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Cyclometallation of 3,5 disubstituted *N*-benzylideneamines by palladium(II). Synthesis and X-ray crystal structure of [Pd(3,5-$F_2C_6H_2CH$=NC_6H_5)Br(PPh_3)$_2$]

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Abstract

The action of $Pd(AcO)_2$ on the imines $C_6R_mH_{5-m}CH$=$N(CH_2)_nC_6H_5$ have been studied. Five-membered *endo* metallacyles were obtained from the imines **1a** (R = 3,5-F_2, *n* = 0), **1b** (R = 3,5-F_2, *n* = 1), **1c** (R = 3,5-$(MeO)_2$, *n* = 0) and **1d** (R = 3,5-$(MeO)_2$, *n* = 1), by activation of a C(aromatic)–H bond, in spite of the presence of MeO or F substituents on the carbon atom adjacent to the metallation position. ^{1}H NMR spectra of the acetate bridged compounds [{Pd(C–N)(μ-AcO)}$_2$] (**2a–d**) obtained show the existence of different isomers in solution. Complexes [PdBr(C–N)(PPh_3)] (**4**) and [PdBr(C–N)(PPh_3)$_2$] (**5**) can be obtained by the action of PPh_3 on the new cyclometallated compounds. [Pd(3,5-$F_2C_6H_2CH$=NC_6H_5)Br(PPh_3)$_2$] crystallizes in the space group $P2_1/a$ with a = 20.224(4), b = 17.447(3), c = 12.290(2) Å, β = 110.12(3)° and Z = 4. The dihedral angle between the metallated phenyl ring and the coordination plane is 86.6°. An N=CH proton and a fluorine atom *ortho* to the Pd–C bond occupy the apical positions in the coordination sphere of the palladium atom.

Keywords: Palladium; Cyclometallation; Benzylideneamine complexes; Dinuclear complexes; X-ray structure; Imine

1. Introduction

In the last decade, much research has been reported on the activation by transition metal complexes of C–H bonds. Cyclopalladation is one of the classical ways to activate C–H bonds in heterosubstituted organic molecules, and its use in organic synthesis has attracted much attention [1].

Schiff bases are suitable ligands to study cyclometallation reactions since they undergo metallation on different carbon atoms (polyfunctional ligands). We have shown that imines have a strong tendency to form endocyclic cyclometallated compounds (with the C=N bond contained within the metallacycle). This tendency, the *endo* effect, is so strong that the action of $Pd(AcO)_2$ on the imine 2,4,6-$Me_3C_6H_2CH$=$NCH_2C_6H_5$, in refluxing acetic acid affords the cyclometallated compound [{Pd{1-CH_2-2-(CH=NCH$_2C_6H_5$)3,5-$Me_2C_6H_2$}-(μ-AcO)}$_2$], where the activation of a C(aliphatic)–H bond with formation of a six-membered *endo* metallacycle takes place in preference to activation of a C(aromatic)–H bond with formation of a five-membered *exo* metallacycle [2].

This *endo* effect is not restricted to cyclopalladation reactions. Recently, it has been shown that oxidative addition of *ortho*-halogenated imines to palladium(0) complexes affords preferentially the *endo* metallacycles [3]. The reaction between [Pt_2Me_4(μ-SMe_2)$_2$] and *N*-benzylideneamines show that the *endo* effect is also important for platinum corresponds [4]. Moreover, selective activation of C–F bonds with the formation of *endo* compounds takes place even in the presence of the weaker C–H, C–Cl or C–Br bonds, when [Pt_2Me_4(μ-SMe_2)$_2$] reacts with ArCH=NCH_2(2-XC_6H_4) (Ar = C_6F_5, 2,3,6-$C_6H_2F_3$ or 2,4,6-$C_6H_2F_3$) [5].

It has been shown that a non-coordinating substituent on the carbon atom adjacent to the metallation position

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hinders the cyclometallation reaction. Thus, the action of $Pd(AcO)_2$ on *N*-2,5-dimethylbenzylideneaniline affords the six-membered *endo* metallacycle by activation of a C(aliphatic)–H bond in preference to the formation of the five-membered *endo* metallacycle, by activation of the C(aromatic)–H bond adjacent to the methyl group [6], although there should be a strong preference for five-membered metallacycles and also a higher tendency to activate C(aromatic)–H bonds than C(aliphatic)–H bonds. In addition, the cyclopalladation of 3,4-dimethoxybenzylideneamines occurs regioselectively at C-6, the less hindered carbon atom [7]. Cyclopalladated compounds have also been prepared from *N*-2,3,4-trimethoxybenzylideneamines, but if the methoxy groups are 2,3,5-, 2,4,5- or 3,4,5-, only Pd^0 is formed in refluxing acetic acid [8]. Recently, van Koten et al. [9] have shown that the cyclopalladation of 2-[(dimethylamino)methyl]naphthalene occurs selectively at position 3 instead of at the earlier reported position 1. They proposed that steric interference of the neighbouring substituents in the 1-metallated transition state can explain the clean palladation at C-3.

In order to obtain additional information on the influence of the steric factors in cyclometallation reactions, we report here the action of $Pd(AcO)_2$ on the *N*-benzylideneamines **1a–d**, in which different metallacycles could, in principle, be obtained by activation of C–H bonds. All these imines have substituents at the carbon atom adjacent to the potential metallation position, which could hinder the formation of *endo* metallacycles.

