Steric and electronic effects on E/Z composition of exocyclic cyclopalladated N-benzylideneamines

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Abstract

Exocyclic six-membered cyclopalladated dimers **2a–2c**, [$\overline{Pd(C-N)}Br]_2$, have been prepared by reaction of palladium(II) acetate with N-benzylidene-2-phenylanilines **1a–1c**, $RCH=NC_6H_4$-2-C_6H_5 {**1a**, $R = 2,6$-$Cl_2C_6H_3$; **1b**, $R = 2,6$-$F_2C_6H_3$ and **1c**, $R = 2,4,6$-$(CH_3O)_3C_6H_2$}, and a subsequent metathesis reaction with LiBr. Reaction of **2** with PPh_3 produced mononuclear compounds **3**, [$\overline{Pd(C-N)}Br(PPh_3)$]. Analysis of the ^1H NMR methinic region of **2** and **3** revealed their E/Z composition. **2a** and **2b** present imines in E and Z configuration in an approximate ratio of 1:1, white **2c** consists almost exclusively of imines in E configuration. Compounds **3** also present imines in E and Z configuration, the former are more abundant in all cases ($\geq 4:1$). The crystal structure of **3c** with the imine in E configuration has been determined. It crystallizes in the monoclinic space group $P2_1/a$ with $a = 19.258(3)$ Å, $b = 13.177(2)$ Å, $c = 14.660(2)$ Å and $\beta = 113.78(2)°$. Steric and electronic effects on the E/Z composition of **2** and **3** and related exocyclic cyclopalladated N-benzylidenebenzylamines suggest that, for compounds of this type, the $E \rightarrow Z$ isomerization takes place via a rotation through the $N=C$ bond which is assisted by π back bonding of the palladium(II) center to the iminic function. © 1997 Elsevier Science S.A.

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1. Introduction

In cyclometallation reactions, N-benzylidenebenzylamines are potentially bifunctional ligands and could produce, depending on whether the $N=C$ bond is included in the metallacycle, endocyclic or exocyclic derivatives (Fig. 1).

Cyclopalladation reactions of N-benzylidenebenzylamines produce regioselectively endocyclic compounds [1–4]. The exocyclic derivatives can be obtained if the *ortho* positions which give rise to endocyclic compounds are replaced by chlorine atoms, fluorine atoms, methyl groups or methoxy groups [5–7]. Alternatively, exocyclic cyclopalladated N-benzylidenebenzylamines have been prepared by oxidative addition of N-benzylidene-2-bromobenzylamines to palladium(0) compounds [2,8].

Exocyclic cyclopalladated N-benzylidenebenzyla-

mines can adopt the E or Z configuration and their E/Z composition is controlled by steric and electronic effects [2,5–8]. Thus, exocyclic cyclopalladated N-benzylidenebenzylamines [2,8] adopt the E configuration and exocyclic cyclopalladated N-2,6-dichlorobenzylidenebenzylamines [5] and N-2,4,6-trimethylbenzylidenebenzylamines adopt the Z configuration [6]. Thus, for these two latter kinds of compound, the steric repulsion between the phenylic group bonded to the methinic carbon atom and the ligand *trans* to the palladated carbon atom favors the Z configuration (Fig. 2A). Steric effects also explain the E/Z composition of exocyclic cyclopalladated N-2,6-dichlorobenzylidene-α-methylbenzylamines and N-2,6-difluorobenzylidene-α-methylbenzylamines which ranges from 1/1 to 1/2 [7]. The presence of imines in E configuration in these cases is consistent with the destabilization of the imines in Z configuration because of the steric repulsion between the phenylic group bonded to the methinic carbon atom and the methyl bonded to the benzylic carbon atom (Fig. 2B). Nevertheless, exocyclic cyclopalladated N-2,4,6-trimethoxybenzylidene-α-methylbenzylamines adopt the E configuration [7], although the steric param-
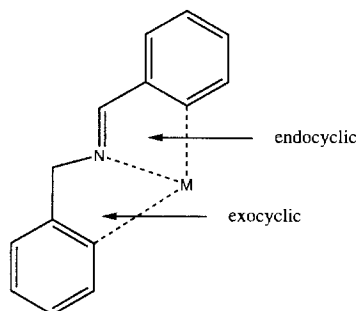
Fig. 1. Endocyclic and exocyclic cyclometallated *N*-benzylidene-benzylamines.

eters of a methoxy substituent are similar to those of a fluorine substituent [9]. This result indicates that electronic effects are also important in the $E \rightarrow Z$ isomerization of exocyclic cyclopalladated *N*-benzylidene-benzylamines and shows that electron donor substituents at the phenyl bonded to the methinic carbon atom can prevent this process.

