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C- and O-metallation of N-benzylideneamines by palladium (II). Synthesis and X-ray crystal structure of [Pd(2-{CH=N-(CH$_2$)$_2$-4'-(MeO)C$_6$H$_4$}-4,5-(MeO)$_2$C$_6$H$_2$)Br(PPh$_3$)]

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Abstract

The action of Pd(AcO)$_2$ on the imines 3,4-(MeO)$_2$C$_6$H$_3$CH=N(CH$_2$)$_n$C$_6$H$_4$R has been studied. Five-membered endo metallacycles were obtained from the imines **1a** (R = H, n = 0), **1b** (R = 2-MeO, n = 0), **1c** (R = 4-MeO, n = 1) and **1d** (R = 4-MeO, n = 2) by activation of the less hindered C(aromatic)–H bond. A six-membered metallacycle, containing a Pd–O bond, was obtained from the imine **1e**, 2,4,6-(MeO)$_3$C$_6$H$_2$CH=NC$_6$H$_5$, by activation of one of the *ortho* O–CH$_3$ bonds. All these results show the strong tendency of imines to form endocyclic compounds and the importance of steric factors in the process. Complexes [PdBr(C–N)(PPh$_3$)] or even [Pd(AcO)(C–N)(PPh$_3$)], in which the acetate acts as a monodentated ligand, can be obtained by the action of PPh$_3$ on the new cyclometallated compounds. [Pd(2-{CH=N-(CH$_2$)$_2$-4'-(MeO)C$_6$H$_4$}-4,5-(MeO)$_2$C$_6$H$_2$)Br(PPh$_3$)] crystallizes in the triclinic space group $P\bar{1}$ with a = 18.388(3), b = 10.167(2), c = 9.858(2) Å, α = 69.00(2), β = 76.79(2), γ = 78.80(3)° and Z = 2.

Keywords: Palladium; X-ray structure; C-metallation; O-metallation; Cyclopalladation; Cyclometallation

1. Introduction

In the last decade much research has been reported on the activation of C–H bonds by transition metal complexes. Cyclometallation is one of the classic ways to activate C–H bonds selectively in heterosubstituted organic molecules [1], and the preparation of cyclopalladated complexes is a field of great interest as a consequence of their useful applications, for example in organic synthesis [2] or in the design of new metallomesogenes [3] or antitumoral drugs [4]. Optically active cyclopalladated derivatives have also been used for the enantiomeric excess determination [5] and optical resolution [6] of amines and phosphines.

Schiff bases are suitable ligands to study cyclometallation reactions since they can 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 in the metallacycle) [7]. This endo effect is not restricted to cyclopalladation reactions. Recently it has been shown that oxidative addition of *ortho* halogenated imines to palladium(0) or platinum(II) complexes preferentially affords the endo metallacycles [8,9]. It should be noted that the 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$_2$Me$_4$(μ-SMe$_2$)$_2$] reacts with ArCH=NCH$_2$(2-XC$_6$H$_4$), Ar = C$_6$F$_5$, 2,3,6-C$_6$H$_2$F$_3$ or 2,4,6-C$_6$H$_2$F$_3$ and X = H, Cl or Br [10].

It has been shown that the presence of non-coordinating substituents in the carbon atom adjacent to the metallation position hinders the cyclometallation reaction [11], nevertheless the action of Pd(AcO)$_2$ on 3,5

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disubstituted imines affords the endo-metallacycles, although the formation of five-membered exo-metallacycles by activation of C(aromatic)–H bonds is also possible [12].

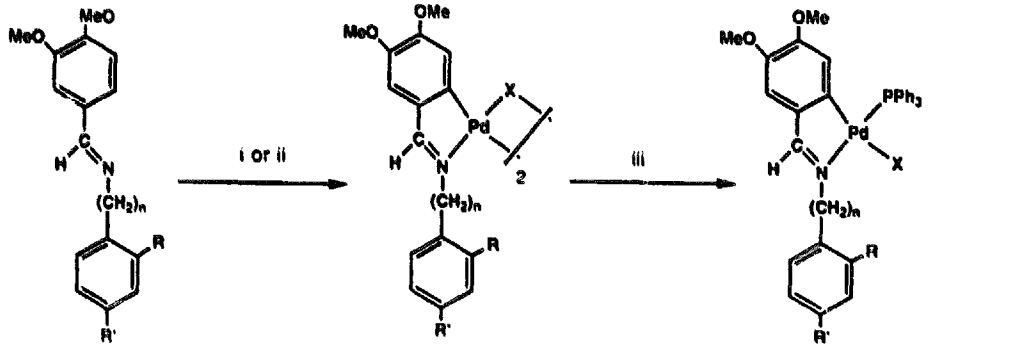
In order to obtain additional information on the factors that influence the ease and mode of cyclometallation reactions, we here report the action of $Pd(AcO)_2$ on the 3,4 disubstituted N-benzylideneamines **1a–d**, in which two different five-membered endo-metallacycles can be formed by activation of C(aromatic)–H bonds. Five- or six-membered exo-metallacycles can also be formed, with the imines **1c** and **1d** respectively.