2. Results and discussion

Imines **1a–d** were treated under dinitrogen with $Pd(AcO)_2$ in anhydrous acetic acid under reflux (**1a** and **1b**) and at 60°C (**1c** and **1d**). Five-membered *endo* metallacycles were obtained by activation of a C(aromatic)–H bond in all cases (see Scheme 1).

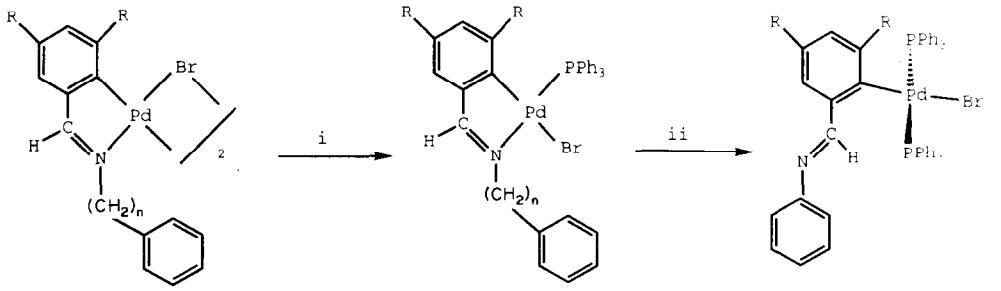
The formation of *endo* metallacycles in spite of the presence of MeO or F substituents on the carbon atom adjacent to the metallation position is remarkable, especially with imines **1b** and **1d**, which could also afford the five-membered *exo* metallacycle by activation of an *ortho* C(aromatic)–H bond of the benzylidene ring [10]. These results show the importance of the so-called *endo* effect in cyclometallation reactions.

It has been shown that a rearrangement occurs in the cyclopalladated compound derived from 3,4,5-trimethoxybenzaldehyde, $[\{PdCl(3,4,5\text{-}(MeO)_3C_6H\text{-}CHO)\}_2]$, to the 2,3,4-trimethoxybenzaldehyde derivative $[\{PdCl(2,3,4\text{-}(MeO)_3C_6HCHO)\}_2]$, in which there is no MeO group adjacent to the Pd–C bond [11]. Such a rearrangement was not observed in the imines studied here, consistent with published results on related imine derivatives [12].

In the IR spectra of these compounds, the $\nu(C{=}N)$ bands is shifted slightly towards lower wavenumbers by ca. 20–30 cm^{-1} with respect to the free imine, suggesting interaction between the nitrogen lone pair and the palladium atom [13]. Bands appearing at ca. 1580 and 1420 cm^{-1} show that the acetate is bridging [14].

The characterization of acetato-bridged cyclometallated compounds is not easy. The ^1H NMR spectra of such compounds are often recorded in the presence of a small amount of pyridine-d_5, which affords the corresponding mononuclear species, and permits an easy assignment of the signals [15]. These acetato-bridged compounds are usually dinuclear, but there is also evidence for the formation of trinuclear or even polynuclear species [16]. Such complexes can be found in two isomeric forms, *trans* or *cis*, depending on the arrangement around the $Pd_2(\mu\text{-}AcO)_2$ unit [17].

In the ^1H NMR spectra of **2** the acetate proton signals appear as a singlet, showing that the arrangement is *trans* relative to the $Pd_2(\mu\text{-}AcO)_2$ unit (depending on the imine, a small amount of the *cis* isomer is also observed). The ^1H NMR spectra of **2c** and **2d** show two series of signals, assignable to the metallated ring and to the N=CH– protons (see Table 1). When pyridine-d_5 is added, the NMR spectra show that there



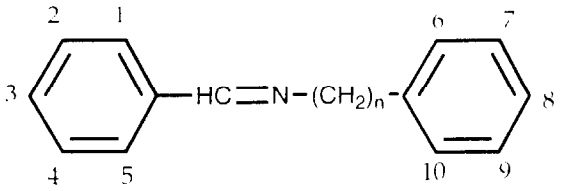
3a (n=0, R=F)
3b (n=1, R=F)
3c (n=0, R=OMe)
3d (n=1, R=OMe)

4a (n=0, R=F)
4b (n=1, R=F)
4c (n=0, R=OMe)
4d (n=1, R=OMe)

5a (n=0, R=F)
5c (n=0, R=MeO)

Scheme 1. (i) PPh_3 (2 eq.), acetone, room temperature, 30 min; (ii) PPh_3 (4 eq.), acetone, room temperature, 1 h.

