Cyclometallated complexes derived from pyrimidin- and pyridazinehydrazones: Structural evidence of intermolecular "chelate metal ring" π–π interactions

Jesús J. Fernández [a,*], Alberto Fernández [a], Margarita López-Torres [a], Digna Vázquez-García [a], Antonio Rodríguez [a], Alexis Varela [a], José M. Vila [b,*]

[a] Departamento de Química Fundamental, Universidad de La Coruña, E-15071 La Coruña, Spain
[b] Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

ABSTRACT

Reaction of $3,4\text{-}(Me)_2C_6H_3C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]$ (**a**) and $3,4\text{-}(Me)_2C_6H_3C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)$ (**b**) with palladium(II) acetate gave the mononuclear cyclometallated complexes $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]\}(OAc)]$ (**1a**) and $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)\}(OAc)]$ (**1b**) with the ligand as terdentate [C,N,N]. Treatment of **a** and **b** with $Li_2[PdCl_4]$ and sodium acetate in methanol at room temperature yielded the mononuclear cyclometallated complexes $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]\}(Cl)]$ (**2a**) and $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)\}(Cl)]$ (**2b**), respectively. Recrystallization of **2b** from a dimethylsulfoxide solution gave $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(4'\text{-}ClC_4H_2N_2)\}][(CH_3)_2S=O]$ after deprotonation of the hydrazine nitrogen. The reaction of **2a** and **2b** with silver trifluoromethanesulfonate and triphenylphosphine, yielded $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]\}\text{-}(PPh_3)][CF_3SO_3]$ (**3a**) and $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)\}(PPh_3)]\text{-}[CF_3SO_3]$ (**3b**) with the phosphine ligand occupying the vacant coordination position after chlorine abstraction; these were deprotonated at the hydrazine nitrogen after treatment with sodium acetate. Reaction of **2a** with $Ph_2P(CH_2)_2AsPh_2$ (arphos), after AgCl removal gave mononuclear complex $Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]\}(Ph_2P(CH_2)_2AsPh_2)][ClO_4]$ (**5a**) with a non-coordinated As atom. Reaction of **2a** and **2b** with a Ag(I) salt and the tertiary diphosphine $Ph_2P(CH_2)_4PPh_2$ (dppb) in 2:1 molar ratio gave the dinuclear complexes $[\{Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]\}\}_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)][CF_3SO_3]_2$ (**6a**) and $[\{Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)\}\}_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)][ClO_4]_2$ (**6b**) with the diphosphine as a bridging ligand. Similarly, treatment of **1b** with silver triflate followed by reaction with the tertiary triphosphine $(Ph_2PCH_2CH_2)_2PPh$ (triphos), in a 3:1 molar ratio, gave the new trinuclear complex $[\{Pd[3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)]\}_3\{\mu_3\text{-}(Ph_2PCH_2CH_2)_2PPh\}][CF_3SO_3]_3$ (**8b**). However, reaction of **2a** and **2b** with (triphos), in 1:1 molar ratio gave the mononuclear complexes $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)[3'\text{-}(CF_3)C_4H_2N_2]\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$ (**7a**) and $[Pd\{3,4\text{-}(Me)_2C_6H_2C(Me)=NN(H)(4'\text{-}ClC_4H_2N_2)\}\text{-}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$ (**7b**) with a is five-coordinated palladium. The crystal structures of **2b**, **3a**, **3b**, **7a** and **7a** have been determined by X-ray crystallography and they show π–π interactions between the metallacycle and the heterocyclic pyrimidine or pyridazine rings, which controls the crystal packing.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In the precedent decades the chemistry of cyclometallated transition metal complexes has attracted much attention. 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 [1–9]. They exhibit a good number of applications which range from the synthesis of new organic and organometallic compounds, to mesogenic species and catalytic materials [10–22] as well as promoting unusual coordination environments [23].

In the past, we have been interested in palladium(II) and platinum(II) cyclometallated complexes derived from terdentate ligands; for example, Schiff bases readily react with palladium(II) salts to give mononuclear cyclometallated complexes with the ligand as terdentate [C,N,N′] [24–27]. Treatment of the latter with neutral ligands such as tertiary mono- or diphosphines produces

cleavage of the metal–Ń bond prior to ring-opening of the five-membered metallacycle; however, removal of the chlorine ligand by reaction with a silver (I) salt yields a vacant coordination site that may be occupied by the phosphine ligand, precluding metal–nitrogen bond cleavage. Nevertheless, in some cases the strength of the Pd–N bond prevents ring-opening, even when an excess of mono- or diphosphine is used [28]. Pd–N bond cleavage may also be achieved by reaction with the tertiary triphosphine (Ph₂PCH₂CH₂)₂PPh (triphos) upon chelation. However, in spite that the tendency of triphos to act as a chelating ligand is patent [23,26,29], in some cases it may behave as a bridging ligand coordinating three different cyclometallated moieties [28,30].

The synthesis and reactivity of the structurally related cyclometallated complexes derived from acetyl- or phenylpyridine phenylhydrazones has been fully studied [31–35] with the corresponding hydrazone having an acidic NH hydrogen which is part of the cyclometallated ring [32]. A similar acidic behavior has been observed in some of the complexes described herein, where the NH group is part of the PdNN(H)CN chelate ring.

