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Synthesis and reactivity towards carbon monoxide of an optically active *endo* five-membered *ortho*-cyclopalladated imine: X-ray molecular structure of *trans*-(μ-Cl)$_2$[Pd(κ^2-*C*,*N*-(*R*)-C$_6$H$_4$-CH=N-CHMe-Ph)]$_2$

Joan Albert [a,*], Lucía D'Andrea [a], Jaume Granell [a], Raquel Tavera [a], Mercè Font-Bardia [b], Xavier Solans [b]

[a] *Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain*
[b] *Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain*

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Abstract

(*R*)-1-Phenylethyl-benzylidene-amine (**1**) reacted with Pd(OAc)$_2$ in acetic acid at 60 °C under nitrogen affording the acetato-bridged dinuclear *endo* five-membered *ortho*-cyclopalladated compound (μ-OAc)$_2$[Pd(κ^2-*C*,*N*-(*R*)-C$_6$H$_4$-CH=N-CHMe-Ph)]$_2$ (**2**) in 65% yield. Compound **2** was converted by a metathesis reaction with LiCl into the corresponding chloro-bridged dinuclear cyclopalladated compound (μ-Cl)$_2$[Pd(κ^2-*C*,*N*-(*R*)-C$_6$H$_4$-CH=N-CHMe-Ph)]$_2$ (**3**). ^{1}H NMR of CDCl$_3$ solutions of compounds **2** and **3** treated separately with py-d_5, (*R*)-1-phenylethylamine and racemic 1-phenylethylamine were consistent with the *endo* cyclopalladated structure and the *R* absolute configuration of the chiral carbon atoms of compounds **2** and **3**. Compounds **2** and **3** reacted with carbon monoxide in methanol affording, as major compounds, methyl 2-formylbenzoate (91% chemical yield) and the epimers of 3-methoxy-2-[(*R*)-1-phenylethyl]isoindolin-1-one (64% chemical yield) in *ca.* 20% diastereomeric excess, respectively. The *trans* isomer of compound **3** crystallized in the $P2_1$ monoclinic space group with $a = 10.430(4)$ Å, $b = 12.082(8)$ Å, $c = 11.168(4)$ Å and $\beta = 95.20(3)°$ and presented C–H···Cl intramolecular and C–H···Pd intermolecular non-conventional hydrogen bonds.

Keywords: Cyclometallation; Optically active imine; Palladium; Non-conventional hydrogen bond; Carbonylation

1. Introduction

Interest in the cyclometallation reaction has been renewed in recent years due to the incorporation of this reaction in catalytic cycles that transform C–H bonds of heterosubstituted organic molecules into C–X bonds (X = B, C, Si, N, O or halogen) [1–11]. In spite of this, the reactivity of the C–M σ bond of cyclometallated compounds has not been extensively studied—especially the processes leading to stereoselective synthesis of organic molecules [12–16].

In this paper, we present an extension of the carbonylation reaction of *endo* five-membered *ortho*-cyclopalladated imines in presence of nucleophiles, which produced racemic 3-nucleophile-2-(aryl or benzyl)isoindolin-1-ones (Fig. 1), with the aim of obtaining this type of compound in a diastereoselective form [17–19]. For this purpose, we prepared the optically active *endo* five-membered *ortho*-cyclopalladated imines **2** and **3** (Scheme 1) and studied their reactivity towards carbon monoxide in methanol.

It should be noted that the bromo- and chloro-bridged *endo* cyclopalladated derivatives of the enantiomer of imine **1** (Scheme 1) have been previously reported, and cationic

* Corresponding author. Tel.: +34 93 4039131; fax: +34 93 4907725.
E-mail address: joan.albert@qi.ub.es (J. Albert).

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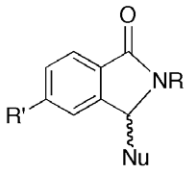


Nu	R	R'	Reference
OAc	$C_6H_5CH_2$	H	17
OMe	4-$CH_3C_6H_4$	OMe	18
OAc	C_6H_5	H	19
OAc	2-$CH_3C_6H_4$	H	19
NHPh	C_6H_5	H	19
OMe	C_6H_5	H	19
OEt	C_6H_5	H	19

Fig. 1. 3-Nucleophile-2-(aryl or benzyl)isoindolin-1-ones prepared by carbonylation of *endo* five-membered *ortho*-cyclopalladated imines in presence of nucleophiles.

derivatives of these cyclopalladated compounds have been used as precatalysts in the telomerization of isoprene and butadiene with methanol [20,21]. Furthermore, *endo* and *exo* five-membered optically active cyclopalladated imines analogous to compounds **2** and **3** have been used as derivating agents for optical resolution of chiral phosphines [22,23] or for optical purity determination of optically active phosphines by NMR [24]. The *endo* and *exo* descriptors were initially introduced to differentiate between the structural isomers of *ortho*-cyclopalladated benzyl-benzylidene-amine (Fig. 2) [17], but the use of these descriptors has been extended to refer in general to cyclometallated imines with the C=N bond inside the metallacycle, *endo* cyclometallated imines, and outside the metallacycle, *exo* cyclometallated imines [25–30].

2. Results and discussion

Scheme 1 shows the compounds prepared in this work and the labelling of the protons, and Table 1 presents the chemical shift of selected protons of compounds **1**–**9**.

2.1. Synthesis and characterization of compounds 1–3

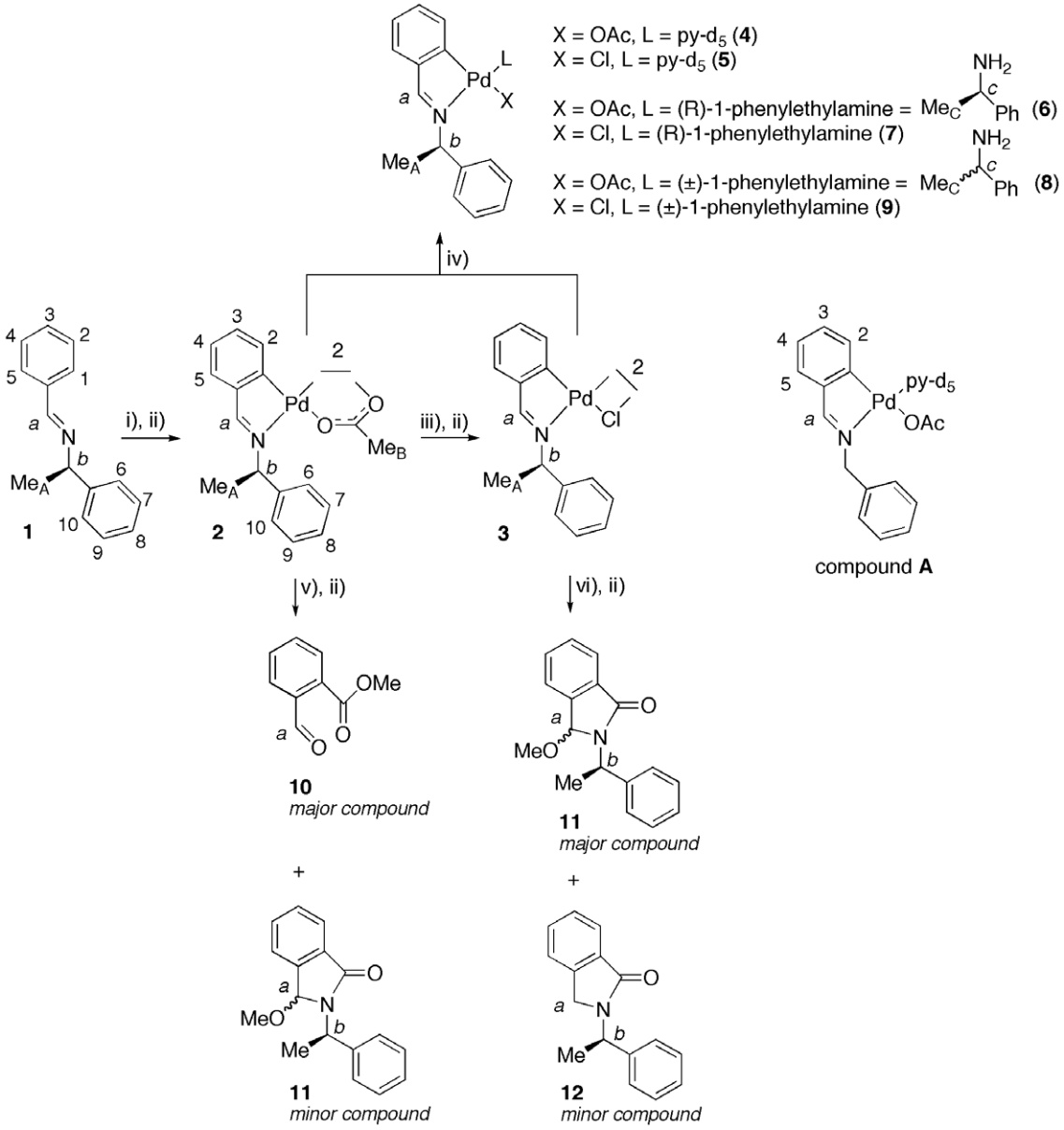
Imine **1** was prepared by an adaptation of the condensation reaction between benzaldehyde and (*R*)-1-phenylethylamine previously reported [31] (Scheme 1) and was purified by distillation at low pressure. **1** was an orange oil which produced satisfactory elemental analysis, IR, ^{1}H NMR, FAB(+) and optical rotation. Its ^{1}H NMR presented a single set of signals, indicating that it should consist of only the *E* geometrical isomer in relation to the carbon nitrogen double bond [32]. ^{1}H–^{1}H COSY and NOESY experiments at 500 MHz allowed the assignation of almost all protons of **1**, and the cross-peaks in the NOESY experiment between *a* and *b*, and *a* and Me_A protons were consistent with an *E* configuration for imine **1**.

