that **2**–**3**(**a**,**b**) are the products of diastereoselective cyclopalladation of the substituted cyclopentadienyl ring in the aldehyde moiety of Schiff bases.

^{1}H NMR spectra of **4a**,**b** contain signals from Me group, the aldimine proton, *one non-substituted* cyclopentadienyl ring (C_5H_5) and 12 broad singlets. This points to the replacement of H in *one* of two C_5H_5 rings in aldimines **1a**,**b** for the palladium atom. Shifts of *ν*(C=N) (to shorter waves) and aldimine proton are small but deshielding of Me protons and non-substituted Cp ring are strong (see Section 3). This points out that the aldehyde part of the molecule seems to be intact and cyclopalladation undergoes into the amine part of the molecule. The aldimine protons in ^{1}H NMR spectra of all **2**–**4** complexes appear as doublets due to coupling with the phosphorus atom through four bonds.

Minor diastereomer **3a** is the product of usual homoannular cyclopalladation of the ruthenocenyl aldehyde fragment in **1b**. Products **4a** and **4b** possess the unusual phane structure as a result of the non-precedent cyclopalladation pathway during which the metal enters into the remote, non-substituted Cp ring of the amine fragment of **1a** and **1b**.

Products of this unusual cyclopalladation reaction are shown in Scheme 1 below.

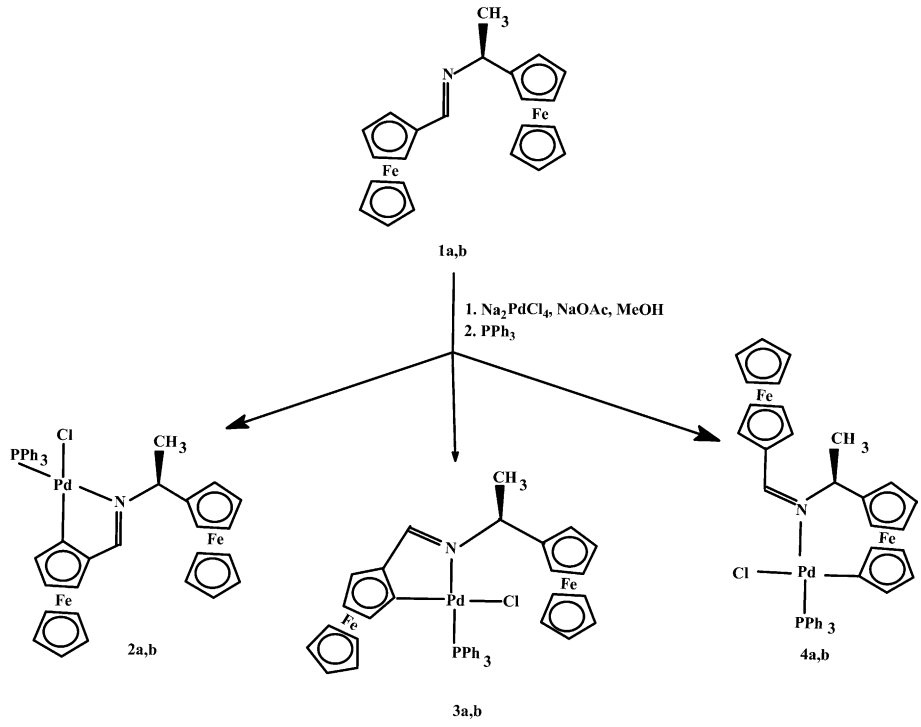
Molecular structures of **3b**, **4b**, and **4a** were unambiguously established by X-ray analysis of single crystals. Crystals of **4a** and **4b** are isostructural, therefore only the structures of **3b** (Fig. 1) and **4b** (Fig. 2) will be discussed.

Mechanism of this abnormal palladation pathway is not clear. Preceding step of any cyclopalladation reaction is known to be a coordination of the metal reagent by a donor atom of the molecule such as nitrogen [14]. Then palladium being a rather strong electrophile replaces hydrogen atom bonded to sp^2 carbon in aryl or heteroaryl group in the suitable position to form five- or six-membered ring. In this special case, perhaps, the unusual products **4** were able to form due to the specific combination of steric factor (bulky three-dimensional metallocenyl groups) and isomerism around the C=N bond.