Following these studies, we now describe the preparation of exocyclic six-membered cyclopalladated derivatives $[\overline{Pd(C\text{-}N)}Br]_2$ (**2**) and $[\overline{Pd(C\text{-}N)}Br(PPh_3)]$ (**3**) of *N*-2,6-dichlorobenzylidene-2-phenylaniline (**1a**), *N*-2,6-difluorobenzylidene-2-phenylaniline (**1b**) and *N*-2,4,6-trimethoxybenzylidene-2-phenylaniline (**1c**). The E/Z composition of dimers **2** follows similar trends to

Fig. 2. Unfavorable steric interactions in exocyclic cyclopalladated *N*-benzylidenebenzylamines.

those discussed above for exocyclic cyclopalladated *N*-benzylidenebenzylamines. Thus, **2a** and **2b** present imines in E and Z configuration in an approximate ratio of 1:1; while, for **2c**, they adopt the E configuration almost exclusively. Interestingly, in compounds **3**, imines in E configuration are more abundant than those in Z configuration ($\geq 4:1$). This result shows that the E/Z composition of exocyclic cyclopalladated *N*-benzylideneamines can also be affected by the ligand in *trans* position to the iminic function.

2. Results

N-benzylidene-2-phenylanilines **1a–1c** (see Scheme 1) were prepared by condensation reaction between 2-phenylaniline and the appropriate aldehyde. **1a–1c** gave satisfactory IR, positive FAB and ^{1}H NMR. In the infrared spectra, the $\nu(C=N)$ appeared quite intense at 1635, 1634 and 1606 cm^{-1}, respectively. The positive FAB of **1** presented intense peaks which were in accordance with their structural features. Thus, **1a** presented intense peaks at $[M]^+$ and $[M-Cl]^+$, **1b** at $[M]^+$ and $[M + H]^+$ and **1c** at $[M + H]^+$ and $[M-CH_3]^+$. The ^{1}H NMR of **1** showed only one set of signals. This result indicated that the *N*-benzylidene-2-phenylanilines **1a–1c** adopted only one configuration around the N=C bond which, according to the literature [10], we assumed to be the E configuration. A NOESY experiment for **1c** was consistent with this assumption since the methinic proton showed NOE with the proton in *ortho* position to the nitrogen atom.