Table 1
Proton [a] NMR data



Compound	Aromatic	HC=N, aliphatic
2a + pyridine-d_5	7.40–7.20 (br m, 5H, H^6–H^{10}) 7.01 (dd, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^5) 6.48 (td, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^3)	8.05 (s, 1H, HC=N) 1.49 (s, 3H, AcO)
3a + pyridine-d_5	7.40–7.20 (br m, 5H, H^6–H^{10}) 7.06 (dd, ^3J(FH) = 7.7, ^4J(HH) = 1.8, 1H, H^5) 6.48 (td, ^3J(FH) = 7.7, ^4J(HH) = 1.8, 1H, H^3)	8.10 (s, 1H, HC=N)
4a	7.80–7.20 (br m, 20H, H^6–H^{10}, PPh_3) 7.10 (dd, ^3J(FH) = 8.2, ^4J(HH) = 2.5, 1H, H^5) 6.25 (br t, ^3J(FH) = 8.5, 1H, H^3)	8.30 [d, ^4J(PH) = 7.1, 1H, HC=N]
5a	7.80–6.91 (br m, 36H, H^5, H^6–H^{10}, PPh_3) 5.73 (br m, 1H, H^3)	8.77 (br s, 1H, HC=N)
2b	7.30–6.90 (br m, 4H, H^6–H^{10}) 6.73 (dd, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^5) 6.55 (td, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^3)	HC=N [b] 4.40 (q AB, 2H, CH_2N) 2.13 (s, 3H, AcO)
3b + pyridine-d_5	7.30–6.90 (br m, 5H, H^6–H^{10}) 6.81 (dd, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^5) 6.40 (td, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^3)	7.71 (s, 1H, HC=N) 5.28 (s, 2H, CH_2N)
4b	7.80–7.20 (br m, 20H, H^6–H^{10}, PPh_3) 6.85 (dd, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^5) 6.12 (td, ^3J(FH) = 7.9, ^4J(HH) = 2.2, 1H, H^3)	7.90 (d, ^4J(PH) = 10.5, 1H, HC=N) 5.35 (s, 2H, CH_2N)
2c (folded)	7.30–6.90 (br m, 5H, H^6–H^{10}) 6.79 (d, ^4J(HH) = 2.0, 1H, H^5) 6.03 (d, ^4J(HH) = 2.1, 1H, H^3)	HC=N [b] 3.82 (s, 3H, MeO) 3.17 (s, 3H, MeO) 1.86 (s, 3H, AcO)
2c (unfolded)	7.30–6.90 (br m, 5H, H^6–H^{10}) 6.88 (d, ^4J(HH) = 2.0, 1H, H^5) 6.54 (d, ^4J(HH) = 2.1, 1H, H^3)	7.63 (s, 1H, HC=N) 3.82 (s, 3H, MeO) 3.17 (s, 3H, MeO) 1.86 (s, 3H, AcO)
2c + pyridine-d_5	7.40–7.20 (br m, 5H, H^6–H^{10}) 6.67 (d, ^4J(HH) = 2.1, 1H, H^5) 6.18 (d, ^4J(HH) = 2.1, 1H, H^3)	7.99 (s, 1H, HC=N) 3.75 (s, 3H, MeO) 3.07 (s, 3H, MeO) 1.49 (s, 3H, AcO)
3c + pyridine-d_5	7.40–7.20 (br m, 5H, H^6–H^{10}) 6.64 (d, ^4J(HH) = 2.1, 1H, H^5) 6.15 (d, ^4J(HH) = 2.1, 1H, H^3)	7.90 (s, 1H, HC=H) 3.72 (s, 3H, MeO) 3.07 (s, 3H, MeO)
5c	7.80–6.91 (br m, 35H, H^6–H^{10}, PPh_3) 6.73 (br d, 1H, H^5) 5.22 (br d, 1H, H^3)	9.15 (br s, 1H, HC=N) 3.63 (s, 3H, MeO) 3.11 (s, 3H, MeO)
2d (folded)	7.30–6.90 (br m, 5H, H^6–H^{10}) 6.34 (d, ^4J(HH) = 2.0, 1H, H^5) 6.23 (d, ^4J(HH) = 2.1, 1H, H^3)	7.04 (s, 1H, HC=N) 4.35 (q AB, 2H, CH_2N) 3.74 (s, 3H, MeO) 3.69 (s, 3H, MeO) 2.12 (s, 3H, AcO)
2d (unfolded)	7.30–6.90 (br m, 5H, H^6–H^{10}) 6.48 (d, ^4J(HH) = 2.01, 1H, H^5) 6.28 (d, ^4J(HH) = 2.1, 1H, H^3)	7.58 (s, 1H, HC=N) 4.80 (s, 2H, CH_2N) 3.79 (s, 3H, MeO) 3.72 (s, 3H, MeO) 2.12 (s, 3H, AcO)
2d + pyridine-d_5	7.40–7.20 (br m, 5H, H^6–H^{10}) 6.46 (d, ^4J(HH) = 2.1, 1H, H^5) 6.10 (d, ^4J(HH) = 2.1, 1H, H^3)	7.63 (s, 1H, HC=N) 4.82 (s, 2H, CH_2N) 3.69 (s, 3H, MeO) 3.02 (s, 3H, MeO) 1.88 (s, 3H, AcO)

Table 1 (continued)

Compound	Aromatic	HC=N, aliphatic
3d + pyridine-d_5	7.45–7.20 (br m, 5H, H^6–H^{10})	7.72 (s, 1H, HC=N)
	6.47 (d, ^4J(HH) = 2.1, 1H, H^5)	5.20 (s, 2H, CH_2N)
	6.11 (d, ^4J(HH) = 2.1, 1H, H^3)	3.70 (s, 3H, MeO)
		3.01 (s, 3H, MeO)
4d	7.80–7.20 (br m, 20H, H^6–H^{10}, PPh_3)	7.89 (d, ^4J(PH) = 11.0, 1H, HC=N)
	6.47 (d, ^4J(HH) = 2.1, 1H, H^5)	5.36 (s, 2H, CH_2N)
	5.73 (br m, 1H, H^3)	3.68 (s, 3H, MeO)
		2.31 (s, 3H, MeO)

[a] In $CDCl_3$; chemical shifts in ppm with respect to internal $SiMe_4$; coupling constants in Hz; numbering as in the structure shown.
[b] Not visible: resonance under aromatic protons.

