

# Cyclometallation of phenylhydrazones: Synthesis, reactivity, crystal structure analysis and novel trinuclear palladium(II) cyclometallated compounds with [C,N,N'] terdentate ligands

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## Abstract

Reaction of the ligand  $C_6H_5N(H)N=CMe(C_5H_4N)$  (**a**) with palladium(II) acetate in toluene gave the mononuclear cyclometallated complex  $[Pd\{C_6H_4N(H)N=CMe(C_5H_4N)\}(AcO)]$  (**1a**). Reaction of **1a** with sodium chloride gave the analogous chlorine compound  $[Pd\{C_6H_4N(H)N=CMe(C_5H_4N)\}(Cl)]$  (**3a**) which could also be prepared by reaction of **a** with lithium tetrachloropalladate and sodium acetate in methanol for 48 h; whereas shorter reaction times afforded the non-cyclometallated complex  $[Pd\{C_6H_5N(H)N=CMe(C_5H_4N)\}(Cl)_2]$  (**2a**). Reaction of the ligand  $2-ClC_6H_4N(H)N=CMe(C_5H_4N) \cdot HCl$  (**b**), with palladium(II) acetate, or with lithium tetrachloropalladate and sodium acetate, yielded the cyclometallated complex  $[Pd2-ClC_6H_3N(H)N=CMe(C_5H_4N)(Cl)]$  (**1b**). Treatment of **3a** and **1b** with silver trifluoromethanesulphonate (triflate) and triphenylphosphine in acetone gave the mononuclear complexes  $[Pd\{2-RC_6H_4N(H)N=CMe(C_5H_4N)\}(PPh_3)][CF_3SO_3]$ , (R = H,  $n = 4$ , **4a**; R = Cl,  $n = 3$ , **2b**) with the ligand as C,N,N' terdentate and substitution of chlorine by triphenylphosphine. Reaction of **3a** and **1b** with silver triflate and the tertiary diphosphine  $Ph_2P(CH_2)_4PPh_2$  (dppb) in a 2:1 molar ratio gave the dinuclear cyclometallated complexes  $[Pd\{2-RC_6H_3N(H)N=CMe(C_5H_4N)\}]_2(\mu-Ph_2P(CH_2)_4PPh_2)[CF_3SO_3]_2$  (R = H, **5a**; R = Cl, **3b**) with a  $\mu_2$ -diphosphine bridging ligand. Similarly, treatment of **3a** and **1b** with silver triflate and the tertiary triphosphines  $MeC(CH_2PPh_2)_3$  (tripod) and  $(Ph_2PCH_2CH_2)_2PPh$  (triphos), in 3:1 molar ratio, gave the novel trinuclear complexes  $[Pd\{C_6H_4N(H)N=CMe(C_5H_4N)\}]_3\{\mu_3-MeC(CH_2PPh_2)_3\}[CF_3SO_3]_3$  (**6a**) and  $[Pd\{2-ClC_6H_3N(H)N=CMe(C_5H_4N)\}]_3\{\mu_3-(PPh_2CH_2CH_2)_2PPh\}[CF_3SO_3]_3$  (**4b**) regioselectively, with the phosphine as a  $\mu_3$ -bridging ligand. When the reaction between **3a** and triphos was carried out in 1:1 molar ratio the mononuclear complex  $[Pd\{C_6H_4N(H)N=CMe(C_5H_4N)\}\{(PPh_2CH_2CH_2)_2PPh-P,P,P\}][ClO_4]$  (**7a**) was obtained. The crystal structures of **2b**, **3a** and **4a** have been determined by X-ray crystallography.

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**Keywords:** Palladium; Cyclometallation; Phosphines; Phenylhydrazones; Crystal structure

## 1. Introduction

Cyclometallated complexes are well documented for a great variety of metal centres and ligands. These

compounds are usually classified according to the metal, to the donor atom, or to chelate ring size; by far the most well-studied examples are five-membered palladacycles containing nitrogen–Pd and C(phenyl)–Pd bonds. The cyclometallation reaction, i.e., the intramolecular activation of aromatic C–H bonds of coordinated ligands by transition metals, has been widely investigated [1–5]. They exhibit a good

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number of applications which range from the synthesis of new organic and organometallic compounds, to mesogenic species and catalytic materials [6–14] as well as promoting unusual coordination environments [15].

In the past, we have been interested in palladium(II) and platinum(II) cyclometallated complexes derived from [C,N,X] (X = N, O, S) terdentate ligands [16–22]. For example, Schiff bases readily react with palladium(II) salts to give mononuclear cyclometallated complexes with the ligand as [C,N,N'] terdentate [18–22]. Treatment of the latter with neutral ligands such as tertiary mono- or diphosphines produced cleavage of the metal–N' bond prior to ring-opening of the five-membered metallacycle. When the cyclometallated compound was treated first with a silver(I) salt the chlorine ligand was removed as silver chloride and the vacant coordination site was occupied by the phosphine [18–22]. The diphosphine chelated to the metal only when the complexes were reacted with excess ligand. Furthermore, reaction of the cyclometallated complexes with the tertiary triphosphine (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh (triphos), produced Pd–N bond cleavage upon chelation of triphos [20]; complexes with triphos coordinating three different cyclometallated palladium(II) moieties were, to the best of our knowledge, hitherto unknown.

In the present paper, we report the synthesis of cyclometallated complexes derived from 2-acetylpyridine phenylhydrazones with the ligand in a C,N,N' terdentate fashion. Although the synthesis of compound **3a** has been previously reported [23], it is included here because: (a) its crystal structure was outstanding, and is now described in this work; (b) it is an intermediate in the preparation of the phosphine derivatives. We have also found that the reaction of the present complexes with tertiary monophosphines, in the absence of AgCF<sub>3</sub>SO<sub>3</sub>, did not produce cleavage of the Pd–N<sub>pyridine</sub> bond. We therefore reasoned that the strong binding of the phenylhydrazone ligand to the palladium atom, leaving only one easily accessible coordination position, should hinder chelation of the bi- or tridentate phosphines. However, this was not the case with di- and triphosphines and chelation could only be prevented by reaction of the cyclometallated complexes with AgCF<sub>3</sub>SO<sub>3</sub> followed by treatment with the tertiary diphosphine Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>, dppb, or with the triphosphines (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh, triphos, and MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>, (tripod); in the latter case, to yield the unprecedented trinuclear cyclometallated complexes with the phosphine acting as a μ<sub>3</sub>-bridging ligand. However, when the cyclometallated complex was only reacted with excess triphos, a mononuclear complex was obtained, with Pd–N<sub>pyridine</sub> bond cleavage.

## 2. Results and discussion

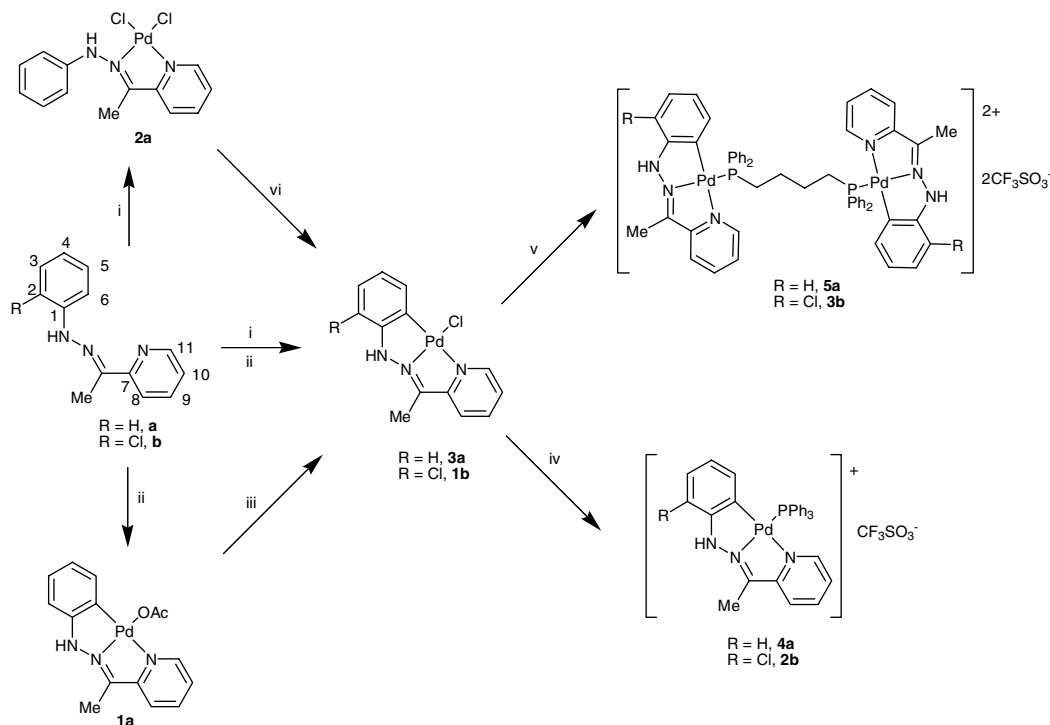
### 2.1. Preparation of the cyclometallated complexes

The compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR spectroscopy and by <sup>1</sup>H, <sup>31</sup>P–{<sup>1</sup>H} and, in part, <sup>13</sup>C–{<sup>1</sup>H} NMR spectroscopy, FAB mass spectrometry and X-ray single crystal diffraction (data in Section 4).