Treatment of imine **1** with $Pd(OAc)_2$ in acetic acid in a 1 to 1 molar ratio under nitrogen afforded the dimeric acetato-bridged five-membered *ortho*-cyclopalladated imine **2**, which was easily converted by metathesis reaction with LiCl into the corresponding chloro-bridged cyclopalladated dimer **3** (Scheme 1). Compounds **2** and **3** were isolated in pure form by chromatography in 65% and 88% yield, respectively. They were air-stable yellow solids, soluble in chloroform and in acetone, and produced satisfactory elemental analysis, IR, ^{1}H NMR, FAB(+) and optical rotation.

The C=N stretching of compounds **2** and **3** appeared at 1606 and 1604 cm^{-1}, respectively, as an intense band shifted to lower wave numbers in relation to **1**, according to the coordination of the iminic nitrogen to the palladium(II) centre [33]. The asymmetric and symmetric stretchings of the carboxylic functions of compound **2** produced broad intense bands at 1566 and 1413 cm^{-1}, respectively, according to a bridging coordination mode of the acetato ligands [34]. The FAB(+) of compounds **2** and **3** afforded intense peaks for the monopositive molecular cations $[M+H^+]$, $[M-(X^-)]$ and $[M/2-(X^-)]$, where X is acetato for **2** and chloro for **3**, in agreement with their dimeric structure with acetato and chloro bridges, respectively [35].

The ^{1}H NMR in $CDCl_3$ of compound **2** produced two sharp sets of signals in *ca.* 3 to 1 ratio, which indicated that it consisted of two isomers, hereafter referred to as **I** (major isomer) and **II** (minor isomer). In dimers **I** and **II**, their monomeric units of formula *trans*-*C*,*O*-Pd{κ^2-*C*,*N*-(*R*)-C_6H_4-CH=N-CHMe-Ph}(κ^1-*O*-OAc) were equivalent, *e.g.* the Me_B protons produced only one singlet signal at 2.20 ppm for **I** and at 2.04 ppm for **II**, showing that their {κ^2-*C*,*N*-(*R*)-C_6H_4-CH=N-CHMe-Ph} ligands were in a *trans* arrangement. Acetato-bridged cyclopalladated dimers present a folded structure (Fig. 3a), usually named open book structure, both in the solid state and in chloroform solution [36]. Thus, we propose that **I** and **II** in $CDCl_3$ solution present a *trans* folded structure belonging to C_2 point group. The unusual upfield chemical shift in relation to imine **1** of the *a* proton of **I** and the Me_A protons of **II** could be an indication of their *trans* folded structure (Table 1) [37]. A ^{1}H–^{1}H NOESY experiment at 400 MHz in $CDCl_3$ showed that **I** and **II** were interconverting in $CDCl_3$ solution but we were not able to deduce from cross-peaks of proximity between protons of **I** or **II** either their axial configuration in relation to the chirality of their carbon atoms or the conformation of their N–CHMe–Ph molecular fragments.

In the ^{1}H NMR at 400 MHz in $CDCl_3$ of compound **3** at room temperature all protons presented sharp signals, except the Me_A protons, for which two broad signals at 1.83 and 1.77 ppm in *ca.* 1.5 to 1 ratio were observed, showing that compound **3** consisted of two isomers in this solvent, hereafter referred to as **III** (major isomer) and **IV** (minor isomer). Chloro-bridged cyclopalladated dimers



Scheme 1. (i) $Pd(OAc)_2$, acetic acid, 60 °C, 4 h; (ii) column chromatography; (iii) LiCl, acetone, room temperature, 4 h; (iv) py-d_5, (*R*)-1-phenylethylamine or (±)-1-phenylethylamine, $CDCl_3$, room temperature; (v) CO, 1.6 bar, methanol, room temperature, 6 h; (vi) CO, 1.6 bar, methanol, room temperature, 24 h.

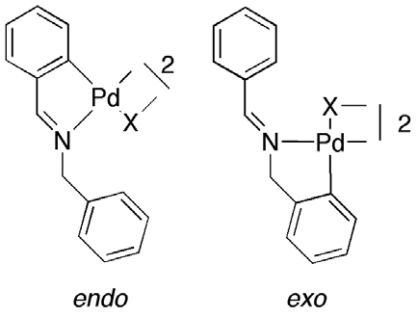


Fig. 2. *endo* and *exo* structural isomers of cyclopalladated benzylbenzylidene-amine.

present a planar structure (Fig. 3b), and in chloroform or dichloromethane solution their *trans* and *cis* isomers can be interconverting between them through intermediate solvento complexes (Fig. 3c) [38]. Therefore, isomers **III** and **IV** could be the *trans* and *cis* isomers of **3**, and the broad signal observed for their Me_A protons in $CDCl_3$ solution at 400 MHz and at room temperature, an indication of a dynamic equilibrium between them through an intermediate mononuclear chloroform solvento complex. It should be noted that in $CDCl_3$ solution at 250 MHz and at 220 K, the Me_A protons of **III** and **IV** gave place to sharp doublets at 1.84 and 1.77 ppm, respectively. Note that both Me_A protons are equivalent in the *trans* and *cis* dimeric molecules of **3** because they belong to the C_2 point group.

Table 1
Chemical shift (in ppm) of selected protons of compounds **1**–**9**

Compound	Proton		
	a	*b*	Me_A
1	8.38	4.56	1.60
2 (Isomer **I**)	6.98[a]	4.67	1.76
2 (Isomer **II**)	7.63	4.61	0.85[a]
3	7.59	5.34[b]	1.79
4	7.66	5.24[b]	1.78
5	7.65	5.96[b]	1.83
6	7.73	5.37[b]	1.83
7	7.62	5.82[b]	1.89
8 (Diastereoisomer *RR*)	7.73	5.36[b]	1.83
8 (Diastereoisomer *RS*)	7.67	5.36[b]	1.81
9 (Diastereoisomer *RR*)	7.62	5.83[b]	1.88
9 (Diastereoisomer *RS*)	7.73	5.83[b]	1.88

Unusual [a]up- and [b]downfield chemical shift in relation to **1**.