Furthermore, the classical concept of "metalloaromaticity" [36] as an indication of aromatic properties in a chelate metallacycle is useful in describing the compound's planar conjugated ring structure, its electron delocalization, ring currents, and tendency toward equivalent, partial bond orders, as well as the impact of these properties in NMR chemical shifts, among others. Since metalloaromaticity affects bond orders and geometrical parameters within the cycles, aromaticity indices based on experimental bond lengths, typically used in the analysis of five or six-membered organic heterocycles, have also been considered in the analysis of the "aromatic" character of five-membered cyclopalladated rings [37]. This "aromatic" character has also been claimed to explain the different reactivity of the complexes towards, for example, ligand-exchange reactions [38] or the superior stability of "exo" cyclometallated rings [39,40].

New structural evidence of metalloaromaticity is given by the existence of π–π stacking interactions, generated by metal chelated rings. An interesting example has been reported recently in the case of a copper (II) 1,10-phenanthroline derivative in which the metallacycle of the N,N type is involved in an intramolecular effective "metal chelate ring/aromatic ring" π–π stacking interaction [41]. Examples of metallacycles of the C,N type, that is, cyclometallated rings, that contribute to π–π stacking interactions within the molecular arrangement, are given by the cyclopalladated phenylhydrazone or azobenzene complexes [35,42].

Herein we report the synthesis of cyclometallated complexes derived from pyrimidin- and pyridazinhydrazones with the ligand in a terdentate *C,N,N′* fashion. In addition, we also report the reaction of these complexes with tertiary mono- di- and triphosphines, as well as with the phosphino arsine Ph₂P(CH₂)₂AsPh₂ (arphos). Treatment with the tertiary diphosphine Ph₂P(CH₂)₄PPh₂, dppb, or with the triphosphine (Ph₂PCH₂CH₂)₂PPh, triphos yielded complexes in which the phosphine is a bridging ligand, this being one of the few examples of a trinuclear cyclometallated complex with triphos as a μ₃-bridging phosphine, however the reaction with arphos yielded a mononuclear complex with an uncoordinated arsenic atom.

We also comment on the crystal structures of several cyclometallated complexes with an aromatic system constituted by the fusion of heterocyclic and phenyl rings, plus two five-membered metallacycles, in which the presence of π–π interactions plays an important role in controlling the crystal packing. Examples of π–π stacking previously reported involved metal chelate-phenyl ring interactions [35,41,42], however in the present paper we describe metallacycle–pyrimidine or –pyrazine ring interactions, and possible interactions between the coordination rings.

2. Results and discussion

2.1. Preparation of the complexes

The compounds and reactions are shown in Schemes 1–3. The compounds described in this paper were characterized by elemental analysis (C, H, N), by IR and ¹H and ³¹P–{¹H} NMR spectroscopy, FAB and ESI mass spectrometry and X-ray single crystal diffraction (data in Section 6).

Reaction of 3,4-Me₂C₆H₃C(Me)=NN(H)[3′-(CF₃)C₄H₂N₂] (**a**) and 3,4-Me₂C₆H₃C(Me)=NN(H)(4′-ClC₄H₂N₂) (**b**) with palladium(II) acetate in toluene at 60 °C, or in dichloromethane at room temperature, gave the mononuclear complexes [Pd{3,4-Me₂C₆H₂C(Me)=NN(H)[3′-(CF₃)C₄H₂N₂]}(OAc)] (**1a**) and [Pd{3,4-Me₂C₆H₂C(Me)=NN(H)(4′-ClC₄H₂N₂)}(OAc)] (**1b**) which were fully characterized (Schemes 1 and 2). The IR spectra showed the ν(C=N) stretch (1547, **1a** and 1588, **1b** cm⁻¹) shifted to lower wavenumbers due to *N*-coordination of the ligand [43,44]. The resonance assigned to the hydrazine HN proton appeared at δ 11.97 (**1a**) and δ 10.3 (**1b**) ppm in the ¹H NMR spectra, downfield shifted as compared to the ligands, as a consequence of the formation of the coordination ring. In the NMR spectrum of **1a** the H11 resonance was shifted to lower frequency due to the coordination of the pyrimidine ring through the adjacent nitrogen atom; absence of the H6 proton resonance was in accordance with metallation. The strong bands assigned to the symmetric and asymmetric ν(COO) vibrations in the IR spectrum, were in agreement with terminal acetate ligands [45] (see Section 6). These findings and the presence of a cluster of peaks in the mass spectra centered at 413 (**1a**) and 379 (**1b**) amu assigned to the [M−AcO] fragment and at 438 (**1b**) amu, assigned to the molecular ion, supported a mononuclear formulation for the complexes.

Treatment of **a** and **b** with Li₂[PdCl₄] and sodium acetate in methanol at room temperature yielded [Pd{3,4-Me₂C₆H₂C(Me)=NN(H)[3′-(CF₃)C₄H₂N₂]}(Cl)] (**2a**) and [Pd{3,4-Me₂C₆H₂C(Me)=NN(H)(4′-ClC₄H₂N₂)}(Cl)] (**2b**). The IR spectra showed the ν(C=N) stretch shifted to lower wavenumbers due to the coordination of the C=N nitrogen. The complexes were insoluble in most organic solvents and only slightly soluble in *d*⁶-DMSO. The ¹H NMR spectra showed the absence of H6 consequent on formation of the Pd–C6 bond. Although in the IR spectra (KBr discs) the presence of bands assigned to the ν(N–H) stretch suggested that the NH groups were present in the complexes, surprisingly, the ¹H NMR spectra of **2a** and **2b** in DMSO-*d*₆ solution did not show the NH resonance. Then, single crystals of **2b** were obtained by slowly evaporating a DMSO solution of the complex and the resolution of the molecular structure showed that the anionic chlorine ligand had been replaced by a solvent molecule and, to preserve the neutrality of the complex, the hydrazone group was deprotonated, putting forward that this was the species present in solution. We found this process was not reversible.