Reaction of C<sub>6</sub>H<sub>5</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N) (**a**) with palladium(II) acetate in toluene at 60 °C gave the mononuclear cyclometallated complex [PdC<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)(AcO)] (**1a**) which was fully characterized. The IR spectrum of **1a** showed the ν(C=N) stretch at 1592 cm<sup>-1</sup>, shifted to lower wavenumbers (as compared to the uncoordinated phenylhydrazone) due to N-coordination of the ligand [24,25]. The resonance assigned to the NH proton appeared at δ 11.60 ppm in the <sup>1</sup>H NMR spectrum, downfield shifted by approximately 4 ppm (as compared to ligand **a**), confirming the formation of the cyclometallated ring (vide infra). The absence of the H6 proton resonance showed that metallation occurred at the C6 carbon. The strong bands assigned to the symmetric and asymmetric ν(COO) vibrations in the IR spectrum, were in agreement with those expected for terminal acetate ligands [26] (see Section 4). These findings and the presence of a cluster of peaks centred at 316 a.m.u. in the mass FAB spectrum corresponding to the [M + H<sup>+</sup>–AcOH] fragment supported a mononuclear formulation for **1a**.

Reaction of 2-ClC<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N) · HCl (**b**) with palladium(II) acetate in dichloromethane did not yield the expected cyclometallated complex, similar to **1a**; instead, complex [Pd{2-ClC<sub>6</sub>H<sub>3</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(Cl)] (**1b**) with a terminal chlorine ligand, was obtained. The <sup>1</sup>H NMR spectrum also showed the resonance corresponding to the NH proton, downfield shifted as compared to the uncoordinated ligand, and absence of the H6 proton signal. Compound **1b** could also be synthesized by reaction of **b** with lithium tetrachloropalladate and sodium acetate in methanol. However, reaction of **b** with Pd<sub>2</sub>(dba)<sub>3</sub> (dba; dibenzylideneacetone) did not give the expected oxidative addition product; instead, a large amount of black palladium and an untreatable reaction mixture were obtained.

Treatment of **a** with lithium tetrachloropalladate and sodium acetate in methanol for 24 h yielded the non-cyclometallated complex [Pd{C<sub>6</sub>H<sub>5</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(Cl)<sub>2</sub>] (**2a**) as an orange solid. In the <sup>1</sup>H NMR spectrum, a doublet signal at δ 6.96 was assigned to the H2 and H6 proton resonances, and a signal at δ 8.66 to the NH proton. The latter was considerably less downfield shifted, as compared to the uncoordinated ligand **a**, than in the cyclometallated derivatives of **a**. The low-frequency shift of the ν(C=N) stretch (as compared



Scheme 1. (i) **3a**, **1b**,  $\text{Li}_2\text{PdCl}_4$ , (methanol, NaAcO); (ii) **1a**,  $\text{Pd}(\text{AcO})_2$ , (toluene), **1b**,  $\text{Pd}(\text{AcO})_2$ , (dichloromethane); (iii) NaCl (acetone/water); (iv) 1,  $\text{AgCF}_3\text{SO}_3$ ; 2,  $\text{PPh}_3$  (acetone, 1:1 molar ratio); (v) 1,  $\text{AgCF}_3\text{SO}_3$ ; 2, dppb (acetone, 2:1 molar ratio); (vi) NaAcO, acetone.

to the free ligand) was indicative of coordination to the nitrogen atom [25,26]. The low conductivity shown by the solutions of **2a** in dry acetonitrile and the presence in the mass FAB spectrum of clusters of peaks at 317  $[\text{M} + 2\text{H}^+ - 2\text{HCl}]$  and 351  $[\text{M} + \text{H}^+ - \text{HCl}]$  a.m.u. were in agreement with the mononuclear formulation proposed for the complex.

Reaction of **a** with lithium tetrachloropalladate and sodium acetate in methanol for 48 h yielded the cyclometallated complex  $[\text{Pd}\{\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})\}-\text{Cl}]]$  (**3a**). The NMR and IR data were similar to those described for **1a**, *vide supra*, with the most noticeable difference being the absence of the MeCOO signal, in the  $^1\text{H}$  NMR spectrum, and the  $\nu(\text{COO})$  bands in the IR spectrum. The presence of a cluster of peaks centred at 352 a.m.u. in the mass FAB spectrum corresponding to the molecular ion confirmed the proposed formulation. The  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum showed the C=N, and C1 signals considerably downfield shifted as compared to the uncoordinated ligand by ca. 10 ppm. The resonance for C6 was shifted to higher frequency by ca. 20 ppm compared to the free donor, confirming metallation of the carbon atom. There was no noticeable quadrupolar broadening of these resonances by coupling with the  $^{105}\text{Pd}$  (22.2% natural abundance,  $I = 5/2$ ) nucleus. Complex **3a** could also be prepared by treatment of a solution of **1a** with an aqueous solution of sodium chloride, or alternatively, by reaction of **2a** with sodium acetate, although this method gave low yields.

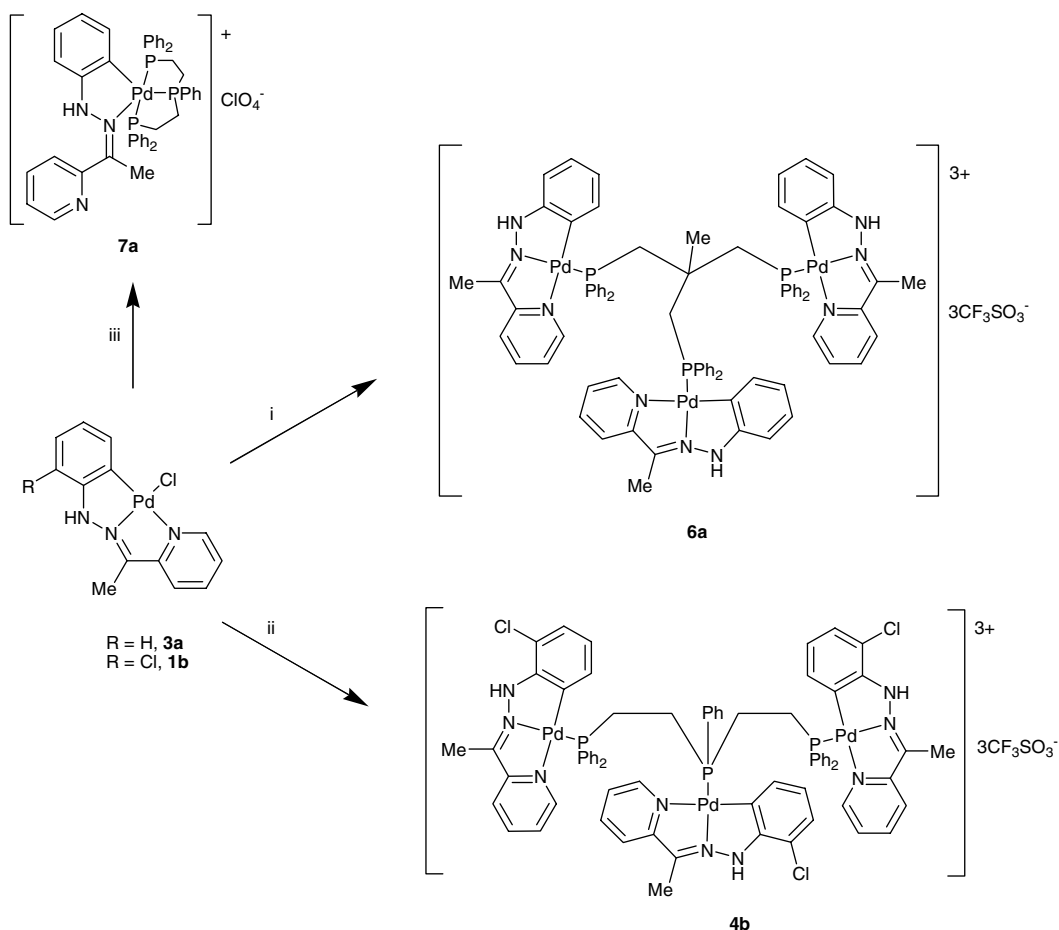
In the course of this work Ghedini et al. [27] have reported mononuclear cyclometallated compounds with 2-benzoyl-*N*-phenylhydrazones, inclusive of the crystal structure of a similar compound to **3a**; however, the comprehensive reaction scheme for the mononuclear compounds described here shows the full synthetic routes between the ligands and compounds.

