Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 663 (2002) 277–283
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Cyclopalladation of Schiff bases from phenylalanine and 2-phenylglicine

Joan Albert [a], J. Magali Cadena [a], Asensio González [b], Jaume Granell [a,*], Xavier Solans [c], Mercè Font-Bardia [c]

[a] Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
[b] Laboratorio de Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona, Pl. Pius XII, s/n, 08028 Barcelona, Spain
[c] Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

Received 17 July 2002; accepted 18 September 2002

Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

The action of palladium acetate on the Schiff bases 4-ClC_6H_4CH=N-$CH(R^2)COOR^1$ (R^1 = Me, Et; R^2 = Ph, CH_2Ph), in acetic acid for 3 h at 70 °C and subsequent treatment of the reaction residues with LiCl in acetone, affords the corresponding chloro-bridged five-membered *endo*-metallacycles $[PdCl(C–N)]_2$, **1a**, **2a**. The action of palladium acetate on the Schiff bases 2,6-$Cl_2C_6H_3CH$=N–$CH(R^2)COOR^1$ (R^1 = Me, Et; R^2 = Ph, CH_2Ph), in chloroform at room temperature and subsequent treatment of the reaction residues with LiCl in acetone, affords the corresponding chloro-bridged five- or six-membered *exo*-metallacycles, by metallation of the amino acid moiety $[PdCl(C–N)]_2$, **3a-*exo***, **4a-*exo***. A small amount of the *endo*-metallacycles was also obtained, probably by oxidative addition of the *ortho* C–Cl bond of these imines to Pd(0) formed in situ. Reaction of dimers **1a**–**4a** with PPh_3 affords the mononuclear complexes $[PdCl(C–N)(PPh_3)]$ **1b**–**4b**.

Keywords: Palladium; Imines; Amino acid; Cyclometallation

1. Introduction

There is growing interest in the synthesis, reactivity and applications of organometallic complexes with biologically important ligands and the term bioorganometallic chemistry is used to describe this new research field on the border between biochemistry and organometallic chemistry [1].

α-Amino acids are highly versatile ligands and can afford two classes of compounds: complexes in which the amino acid is coordinated to an organometallic fragment via their donor atoms (amino, carboxylato or other basic groups) and complexes in which the amino acid is coordinated to the metal through a carbon–metal bond, this last class being comparatively rare [1a]. Some C–N chelates have been synthesized by metallation of amino acid derivatives by palladium. Ryabov et al. reported the cyclopalladation of the (*R*)-*N*,*N*-dimethyl-2-phenylglycine methyl ester by palladium acetate [2], Fuchita et al. described the metallation of the primary benzylamine derivative (*R*)-2-phenylglycine methyl ester [3] and Grigg et al. reported the synthesis of *ortho*-palladated imines of α-amino acids [4]. Recently, Beck and coworkers described the cyclopalladation of several Schiff bases from α-amino acid and peptide esters [5].

As part of our studies on the cyclometallation of N-donor ligands, we examined the action of palladium acetate on imines from phenylalanine and 2-phenylglycine. These ligands were obtained by condensation of the corresponding benzaldehyde with the α-amino acid ester.

Imines can undergo metallation on different carbon atoms, giving organometallic complexes of different structures: *endo*-metallacycles, if the C=N bond is included in the metallacycle, or *exo*-derivatives. In

* Corresponding author. Fax: +34-93-411-1492
E-mail address: jgranell@kripto.qui.ub.es (J. Granell).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01928-9