The cyclopalladation reaction of **1** with palladium(II) acetate was studied (Scheme 1). The reaction conditions were chosen in order to avoid reactions which could give rise to the formation of endocyclic compounds. Thus, **1a** was treated in acetic acid at 60°C since, according to the behavior of related ligands [5,11,12], oxidative addition of C–Cl bonds to palladium(0) formed in site was observed at higher temperature. Nevertheless, for **1b**, more drastic reaction conditions were used (acetic acid, reflux) since oxidative addition of C–F bonds to palladium(0) did not take place. On the other hand, **1c** was *ortho*-palladated in chloroform at room temperature because activation of the O–Csp^3 bond of one of the *ortho* methoxy groups could be a competitive process in acetic acid or at higher temperature [4]. In the above discussed reaction conditions and in a subsequent metathesis reaction with LiBr, the bromo bridged exocyclic six-membered cyclopalladated dimers **2** were obtained in 30–50% yield [1].
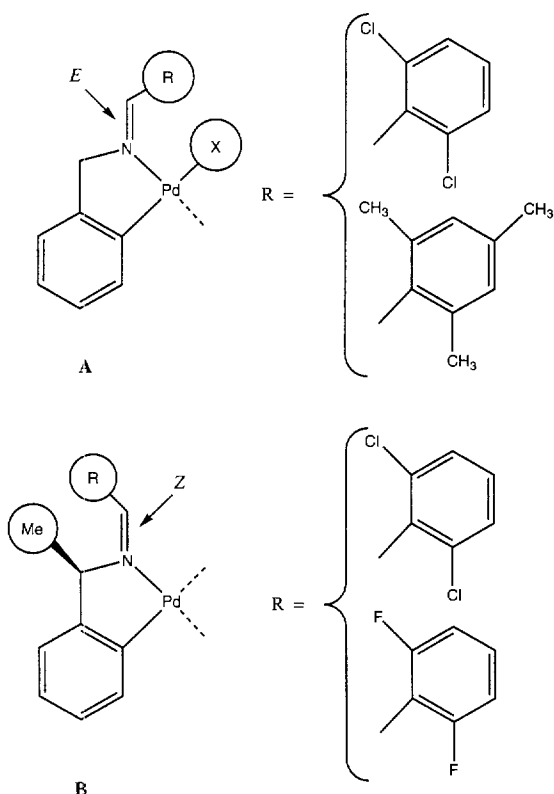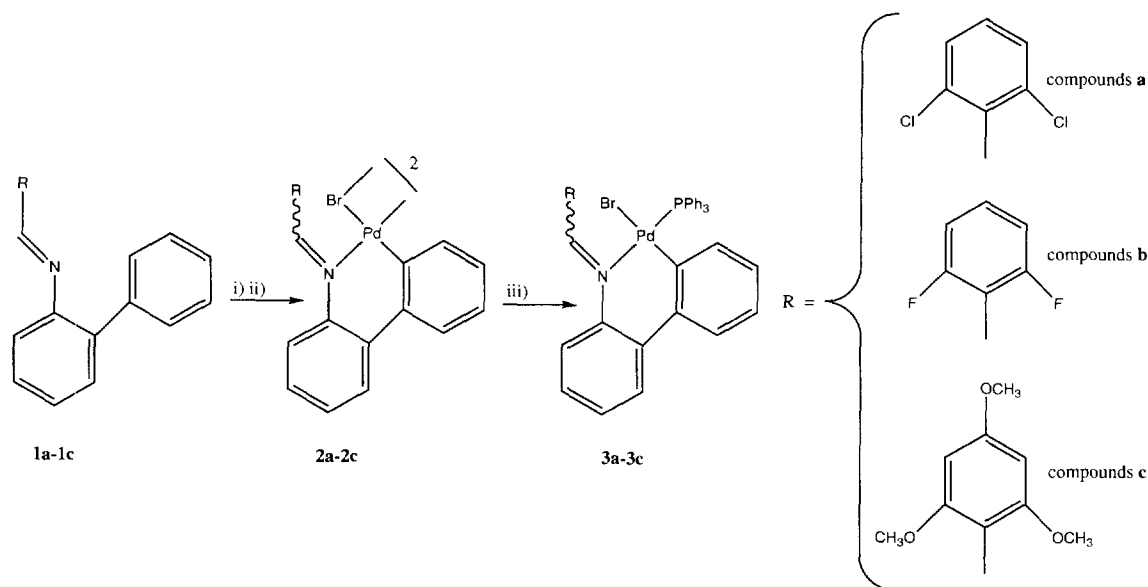
Scheme 1. (i) Pd(O$_2$CMe)$_2$; **1a**, acetic acid, 60°C, 2 h; **1b**, acetic acid reflux, 45 min; **1c**, CHCl$_3$, RT, 24 h. (ii) LiBr, EtOH, RT, 30 min. (iii) PPh$_3$, acetone, RT, 30 min.

2a–2c gave satisfactory elemental analyses, IR, positive FAB and ^{1}H NMR. In the infrared spectra, the ν(C=N) appeared quite intense at 1629, 1630 and 1600 cm^{-1}, respectively, and the positive FAB showed intense peaks corresponding to [M]$^+$ and [M–Br]$^+$, like analogous [Pd(C-N)Br]$_2$ dinuclear cyclopalladated compounds [13]. The ^{1}H NMR of **2a** and **2b** showed different set of signals which we assigned to conformational isomers of the (E, E), (E, Z) and (Z, Z) geometrical isomers that would constitute **2a** and **2b** [7].

In order to establish the E/Z composition of **2a** and **2b** we studied their ^{1}H NMR in the methinic region (between 8.4 and 9 ppm). In this interval eight singlets appeared which were assigned to methinic protons of which those with a chemical shift close to that of the methinic proton of the free imines were assigned to the imines in E configuration; while those low-field shifted in relation to the methinic proton of the free imines were assigned to the imines in Z configuration [7]. Integration of these two groups of signals allowed us to establish the E/Z composition of **2a** and **2b**, which was approximately 1:1. In contrast, **2c** presented almost exclusively imines in E configuration since its ^{1}H NMR spectrum showed almost exclusively one set of signals which, according to the chemical shift of the methinic proton in relation to the free imine [7], was assigned to the (E, E) geometrical isomer.