Coordination square {Pd[ClCNP]} is the same in both molecules (**3b** and **4b**) but bond lengths and bond angles are different. The main difference is in significant decrease of the angles P–Pd–N and N–Pd–C and the increase of the N–Pd–Cl angle in **3b** comparing with **4b**. The bond angle P–Pd–N in **3b** has the minimum value among 11 cyclopalladated azomethines of ferrocenyl series whose structures are collected in the Cambridge Bank of Structural Data. There are no analogues of **4** in the literature.

Conformations of the ligand CpRuCp–C=NC(Me)–CpFeCp in **3b** and **4b** are dissimilar. Torsion angles Ru–C(Cp)–C=N, C(Cp)–C=N–C, C=N–C(Me)–C(Cp) and N–C(Me)–C(Cp)–Fe are equal to 89.0°, 177.5°, 23.1 and 165.2° (**3b**), 110.8°, 175.6°, 98.3° and 39.7° (**4b**) correspondingly. The difference is in the turn around the C2–N1 bond and in the different placement of Me group with respect to the coordination plane {Pd[ClCNP]} (Fig. 3).

In the structure **4b** Me group and Cp ring are placed on the opposite sites of the square forming rather short axial contacts Pd···H3 (CH_3) 2.85 Å, Pd···H8 (Cp) 2.71 Å. In **3b** similar contacts are formed by the H atoms of the Ph_3P ligand (Fig. 4). Axial contacts C–H···M with planar square d^8 transition metals are conventially considered as agostic bonds which make contribution into the stability of the molecule.



Scheme 1.

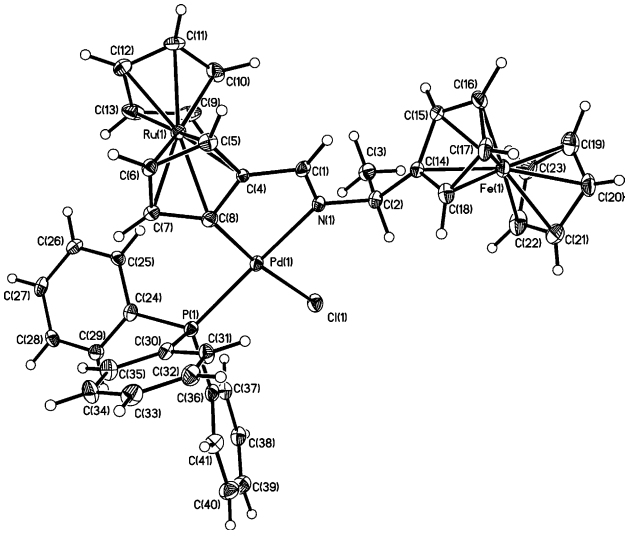


Fig. 1. Molecular structure of the normal product of cyclopalladation **3b**.

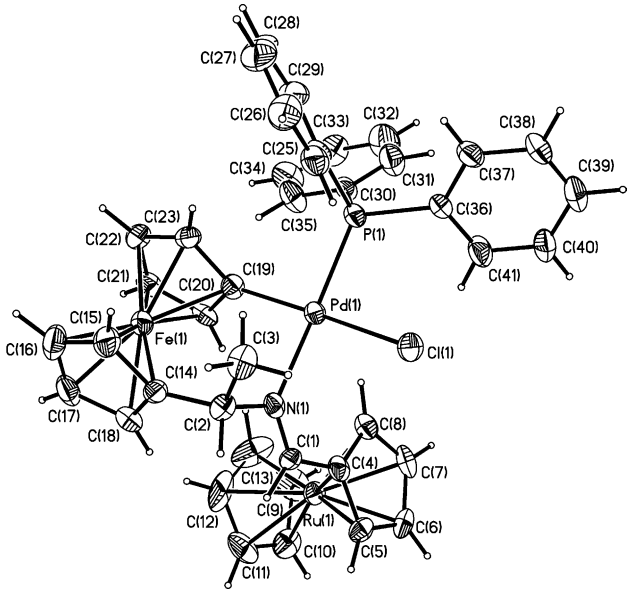


Fig. 2. Molecular structure of the abnormal product of cyclopalladation **4b**.