There are few reports about the activation of $O-CH_3$ bonds by Group 10 transition metal compounds. Shaw and coworkers [13] described the O-metallation of diphenyl(2-methoxyphenyl)phosphine by platinum(II) and Colbran and coworkers [14] reported the O-metallation of 2-(2,5-dimethoxyphenyl)-1,10-phenanthroline by palladium(II) with formation of the corresponding O,N,N coordination compound. Here we report the action of $Pd(AcO)_2$ on the imine **1e**. This ligand could afford a six-membered endo-metallacycle by selective activation of an *ortho* $O-CH_3$ bond, with the formation of an O-metallated chelate. Analogous bidentate N,O ligands, derived from salicylaldehyde, have recently been prepared in order to assess their potential as intermediates for catalytic selective allylic functionalization [15].

2. Results and discussion

The action of $Pd(AcO)_2$ on the imines **1b–d** in anhydrous acetic acid at 60°C under nitrogen and the treatment of the residue obtained with LiBr in ethanol affords, after chromatographic purification, the dinuclear bromo-bridged complexes **2b–d** (see Scheme 1). If the imines **1a**, **1b** and **1c** were treated with $Pd(AcO)_2$ under the above-mentioned conditions but without the subsequent reaction with LiBr, the acetato-bridged complexes **3** were obtained after chromatographic purification. The action of LiBr on **3a** affords the bromo-bridged derivative **2a** in good yield.

Under these experimental conditions the metallation of the less hindered C(aromatic)–H bond is achieved, with formation of five-membered metallacycles in all cases. The purification of the corresponding dinuclear acetato-bridged derivatives is not easy because of their high solubility, which hinders crystallization. In addition, when these acetato derivatives are eluted with chloroform–methanol (100/2) through a column of SiO_2, a certain amount of chloro-bridged derivatives is formed, which hinders their purification. The chloride ligand probably comes from the chloroform used as eluant. Nevertheless, it was possible to obtain pure samples of the acetato-bridged cyclopalladated derivatives **3a–c** by column chromatography. The acetato bands appear at ca. 1580 and 1420 cm^{-1} in the IR spectra of compounds **3**, showing that it is a bridging ligand [16]. The acetate proton signals appear as a singlet at $\delta = 1.80–2.10$ in the ^1H NMR spectra of **3** (see Table 1), in good agreement with a dinuclear acetato-bridged structure with a *trans* arrangement of the C–N ligands relative to the $Pd_2(\mu\text{-}AcO)_2$ fragment. The $\nu(C{=}N)$ band is slightly shifted towards lower wavenumbers, with respect to the free imine, in the IR spectra of **2** and **3**, suggesting interaction between the nitrogen lone pair and the palladium atom [17]. The aromatic and methinic proton signals in the ^1H NMR spectra of **2** (the spectrum of **2a** was recorded in the



1a, R = R' = H, n = 0
1b: R = MeO, R' = H, n = 0
1c; R = H, R' = MeO, n = 1
1d; R = H, R' = MeO, n = 2

2a,b,c,d, X = Br
3a,b,c X = AcO

4a,b,c,d, X = Br
5a,b, X = AcO

Scheme 1. (i) $Pd(AcO)_2$/AcOH at 60°C, 4 h and LiBr/EtOH at 25°C, 15 min to obtain **2**; (ii) $Pd(AcO)_2$/AcOH at 60°C, 4 h to obtain **3**; (iii) PPh_3, acetone, at 25°C, 30 min.

presence of py-d_5 due to its insolubility) and **3** show that in all cases an endo-metallacycle was formed by metallation of the less hindered C–H bond.

Imines **1c** and **1d** might also afford a five- and six-membered exo-metallacycle by activation of C(aromatic)–H bonds, but their formation was not observed. All these results show the strong tendency of imines to form endocyclic compounds and the importance of the steric factors in the process.

2.1. Reaction with PPh_3

The action of PPh_3 on the cyclometallated compounds **2**, $[PdBr(C-N)]_2$, 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. Aromatic protons of the palladated ring in **4** appear high-field shifted in the ^1H NMR spectra. This effect is caused by a phosphine phenyl ring, and indicates a *cis* arrangement of the phosphine and the metallated carbon atom [11a]. The methinic proton signal in **4** appears high-field shifted, relative to that of the free imine, and coupled with the phosphorus atom, $^4J(PH)$ being ca. 6–8 Hz, in good agreement with an endocyclic structure with a *trans* arrangement between phosphorus and nitrogen atoms [18]. The $^{31}P\{^1H\}$ NMR spectra (see Experimental section) confirm the *trans* arrangement between the phosphine and the iminic nitrogen in **4**.