## 2.2. Crystal structure of **3a**

Suitable crystals were grown by slowly evaporating a chloroform/*n*-hexane solution of the complex. The molecular structure is illustrated in Fig. 1. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The structure consists of discrete molecules separated by Van der Waals distances in which the palladium atom is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the phenyl ring, the N(2) and pyridine N(3) nitrogen atoms, and to the Cl(1) chlorine atom. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of  $90^\circ$  with the most noticeable distortions corresponding to the N(2)–Pd(1)–N(3) angle of  $78.85(8)^\circ$  and the N(3)–Pd(1)–Cl(1) angle of  $101.04(6)^\circ$ . The sum of the angles about palladium is approximately  $360^\circ$ .

The Pd(1)–N(2) 1.975(2) Å and Pd(1)–N(3) 2.150(2) bond distances are similar to others reported for related compounds [21,23,28–30]. The Pd(1)–N(3) bond length



Scheme 2. (i) 1,  $\text{AgCF}_3\text{SO}_3$ ; 2, tripod (acetone, 3:1 molar ratio); (ii), 1,  $\text{AgCF}_3\text{SO}_3$ ; 2, triphos (acetone, 3:1 molar ratio); (iii) 1, triphos (acetone, 1:1 molar ratio); 2,  $\text{NaClO}_4$ .

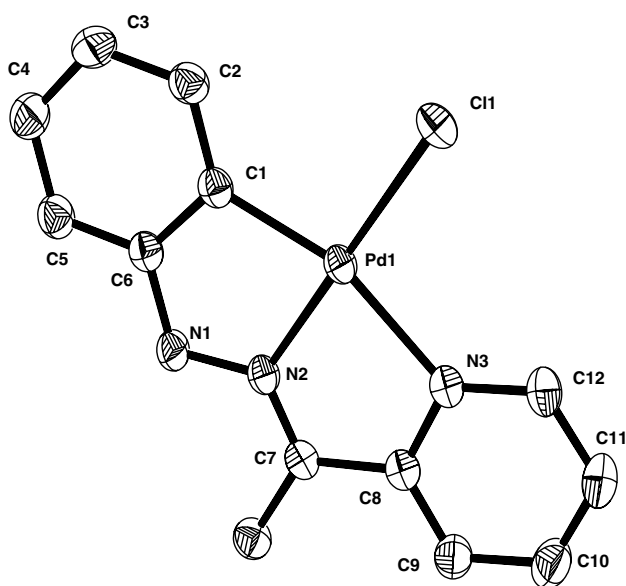


Fig. 1. Molecular structure of  $[\text{Pd}\{\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})\}(\text{Cl})]$  (**3a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

is longer than  $\text{Pd}(1)\text{--N}(2)$  distance, showing the stronger *trans* influence of the  $\text{C}(1)$  carbon atom as compared to the  $\text{Cl}(1)$  chlorine. The  $\text{Pd}(1)\text{--C}(1)$  bond distance of  $1.980(3)$  Å is somewhat shorter than the value predicted from their covalent radii [31] but similar to values found earlier [21,23,28–30].

The geometry around the palladium atom  $[\text{Pd}(1), \text{C}(1), \text{N}(2), \text{N}(3), \text{Cl}(1)]$  is planar (r.m.s. = 0.0186, plane1). The metallated ring  $[\text{Pd}(1), \text{C}(1), \text{C}(6), \text{N}(1), \text{N}(2), \text{plane 2}]$  and the coordination ring  $[\text{Pd}(1), \text{N}(2), \text{C}(7), \text{C}(8), \text{N}(3), \text{plane 3}]$  are also planar (r.m.s. = 0.0027 and 0.0080, respectively). Planes 1, 2, 3, the metallated phenyl ring and the pyridine ring are nearly coplanar (largest angle  $3.7^\circ$  between the metallated phenyl and the pyridine rings).

### 2.3. Reactivity of the cyclometallated complexes

Treatment of **3a** and **1b** with silver trifluoromethanesulphonate (triflate) and triphenylphosphine in acetone gave the mononuclear complexes  $[\text{Pd}\{\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})\}(\text{PPh}_3)][\text{F}_3\text{CSO}_3]$  (**4a**)

Table 1  
Crystal and structure refinement data

	<b>3a</b>	<b>4a</b>	<b>2b</b>
Formula	C <sub>13</sub> H <sub>12</sub> N <sub>3</sub> ClPd	C <sub>32</sub> H <sub>27</sub> F <sub>3</sub> N <sub>3</sub> O <sub>3</sub> PPdS	C <sub>32</sub> H <sub>26</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>3</sub> PPdS · CHCl <sub>3</sub>
M <sub>r</sub>	352.11	728.00	881.81
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	10.288(1)	10.180(1)	10.654(1)
<i>b</i> (Å)	11.532(1)	12.502(9)	11.844(1)
<i>c</i> (Å)	21.742(2)	13.986(11)	14.647(1)
$\alpha$ (°)		116.238(1)	81.057(1)
$\beta$ (°)		97.976(1)	80.041(1)
$\gamma$ (°)		96.478(1)	86.990(1)
V (Å <sup>3</sup> )	2579.5(3)	1550.5(2)	1797.7(1)
Z	8	2	2
$\mu$ (mm <sup>-1</sup> )	1.629	1.559	1.629
Crystal size (mm)	0.55 × 0.40 × 0.35	0.34 × 0.18 × 0.10	0.50 × 0.45 × 0.20
2 $\theta$ <sub>max</sub> (°)	56.6	56.6	56.6
<i>Reflections</i>			
Collected	17058	9986	12422
Unique	3195 ( <i>R</i> <sub>int</sub> = 0.04)	7017 ( <i>R</i> <sub>int</sub> = 0.02)	8532 ( <i>R</i> <sub>int</sub> = 0.02)
Transmissions	0.59, 0.46	0.92, 0.78	0.83, 0.64
<i>R</i> [ <i>F</i> , <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0285	0.0453	0.0330
<i>wR</i> [ <i>F</i> <sup>2</sup> , all data]	0.0726	0.1298	0.0895
max $\rho$ (e Å <sup>-3</sup> )	0.264	0.861	0.557
Extinction coefficient			0.0087(5)

Table 2  
Selected bond distances (Å) and angles (°) for complexes **3a**, **4a** and **2b**