Determination of structure and stereochemistry of **3b** and **4b** permits to deduce both for **2a**,**b** and **4a** as well.

To summarize, cyclopalladation of **1a**,**b** proceeds abnormally for metallocenyl azomethines. It proceeds in two pathways: (i) conventional cyclopalladation with the formation of five-membered metallocycle including double bond C=N to give two diastereomers; (ii) palladation into the remote (unsubstituted) Cp ring of the amine fragment of the molecule. Ratio between (i) and (ii) is about 3:1. Pathway (i) is non-regioselective and has low stereoselectivity. Chiral R_C α-centre induces preferentially the formation of chiral plane of S_P configuration like in the case of *N*,*N*-dimethyl-α-ferrocenylethylamine [15] but with less diastereoselectivity (about 30% comparing to 70% for tertiary amine). Pathway (ii) does not introduce planar chirality, so the unprecedented "phane" product has no diastereomers.

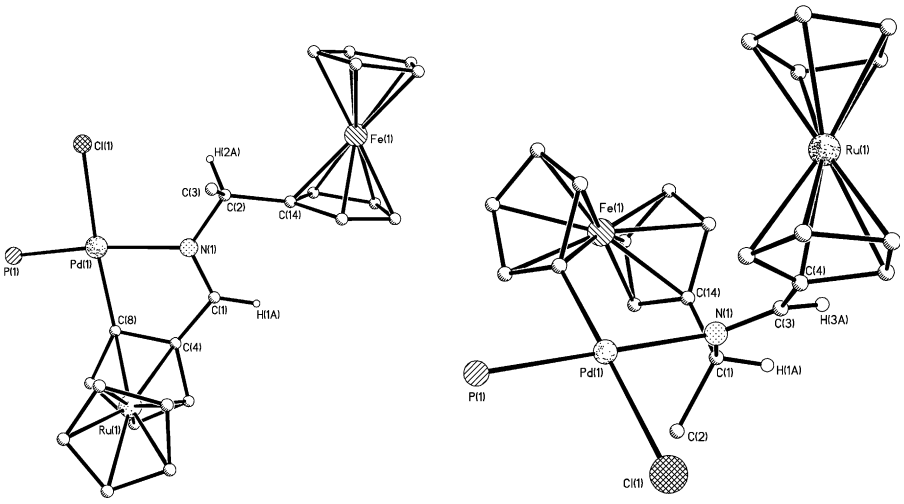


Fig. 3. The different placement of Me group with respect to the coordination plane {Pd[ClCNP]} in **3b** and **4b**.

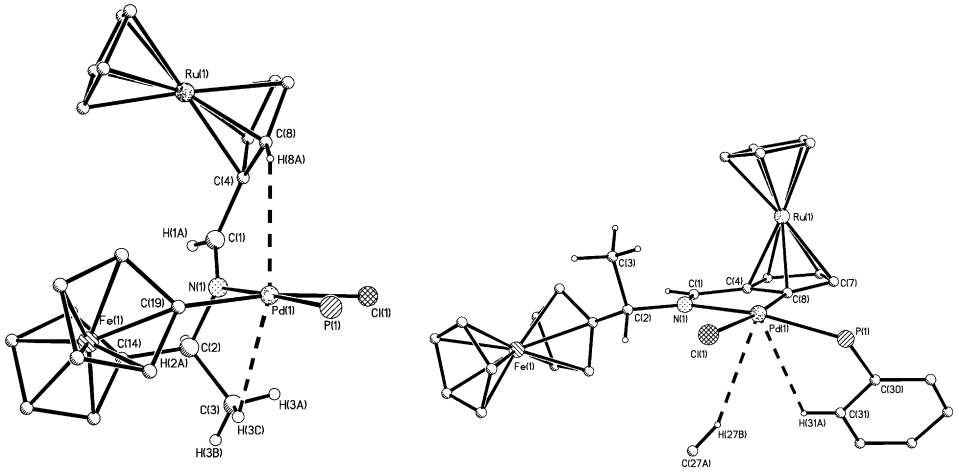


Fig. 4. Short axial contacts involving the palladium atom in **3b** and **4b**.