is only one compound in solution, obviously the mononuclear complex [Pd(AcO)(C–N)(py-d_5)]. Consequently, the two isomeric forms of the acetato-bridged compounds **2** in solution are a function of the dinuclear structure. The CH_2N protons appear as an AB quartet for one of the conformational isomers in solution, showing that these protons are diastereotopic. This is consistent with an open book structure (folded), which has been previously found by X-ray diffraction studies of some cyclopalladated acetate-bridge dimers [18]. The CH_2N protons appears as a singlet for the other isomer, showing that these protons are isochronous. This can be explained if this isomer adopts an unfolded structure (see Scheme 2). Molecular models allow this possibility and rule out the planar structure of some halo-bridged cyclometallated derivatives found by X-ray studies [19]. The chemical shifts of the two series of signals are also consistent with these two different structures, since the signals of the folded isomer appear at higher field owing to interaction with the other fragment of the dinuclear molecule.

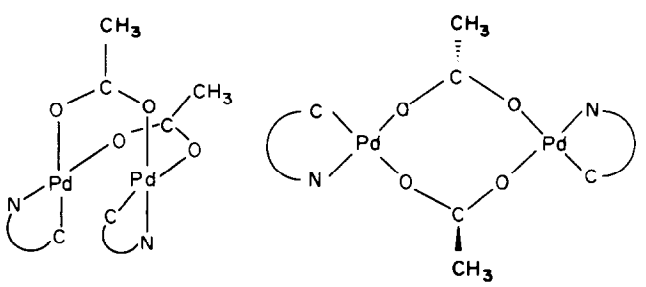
The reaction between compounds **2** and LiBr in ethanol afforded the bromo-bridged cyclometallated compounds **3**. These compounds are almost insoluble and their ^{1}H NMR spectra were obtained in presence of pyridine-d_5, which affords the corresponding monomeric compounds [PdBr(C–N)(py-d_5)].

2.1. Reaction with PPh_3

The action of PPh_3 on the cyclometallated compounds **3** [{PdBr(C–N)}$_2$] in a 2:1 molar ratio was studied in order to obtain mononuclear complexes. Compounds **4** [PdBr(C–N)(PPh_3)] were obtained in all cases, but compounds **5**, [PdBr(C–N)(PPh_3)$_2$], were also formed with aniline derivatives (imines **1a** and **1c**). Aromatic protons of the palladated ring in compounds **4** resonate at higher field in the ^{1}H-NMR spectra. This is caused by a phosphine phenyl ring, and indicates a *cis* arrangement of the phosphine and the metallated carbon atom and, in consequence, a *trans* arrangement between phosphorus and nitrogen atoms [6,10]. The N=CH– proton signal in **4** appears shifted to high field relative to that of the free imine and, coupled with the phosphorus atom, ^4J(PH) being ca. 6–12 Hz, consistent with an endocyclic structure with a *trans* arrangement between phosphorus and nitrogen atoms [6].

The action of PPh_3 on cyclometallated compounds **3** in a 4:1 molar ratio gives complexes **5**, *trans*-[PdBr(C–N)(PPh_3)$_2$], without a Pd–N bond, only if the imine is an aniline derivative. In ^{1}H NMR spectra, the N=CH– proton signal is shifted down field (δ = 8.75 and 9.15 ppm for **5a** and **5c**, respectively) compared with compounds **4**, which contain only one PPh_3 molecule per palladium atom. This shift shows a close approach between this proton and the palladium atom, and can be explained by the paramagnetic anisotropy of the metal [20] or by the existence of a weak three-centre, four-electron interaction C–H · · · M [21]. The X-ray structure of **5a** confirms the proximity of these atoms (see below).

The stability of the Pd–N bond in cyclometallated derivatives is, in general, highly dependent on the basicity of the nitrogen atom. Thus, whereas the action of an excess of PPh_3 on *N*-benzylideneaniline derivatives gives complexes without Pd–N bonds, *N*-benzylidenebenzylamine derivatives with a more basic nitrogen atom form only cyclometallated compounds [6]. The results described here are consistent with this, since it is possible to prepare compounds **5** without a Pd–N bond only with benzylideneaniline derivatives. It should be noted that in the preparation of aniline derivatives [PdBr(C–N)(PPh_3)] the formation of **5** is also observed, even if a stoichiometric amount of PPh_3 is used, and careful recrystallization is needed to obtain **4a** pure. This result has not been reported before in the study of



Scheme 2.

analogous cyclopalladated compounds without substituents in *ortho* positions to the Pd–C bond. The chelating nature of the imine ligand (*C*- and *N*-bonded in **4**) implies that substituents adjacent to palladium should be in the coordination plane and, in consequence there is a strong interaction with the PPh_3 that increases the reactivity of the Pd–N bond. These results show that the existence of such substituents permits fine-tuning of the reactivity of cyclopalladated compounds, since their presence is not sufficient to permit the preparation of **5** if the imine is a benzylamine derivative, but it increases the reactivity of the Pd–N bond in the aniline derivatives. Analogous results have been found for cycloplatinated imine derivatives, in which the presence of a fluorine substituent *ortho* to the Pt–C bond hinders the formation of the cycloplatinated species [PtMe(C–N)(PPh_3)] [22].

In the ^{19}F NMR spectra of **4a** and **4b** (see Experimental), the signal of the fluorine atom adjacent to the Pd–C bond appears at $\delta = -83.1$ and -84.1 ppm (relative to CF_3COOH) respectively, and it is coupled with the phosphorus atom.