Reaction of **2** with PPh$_3$ produced the mononuclear derivatives **3** (Scheme). Compounds **3** gave satisfactory elemental analyses, infrared spectra positive FAB, ^{1}H NMR and ^{31}P NMR. The infrared spectra showed the bands of the coordinated imine and phosphine ligands and, in the positive FAB, the most abundant peak was

the loss of the bromo ligand ([M–Br]$^+$), like analogous [Pd(C-N)Br(PPh$_3$)]mononuclear compounds [13].

The ^{1}H NMR of **3** showed signals corresponding to isomers with the imine in E or Z configuration. Some of these geometrical isomers showed broad signals or consisted of two sets of signals, which was consistent with a slow interconversion between their conformational isomers at room temperature [14–16]. The phosphine was *cis* to the palladated carbon atom, which was inferred by coupling constants of the methinic protons with the phosphorus atoms, large up-field shift of the protons of the metallated phenyl ring and chemical shift of the phosphorus atoms in the interval 36–33 ppm [6]. Interestingly, in compounds **3**, imine ligands in E configuration were more abundant than those in Z configuration. Integration of the methinic protons allowed us to establish their proportion which was in all cases equal to or grater than 4:1. This result shows that ligands in *trans* position to the iminic function can also influence the E/Z composition of exocyclic cyclopalladated N-benzylideneamines.

3. Discussion

It is generally assumed that N-benzylideneanilines undergo $E \to Z$ isomerization due to a lateral shift of the phenyl bonded to the nitrogen atom, in which the nitrogen atom changes its hybridization from sp^2 to sp in the transition state; since the alternative rotation mechanism, which would proceed through heterolytic cleavage of the π bond of the nitrogen–carbon double bond, would require higher activation energy [10,17–19].
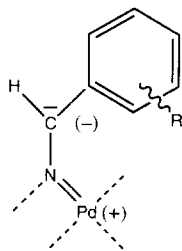
Fig. 3. Transition state for the $E \to Z$ isomerization of exocyclic cyclopalladated N-benzylideneamines.

In exocyclic cyclopalladated N-benzylideneamines coordination of the nitrogen atom to palladium(II) prevents the lateral shift mechanism. Moreover, a mechanism for the $E \to Z$ isomerization of exocyclic cyclopalladated N-benzylideneamines, initiated by cleavage of the Pd–N bond and a subsequent lateral shift of the group bonded to the nitrogen atom, does not seem likely since the Pd–N bond is quite stable for compounds of this kind [5–7,20,21]. Therefore, for exocyclic cyclopalladated N-benzylideneamines, the $E \to Z$ isomerization must proceed through the alternative rotation mechanism. Moreover, π back bonding of the palladium(II) to the iminic function would favor the rotation mechanism through the transition state shown in Fig. 3.

It should be noted that the proposed transition state for the $E \to Z$ isomerization of exocyclic cylopalladated N-benzylideneamines is consistent with the well known π back bonding properties of d^8 metal centers [22] which also apply for cyclometallated compounds [23–25].

E/Z composition of exocyclic cyclopalladated N-benzylideneamines is consistent with the proposed transition state for their $E \to Z$ isomerization (Fig. 3). Thus, acceptor (chlorine or fluorine) or donor (methoxy) electron substituents at the ortho positions of the phenyl bonded to the methinic carbon atom would stabilize or destabilize, respectively, the proposed transition state and would therefore favor or prevent the $E \to Z$ isomerization which is in fact the experimental result (Refs. [5,7] and this study). Nevertheless, exocyclic cyclopalladated N-2,4,6-trimethylbenzylidenebenzylamines adopt the Z configuration [6], although the methyl group is an electron donor. This result shows that $E \to Z$ isomerization of exocyclic N-benzylideneamines is mainly controlled by steric effects since the effective volume of a methyl group is bigger than that of a methoxy substituent [9].

Finally, the preference of compounds **3** for the E configuration should reflect the changes in bond distances and angles around palladium(II) and in π back bonding properties of palladium(II) when we compare mononuclear compounds [$\overline{Pd(C-N)}$Br(PPh$_3$)] with dimers [$\overline{Pd(C-N)}$Br]$_2$. Thus, mononuclear compounds [$\overline{Pd(C-N)}$Br(PPh$_3$)] in relation to dimers [$\overline{Pd(C-N)}$Br]$_2$

show a lengthening of the Pd–N distance because of the *trans* influence of PPh$_3$ ligand [6,24]. This decreases the steric repulsion between the bromo ligand and the phenylic group bonded to the methinic carbon atom and therefore favors the E configuration. Moreover, the π acceptor electron properties of the PPh$_3$ ligand [26] should diminish the π back bonding properties of the Pd(PPh$_3$) unit in relation to the PdBr unit and this should be reflected kinetically by a retardation of the $E \to Z$ isomerization, although we have no evidence for this.