3. Crystal structure of [Pd{3,4-(Me)₂C₆H₂C(Me)NN(4′-ClC₄H₂N₂)}{(CH₃)₂SO}]

Suitable crystals were grown by slowly evaporating a dimethylsulfoxide 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 asymmetric unit contains one molecule of the complex lying on a crystallographic mirror plane, except for the DMSO methyl. The structure consists of discrete molecules 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(1)
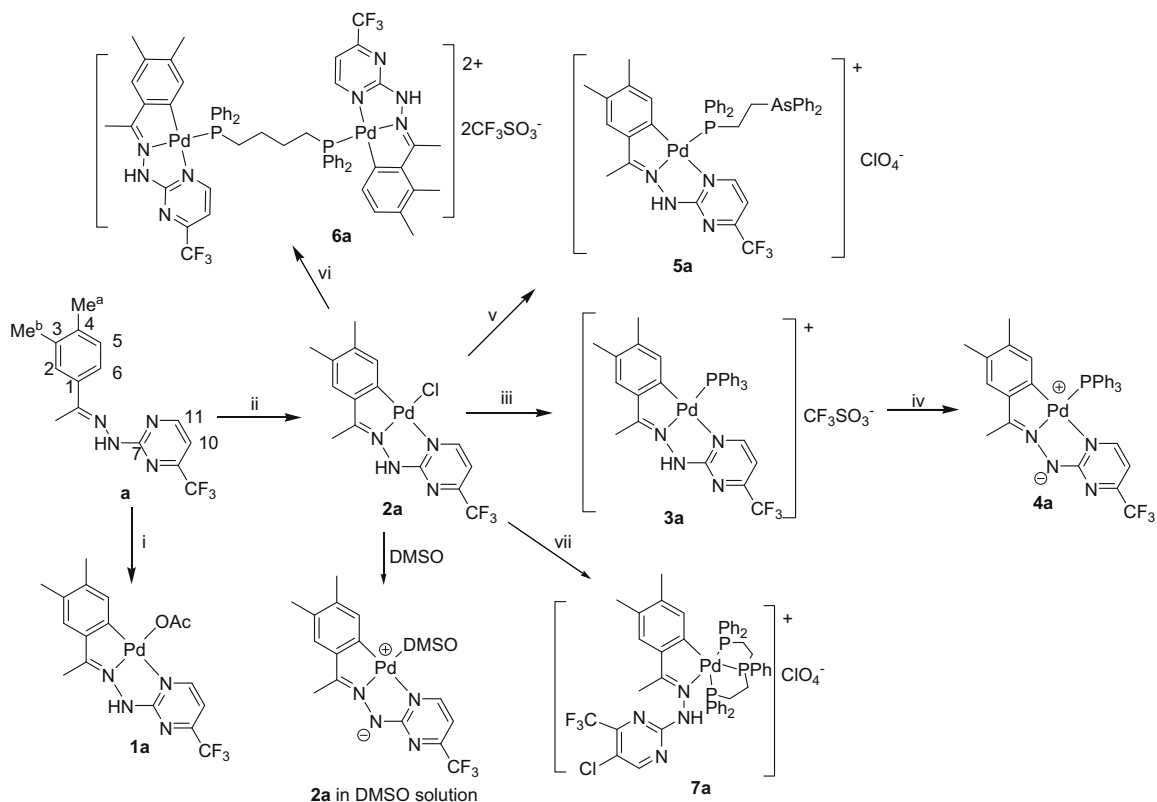
Scheme 1. (i) Pd(AcO)$_2$, (toluene or dichloromethane); (ii) Li$_2$PdCl$_4$, (methanol, NaAcO); (iii) 1: AgCF$_3$SO$_3$; 2: PPh$_3$ (acetone, 1:1molar ratio); (iv) NaAcO (methanol); (v) 1: AgCF$_3$SO$_3$; 2: arphos (acetone, 1:1 molar ratio); (vi) 1: AgCF$_3$SO$_3$; 2: dppb (acetone, 2:1 molar ratio); (vii) triphos (acetone, 1:1molar ratio); 2: NaClO$_4$.
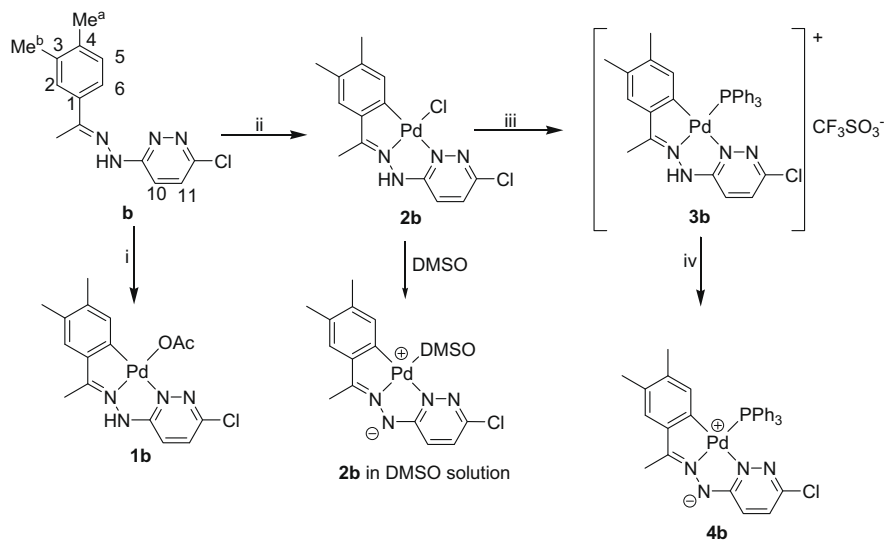