The $^{31}P\{^1H\}$ NMR spectra (see Experimental) confirm the *trans* arrangement of the phosphine and the imine nitrogen in **4** and the *trans* arrangement of the phosphorus atoms in **5**. The signals appear as a doublet in **4a** and **4b**, $J(FP) = 39.8$ and 39.5 Hz, respectively. In contrast, this coupling is clearly lower in **5a**, $J(FP) = 10.3$ Hz, and can only be observed at low temperature (220 K) after Gaussian–Lorentz multiplication of the FID to enhance resolution. The different coupling constants in compounds **4** and **5** may be a consequence of their different structures, since there is formal four-bond coupling in each case. This difference can be explained if it is assumed that in complexes **4** there is through-space coupling between the phosphorus and the fluorine adjacent to the Pd–C bond, which are very close, as seen in molecular models. The different values of $J(FP)$ can also be explained by an extension of the well known Karplus–Conroy relation [23], which correlates $^3J(H–H)$ or more generally $^3J(A–B)$ with the conformation the dihedral angle enclosed by the A–C–C–B connection. In **4a** both nuclei are coplanar, as a consequence of the chelation of the imine, and a maximum J value is expected, but in **5a** the dihedral angle between the coordination plane and the metallated ring

Table 2
Summary of crystallographic data for **5a**

Formula	$C_{49}H_{38}BrF_2NP_2Pd$
Molecular mass	927.11
Crystallographic system	Monoclinic
Space group	$P2_1/a$
a (Å)	20.224(4)
b (Å)	17.447(3)
c (Å)	12.290(2)
β (°)	100.12(3)
V (Å^3)	4072(2)
d_{calc} (g cm^{-3})	1.512
Z	4
$F(000)$	1872.0
Crystal size (mm^3)	$0.1\times0.1\times0.2$
μ (Mo Kα) (cm^{-1})	16.13
λ (Mo Kα) (Å)	0.71069
T (°C)	25
Total No. of reflections	4345
No. of reflections with $I \geq 2.5\sigma(I)$	3156
R	0.048
R_w	0.054

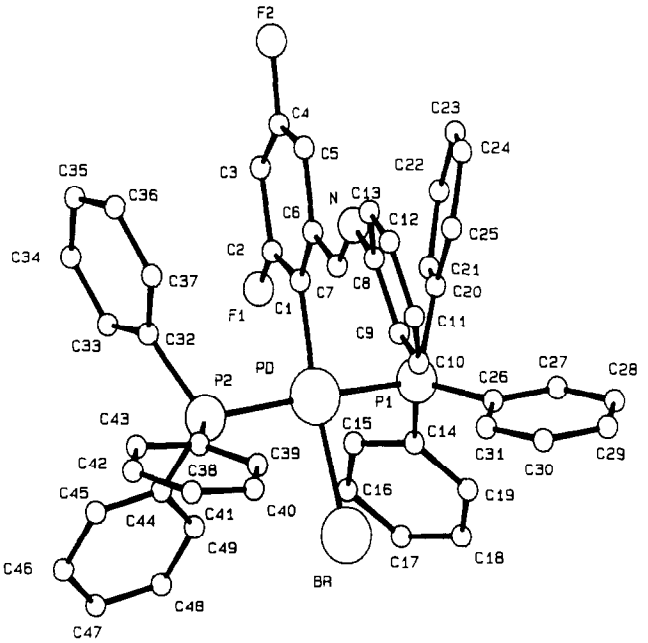


Fig. 1. Molecular structure of **5a**.

is nearly 90° (see crystal structure discussion) and a minimum J value is expected.

2.2. Molecular structure of 5a

The crystal structure of **5a** has been determined (Fig. 1). Crystallographic data and selected bond lengths and angles are listed in Tables 2 and 3 and atomic coordinates for non-hydrogen atoms are given in Table 4.

The crystal structure consists of discrete molecules separated by van der Waals distances. The palladium atom is square-planar, coordinated to carbon, bromine and the two phosphorus atoms. The coordination plane shows some tetrahedral distortion, the deviation from the mean plane being +0.140(1), +0.169(8), −0.179(3) and −0.169(3) Å for Br, C-1, P-1 and P-2, respectively. The phosphorus atoms are *trans*. The angles between adjacent atoms in the coordination sphere lie in the range 91.7(3) (C-1–Pd–P-2) 87.3(3)° (P-1–Pd–Br). The distances between palladium and the coordinated atoms are similar to those reported for analogous cyclopalladated compounds [10,16b,24].

The dihedral angle between the metallated ring and the coordination plane is 86.6(4)°. The fluorine atom *ortho* to the Pd–C bond and the N=CH– proton occupy apical sites in the coordination sphere, the Pd · · · F and Pd · · · H distances being 3.16(1) and 2.72(2)° Å, respectively. Occasionally the apical sites of formally square-planar cyclopalladated compounds are occupied by atoms such as the imine nitrogen [16b,24], *ortho*-methyl groups as in lutidine [25], and a hydrogen atom of a $CH_3CH=N$ group [26].

The metallated phenyl ring and the N=CH– moiety are nearly planar, the dihedral angle between them being 6.28°. The metallated phenyl and the aniline groups are *trans* to the C=N bond, showing that the imine is in the *E*-conformation. The dihedral angle between the moieties is 16.9°.