The action of PPh_3 on the cyclometallated compounds **3**, $[Pd(AcO)(C-N)]_2$, in a 2:1 molar ratio was also studied, and mononuclear complexes **5**, $[Pd(AcO)(C-N)(PPh_3)]$, were obtained. IR spectra show $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ separated by 220 cm^{-1}, consistent with unidentate acetate coordination [19]. The acetate proton signals appear as a singlet at $\delta = 1.1-1.0$ in the ^1H NMR spectra of these compounds. The different δ values in relation to those observed in the spectra of the dinuclear compounds **3a–c**, where the acetate is a bridging ligand, confirm the mononuclear coordination of the acetate group in **5**. The monodentate nature of the acetate ligand is unusual for palladium complexes, which generally prefer the acetate group as a bridging ligand between two palladium atoms or as a bidentate ligand to a single palladium, but some palladium compounds, with monodentate acetato ligand, have been characterized by X-ray crystal structure determination [20]. The ^1H and ^{31}P NMR spectra of compounds **5** indicate a *trans* arrangement between phosphorus and nitrogen atoms.

2.2. Molecular structure of 4d

The crystal structure of **4d** has been determined (Fig. 2). 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 in a square-planar environment, coordinated to carbon, nitrogen, bromine and phosphorus atoms. The coordination plane shows some tetrahedral distortion, the deviation from the mean plane being +0.065, +0.089, −0.076 and −0.110 Å for P, N, Br and C11 respectively. The angles between adjacent atoms in the coordination sphere lie in the range 72.1(6) (C11–Pd–N) to 98.9(3)° (C11–Pd–P). The distances between palladium and the coordinated atoms are similar to those reported for other analogous cyclopalladated compounds [21].

The metallacycle is roughly planar, the greatest deviation from the mean plane being −0.119 Å for C10. The dihedral angle between the metallacycle and the coordination plane is 8.6°. The metallated phenyl ring and the aniline ring are in *trans* position relative to the C=N bond, showing that the imine is in the E conformation.

2.3. Activation of $O-CH_3$ bonds

The action of palladium acetate on the imine **1e** in refluxing acetic acid affords **3e**, which by reaction with PPh_3 in acetone affords **5e** (see Scheme 2). Two different endo-metallacycles can be obtained from this ligand: a six-membered metallacycle by activation of an $O-CH_3$ bond, with formation of an O-metallated chelate, or a seven-membered metallacycle by activation of a C(aliphatic)–H bond of one of the methoxy substituents in *ortho* position. A palladium catalytic C–H activation of methoxy groups, that permits the synthesis of substituted pyrans, has recently been described [22].

The analytical data, as well as the ^1H and ^{13}C NMR spectra of **3e** and **5e**, unambiguously show the formation of the O-metallated derivative. In the ^1H NMR spectrum the MeO groups appear as two singlets at $\delta = 3.77$ and 3.57 for **3e** and 3.70 and 3.57 for **5e**, each of which integrates three protons. In the same way the ^{13}C NMR spectrum confirms the proposed structure (see Experimental section). Aromatic protons of the O-metallated ring appear high-field shifted in the ^1H NMR spectrum of **5e**, indicating a *cis* arrangement between this ring and the phosphine ligand. This arrangement is also confirmed by the high value of $J(PH)$ of the methinic proton (15.0 Hz). IR spectra of compounds **3e** and **5e** show ν_{asym} (CO_2) and ν_{sym} (CO_2) separated by 220 cm^{-1}, consistent with unidentate acetate coordination [19]. The acetate proton signals appear as a singlet at $\delta = 1.20-0.90$ ppm in these compounds, in good agreement with the mononuclear coordination of the acetato ligand (see above). The monodentate nature of the acetato group and the fact that signals above $M/2$