Scheme 2. (i) Pd(AcO)$_2$, (toluene or dichloromethane); (ii) Li$_2$PdCl$_4$, (methanol, NaAcO); (iii) 1: AgCF$_3$SO$_3$; 2: PPh$_3$ (acetone, 1:1molar ratio); (iv) NaAcO (methanol); (v) 1: AgCF$_3$SO$_3$; 2: arphos (acetone, 1:1 molar ratio); (vi) 1: AgCF$_3$SO$_3$; 2: dppb (acetone, 2:1 molar ratio); (vii) triphos (acetone, 1:1molar ratio); 2: NaClO$_4$.

and the pyridazine N(3) nitrogen atoms, and to the S(1) sulfur atom of the coordinated DMSO. 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(1)–Pd(1)–N(3) angle of 77.62(9)° and the C(1)–Pd(1)–S(1) angle of 100.77(8)°. The sum of the angles about palladium is approximately 360°.

The Pd(1)–N(1) 1.983(2) Å and Pd(1)–N(3) 2.092(2) bond distances are similar to others reported for related compounds [28,32,33,35,46–48]. The Pd(1)–N(3) bond length is longer than Pd(1)–N(1) distance, showing the stronger *trans* influence of the C(1) carbon atom as compared to the S(1) sulfur.

The geometry around the palladium atom [Pd(1), C(1), N(1), N(3), S(1)] is planar (r.m.s. = 0.000, plane1). The metallated ring [Pd(1), C(1), C(6), C(7), N(1), plane 2] and the coordination ring [Pd(1), N(1), N(2), C(8), N(3), plane 3] are also planar (r.m.s. = 0.000). Planes 1, 2, 3, the metallated phenyl ring and the pyridazine ring are coplanar.
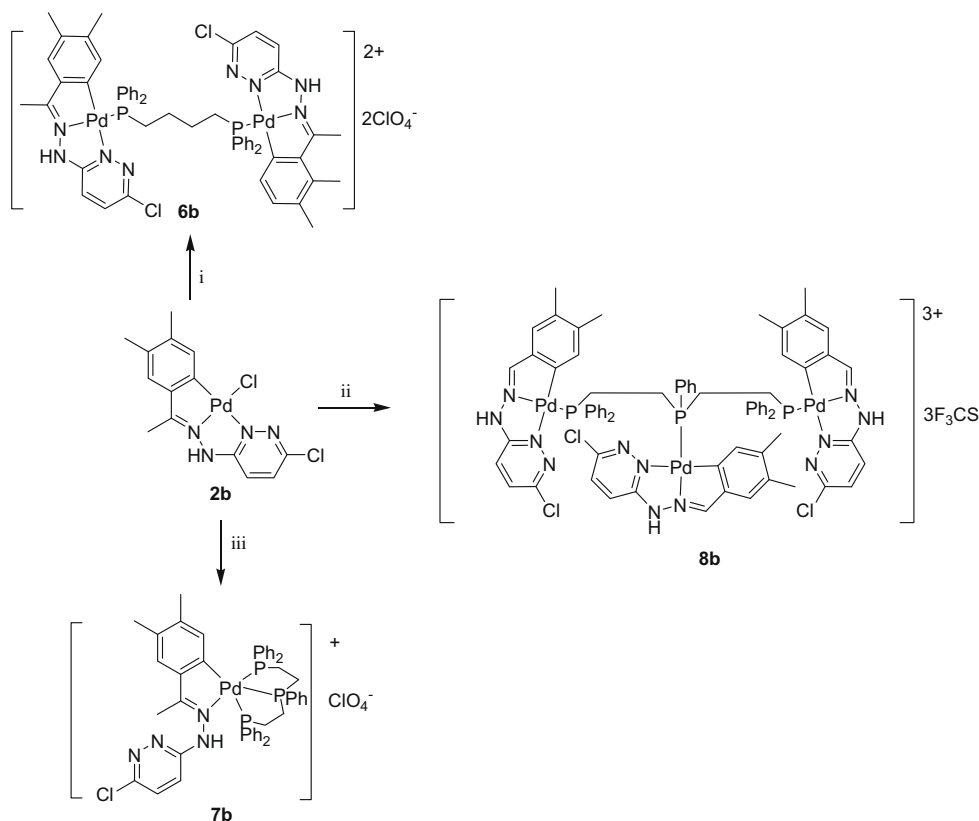
Scheme 3. (i) 1: AgCF$_3$SO$_3$; 2: dppb (acetone, 2:1 molar ratio); (ii) 1: AgCF$_3$SO$_3$; 2: triphos (acetone, 3:1 molar ratio); (iii) triphos (acetone, 1:1 molar ratio); 2: NaClO$_4$.
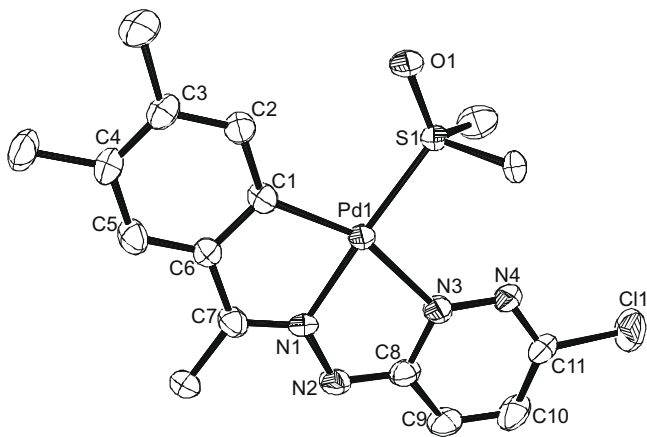

Fig. 1. Molecular structure of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(4′-ClC$_4$H$_2$N$_2$)}{(CH$_3$)$_2$S=O}], with labelling scheme. Hydrogen atoms have been omitted for clarity.

