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# New cyclometalated palladium(II) complexes with iminophosphines Crystal structures of $[Pd(C \times N)(o-Ph_2PC_6H_4-CH=NR)][PF_6]$ (C×N=azobenzene, R=Et; C×N=2-phenylpyridine, R=Me)

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### Abstract

The synthesis of new cyclometalated compounds of palladium(II) with the mixed-donor bidentate ligands  $o-Ph_2PC_6H_4-CH=NR$  is described. Two series of complexes  $[Pd(C\times N)(o-Ph_2PC_6H_4-CH=NR)][PF_6]$  have been prepared using either azobenzene or 2-phenylpyridine as cyclometalated ligands  $[C\times N=$ azobenzene (azb); R=Me (1a), Et (2a), <sup>n</sup>Pr (3a), <sup>i</sup>Pr (4a), <sup>i</sup>Bu (5a), Ph (6a), NH–Me (7a);  $C\times N=$ 2-phenylpyridine (phpy); R=Me (1b), Et (2b), <sup>n</sup>Pr (3b), <sup>i</sup>Pr (4b), <sup>i</sup>Bu (5b), Ph (6b), NH–Me (7b)]. The new complexes were characterized by partial elemental analyses and spectroscopic methods (IR, FAB, <sup>1</sup>H and <sup>31</sup>P NMR). The molecular structures of compounds 2a (monoclinic,  $P 2_1/n$ ) and 1b (monoclinic, C 2/c) have been determined by a single-crystal diffraction study. In both cases this technique revealed the relative trans configuration between the phosphorus atom and the nitrogen atom of the ortho-metalated ligand. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclometalated palladium(II) complexes; Iminophosphine ligands; Crystal structures

## 1. Introduction

Azobenzenes and heteroaromatic ligands such as 2phenylpyridine can easily be orthometalated by Pd(II) salts via  $C(sp^2)$ -H bond cleavage [1,2] to usually give the corresponding acetato or halide-bridged dimers. These dinuclear complexes have been thoroughly studied [3] and employed as precursors of mononuclear cyclometalates of general formula M(C×N)LX (M=Pd, Pt; C×N=orthometalated ligand; L=neutral monodentate ligand such as pyridines and phosphines; X=halide) [4–6]. However, there is an apparent lack of data for analogous reactions with neutral bidentate ligands [7], which imply the loss of both halide ligands and the presence of an appropiate anion. It should be noted that since a number of orthometalated complexes of the platinum group elements have been implicated as potential photosensitizers [8–14] there has been a growing interest in this kind of compounds.

On the other hand, there has also recently been considerable interest in the chemistry of polydentate ligands with both hard and soft donor atoms [15-21]. In this sense, the metal complexes with N and P donor atoms display a variety of coordination well beyond those of P-P or N-N ligands [22]. Furthermore, this N.P-ligands show a particular behaviour binding soft metal centres such as Pd(II) and Pt(II) that make their complexes good precursors in catalytic processes [23-29]. Thus, the hard-ligand components can readily dissociate generating a vacant site on the metal ion for potential substrate binding. Among the most widely studied ligands with this characteristics are the pyridylphosphines and the iminophosphines that we present in this work, which have been profusely reported since 1992 in complexes with rhodium [25], iridium [23], ruthenium [30] and palladium [27-34].

Here we report the preparation of some ortho-metalated palladium(II) derivatives  $[C \times N=azobenzene (azb) \text{ or } 2-phenylpyridine (phpy)]$  with the mixed-donor bidentate

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iminophosphine ligands (N,P-donors). The iminophosphine ligands were prepared via Schiff-base reaction between *o*-(diphenylphosphino)benzaldehyde and the corresponding amine [25].

#### 2. Experimental

C, H and N analyses were carried out with a Perkin– Elmer 240C microanalyser. IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. NMR data were recorded on a Bruker AC 200E (<sup>1</sup>H) or a Varian Unity 300 (<sup>1</sup>H, <sup>31</sup>P) spectrometer. Conductance measurements were performed with a Crison 525 conductimeter (in acetone;  $c=10^{-3}$  M). Mass spectrometric analyses were performed on a FISONS VG AUTOSPEC double-focusing spectrometer, operated in positive mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-keV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000.

The cyclometalated precursors  $[{Pd(C \times N)(\mu-Cl)}_2]$ (C×N=azobenzene or 2-phenylpyridine) were prepared as described in the literature [35,5]. The iminophosphine [25] ligands were prepared according to reported procedures and all the solvents were dried by standard methods before use.