2.2. *endo* Structure and configurational stability of the chiral carbon atoms of compounds **2** and **3**

Although it is likely that compounds **2** and **3** present an *endo* structure [17,20–30] and that their chiral carbon atoms are configurationally stable [20–24], we checked these two items by NMR. For this purpose, $CDCl_3$ solutions of compounds **2** and **3** were treated separately with py-d_5, (*R*)-1-phenylethylamine and racemic 1-phenylethylamine, and the resulting solutions were studied by NMR. In all cases, a colour change of the initial orange or pale yellow solution to a colourless solution indicated the quantitative transformation of the dimeric cyclopalladated compounds **2** and **3** in the corresponding mononuclear cyclopalladated compounds **4**–**9** (Scheme 1). This was confirmed by the ^{1}H NMR at 400 MHz of the final colourless solutions. In compounds **4**–**9**, the upfield shift of the *ortho*-palladated aromatic ring protons was an indication of the *trans* disposition of the L ligand in relation to the iminic nitrogen (Scheme 1) [26,39].

^{1}H–^{1}H NOESY and COSY experiments for the solutions containing compounds **4** and **5** made it possible to establish unambiguously the *endo* structure of compounds **2** and **3**. Thus, a strong NOE between the *a* and 5 protons allowed the assignation of the 5 proton and, starting from this proton, the ^{1}H–^{1}H COSY experiment, permitted the assignation of the 4–2 protons [40]. The 5–2 protons turned out to be those of the *ortho*-metallated ring since they produced a coupling pattern for a 1,2-disubstituted aromatic ring and were upfield shifted in relation to the non-metallated phenyl protons [26,39].

In addition, the ^{1}H NMR at 400 MHz of the solutions containing compounds **6**–**9** confirmed that the chiral carbon atoms of compounds **2** and **3** were configurationally stable. This was unequivocally established because the ^{1}H NMR spectra of the solutions containing compounds **6** and **7**, which presented (*R*)-1-phenylethylamine coordinated to the palladium(II) centres, produced a single set of signals, showing that compounds **6** and **7** consisted of only the *RR* diastereoisomer, while the ^{1}H NMR spectra of the solutions containing compounds **8** and **9**, which presented racemic 1-phenylethylamine coordinated to the palladium(II) centres, produced two sets of signals in a 1 to 1 ratio, indicating that compounds **8** and **9** consisted of a mixture in a 1 to 1 molar ratio of the *RR* and *RS* diastereoisomers.

2.3. Non-conventional hydrogen bonds in solution

Notably, the chemical shift of the *b* proton of compounds **3**–**9** appeared quite downfield shifted in relation to imine **1**, between 0.68 and 1.40 ppm (Table 1). This

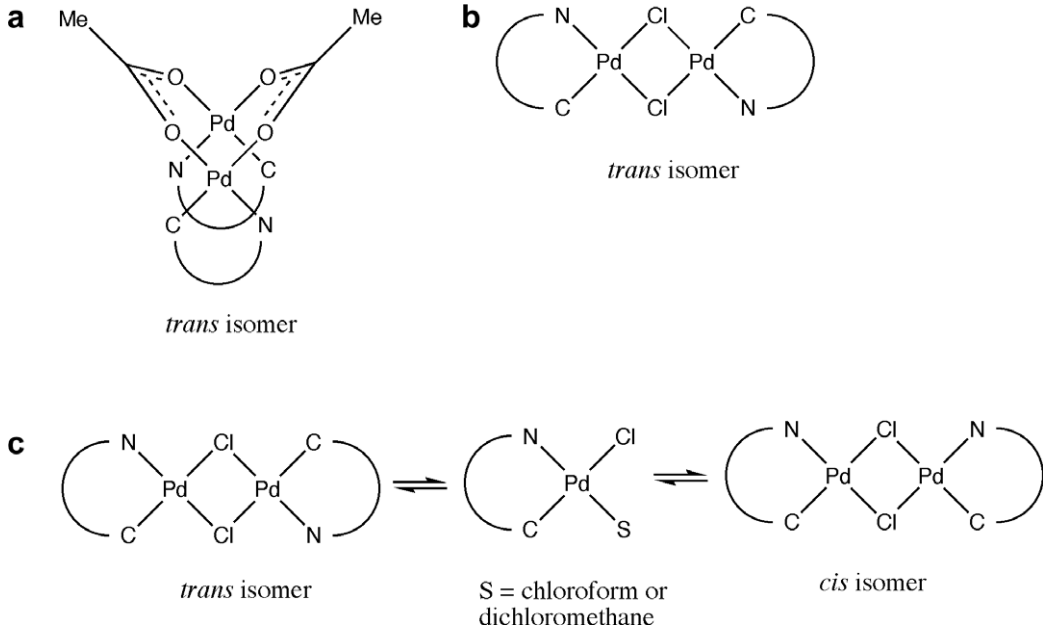
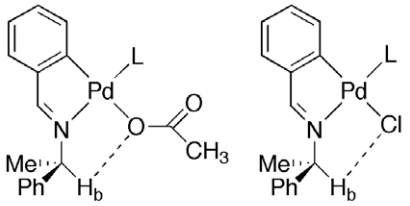


Fig. 3. (a) Folded structure of acetato-bridged cyclopalladated dimers, (b) planar structure of chloro-bridged cyclopalladated dimers and (c) dynamic equilibrium between *trans* and *cis* isomers of chloro-bridged cyclopalladated dimers.



compounds **4**, **6** and **8** compounds **3**, **5**, **7** and **9**

Fig. 4. Proposed intramolecular C–H_b···X non-conventional hydrogen bond in $CDCl_3$ solution for compounds **3**–**9**.

could indicate that in $CDCl_3$ solution these compounds present an intramolecular C–H_b···X non-conventional hydrogen bond, where X is either the κ^1-oxygen atom of the acetato ligand or the chlorine atom of the chloro ligand (Fig. 4). An analogous intramolecular C–H···Cl non-conventional hydrogen bond has previously been reported in the solid state for a mononuclear *endo* cyclopalladated ferrocenylbenzylimine [41]. It should be noted that (i) non-conventional hydrogen bonds [42] can explain the conformation and association of molecules, both in the solid state and in solution [43–46], and (ii) the chemical shift of the hydrogen atom involved in non-conventional hydrogen bonds is shifted to downfield due to the transfer of part of its electronic density to the acceptor atomic centres, as in conventional hydrogen bonds [46,47].

In order to obtain more information on this kind of interaction we prepared in $CDCl_3$ solution compound *trans*-*N*,*N*-[Pd(κ^2-*C*,*N*-C_6H_4-CH=N-CH_2-C_6H_5)(OAc)(py-d_5)] (compound **A** in Scheme 1) and registered its ^{1}H NMR in this solvent. In this case, the CH_2 protons of compound **A** resonate at 4.86 ppm, very close to the CH_2 protons of benzyl-benzylidene-amine, which resonate at 4.74 ppm [40]. In addition, the chemical shift of the *c* proton of compounds **6**–**9** in $CDCl_3$ appeared in the interval between 4.56 and 4.16 ppm, very close to the *c* proton of (*R*)-1-phenethylamine, which resonate at 4.57 ppm in $CDCl_3$ solution. These latter results suggest that a fine-tuning of steric and electrostatic effects are cooperating in order to establish the proposed intramolecular C–H_b···X non-conventional hydrogen bond in compounds **3**–**9**. It should be noted that compounds **3**–**9** should present in solution a conformation in which the *b* proton is near the coordination plane of the palladium(II) centre in order to diminish steric repulsions. Thus, the paramagnetic anisotropy of the palladium(II) centre should not be the origin of the unusual downfield chemical shift of the *b* proton of compounds **3**–**9** [48].