3. Experimental

Solvents were purified by known methods. ^{1}H and ^{31}P NMR spectra were registered on Bruker 400 HX instrument.

3.1. (α-Ferrocenylethyl)iminomethylferrocene (*1a*)

The well-ground mixture of ferrocene aldehyde (0.107 g, 0.5 mM) and α-ferrocenylethylamine (0.115 g, 0.5 mM) was kept in desiccator over P_2O_5 for five days. The solid product was crystallized from hexane to give 0.129 g (61.2%) of **1a**. IR spectrum (KBr): ν(C=N) 1624 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.49 (d, 3H, CH_3, J 6.8 Hz), 4.13 (broad s, 15H, 2 Cp + C_5H_4 + CH), 4.31 (broad s, 2H, β-H C_5H_{4ald}). 4.60 (1H) and 4.63 (1H) (α-H C_5H_{4ald}), 8.09 (s, 1H, HC=N). $C_{23}H_{23}Fe_2N$ calcd.: 64.93; H 5.45; N 3.29%. Found: C 64.85; H 5.56; N 3.17%.

3.2. (α-Ferrocenylethyl)iminomethylruthenocene (*1b*)

Similarly 0.102 g (43.3%) of **1b** was obtained from 0.130 g of ruthenocene aldehyde and 0.115 g of α-ferrocenylethylamine. IR spectrum (KBr): ν(C=N) 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.47 (d, 3H, CH_3, J 6.8 Hz), 4.12 (broad s, 4,5H, C_5H_{4am} + 0.5 q CH), 4.14 (q, HC, J 6.8 Hz), 4.16 (s 5.5H Cp_{am} + 0.5 q CH) 4.57 (s, 5H, Cp_{ald}), 4.68 (broad s, 2H, β-H C_5H_{4ald}), 4.97 and 5.08 (broad s, 1H and 1H, α-C_5H_{4ald}), 7.97 (s, 1H, HC=N). $C_{23}H_{23}Fe_2N$ calc.: C 64.93; H 5.45; N 3.29%. Found: C 64.85; H 5.56; N 3.17%.

3.3. Cyclopalladation of aldimines *1a,b*

General procedure. Methanolic solution of equimolar amounts of Na_2PdCl_4 and $NaOCOCH_3 \cdot 3H_2O$ was added to the suspension of a Schiff base in MeOH.

Mixture was stirred for seven days, then precipitate was filtered off and dried.

A. In this way 0.15 g of **1a** afforded 0.18 g (86.3%) of the cyclopalladated product which was treated with triphenylphosphine (50% excess) in $CHCl_3$. Solution was concentrated and chromatographed on SiO_2 (TLC, eluent $CHCl_3$). Mixture of diastereomers **2**–**3a** (very close first and second bands) and complex **4a** (third band) were collected. Both products were crystallized from methanol.