<b>3a</b>	<b>4a</b>	<b>2b</b>			
Pd(1)–C(1)	1.980(3)	Pd(1)–C(1)	2.014(4)	Pd(1)–C(1)	2.007(2)
Pd(1)–N(2)	1.975(2)	Pd(1)–N(2)	2.028(3)	Pd(1)–N(2)	2.016(2)
Pd(1)–N(3)	2.150(2)	Pd(1)–N(3)	2.175(3)	Pd(1)–N(3)	2.155(3)
Pd(1)–Cl(1)	2.3166(7)	Pd(1)–P(1)	2.278(1)	Pd(1)–P(1)	2.2816(6)
C(1)–C(6)	1.409(4)	C(1)–C(6)	1.415(6)	C(1)–C(6)	1.415(3)
C(6)–N(1)	1.404(4)	C(6)–N(1)	1.390(5)	C(6)–N(1)	1.402(3)
N(1)–N(2)	1.362(3)	N(1)–N(2)	1.353(5)	N(1)–N(2)	1.375(3)
C(1)–Pd(1)–N(2)	82.50(10)	C(1)–Pd(1)–N(2)	81.70(15)	C(1)–Pd(1)–N(2)	81.58(8)
C(1)–Pd(1)–N(3)	161.35(10)	C(1)–Pd(1)–N(3)	157.97(15)	C(1)–Pd(1)–N(3)	158.39(9)
N(2)–Pd(1)–N(3)	78.85(8)	N(2)–Pd(1)–N(3)	76.42(13)	N(2)–Pd(1)–N(3)	76.91(7)
C(1)–Pd(1)–Cl(1)	97.59(8)	C(1)–Pd(1)–P(1)	94.02(12)	C(1)–Pd(1)–P(1)	94.07(7)
N(3)–Pd(1)–Cl(1)	101.04(6)	N(3)–Pd(1)–P(1)	107.96(9)	N(3)–Pd(1)–P(1)	107.52(5)
C(6)–C(1)–Pd(1)	111.2(2)	C(6)–C(1)–Pd(1)	110.5(3)	C(6)–C(1)–Pd(1)	110.4(2)
C(1)–C(6)–N(1)	117.3(2)	C(1)–C(6)–N(1)	118.4(4)	C(1)–C(6)–N(1)	120.0(2)
N(2)–N(1)–C(6)	114.2(2)	N(2)–N(1)–C(6)	115.4(3)	N(2)–N(1)–C(6)	112.3(2)
N(2)–N(1)–Pd(1)	114.9(2)	N(2)–N(1)–Pd(1)	114.0(3)	N(2)–N(1)–Pd(1)	115.7(1)

and [Pd{2-ClC<sub>6</sub>H<sub>3</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(PPh<sub>3</sub>)](F<sub>3</sub>CSO<sub>3</sub>) (**2b**) with the phosphine ligand occupying the vacant coordination position left by the chlorine ligand after AgCl removal. The <sup>1</sup>H NMR spectra of the complexes showed the hydrazine NH proton signal at  $\delta$  10.31 (<sup>4</sup>*J*(HNP) = 4.4 Hz) and  $\delta$  8.80 for **4a** and **2b**, respectively. The upfield shift of the H5 and H11 resonances (as compared to **3a** and **1b**) was due to shielding by the phosphine phenyl rings [32,33], confirming coordination of the ligand. The <sup>31</sup>P–{<sup>1</sup>H} NMR spectra showed a singlet resonance at ca.  $\delta$  42 in accordance

with a phosphorus-to-nitrogen *trans* geometry [34–37]. The conductivity measurements carried out in dry acetonitrile showed the complexes to be 1:1 electrolytes.

As we [18–22] have shown before, when cyclometalated complexes derived from terdentate C,N,N' ligands with Pd–N bonds were reacted with tertiary phosphines in the appropriate molar ratio, species with the phosphine coordinated to the metal centre were obtained, with cleavage of, at least, one Pd–N bond; this was prevented in those cases where a vacant coordination was created by initial treatment with a silver(I) salt.

However, when the complexes **3a** and **1b** reported here were reacted directly with triphenylphosphine, without previous removal of the chlorine ligand, no breakage of the Pd–N bond was observed, putting forward the greater strength of the Pd–N<sub>pyridine</sub> bond in these compounds. The compounds obtained were 1:1 electrolytes, bearing the same cation, with the anion being Cl<sup>−</sup> instead of CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>.

#### 2.4. Crystal structures of **4a** and **2b**

Suitable crystals were grown by slowly evaporating dichloromethane/*n*-hexane and chloroform/*n*-hexane solutions of the complexes **4a** and **2b**, respectively. The molecular structures are illustrated in Figs. 2 and 3. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

Both crystal structures comprise one [Pd{2-RC<sub>6</sub>H<sub>n</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(PPh<sub>3</sub>)]<sup>+</sup> (R = H, *n* = 4, **4a**; R = Cl, *n* = 3, **2b**) cation and one CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> anion per asymmetric unit.

The palladium atom is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the phenyl ring, the N(2) and pyridine N(3) nitrogen atoms, and to the phosphorus atom of the triphenylphosphine ligand P(1). The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90° with the most noticeable distortions corresponding to the N(2)–Pd(1)–N(3) [76.4(1)° and

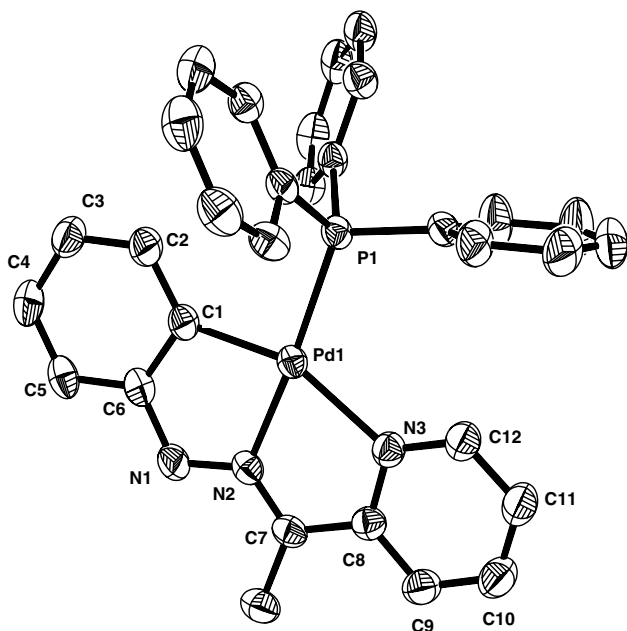


Fig. 2. Cation of [Pd{C<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(PPh<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>]<sup>−</sup> (**4a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

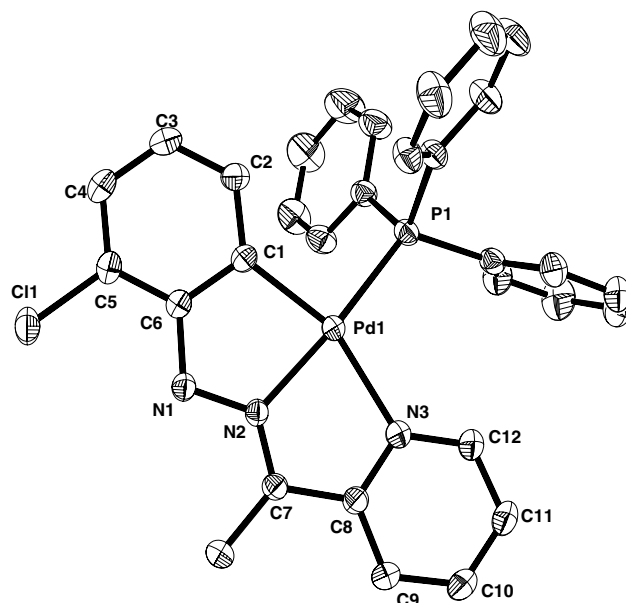


Fig. 3. Cation of [Pd{2-ClC<sub>6</sub>H<sub>3</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(PPh<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>]<sup>−</sup> (**2b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

76.91(7)° for **4a** and **2b**, respectively] and N(3)–Pd(1)–P(1) [107.96(9)° and 107.52(5)° for **4a** and **2b**, respectively] angles. The sum of the angles about palladium is approximately 360°.

The Pd–C [2.014(4) and 2.007(2) Å, for **4a** and **2b**, respectively], Pd–P [2.278(1) and 2.2816(6) Å, for **4a** and **2b**, respectively], Pd–N(2) [2.028(3) and 2.016(2) Å, for **4a** and **2b**, respectively] and Pd–N(3) [2.175(3) and 2.155(3) Å, for **4a** and **2b**] bond distances are within the expected values for these type of complexes [23,29,38,39]. The Pd–N(3) bond length shows the larger *trans* influence of the C(1) carbon as compared to the P(1) phosphorus.