#### 2.1. Preparation of the complexes

Complexes  $[Pd(C \times N)(o-Ph_2PC_6H_4-CH=NR)][PF_6]$  $[C \times N=azobenzene (azb); R=Me (1a), Et (2a), "Pr (3a), "Pr (4a), "Bu (5a), Ph (6a), NH-Me (7a); C \times N=2-phenylpyridine (phpy); R=Me (1b), Et (2b), "Pr (3b), "Pr (4b), "Bu (5b), Ph (6b), NH-Me (7b)]$ 

The complexes were obtained by treating [{Pd(C×N)(F-Cl)}<sub>2</sub>] (C×N=azobenzene or 2-phenylpyridine) with the corresponding iminophosphine (molar ratio 1:2) in acetone according to the following general method. To an acetone (5 ml) suspension of the precursor [{Pd(C×N)(F-Cl)}<sub>2</sub>] (0.07 mmol.) was added the stoichiometric amount of the previously prepared iminophosphine dissolved in acetone (5 ml) and KPF<sub>6</sub> (0.140 mmol.). The reaction changed colour immediately and the mixture was refluxed for 15 min. The hot solution was filtered through celite and then concentrated under reduced pressure to half volume. Addition of hexane caused precipitation of the new complexes, which were filtered off, air-dried and recrystallized from acetone–hexane.

 $[Pd(azb){P(o-C_{6}H_{4}-CH=N-R)Ph_{2}}][PF_{6}] (R=Me)$ (1a)was obtained in 72% yield. Anal. calc. for  $C_{32}F_{6}H_{27}N_{3}P_{2}Pd$ : C, 52.2; H, 3.7; N, 5.7. Found: C, 52.3; H, 3.5; N, 5.5%.  $\Lambda_{M}$ =134  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. IR (cm<sup>-1</sup>): 1646 (C=N str). FAB-MS (positive mode) m/z: 590 [Pd(azb){P(o-C\_{6}H\_{4}-CH=N-Me)Ph\_{2}}]^{+}.  $[Pd(azb){P(o-C_{6}H_{4}-CH=N-R)Ph_{2}}][PF_{6}] (R=Et)$ (2a)was obtained in 82% yield. Anal. calc. for C<sub>33</sub>F<sub>6</sub>H<sub>29</sub>N<sub>3</sub>P<sub>2</sub>Pd: C, 52.8; H, 3.9; N, 5.6. Found: C, 52.6; H, 3.8; N, 5.5%.  $\Lambda_{M}$ =145  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. IR (cm<sup>-1</sup>): 1644 (C=N str). FAB-MS (positive mode) m/z: 604 [Pd(azb){P(o-C\_{6}H\_{4}-CH=N-Et)Ph\_{2}]^{+}.

 $[Pd(azb){P(o-C_6H_4-CH=N-R)Ph_2}][PF_6] (R=^n Pr)$ (**3a**)was obtained in 75% yield. Anal. calc. for $C_{34}F_6H_{31}N_3P_2Pd: C, 53.4; H, 4.1; N, 5.5. Found: C, 53.3;$  $H, 4.0; N, 5.5%. <math>\Lambda_M = 132 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . IR (cm<sup>-1</sup>): 1638 (C=N str). FAB-MS (positive mode) m/z: 618 [Pd(azb){P(o-C\_6H\_4-CH=N-^nPr)Ph\_2}]^+.

 $[Pd(azb){P(o-C_{6}H_{4}-CH=N-R)Ph_{2}}][PF_{6}] (R='Pr)$ (**4a**)was obtained in 82% yield. Anal. calc. forC<sub>34</sub>F<sub>6</sub>H<sub>31</sub>N<sub>3</sub>P<sub>2</sub>Pd: C, 53.4; H, 4.1; N, 5.5. Found: C, 53.5; $H, 4.3; N, 5.5%. <math>\Lambda_{M}$ =117  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. IR (cm<sup>-1</sup>): 1646 (C=N str). FAB-MS (positive mode) m/z: 618 [Pd(azb){P(o-C\_{6}H\_{4}-CH=N-^{i}Pr)Ph\_{2}}]^{+}.

 $[Pd(azb){P(o-C_6H_4-CH=N-R)Ph_2}][PF_6] (R='Bu)$ (**5a**)was obtained in 76% yield. Anal. calc. forC<sub>35</sub>F<sub>6</sub>H<sub>33</sub>N<sub>3</sub>P<sub>2</sub>Pd: C, 54.0; H, 4.2; N, 5.4. Found: C, 54.2; $H, 4.3; N, 5.5%. <math>\Lambda_M = 134 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . IR (cm<sup>-1</sup>): 1626 (C=N str). FAB-MS (positive mode) m/z: 632 [Pd(azb){P(o-C\_6H\_4-CH=N-'Bu)Ph\_2}]^+.

 $[Pd(azb){P(o-C_{6}H_{4}-CH=N-R)Ph_{2}}][PF_{6}] (R=Ph)$ (**6a**)was obtained in 90% yield. Anal. calc. forC<sub>37</sub>F<sub>6</sub>H<sub>29</sub>N<sub>3</sub>P<sub>2</sub>Pd: C, 55.7; H, 3.6; N, 5.3. Found: C, 55.8; $H, 3.5; N, 5.5%. <math>\Lambda_{M}$ =125  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. IR (cm<sup>-1</sup>): 1618 (C=N str). FAB-MS (positive mode) m/z: 652 [Pd(azb){P(o-C\_{6}H\_{4}-CH=N-Ph)Ph\_{2}]^{+}.