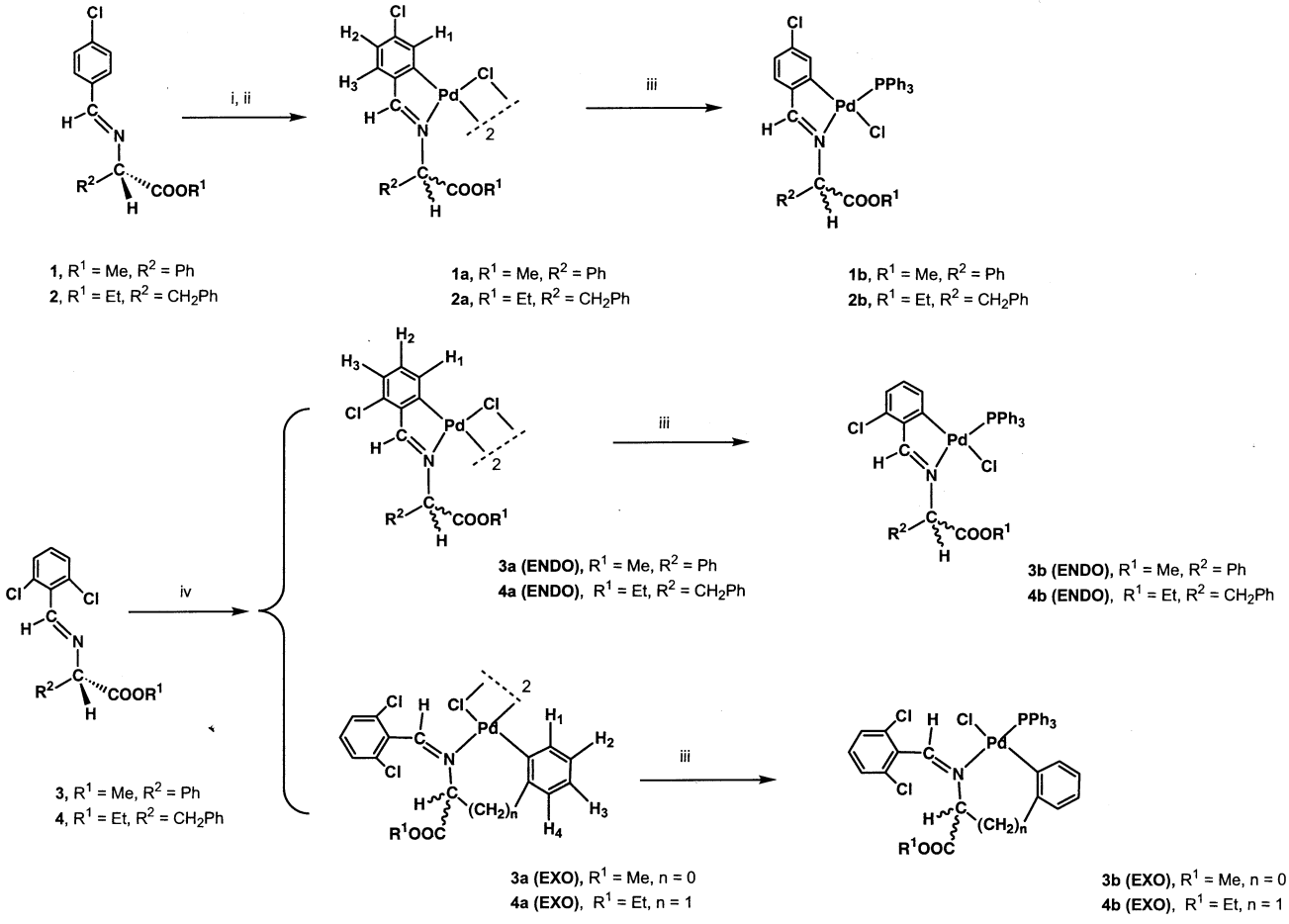
addition, imines can exist in *E* or *Z* isomers, but in general, N-substituted aldimines adopt the more stable E form [6]. *endo*- or *exo*-Metallacycles can be obtained from imines in the *E* form but the *Z* isomer can afford only *exo*-metallacycles [7].

2. Results and discussion

The Schiff bases **1** and **2** were treated with palladium acetate in acetic acid for 3 h at 70 °C. Subsequent treatment of the reaction residues with LiCl in acetone afforded, after purification by SiO_2 column chromatography, the corresponding chloro-bridged cyclopalladated dimers **1a** and **2a**, in a yield of 25 and 40%, respectively (Scheme 1). Overall NMR data showed that only the *endo*-derivative was formed, which is consistent with reports of the strong tendency of imines to form *endo*-metallacycles [8]. These imines might also afford *exo*-metallacycles (of five- and six-membered, respectively) by activation of a $C_{aromatic}$–H bond of the amino acid moiety but their formation was not observed. The low yield of the metallation reaction can be explained by the instability of the imines.

It has been shown that *exo*-metallacycles can be obtained by cyclopalladation of imines if the *ortho* positions of the benzal ring (which leads to the formation of *endo*-metallacycles) are blocked by substituents such as chlorine atoms [7a]. Following and expanding this strategy to prepare *exo*-cyclic imine cyclopalladated derivatives, the action of palladium acetate on imines **3** and **4**, derived from 2,6-dichlorobenzaldehyde, was studied.

The reaction was performed in chloroform at room temperature and the reaction residues were treated with LiCl in acetone. After purification by SiO_2 column chromatography, the corresponding chloro-bridged cyclopalladated dimers **3a** and **4a** were isolated. NMR data showed that these complexes are the *exo*-derivatives, with a $C_{aromatic}$–Pd bond, containing the imine in the Z form. A small amount of the *endo*-metallacycles was also obtained, probably by oxidative addition of the *ortho* C–Cl bond of these imines to Pd(0) formed in situ [7a,9].



Scheme 1. (i) $Pd(AcO)_2$, AcOH, 3 h, 70 °C; (ii) LiCl, acetone, room temperature, 30 min; (iii) PPh_3, acetone; (iv) $Pd(AcO)_2/CHCl_3$, room temperature, 2 h.

Reaction of dimers **1a**–**4a** with PPh_3 afforded the mononuclear complexes [PdCl(C–N)(PPh_3)] **1b**–**4b**. The high-field shift of the aromatic protons of the palladated ring in these complexes, due to the aromatic rings of the phosphine, indicates the *cis* disposition of the phosphorus relative to the metallated carbon atom, and the chemical shift of the phosphorus confirms this arrangement [7]. This arrangement is usual in cyclopalladated compounds containing phosphines [10].

The structure of **4b-*exo*** was determined by X-ray diffraction (Fig. 1, Table 1). The crystal structure consists of discrete molecules separated by van der Waals distances. The palladium atom is in a square-planar environment, coordinated to carbon, chlorine, nitrogen and phosphorus atoms. The coordination plane shows a tetrahedral distortion, the deviation from the mean plane being: −0.049(1), −0.064(5), +0.051(4) and 0.062(5) Å for Cl, C1, P and N, respectively. The distances between palladium and the coordinated atoms are similar to those reported for analogous compounds [7,11], the angles between adjacent atoms in the coordination sphere lie in the range 81.79(16) (C1–Pd–N) to 94.00(12) (C1–Pd–P). The phosphorus and nitrogen atoms adopt a *trans* arrangement, the metallacycle does not contain the C=N bond and the imine is in the *Z*-form.