2.4. X-ray molecular structure of the trans isomer of compound 3

Suitable crystals for an X-ray diffraction study were obtained from compound **3**. The selected crystal was con-

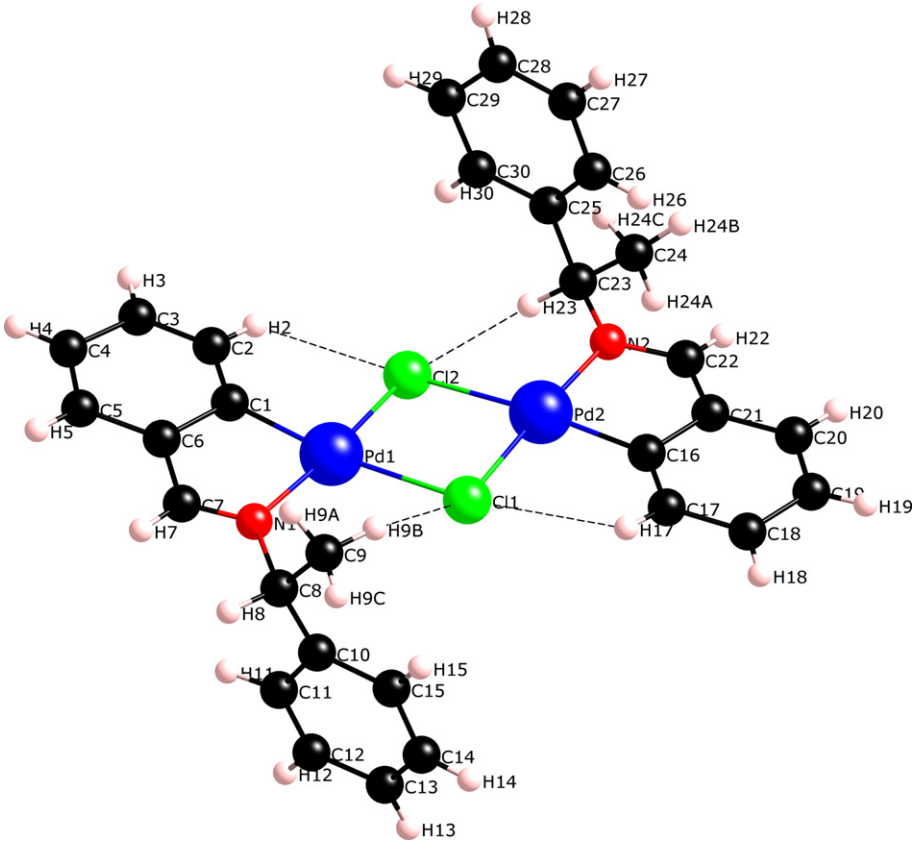


Fig. 5. X-ray molecular structure and atom labelling scheme for the *trans* isomer of **3**. Dashed lines indicate intramolecular C–H···Cl non-conventional hydrogen bonds.

stituted by molecules of the *trans* isomer of **3**, pertained to the $P2_1$ monoclinic space group and produced a satisfactory Flack × parameter of −0.01(7)—assuming that its molecules presented an *R* absolute configuration at the chiral carbon atoms. Figs. 5 and 6 show the X-ray molecular structure of the *trans* isomer of **3** and the labelling of the atoms for the discussion that follows (Fig. 5) and a simplified view of the crystal down the *c*-axis (Fig. 6). Tables 2–4 give bonding parameters for intra- and intermolecular non-conventional hydrogen bonds (Table 2), selected distances and angles (Table 3) and planes of atoms (Table 4) for the molecule of the *trans* isomer of **3**.

An automatic search for π–π stacking interactions and non-conventional hydrogen bonds in the crystal structure did not find π–π stacking interactions, but it revealed the presence of the intra- and intermolecular non-conventional hydrogen bonds given in Table 2 [51]. The intramolecular hydrogen bonds C2–H2···Cl2 and C17–H17···Cl1 were forced by the *trans* planar configuration of the molecule (Fig. 5). In spite of this, the intramolecular hydrogen bonds C9–H9B···Cl1 and C23–H23···Cl2 were not imposed by geometrical constraints and, it seems likely, that they determined the molecular conformation in the crystal. It is worth highlighting that the intramolecular hydrogen bond C9–H9B···Cl1 forced a Pd1–N1–C8–H8 torsion angle of 173° that prepared the H8 atom for the intermolecular interaction C8–H8···Pd2 which, in its turn, generated chains of molecules along the *b* axis of the crystal (Fig. 6).

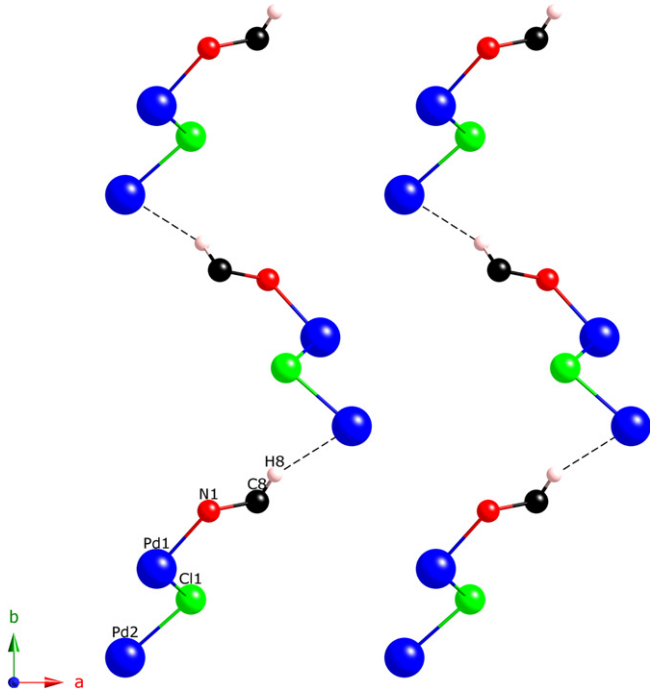


Fig. 6. View of the crystal structure of the *trans* isomer of **3** down the *c*-axis. Dashed lines indicate intermolecular C–H···Pd non-conventional hydrogen bonds. For simplicity, only the molecular fragments H8–C8–N1–Pd1–Cl1–Pd2 involved in the formation of intermolecular C–H···Pd non-conventional hydrogen bonds are represented.

Table 2
Non-conventional hydrogen bonds for the *trans* isomer of **3**

Non-conventional hydrogen bonds	D–H[c]	H···A[d,e]	D···A	D–H···A
C2–H2···Cl2[a]	0.93	2.67	3.235(16)	120
C9–H9B···Cl1[a]	0.96	2.69	3.504(15)	143
C17–H17···Cl1[a]	0.93	2.76	3.271(15)	116
C23–H23···Cl2[a]	0.98	2.75	3.357(15)	120
C8–H8···Pd2[b]	0.98	2.71	3.638	159

Distances in Å, angles in °, D = donor, A = acceptor.
[a] Intramolecular.
[b] Intermolecular.
[c] Calculated.
[d] Interval for an H···Cl non-conventional hydrogen bond: 2.40–2.90 Å [49].
[e] Interval for an H···Pd non-conventional hydrogen bond: 2.30–2.90 [50].

