

Cyclopalladation of Schiff bases from phenylalanine and 2-phenylglycine

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

Abstract

The action of palladium acetate on the Schiff bases 4-ClC₆H₄CH=N-CH(R²)COOR¹ (R¹ = Me, Et; R² = Ph, CH₂Ph), 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-Cl₂C₆H₃CH=N-CH(R²)COOR¹ (R¹ = Me, Et; R² = Ph, CH₂Ph), 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 PPh₃ affords the mononuclear complexes [PdCl(C-N)(PPh₃)] **1b–4b**.

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1. Introduction

There is growing interest in the synthesis, reactivity and applications of organometallic complexes with biologically important ligands and the term bioorgano-metallic chemistry is used to describe this new research field on the border between biochemistry and organo-metallic 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

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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].

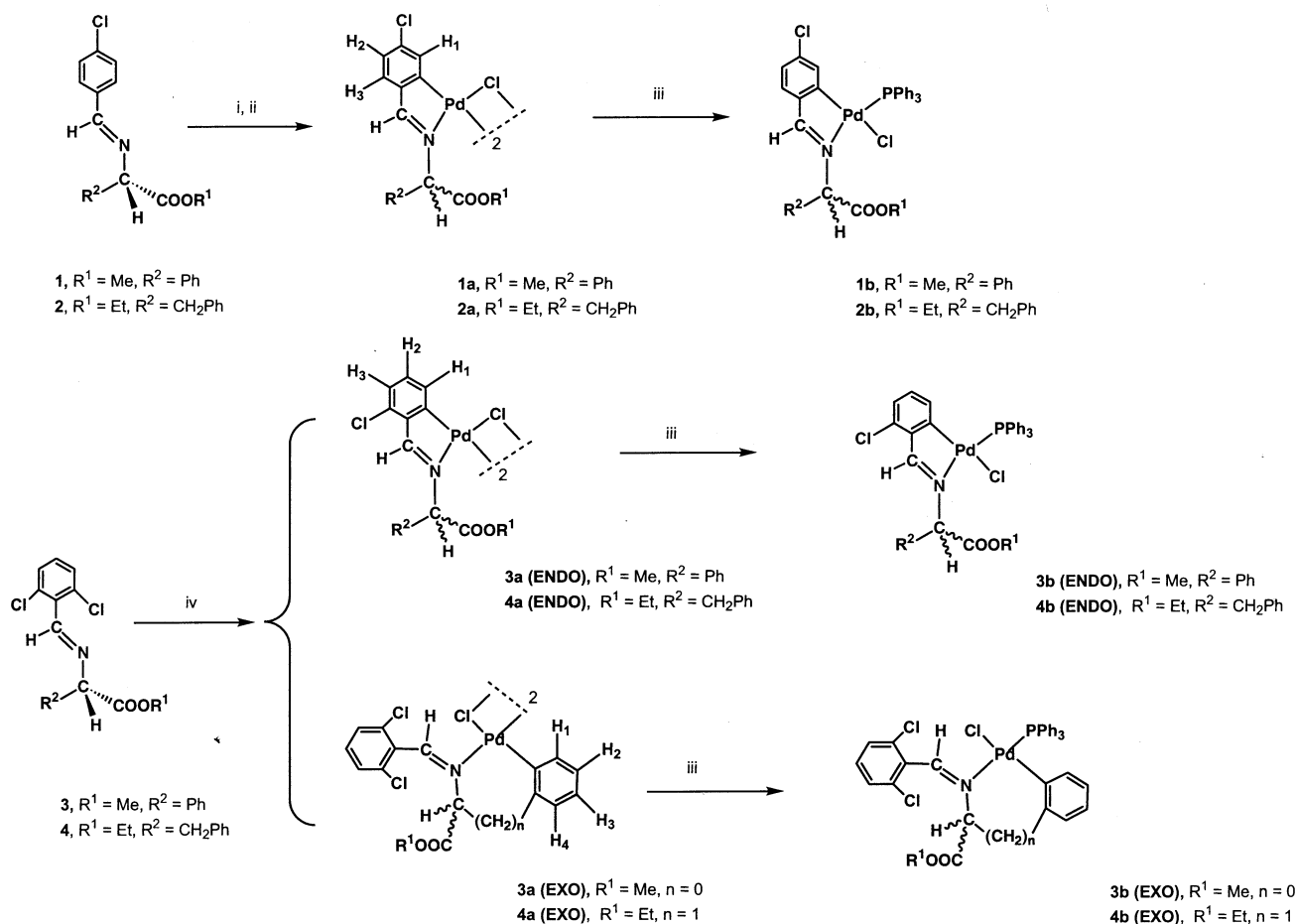
2. Results and discussion

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 SiO₂ 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 SiO₂ 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].

