Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 690 (2005) 3976–3982

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

# 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*

Received 30 March 2005; received in revised form 26 May 2005; accepted 26 May 2005
Available online 5 July 2005

## 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).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.05.035

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 $\nu$(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.