3. Experimental

^1H, $^{31}P\{^1H\}$, ^{19}F NMR and $^{13}C\{^1H\}$ NMR spectra were obtained using Varian XL-200 (200 MHz), Bruker

Table 3
Selected bond distances (Å) and angles (°) for **5a**

Br–Pd	2.486(1)	C(2)–C(1)	1.456(13)
P(1)–Pd	2.323(3)	C(6)–C(1)	1.408(14)
P(2)–Pd	2.336(2)	C(3)–C(2)	1.460(15)
C(1)–Pd	2.023(8)	C(4)–C(3)	1.366(17)
C(14)–P(1)	1.773(6)	C(5)–C(4)	1.473(15)
C(20)–P(1)	1.819(5)	C(6)–C(5)	1.447(14)
C(26)–P(1)	1.841(5)	C(7)–C(6)	1.461(12)
C(32)–P(2)	1.847(5)	C(9)–C(8)	1.395
C(38)–P(2)	1.850(5)	C(13)–C(8)	1.395
C(44)–P(2)	1.783(6)	C(10)–C(9)	1.395
C(2)–F(1)	1.212(13)	C(11)–C(10)	1.395
C(4)–F(2)	1.442(11)	C(12)–C(11)	1.395
C(7)–N	1.200(13)	C(13)–C(12)	1.395
C(8)–N	1.460(11)		
P(1)–Pd–Br	87.3(1)	C(6)–C(1)–C(2)	121.5(8)
P(2)–Pd–Br	92.3(1)	C(1)–C(2)–F(1)	126.1(10)
P(2)–Pd–P(1)	169.5(1)	C(3)–C(2)–F(1)	115.7(10)
C(1)–Pd–Br	173.1(3)	C(3)–C(2)–C(1)	118.2(11)
C(1)–Pd–P(1)	89.9(3)	C(4)–C(3)–C(2)	115.1(11)
C(1)–Pd–P(2)	91.7(3)	C(3)–C(4)–F(2)	119.3(10)
C(14)–P(1)–Pd	106.7(3)	C(5)–C(4)–F(2)	108.8(10)
C(20)–P(1)–Pd	118.0(3)	C(5)–C(4)–C(3)	131.8(10)
C(20)–P(1)–C(14)	104.2(3)	C(6)–C(5)–C(4)	109.1(10)
C(26)–P(1)–Pd	115.5(2)	C(5)–C(6)–C(1)	124.0(9)
C(26)–P(1)–C(14)	109.8(3)	C(7)–C(6)–C(1)	118.9(8)
C(26)–P(1)–C(20)	102.0(3)	C(7)–C(6)–C(5)	117.1(10)
C(32)–P(2)–Pd	114.6(3)	C(6)–C(7)–N	120.9(9)
C(38)–P(2)–Pd	114.4(3)	C(9)–C(8)–N	121.5(6)
C(38)–P(2)–C(32)	103.3(4)	C(13)–C(8)–N	118.5(6)
C(44)–P(2)–Pd	113.8(3)	C(13)–C(8)–C(9)	120.0
C(44)–P(2)–C(32)	101.6(3)	C(10)–C(9)–C(8)	120.0
C(44)–P(2)–C(38)	107.8(4)	C(11)–C(10)–C(9)	120.0
C(8)–N–C(7)	121.5(9)	C(12)–C(11)–C(10)	120.0
C(2)–C(1)–Pd	115.4(8)	C(13)–C(12)–C(11)	120.0
C(6)–C(1)–Pd	123.1(6)	C(12)–C(13)–C(8)	120.0

WP 80SY (32.4 MHz), Varian XL300 FT (282.2 MHz) and Varian XL-200 (50.3 MHz) spectrometers, respectively. IR spectra were recorded as KBr discs on a Nicolet 520 FT-IR spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC) and by the Serveis Científico-Tècnics de la Universitat de Barcelona.

3.1. Materials and synthesis

Solvents were dried and distilled before use. The imines were obtained from the corresponding benzaldehydes and the appropriate amines under standard conditions (refluxing ethanol) [27].

3.1.1. Compounds **2a** and **2b**

A stirred suspension of $Pd(O_2CMe)_2$ (2.23 mmol, 0.5 g) in acetic acid (30 cm^3) was treated with the corresponding imine (2.23 mmol) and heated under reflux for 45 min. The resulting solution was concentrated in vacuo and the residue purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100:2) as eluent. Compounds **2a** and **2b** were eluted in the first intensely coloured band and isolated in the solid state after concentration of the solvents and addition of diethyl ether: **2a**, yield 391 mg (46%). Found: C, 46.3; H, 2.9; N, 3.6. $C_{30}H_{22}F_4N_2O_4Pd_2$ requires C, 47.20; H, 2.90; N, 3.70%. **2b**, yield 298 mg (34%). Found: C, 48.5; H, 3.3; N, 3.4. $C_{32}H_{26}F_4N_2O_4Pd_2$ requires C, 48.60; H, 3.30; N, 3.55%).

3.1.2. Compounds **2c** and **2d**

A stirred suspension of $Pd(O_2CMe)_2$ (2.23 mmol, 0.5 g) in acetic acid (30 cm^3) was treated with the corresponding imine (2.23 mmol) for 4 h at 60°C under dinitrogen using Schlenk techniques. The resulting solution was concentrated in vacuo and the residue of the reaction was purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100:2) as eluent. Compounds **2c** and **2d** were eluted in the first intensely coloured band and isolated in the solid state after concentration of the solvents and addition of diethyl ether: **2c**, yield 362 mg (40%). Found: C, 49.7; H, 4.0; N, 3.5. $C_{34}H_{34}N_2O_8Pd_2$ requires C, 50.35; H, 4.20; N, 3.45%. **2d**, yield 393 mg (42%). Found: C, 51.2; H, 4.3; N, 3.2. $C_{36}H_{38}N_2O_8Pd_2$ requires C, 51.50; H, 4.55; N, 3.35%.