All the new organometallic compounds obtained were characterized by elemental analysis, IR spectra, and ^1H and ^{31}P-NMR spectra. In some cases, 2D-NMR experiments and positive FAB-mass spectra were carried out to complete the characterization. It should be noted that complete racemization of the Schiff base takes place during the cyclopalladation reaction.

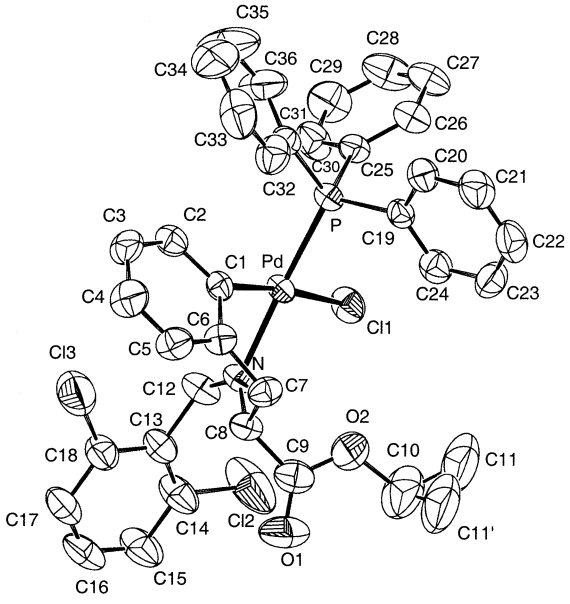


Fig. 1. ORTEP plot of the structure of **4b-*exo***.

All the free ligands and *endo*-metallacycles, which bear a chloro substituent at the C2 position of the aryl ring, show a downfield shift of the imine resonance which is consistent with a N=CH···Cl interaction between the imine proton and the chlorine atom. Similar shifts have been previously observed for analogous compounds with chloro or fluoro substituents. This interaction, which reinforces the planarity of the ArC=N fragment, has been confirmed in some cases by X-ray crystal structure determination [12].

In conclusion the results here reported show that imines derived from amino acids have a strong tendency to afford *endo*-metallacycles. Nevertheless the *exo*-derivatives can be obtained if the *ortho* positions of the benzal ring (which leads to the formation of *endo*-metallacycles) are blocked by chloro substituents. There is no clear explanation of this *endo*-effect. The aromaticity of the five-membered metallacycle, involving the two conjugated bonds C=C, C=N and the filled *d* orbital of the metal of appropriate symmetry has been proposed to explain the greater stability of *endo*-cyclic compounds [13]. Besides this, kinetic studies of the influence of temperature and pressure on a wide variety of imines have also been reported. In these studies the formation of a highly ordered transition state, in which there is a four centered interaction between the carbon and hydrogen bonds of the C–H bond to be activated, the oxygen atom of the acetate ligand and the palladium atom, is proposed to explain the *endo*-effect [8a,8b,14].

3. Experimental

^1H-NMR spectra at 200 MHz were recorded on a Varian Gemini 200 spectrometer and ^1H-NMR at 500 MHz and $^{31}P\{^1H\}$ at 101.26 MHz were recorded, respectively, on a Varian VXR 500 or a Bruker DRX 250 spectrometers. Chemical shifts (in ppm) were

Table 1
Selected bond lengths (Å) and angles (°) for **4b-*exo***

Bond lengths			
Pd–C(1)	1.999(4)	O(1)–C(9)	1.187(7)
Pd–N	2.096(3)	O(2)–C(9)	1.312(8)
Pd–P	2.2460(10)	O(2)–C(10)	1.454(10)
Pd–Cl(1)	2.3863(12)	N–C(12)	1.267(6)
Cl(2)–C(14)	1.721(6)	N–C(8)	1.486(6)
Cl(3)–C(18)	1.738(6)		
Bond angles			
C(1)–Pd–N	81.73(16)	C(9)–O(2)–C(10)	119.3(6)
C(1)–Pd–P	94.00(12)	C(12)–N–C(8)	120.1(3)
N–Pd–P	172.64(10)	C(12)–N–Pd	121.3(3)
C(1)–Pd–Cl(1)	172.55(12)	C(8)–N–Pd	117.9(2)
N–Pd–Cl(1)	90.84(11)	N–C(8)–C(9)	111.6(4)
P–Pd–Cl(1)	93.44(4)	N–C(8)–C(7)	108.5(3)

measured relative to $SiMe_4$ for ^1H and to 85% H_3PO_4 for ^{31}P. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Mass spectra were recorded on a Fisons VG-Quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzylalcohol for FAB analysis and then bombarded with cesium atoms.

3.1. Materials and synthesis

All solvents were dried and degassed by standard methods. All chemicals were of commercial grade and used as received. Crystals of **4b-*exo*** for X-ray structure determination were obtained from a Et_2O solution. The proton NMR spectra of cyclopalladated compounds **1a**–**4a** were performed in $CDCl_3$ the presence of a few drops of pyridine-d_5 to obtain the corresponding mononuclear complexes [PdCl(C–N)py].