Table 1
Proton [a] NMR data

Compound	Aromatic	Others
2a + py-d_5	7.39 (s, 1H, H^5) 7.15–7.05 (br, m, 3H) 6.97 (s, 1H, H^2) 6.80–6.70 (br m, 2H)	7.90 (s, 1H, HC=N) 3.92 (s, 3H, MeO) 3.82 (s, 3H, MeO)
3a	7.20–7.10 (br m, 3H) 6.85 (s, 1H, H^5) 6.80–6.70 (br m, 2H) 5.98 (s, 1H, H^2)	7.58 (s, 1H, HC=N) 3.89 (s, 3H, MeO) 3.55 (s, 3H, MeO) 1.90 (s, 3H, AcO)
4a	7.86–7.33 (br m, 20H, H^6–H^{10}, PPh_3) 6.95 (s, 1H, H^5) 6.05 [d, J(HP) = 6.1 Hz, 1H, H^2]	8.16 [d, J(HP) = 8.5 Hz; 1H, HC=N] 3.79 (s, 3H, MeO) 2.88 (s, 3H, MeO)
5a	7.86–7.32 (br m, 20H, H^6–H^{10}, PPh_3) 6.97 (s, 1H, H^5) 6.03 [d, J(HP) = 5.8 Hz, 1H, H^2]	8.09 [d, J(HP) = 6.4 Hz, 1H, HC=N] 3.82 (s, 3H, MeO) 2.93 (s, 3H, MeO) 1.04 (s, 3H, AcO)
2b	7.40–7.29 (br m, 3H, H^7, H^8, H^{10}) 7.05 (s, 1H, H^5) 6.97(t, J(HH) = 7.8 Hz, 1H, H^9) 6.85 (s, 1H, H^2)	7.90 (s, 1H, HC=N) 3.92 (s, 3H, MeO) 3.86 (s, 3H, MeO) 3.81 (s, 3H, MeO)
3b	7.12 (t, J(HH) = 7.8 Hz, 1H, H^8) 6.85 (s, 1H, H^5) 6.78 (d, J(HH) = 7.8 Hz, 1H, H^{10}) 6.66 (t, J(HH) = 7.8 Hz, 1H, H^9) 6.34 (d, J(HH) = 7.8 Hz, 1H, H^7) 6.11 (s, 1H, H^2)	7.70 (s, 1H, HC=N) 3.88 (s, 3H, MeO) 3.79 (s, 3H, MeO) 3.66 (s, 3H, MeO) 1.81 (s, 3H, AcO)
4b	7.86–7.33 (br m, 18H, H^7, H^8, H^{10}, PPh_3) 7.05–6.95 (m, 2H, H^5, H^9) 6.05 [d, J(HP) = 6.2 Hz, 1H, H^2]	8.15 [d, J(HP) = 8.1 Hz, 1H, HC=N] 3.87 (s, 3H, MeO) 3.79 (s, 3H, MeO) 2.89 (s, 3H, MeO)
5b	7.86–7.32 (br m, 18H, imine, PPh_3) 6.95 (m, 2H) 6.00 [d, J(HP) = 5.2 Hz, 1H, H^2]	8.11 [d, J(HP) = 6.8 Hz, 1H, HC=N] 3.87 (s, 3H, MeO) 3.78 (s, 3H, MeO) 2.92 (s, 3H, MeO) 1.04 (s, 3H, AcO)
2c	7.32 (d, J(HH) = 8.2 Hz, 2H, H^6, H^{10}) 7.10 (s, 1H, H^5) 6.91 (d, J(HH) = 8.2 Hz, 2H, H^7, H^9) 6.70 (s, 1H, H^2)	7.51 (s, 1H, HC=N) 4.88 (br m, 2H, CH_2N) 3.90 (s, 3H, MeO) 3.81 (s, 3H, MeO) 3.77 (s, 3H, MeO)
3c	7.0–6.50 (br m, 7H, H^2, H^5, H^6, H^7, H^9, H^{10} and HC=N)	4.20 (q AB, 2H, CH_2N) 3.84 (s, 3H, MeO) 3.80 (s, 3H, MeO) 3.77 (s, 3H, MeO) 2.17 (s, 3H, AcO)
4c	7.86–7.33 (br m, 17H, H^6, H^{10}, PPh_3) 6.93 (d, J(HH) = 8.4 Hz, 2H, H^7, H^9) 6.72(s, 1H, H^5) 5.93 [d, J(HP) = 6.2 Hz, 1H, H^2]	HC=N [b] 5.28 (s, 2H, CH_2N) 3.72 (s, 3H, MeO) 2.83 (s, 3H, MeO) 3.84 (s, 3H, MeO)
2d	7.23 (m, 3H, H^5, H^6, H^{10}) 6.79 (d, J(HH) = 8.6 Hz, 2H, H^7, H^9) 6.68 (s, 1H, H^2)	7.37 (s, 1H, HC=N) 3.91 (s, 3H, MeO) 3.78 (m, 8H, MeO, CH_2) 3.18 (t, J(HH) = 6.2 Hz, 2H, CH_2)
4d	7.86–7.33 (br m, 17 H, H^6, H^{10}, PPh_3) 6.80 (d, J(HH) = 8.4 Hz, 2H, H^7, H^9) 6.72 (s, 1H, H^5) 5.94 [d, J(HP) = 6.2 Hz, 1H, H^2]	HC=N [b] 4.19 (br, t, 2H, CH_2) 3.77 (s, 3H, MeO) 3.75 (s, 3H, MeO) 3.15 (t, J(HH) = 6.2 Hz, 2H, CH_2) 2.83 (s, 3H, MeO)

Table 1 (continued)