*(Triphenylphosphine)2-((α-ferrocenylethyl)iminomethylferrocenyl-C,N)palladium(II) chloride (mixture of diastereomers **2**–**3a**)*. IR spectrum (KBr): ν(C=N) 1600 cm^{-1}. ^{31}P NMR ($CDCl_3$), δ (ppm): 37.84 (**2a**, major diastereomer), 38.00 (**3a**, minor diastereomer). ^1H NMR ($CDCl_3$), δ (ppm): diastereomer **2a**: 1.68 (d, 3H, CH_3, J 7.2 Hz), 3.32 (broad s, 1H, subst. Cp_{ald}), 3.68 (s, 5H, Cp_{ald}), 3.97 (broad s, 1H, subst. Cp_{ald}), 4.19 (s, 5H, Cp_{am}), 4.24 (broad s, 3H, Cp_{am}), 4.28 (s, 5H, Cp_{am}), 4.59 (s, 1H, subst. Cp_{ald}), 5.75 (q, 1H, CH, J 7.2 Hz), 7.43 (broad s) and 7.82 (m, 16H, Ph and CH=N); diastereomer **3a**: 1.75 (d, 3H, CH_3, J 7.2 Hz), 3.25 (broad s, 1H, subst. Cp_{ald}), 3.84 (s, 5H, Cp_{ald}), 3.97 (broad s, 1H, subst. Cp_{ald}), 4.19 (s, 5H, Cp_{am}), 4.23 (broad s, 2H, Cp_{am}), 4.27 (broad s, 2H, Cp_{am}), 4.33 (1H, subst. Cp_{ald}), 5.55 (q, 1H, CH, J 7.2 Hz), 7.44 (m, 9H, Ph), 7.71 (d, 1H, CH=N, $^4J_{HP}$ 9.4 Hz), 7.79 (m, 6H, Ph). $C_{41}H_{37}ClFe_2NPPd$. Calc. C 59.45; H 4.50; N 1.69; Cl 4.28%. Found: C 59.28; H. 4.47; N 1.76; Cl 4.25%.

*1′-[(Triphenylphosphine)(chloride)palladio-N]-1-(α-ferrocenylethyl)iminomethylferrocene (**4a**)*. IR spectrum (KBr): ν(C=N) 1630 cm^{-1}. ^{31}P NMR ($CDCl_3$), δ (ppm): 32.28. ^1H NMR ($CDCl_3$), δ (ppm): 2.13 (d, 3H, CH_3, $^4J_{HP}$ 7.4 Hz), 3.31, 3.55, 3.80 (broad s, 1H each), 3.50 (s, MeOH), 3.85 (broad s and m, 2H, 1H and subst. Cp), 3.96, 4.07, 4.15, and 4.24 (broad s, 1H each), 4.40 (s, Cp), 4.51, 4.61, 5.16, and 6.07 (broad s, 1H each), 7.2–7.6 (m, 15H, Ph), 8.17 (d, 1H, CH=N, $^4J_{HP}$ 11.5 Hz). $C_{41}H_{37}ClFe_2NPPd \cdot CH_3OH$. Calc.: C 58.64; H 4.80; N 1.63%. Found: C 58.40; H 4.64; N 1.48%.

B. From 0.085 g (0.182 mM) of **1b** was similarly obtained 0,084 g (76%) of the product. After the treatment with Ph_3P (50% excess) in CH_2Cl_2 the solution was

Table 1
Crystal data and structure refinement for **3b**, **4a** and **4b**

	4b	**3b**	**4a**
Formula	$C_{42}H_{41}ClFeNOPPdRu$	$C_{42}H_{41}ClFeNOPPdRu$	$C_{42}H_{41}ClFe_2NOPPd$
Molecular weight	905.50	905.50	860.28
Crystal colour, habit	Light-yellow plate	Light-yellow needle	Red plate
Crystal size (mm)	$0.25 \times 0.15 \times 0.15$	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.20 \times 0.10$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Cell constants			
a (Å)	13.726(3)	16.855(2)	13.782(5)
b (Å)	8.954(2)	12.568(2)	9.004(4)
c (Å)	30.084(6)	18.471(2)	29.587(8)
β (°)	90.93(3)	111.963(3)	91.901(3)
V (Å^3)	3697(1)	3628.6(8)	3670(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.422	1.448	1.557
Temperature (K)	295	120	295
Radiation		Mo Kα (λ = 0.71073)	
Scan mode	$\theta - 5/3\theta$	ϕ and ω	$\theta - 5/3\theta$
$2\theta_{max}$ (°)	44	58	50
Absorption coefficient μ(Mo Kα) (mm^{-1})	1.422	1.448	1.416
Absorption correction	psi-scan	SADABS	psi-scan
$T_{max.}$ and $T_{min.}$	0.577 and 0.313	0.746 and 0.529	0.755 and 0.521
Structure solution		Direct method	
Refinement method		Full-matrix least-squares on F^2	
Number of reflections collect	4981	39577	6848
Number of independent reflections	4457 (R_{int} = 0.0259)	9517 (R_{int} = 0.0950)	6313 (R_{int} = 0.0402)
Number of observed reflections ($I > 2\sigma(I)$)	3315	4998	1638
Number of parameters	460	442	441
R_1 (on F for observed reflections)	0.0503	0.0570	0.0528
wR_2 (on F^2 for all reflections)	0.1555	0.1263	0.0934
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP, \quad P = 1/3(F_o^2 + 2F_c^2)$		
a	0.0915	0.0510	0.0010
b	31.8114	2.5000	0.5000
F(000)	1824	1824	1752
GOOF	0.946	0.926	0.799
Largest different peak and hole (e Å^{-3})	1.533 and 0.131	1.657 and 0.161	0.555 and −1.354