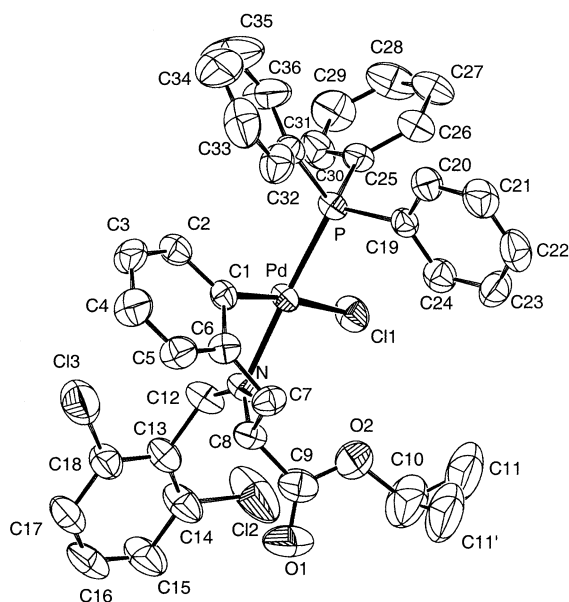


Scheme 1. (i) Pd(AcO)₂, AcOH, 3 h, 70 °C; (ii) LiCl, acetone, room temperature, 30 min; (iii) PPh₃, acetone; (iv) Pd(AcO)₂/CHCl₃, room temperature, 2 h.

Reaction of dimers **1a–4a** with PPh_3 afforded the mononuclear complexes $[\text{PdCl}(\text{C}=\text{N})(\text{PPh}_3)]$ **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.



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 Científic-Tècnics de la Universitat de Barcelona. Infra-red 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 mono-nuclear complexes $[\text{PdCl}(\text{C}=\text{N})\text{py}]$.

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) δ = 3.73 (s, 3H, *Me*); 5.19 (s, 1H, *HCCOOMe*); 7.50–7.30 (m, 7H, *aromatic*); 7.75 (d, 2H, *aromatic*, J_{HH} = 8.4 Hz); 8.28 (s, 1H, *HC=N*).

2: ^1H -NMR (200 MHz, CDCl_3) δ = 1.24 (t, 3H, $\text{CH}_3\text{CH}_2\text{O}$, J_{HH} = 7.2 Hz); 3.15 (dd, 1H, J_{HH} = 13.4 Hz, J_{HH} = 9 Hz, CH_2N); 3.40 (dd, 1H, dd, 1H, J_{HH} = 13.4 Hz, J_{HH} = 5.2 Hz, CH_2N); 4.18 (m, 3H, *HCCOOEt*, CH_2O); 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, *HC=N*).

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

4: ^1H -NMR (200 MHz, CDCl_3) δ = 1.27 (t, 3H, $\text{CH}_3\text{CH}_2\text{O}$, J_{HH} = 7.4 Hz); 3.10 (dd, 1H, J_{HH} = 13.4 Hz, J_{HH} = 9 Hz, CH_2Ph); 3.45 (dd, 1H, dd, 1H, J_{HH} = 13.4 Hz, J_{HH} = 5.2 Hz, CH_2Ph); 4.18 (m, 2H, *HCCOOEt*, CH_2CH_3); 7.20–7.15 (m, 8H, *aromatic*); 8.19 (s, 1H, *HC=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 $\text{C}_{32}\text{H}_{26}\text{Cl}_4\text{N}_2\text{O}_4\text{Pd}_2$: 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** , δ = 3.83 (s, 3H, *Me*); 6.05 (s, 1H, *HCCOOMe*); 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, *HC=N*).