Table 3
Selected bond distances (Å) and angles (°) for the *trans* isomer of **3**

Pd1–Cl1	2.488(4)	Pd2–Cl1	2.313(4)
Pd1–Cl2	2.324(4)	Pd2–Cl2	2.456(4)
Pd1–N1	2.079(11)	Pd2–N2	1.968(13)
Pd1–C1	1.937(14)	Pd2–C16	1.958(13)
N1–C7	1.226(19)	N2–C22	1.30(2)
C6–C7	1.46(2)	C21–C22	1.41(3)
C1–C6	1.44(2)	C16 –C21	1.43(2)
N1–C8	1.464(19)	N2–C23	1.41(2)
C8–C9	1.517(19)	C23–C24	1.54(2)
Pd1–Cl2–Pd2	95.01(13)	Pd1–Cl1–Pd2	94.44(13)
Cl1–Pd1–Cl2	84.63(12)	Cl1–Pd2–Cl2	85.58(12)
Cl2–Pd1–C1	92.1(4)	Cl1–Pd2–C16	93.4(4)
C1–Pd1–N1	83.0(5)	C16–Pd2–N2	84.0(6)
N1–Pd1–Cl1	100.4(3)	N2–Pd2–Cl2	96.8(4)
C1–Pd1–Cl1	171.5(4)	C16–Pd2–Cl2	173.5(4)
N1–Pd1–Cl2	174.9(3)	N2–Pd2–Cl1	177.1(4)
N1–C8–C9	109.3(11)	N2–C23–C24	118.1(13)

Table 4
Selected planes of atoms for the *trans* isomer of **3**

Plane 1					
Atoms	Pd1	Cl1	Cl2	N1	
Deviation	0.010(1)	0.000(3)	−0.004(3)	−0.005(11)	
Equation	$7.822(19)x - 7.92(2)y + 0.238(17)z = 1.38(3)$				
Plane 2					
Atoms	Pd2	Cl1	Cl2	N2	
Deviations	0.020(1)	−0.009(3)	0.000(3)	−0.011(13)	
Equation	$7.22(3)x - 8.61(3)y + 0.596(17)z = 0.78(3)$				
Plane 3					
Atoms	Pd1	Pd2	Cl1	Cl2	
Deviations	0.047(1)	0.047(1)	−0.047(3)	−0.047(3)	
Equation	$7.505(4)x - 8.297(6)y + 0.420(15)z = 1.095(15)$				
Plane 4					
Atoms	Pd1	N1	C1	C6	C7
Deviations	−0.008(1)	0.010(11)	0.009(15)	−0.004(16)	−0.007(15)
Equation	$8.04(3)x - 7.68(4)y - 1.27(7)z = 0.64(6)$				
Plane 5					
Atoms	Pd2	N2	C16	C21	C22
Deviations	−0.027(1)	0.052(13)	0.009(13)	0.021(16)	−0.055(16)
Equation	$7.96(3)x - 7.80(5)y - 0.45(7)z = 1.38(8)$				

Deviations in Å. Equations in fractional coordinates.

We also notice that the intramolecular hydrogen bond C23–H23···Cl2 is of the same type than that we have proposed for compounds **3**–**9** in $CDCl_3$ solution. This reinforces the idea that the downfield shift of the *b* proton of compounds **3**–**9** in $CDCl_3$ solution is a consequence of an intramolecular C–H_b···X non-conventional hydrogen bond, where X is either the κ^1-oxygen atom of the acetato ligand or the chlorine atom of the chloro ligand of compounds **3**–**9** (Fig. 4). Note also that H23 is not very displaced from the coordination plane of Pd2 since the dihedral angle H23–Cl2–Pd2–Cl1 is 171°.

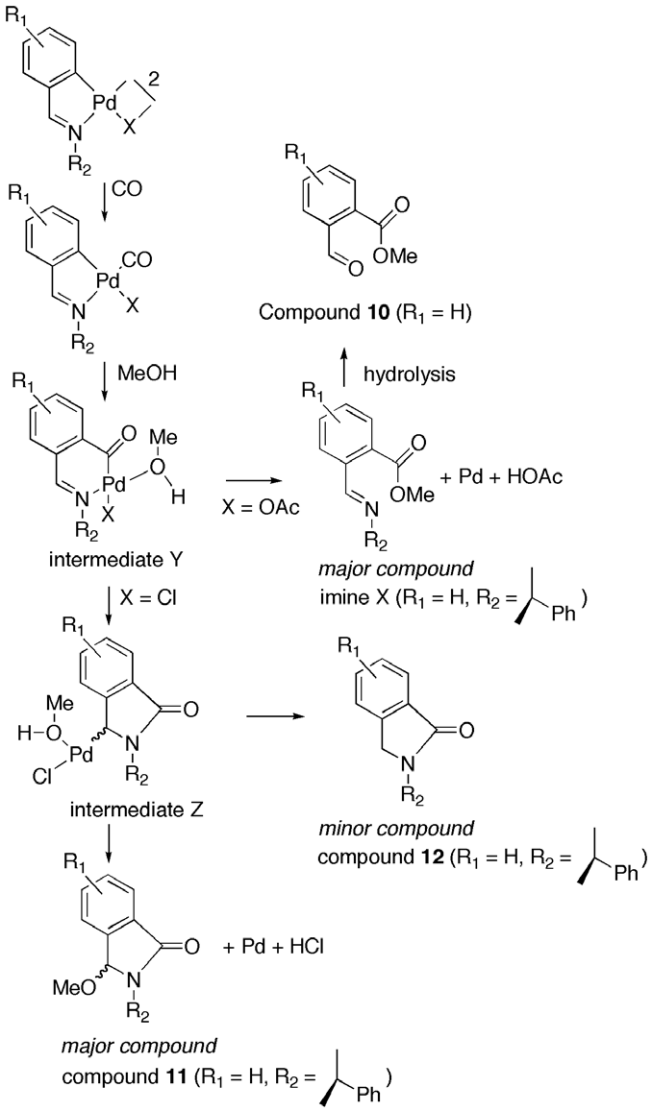
Distances and angles for the molecule of the *trans* isomer of **3** (Table 3) were between the normal intervals for analogous chloro-bridged cyclopalladated dimers [52–54]. As expected [55], the Pd1–Cl1 [2.488(4) Å] and Pd2–Cl2 [2.456(4) Å] distances were larger than those of Pd1–Cl2 [2.324(4) Å] and Pd2–Cl1 [2.313(4) Å] due to the greater *trans* influence of the C1 and C16 coordinated carbon atoms in relation to the N1 and N2 coordinated nitrogen atoms. The coordination angles of the palladium atoms were close to 90° and 180°. The chelate bite angles, C1–Pd1–N1 and C16–Pd2–N2, were 83.05(5)° and 84.0(6)°, respectively (Table 3). Each palladium atom together with its coordinated nitrogen and chlorine atoms determined a plane—planes 1 (Pd1, Cl1, Cl2 and N1) and 2 (Pd2, Cl1, Cl2 and N2) in Table 4. The deviations of the C1 and C16 metallated carbon atoms from planes 1 and 2 were 0.281(15) and −0.185(13) Å, respectively. The $(\mu\text{-Cl})_2Pd_2$ central core of the molecule and both *endo* five-membered metallacycles were planar, planes 3–5 in Table 4, but the molecule was somewhat folded since the angle between the planes 1 (Pd1, Cl1, Cl2 and N1) and 2 (Pd2, Cl1, Cl2 and N2) was 4.9(3)°.

2.5. Carbonylation of compounds *2* and *3*

Scheme 2 shows the mechanism proposed for the carbonylation reaction of *endo* five-membered *ortho*-cyclopalladated imines in methanol, leading to methyl 2-formylbenzoates or 3-methoxy-2-(aryl or benzyl)isoindolin-1-ones, including the compounds prepared in this work by the carbonylation reaction of compounds **2** and **3** [18].

Compounds **2** and **3** were treated in methanol at room temperature with carbon monoxide at 1.6 bar in a glassware reactor for 6 and 24 h, respectively (Scheme 1). In both cases a voluminous precipitate of palladium(0) and a colourless solution were formed. Removal of the palladium(0) by filtration and subsequent concentration of the obtained colourless solution afforded an oily material, which was studied by TLC and subjected to column chromatography.