 $\begin{array}{ll} [\mathrm{Pd(azb)}\{\mathrm{P(o-C_6H_4-CH=N-R)Ph_2}\}][\mathrm{PF_6}] & (\mathrm{R=NH-Me}) & (\mathbf{7a}) & \mathrm{was} & \mathrm{obtained} & \mathrm{in} & 88\% & \mathrm{yield.} & \mathrm{Anal.} & \mathrm{calc.} & \mathrm{for} \\ \mathrm{C_{32}F_6H_{28}N_4P_2Pd:} & \mathrm{C}, 51.2; & \mathrm{H}, 3.7; & \mathrm{N}, 7.5. & \mathrm{Found:} & \mathrm{C}, 51.2; \\ \mathrm{H}, 3.5; & \mathrm{N}, 7.5\%. & \Lambda_{\mathrm{M}} = 144 & \Omega^{-1} & \mathrm{cm}^2 & \mathrm{mol}^{-1}. & \mathrm{IR} & (\mathrm{cm}^{-1}): \\ 3406 & (\mathrm{N-H} & \mathrm{str.}), & 1630 & (\mathrm{C=N} & \mathrm{str}). & \mathrm{FAB-MS} & (\mathrm{positive} & \mathrm{mode}) & \mathrm{m/z:} & 605 & [\mathrm{Pd(azb)}\{\mathrm{P(o-C_6H_4-CH=N-NHMe)Ph_2}\}]^+. \end{array}$ 

 $\begin{array}{l} [Pd(phpy)\{P(o-C_{6}H_{4}-CH=N-R)Ph_{2}\}][PF_{6}] \quad (R=Me) \\ \textbf{(1b)} was obtained in 69\% yield. Anal. calc. for \\ C_{31}F_{6}H_{26}N_{2}P_{2}Pd: C, 52.5; H, 3.7; N, 3.9. Found: C, 52.3; \\ H, 3.5; N, 3.8\%. \Lambda_{M}=140 \ \Omega^{-1} \ cm^{2} \ mol^{-1}. \ IR \ (cm^{-1}): \\ 1642 \ (C=N \ str). \ FAB-MS \ (positive \ mode) \ m/z: 563 \\ [Pd(phpy)\{P(o-C_{6}H_{4}-CH=N-Me)Ph_{2}\}]^{+}. \end{array}$ 

 $\begin{array}{ll} [Pd(phpy)\{P(o-C_{6}H_{4}-CH=N-R)Ph_{2}\}][PF_{6}] & (R=Et) \\ (2b) was obtained in 75\% yield. Anal. calc. for \\ C_{32}F_{6}H_{28}N_{2}P_{2}Pd: C, 53.2; H, 3.9; N, 3.9. Found: C, 53.5; \\ H, 3.8; N, 3.8\%. \Lambda_{M} = 148 \ \Omega^{-1} \ cm^{2} \ mol^{-1}. \ IR \ (cm^{-1}): \\ 1638 \ (C=N \ str). \ FAB-MS \ (positive \ mode) \ m/z: 577 \\ [Pd(phpy)\{P(o-C_{6}H_{4}-CH=N-Et)Ph_{2}\}]^{+}. \end{array}$ 

 $\begin{array}{l} [Pd(phpy)\{P(o-C_{6}H_{4}-CH=N-R)Ph_{2}\}][PF_{6}] \quad (R=^{n}Pr) \\ \textbf{(3b)} was obtained in 71\% yield. Anal. calc. for \\ C_{33}F_{6}H_{30}N_{2}P_{2}Pd: C, 53.8; H, 4.1; N, 3.8. Found: C, 53.9; \\ H, 4.2; N, 3.6\%. \Lambda_{M}=129 \ \Omega^{-1} \ cm^{2} \ mol^{-1}. \ IR \ (cm^{-1}): \\ 1641 \ (C=N \ str). \ FAB-MS \ (positive \ mode) \ m/z: \ 591 \\ [Pd(phpy)\{P(o-C_{6}H_{4}-CH=N-^{n}Pr)Ph_{2}\}]^{+}. \end{array}$ 

 $[Pd(phpy){P(o-C_6H_4-CH=N-R)Ph_2}][PF_6]$  (R=<sup>*i*</sup>Pr)

Table 1

Crystal data and summary of data collection and refinement for  $[Pd(azb){P(o-C_6H_4-CH=N-Et)Ph_2}][PF_6]$  (2a) and  $[Pd(phpy){P(o-C_6H_4-CH=N-Me)Ph_3}][PF_6]$  (1b)

	2a	1b
Empirical formula	$C_{33}H_{29}F_6N_3P_2Pd$	$C_{31}H_{26}F_6N_3P_2Pd$
Form. weight	749.3	708.8
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
Unit cell	a=9.293(2) Å	a=21.253(4) Å
dimensions	b=14.3842(10) Å	b=15.379(3) Å
	c=23.938(2) Å	c=19.274(4) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 100.783(10)^{\circ}$	$\beta = 104.29(3)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
$V(\text{\AA}^3)$	3143,1(7)	6105 (2)
Ζ	4	8
$D_{\rm calcd}  ({\rm Mg/m^3})$	1.585	1.543
$F (\mathrm{mm}^{-1})$	0.757	0.773
$\lambda$ (Å)	0.71073	0.71073
Obs. refl.	6209	4887
<i>R</i> 1, <i>R</i> w2	0.0454, 0.1115	0.0366, 0.0903
GooF	1.044	1.129