3.1.1. Synthesis of imines *1*–*4*

A mixture of 1.7 mmol of amino acid ester (phenylalanine ethyl ester and phenylglycine methyl ester) and 1.7 mmol of the corresponding aldehyde and $MgSO_4$ was stirred in CH_2Cl_2 for 20 h to obtain the ligands **1**–**4**. The solution was filtered and concentrated in vacuo and the oil obtained was characterized by ^1H-NMR and IR spectra and was used without further purification.

1: ^1H-NMR (200 MHz, $CDCl_3$) $\delta = 3.73$ (s, 3H, *Me*); 5.19 (s, 1H, *H*CCOOMe); 7.50–7.30 (m, 7H, *aromatic*); 7.75 (d, 2H, *aromatic*, $J_{HH} = 8.4$ Hz); 8.28 (s, 1H, *H*C=N).

2: ^1H-NMR (200 MHz, $CDCl_3$) $\delta = 1.24$ (t, 3H, C*H*$_3$CH$_2$O, $J_{HH} = 7.2$ Hz); 3.15 (dd, 1H, $J_{HH} = 13.4$ Hz, $J_{HH} = 9$ Hz, C*H*$_2$N); 3.40 (dd, 1H, dd, 1H, $J_{HH} = 13.4$ Hz, $J_{HH} = 5.2$ Hz, C*H*$_2$N); 4.18 (m, 3H, *H*CCOOEt, C*H*$_2$O); 7.20–7.15 (m, 5H, *aromatic*); 7.33 (d, 2H, $J_{HH} = 8.8$ Hz, *aromatic*); 7.62 (d, 2H, $J_{HH} = 8.8$ Hz, *aromatic*); 7.85 (s, 1H, *H*C=N).

3: ^1H-NMR (200 MHz, $CDCl_3$) $\delta = 3.76$ (s, 3H, *Me*); 5.32 (s, 1H, *H*CCOOMe); 7.50–7.30 (m, 6H, *aromatic*); 7.52 (d, 2H, *aromatic*, $J_{HH} = 7.2$ Hz); 8.53 (s, 1H, *H*C=N).

4: ^1H-NMR (200 MHz, $CDCl_3$) $\delta = 1.27$ (t, 3H, C*H*$_3$CH$_2$O, $J_{HH} = 7.4$ Hz); 3.10 (dd, 1H, $J_{HH} = 13.4$ Hz, $J_{HH} = 9$ Hz, C*H*$_2$Ph); 3.45 (dd, 1H, dd, 1H, $J_{HH} = 13.4$ Hz, $J_{HH} = 5.2$ Hz, C*H*$_2$Ph); 4.18 (m, 2H, HCCOOEt, C*H*$_2$CH$_3$); 7.20–7.15 (m, 8H, *aromatic*); 8.19 (s, 1H, *H*C=N).

3.1.2. Synthesis of compounds *1a*–*4a*

A stirred suspension of palladium acetate (2.22 mmol, 500 mg) in AcOH (30 ml) was treated with the corresponding ligand **1**–**2** (2.22 mmol) for 3 h at 70 °C under nitrogen. The resulting solution was concentrated in vacuo, and the solid obtained was dissolved in acetone (20 ml) and was treated with LiCl (2.44 mmol, 104 mg) for 30 min at room temperature (r.t.). The solution was concentrated in vacuo and the precipitate formed was purified by column chromatography over SiO_2 with chloroform–acetone (100:4) as eluent to obtain **1a** and **2a** in a yield of 25 and 40%, respectively.

The cyclometallated complexes **3a** and **4a** were similarly prepared by reaction between palladium acetate and the corresponding imine in $CHCl_3$ for 2 h at r.t. The resulting solution was concentrated in vacuo, and the solid obtained was dissolved in acetone (20 ml) and was treated with LiCl (2.44 mmol, 104 mg) for 30 min at r.t. The solution was concentrated in vacuo and the precipitate formed was purified by column chromatography over SiO_2 with $CHCl_3$:MeOH (100:1) as eluent. The compounds were obtained in a yield of 5% for **3a-*endo***, 20% for **3a-*exo***, 8% for **4a-*endo***, and 25% for **4a-*exo***.

1a: Characterization data: Anal. Calc. (found) for $C_{32}H_{26}Cl_4N_2O_4Pd_2$: C, 44.84 (44.7); H, 3.06 (2.9); N, 3.27 (3.3)%. ^1H-NMR (200 MHz, $CDCl_3$): **1a + pyridine-*d*$_5$**, $\delta = 3.83$ (s, 3H, *Me*); 6.05 (s, 1H, *H*CCOOMe); 6.75 (s, 1H, *H*^{1}); 7.01 (d, 1H, $J_{HH} = 8.0$ Hz, *H*^{2}), 7.15 (d, 1H, $J_{HH} = 8.0$ Hz, *H*^{3}); 7.45 (m, 5H, *aromatic*); 7.86 (s, 1H, *H*C=N).