The spatial arrangement of the molecules shows they are set in rows with alignment of the palladium atoms parallel to the *a* and *c* crystallographic axes and defining a plane that contains the molecular planes. These planes are parallel with an interplanar distance of 3.61 Å (Fig. 2).

The presence of an aromatic system constituted by the fusion of the heterocyclic and phenyl rings, plus two five-membered metallacycle and coordination rings, indicated that, in this type of structures, π–π interactions can play an important role in controlling the crystal packing. Consequently π–π interactions between the pyridazine and the metallacycle [Pd(1), C(1), C(6), C(7), N(1), plane 2] rings (distance between ring centers, 3.69 Å) as well as between the two coordination [Pd(1), N(1),

N(2), C(8), N(3), plane 3] rings (distance between ring centers, 3.69 Å) were observed (Fig. 2). In fact, within the packing dimmer, the cyclometallated and the pyridazine rings, and the two coordination rings are not stacked in a roughly "face-to-face" manner showing a so-called "slipped stacking" [49]. Similar interactions have been described previously [35,41,42] and strongly suggest an active electronic delocalization within the metal chelate rings, such that it could exhibit some degree of "metalloaromaticity". However, in the present case the π–π bonded rings were the metallacycle ring and the heterocyclic pyridazine ring. The two coordination rings were also parallel and within the distance expected for a π–π "slipped stacking"; whether this disposition is consequence of an attractive interaction between the "metalloaromatic" rings or is required by metallacycle–pyridazine interaction cannot be established at present.

Reaction of **2a** and **2b** with triphenylphosphine, after chlorine removal with silver trifluoromethanesulfonate, gave [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$]}-(PPh$_3$)][CF$_3$SO$_3$] (**3a**) and [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$)}-(PPh$_3$)][CF$_3$SO$_3$] (**3b**) with the phosphine ligand occupying the vacant coordination position after AgCl removal. The ^{1}H NMR spectra of the complexes showed the hydrazine NH proton signal at δ 11.8 (**3a**) and 11.52 (**3b**) (^4J(HNP) = 5.4 Hz). The upfield shift of the H5 [δ 5.7 ppm; ^4J(H5P) *ca.* 5 Hz] and H11 (in **3a**) resonances (as compared to the parent complexes) was due to shielding by the phosphine phenyl rings [50,51], confirming coordination of the ligand. The ^{31}P–{^{1}H} NMR spectra showed a singlet resonance *ca.* δ 39 in accordance with a *trans* phosphorus-to-nitrogen geometry [52–55]. The conductivity measurements carried out in dry acetonitrile were in agreement with 1:1 electrolytes. The ESI mass spectra showed the peaks corresponding to the loss of the triflate counterions.

Table 1
Crystallographic data for complexes **2b**, **3a**, **3b**, **7a** and **7b**.

	2b	3a	3b	7a	7b
Empirical formula	$C_{16}H_{19}Cl\,N_4OPdS$	$C_{35}H_{30}Cl_3F_6N_4O_3PPdS$	$C_{33}H_{29}N_4O_3F_3ClPPdS$	$C_{49.25}H_{47.25}N_4O_4F_3Cl_{1.75}P_3Pd$	$C_{48}H_{47}N_4O_4Cl_2P_3Pd$
Formula mass	457.26	941.41	791.48	1077.51	1014.11
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/c$
a (Å)	10.333(1)	11.141(1)	20.923(2)	10.938(1)	18.918(1)
b (Å)	7.225(1)	14.091(1)	14.766(1)	22.288(1)	11.828(1)
c (Å)	12.123(1)	25.970(3)	23.208(2)	20.8394(1)	22.616(1)
β (°)	99.218(1)	99.307(2)	108.639(2)	91.994(1)	111.086 (1)
V (Å^3)	893.4(1)	4023.2(8)	6793.8(10)	5077.2(4)	4721.8(5)
Z	2	4	8	4	4
μ (mm^{-1})	1.316	0.819	0.790	0.609	0.654
Maximum, minimum transmissions	0.87, 0.57	0.90, 0.76	0.90, 0.86	0.86, 0.78	0.95, 0.90
ρ_{calc} (g cm^{-3})	1.700	1.559	1.548	1.410	1.423
θ Range (°)	2.00–28.26	1.59–28.44	1.72–28.30	1.34–28.30	1.86–28.19
Reflections collected	12263	28398	45614	6944	59671
Independent reflections	2380 (R_{int} = 0.034)	9958 (R_{int} = 0.055)	8426 (R_{int} = 0.133)	12596 (R_{int} = 0.038)	11585 (R_{int} = 0.056)
$R_1{}^a$	0.0227	0.0485	0.0593	0.0456	0.0430
$wR_2{}^b$	0.0540	0.1358	0.1475	0.1547	0.1232

^{a} $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$, $[F > 4\sigma(F)]$.
^{b} $wR_2 = [\sum [w(F_o^2 - F_c^2)^2 \sum w(F_o^2)^2]^{1/2}$, all data.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **2b**, **3a**, **3b**, **7a** and **7b**.