2a: Characterization data: Anal. Calc. (found) for $\text{C}_{36}\text{H}_{34}\text{Cl}_4\text{N}_2\text{O}_4\text{Pd}_2$: C, 47.35 (47.6); H, 3.75 (3.6); N, 3.07 (3.0)%. MS-positive FAB: 912 (M^+), 877 $\{(\text{M} - \text{Cl})^+\}$. ^1H -NMR (200 MHz, CDCl_3): δ = 1.28 (t, 3H, J_{HH} = 7.2 Hz, $\text{CH}_3\text{CH}_2\text{O}$); 3.40 (br m, 1H, CH_2CHN); 3.60 (m, 1H, CH_2N); 4.24 (q, 2H, J_{HH} = 6.6 Hz, CH_2CH_3); 4.60 (br m, 1H, *HCCOOEt*); 7.03 (s, 1H, H^1); 7.20–7.40 (m, 7H, *aromatic*); 7.64 (s, 1H, *HC=N*). ^1H -NMR (200 MHz, CDCl_3) **2a** + **pyridine- d_5** , δ = 1.20 (t, 3H, J_{HH} = 7.0 Hz, $\text{CH}_3\text{CH}_2\text{O}$); 3.30 (dd, 1H, J_{HH} = 12.8 Hz, J_{HH} = 6.6 Hz, CH_2CHN); 3.60 (dd, 1H, J_{HH} = 12.8 Hz, J_{HH} = 5.8 Hz, CH_2CHN); 4.17 (q, 2H, J_{HH} = 7.0 Hz, CH_2CH_3); 5.60 (br m, 1H, *HCCOOEt*); 6.10 (s, 1H, H^1); 7.0–7.40 (m, 7H, *aromatic*); 7.81 (s, 1H, *HC=N*).

3a-endo: Characterization data: Anal. Calc. (found) for $\text{C}_{32}\text{H}_{26}\text{Cl}_4\text{N}_2\text{O}_4\text{Pd}_2$: C, 44.84 (45.1); H, 3.06 (3.0); N, 3.27 (3.2). MS-positive FAB: 857 (M^+), 820 $\{(\text{M} - \text{Cl})^+\}$. ^1H -NMR (200 MHz, CDCl_3): δ = 3.84 (s, 3H, *Me*); 6.02 (s, 1H, *HCCOOMe*); 6.96 (m, 2H, *aromatic*); 7.35–7.49 (m, 6H, *aromatic*); 8.07 (s, 1H, *HC=N*). ^1H -NMR (200 MHz, CDCl_3) **3a-endo** + **pyridine- d_5** : δ = 3.81 (s, 3H, *Me*); 6.02 (br, 1H, H^1); 6.75 (s, 1H, *HCCOOMe*); 6.85–6.91 (m, 2H, *aromatic*); 7.36–7.45 (m, 5H, *aromatic*); 8.24 (s, 1H, *HC=N*).

3a-exo: Characterization data: Anal. Calc. (found) for $\text{C}_{32}\text{H}_{24}\text{Cl}_6\text{N}_2\text{O}_4\text{Pd}_2$: C, 41.50 (41.5); H, 2.61 (2.5); N, 3.02 (2.9). MS-positive FAB: 926 (M^+), 890 $\{(\text{M} - \text{Cl})^+\}$. ^1H -NMR (200 MHz, CDCl_3) δ = 3.67 (s, 3H, *Me*); 5.49 (s, 1H, *HCCOOMe*); 6.90–7.05 (m, 3H,

aromatic); 7.35–7.40 (m, 4H, aromatic); 9.05 (s, 1H, HC=N). ¹H-NMR (200 MHz, CDCl₃), **3a-exo** + pyridine-*d*₅, δ = 3.65 (s, 3H, Me); 5.62 (s, 1H, HCCOOMe); 6.18 (br, 1H, aromatic); 6.95 (t, 1H, $J_{\text{HH}} = 8.0$, H^2); 7.03–7.18 (m, 2H, H^3 , H^4); 7.31–7.49 (m, 3H, aromatic); 9.75 (br, 1H, HC=N).

4a-endo: Characterization data: Anal. Calc. (found) for C₃₆H₃₄Cl₄N₂O₄Pd₂: 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)⁺}. ¹H-NMR (200 MHz, CDCl₃): δ = 1.30 (t, 3H, $J_{\text{HH}} = 7.2$ Hz, CH₃CH₂O); 3.4–3.7 (m, 2H, CH₂CHN); 4.24 (q, 2H, $J_{\text{HH}} = 7.2$ Hz, CH₃CH₂O); 4.60 (br, 1H, HCCOOEt); 6.98 (m, 2H, aromatic); 7.25–7.31 (m, 6H, aromatic); 7.94 (s, 1H, HC=N). ¹H-NMR (200 MHz, CDCl₃), **4a-endo** + pyridine-*d*₅: δ = 1.21 (t, 3H, $J_{\text{HH}} = 7.0$ Hz, CH₃CH₂O); 3.50 (dd, 2H, CH₂CHN); 4.19 (q, 2H, $J_{\text{HH}} = 7.0$ Hz, CH₂CH₃); 5.60 (br, 1H, HCCOOEt); 6.0 (d, 1H, $J_{\text{HH}} = 6.0$ Hz, H^1); 6.98 (m, 2H, H^2 , H^3); 7.24–7.38 (m, 5H, aromatic); 8.2 (s, 1H, HC=N).