2a: Characterization data: Anal. Calc. (found) for $C_{36}H_{34}Cl_4N_2O_4Pd_2$: C, 47.35 (47.6); H, 3.75 (3.6); N, 3.07 (3.0)%. MS-positive FAB: 912 (M^+), 877 {$(M-Cl)^+$}. ^1H-NMR (200 MHz, $CDCl_3$): $\delta = 1.28$ (t, 3H, $J_{HH} = 7.2$ Hz, C*H*$_3$CH$_2$O); 3.40 (br m, 1H, C*H*$_2$CHN); 3.60 (m, 1H, C*H*$_2$N); 4.24 (q, 2H, $J_{HH} = 6.6$ Hz, *CH*$_2$CH$_3$); 4.60 (br m, 1H, *H*CCOOEt); 7.03 (s, 1H, *H*^{1}); 7.20–7.40 (m, 7H, *aromatic*); 7.64 (s, 1H, *H*C=N). ^1H-NMR (200 MHz, $CDCl_3$) **2a + pyridine-*d*$_5$**, $\delta = 1.20$ (t, 3H, $J_{HH} = 7.0$ Hz, C*H*$_3$CH$_2$O); 3.30 (dd, 1H, $J_{HH} = 12.8$ Hz, $J_{HH} = 6.6$ Hz, C*H*$_2$CHN); 3.60 (dd, 1H, $J_{HH} = 12.8$ Hz, $J_{HH} = 5.8$ Hz, C*H*$_2$CHN); 4.17 (q, 2H, $J_{HH} = 7.0$ Hz, *CH*$_2$CH$_3$); 5.60 (br m, 1H, *H*CCOOEt); 6.10 (s, 1H, *H*^{1}); 7.0–7.40 (m, 7H, *aromatic*); 7.81 (s, 1H, *H*C=N).

3a-*endo*: Characterization data: Anal. Calc. (found) for $C_{32}H_{26}Cl_4N_2O_4Pd_2$: C, 44.84 (45.1); H, 3.06 (3.0); N, 3.27 (3.2). MS-positive FAB: 857 (M^+), 820 {$(M-Cl)^+$}. ^1H-NMR (200 MHz, $CDCl_3$): $\delta = 3.84$ (s, 3H, *Me*); 6.02 (s, 1H, *H*CCOOMe); 6.96 (m, 2H, *aromatic*); 7.35–7.49 (m, 6H, *aromatic*); 8.07 (s, 1H, *H*C=N). ^1H-NMR (200 MHz, $CDCl_3$), **3a-*endo* + pyridine-*d*$_5$**: $\delta = 3.81$ (s, 3H, *Me*); 6.02 (br, 1H, *H*^{1}); 6.75 (s, 1H, *H*CCOOMe); 6.85–6.91 (m, 2H, *aromatic*); 7.36–7.45 (m, 5H, *aromatic*); 8.24 (s, 1H, *H*C=N).

3a-*exo*: Characterization data: Anal. Calc. (found) for $C_{32}H_{24}Cl_6N_2O_4Pd_2$: C, 41.50 (41.5); H, 2.61 (2.5); N, 3.02 (2.9). MS-positive FAB: 926 (M^+), 890{$(M-Cl)^+$}. ^1H-NMR (200 MHz, $CDCl_3$) $\delta = 3.67$ (s, 3H, *Me*); 5.49 (s, 1H, *H*CCOOMe); 6.90–7.05 (m, 3H,

aromatic); 7.35–7.40 (m, 4H, *aromatic*); 9.05 (s, 1H, *H*C=N). ^{1}H-NMR (200 MHz, $CDCl_3$), **3a-*exo* + pyridine-d_5**, $\delta = 3.65$ (s, 3H, *Me*); 5.62 (s, 1H, *H*CCOOMe); 6.18 (br, 1H, *aromatic*); 6.95 (t, 1H, $J_{HH} = 8.0$, H^2); 7.03–7.18 (m, 2H, H^3, H^4); 7.31–7.49 (m, 3H, *aromatic*); 9.75 (br, 1H, *H*C=N).

4a-*endo*: Characterization data: Anal. Calc. (found) for $C_{36}H_{34}Cl_4N_2O_4Pd_2$: C, 47.35 (47.4); H, 3.75 (3.6); N, 3.07 (3.0); Cl, 15.56 (15.9)%. MS-positive FAB: 913 (M^+), 877 {$(M-Cl)^+$}. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.30$ (t, 3H, $J_{HH} = 7.2$ Hz, CH_3CH$_2$O); 3.4–3.7 (m, 2H, CH_2CHN); 4.24 (q, 2H, $J_{HH} = 7.2$ Hz, CH$_3$CH_2O); 4.60 (br, 1H, *H*CCOOEt); 6.98 (m, 2H, *aromatic*); 7.25–7.31 (m, 6H, *aromatic*); 7.94 (s, 1H, *H*C=N). ^{1}H-NMR (200 MHz, $CDCl_3$), **4a-*endo* + pyridine-d_5**: $\delta = 1.21$ (t, 3H, $J_{HH} = 7.0$ Hz, CH_3CH$_2$O); 3.50 (dd, 2H, CH_2CHN); 4.19 (q, 2H, $J_{HH} = 7.0$ Hz, CH_2CH$_3$); 5.60 (br, 1H, *H*CCOOEt); 6.0 (d, 1H, $J_{HH} = 6.0$ Hz, H^1); 6.98 (m, 2H, H^2, H^3); 7.24–7.38 (m, 5H, *aromatic*); 8.2 (s, 1H, *H*C=N).