4. X-ray crystallographic studies

The crystal structure of **3c** with the imine E in configuration, thereafter referred to as the E isomer of **3c**, has been determined. Fig. 4 shows its molecular structure, together with the numbering scheme, and Table 1 gives selected bond distances and angles. The crystal structure confirms the NMR findings. Thus, the mononuclear cyclopalladated compound is exocyclic and the PPh$_3$ ligand is *cis* to the metallated ring. The bond distances and angles around the palladium atom are in the normal intervals [6,24,27]. The palladium atom is in a roughly distorted square planar geometry. The deviations from the coordination plane are as follows: Pd, -0.042 Å; Br, -0.097 Å; P, 0.121 Å; N, 0.146 Å and C(1), -0.128 Å. The six-membered metallacycle is not
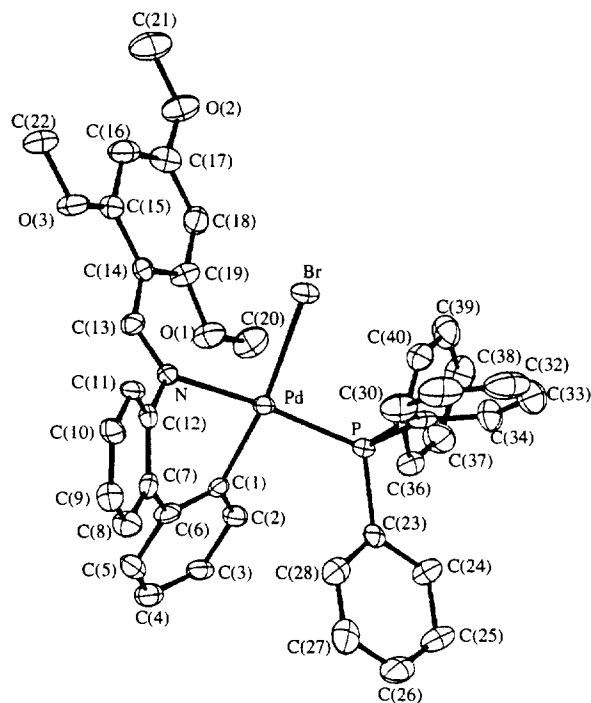

Fig. 4. X-ray molecular structure of the E isomer of **3c** (labels of some carbon atoms of the PPh$_3$ ligand have been omitted for clarity).

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

Bond distances		Angles	
Pd–C(1)	2.030(6)	C(1)–Pd–N	83.2(2)
Pd–N	2.094(5)	C(1)–Pd–P	94.5(2)
Pd–P	2.237(2)	N–Pd–P	170.3(2)
Pd–Br	2.5098(9)	C(1)–Pd–Br	171.6(2)
N–C(12)	1.415(7)	N–Pd–Br	89.66(13)
C(7)–C(12)	1.419(9)	P–Pd–Br	93.33(5)
C(6)–C(7)	1.478(9)	C(12)–N–Pd	106.5(4)
C(1)–C(6)	1.376(8)	C(7)–C(12)–N	119.1(6)
N–C(13)	1.272(7)	C(12)–C(7)–C(6)	118.5(6)
		C(1)–C(6)–C(7)	122.4(6)
		C(6)–C(1)–Pd	118.7(5)

planar and presents the Pd and C(1) atoms out of the plane defined by the remaining four atoms of the metallacycle: 1.732 Å and 0.718 Å, respectively.

In order to accommodate the square-planar coordination of the palladium atom in the six-membered metallacycle the aromatic rings of the biphenyl group are not coplanar (the dihedral angle between C(1)–C(6)–C(7)–C(12) is 40.5°) and the palladium atom is out of the plane defined by the iminic function (0.363 Å). Therefore, although the imine adopts the E configuration, the dihedral angle between Pd–N–C(13)–C(14) is 9.9°. Finally, the phenyl rings bonded to the iminic function and the iminic function are not coplanar (the dihedral angles between N–C(13)–C(14)–C(15) and C(13)–N–C(12)–C(7) are 22.7° and 133.9°, respectively).