4a-exo: Characterization data: Anal. Calc. (found) for C₃₆H₃₂Cl₆N₂O₄Pd₂: C, 44.02 (44.0); H, 3.28 (3.2); N, 2.85 (2.9)%. ¹H-NMR (250 MHz, CDCl₃), **4a-exo** + pyridine-*d*₅, δ = 0.97 (t, 3H, CH₃CH₂); 3.07–3.85 (m, 5H, CH₂Ph, CHCOO, CH₃CH₂); 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 PPh₃, the mixture of reaction was stirred for 30 min at r.t. and then concentrated in vacuo. The solid formed was washed with Et₂O 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 C₃₄H₂₈Cl₂NO₂PPd: C, 59.11 (59.1); H, 4.09 (3.9); N, 2.03 (2.0)%. MS-positive FAB: 689 (M⁺), 654{(M–Cl)⁺}. ³¹P{¹H}-NMR: δ = 40.88, s. ¹H-NMR (200 MHz): δ = 3.77 (s, 3H, Me); 6.23 (dd, 1H, $J_{\text{HP}} = 6.0$ Hz, $J_{\text{HH}} = 1.6$ Hz, H^1), 6.84 (dd, 1H, $J_{\text{HH}} = 8.0$ Hz, $J_{\text{HH}} = 1.4$ Hz, H^2), 6.89 (s, 1H, HCCOOMe); 7.11 (d, 1H, $J_{\text{HH}} = 8.2$ Hz, H^3); 7.35–7.78 (m, 20 H, aromatic); 8.01 (d, 1H, $J_{\text{HP}} = 7.6$ Hz, HC=N).

2b Characterization data: Anal. Calc. (found) for C₃₆H₃₂Cl₂NO₂PPd: C, 60.14 (60.5); H, 4.49 (4.5); N, 1.95 (1.9)%. MS-positive FAB: 719 (M⁺), 684 {(M–Cl)⁺}. ³¹P{¹H}-NMR: δ = 40.92, s. ¹H-NMR (200 MHz, CDCl₃): δ = 1.12 (t, 3H, $J_{\text{HH}} = 7.0$ Hz, CH₃CH₂O); 3.16 (dd, 1H, $J_{\text{HH}} = 13.2$ Hz, $J_{\text{HH}} = 8.0$ Hz, CH₂CHN); 3.65 (dd, 1H, $J_{\text{HH}} = 13.2$ Hz, $J_{\text{HH}} = 5.6$ Hz, CH₂CHN); 4.10 (q, 2H, $J_{\text{HH}} = 7.0$ Hz, CH₂CH₃); 5.80 (br m, 1H, HCCOOEt); 6.25 (d, 1H,

$J_{\text{HH}} = 2.0$ Hz, H^1), 6.80 (dd, 1H, $J_{\text{HH}} = 8.2$ Hz, $J_{\text{HH}} = 2.0$ Hz, H^2), 7.11 (d, 1H, $J_{\text{HH}} = 8.2$ Hz, H^3), 7.20–7.70 (m, 20 H, aromatic); 8.05 (s, 1H, HC=N).

3b-endo Characterization data: Anal. Calc. (found) for C₃₄H₂₈Cl₂NO₂PPd: C, 59.11 (59.3); H, 4.09 (4.1); N, 2.03 (1.9)%. ³¹P{¹H}-NMR: δ = 41.86, s. ¹H-NMR (200 MHz, CDCl₃): δ = 3.78 (s, 3H, Me); 6.26 (t, 1H, $J_{\text{HH}} = 6.0$ Hz, $J_{\text{HP}} = 13$ Hz, H^1); 6.45 (t, 1H, $J_{\text{HH}} = 7.6$ Hz, H^2); 6.80 (d, 1H, $J_{\text{HH}} = 8.2$, H^3); 6.94 (br, 1H, HCCOOMe); 7.33–7.81 (m, 20H, aromatic); 8.56 (s, 1H, $J_{\text{HP}} = 8.2$ Hz, HC=N).