For the oily material obtained from the carbonylation of compound **2**, the second eluted band was the most important one. This band, after concentration of the solvents, afforded methyl 2-formylbenzoate in 91% chemical yield, compound **10** in Schemes 1 and 2. This was confirmed by the IR and ^{1}H NMR of the obtained white solid, which



Scheme 2. Mechanism for the carbonylation reaction of *endo* five-membered *ortho*-cyclopalladated imines in methanol, leading to methyl 2-formylbenzoates or 3-methoxy-2-(aryl or benzyl)isoindolin-1-ones.

were identical to those previously reported for 2-formylbenzoate [56]. The third band contained a small amount of a sample enriched in the epimers of 3-methoxy-2-[(*R*)-1-phenylethyl]isoindolin-1-one in *ca.* 20% diastereomeric excess, compound **11** in Schemes 1 and 2. The diastereomeric excess of these epimers was determined by the integration of their methoxy protons, which appeared as singlet signals, at 2.93 ppm for the major epimer, hereafter referred to as **V**, and at 2.47 ppm for the minor epimer, hereafter referred to as **VI**. It should be noted that 2-formylbenzoate was formed by hydrolysis of the carbon nitrogen double bond of its precursor imine (imine X in Scheme 2) since this imine was the major compound present in the oily material obtained from the carbonylation of **2**, as it showed its ^{1}H NMR at 400 MHz.

In the case of the oily material obtained from the carbonylation of compound **3**, the third eluted band was the

major one. This band, after concentration of the solvents, produced a yellow oil, which was a mixture of the epimers of 3-methoxy-2-[(*R*)-1-phenylethyl]isoindolin-1-one, compound **11** in Schemes 1 and 2, and 2-[(*R*)-1-phenylethyl]isoindolin-1-one, compound **12** in Schemes 1 and 2, in *ca.* 7 to 1 molar ratio. The epimers of **11** were the major components of this mixture. This sample is henceforth referred to as sample A. The mass of sample A and its molar composition made it possible to determine that the epimers of **11** were obtained in 64% chemical yield in the carbonylation of **3**. In sample A, the major epimer of **11** was epimer **V**, which was present in this sample in *ca.* 20% diastereomeric excess, as was also the case in the sample containing a small amount of the epimers of **11** obtained from the carbonylation of **2**.

A ^{1}H–^{1}H NOESY experiment at 400 MHz in $CDCl_3$ for sample A did not allow us to carry out the determination of the relative configuration of the chiral carbon atoms in the epimers of **11**. Nevertheless, since: (i) the NOESY experiment did not present exchange peaks between the epimers of **11**, (ii) the molar ratio between the three components of sample A remained unchanged after several weeks, an occurrence which was checked by ^{1}H NMR and (iii) an HPLC analysis of sample A with a chiral column afforded three well-separated signals for its three components, we concluded that the epimers of **11** were configurationally stable, which was consistent with precedents in the literature [57].

The fourth eluted band during the chromatography of the oily material obtained in the carbonylation of **3** produced a small amount of another sample, hereafter referred to as sample B, which was enriched in compound **12**. Thus, from samples A and B, it was possible to assign the characteristic NMR proton resonances and IR absorptions for compounds **11** and **12** (see Section 3). Furthermore, the FAB(+) mass spectrum of sample A produced the most abundant peaks at 268 and 236, which corresponded to the molecular monopositive cations $[M_{11}+H^+]$ and $[M_{11}+H^+$-MeOH], and the CI mass spectrum of sample B displayed the most abundant peak at 268, which corresponded to the molecular monopositive cation $[M_{12}+H^+]$, where M_{11} and M_{12} were the masses of the most abundant isotopomer of **11** and **12**, respectively.

It seems likely that (i) compound **12** could be formed by methanolysis of the Pd–C σ bond of the intermediate α-aminoalkylpalladium complex (Z in Scheme 2) or else by reductive elimination of palladium(0) in a hydridepalladium complex formed by *β* elimination of a methyl hydrogen of the methanol ligand of intermediate Z, and that (ii) the induction of the diastereoselection observed in the synthesis of compound **11** takes place during the transformation of the intermediate acylpalladium complex (Y in Scheme 2) into the intermediate α-aminoalkylpalladium complex (Z in Scheme 2). We notice that this latter transformation corresponds to an intramolecular insertion of the carbon nitrogen double bond of the acylpalladium complex Y into its Pd–C σ bond [58].

Finally, it should be noted that the selectivity change in the carbonylation products of compounds **2** and **3**, when the acetato ligands are replaced by chloro ligands in the starting *endo* five-membered *ortho*-cyclopalladated imine, is remarkable and reproduces well the results previously reported [17–19,59].

3. Experimental

3.1. Instruments and reagents

Elemental analyses of C, H and N were performed with an Eager 1108 microanalyzer. Infrared spectra were recorded on a Nicolet Impact-400 spectrophotometer using pressed discs of dispersed samples of compounds **2** and **3** in KBr, a thin film of **1** between NaCl windows and a $CHCl_3$ solution of compounds **10**–**12** in a NaCl cell. ^{1}H NMR at 500, 400, 250 and 200 MHz were recorded in Varian Inova, Varian Mercury, Bruker DRX and Varian Gemini instruments, respectively. Chemical shifts are reported in *δ* values (ppm) relative to $SiMe_4$ and coupling constants in Hz. FAB(+) mass spectra were obtained with a VG-Quatro Fisions instrument, using 3-nitrobenzylalcohol as matrix. The CI mass spectrum was obtained with a ThermoFinnigan TRACE DSQ instrument, using NH_3 as reactive gas. The HPLC analysis was carried out in a Waters 717 Plus autosampler chromatograph with a Waters 996 multidiode array detector, fitted with a Chiracel OD-H chiral column. The eluent was a mixture of *n*-hexane/^{i}PrOH (95/5). Optical rotations were measured with a polarimeter Perkin Elmer 241MC at the D line of Na (589 nm) with a cell of 1 mL and an optical path of 10 cm. All chemicals and solvents were of commercial grade and used as received. Carbon monoxide was CON47 Alphagaz, which contained less than 1 ppm of hydrogen. Compound (μ-OAc)$_2$[Pd(κ^2-*C*,*N*-C_6H_4-CH=N-CH_2-Ph)]$_2$ was prepared as previously reported [40].

3.2. Preparation of *1*

1.433 g (13.50 mmol) of benzaldehyde and 1.651 g (13.62 mmol) of *R*-(+)-1-phenylethylamine were treated at reflux of ethanol (20 mL) for 4 h. The resulting solution was concentrated in vacuum and the oil obtained was purified by distillation in a Büchi oven for distillation. The Schiff base **1** was obtained as an orange oil in 84% yield (2.376 g). Characterization data: Anal. Calc. for $C_{15}H_{15}N$: C, 86.08, H, 7.22; N, 6.69. Found: C, 84.02; H, 7.2; N, 6.7%. IR (NaCl, cm^{-1}): 1653 (C=N st). FAB(+) (most intense peaks): $[M+H^+] = 210$, $[M+H^+-CH_4] = 194$. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 8.38 (s, H_a), 7.81–7.79 (m, H_1 and H_5), 7.46 (dd, H_6 and H_{10}, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 1.1$ Hz), 7.43–7.40 (m, H_2, H_4 and H_3), 7.36 (t, H_7 and H_9, $^3J_{HH} = 7.7$ Hz), 7.26 (tt, H_8, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.5$ Hz), 4.56 (q, H_b, $^3J_{HH} = 6.6$ Hz), 1.60 (d, Me_A, $^3J_{HH} = 6.7$ Hz). $[\alpha]_{589}^{27}$ ($c = 0.36$ g/100 mL, $CHCl_3$) (literature [31], $c = 1.0$ g/100 ml) = −64.4° (−64.7°).