5. Final remarks

The present study contributes to our understanding of the steric and electronic factors that influence the E/Z composition of exocyclic cyclopalladated N-benzylideneamines and may lead to its effective control by an appropriate substitution of the imine ligand or an appropriate derivatization of the starting cyclopalladated dimer. Moreover, an effective control of the E or Z configuration adopted by exocyclic cyclopalladated N-benzylideneamines is a prior step before asymmetric elaboration of their nitrogen–carbon double bond, which could open the way to new optically active amines.

6. Experimental section

Infrared spectra were recorded on a Nicolet 520-FTIR spectrophotometer using KBr pellets. ^{1}H NMR at 200 MHz and ^{31}P{^{1}H} at 101.2 MHz were recorded respectively on Varian Gemini 200 and Bruker DRX-250 instruments. Chemical shifts (in ppm) were measured relative to SiMe$_4$ for ^{1}H and relative to 85% H$_3$PO$_4$ for ^{31}P. The solvents used were CDCl$_3$ in ^{1}H and CHCl$_3$ in

^{31}P. Positive FAB mass spectra were obtained with a VG-Quattro Fisons instrument, using 3-nitrobenzylalcohol as matrix. All chemicals were of commercial grade and used as received. Solvents were distilled before use, as follows: chloroform and dichloromethane over CaO; acetone, ethanol and methanol over CaCl$_2$; and diethylether over sodium and benzophenone.

6.1. Preparation of 1

20 mmol of 2-phenylaniline (3.850 g) were treated with 20 mmol of the appropriate aldehyde in ethanol (30 cm^3) at reflux for 4 h and the resulting solution concentrated in vacuum. Compounds **1** were purified by recrystallization in ethanol. **1a**: (pale yellow, 3.734 g, 57%). IR (cm^{-1}) 1635s ν(C=N). RMN ^{1}H: 8.68 s (1H, methinic proton), 7.60–7.12 (12H, aromatic protons). Positive FAB: 326 ([M + H]$^+$), 290 ([M–Cl]$^+$). **1b**: (pale yellow, 3.170 g, 54%). IR(cm^{-1}) 1634s ν(C=N). RMN ^{1}H: 8.63 s (1H, methinic proton), 7.54 d $^3J_{HH}$ = 8.5 Hz (2H, aromatic protons), 7.50–7.07 (8H, aromatic protons), 6.92 t $^3J_{FH}$ = $^3J_{HH}$ = 8.5 Hz (2H, aromatic protons). Positive FAB: 294 ([M + H]$^+$), 293 ([M]$^+$). **1c**: (pale yellow, 4.519 g, 65%). IR(cm^{-1}) 1606s ν(C=N). RMN ^{1}H: 8.73 s (1H, methinic proton), 7.59 d $^3J_{HH}$ = 8.5 Hz (2H, aromatic protons), 7.45–7.18 (6H, aromatic protons), 7.12 d $^3J_{HH}$ = 8.5 Hz (1H, aromatic protons), 6.12 s (2H, aromatic protons), 3.86 s (3H, aliphatic protons), 3.78 s (6H, aliphatic protons). Positive FAB: 348 ([M + H]$^+$), 332 ([M–Me]$^+$).

6.2. Preparation of 2a

A suspension formed by 2.23 mmol (0.500 g) of Pd(O$_2$CMe)$_2$, 2.23 mmol (0.726 g) of **1a** and 30 cm^3 of acetic acid was stirred at 60°C for 2 h and the resulting solution was concentrated to dryness. 4.46 mmol (0.387 g) of LiBr and 30 cm^3 of ethanol were added to the residue and the suspension was stirred at room temperature for 30 min. The precipitate was filtered off and eluted through a column of SiO$_2$ with chloroform. **2a** was isolated as a yellow powder (0.441 g, 39%) from the first colored band by concentration of the solvent and addition of ethanol (10 cm^3) to the residue. Found (Anal. Calc. for C$_{38}$H$_{24}$Br$_2$Cl$_4$N$_2$Pd$_2$): C, 45,2 (44.61); H, 2.5 (2.36); N, 2.7 (2.74)%. IR(cm^{-1}) 1629s ν(C=N). ^{1}H NMR (E/Z composition 1:1): 9.05–8.40 eight br singlets (methinic protons), 7.80–6.30 (aromatic protons). Positive FAB (selected data): 1024 ([M]$^+$), 943 ([M–Br]$^+$).