(4b)was obtained in 80% yield. Anal. calc. for  $C_{33}F_6H_{30}N_2P_2Pd$ : C, 53.8; H, 4.1; N, 3.8. Found: C, 53.7; H, 4.2; N, 3.6%.  $\Lambda_M = 131 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ . IR (cm<sup>-1</sup>): 1640 (C=N str). FAB-MS (positive mode) m/z: 591 [Pd(phpy){P(o-C\_6H\_4-CH=N-^iPr)Ph\_2}]^+.

[Pd(phpy){P(o-C<sub>6</sub>H<sub>4</sub>-CH=N-R)Ph<sub>2</sub>}][PF<sub>6</sub>] (R=<sup>*t*</sup>Bu) (**5b**)was obtained in 85% yield. Anal. calc. for C<sub>34</sub>F<sub>6</sub>H<sub>32</sub>N<sub>2</sub>P<sub>2</sub>Pd: C, 54.4; H, 4.3; N, 3.7. Found: C, 54.2; H, 4.4; N, 3.5%.  $\Lambda_{\rm M}$ =142  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. IR (cm<sup>-1</sup>): 1640 (C=N str). FAB-MS (positive mode) m/z: 605 [Pd(phpy){P(o-C<sub>6</sub>H<sub>4</sub>-CH=N<sup>-1</sup>Bu)Ph<sub>2</sub>}]<sup>+</sup>.

 $[Pd(phpy){P(o-C_6H_4-CH=N-R)Ph_2}][PF_6] (R=Ph)$ (**6b**)was obtained in 65% yield. Anal. calc. forC<sub>36</sub>F<sub>6</sub>H<sub>28</sub>N<sub>2</sub>P<sub>2</sub>Pd: C, 53.5; H, 3.5; N, 3.5. Found: C, 53.7; $H, 3.7; N, 3.5%. <math>\Lambda_M = 137 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . IR (cm<sup>-1</sup>): 1638 (C=N str). FAB-MS (positive mode) m/z: 661 [Pd(phpy){P(o-C\_6H\_4-CH=N-Ph)Ph\_2}]^+.

 $[Pd(phpy){P(o-C_6H_4-CH=N-R)Ph_2}][PF_6] (R=NH-Me) (7b) was obtained in 66% yield. Anal. calc. for C_{31}F_6H_{27}N_3P_2Pd: C, 49.0; H, 3.5; N, 3.7. Found: C, 49.2; H, 3.5; N, 3.5\%. <math>\Lambda_M = 137 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . IR (cm<sup>-1</sup>): 3406 (N-H str.), 1680 (C=N str). FAB-MS (positive mode) m/z: 614 [Pd(phpy){P(o-C\_6H\_4-CH=N-NHMe)Ph\_2}]^+.

Crystal Structure determination of  $[Pd(azb)(o-Ph_2PC_6H_4-CH=NEt)][PF_6]$  (2a) and  $[Pd(phpy)(o-Ph_2PC_6H_4-CH=NMe)][PF_6]$  (1b)

X-ray diffraction experiments were carried out on a Siemens P4 diffractometer equipped with a graphite monochromator for Mo  $K_{\alpha}$  radiation. The crystallographic data are shown in Table 1. Empirical  $\Psi$ -scan mode absorption correction was made.

Data for **2a** were collected using a single crystal of approximate dimensions  $0.20 \times 0.25 \times 0.22$  mm. Accurate cell parameters were determined by least-squares fitting of 25 high-angle reflections. The scan method was  $\omega$  with the range of hkl ( $0 \le h \le 11, -14 \le k \le 14, -14 \le l \le 14$ ) corresponding to  $2\Theta_{\text{max}} = 50^{\circ}$ . The structure was solved by the Patterson methods and refined anisotropically on  $F^2$  [36]. Hydrogen atoms were introduced in calculated positions. The final *R* factor was 0.0454 [ $R_w = 0.1115$ , where w = 1/2]



Table 2 NMR data (ppm; J in Hz) for the palladium(II) complexes (solvent  $\text{CDCl}_3$ )