4a-*exo*: Characterization data: Anal. Calc. (found) for $C_{36}H_{32}Cl_6N_2O_4Pd_2$: C, 44.02 (44.0); H, 3.28 (3.2); N, 2.85 (2.9)%. ^{1}H-NMR (250 MHz, $CDCl_3$), **4a-*exo* + pyridine-d_5**, $\delta = 0.97$ (t, 3H, CH_3CH$_2$); 3.07–3.85 (m, 5H, CH_2Ph, C*H*COO, CH$_3$$CH_2$); 6.48 (d, 1H, H^1), 6.7 (br,1H, H^2); 6.90 (d, 2H, aromatic) 7.22–7.40 (m, 3H, aromatic); 9.71 (s, 1H, HC=N).

3.1.3. Synthesis of compounds *1b–4b*

A suspension formed by 0.11 mmol (100 mg) of compound **1a** in 20 ml of acetone was treated with 0.22 mmol (57 mg) of PPh_3, the mixture of reaction was stirred for 30 min at r.t. and then concentrated in vacuo. The solid formed was washed with Et_2O and the yellow solid was obtained in a yield of 80%.

Compounds **2b**, **3b-*endo***, **3b-*exo***, **4b-*endo***, **4b-*exo*** were prepared in similar ways, in yields of 75, 74, 80, 85 and 80%, respectively.

1b Characterization data: Anal. Calc. (found) for $C_{34}H_{28}Cl_2NO_2PPd$: C, 59.11 (59.1); H, 4.09 (3.9); N, 2.03 (2.0)%. MS-positive FAB: 689 (M^+), 654{$(M-Cl)^+$}. ^{31}P{^{1}H}-NMR: $\delta = 40{,}88$, s. ^{1}H-NMR (200 MHz): $\delta = 3.77$ (s, 3H, *Me*); 6.23 (dd, 1H, $J_{HP} = 6.0$ Hz, $J_{HH} = 1.6$ Hz, H^1), 6.84 (dd, 1H, $J_{HH} = 8.0$ Hz, $J_{HH} = 1.4$ Hz, H^2), 6.89 (s, 1H, *H*CCOOMe); 7.11 (d, 1H, $J_{HH} = 8.2$ Hz, H^3); 7.35–7.78 (m, 20 H, *aromatic*); 8.01 (d, 1H, $J_{HP} = 7.6$ Hz, *H*C=N).

2b Characterization data: Anal. Calc. (found) for $C_{36}H_{32}Cl_2NO_2PPd$: C, 60.14 (60.5); H, 4.49 (4.5); N, 1.95 (1.9)%. MS-positive FAB: 719 (M^+), 684 {$(M-Cl)^+$}. ^{31}P{^{1}H}-NMR: $\delta = 40{,}92$, s. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.12$ (t, 3H, $J_{HH} = 7.0$ Hz, CH_3CH$_2$O); 3.16 (dd, 1H, $J_{HH} = 13.2$Hz, $J_{HH} = 8.0$ Hz, CH_2CHN); 3.65 (dd, 1H, $J_{HH} = 13.2$ Hz, $J_{HH} = 5.6$Hz, CH_2CHN); 4.10 (q, 2H, $J_{HH} = 7.0$ Hz, CH_2CH$_3$); 5.80 (br m, 1H, *H*CCOOEt); 6.25 (d, 1H, $J_{HH} = 2.0$ Hz, H^1), 6.80 (dd, 1H, $J_{HH} = 8.2$ Hz, $J_{HH} = 2.0$ Hz, H^2), 7.11 (d, 1H, $J_{HH} = 8.2$ Hz, H^3), 7.20–7.70 (m, 20 H, *aromatic*); 8.05 (s, 1H, *H*C=N).

3b-*endo* Characterization data: Anal. Calc. (found) for $C_{34}H_{28}Cl_2NO_2PPd$: C, 59.11 (59.3); H, 4.09 (4.1); N, 2.03 (1.9)%. ^{31}P{^{1}H}-NMR: $\delta = 41.86$, s. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 3.78$ (s, 3H, *Me*); 6.26 (t, 1H, $J_{HH} = 6.0$ Hz, $J_{HP} = 13$ Hz; H^1); 6,45 (t, 1H, $J_{HH} = 7.6$ Hz, H^2); 6.80 (d, 1H, $J_{HH} = 8.2$, H^3); 6.94 (br, 1H, *H*CCOOMe); 7.33–7.81 (m, 20H, *aromatic*); 8.56 (s, 1H, $J_{HP} = 8.2$ Hz, *H*C=N).

3b-*exo* Characterization data: Anal. Calc. (found) for $C_{34}H_{27}Cl_3NO_2PPd$: C, 56.30 (56.5); H, 3.75 (3.9); N, 1.93 (1.8)%. ^{31}P{^{1}H}-NMR: $\delta = 41.15$, s. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 3.76$ (s, 3H, *Me*); 5.48 (br s, 1H, *H*CCOOMe); 6.44 (m, 2H, H^1, H^2); 6.87 (br t, 1H, H^3); 7.10 (d, 1H, $J_{HH} = 7.4$ Hz, *aromatic*) 7.34–7.85 (m, 18H, *aromatic*); 9.61 (br d, 1H, $J_{HP} = 4.8$ Hz, *H*C=N).