3.3. Preparation of **2**

A suspension formed by 2.22 mol (0.500 g) of $Pd(OAc)_2$, 2.22 mmol (0.465 g) of **1** and 20 mL of acetic acid was stirred under nitrogen at 60 °C for 4 h. The resulting red solution was concentrated in vacuum and the residue was eluted through a silica gel column chromatography with a solution of methanol in chloroform in a 2 to 100 volume ratio. The orange bands were collected and concentrated under vacuum. Addition of diethylether (5 mL) to the residue produced the precipitation of **2** as a yellow powder, which was filtered and dried under vacuum. Yield: 65% (0.539 g). Characterization data: Anal. Calc. for $C_{34}H_{34}O_4N_2Pd_2$: C, 54.63; H, 4.58; N, 3.75%. Found: C, 54.0; H, 4.5; N, 3.8%. IR (KBr, cm^{-1}): 1606 (C=N st), 1595 st as (carboxylato), 1420 st s (carboxylato). FAB(+) (most intense peaks): $[M+H^+] = 749$, $[M-(OAc^-)] = 690$, $[(M/2)-(OAc^-)] = 315$. ^1H NMR (400 MHz, $CDCl_3$, 298 K) (selected data) (**I** and **II** isomers in 3 to 1 molar ratio): 7.63 (d, H_a, $^4J_{HH} = 1.2$ Hz, **II**), 6.98 (d, H_a, $^4J_{HH} = 1.2$ Hz, **I**), 4.67 (q, H_b, $^3J_{HH} = 6.8$ Hz, **II**), 4.61 (q, H_b, $^3J_{HH} = 6.8$ Hz, **I**), 2.20 (s, Me_B, **I**), 2.04 (s, Me_B, **II**), 1.76 (d, Me_A, $^3J_{HH} = 6.8$ Hz, **I**), 0.85 (d, Me_A, $^3J_{HH} = 7.2$ Hz, **II**). $[\alpha]_{589}^{23.5}$ ($c = 0.29$ g/100 mL, $CHCl_3$) = +179.9°.

3.4. Preparation of **3**

A suspension formed by 0.180 g (4.20 mmol) of LiCl, 0.801 g (1.07 mmol) of **2** and 30 mL of acetone was stirred at room temperature for 4 h. The resulting suspension was concentrated under vacuum and the residue was eluted through a silica gel column chromatography with a solution of methanol in chloroform in a 2 to 100 volume ratio. The coloured band was collected and concentrated under vacuum. Addition of diethylether (5 mL) to the residue produced the precipitation of **3** as a yellow powder, which was filtered and dried under vacuum. Yield: 88% (0.663 g). Characterization data: Anal. Calc. for $C_{30}H_{28}N_2Cl_2Pd_2$: C, 51.45; H, 4.03; N, 4.00. Found: C, 51.0; H, 4.2; N, 3.8%. IR (KBr, cm^{-1}): 1604 (C=N st). FAB(+) (*m/z*): $[M+H^+] = 701$, $[M-(Cl^-)] = 665$, $[(M/2)-(Cl^-)] = 315$. ^1H NMR (400 MHz, $CDCl_3$, 298 K) (**III** and **IV** isomers in 1.5 to 1 molar ratio): 7.59 (s, H_a, **III** and **IV**), 7.40 (m, 4 H, H_{ar}, **III** and **IV**, $^3J_{HH} = 6.0$ Hz), 7.36–7.32 (m, 2H, H_{ar}, **III** and **IV**), 7.10–7.08 (m, 1H, H_{ar}, **III** and **IV**), 7.04–6.99 (m, 2H, H_{ar}, **III** and **IV**), 5.34 (q, H_b, **III** and **IV**, $^3J_{HH} = 6.7$ Hz), 1.82 (br signal, Me_A, **III**) 1.77 (br signal, Me_A, **IV**). Optical rotation: $[\alpha]_{589}^{23.5}$ ($c = 0.28$ g/100 mL, $CHCl_3$) = + 255.7°.

3.5. NMR tube reactions

An orange or pale yellow solution formed by 10 mg of the corresponding dimeric cyclopalladated compound in 0.7 mL of $CDCl_3$ was treated with a drop of the corresponding L ligand and shaken for a few seconds. The formation of a colourless solution indicated the quantitative formation of the corresponding monomeric cyclopalladated compound, as showed the ^1H NMR of the final colourless solution. Characterization data: ^1H NMR ($CDCl_3$, 298 K) (selected data): Compound **4** (400 MHz): 7.66 (d, H_a, $^4J_{HH} = 1.0$ Hz), 7.14 (dd, H_5, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz), 6.97 (td, H_4, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.0$ Hz), 6.88 (td, H_3, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz), 6.18 (dd, H_2, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 0.7$ Hz), 5.24 (q, H_b, $^3J_{HH} = 6.9$ Hz), 1.90 (s, Me_B), 1.78 (d, Me_A, $^3J_{HH} = 6.9$ Hz). Compound **5** (400 MHz): 7.65 (s, H_a), 7.15 (d, H_5, $^3J_{HH} = 7.0$ Hz), 7.00 (t, H_4, $^3J_{HH} = 7.3$ Hz), 6.91 (t, H_3, $^3J_{HH} = 7.5$ Hz), 6.14 (d, H_2, $^3J_{HH} = 7.6$ Hz), 5.96 (q, H_b, $^3J_{HH} = 6.9$ Hz), 1.83 (d, Me_A, $^3J_{HH} = 6.9$ Hz). Compound **6** (*RR* diastereoisomer) (400 MHz): 7.73 (d, H_a, $^4J_{HH} = 1.1$ Hz,), 7.09 (td, H_4, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.7$ Hz), 7.04 (td, H_3, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz), 6.86 (dd, H_2, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 0.9$ Hz), 5.37 (q, H_b, $^3J_{HH} = 6.8$ Hz), 4.26–4.16 (m, H_c), 3.64 (d, 1H, NH_2, $^2J_{HH} = 8.7$ Hz), 1.98 (s, Me_B), 1.83 (d, Me_C, $^3J_{HH} = 6.8$ Hz), 1.75 (d, Me_A, $^3J_{HH} = 6.9$ Hz). Compound **7** (*RR* diastereoisomer) (400 MHz): 7.62 (d, H_a, $^4J_{HH} = 0.7$ Hz), 7.17 (dd, H_5, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.6$ Hz), 7.11 (td, H_4, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.6$ Hz), 7.06 (td, H_3, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 0.8$ Hz), 6.85 (d, H_2, $^3J_{HH} = 7.5$ Hz), 5.82 (q, H_b, $^3J_{HH} = 6.8$ Hz), 4.56–4.46 (m, H_c), 3.58 (t, 1H, NH_2, $^2J_{HH} = 10.7$ Hz), 3.28 (d, 1H, NH_2, $^2J_{HH} = 9.4$ Hz), 1.89 (d, Me_A, $^3J_{HH} = 6.9$ Hz), 1.81 (d, Me_C, $^3J_{HH} = 6.9$ Hz). Compound **8** (*RR* and *RS* diastereoisomers in 1 to 1 molar ratio) (400 MHz): 7.73 (d, H_a, $^4J_{HH} = 1.1$ Hz, *RR*), 7.67 (d, H_a, $^4J_{HH} = 1.1$ Hz, *RS*), 6.86 (dd, H_2, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 0.8$ Hz, *RR*), 6.85 (dd, H_2, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 0.7$ Hz, *RS*), 5.36 (q, H_b, $^3J_{HH} = 6.8$ Hz, *RR* and *RS*), 4.24–4.16 (m, H_c, *RR* and *RS*), 3.63 (t, 1H, NH_2, $^2J_{HH} = 8.6$ Hz, *RR* and *RS*), 1.98 (s, Me_B, *RR* and *RS*), 1.83 (d, Me_C, $^3J_{HH} = 6.9$ Hz, *RR*), 1.81 (d, Me_C, $^3J_{HH} = 6.9$ Hz, *RS*), 1.75 (d, Me_A, $^3J_{HH} = 6.9$ Hz, *RR*), 1.73 (d, Me_A, $^3J_{HH} = 6.9$ Hz, *RS*). Compound **9** (*RR* and *RS* diastereoisomers in 1 to 1 molar ratio) (400 MHz): 7.73 (s, H_a, *RS*), 7.62 (s, H_a,*RR*), 7.17 (d, H_5, $^3J_{HH} = 7.1$ Hz, *RR* and *RS*), 7.11 (td, H_4, $^3J_{HH} = 7.2$ Hz, *RR* and *RS*), 7.05 (td, H_3, $^3J_{HH} = 7.3$ Hz, *RR* and *RS*), 6.85 (d, H_2, $^3J_{HH} = 7.4$ Hz, *RR* and *RS*), 5.83 (q, H_b, $^3J_{HH} = 6.7$ Hz, *RR* and *RS*), 4.55–4.47 (m, H_c, *RR* and *RS*), 3.58 (t, 1H, NH_2, $^2J_{HH} = 11.2$ Hz, *RR*), 3.52 (t, 1H, NH_2, $^2J_{HH} = 11.0$ Hz, *RS*), 3.31 (d, 1H, NH_2, $^2J_{HH} = 11.2$ Hz, *RS*), 3.27 (d, 1H, NH_2, $^2J_{HH} = 11.2$ Hz, *RR*), 1.88 (t, Me_A, $^3J_{HH} = 7.6$ Hz, *RR* and *RS*), 1.81 (d, Me_C, $^3J_{HH} = 6.9$ Hz, *RR*), 1.78 (d, Me_C, $^3J_{HH} = 6.9$ Hz, *RS*). Compound **A** (200 MHz): 7.70 (s, H_a), 7.16 (d, H_5, $^3J_{HH} = 7.0$ Hz), 6.97 (t, H_4, $^3J_{HH} = 7.0$ Hz), 6.88 (t, H_3, $^3J_{HH} = 7.0$ Hz), 6.03 (d, H_2, $^3J_{HH} = 7.0$ Hz), 4.86 (s, CH_2), 1.91 (s, OAc).