The coordination sphere around palladium [Pd(1), C(1), N(2), N(3), P(1)] is planar (r.m.s. = 0.0345 and 0.0759, for **4a** and **2b**, respectively; plane 1) with a small tetrahedral distortion, probably caused by the steric hindrance of the triphenylphosphine ligand. The metallated [Pd(1), C(6), N(1), N(2)] and the coordination [Pd(1), N(2), C(7), C(8), N(3)] rings are also planar (r.m.s. = 0.0088 and 0.0175 for **4a** and **2b**, respectively; plane 2, and 0.0255 and 0.0221 for **4a** and **2b**, respectively; plane 3) and coplanar with the metallated phenyl and pyridine rings; consequently the **4a** and **2b** cations are planar with the exception of the phosphine phenyls.

Hydrogen bonding between the N(1)–H(1) hydrogen and O(1) oxygen atom of the triflate anion was found in complex **2b** [N(1)–H(1), 0.81(3) Å; O(1)⋯H(1), 2.43(3) Å; N(1)–H(1)⋯O(1), 3.160(3) Å, 151(3)°].

Reaction of **3a** and **1b** with silver triflate and the tertiary diphosphine Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>(dppb) in a 2:1 molar

ratio gave the dinuclear cyclometallated complexes  $[\{\text{Pd}\{\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})\}_2(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)\text{-}[\text{CF}_3\text{SO}_3]_2$  (**5a**) and  $[\{\text{Pd}\{2\text{-ClC}_6\text{H}_3\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})\}_2(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)\text{-}[\text{CF}_3\text{SO}_3]_2$  (**3b**) which were fully characterized (see Section 4). The  $^1\text{H}$  NMR spectra of the complexes were analogous to those described for complexes **4a** and **2b**, suggesting a similar coordination situation for the palladium atoms. The symmetric nature of the complexes was established by the presence of only one singlet signal in the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  spectra ca.  $\delta$  29.5. The conductivity measurements carried out in dry acetonitrile have shown the complexes to be 1:2 electrolytes. The mass-FAB spectra have shown the presence of clusters of peaks centred at 1209 and 1277 uma, for **5a** and **3b**, respectively, corresponding to the loss of one triflate counteranion.

### 2.5. Reactions with triphosphines

Treatment of **3a** with silver triflate followed by reaction with the tertiary triphosphine  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$  (tripod) in a 3:1 molar ratio, gave the unprecedented trinuclear complex  $[\{\text{Pd}[\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})]\}_3\{\mu_3\text{-CH}_3\text{C}(\text{CH}_2\text{Ph}_2)_3\}][\text{CF}_3\text{SO}_3]_3$  (**6a**) as an air-stable solid, which was fully characterized (see Section 4). The conductivity data in acetonitrile solution showed the compound was a 1:3 electrolyte. The  $^1\text{H}$  NMR spectrum of the complex showed only one set of signals in accordance with three equivalent cyclometallated moieties, each of which was bonded to one of the phosphorus atoms of the terdentate phosphine ligand, and whose pattern was similar to that of compound **4a**, i.e., with the NH signal ca.  $\delta$  10 and the resonances corresponding to H5 and H11 protons shifted to high field, due to the shielding effect of the phosphine phenyl rings. Likewise, only one signal at  $\delta$  3.3 (multiplet, 6H) was assigned to the three phosphine methylene groups. The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectrum showed only one singlet resonance at  $\delta$  23.2, for the three equivalent phosphorus nuclei, a value in agreement with a P–Pd–N *trans* geometry [34–37].

Treatment of **1b** with silver triflate followed by reaction with the tertiary triphosphine  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$  (triphos), in a 3:1 molar ratio, gave the new trinuclear complex  $[\{\text{Pd}[2\text{-ClC}_6\text{H}_3\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})]\}_3\{\mu_3\text{-}(\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh}\}][\text{CF}_3\text{SO}_3]_3$  (**4b**) as an air-stable solid, which was fully characterized (see Section 4). The conductivity data in acetonitrile solution showed the compound was a 1:3 electrolyte. The  $^1\text{H}$  NMR spectrum showed two groups of resonances with an integration ratio of 2:1; one assigned to the two equivalent cyclometallated groups coordinated to the terminal phosphorus atoms, and the other one to the cyclometallated moiety bonded to the central phosphorus atom. The NH proton resonances were at  $\delta$  10.01 for the former, and at  $\delta$  9.90 for the latter. The signals corresponding to the H5 and H11 protons were shifted to lower frequency, as com-

pared to **1b**, both in the terminal cyclometallated groups, as well as in the central one, by the influence of the phosphine phenyl rings (see Section 4). The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectrum showed a doublet at  $\delta$  35.9 assigned to the two equivalent terminal phosphorus nuclei, and a triplet at  $\delta$  33.1, for the central phosphorus nucleus. All chemical shifts were characteristic of a P–Pd–N *trans* geometry [34–37].

Treatment of **3a** with the tertiary triphosphine  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}$  (triphos), in a 1:1 molar ratio, followed by sodium perchlorate, gave the mononuclear complex  $[\text{Pd}\{\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})\}\{(\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh-P,P,P}\}][\text{ClO}_4]$  (**7a**) as an air-stable solid, which was fully characterized (see Section 4). The conductivity data in acetonitrile solution showed the compound was a 1:1 electrolyte. The FAB-mass spectrum showed a set of peaks centred at 851 uma assigned to the  $[\text{M} + \text{H}^+ - \text{HClO}_4]$  fragment.

The phosphorus resonances in the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectrum were downfield shifted from their values in the free phosphine suggesting coordination of the three phosphorus atoms to the metal centre. A triplet resonance at  $\delta$  94.2 was assigned to the central  $^{31}\text{P}$  nucleus, *trans* to the phenyl carbon atom, and a doublet at  $\delta$  21.8 was assigned to the two equivalent mutually *trans* phosphorus nuclei. The latter signal appeared at lower frequency in accordance with the high *trans* influence of the phosphine ligand [34]. The resonance of the proton in the *ortho* position to the metallated carbon appeared as a triplet showing coupling to the central  $^{31}\text{P}$  atom [ $J(\text{PH5}) = 7.1$  Hz]; no coupling was observed to the terminal phosphorus nuclei. These data are in accordance with a disposition in which the metallated ring is nearly perpendicular to the plane defined by the three phosphorus atoms [15,40]. The shift of the  $\nu(\text{C}=\text{N})$  stretching vibration to lower wavenumbers indicates the existence of palladium–nitrogen interaction. These results strongly agree with those previously obtained by us in related penta-coordinated palladium(II) species, and hence we propose a similar disposition of the triphos ligand in this case [15,40]. The H11 proton resonance appeared at  $\delta$  8.49, downfield shifted as compared to the phosphine derivatives of ligand **a** mentioned above, indicating that H11 does not fall within the shielding zone of the phosphine phenyl rings, due to the cleavage of the Pd–N<sub>pyridine</sub> bond.

### 3. Conclusions

We have shown that 2-acetylphenylhydrazones may be readily metallated at the phenyl ring by palladium(II) salts rendering mononuclear cyclometallated compounds with chlorine or mono-coordinated acetate ligands, and with the organic moiety as terdentate through the aromatic carbon atom, and the azomethine

and pyridine nitrogen atoms, with two fused rings at the metal centre: the metallacycle and the coordination ring. Varying the reaction conditions, in the present case a lower reaction time suffices, may only lead to coordination compounds with absence of a Pd–C bond, that in turn may be transformed into the corresponding cyclometallated species. The reactivity of the latter towards tertiary phosphines leads to the mono-, di or trinuclear compounds. These trinuclear species are the first examples of a triphosphine acting as a  $\mu_3$ -bridging ligand and linking three cyclometallated moieties together. The strength of the Pd–N<sub>pyridine</sub> bond hinders ring opening upon reaction of the compounds with triphenylphosphine, even in the absence of a silver(I) salt. However, with bi- or tridentate phosphines chelation prevails and Pd–N<sub>pyridine</sub> bond cleavage may only be prevented by treatment of the compounds with silver trifluoromethanesulfonate, prior to the reaction with the corresponding phosphine.

## 4. Experimental

**Safety note.** Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

### 4.1. General procedures

Solvents were purified by standard methods [41]. Chemicals were reagent grade. The phosphines PPh<sub>3</sub>, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>(dppb), (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh (triphos) and MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub> (tripod) were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometers. NMR spectra were obtained as CDCl<sub>3</sub> solutions and referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C–{<sup>1</sup>H}) or 85% H<sub>3</sub>PO<sub>4</sub> <sup>31</sup>P–({<sup>1</sup>H}) and were recorded on a Bruker AC-2005 spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol (3-NBA), 2-hydroxyethyl disulfide (2-HEDS) or 3-mercaptopropanediol (1-thioglycerol) were used as the matrix. Conductivity measurements were made on a CRISON GLP 32 conductivitymeter using 10<sup>−3</sup> mol dm<sup>−3</sup> solutions in dry acetonitrile.