Compound	Aromatic	Others
3e	7.40–7.20 (br m, 5H, H^6–H^{10})	HC=N [b]
	6.21 [d, J(HH) = 2.1 Hz, 1H, H^4]	3.77 (s, 3H, MeO)
	5.44 [d, J(HH) = 2.1 Hz, 1H, H^2]	3.57 (s, 3H, MeO)
		1.18 (s, 3H, AcO)
5e	7.86–7.32 (br m, 20H, H^6–H^{10}, PPh_3)	8.35 [d, J(HP) = 15.0 Hz, HC=N]
	5.65 (br s, 1H, H^4)	3.73 (s, 3H, MeO)
	5.37 [br s, 1H, H^2]	3.59 (s, 3H, MeO)
		0.89 (s, 3H, AcO)

[a] In $CDCl_3$; chemical shift (ppm) with respect to internal $SiMe_4$; coupling constants in Hertz; numbering as in Fig. 1. [b] Not visible: resonance under aromatic protons.

were not observed in the FAB spectrum suggest a dinuclear μ-oxo-bridged structure for **3e**. Some related oxo-bridged palladium complexes have been reported to adopt a binuclear [23] or even a trinuclear [24] structure.

The reaction described here permits the synthesis of bidentate N,O ligands by selective activation of an *ortho* O–CH_3 bond, and shows that the endo effect is not only restricted to the activation of C–H bonds by transition metal compounds but can also be extended to other different reactions.

3. Experimental

^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were obtained using Varian XL-200 (200 MHz), Bruker WP 80SY (32.4 MHz) and Varian XL-200 (50.3 MHz) spectrometers respectively. IR spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC) and the Serveis Científico-Tècnics de la Universitat de Barcelona.

Table 2
Crystal data and structure refinement for **4d**

Empirical formula	$C_{36}H_{35}BrNO_3PPd$
Formula weight	746.97
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 18.388(3) Å, α = 69.00(2)°
	b = 10.167(2) Å, β = 76.79(2)°
	c = 9.858(2) Å, γ = 78.80(3)°
Volume	1662.2(5) Å^3
Z	2
Density (calculated)	1.492 Mg m^3
Absorption coefficient	1.906 mm^{-1}
F(000)	756
Crystal size	0.1 × 0.1 × 0.2 mm^3
Theta range for data collection	2.16 to 30.01°
Index ranges	$-24 \leq h \leq 25$, $-12 \leq k \leq 14$,
	$0 \leq l \leq 13$
Reflections collected	9677
Independent reflections	9677 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9614/0/179
Goodness-of-fit on F^2	0.697
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0598, wR_2 = 0.1343
R indices (all data)	R_1 = 0.2578, wR^2 = 0.5024
Extinction coefficient	0.0000(12)
Largest diff. peak and hole	0.888 and −1.268 e Å^{-3}

3.1. Materials and synthesis

Solvents were dried and distilled before use. The amines and aldehydes were obtained from standard sources and used as received.

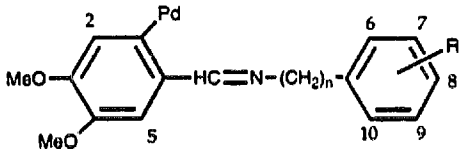


Fig. 1.

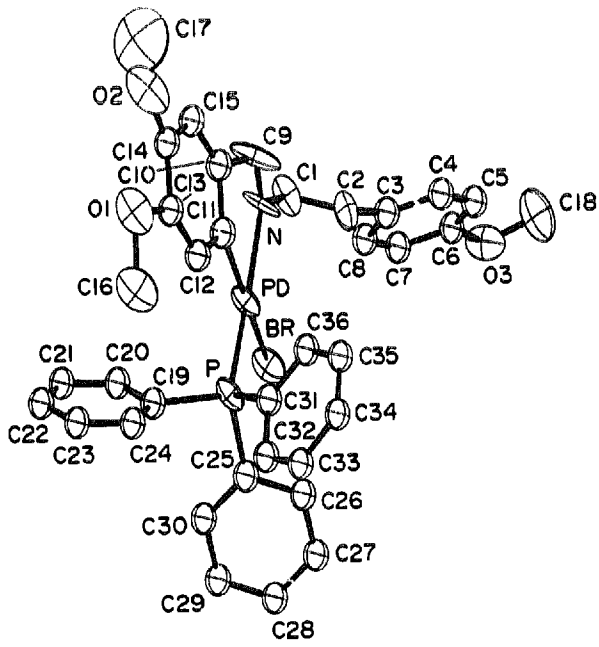


Fig. 2. Molecular structure of **4d**.