	2b	3a	3b	7a	7b
Pd(1)–C(1)	2.018(3)	2.020(4)	2.003(5)	2.067(3)	2.059(3)
Pd(1)–P(1)		2.233(1)	2.268(1)	2.305(1)	2.320(1)
Pd(1)–N(1)	1.983(2)	2.032(3)	2.009(4)	2.410(3)	2.448(3)
Pd(1)–N(3)	2.092(2)	2.188(3)	2.107(4)		
Pd(1)–S(1)	2.260(1)				
Pd(1)–P(2)				2.313(1)	2.323(1)
Pd(1)–P(3)				2.329(1)	2.297(1)
C(1)–C(6)	1.416(4)	1.422(5)	1.426(6)	1.399(5)	1.405(4)
C(6)–C(7)	1.467(4)	1.449(6)	1.475(7)	1.465(5)	1.473(4)
N(1)–C(7)	1.304(3)	1.291(5)	1.299(6)	1.283(4)	1.295(4)
N(1)–N(2)	1.378(3)	1.375(5)	1.380(6)	1.383(4)	1.395(3)
N(2)–C(8)	1.325(4)	1.364(5)	1.377(7)	1.363(5)	1.364(4)
C(8)–N(3)	1.378(3)	1.368(5)	1.339(6)	1.332(5)	1.319(4)
C(1)–Pd(1)–N(1)	81.40(10)	80.86(15)	81.15(19)	74.60(12)	74.59(10)
N(1)–Pd(1)–P(1)		171.27(9)	176.59(13)	115.34(8)	97.92(7)
C(1)–Pd(1)–P(1)		94.77(12)	101.82(14)	92.30(10)	92.68(8)
N(1)–Pd(1)–N(3)	77.62(9)	76.43(12)	77.79(17)		
C(1)–Pd(1)–N(3)	159.01(10)	157.10(14)	158.64(18)		
P(1)–Pd(1)–N(3)		108.12(8)	99.34(12)		
N(1)–Pd(1)–S(1)	177.83(7)				
C(1)–Pd(1)–S(1)	100.77(8)				
S(1)–Pd(1)–N(3)	100.21(6)				
P(2)–Pd(1)–P(1)				86.72(3)	85.53(3)
P(2)–Pd(1)–N(1)				110.30(7)	114.74(6)
C(1)–Pd(1)–P(2)				174.94(10)	170.64(9)
N(1)–Pd(1)–P(3)				107.34(8)	116.66(7)
P(1)–Pd(1)–P(3)				36.84(3)	145.10(3)
P(2)–Pd(1)–P(3)				84.42(3)	84.24(3)
C(1)–Pd(1)–P(3)				92.94(10)	92.09(8)

4. Crystal structures of 3a and 3b

Suitable crystals were grown by slowly evaporating chloroform/ n-hexane solutions of the complexes **3a** and **3b**. The molecular structures are illustrated in Figs. 3 and 4. 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 cation, one CF$_3$SO$_3{}^-$ anion and, in the case of **3a**, a chloroform molecule 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(1) and the heterocyclic 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(1)–Pd(1)–N(3) [76.4(1)° and 77.8(2)° for **3a** and **3b**, respectively] and N(3)–Pd(1)–P(1) [108.1(8)° for **3a**] and C(1)–Pd(1)–P(1) [101.8(1)° for **3b**] angles. The sum of the angles about palladium is approximately 360°.

The Pd–C [2.020(4) and 2.003(5) Å, for **3a** and **3b**, respectively], Pd–P [2.233(1) and 2.268(1) Å, for **3a** and **3b**, respectively], Pd–N(1) [2.032(3) and 2.009(4) Å, for **3a** and **3b**, respectively] and Pd–N(3) [2.188(3) and 2.107(4) Å, for **3a** and **3b**] bond distances are within the expected values for these type of complexes
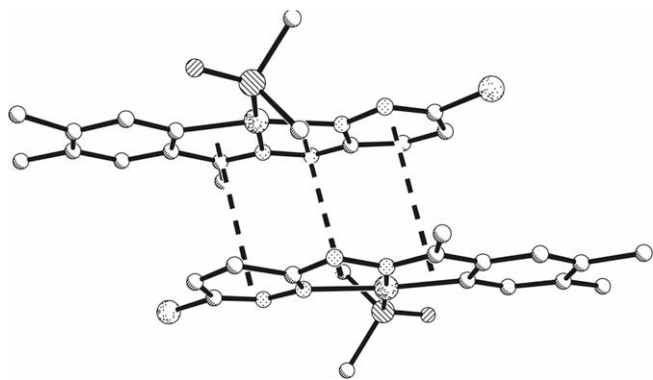
Fig. 2. Intermolecular π,π-stacking interactions. Dashed lines link ring centers involved in each stacking interaction.
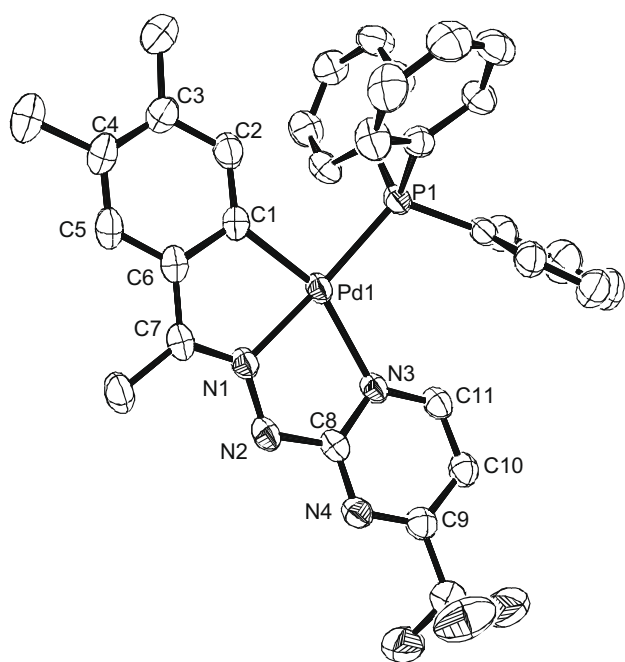