4b-*endo* Characterization data: Anal. Calc. (found) for $C_{36}H_{32}Cl_2NO_2PPd$: C, 60.14 (60.1); H, 4.49 (4.6); N, 1.95 (1.9)%. MS-positive FAB: 718.8 $[M]^+$), 684{$[M-Cl]^+$}. ^{31}P{^{1}H}-NMR: $\delta = 41.89$, s. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.13$ (t, 3H, $J_{HH} = 7.0$ Hz, CH_3CH$_2$O); 3.18 (dd, 1H, $J_{HH} = 13.6$ Hz, $J_{HH} = 8.4$Hz, CH_2CHN); 3.69 (dd, 1H, $J_{HH} = 13.2$ Hz, $J_{HH} = 5.6$ Hz, CH_2CHN); 4.12 (q, 2H, $J_{HH} = 7.1$ Hz, CH$_3$$CH_2$O); 5.81 (br, 1H, *H*CCOOEt); 6.26 (t, 1H, $J_{HH} = J_{HP} = 6.2$ Hz, H^1); 6.45 (t, 1H, $J_{HH} = 8.2$ Hz, H^2); 6.82 (d, 1H, $J_{HH} = 8.0$ Hz, H^3); 7.19–7.78 (m, 20H, *aromatic*); 8,66 (d, 1H, $J_{HP} = 8.0$ Hz, *H*C=N).

4b-*exo* Characterization data: Anal. Calc. (found) for $C_{36}H_{31}Cl_3NO_2PPd$: C, 57.39 (57.2); H, 4.15 (4.0); N, 1.86 (1.7)%. ^{31}P{^{1}H}-NMR: $\delta = 33.78$, s. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.20$ (t, 3H, CH_3CH$_2$); 3.43 (br, 1H, *H*CHPh); 3.87–4.20 (br, 4H, HC*H*Ph, C*H*COO, CH$_3$CH_2); 6.31 (t, 1H, $J_{HH} = 7.0$ Hz, H^2), 6.60 (m, 2H, H^1, H^3); 6.75 (d, 1H, $J_{HH} = 8.0$ Hz, H^4) 7.25–7.43 (m, 12H, *aromatic*); 7.58–7.71 (m, 6H, *aromatic*), 9.26 (br, 1H, *H*C=N).

3.2. Crystal structure determination

A summary of crystallographic data and some details of the refinement are given in Table 2. A prismatic crystal was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from automatic centering of 25 reflections ($3 < \theta < 31^\circ$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K_α radiation. 14 156 reflections were measured in the range $1.67 < \theta < 31.60$, 5527 of which were non-equivalent by symmetry [R_{int}(on I) = 0.027]. 4602 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made.

Table 2
Crystal data and structure refinement for **4b-*exo***

Empirical formula	$C_{36}H_{31}Cl_3NO_2PPd$
Formula weight	753.34
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	11.5890(10)
b (Å)	24.4350(10)
c (Å)	13.2510(10)
α (°)	90.0000(10)
β (°)	114.3590(10)
γ (°)	90.0000(10)
V (Å^3)	3418.3(4)
Z	4
D_{calc} (Mg m^{-3})	1.464
Absorption coefficient (mm^{-1})	0.857
$F(000)$	1528
Crystal size (mm)	0.1 × 0.1 × 0.2
Theta range for data collection (°)	1.67–31.60
Index ranges	$0 \le h \le 13$, $0 \le k \le 35$, $-14 \le l \le 16$
Reflections collected/unique	14 156/5527 [$R_{int} = 0.0276$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5527/0/400
Goodness-of-fit on F^2	1.131
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0458$, $wR_2 = 0.1346$
R indices (all data)	$R_1 = 0.0633$, $wR_2 = 0.1578$
Largest difference peak and hole (e Å^2)	0.755 and −0.820

The structure was solved by Direct methods, using SHELXS computer program and refined by full-matrix least-squares method with SHELX97 computer program [15]. The function minimized was $\Sigma w[[F_o]^2-[F_c]^2]^2$, where $w=[\sigma^2(I)+(0.0902P)^2+4.1415P]^{-1}$, and $P=([F_o]^2+2[F_c]^2)/3$, f, f' and f'' were taken from International Tables of X-ray Crystallography [16]. All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atoms which are linked.

4. Supplementary material

Crystallographic data (excluding structure factors) for **4b-*exo*** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 189590. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Ministerio de Ciencia y Tecnología (projects: BQU2000-0652) and by the Comissionat per a Universitats i Recerca (project: 2001SGR-00054).