Table 3
Bond lengths (Å) and angles (°) for **4d**

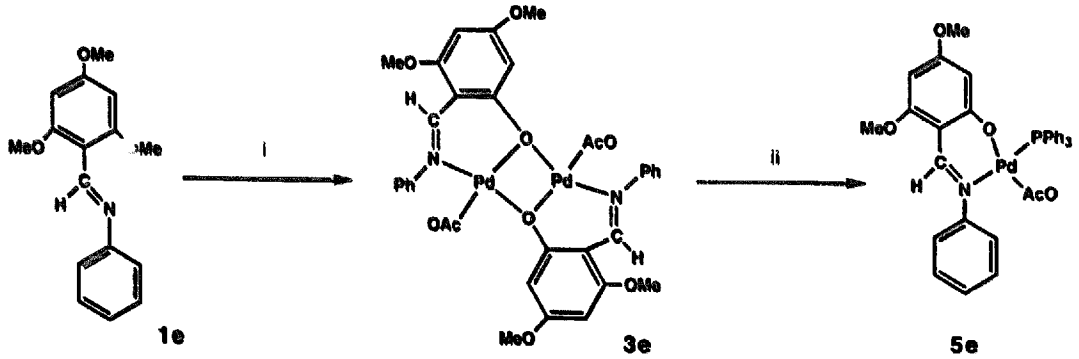
Pd–C(11)	2.016(8)	O(2)–C(14)	1.42(3)
Pd–N	2.168(14)	O(3)–C(18)	1.39(2)
Pd–P	2.250(4)	O(3)–C(6)	1.465(14)
Pd–Br	2.489(3)	N–C(9)	1.12(3)
O(1)–C(13)	1.57(2)	N–C(1)	1.53(2)
O(1)–C(16)	1.59(3)	C(1)–C(2)	1.47(2)
O(2)–C(17)	1.03(6)	C(2)–C(3)	1.44(2)
C(9)–C(10)	1.56(3)		
C(11)–Pd–N	72.1(6)	C(4)–C(3)–C(2)	129.9(11)
C(11)–Pd–P	98.9(3)	C(8)–C(3)–C(2)	110.1(11)
N–Pd–P	170.5(5)	C(7)–C(6)–O(3)	116.1(10)
C(11)–Pd–Br	166.5(3)	C(5)–C(6)–O(3)	123.7(10)
N–Pd–Br	96.3(5)	N–C(9)–C(10)	113(2)
P–Pd–Br	92.98(13)	C(11)–C(10)–C(9)	106.8(11)
C(13)–O(1)–C(16)	98.4(14)	C(15)–C(10)–C(9)	132.8(11)
C(17)–O(2)–C(14)	129(5)	C(12)–C(11)–Pd	118.0(6)
C(18)–O(3)–C(6)	108(2)	C(10)–C(11)–Pd	120.5(6)
C(9)–N–C(1)	116(2)	C(14)–C(13)–O(1)	100.6(11)
C(9)–N–Pd	123(2)	C(12)–C(13)–O(1)	139.2(11)
C(1)–N–Pd	121.0(13)	C(13)–C(14)–O(2)	126.2(11)
C(2)–C(1)–N	108.2(14)	C(15)–C(14)–O(2)	113.3(12)
C(3)–C(2)–C(1)	131(2)		

3.1.1. Imines 1a–e

2.5 mmol of the aldehyde, 5 Å molecular sieves (7.0 g), activated for 24 h at 250°C, and the stoichiometric amount of the corresponding amine were suspended in dry toluene and the reaction mixtures were refluxed for 4 h. Then the molecular sieves were removed by filtration and washed with toluene until the washings became colourless. The solutions were concentrated to dryness on a vacuum line. The oils obtained contain the imines, nearly in pure form, and were used without further purification.

3.1.2. Compounds 2b, 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 nitrogen, using Schlenk techniques. The resulting solution was concentrated to dryness in vacuo. The residue obtained was dissolved in ethanol (20 cm^3) and treated with an excess of LiBr (4.46 mmol, 0.386 g) for 15 min at room temperature. The precipitates formed were filtered, washed with ethanol and purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100/2) as eluant. Compounds **2b**, **2c** and **2d** were eluted in the first intense coloured band and isolated, in the solid state, after concentration of the solvents and addition of ether. **2b** (0.285 g, 30%) (Anal. Found: C, 42.6; H, 3.6; N, 3.3. $C_{32}H_{32}Br_2N_2O_6Pd_2$ Calc.: C, 42.10 H, 3.50; N, 3.10%). **2c** (0.254 g, 25%) (Anal. Found: C, 43.3; H, 3.8; N, 3.0. $C_{34}H_{36}Br_2N_2O_6Pd_2$ Calc.: C, 43.40; H, 3.80; N, 3.00%). **2d** (0.400 g, 40%) (Anal. Found: C, 45.0; H, 4.1; N, 2.9. $C_{36}H_{40}Br_2N_2O_6Pd_2$ Calc.: C, 44.6; H, 4.10; N, 2.90%).