Fig. 3. Cation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$]}(PPh$_3$)]·[CF$_3$SO$_3$] (**3a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

[28,32,47,56,57]. The Pd–N(3) bond length shows the greater *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. = 0.0544 and 0.0369, for **3a** and **3b**, respectively; plane 1) with a small tetrahedral distortion, probably caused by the steric hindrance of the triphenylphosphine ligand. The metallated [Pd(1), C(1), C(6), C(7), N(1), plane 2] and the coordination [Pd(1), N(1), N(2), C(8), N(3), plane 3] rings are also planar (r.m.s. = 0.0031 and 0.0196 for **3a** and **3b**, respectively; plane 2, and 0.0347 and 0.0157 for **3a** and **3b**, respectively; plane 3) and coplanar with the metallated phenyl and pyridine rings; consequently the **3a** and **3b** cations are planar with the exception of the phosphine phenyls.

Hydrogen bonding between the N(2)–H(2a) hydrogen and O(1) oxygen atom of the triflate anion was found in complex **3a** [N(2)–H(2a), 0.78 Å; **N(2)**–H(2)···**O(1)**, 2.926(5) Å, 177°] and between the N(2)–H(1) hydrogen and O(3) in **3b** [N(2)–H(1), 0.87(6)Å; O(3)···H(1), 2.07(6)Å; **N(2)**–H(1)···**O(3)**, 2.94(2) Å, 178(5)°].

In the structure of **3a** the cations are arranged as dimmers with π–π stacking interactions between the coordination rings [Pd(1),

N(1), N(2), C(8), N(3), plane 3] (distance between ring centers, 3.62 Å) as well as between the metallacylce [Pd(1), C(1), C(6), C(7), N(1), plane 2] and the pyrimidine ring (distance between ring centers, 3.69 Å) (Fig. 5).

As for the crystal structure of **3b** the cations are arranged in lines parallel to the crystallographic *b* axis and, with the exception of the phosphine rings the molecular planes are parallel to each other. π–π Stacking interactions are present between the pyridazine and the metallated phenyl rings (distance between ring centers, 3.66 Å) of two adjacent rows (Fig. 6).

Acetylpyridine phenylhydrazone derivatives, where the NH nitrogen is part of the cyclometallated ring, behave as protic acids [32]. The deprotonation experimented by **2a** and **2b** in DMSO led us to think that a similar behavior could be observed for **3a** and **3b**. Consequently, treatment of the cyclometallated complexes **3a** and **3b** with a base (sodium acetate) in methanol produced deprotonation of the hydrazine nitrogen to give the neutral complexes [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN[3′-(CF$_3$)C$_4$H$_2$N$_2$]}(PPh$_3$)] (**4a**) and [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN[3′-(CF$_3$)C$_4$H$_2$N$_2$]}(PPh$_3$)] (**4b**). Absence of the ν(N–H) stretch in the IR spectra and of the NH resonance in the ^{1}H NMR spectra evidenced deprotonation of the NH group. In the ^{31}P–{^{1}H} NMR spectra the phosphorus resonance was at δ 39.40 (**3a**) and 38.54 (**3b**) ppm, slightly highfield shifted. Conductivity measurements in acetonitrile were in accordance with the molecular nature of **4a** and **4b**. Treatment of the latter compounds with acetic acid gave the corresponding NH protonated compounds as the acetate salts.

Treatment of **2a** with Ph$_2$P(CH$_2$)$_2$AsPh$_2$ (arphos), after AgCl removal with silver perchlorate, in 1:1 molar ratio gave the mononuclear complex Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$]} (Ph$_2$P(CH$_2$)$_2$AsPh$_2$)][ClO$_4$] (**5a**). Along with the δP value, coupling of the H5 proton resonance, δ 5.63 ppm, to the ^{31}P nucleus showed coordination of the arsinophosphine through the phosphorus atom. The H4 resonance, δ 6.04, was upfield shifted due to shielding by the phosphine phenyl rings. Conductivity measurements carried out in dry acetonitrile were in agreement with 1:1 electrolytes, and the FAB mass spectrum showed the peaks centered at 855 assigned to [M−ClO$_4$].

Reaction of **2a** and **2b** with a Ag(I) salt Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb) in a 2:1 molar ratio gave the dinuclear cyclometallated complexes [{Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$]}}$_2$(μ-Ph$_2$P(CH$_2$)$_4$-PPh$_2$)][CF$_3$SO$_3$]$_2$ (**6a**) and [{Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)= NN(H)(4′-ClC$_4$H$_2$N$_2$)}}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)][ClO$_4$]$_2$ (**6b**), as 1:2 electrolytes, which were fully characterized (see Section 6). The symmetric nature of the complexes was established by the presence of only one singlet signal in the ^{31}P–{^{1}H} spectra (δ 26.82, **6a** and 31.03, **6b** ppm). The mass-FAB spectra showed clusters of peaks centered at 1253 (**6a**) and 1185 (**6b**) uma, assigned to loss of triflate (**6a**) or perchlorate (**6b**) counteranions.