3.6. Preparation of **10**

A 250 mL cylindrical glassware reactor was charged in a ventilated fume hood with 0.151 g (0.20 mmol) of compound **2**, 25 mL of MeOH and carbon monoxide at

1.6 bar. The resulting suspension was stirred at room temperature for 6 h. After this time, a voluminous precipitate of palladium(0) was formed and the reactor was opened to release the excess of carbon monoxide. The palladium(0) was filtered and the solvent of the resulting solution was concentrated under vacuum. The residue of the solution was eluted through a short silica gel column chromatography (*ca.* 10 cm), initially with chloroform and thereafter with solutions of methanol in chloroform, increasing gradually the volume ratio between methanol and chloroform from 0.5 to 100 to 2 to 100. Compound **10** was isolated as a white solid in 91% yield after concentration under vacuum of the solvent of the second eluted band. Characterization data: IR ($CHCl_3$ solution, cm^{-1}): 1723 (C=O st, ester), 1700 (C=O st, aldehyde), 1284 (CO–O st a), 1257 (CO–O st s). ^1H NMR (400 MHz, $CDCl_3$, 298 K): 10.62 (s, H_a), 7.99–7.94 (m, 2H, H_{ar}), 7.67–7.64 (m, 2H, H_{ar}), 3.98 (s, Me).

3.7. Preparation of samples A and B

A 250 mL cylindrical glassware reactor was charged in a ventilated fume hood with 0.155 g (0.22 mmol) of compound **3**, 25 mL of MeOH and carbon monoxide at 1.6 bar. The resulting suspension was stirred at room temperature for 24 h. After this time, a voluminous precipitate of palladium(0) was formed and the reactor was opened to release the excess of carbon monoxide. The palladium(0) was filtered and the solvent of the resulting solution was concentrated under vacuum. The residue of the solution was eluted through a silica gel column chromatography with chloroform. Four bands were eluted, the most important being the last two bands. Concentration of the solvent of the third eluted band afforded 0.085 g of a yellow oil (sample A), which was a mixture of compounds **11** and **12** in *ca.* 7 to 1 molar ratio. Concentration of the solvent of the fourth eluted band afforded 0.011 g of an oil (sample B), which was a mixture of compounds **12** and **11** in *ca.* 4 to 1 molar ratio. Characterization data: Compound **11** (**V** and **VI** epimers in 1.5 to 1 molar ratio): IR ($CHCl_3$ solution, cm^{-1}): 1693 (C=O st). FAB(+) (*m*/*z*) (most intense peaks): $[M+H]^+ = 268$, $[M+H^+-MeOH] = 236$. ^1H NMR (400 MHz, $CDCl_3$, 298 K) (selected data): 6.02 (s, H_a,**VI**), 5.68 (q, H_b, $^3J_{HH} = 7.3$ Hz, **V**), 5.60 (s, H_a, **V**), 5.39 (q, H_b, $^3J_{HH} = 7.4$ Hz, **VI**), 2.92 (s, MeO, **V**), 2.47 (s, MeO, **VI**), 1.88 (d, Me, $^3J_{HH} = 7.3$ Hz, **VI**), 1.80 (d, Me, $^3J_{HH} = 7.3$ Hz, **V**). HPLC (t_R) = 22.5 min (**V**), 24.4 min (**VI**). Compound **12**: IR ($CHCl_3$ solution, cm^{-1}): 1676 (C=O st). CI-MS/NH_3 (*m*/*z*) (most intense peak): $[M+H^+] = 238$. ^1H NMR (400 MHz, $CDCl_3$, 298 K) (selected data): 7.88 (d, 1H, H_{ar}, $^3J_{HH} = 7.0$ Hz), 5.82 (q, H_b, $^3J_{HH} = 7.1$ Hz), 4.34 (d, 1H, CH_2, $^2J_{HH} = 17.0$ Hz), 4.00 (d, 1H, CH_2, $^2J_{HH} = 17.0$ Hz), 1.70 (d, Me, $^3J_{HH} = 7.1$ Hz). HPLC (t_R) = 39.4 min.

3.8. Crystal structure

Crystals for the X-ray molecular structure determination of **3** were obtained by cooling at 4 °C a solution of **3** in ethyl acetate/dichloromethane (1/1). A prismatic crystal was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Intensities were collected with graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods using the SHELXS [60] computer program and refined by the full-matrix least-squares method, with the SHELXL97 [61] computer program. A summary of crystallographic data and some details of the refinement are given in Table 5.

Table 5
Crystallographic data for the *trans* isomer of compound **3**

Empirical formula	$C_{30}H_{28}Cl_2N_2Pd_2$
Formula weight	700.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	10.430(4)
b (Å)	12.082(8)
c (Å)	11.168(4)
β (°)	95.20(3)
Volume	1401.5(12) $Å^3$
Z	2
$D_{calc}(Mg/m^3)$	1.659
Absorption coefficient (mm^{-1})	1.495
F(000)	696
Crystal size (mm)	$0.2 \times 0.1 \times 0.1$
θ Range for data collection (°)	2.49–29.97
Limiting indices	$-14 \leqslant h \leqslant 14$ $0 \leqslant k \leqslant 16$ $0 \leqslant l \leqslant 15$
Reflections collected/unique [R_{int}]	4749/4253 [0.040]
Completeness to theta = 29.97° (%)	98.8
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4253/4/325
Goodness-of-fit on F^2	0.753
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$ $wR_2 = 0.0478$
R indices (all data)	$R_1 = 0.2676$ $wR_2 = 0.0760$
Flack × parameter	−0.01(7)
Largest difference in peak and hole (e $Å^3$)	0.405 and −0.520

4. Supplementary material

CCDC 633319 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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