Complex	$^{1}$ H (SiMe <sub>4</sub> )	$^{31}P(H_{3}PO_{4})$
1a	6.26 (m, 1H, 3'-azb)	40.2 (s, NP)
	6.82 (m, 1H, 4'-azb)	102.4 (spt, $PF_6$ , $J=710$ )
	7.03 (dd, 1H, 3"-NP, $J_{\rm HH}$ =10.8; $J_{\rm HP}$ =10.5)	
	7.23 (m, 1H, 5'-azb)	
	7.55 (m, 16H; 2,3,4,5,6-azb; 4"-NP; Ph)	
	7.80  (m, 1H, 5''-NP)	
	8.05 (d, 1H, 6'-azb) 8.17 (d, 1H, $('', ND, L, -7.5, L, -7.2)$	
	8.1/ (dd, 1H, 6"-NP, $J_{HH}$ = 7,5; $J_{HP}$ = 7,2) 8.57 (c. 1H, CH-N)	
29	0.37 (s, 1H, CH-N) 0.73 (t 3H CH - $I=7.3$ )	38.9 (s. NP)
24	3.30  (cd  2H  -CH -  I=7.0)	102.4  (spt PF I=710)
	6.33 (m, 1H, 3'-azb)	102.4 (Spt, 11 <sub>6</sub> , 9 /10)
	6.83 (m, 2H, 4'-azb; 6-NP)	
	7.16 (m, 1H, 5'-azb)	
	7.40 (m, 16H, 2,3,4,5,6-azb; 4"-NP; Ph)	
	7.77 (m, 1H, 5"-NP)	
	8.00 (d, 1H, 6'-azb, J=1.17)	
	8.16 (dd, 1H, 6"-NP, $J_{HH} = 7,4$ ; $J_{HP} = 7,1$ )	
_	8.57 (s, 1H, CH=N)	
3a	0.29 (t, 3H, CH <sub>3</sub> -)	38.3 (s, NP)
	$1.70 \text{ (m, 2H, -CH}_2\text{-})$	102.4 (spt, $PF_6$ , $J=710$ )
	3.28 (t, 2H, -CH <sub>2</sub> -, $J=0.9$ )	
	6.40  (m, 1H, 3 - azb)	
	6.63 (iii, 1H, 4 - a20) 6.94 (dd 1H 3"-NP $I = 8.1$ : $I = 8.0$ )	
	7.25  (m. 1H. 5'-azb)	
	7.25 (m, 16H, 2.3.4.5.6-Azb; 4"-NP: Ph)	
	7.84 (m, 1H, 5"-NP)	
	8.06 (d, 1H, 6'-azb, $J=7,8$ )	
	8.22 (m, 1H, 6"-NP)	
	8.56 (s, 1H, CH=N)	
4a	0.78 (s-br, 6H, 2CH <sub>3</sub> -)	38.6 (s, NP)
	3,64 (spt, 1H, CH)	102.4 (spt, $PF_6$ , $J=710$ )
	6.40  (m, 1H, 3'-azb)	
	6.82 (m, 2H, 4'-azb; 3-NP)	
	7.36 (m, 1/H, 2,3,4,5,6,8-AZD; 4 $^{\circ}$ -NP; Ph)	
	7.61 (III, 1H, $3 - NF$ ) 8.00 (d. 1H, 6' orthe $I = 7.5$ )	
	8.00 (d, 1H, 0 - az0, $J = 7, 3$ ) 8.20 (dd 1H 6"-NP $L = 11.4$ : $L = 11.2$ )	
	$8.20$ (dd, 111, 0 -141, $J_{HH} = 11.4$ , $J_{HP} = 11.2$ ) 8 51 (s 1H CH=N)	
5a	0.82 (s, 9H, 3CH)	39.1 (s. NP)
eu -	6.46 (m, 1H, 3'-azb)	102.5  (spt, PF, J=710)
	6.82 (m, 2H, 4'-azb; 3-NP)	
	7.20 (m, 1H, 5'-azb)	
	7.49 (m, 16H, 2,3,4,5,6-azb; 4"-NP; Ph)	
	7.84 (m, 1H, 5"-NP)	
	7.96 (d, 1H, 6'-azb, $J=8,7$ )	
	8.22 (dd, 1H, 6"-NP, $J_{\rm HH}$ =6,9; $J_{\rm HP}$ =6,7)	
	8.60 (d, 1H, CH=N, $J=3,3$ )	
6a	6.37 (m, 1H, 3'-azb)	38.7 (s, NP) 102.5 (art DE $I = 710$ )
	0.85 (III, 1II, 4 - d2D) 7.02 (m. 2H. 5' orb; 2' ND)	$102.5 \text{ (spt, PF}_6, J = /10)$
	7.05 (III, 2H, 3 - $az0$ , 3 - $NF$ ) 7.41 (m, 21H, 2.3.4.5.6 azb; 4" NP: Pb)	
	7.41 (iii, 2111, 2,3,4,3,0-a20, 4 -101, 111) 7.90 (m. 1H. 5"-NP)	
	800 (d 1H, 6'-azb, J=75)	
	8.40 (m, 1H, 6'-NP)	
	8.58 (s, 1H, CH=N)	
7a	2.45 (d, 3H, Me)	39.0 (s, NP)
	6.01 (m, 1H, NH)	102.5 (spt, PF <sub>6</sub> , J=710)
	6.14 (m, 1H, 3'-azb)	· · · · ·
	6.72 (m, 1H, 4'-azb)	
	6.95 (dd, 1H, 3"-NP, $J_{\rm HH}$ =10.9; $J_{\rm HP}$ =10.7)	
	7.15 (m, 1H, 5'-azb)	
	7.50 (m, 18H, 2,3,4,5,6,6'-Azb; 4",5"-NP; Ph)	
	7.79 (m, 1H, 6"-NP)	
	/.9/ (d, 1H, CH=N, $J=/.8)$	