References

[1] (a) K. Severin, R. Bergs, W. Beck, Angew. Chem. Int. Ed. 37 (1998) 1634;
(b) G. Jaouen, A. Vessiers, I.S. Butler, Acc. Chem. Res. 26 (1993) 361;
(c) H. Chen, S. Ogo, R.H. Fish, J. Am. Chem. Soc. 118 (1996) 4993;
(d) A.D. Ryabov, Angew. Chem. Int. Ed. 30 (1991) 931.
[2] A.D. Ryabov, V.A. Polyakov, A.K. Yatsimirki, Inorg. Chim. Acta 91 (1984) 59.
[3] Y. Fuchita, K. Yoshinaga, Y. Ikeda, J. Kinoshita-Kawashima, J. Chem. Soc. Dalton Trans. (1997) 2495.
[4] R. Grigg, J. Devlin, J. Chem. Soc. Chem. Commun. (1986) 631.
[5] (a) A. Bohm, B. Schreiner, N. Steiner, R. Urban, K. Sünkel, K. Polborn, W. Beck, Z. Naturforsch. 53b (1998) 191;
(b) A. Bohm, K. Polborn, K. Sünkel, W. Beck, Z. Naturforsch. 53b (1998) 448;
(c) A. Bohm, K. Polborn, W. Beck, Z. Naturforsch. 54b (1999) 300.
[6] C.G. McCarthy, in: S. Patai (Ed.), The Chemistry of the Carbon–Nitrogen Double Bond, Wiley, Chichester, 1970, pp. 364–372, 405–408.
[7] (a) J. Albert, M. Gómez, J. Granell, J. Sales, X. Solans, Organometallics 9 (1990) 1405;
(b) J. Albert, J. Granell, J. Sales, M. Font-Bardia, X. Solans, Organometallics 14 (1995) 1393.
[8] (a) M. Gómez, J. Granell, M. Martinez, J. Chem. Soc. Dalton Trans. (1998) 37;
(b) M. Gómez, J. Granell, M. Martinez, Organometallics 16 (1997) 2539;
(c) G. De Munno, M. Ghedini, F. Neve, Inorg. Chim. Acta 239 (1995) 155;
(d) R. Bosque, C. López, M. Font-Bardia, X. Solans, J. Chem. Soc. Dalton Trans. (1995) 4053;
(e) R. Bosque, C. López, J. Sales, J. Organomet. Chem. 498 (1995) 147;
(f) R. Bosque, C. López, J. Sales, J. Chem. Soc. Dalton Trans. (1995) 2445.
[9] J. Albert, J. Barro, J. Granell, J. Organomet. Chem. 408 (1991) 115.
[10] The destabilizing effect of two soft ligands in mutual *trans* positions has been called *antisymbiosis*, see: (a) J.A. Davies, F.R. Hartley, Chem. Rev. 81 (1981) 79; (b) R.G. Pearson, Inorg. Chem. 12 (1973) 712; (c) R. Navarro, E.P. Urriolabeitia, J. Chem. Soc. Dalton Trans (1999) 4111. Recently the term *transphobia* has been proposed to describe the difficulty of coordinating mutually *trans* phosphine and aryl ligands in palladium complexes, see: (d) J. Vicente, J.A. Abad, A.D. Frankland, M.C. Ramírez de Arellano, Chem. Eur. J. 5 (1999) 3066; (e) J. Vicente, A. Arcas, D. Bautista, P.G. Jones, Organometallics 16 (1997) 2127.
[11] (a) J. Vicente, I. Saura-Llamas, M.G. Palin, P.G. Jones, M.C. Ramírez de Arellano, Organometallics 16 (1997) 826;
(b) M.A. Cinelli, S. Gladiali, G. Minghetti, S. Stoccoro, A. Demartin, J. Organomet. Chem. 401 (1991) 371;
(c) J.M. Vila, M.T. Pereira, J.M. Ortigueira, M. López Torres, J.M. Castineiras, D. Lata, J.J. Fernández, A. Fernández, J. Organomet. Chem. 556 (1998) 31.
[12] (a) J. Bernstein, J. Chem. Soc. Perkin Trans. II (1972) 946;
(b) T. Inabe, I. Gaultier-Luneau, N. Hoshino, K. Okinawa, H. Okamoto, T. Mitani, U. Nagashima, Y. Maruyama, Bull. Chem. Soc. Jpn. 64 (1991) 801;

(c) M. Crespo, M. Martínez, J. Sales, X. Solans, M. Font-Bardia, Organometallics 11 (1992) 1288;
(d) M. Crespo, X. Solans, M. Font-Bardía, Organometallics 14 (1995) 355;
(e) M. Crespo, X. Solans, M. Font-Bardía, J. Organomet. Chem. 518 (1996) 105;
(f) J. Albert, J. Granell, J. Mínguez, G. Muller, D. Sainz, P. Valerga, Organometallics 16 (1997) 3561.

[13] (a) C. Navarro-Raninger, I. López-Solera, A. Alvarez-Valdés, J.M. Rodríguez-Ramos, J.R. Masaguer, J.L. García-Ruano, Organometallics 12 (1993) 4104;
(b) A. Crispini, M. Ghedini, J. Chem. Soc. Dalton Trans (1997) 75;
(c) M. Crespo, C. Grande, A. Klein, M. Font-Bardía, X. Solans, J. Organomet. Chem. 563 (1998) 179.

[14] M. Gómez, J. Granell, M. Martinez, Eur. J. Inorg. Chem. (2000) 217.

[15] G.M. Sheldrick, A Computer Program for Determination of Crystal Structure, University Göttingen, Göttingen, Germany, 1997.

[16] International Tables of X-ray Crystallography, vol. IV, Kynoch Press, 1974, pp. 99–100 and 149.