6.3. Preparation of 2b

A stirred suspension formed by 2.23 mmol (0.500 g) of Pd(O$_2$CMe)$_2$, 2.23 mmol (0.653 g) of **1b** and 30 cm^3

of acetic acid was kept under reflux for 45 min and the resulting solution was concentrated to dryness. 4.46 mmol (0.387 g) of LiBr and 30 cm^3 of ethanol were added to the residue and the resulting suspension was stirred at room temperature for 30 min. The precipitate was filtered off and eluted through a column of SiO$_2$ with chloroform. **2b** was isolated as a brown powder (0.400 g, 37%) from the first two intensely colored bands by concentration of the solvent and addition of ethanol (10 cm^3) to the residue. Found (Anal. Calc. for C$_{38}$H$_{24}$Br$_2$F$_4$N$_2$Pd$_2$): C, 46.8 (47.68); H, 2.6 (2.53); N, 2.8 (2.93)%. IR(cm^{-1}) 1631s ν(C=N). ^{1}H NMR (E/Z composition 1:1): 9.00–8.35 eight br singlets (methinic protons), 7.80–6.40 (aromatic protons). Positive FAB (selected data): 958 ([M]$^+$), 877 ([M–Br]$^+$).

6.4. Preparation of 2c

A solution formed by 2.23 mmol (0.500 g) of Pd(O$_2$CMe)$_2$, 2.23 mmol (0.774 g) of **1c** and 30 cm^3 of chloroform was stirred at room temperature for 24 h and the resulting solution was concentrated to dryness. 4.46 mmol (0.387 g) of LiBr and 30 cm^3 of ethanol were added to the residue and the resulting suspension was stirred at room temperature for 30 min. The precipitate was filtered off and eluted through a column of SiO$_2$ with chloroform. **2c** was isolated as a yellow powder (0.557 g, 47%) from the first colored band by concentration of the solvent and addition of ethanol (10 cm^3) to the residue. Found (Anal. Calc. for C$_{44}$H$_{40}$Br$_2$N$_2$O$_6$Pd$_2$): C, 48.5 (49.60); H, 3.7 (3.78); N, 2.5 (2.63)%. IR (cm^{-1}) 1600s ν(C=N). ^{1}H NMR: 8.40 s (1H, methinic proton), 7.80–6.80 (8H, aromatic protons), 6.24 s (2H, aromatic protons), 3.95 s (6H, aliphatic protons), 3.90 s (3H, aliphatic protons). Positive FAB (selected data): 1066 ([M]$^+$), 985 ([M–Br]$^+$).

6.5. Preparation of 3

A stirred suspension of 30 cm^3 of acetone and 0.10 mmol of the corresponding compound **2** was treated with PPh$_3$ (0.20 mmol, 0.052 g) at room temperature for 30 min. The resulting solution was concentrated in vacuum and the residue eluted through a column of SiO$_2$ with chloroform for the preparation of **3a** and **3b** and chloroform and methanol (100:2) for the preparation of **3c**. The yellow bands were collected and concentrated in vacuum. Compounds **3** were obtained as pale yellow solids after addition of diethyl ether (10 cm^3) to the residues. **3a**: (0.090 g, 60%). Found (Anal. Calc. for C$_{37}$H$_{27}$BrCl$_2$NPPd): C, 57.8 (57.43); H, 3.7 (3.52); N, 1.9 (1.81)%. IR(cm^{-1}) 1632s ν(C=N). ^{1}H NMR (E/Z composition 5:1): 9.10 br d $^4J_{PH}$ = 5.0 Hz (methinic proton of the isomer with the imine in Z configuration), 8.71 d $^4J_{PH}$ = 11.1 Hz (methinic proton of the isomer