Table 2. Continued				
Complex	$^{1}$ H (SiMe <sub>4</sub> )	$^{31}P(H_{3}PO_{4})$		
1b	3.59 (s, 1H, Me)	40.8 (s, NP)		
	6.32 (m, 1H, 3'-phpy)	102.3 (spt, $PF_6$ , $J=710$ )		
	6.64 (m, 1H, 4'-phpy)			
	6.90 (dd, 1H, 3"-NP, $J_{\rm HH}$ = 10.5; $J_{\rm HP}$ = 10.7)			
	7.00  (m, 1H, 5'-phpy)			
	7.46 (m, 14H; 5,6°-pnpy; 4 $^{\circ}$ ,5°-NP; Pn) 7.72 (d. 1H, 2 phpy, $J=6.4$ )			
	7.75 (u, 111, 5-pipy, $J = 0.4$ ) 7.78 (m, 2H, $A_{-}$ phpy, $G''_{-}$ NP)			
	8.41  (m. 1H. 6-phpy)			
	8.52 (s. 1H, CH=N)			
2b	0.89 (t, 3H, CH <sub>3</sub> -)	38.9 (s, NP)		
	3.99 (s-br, 2H, -CH <sub>2</sub> -)	102.4 (spt, $PF_6$ , $J=710$ )		
	6.47 (m, 1H, 3'-phpy)			
	6.65 (m, 1H, 4'-phpy)			
	6.79 (dd, 1H, 3"-NP, $J_{\rm HH} = 10.8$ ; $J_{\rm HP} = 10.5$ )			
	7.01 (m, 1H, 5'-phpy)			
	7.56 (m, 15H; 3,5,6'-phpy; 4",5"-NP; Ph)			
	7.89 (m, 2H, 4-phpy, 6"-NP)			
	8.37 (m, 1H, 6-phpy)			
21	8.58 (s, 1H, CH=N) 0.25 (c, 2H, CH)	29.4 ()		
30	$(1, 5H, CH_3)$	58.4 (8) 102.2 (apt DE $I = 710$ )		
	$3.27 \text{ (m. 2HCH_2^-)}$	$102.3$ (spt, $FF_6$ , $J = 710$ )		
	6.47  (m. 1H. 3'-nhny)			
	6.63  (m. 1H, 4'-phpy)			
	6.79 (dd, 1H, 3"-NP, $J_{\mu\mu}$ = 10.1; $J_{\mu\nu}$ = 10.7)			
	7.02 (m, 1H, 5'-phpy)			
	7.47 (m, 14H; 5,6'-phpy; 4",5"-NP; Ph)			
	7.75 (d, 1H, 3-phpy, J=8,0)			
4b	1.10 (d, 3H, $CH_3$ -, $J=6,0$ )	38.4 (s, NP)		
	1.40 (d, 3H, $CH_{3-}$ , $J=6,0$ )	102.4 (spt, $PF_6$ , $J=710$ )		
	4.33 (spt, 1H, CH, $J=6,0$ )			
	6.56 (m, 1H, 3'-phpy)			
	6.70 (m, 1H, 4 -pnpy) 6.78 (44 1H 2" ND L = 10.5, L = 10.8)			
	$0.76$ (dd, 1H, 5 - NP, $J_{\rm HH} = 10.3$ ; $J_{\rm HP} = 10.8$ ) 7.07 (m. 1H, 5' nbny)			
	7.07 (m, 11, 5 -phpy) 7.40 (m. 13H: 5.6'-nhny: 4"-NP: Ph)			
	7.73 (m. 1H. 5"-NP)			
	7.79 (d, 1H, 3-phpy, $J=7.8$ )			
	7.93 (m, 1H, 4-phpy)			
	8.05 (dd, 1H, 6"-NP, $J_{\rm HH}$ =10.8; $J_{\rm HP}$ =3,0)			
	8.31 (m, 1H, 6-phpy)			
	8.61 (s, 1H, CH=N)			
5b	1.26 (s-br, 6H, 2CH <sub>3</sub> -)	38.2 (s, NP)		
	1.61 (s, 3H, CH <sub>3</sub> -)	102.4 (spt, $PF_6$ , $J=711$ )		
	6.55 (m, 1H, 3'-phpy)			
	6.68 (m, 2H, 4'-phpy; 3'-NP) 7.01 (m, 1H, $5'$ physic)			
	7.01 (m, 1H, 5 -pnpy) 7.56 (m, 15H: 3.5.6' nbny: $4''$ 5" NP: Pb)			
	7.50 (m, 1511, 5,5,0 - pnpy, 4, 5 - 141, 1 m) 7.85 (m, 1H, $A_{-}$ nhpy)			
	8.03  (m. 1H. 6"-NP)			
	8.33 (s-br, 1H, 6-phpy)			
	8.64 (d, 1H, CH=N, J=3.0)			
6b	6.35 (m, 1H, 3'-phpy)	38.7 (s, NP)		
	6.55 (m, 2H, 4'-phpy; 3"-NP)	102.5 (spt, PF <sub>6</sub> , J=710)		
	7.10 (m, 1H, 5'-phpy)			
	7.60 (m, 20H; 3,5,6'-phpy; 4",5"-NP; Ph)			
	7.85 (m, 1H, 4-phpy)			
	8.03 (m, 1H, 6"-NP)			
	8.33 (s-br, 1H, 6-phpy)			
	8.64 (d, 1H, CH=N, $J=3,0$ )			