### 4.2. Syntheses

#### 4.2.1. Preparation of C<sub>6</sub>H<sub>5</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N) **a**

A mixture of phenylhydrazine (1.02 g, 8.42 mmol), 2-acetylpyridine (0.92 g, 8.42 mmol) and 0.1 cm<sup>3</sup> of acetic acid in 50 cm<sup>3</sup> of ethanol was stirred for 4 h at room

temperature (r.t.). The yellow precipitate formed was filtered off and dried in air. Yield 58%. Anal. Found: C, 73.7; H, 6.1; N, 19.8. C<sub>13</sub>H<sub>13</sub>N<sub>3</sub> requires C, 73.9; H, 6.2; N, 19.9%. IR:  $\nu$ (C=N), 1604s cm<sup>−1</sup>,  $\nu$ (N–H), 3205, 3175m cm<sup>−1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, J Hz): 2.40 [s, 3H, Me]; 7.60 [s, 1H, NH]; 8.57 [dd, 1H, H11, <sup>3</sup>J(H11H10) = 3.9, <sup>4</sup>J(H11H9) = 0.9]; 6.91 [dt, 1H, <sup>3</sup>J(HH) = 6.8, <sup>4</sup>J(HH) = 1.5], 7.3 [m, 5H]; 7.69 [dt, 1H, <sup>3</sup>J(HH) = 8.3, <sup>4</sup>J(HH) = 1.9]; 8.19 [d, 1H, <sup>3</sup>J(HH) = 8.3]. <sup>13</sup>C–<sup>1</sup>H NMR (50.28 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 148.8, 147.5, 144.4 (C=N, C1, C7); 147.3 (C11); 129.2 (C3, C5); 136.6 (C9); 122.8, 120.7 (C8, C10); 113.5 (C2, C6); 122.2 (C4); 10.0 (Me). Specific molar conductivity,  $\Lambda_m$  = 2.9 ohm<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup> (in acetonitrile).

Compound **b** was prepared similarly from 2-chlorophenylhydrazine hydrochloride as a yellow solid.

#### 4.2.2. 2-ClC<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N) · HCl **b**

Yield 78%. Anal. Found: C, 58.6; H, 4.7; N, 10.1. C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>Cl · HCl requires C, 58.2; H, 4.9; N, 10.4%. IR:  $\nu$ (C=N), 1609s cm<sup>−1</sup>,  $\nu$ (N–H), 3265m cm<sup>−1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, J Hz): 2.68 [s, 3H, Me]; 6.99 [t, 1H, <sup>3</sup>J(HH) = 7.5]; 7.4 [m, 2H]; 7.6 [m, 1H]; 8.01 [d, 1H, <sup>3</sup>J(HH) = 7.8]; 8.3 [m, 2H]; 8.61 [s, 1H, NH]; 8.97 [d, 1H, H11, <sup>3</sup>J(H11H10) = 4.8]; specific molar conductivity,  $\Lambda_m$  = 42.3 ohm<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup> (in acetonitrile).

#### 4.2.3. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(OAc)] **1a**

A pressure tube containing C<sub>6</sub>H<sub>5</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N), **a**, (138 mg, 0.65 mmol), palladium(II) acetate (146 mg, 0.65 mmol) and 20 cm<sup>3</sup> of dry toluene was sealed under argon. The resulting mixture was heated at 60 °C for 12 h. After cooling to r.t., the solution was filtered through cellite to remove the black palladium formed. The solvent was removed under vacuum to give a yellow solid. Yield 51%. Anal. Found: C, 48.0; H, 4.1; N, 11.0. C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>Pd requires C, 47.9; H, 4.0; N, 11.2%. IR:  $\nu$ (C=N), 1592s cm<sup>−1</sup>,  $\nu$ (N–H), 3125m cm<sup>−1</sup>;  $\nu_{as}$ (COO), 1504m cm<sup>−1</sup>;  $\nu_s$ (COO), 1385m cm<sup>−1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, J Hz): 2.04 [s, 3H, AcO]; 2.24 [s, 3H, Me]; 6.2, 6.1 [m, 3H, H2, H3, H4]; 6.8 [m, 3H, H5, H8, H10]; 7.60 [t, 1H, H9, <sup>3</sup>J(H10H9) = 7.8]; 7.95 [d, 1H, H11, <sup>3</sup>J(H11H10) = 4.4]; 11.6 [s, 1H, NH]. FAB-MS:  $m/z$  = 316 [M + H<sup>+</sup> – AcOH], (in 3-NBA and 2-HEDS).

#### 4.2.4. Preparation of [Pd{2-ClC<sub>6</sub>H<sub>3</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(Cl)] **1b**

**Method 1.** A pressure tube containing 2-ClC<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N) · HCl (**b**) (22 mg, 0.08 mmol), palladium(II) acetate (18 mg, 0.08 mmol) and 20 cm<sup>3</sup> of dry dichloromethane was sealed under argon. The resulting mixture was stirred for 12 h at room tem-



perature (r.t.) and the solvent removed under vacuum to give a yellow solid. Yield 58%.

**Method 2.** A stirred solution of lithium tetrachloropalladate (200 mg, 0.76 mmol) in methanol 50 cm<sup>3</sup> was treated with 2-ClC<sub>6</sub>H<sub>4</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)·HCl (**a**) (200 mg, 0.76 mmol) and sodium acetate (63 mg, 0.76 mmol). The mixture was stirred at room temperature for 24 h. The yellow precipitate formed was filtered off, and dried in air. Yield 65%. Anal. Found: C, 40.3; H, 2.9; N, 11.0. C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>Cl<sub>2</sub> Pd requires C, 40.4; H, 2.9; N, 10.9%. IR:  $\nu(\text{C}=\text{N})$ , 1577s cm<sup>-1</sup>,  $\nu(\text{N}-\text{H})$ , 3270m cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, *J*Hz): 2.42 [s, 3H, Me]; 6.60 [t, 1H, H4, <sup>3</sup>*J*(H4H3) = 7.3]; 6.94, 7.12 [d, 2H, H3, H5, <sup>3</sup>*J*(HH) = 7.3, 6.8]; 7.62 [t, 1H, H10, <sup>3</sup>*J*(H10H9) = 7.8]; 7.82 [d, 1H, H8, <sup>3</sup>*J*(H9H8) = 7.8]; 8.10 [t, 1H, H9, <sup>3</sup>*J*(H10H9) = 7.8]; 8.39 [d, 1H, H11, <sup>3</sup>*J*(H11H10) = 3.9]; 10.14 [s, 1H, NH]. FAB-MS: *m/z* = 351 [M + H<sup>+</sup> - HCl], (in 3-NBA).

#### 4.2.5. Preparation of [Pd{C<sub>6</sub>H<sub>5</sub>N(H)N=CMe-(C<sub>5</sub>H<sub>4</sub>N)}(Cl)<sub>2</sub>] **2a**

A stirred solution of lithium tetrachloropalladate (200 mg, 0.76 mmol) in methanol 50 cm<sup>3</sup> was treated with C<sub>6</sub>H<sub>5</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N) (**a**) (162 mg, 0.76 mmol) and sodium acetate (63 mg, 0.76 mmol). The mixture was stirred to room temperature for 24 h. The orange precipitate formed was filtered off, and dried in air. Yield 88%. Anal. Found: C, 40.4; H, 3.3; N, 10.7. C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>Cl<sub>2</sub>Pd requires C, 40.2; H, 3.4; N, 10.8%. IR:  $\nu(\text{C}=\text{N})$ , 1596s cm<sup>-1</sup>,  $\nu(\text{N}-\text{H})$ ; 3227s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, *J*Hz): 2.32 [s, 3H, Me]; 6.96 [d, 2H, H2, H6, <sup>3</sup>*J*(H3H2) = 7.8]; 7.13 [t, 1H, H4, <sup>3</sup>*J*(H5H4) = 7.8]; 7.37 [t, 2H, H3, H5, <sup>3</sup>*J*(H4H3) = 7.8]; 7.75 [dt, 1H, H10, <sup>3</sup>*J*(H11H10) = 6.8, <sup>4</sup>*J*(H10H8) = 1.4]; 7.95 [dd, 1H, H8, <sup>3</sup>*J*(H9H8) = 7.8, <sup>4</sup>*J*(H10H8) = 1.4]; 8.25 [dt, 1H, H9, <sup>4</sup>*J*(H11H9) = 1.4, <sup>3</sup>*J*(H9H8) = 7.8]; 8.66 [s, 1H, NH]; 9.18 [dd, 1H, H11, <sup>3</sup>*J*(H11H10) = 6.8, <sup>4</sup>*J*(H11H9) = 1.4]. FAB-MS: *m/z* = 317 [M + 2H<sup>+</sup> - 2HCl], 351 [M + H<sup>+</sup> - HCl] (in 3-NBA).