3b-exo Characterization data: Anal. Calc. (found) for C₃₄H₂₇Cl₃NO₂PPd: C, 56.30 (56.5); H, 3.75 (3.9); N, 1.93 (1.8)%. ³¹P{¹H}-NMR: δ = 41.15, s. ¹H-NMR (200 MHz, CDCl₃): δ = 3.76 (s, 3H, Me); 5.48 (br s, 1H, HCCOOMe); 6.44 (m, 2H, H^1 , H^2); 6.87 (br t, 1H, H^3); 7.10 (d, 1H, $J_{\text{HH}} = 7.4$ Hz, aromatic) 7.34–7.85 (m, 18H, aromatic); 9.61 (br d, 1H, $J_{\text{HP}} = 4.8$ Hz, HC=N).

4b-endo Characterization data: Anal. Calc. (found) for C₃₆H₃₂Cl₂NO₂PPd: C, 60.14 (60.1); H, 4.49 (4.6); N, 1.95 (1.9)%. MS-positive FAB: 718.8 [M]⁺, 684{(M–Cl)⁺}. ³¹P{¹H}-NMR: δ = 41.89, s. ¹H-NMR (250 MHz, CDCl₃): δ = 1.13 (t, 3H, $J_{\text{HH}} = 7.0$ Hz, CH₃CH₂O); 3.18 (dd, 1H, $J_{\text{HH}} = 13.6$ Hz, $J_{\text{HH}} = 8.4$ Hz, CH₂CHN); 3.69 (dd, 1H, $J_{\text{HH}} = 13.2$ Hz, $J_{\text{HH}} = 5.6$ Hz, CH₂CHN); 4.12 (q, 2H, $J_{\text{HH}} = 7.1$ Hz, CH₃CH₂O); 5.81 (br, 1H, HCCOOEt); 6.26 (t, 1H, $J_{\text{HH}} = J_{\text{HP}} = 6.2$ Hz, H^1); 6.45 (t, 1H, $J_{\text{HH}} = 8.2$ Hz, H^2); 6.82 (d, 1H, $J_{\text{HH}} = 8.0$ Hz, H^3); 7.19–7.78 (m, 20H, aromatic); 8.66 (d, 1H, $J_{\text{HP}} = 8.0$ Hz, HC=N).

4b-exo Characterization data: Anal. Calc. (found) for C₃₆H₃₁Cl₃NO₂PPd: C, 57.39 (57.2); H, 4.15 (4.0); N, 1.86 (1.7)%. ³¹P{¹H}-NMR: δ = 33.78, s. ¹H-NMR (250 MHz, CDCl₃): δ = 1.20 (t, 3H, CH₃CH₂); 3.43 (br, 1H, HCHPh); 3.87–4.20 (br, 4H, HCHPh, CHCOO, CH₃CH₂); 6.31 (t, 1H, $J_{\text{HH}} = 7.0$ Hz, H^2), 6.60 (m, 2H, H^1 , H^3); 6.75 (d, 1H, $J_{\text{HH}} = 8.0$ Hz, H^4) 7.25–7.43 (m, 12H, aromatic); 7.58–7.71 (m, 6H, aromatic), 9.26 (br, 1H, HC=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 [$R_{\text{int}}(\text{on } I) = 0.027$]. 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 ₃ NO ₂ PPd
Formula weight	753.34
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	11.5890(10)
<i>b</i> (Å)	24.4350(10)
<i>c</i> (Å)	13.2510(10)
α (°)	90.0000(10)
β (°)	114.3590(10)
γ (°)	90.0000(10)
<i>V</i> (Å ³)	3418.3(4)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ^{−3})	1.464
Absorption coefficient (mm ^{−1})	0.857
<i>F</i> (000)	1528
Crystal size (mm)	0.1 × 0.1 × 0.2
Theta range for data collection (°)	1.67–31.60
Index ranges	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 35, −14 ≤ <i>l</i> ≤ 16
Reflections collected/unique	14 156/5527 [<i>R</i> _{int} = 0.0276]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5527/0/400
Goodness-of-fit on <i>F</i> ²	1.131
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0458, <i>wR</i> ₂ = 0.1346
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0633, <i>wR</i> 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 SHELXL97 computer program [15]. The function minimized was $\sum w[[F_o]^2 - [F_c]^2]^2$, 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>).

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