Table 2. Continued

Complex	<sup>1</sup> H (SiMe <sub>4</sub> )	$^{31}P(H_{3}PO_{4})$
7b	2.89 (d, 3H, Me)	39.2 (s, NP)
	6.32 (m, 2H; 3'-phpy; NH)	102.4 (spt, $PF_6$ , $J=710$ )
	6.56 (m, 1H, 4'-phpy)	
	6.85 (dd, 1H, 3"-NP, $J_{\rm HH}$ =10.9; $J_{\rm HP}$ =10.9)	
	6.98 (m, 1H, 5'-phpy)	
	7.45 (m, 14H; 5,6'-phpy; 4",5"-NP; Ph)	
	7.73 (d, 1H, 3-phpy, $J=8,0$ )	
	7.87 (m, 3H, 4-phpy, 6'-NP, CH=N)	
	8.73 (m, 1H, 6-phpy)	

 $\sigma^{2}(F_{o}^{2})+(0.0581P)^{2}$  and  $P=(F_{o}^{2}+2F_{c}^{2})/3]$  over 2607 observed reflections  $[I>2\sigma(I)]$ .

Data for **1b** were collected using a single crystal of approximate dimensions  $0.20 \times 0.23 \times 0.25$  mm. Accurate cell parameters were determined by least-squares fitting of 46 high-angle reflections. The scan method was  $\omega$  with the range of hkl ( $-25 \le h \le 1$ ,  $-18 \le k \le 1$ ,  $-22 \le l \le 23$ ) corresponding to  $2\Theta_{\text{max}} = 50^{\circ}$ . The structure was solved by the Patterson methods and refined anisotropically on  $F^2$  [36]. Hydrogen atoms were introduced in calculated positions. The final *R* factor was  $0.0366 [R_w = 0.0903$ , where  $w = 1/\sigma^2(F_o^2) + (0.0394P)^2$  and  $P = (F_o^2 + 2F_c^2)/3$ ] over 3424 observed reflections  $[I > 2\sigma(I)]$ .

## 3. Results and discussion

In acetone, the chloro-bridged cyclometalated dimers  $[{Pd(C \times N)(F-Cl)}_2]$  (C×N=azobenzene or 2-phenylpyridine) react under mild conditions with iminophosphines (molar ratio 1:2) in the presence of the stoichiometric amount of KPF<sub>6</sub> to give the corresponding square-planar cationic complexes [Pd(C×N)(*o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-CH=NR)][PF<sub>6</sub>] presented in Scheme 1.

The new azobenzene derivatives with iminophosphines are air-stable orange solids, while the 2-phenylpyridinate complexes present a pale yellow colour. Measurements of their molar conductivity in acetone solutions indicate that all the complexes behave as 1:1 electrolytes [37], in accordance with the proposed formulae. There are two possible conformations for the new complexes, depending on the relative positions adopted by the four atoms directly bonded to the palladium centre. As we represent in Scheme 1, the new complexes with ortho-metalated azobenzene or 2-phenylpyridine exhibit a P,N-trans geometry. This is concluded from the X-ray crystal structure determination of complexes **2a** and **1b** (discussed below), and in accordance with previously reported data for related compounds [3,4,8,9].

Infrared spectra of all compounds show the characteristic absorptions of the  $PF_6^-$  anion at ca. 840 vs. and 558 s

cm<sup>-1</sup>, together with the bands assigned to the corresponding cyclometalated ligand. Two medium intensity bands at 1578 and 1552 cm<sup>-1</sup> were observed in the IR spectra of the the azobenzene compounds, while relevant bands for 2-phenylpyridinate compounds appeared at 1604 and 1576 cm<sup>-1</sup>. The presence of iminophosphine ligands coordinated to palladium(II) is detected by a single strong band in the 1650–1620 cm<sup>-1</sup> region attributed to the C=N stretching vibrations, shifted to lower frequencies than in the free ligands. The positive FAB-mass data of the complexes, with the m/z values for the observed fragments, are collected in the expected isotopomer distribution.

The <sup>1</sup>H and <sup>31</sup>P-NMR data of the iminophosphine complexes are collected in Table 2. The <sup>31</sup>P-NMR spectra consist on singlets with chemical shifts in the usual range of Pd(II) complexes, and the typical septuplet resonance showed by the  $PF_6^-$  anion. Unlike the dichloro-bridged precursors, whose low solubility prevented the acquisition of good-quality spectra [5,35,38], the mononuclear complexes are soluble in common organic solvents, and extensive <sup>1</sup>H-RMN study has been done. Thus, assignments of resonances were made through comparison with spectra of the free ligands and of similar compounds [5,8,9,12] helped by the use of homonuclear shift correlation spectroscopy (COSY).