evaporated to dryness and methanol was added. Insoluble residue was recrystallized from the mixture MeOH–CH_2Cl_2, and minor diastereomer **3b** was obtained. From methanolic solution in refrigerator crystals of isomer **4b** were isolated. After evaporation of solvent and freezing a mixture of isomers **2b** and **3b** was obtained, the first being predominant.

(R,S*)(Triphenylphosphine)((2-(α-ferrocenylethyl) iminomethyl)ruthenocenyl-C,N)palladium(II) chloride* (**2b**). IR spectrum (KBr): ν(C=N) 1606 cm^{-1}. ^{31}P NMR ($CDCl_3$), δ (ppm): 37.31. ^1H NMR ($CDCl_3$), δ (ppm): 1.66 (d, 3H, CH_3, J 7.4 Hz), 3.45 (broad s, 1H, subst. Cp_{ald}), 4.17 and 4.22 (m, 14H, Cp_{am}, subst. Cp_{am}, Cp_{ald}), 4.46 (broad s, 1H, Cp_{ald}), 4.57 (broad s, 1H, Cp_{ald}), 5.66 (q, 1H, CH, J 7.4 Hz), 7.42, 7.54 and 7.92 (m, 15H, Ph), 7.70 (d, 1H, CH=N, $^4J_{HP}$ 9.3 Hz). $C_{41}H_{37}ClFeNPPdRu$. Calcd.: C 56.38; H 4.27%. Found: C 56.38; H 4.38%.

*(R*R*)(Triphenylphosphine)((2-(α-ferrocenylethyl) iminomethyl)ruthenocenyl-C,N)palladium(II) chloride* **(3b).** IR spectrum (KBr): ν(C=N) 1606 cm^{-1}. ^{31}P NMR ($CDCl_3$), δ (ppm): 37.53. ^1H NMR ($CDCl_3$), δ (ppm): 1.58 (d, 3H, CH_3, J 7.3 Hz), 3.43 (broad s, 1H, subst. Cp_{ald}), 4.16 (s, 5H, Cp_{am}), 4.21 (broad s, 2H, Cp_{am}), 4.23 (broad s, 1H, subst. Cp_{ald}), 4.26 (broad s, 2H, Cp_{am}), 4.34 (s, 5H, Cp_{ald}), 5.30 (s, CH_2Cl_2), 5.51 (q, 1H, CH, J 7.3 Hz), 7.42 (m, 9H, Ph), 7.60 (d, 1H, CH=N, $^4J_{HP}$ 9.3 Hz), 7.77 (m, 6H, Ph). $C_{41}H_{37}ClFeNPPdRu \cdot CH_2Cl_2$. Calcd.: C 52.63; H 4.10%. Found: C 53.76; H 4.10%.