Scheme 2. (i) $Pd(AcO)_2$/AcOH at 60°C, 4 h; (ii) PPh_3, acetone, at 25°C, 30 min.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4d**

Atom	x	y	z	U_{eq}
Pd	2702(1)	2599(1)	7299(2)	61(1)
Br	2102(1)	727(2)	9453(2)	77(1)
P	1597(3)	3638(4)	6562(5)	57(1)
O(1)	3489(10)	6298(16)	1438(17)	124(5)
O(2)	4878(12)	5612(22)	1723(28)	122(7)
O(3)	3601(7)	−1906(15)	16443(14)	95(4)
N	3840(9)	1914(18)	7749(19)	72(5)
C(1)	4001(11)	736(17)	9180(18)	73(6)
C(2)	3783(11)	1340(21)	10390(20)	83(6)
C(3)	3787(7)	678(11)	11947(10)	77(5)
C(4)	3954(7)	1202(9)	12948(14)	96(6)
C(5)	3918(7)	365(13)	14422(12)	63(5)
C(6)	3714(7)	−996(12)	14895(9)	89(6)
C(7)	3546(6)	−1520(9)	13894(12)	64(5)
C(8)	3583(6)	−683(12)	12420(11)	58(4)
C(9)	4334(13)	2454(27)	7015(32)	108(9)
C(10)	4173(6)	3401(10)	5452(10)	54(4)
C(11)	3398(5)	3762(11)	5582(10)	57(4)
C(12)	3088(5)	4721(12)	4386(13)	58(4)
C(13)	3534(7)	5318(11)	3060(11)	114(8)
C(14)	4329(6)	4957(12)	2931(10)	68(5)
C(15)	4639(4)	3998(12)	4127(13)	65(5)
C(16)	2596(16)	6607(25)	1630(30)	141(10)
C(17)	5453(33)	5336(68)	1532(69)	293(31)
C(18)	3854(15)	−1259(24)	17244(25)	117(9)
C(19)	1537(6)	3234(12)	4866(10)	75(5)
C(20)	1849(6)	1911(10)	4748(11)	54(4)
C(21)	1876(7)	1636(10)	3453(14)	98(7)
C(22)	1590(8)	2684(14)	2276(11)	95(6)
C(23)	1278(7)	4006(12)	2394(11)	89(6)
C(24)	1252(6)	4281(9)	3688(13)	58(4)
C(25)	725(6)	2960(14)	7793(13)	89(6)
C(26)	489(8)	3287(13)	9091(15)	67(5)
C(27)	−164(8)	2813(16)	10038(12)	147(10)
C(28)	−580(7)	2013(16)	9687(14)	129(9)
C(29)	−344(7)	1687(13)	8388(15)	73(5)
C(30)	308(7)	2160(13)	7441(11)	67(5)
C(31)	1402(6)	5516(9)	6293(12)	55(4)
C(32)	715(5)	6263(11)	5942(12)	79(6)
C(33)	538(5)	7670(11)	5892(12)	48(4)
C(34)	1047(7)	8331(9)	6193(15)	104(7)
C(35)	1735(7)	7584(13)	6544(15)	159(11)
C(36)	1912(5)	6176(12)	6595(12)	51(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.1.3. Compounds 3a, 3b and 3c

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 nitrogen, using Schlenk techniques. The resulting solution was concentrated to dryness in vacuo. The residue obtained was purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100/2) as eluant. Compounds **3** were eluted in the first intense coloured band and isolated, in the solid state, after concentration of the solvents and addition of ether. **3a** (0.488 g, 54%) (Anal. Found: C, 50.6; H, 4.3; N, 3.3. $C_{34}H_{34}N_2O_8Pd_2$ Calc.: C, 50.30; H, 4.20; N, 3.45%). **3b** (0.514 g, 53%) (Anal. Found: C, 50.0; H, 4.3; N, 3.1. $C_{36}H_{38}N_2O_{10}Pd_2$ Calc.: C, 49.60; H, 4.36; N, 3.21%). **3c** (0.200 g, 20%) (Anal. Found: C, 49.6; H, 4.6; N, 3.1. $C_{38}H_{42}N_2O_{10}Pd_2$ Calc.: C, 50.70; H, 4.65; N, 3.10%).

3.1.4. Compound 2a

A stirred suspension of **3a** (0.5 mmol) was treated with LiBr (1.0 mmol, 0.087 g) in ethanol for 15 min at room temperature. The precipitate formed was filtered and washed with ethanol. **2a** (0.390 g, 90%) (Anal. Found: C, 41.8; H, 3.2; N, 3.2. $C_{30}H_{28}Br_2N_2O_4Pd_2$ Calc.: C, 42.2 H, 3.30; N, 3.30%).