#### 4.2.6. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>N(H)N=CMe-(C<sub>5</sub>H<sub>4</sub>N)}(Cl)] **3a**

**Method 1.** Complex **3a** was obtained following a similar procedure to the one used for **2a** but stirring the reaction mixture for 48 h, as a yellow solid. Yield 80%.

**Method 2.** An aqueous solution of NaCl (ca. 10<sup>-2</sup> M) was added dropwise to a solution of **1a** (68 mg, 0.08 mmol) in 15 cm<sup>3</sup> of acetone. The resulting mixture was stirred for 24 h. The orange precipitate formed was filtered off, washed with water and dried under vacuum to give complex **3a** as an orange solid. Yield 85%. Anal. Found: C, 44.4; H, 3.3; N, 11.8. C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>ClPd requires C, 44.3; H, 3.4; N, 11.9%. IR:  $\nu(\text{C}=\text{N})$ , 1599s cm<sup>-1</sup>,  $\nu(\text{N}-\text{H})$ , 3228s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz,

CDCl<sub>3</sub>,  $\delta$  ppm, *J*Hz): 2.32 [s, 3H, Me]; 6.5 [m, 2H, H2, H4]; 6.83 [dt, 1H, H3, <sup>3</sup>*J*(H4H3) = 7.6, <sup>4</sup>*J*(H5H3) = 1.4]; 7.11 [dd, 1H, H5, <sup>3</sup>*J*(H5H4) = 7.3, <sup>4</sup>*J*(H5H3) = 1.4]; 7.52 [dt, 1H, H10, <sup>3</sup>*J*(H11H10) = 5.5, <sup>4</sup>*J*(H10H8) = 0.9]; 7.68 [d, 1H, H8, <sup>3</sup>*J*(H9H8) = 7.8]; 8.03 [dt, 1H, H9, <sup>3</sup>*J*(H10H9) = 7.8, <sup>4</sup>*J*(H11H9) = 1.4]; 8.32 [dd, 1H, H11, <sup>3</sup>*J*(H11H10) = 5.5, <sup>4</sup>*J*(H11H9) = 1.4]; 10.7 [s, 1H, NH]. <sup>13</sup>C-{<sup>1</sup>H} NMR (50.28 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 158.0, 156.0, 144.0 (C=N, C1, C7); 148.6 (C11); 134.8 (C6); 140.6, 135.4, 125.8, 125.5, 123.2, 119.4, 108.7 (C2, C3, C4, C5, C8, C9, C10); 12.8 (Me). FAB-MS: *m/z* = 316 [M + H<sup>+</sup> - HCl], (in 3-NBA).

#### 4.2.7. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>N(H)N=CMe-(C<sub>5</sub>H<sub>4</sub>N)}(PPh<sub>3</sub>)] [F<sub>3</sub>CSO<sub>3</sub>] **4a**

Silver trifluoromethanesulfonate (46 mg, 0.18 mmol) was added to a solution of **2a** (63.9 mg, 0.18 mmol) in acetone (15 cm<sup>3</sup>). The resulting mixture was stirred for 2 h and filtered through celite to remove the AgCl precipitate. PPh<sub>3</sub> (47.3 mg, 0.18 mmol) was added to the filtrate, the solution stirred for another 2 h and the solvent removed to give an orange solid which was recrystallized from acetone/hexane. Yield 41%. Anal. Found: C, 52.6; H, 3.9; N, 5.8. C<sub>32</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>F<sub>3</sub> PSPd requires C, 52.7; H, 3.7; N, 5.7%. IR:  $\nu(\text{C}=\text{N})$ , 1599s cm<sup>-1</sup>,  $\nu(\text{N}-\text{H})$ , 3125s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, *J*Hz): 2.49 [s, 3H, Me]; 5.90 [d, 1H, H11, <sup>3</sup>*J*(H11H10) = 4.5]; 6.05 [m, 2H, H4, H5]; 6.75 [m, 2H]; 6.95 [d, 1H, H2, <sup>3</sup>*J*(H3H2) = 7.8]; 10.31 [d, 1H, NH, <sup>4</sup>*J*(P-NH) = 4.4]. <sup>31</sup>P-<sup>1</sup>H NMR (80.96 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 42.0s. Specific molar conductivity,  $\Lambda_m$  = 136.4 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile).

Compounds **2b** and **5a** were obtained following a similar procedure, using a complex/diphosphine 1:1 and 2:1 molar ratios, respectively, as yellow solids.

#### 4.2.8. [Pd{2-ClC<sub>6</sub>H<sub>3</sub>N(H)N=CMe(C<sub>5</sub>H<sub>4</sub>N)}(PPh<sub>3</sub>)] [F<sub>3</sub>CSO<sub>3</sub>] **2b**

Yield 54%. Anal. Found: C, 50.4; H, 3.5; N, 5.7. C<sub>32</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub>F<sub>3</sub>PSClPd requires C, 50.4; H, 3.4; N, 5.5%. IR:  $\nu(\text{C}=\text{N})$ , 1569s cm<sup>-1</sup>,  $\nu(\text{N}-\text{H})$ , 3180m cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, *J*Hz): 2.64 [s, 3H, Me]; 6.1 [m, 3H, H4, H5, H11]; 6.85 [m, 2H]; 8.80 [s, 1H, N-H]. <sup>31</sup>P-<sup>1</sup>H NMR (80.96 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 41.5s. Specific molar conductivity,  $\Lambda_m$  = 125.6 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (in acetonitrile). FAB-MS: *m/z* = 613 [MH-CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup> (in 3-NBA).

#### 4.2.9. Preparation of [Pd{C<sub>6</sub>H<sub>4</sub>N(H)N=CMe-(C<sub>5</sub>H<sub>4</sub>N)}]<sub>2</sub>( $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>)] [F<sub>3</sub>CSO<sub>3</sub>]<sub>2</sub> **5a**

Yield 46%. Anal. Found: C, 49.5; H, 3.9; N, 6.1. C<sub>56</sub>H<sub>52</sub>N<sub>6</sub>O<sub>6</sub>F<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Pd<sub>2</sub> requires C, 49.5; H, 3.9; N, 6.2%. IR:  $\nu(\text{C}=\text{N})$ , 1598s cm<sup>-1</sup>,  $\nu(\text{N}-\text{H})$ , 3220s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, *J* Hz): 2.40 [s, 3H, Me]; 5.88 [t, 2H, H4, <sup>3</sup>*J*(H4H3) = 7.3]; 6.09 [dt, 1H, H5, <sup>3</sup>*J*(H5H4) = 7.3, <sup>4</sup>*J*(PH5) = 5.3]; 6.19 [d, 1H,

H11,  $^3J(\text{H11H10}) = 4.9$ ]; 6.6 [m, 2H]; 6.79 [d, 1H, H2,  $^3J(\text{H3H2}) = 7.3$ ]; 10.06 [d, 1H, NH,  $^4J(\text{P-HN}) = 3.4$ ].  $^{31}\text{P}-\{^1\text{H}\}$  NMR (80.96 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 29.8s. Specific molar conductivity,  $\Lambda_m = 217 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (in acetonitrile). FAB-MS:  $m/z = 1209$  [ $\text{M} + \text{H}^+ - \text{CF}_3\text{SO}_3\text{H}$ ], 743 [ $\text{M} + 2\text{H}^+ - 2\text{CF}_3\text{SO}_3\text{H-L-Pd}$ ], (in 2-HEDS).