3.1.3. Compounds **3a** and **3b**

A stirred suspension of compound **2a** or **2b** (0.5 mmol) in EtOH (30 cm^3) was treated with LiBr (1 mmol, 0.087 g) for 15 min at room temperature. The precipitate was filtered off and washed with ethanol: **3a** yield 245 mg (61%). Found: C, 39.3; H, 2.1; N, 3.5. $C_{26}H_{16}Br_2F_4N_2Pd_2$ requires C, 38.80; H, 2.00; N, 3.50%. **3b**, yield 354 mg (85%). Found: C, 41.3; H, 2.4; N, 3.4. $C_{28}H_{20}Br_2F_4N_2Pd_2$ requires C, 40.40; H, 2.40; N, 3.35%.

Table 4
Final atomic coordinates ($\times 10^4$; Pd, Br and P-1 and P-2 $\times 10^5$) of **5a**

Atom	x	y	z	B_{eq} [a]
Pd	14176(3)	21899(4)	19575(7)	2.16(3)
Br	24231(7)	25263(8)	13221(13)	5.20(7)
P(1)	9598(12)	33946(14)	13122(24)	2.51(11)
P(2)	17664(12)	9079(14)	22570(25)	2.78(12)
F(1)	−160(3)	1661(4)	763(6)	4.47(33)
F(2)	−1020(4)	1705(4)	3847(7)	6.61(45)
N	1528(5)	2458(6)	5601(10)	4.60(53)
C(1)	641(4)	2018(5)	2619(9)	2.45(42)
C(2)	−29(5)	1764(6)	1791(11)	3.69(56)
C(3)	−612(6)	1632(8)	2212(12)	5.09(71)
C(4)	−470(5)	1792(6)	3358(12)	3.88(57)
C(5)	187(6)	2007(7)	4289(11)	4.77(59)
C(6)	739(4)	2108(5)	3803(10)	2.93(45)
C(7)	1435(5)	2322(5)	4602(9)	2.52(44)
C(8)	2227(3)	2629(5)	6425(7)	5.27(4)
C(9)	2764(3)	2906(5)	6060(7)	5.27(4)
C(10)	3425(3)	3069(5)	6873(7)	5.27(4)
C(11)	3549(3)	2956(5)	8050(7)	5.27(4)
C(12)	3012(3)	2679(5)	8415(7)	5.27(4)
C(13)	2351(3)	2516(5)	7602(7)	5.27(4)
C(14)	836(4)	3435(4)	−187(5)	4.26(3)
C(15)	534(4)	2787(4)	−834(5)	4.26(3)
C(16)	412(4)	2769(4)	−2022(5)	4.26(3)
C(17)	591(4)	3399(4)	−2563(5)	4.26(3)
C(18)	892(4)	4046(4)	−1917(5)	4.26(3)
C(19)	1015(4)	4064(4)	−728(5)	4.26(3)
C(20)	102(3)	3638(4)	1385(6)	3.69(3)
C(21)	−523(3)	3632(4)	434(6)	3.69(3)
C(22)	−1165(3)	3761(4)	591(6)	3.69(3)
C(23)	−1182(3)	3898(4)	1700(6)	3.69(3)
C(24)	−558(3)	3904(4)	2651(6)	3.69(3)
C(25)	84(3)	3774(4)	2494(6)	3.69(3)
C(26)	1502(3)	4211(3)	2065(6)	4.06(3)
C(27)	1263(3)	4963(3)	1819(6)	4.06(3)
C(28)	1674(3)	5570(3)	2428(6)	4.06(3)
C(29)	2324(3)	5425(3)	3283(6)	4.06(3)
C(30)	2563(3)	4673(3)	3528(6)	4.06(3)
C(31)	2152(3)	4066(3)	2919(6)	4.06(3)
C(32)	1129(3)	268(4)	2578(6)	4.13(3)
C(33)	622(3)	−131(4)	1697(6)	4.13(3)
C(34)	94(3)	−537(4)	1939(6)	4.13(3)
C(35)	74(3)	−543(4)	3062(6)	4.13(3)
C(36)	581(3)	−144(4)	3943(6)	4.13(3)
C(37)	1108(3)	262(4)	3701(6)	4.13(3)
C(38)	2591(3)	746(4)	3492(6)	4.42(3)
C(39)	3017(3)	1375(4)	3976(6)	4.42(3)
C(40)	3663(3)	1265(4)	4860(6)	4.42(3)
C(41)	3882(3)	527(4)	5260(6)	4.42(3)
C(42)	3456(3)	−101(4)	4777(6)	4.42(3)
C(43)	2810(3)	8(4)	3893(6)	4.42(3)
C(44)	1857(4)	455(4)	1015(5)	4.08(3)
C(45)	2087(4)	−301(4)	1060(5)	4.08(3)
C(46)	2177(4)	−634(4)	89(5)	4.08(3)
C(47)	2036(4)	−211(4)	−929(5)	4.08(3)
C(48)	1806(4)	546(4)	−974(5)	4.08(3)
C(49)	1716(4)	879(4)	−3(5)	4.08(3)

[a] $B_{eq} = 8\pi^2/3\Sigma U_{ij} A_i^* A_j^* A_i A_j$.