Fig. 1 shows the aromatic section of the <sup>1</sup>H-COSY spectrum of 4b, where nine resonances are observed integrating for a total of 23 aromatic protons in the 6.0-9.0 ppm range. Several second order couplings were observed in this experiment, making easier the proposed assignment. Resonances attributed to H(5), H(6') and H(4'') protons are hidden by the broad signals of phenyl groups, while the rest of signals are fairly distinguishable, even those of H(3)-H(5'') and H(3'')-H(4'') which appear partly overlapped and were listed as multiplets integrating two protons. The two signals that integrate for one proton each observed downfield between 8.20 and 8.60 ppm were assigned to the H(6) and >CH=N- protons, adjacent to the coordinated nitrogens of the phenylpyridine and iminophosphine ligands respectively. The appreciable coupling to the phosphorus atom exhibited by the H(6), H(3'),



Fig. 1. <sup>1</sup>H-<sup>1</sup>H COSY spectrum of **4b** in the aromatic region.

H(3'') and H(6'') protons (expected as doublets resonances a priori), is the most remarkable aspect of the <sup>1</sup>H-NMR spectra.

#### 3.1. X-ray structures of 2a and 1b

The planar coordination around palladium is tetrahedrally distorted in both cases. Selected bond distances and angles are presented in Table 3. In **2a** (Fig. 2) the planar arrangement around palladium is slightly distorted with a twist angle between the planes through Pd,C(1),N(2) and through Pd,N(3),P of 9.6(3) °, and compound **1b** (Fig. 3) shows a larger distortion with a twist angle between the

Table 3 Selected bond lenghts (Å) and angles (°) for 2a and 1b

	Lengths	Angles		
2a	Pd-C(1)	1.996(8)	C(1)-Pd-N(2)	78.4(3)
	Pd-N(2)	2.108(6)	C(1)– $Pd$ – $N(3)$	172.6(3)
	Pd-N(3)	2.135(5)	N(2)-Pd-N(3)	97.7(2)
	Pd–P	2.246(2)	C(1)-Pd-P	101.3(3)
			N(2)-Pd-P	173.6(2)
			N(3)–Pd–P	83.2(2)
1b	Pd-C(1)	1.993(4)	C(1)– $Pd$ – $N(1)$	80.8(2)
	Pd-N(1)	2.088(3)	C(1)-Pd-N(2)	168.5(2)
	Pd-N(2)	2.120(4)	N(1)-Pd-N(2)	98.3(2)
	Pd-P(1)	2.2087(13)	C(1)-Pd-P(1)	99.03(14)
			N(1)-Pd-P(1)	163.87(12)
			N(2)-Pd-P(1)	85.04(12)



Fig. 2. Structure of the  $[Pd(azb){P(o-C_6H_4-CH=N-Et)Ph_2}]^+$  cation in the single crystal structure of **2a**. For clarity, all hydrogen atoms have been omitted.

planes through Pd, C(1), N(1) and through Pd, P(1), N(2) of  $20.9^{\circ}$ . The Pd–P bond length in compound **2a** [2.246(2) Å)] is clearly larger than in **1b** [2.2087(13) Å)] but this variation is easily explained in terms of the different electron-donor nature of the nitrogen in trans-arrangement.

The narrow NMC bite angle is characteristic of orthometalated and cyclometalated transition metal complexes [39]. In **2a** that C(1)PdN(2) bite angle is 78.4(3)°, similar to that found in others (phenylazophenyl) palladium complexes [40] while in **1b** is 80.8(2)°.

In **2a** the chelating ring (PdC(1)C(6)N(1)N(2)) is planar within 0.01 Å. Planar [40] and not planar [41] geometries



Fig. 3. Structure of the  $[Pd(phpy){P(o-C_6H_4-CH=N-Me)Ph_2}]^+$  cation in the single crystal structure of **1b**.

have been reported for these rings. The dihedral angle formed by the free phenyl group with the best weighted least-squares plane of the palladium–azophenyl moiety is  $49.2(2)^{\circ}$ . The N(1)–N(2) distance is 1.278(7)Å, this value is slightly longer than that observed for the N=N bond in trans-azobenzene [42].

In **1b** The five-membered ring chelate is approximately planar, the largest deviation from the mean plane defined by the five atoms is 0.05 Å for C(7). The phenyl and the pyridyl rings of the ortho-metalated phenylpyridine ligand have an angle of  $11.8^{\circ}$  between their planes. There is a potential crystallographic ambiguity in the assignment of the C and N atoms of the cyclometalated ligand; however the thermal parameters and the bond lengths are all consistent with the assignment that we have made.

The torsion angles of  $-2.9^{\circ}$  for C(18)–C(17)–C(12)– P(1) and 48.4° for the Pd–P(1)–C(12)–C(17) units point to a perturbed envelope conformation of the six-membered ring chelate.

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