Compound **3b** was prepared similarly, as a green solid.

4.2.10. [ $\text{Pd}[2\text{-ClC}_6\text{H}_3\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})]$ ] $_2$ -  
( $\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ )] [ $\text{F}_3\text{CSO}_3$ ] $_2$  **3b**

Yield 54%. Anal. Found: C, 47.2; H, 3.5; N, 6.0.  $\text{C}_{56}\text{H}_{50}\text{N}_6\text{O}_6\text{Cl}_2\text{F}_6\text{P}_2\text{S}_2\text{Pd}_2$  requires C, 47.1; H, 3.5; N, 5.9%. IR:  $\nu(\text{C}=\text{N})$ ,  $1599\text{s cm}^{-1}$ ,  $\nu(\text{N-H})$ ,  $3202\text{m cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 2.59 [s, 3H, Me]; 6.0 [m, 2H, H4, H5]; 6.42 [d, 1H, H11,  $^3J(\text{H11H10}) = 4.9$ ]; 6.61 [d, 1H, H3,  $^3J(\text{H4H3}) = 7.8$ ]; 6.82 [t, 1H,  $^3J(\text{HH}) = 6.1$ ]; 9.01 [d, 1H, NH,  $^4J(\text{P-HN}) = 3.4$ ].  $^{31}\text{P}-\{^1\text{H}\}$  NMR (80.96 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 29.3s. Specific molar conductivity,  $\Lambda_m = 250 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (in acetonitrile). FAB-MS:  $m/z = 1277$  [ $\text{M} + \text{H}^+ - \text{CF}_3\text{SO}_3\text{H}$ ], 778 [ $\text{M} + 2\text{H}^+ - 2\text{CF}_3\text{SO}_3\text{H-L-Pd}$ ], (in 2-HEDS).

Compounds **6a** and **4b** were obtained following a similar procedure as orange solids, but using a complex/triposphine 3:1 molar ratio.

4.2.11. [ $\text{Pd}[\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})]$ ] $_3$ { $\mu_3\text{-CH}_3\text{C}(\text{CH}_2\text{Ph}_2)_3\text{P}$ }] [ $\text{F}_3\text{CSO}_3$ ] $_3$  **6a**

Yield 40%. Anal. Found: C, 49.5; H, 3.7; N, 6.1.  $\text{C}_{83}\text{H}_{75}\text{N}_9\text{O}_9\text{F}_9\text{P}_3\text{S}_3\text{Pd}_3$  requires C, 49.3; H, 3.7; N, 6.2%. IR:  $\nu(\text{C}=\text{N})$ ,  $1598\text{s cm}^{-1}$ ,  $\nu(\text{N-H})$ ,  $3206\text{s cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 2.05 [s, 3H, Me], 2.44 [s, 9H, Me], 3.3 [m, 6H,  $\text{CH}_2$ ], 6.07, 6.47 [m, 3H, H4, H5, H11], 10.9 [s, 1H, NH].  $^{31}\text{P}-\{^1\text{H}\}$  NMR (80.96 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 23.2s. Specific molar conductivity,  $\Lambda_m = 374 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (in acetonitrile). FAB-MS:  $m/z = 942$  [ $\text{M} + 3\text{H}^+ - 3\text{CF}_3\text{SO}_3\text{H-L-Pd}$ ], (in 3-NBA and 2-HEDS).

4.2.12. [ $\text{Pd}[2\text{-ClC}_6\text{H}_3\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})]$ ] $_3$ { $\mu_3\text{-PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh}$ }] [ $\text{F}_3\text{CSO}_3$ ] $_3$  **4b**

Yield 23%. Anal. Found: C, 44.7; H, 3.3; N, 6.1.  $\text{C}_{76}\text{H}_{66}\text{N}_9\text{O}_9\text{Cl}_3\text{F}_9\text{P}_3\text{S}_3\text{Pd}_3$  requires C, 44.8; H, 3.3; N, 6.2%. IR:  $\nu(\text{C}=\text{N})$ ,  $1583\text{s cm}^{-1}$ ,  $\nu(\text{N-H})$ ,  $3220\text{m cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 2.48, 2.63 [s, 6H, Me, *s*, 3H, Me], 2.9 [m, 4H,  $\text{CH}_2$ ], 3.3 [m, 4H,  $\text{CH}_2$ ], 5.4, 5.7 [t, 1H, H5, *t*, 2H, H5,  $J(\text{PH5}) = 7.5$ ,  $^3J(\text{H4H5}) = 7.5$ ]; 5.87 [m, 1H, H4]; 6.10 6.32 [d, 1H, H11, *d*, 2H, H11,  $^3J(\text{H11H10}) = 5.1$ ]; 6.47, 6.59 [d, 1H, H3, *d*, 2H, H3,  $^3J(\text{H4H3}) = 7.7$ ]; 9.90, 10.01 [s, 1H, NH, *s*, 2H, N-H].  $^{31}\text{P}-\{^1\text{H}\}$  NMR (80.96 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 35.9d, 33.1t,  $J(\text{PP}) = 34.7$ . Data in italics are for the cyclometallated fragment bonded to the central phosphorus atom. Specific molar conductivity,  $\Lambda_m = 370 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (in acetonitrile). FAB-MS:

$m/z = 886$  [ $\text{M} + 3\text{H}^+ - 3\text{CF}_3\text{SO}_3\text{H-L-Pd}$ ], (in 3-NBA, 2-HEDS and 1-thioglycerol).

4.2.13. Preparation of [ $\text{Pd}[\text{C}_6\text{H}_4\text{N}(\text{H})\text{N}=\text{CMe}(\text{C}_5\text{H}_4\text{N})]$ ] $_3$ { $(\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh-P,P,P}$ }] [ $\text{ClO}_4$ ] **7a**

( $\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh}$  (98 mg, 0.18 mmol) was added to a suspension of **3a** (65 mg, 0.18 mmol) in acetone (20  $\text{cm}^3$ ). The mixture was stirred for 1 h, after which an excess of sodium perchlorate was added. The mixture was stirred for a further 4 h and the orange complex precipitated out by addition of water, filtered off and dried in vacuo. Yield 90%. Anal. Found: C, 59.1; H, 4.8; N, 4.1.  $\text{C}_{47}\text{H}_{45}\text{N}_3\text{O}_4\text{ClP}_3\text{Pd} \cdot \text{CH}_2\text{Cl}_2$  requires C, 59.3; H, 4.7; N, 4.4%. IR:  $\nu(\text{C}=\text{N})$ ,  $1562\text{s cm}^{-1}$ ,  $\nu(\text{N-H})$ ,  $3052\text{s cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz): 1.85 [s, 3H, Me]; 6.07 [t, 1H, H5,  $^3J(\text{H5H4}) = 7.1$ ,  $^4J(\text{PH5}) = 7.1$ ]; 6.30 [t, 1H, H4,  $^3J(\text{H3H4}) = 7.1$ ]; 8.49 [s, 1H, H11,  $^3J(\text{H10H11}) = 3.9$ ].  $^{31}\text{P}-\{^1\text{H}\}$  NMR (80.96 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 94.2t, 21.8d [ $J(\text{PP}) = 21.8$ ]. Specific molar conductivity,  $\Lambda_m = 150.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (in acetonitrile). FAB-MS:  $m/z = 851$  [ $\text{M} + \text{H}^+ - \text{HClO}_4$ ], (in 3-NBA).

4.2.14. X-ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the  $\omega$  scan method using graphite-monochromated Mo  $\text{K}\alpha$  radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares on  $F^2$ . Hydrogen atoms were included in calculated positions (except the N-NH hydrogens which were located in a difference Fourier map) and refined in riding mode. The S(1), C(1s), F(3) and O(1), atoms of the trifluoromethanesulphonate ion in complex **4a** were found to be disordered over two positions (with occupancies of approximately 50%). The refinement was carried out taking into account both components. Refinement converged at a final  $R = 0.0285$ , 0.0453 and 0.0330 (for complexes **3a**, **4a** and **2b**, respectively, observed data,  $F$ ) and  $wR2 = 0.0726$ , 0.1298 and 0.0895 (for complexes **3a**, **4a** and **2b**, respectively, unique data,  $F^2$ ), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [42].

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication No. 259264 (**2b**), No. 259265 (**3a**), and No. 259266 (**4a**). Copies of the

data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk.

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