3.1.4. Compounds **3c** and **3d**

A stirred suspension of compound **2c** or **2d** (0.5 mmol) in EtOH (30 cm^3) was treated with LiBr (1

mmol, 0.087 g) for 15 min at room temperature. The precipitate was filtered off and purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100 : 2) as eluent. Compounds **3c** and **3d** were eluted in the first intensely coloured band and isolated in the solid state after concentration of the solvents and addition of ethanol: **3c**, yield 239 mg (56%). Found: C, 42.3; H, 3.3; N, 3.3. $C_{30}H_{28}Br_2N_2O_4Pd_2$ requires C, 42.25; H, 3.30; N, 3.30%. **3d**, yield 251 mg (57%). Found: C, 42.8; H, 3.6; N, 3.1. $C_{32}H_{32}Br_2N_2O_4Pd_2$ requires C, 43.60; H, 3.65; N, 3.15%.

3.1.5. Compounds **4**

Stirred suspensions of compounds **3** (0.25 mmol) were treated with PPh_3 (0.5 mmol, 0.13 g) in acetone (30 cm^3) for 30 min at room temperature and then filtered. The filtrate was concentred in vacuo and the solid obtained after addition of diethyl ether was carefully recrystallized from chloroform–diethyl ether to obtain compounds **4**: **4a**, yield 232 mg (70%). Found: C, 55.6; H, 3.2; N, 2.1. $C_{31}H_{23}BrF_2NPPd$ requires C, 55.99; H, 3.49; N, 2.10%; δ_F ($CDCl_3$) −83.9 (1 F, dt, J(PF) 39.8 Hz, J(HF) 8.8 Hz, J(FF) 8.8 Hz) and −122.7 (1F, br q, J(HF) 8.8 Hz, J(FF) 8.8 Hz); δ_P ($CHCl_3$) 37.1 (d, J(PF) 39.8 Hz). **4b**, yield 295 mg (87%). Found: C, 56.4; H, 3.7; N, 2.1. $C_{32}H_{25}BrF_2NPPd$ requires C, 56.60; H, 3.70; N, 2.05%; δ_F ($CDCl_3$) −84.11 (1 F, dt, J(PF) 39.8 Hz, J(HF) 8.2 Hz, J(FF) 8.2 Hz) and −122.7 (1F, q, J(HF) 8.2, J(FF) 8.2 Hz); δ_P ($CHCl_3$) 36.0 (d, J(FP) 39.8 Hz). **4d**, yield 221 mg (63%). Found: C, 57.3; H, 4.4; N, 1.9. $C_{34}H_{31}BrNO_2PPd$ requires C, 58.10; H, 4.40; N, 2.00%; δ_P ($CHCl_3$) 38.6 (s).

3.1.6. Compounds **5**

A stirred suspension of compound **3a** or **3c** (0.25 mmol) was treated with PPh_3 (1 mmol, 0.26 g) in acetone (30 cm^3) for 1 h at room temperature. The precipitate was filtered off and washed with diethyl ether: **5a**, yield 338 mg (73%). Found: C, 63.3; H, 4.3; N, 1.5. $C_{49}H_{38}BrF_2NP_2Pd$ requires C, 63.50; H, 4.10; N, 1.50%; δ_F ($CDCl_3$) −91.2 (br s) and −127.7 (br s); δ_P ($CHCl_3$) 22.7 (d, J(FP) 10.3 Hz). **5c**, yield 271 mg (57%). Found: C, 63.1; H, 4.8; N, 1.4. $C_{51}H_{44}BrNO_2P_2Pd$ requires C, 64.40; H, 4.65; N, 1.45%; δ_P ($CHCl_3$) 23.1 (s).

3.2. Data collection

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($12 \leq \theta \leq 21°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique; 4345 reflections were measured in the range $2 \leq \theta \leq 30°$, 3156 of which were assumed as observed by applying the condition $I \geq 2.5\sigma(I)$. R_{int} (on F) = 0.009, where $R_{int} = \Sigma[|F_o| - |F_o|]/\Sigma|F_o|$. Three reflections were measured every 2 h as orientation and intensity controls, and significant intensity decay was not observed. Lorentz polarization and absorption corrections were made (maximum and minimum transmission factors 0.90 and −0.74, respectively).

3.3. Structure solution and refinement

The structure was solved by Patterson synthesis, using the SHELXS computer program [28] for crystal structure determination, and refined by the full-matrix least-squares method, with the SHELX-76 program [29]. The function minimized was $\Sigma w[|F_o| - k|F_c|]^2$, where $w = \sigma^{-2}(F_o)$; f, f' and f'' were taken from Ref. [30]. All the atoms of phenyl groups were refined with constrained geometry and with an overall isotropic temperature factor, and the remaining atoms were refined anisotropically. The final R factor was 0.048 (wR = 0.054) for all observed reflections. The number of refined parameters was 176. Maximum shift/c.s.d. = 0.4 and maximum and minimum peaks in the final difference synthesis were 0.06 and −0.5 e $Å^{-3}$, respectively.

4. Supplementary material

Tables of structure factors and thermal parameters are available from the authors, and the usual structural details have been deposited with the Cambridge Crystallographic Data Centre.

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