3.1.5. Compounds 4a–d

A stirred suspension of compounds **2** (0.25 mmol) was 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 concentrated in vacuo and the solid obtained after addition of ether was recrystallized from chloroform–ether to obtain compounds **4**. **4a** (0.280 g, 81%) (Anal. Found: C, 57.1; H, 4.2; N, 1.9. $C_{33}H_{28}BrNO_2PPd$ Calc.: C, 57.5; H, 4.20; N, 2.00%); δ_P ($CHCl_3$) 44.0 ppm. **4b** (0.230 g, 64%) (Anal. Found: C, 56.0; H, 4.5; N, 2.0. $C_{34}H_{31}BrNO_3PPd$ Calc.: C, 56.80; H, 4.30; N, 1.95%); δ_P ($CHCl_3$) 43.0 ppm. **4c** (0.360 g, 98%) (Anal. Found: C, 56.7; H, 4.5; N, 1.9. $C_{35}H_{33}BrNO_3PPd$ Calc.: C, 57.35; H, 4.50; N, 1.90%); δ_P ($CHCl_3$) 42.3 ppm. **4d** (0.325 g, 87%) (Anal. Found: C, 58.4; H, 4.7; N, 1.9. $C_{36}H_{35}BrNO_3PPd$ Calc.: C, 57.90; H, 4.70; N, 1.90%); δ_P ($CHCl_3$) 44.8 ppm.

3.1.6. Compounds 5a,b

A stirred suspension of compounds **3** (0.25 mmol) was 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 concentrated in vacuo and the solid obtained after addition of ether was recrystallized from chloroform–ether to obtain compounds **5**. **5a** (0.267 g, 80%) (Anal. Found: C, 60.7; H, 5.0; N, 2.1. $C_{35}H_{32}NO_4PPd$ Calc.: C, 62.90; H, 4.80; N, 2.10%); δ_P ($CHCl_3$) 41.1 ppm. **5b** (0.272 g, 78%) (Anal. Found: C, 62.1; H, 5.0; N, 1.9. $C_{36}H_{34}NO_5PPd$ Calc.: C, 61.94; H, 5.00; N, 2.00%); δ_P ($CHCl_3$) 41.2 ppm.

3.1.7. Compound 3e

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 refluxed for 45 min, under nitrogen, using Schlenk techniques. The resulting solution was concentrated to dryness in vacuo. The residue obtained was purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100/2) as eluant. Compound **3e** was eluted in the first intense coloured band and isolated, in the solid state, after

concentration of the solvents and addition of ether. **3e** (0.219 g, 24%) (Anal. Found: C, 48.1; H, 4.0; N, 3.2. $C_{34}H_{34}N_2O_{10}Pd_2$ Calc.: C, 48.41; H, 4.07; N, 3.32%); δ_C ($CDCl_3$) 21.9 (s, CH_3COO), 55.0, 55.2 (s, CH_3O), 88.1, 92.7, 124.5, 126.3, 128.7 (s, CH, aromatics), 106.2, 150.9, 154.9, 155.1, 161.3 (s, quaternary aromatics), 165.8 (s, HC=N), 184.2 (s, COO).

3.1.8. Compound 5e

A stirred suspension of compound **3e** (0.25 mmol) was 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 concentrated in vacuo and the solid obtained after addition of ether was carefully recrystallized from chloroform–ether to obtain compound **5e** (0.220 g, 65%) (Anal. Found: C, 61.6; H, 4.7; N, 2.0. $C_{35}H_{32}NO_5PPd$ Calc.: C, 61.45; H, 4.70; N, 2.05%); δ_P ($CHCl_3$) 20.2, s; δ_C ($CDCl_3$) 22.2 (s, CH_3COO), 55.6, 56.0 (s, CH_3O), 88.6, 95.8, 124.8, 126.0, 131.0 (s, CH, aromatics), 128.4–128.9 (m, CH aromatics), 135.0–135.5 (m, CH aromatics), 106.2, 152.0, 162.2, 165.8, 167.0 (s, quaternary aromatics), 157.0 (s, HC=N), 178.4 (s, COO).

3.2. Data collection

A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm^3) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8 \leq \theta \leq 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromated Mo Kα radiation, using the $\omega/2\theta$-scan technique. 9677 reflections were measured in the range $2.16 \leq \theta \leq 30.01°$, 1545 of which were assumed to be observed, applying the condition $I \geq 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls, significant intensity decay was not observed. Corrections were made for Lorentz-polarization but not for absorption.

3.3. Structure solution and refinement

The structure was solved by Patterson synthesis, using the SHELXS computer program [25] for crystal structure determination, and refined by the full-matrix least-squares method using the SHELX93 computer program [26] with 9614 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.1515P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from *International Tables of X-Ray Crystallography* [27]. The extinction coefficient was 0.059, wR (on $|F|^2$) 0.134 and goodness of fit 0.615 for all observed reflections. All atoms of phenyl groups were refined isotropically and geometrically constrained, with C–C bond length 1.39 Å, C–C–C bond angle 120° and a planar form for the ring. The number of refined parameters was 179. Max. shift/e.s.d. 4.9, mean shift/e.s.d. 0.07. Max. and min. peaks in the final difference synthesis were 0.888 and -1.268 e $Å^{-3}$ respectively.

4. Supplementary material available

Tables of structure factors and thermal parameters are available from the authors.

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