with the imine in E configuration), 7.75–6.30 (aromatic protons). ^{31}P{^{1}H} RMN: 35.13 s, 34.48 s. Positive FAB (selected data): 694 ([M–Br]$^+$). **3b**: (0.105 g, 68%). Found (Anal. Calc. for C$_{37}$H$_{27}$BrF$_2$NPPd): C, 59.6 (59.98); H, 3.7 (3.67); N, 1.8 (1.89)%. IR (cm^{-1}) 1625s ν(C=N). ^{1}H NMR (E/Z composition 5:1): 9.10 br signal (methinic proton of the isomer with the imine in Z configuration), 8.65 d $^4J_{PH}$ = 11.6 Hz and 8.62 d $^4J_{PH}$ = 11.6 Hz (methinic protons of two conformational isomers of the isomer with the imine in E configuration), 7.80–6.30 (aromatic protons). ^{31}P{^{1}H} RMN: 34.96 s, 34.24 s. Positive FAB (selected data): 660 ([M–Br]$^+$). **3c**: (0.105 g, 70% yield). Found (Anal. Calc. for C$_{40}$H$_{35}$NO$_3$BrPPd): C, 59.9 (60.43); H, 4.4 (4.44); N, 1.7 (1.76)%. IR(cm^{-1}) 1607s ν(C=N). ^{1}H NMR (E/Z composition 4:1): 9.07 d $^4J_{PH}$ = 5.0 Hz and 9.00 d $^4J_{PH}$ = 5.0 Hz (methinic protons of two conformational isomers of the isomer with the imine in Z configuration), 8.78 d $^4J_{PH}$ = 12.6 Hz and 8.76 d $^4J_{PH}$ = 12.6 Hz (methinic protons of two conformational isomers of the isomer with the imine in E configuration), 7.75–6.49 and 6.07–6.85 (aromatic protons), 3.89–3.43 (aliphatic protons). ^{31}P{^{1}H} RMN: 34.54 s, 33.72 s, 33.34 s. Positive FAB (selected data): 660 ([M–Br]$^+$).

6.6. Crystal structure determination

A summary of crystallographic data and some details of the refinement are given in Table 2. Suitable crystals for the structure determination of the E isomer of **3c** were grown by slow evaporation of the solvents of a solution of **3c** in CH$_2$Cl$_2$/MeOH (1/1). A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections (8 < Θ < 12°) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using $\omega/2\Theta$ scan-technique. 9937 reflections were measured in the range 2.15 ≤ Θ ≤ 30.06°. 6181 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization, but not absorption corrections, were made.

The structure was solved by Patterson synthesis, using SHELXS computer program [28] and refined by full-matrix least-squares method with SHELXL computer program [29] using 9937 reflections. The function minimized was $\Sigma w\|Fo|^2 - |Fc|^2|^2$, where $w = [\sigma^2(I) + (0.0526P)^2]^{-1}$, and $P = (|Fo|^2 + 2|Fc|^2)/3$. f, f' and f'' were taken from International Tables of X-Ray Crystallography [30]. The extinction coefficient was 0.0000(3). All hydrogen atoms were computed and

Table 2
Crystal data and structure refinement for the E isomer of **3c**

Empirical formula	$C_{40}H_{35}BrNO_3PPd$
Formula weight	794.97
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_1/a$
Unit cell dimensions	$a = 19.258(3)$ Å
	$b = 13.177(2)$ Å
	$c = 14.660(2)$ Å
	$\beta = 113.78(2)°$
Volume	3404.3(9) Å^3
Z	4
Density (calculated)	1.551 mg/m^3
Absorption coefficient	1.806 mm^{-1}
$F(000)$	1608
Crystal size	$0.1 \times 0.1 \times 0.2$ mm
Θ range for data collection	2.15 to 30.06°
Index ranges	$-27 < = h < = 24$
	$0 < = k < = 18$
	$0 < = l < = 20$
Reflections collected	9937
Independent reflections	9937 [$R(int) = 0.0000$]
Observed reflections [$I > 2\sigma(I)$]	6181
Refinement method	Full-matrix least-squares on F^2
Refined parameters	426
Goodness of fit on F^2	0.976
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0479, wR2 = 0.1024$
R indices all data	$R1 = 0.1691, wR2 = 0.2411$
Extinction coefficient	0.0000(3)
Largest diff. peak and hole	0.432 and -0.664 e Å^{-3}

refined with an overall isotropic temperature factor using a riding model. The final R (on F) factor was 0.047, wR (on $|F|^2$) = 0.102 and goodness of fit = 0.976 for all observed reflections. Number of refined parameters was 426. Max. shift/esd and mean shift/esd were 1.2 and 0.01, respectively. Max. and min. peaks in final difference synthesis were 0.432 and -0.664 e Å^{-3}, respectively.

7. Supplementary material

Additional material available from the Cambridge Crystallographic Data Center comprises atomic coordinates, hydrogen atom coordinates, bond lengths and angles, anisotropic displacement parameters and observed and calculated structure factors.

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