1′-[(Triphenylphosphine)(chloride)palladio-N]-1-(α-ferrocenylethyliminomethyl)ruthenocene (***4b***). IR spectrum (KBr): ν(C=N) 1636 cm^{-1}. ^{31}P NMR ($CDCl_3$), δ (ppm): 32.35. ^1H NMR ($CDCl_3$), δ (ppm): 2.13 (d, 3H, CH_3, J 6.7 Hz), 3.25 (broad s, 1H), 3.48, 3.50, 3.51, and 3.63 (broad singlets, 1H each), 3.83 (q, 1H, CH), 3.84, 3.94, 4.05, and 4.22 (broad singlets, 1H each), 4.74 (s, 5H, Cp), 4.85, 4.88, 5.14, and 6.90 (broad singlets, 1H each), 7.3-7.7 (m 15H, Ph), 8.00 (d, 1H, CH=N, $^4J_{HP}$ 11.0 Hz).

4. X-ray crystallography

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo Kα radiation, ω-scans with a 0.3° step in ω and 10 s per frame exposure at 120 K (**3b**) and CAD4 Enraf-Nonius at 295 K (**4a** and **4b**). Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software [16] and semi-empirical method SADABS [17]. The empirical absorption correlation of **4a** and **4b** based on the azimuthal scans of 20 reflections was applied [18].

Structures were solved by direct method and refined by full-matrix least squares against F^2 in the anisotropic (H-atoms isotropic) approximation using SHELXTL-97 package. All hydrogen atoms in **3b**,**4a** and **4b** were placed in geometrically calculated positions and included in final the refinement using the "riding" model with the $U_{iso}(H)$ parameters equal to $1.2U_{eq}(C_i)$ or $1.5U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are, respectively, the equivalent thermal parameters of the methine and methylene carbon atoms to which corresponding H atoms are bonded. The MeOH molecules in the structures **4a** and **4b** are disordered over two

Table 3
Selected bond and tilting angles [°] in **4a**, **4b**, and **3b**

	4a	4b	3b
Cl–Pd–C	170.9(3)	172.1(3)	173.0(2)
P–Pd–C	89.2(3)	88.6(3)	90.1(2)
P–Pd–Cl	95.1(1)	94.9(1)	96.63(5)
N–Pd–Cl	85.6(2)	86.0(2)	92.7(1)
N–Pd–C	89.8(3)	90.2(3)	81.2(2)
C=N–C(Me)	117.8(9)	117.1(8)	120.5(4)
Cp/Cp (coord)	3.4	3.3	4.3
Cp/Cp (non-coord)	4.0	3.2	0.2
ΔPd/plane	0.096	0.083	0.088
ΔFe/Cp	1.629–1.637	1.636, 1.640	1.636, 1.654
ΔRu/Cp	–	1.795,1.797	1.798, 1.809

Table 2
Selected bond lengths [Å] in **4a**, **4b**, and **3b**

	4a	4b	3b
Pd–Cl	2.399(3)	2.392(3)	2.389(1)
Pd–N	2.124(8)	2.122(7)	2.138(4)
Pd–P	2.268(3)	2.262(3)	2.253(1)
Pd–C	2.009(8)	1.993(9)	2.000(5)
Cp–M–Cp	Fe2–Cp	Ru1–Cp	Fe1–Cp
(non-coord)	C4–C8 2.01–2.04	C4–C8 2.14–2.17	C14–C18 2.026–2.044
	C9–C13 1.98-2.06	C9–C13 2.15–2.16	C19–C23 2.038–2.053
Cp–M–Cp	Fe1–Cp	Fe1–Cp	Ru1–Cp
(coord)	C14–C18 2.02–2.04	C14–C18 2.03–2.06	C4–C8 2.111–2.208
	C19–C23 2.01–2.06	C19–C23 2.01–2.06	C9–C13 2.166–2.192
P–C	1.80, 1.82, 1.83(1)	1.81, 1.82, 1.83(1)	1.818, 1.821, 1.832(5)
N–C(Me)	1.47(1)	1.48(1)	1.500(6)
N=C	1.31(1)	1.25(1)	1.275(6)

positions and were refined with the site occupancy factors equal to 0.61 and 0.39 (**4a**) and 0.5 (**4b**). Crystal data and structure refinement are given in Table 1.

The crystallographic data for complexes **3b, 4a** and **4b** are summarized in Tables 2 and 3.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Nos. CCDC-266417, 266418, 266419. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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