Treatment of **1b** with silver triflate followed by reaction with (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (triphos), in a 3:1 molar ratio, gave the new trinuclear complex [{Pd[3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$)]}$_3$-{μ_3-(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-P,P,P}][CF$_3$SO$_3$]$_3$ (**8b**), as a 1:3 electrolyte. The ^{1}H NMR spectrum showed two sets of signals with an integration ratio of 2:1, for the three cyclometallated moieties, with one set assigned to the 2 equiv. cyclometallated groups coordinated to the terminal phosphorus atoms, and the other to the metallacycle bonded to the central phosphorus atom. The H5 resonances were assigned as doublets at 5.19 [terminal; ^4J(PH) = 4.8 Hz] and 4.53 ppm [central; ^4J(PH5) = 4.5 Hz], highfield shifted by the influence of the phosphine phenyl rings; the NH proton resonances also showed coupling to the ^{31}P nuclei 11.35 and 11.14 [^4J(PH) = 5.1 Hz] ppm. The ^{31}P–{^{1}H} NMR spectrum showed a doublet at δ 27.5 and a triplet at δ 24.7 assigned to the 2 equiv. terminal phosphorus nuclei and to the central phosphorus nucleus, respectively. The ESI mass spectrum showed a cluster of peaks
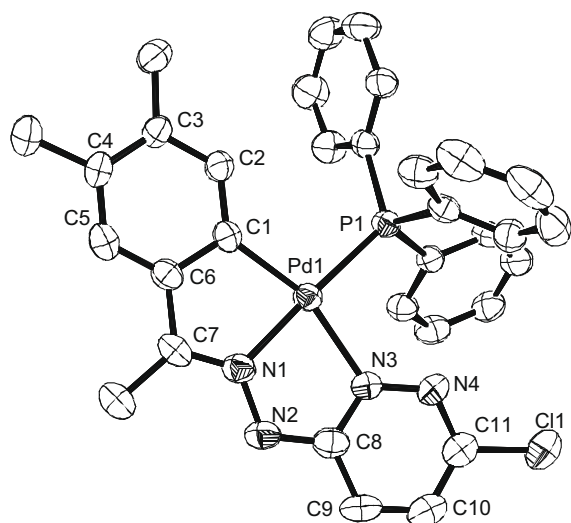
Fig. 4. Cation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4'-ClC$_4$H$_2$N$_2$)}(PPh$_3$)][CF$_3$SO$_3$] (**3b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.
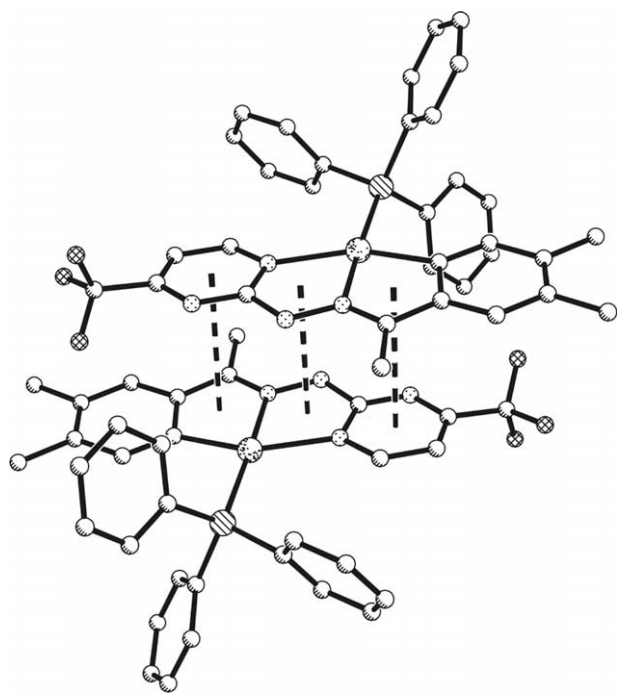

Fig. 5. Intermolecular π,π-stacking interactions in the crystal of **3a**. Dashed lines link ring centers involved in each stacking interaction.

centered at 1972 uma assigned to the trinuclear fragment [M−CF$_3$SO$_3$]$^+$.

Reaction of **2a** and **2b** with the tertiary triphosphine (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (triphos), in a 1:1 molar ratio, followed by sodium perchlorate, gave the mononuclear complexes [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3'-(CF$_3$)C$_4$H$_2$N$_2$]}{(PPh$_2$CH$_2$CH$_2$)$_2$PPh-P, P,P}][ClO$_4$] (**7a**) and [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4'-ClC$_4$H$_2$N$_2$)}-{(PPh$_2$CH$_2$CH$_2$)$_2$PPh-P,P,P}][ClO$_4$] (**7b**), as air-stable 1:1 electrolytes, which were fully characterized (see Section 6). The FAB mass spectra showed a set of peaks centered at 947 (**7a**) and 912 (**7b**) uma assigned to the [M−ClO$_4$] fragments.

A triplet resonance *ca.* δ 87 ppm was assigned to the central ^{31}P nucleus, *trans* to the phenyl carbon atom, and a doublet *ca.* δ 42 ppm was assigned to the 2 equiv. mutually *trans* phosphorus

nuclei. The latter signal appeared at lower frequency in accordance with the higher *trans* influence of the phosphine ligand [53]. The resonance of the proton in the *ortho* position to the metallated carbon appeared as a doublet showing coupling to the central ^{31}P atom [*J*(PH5) *ca.* 9 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 [23,26,28,29]. The conductivity data in acetonitrile solution showed the compounds were 1:1 electrolytes. The FAB mass spectra showed a set of peaks centered at 947 and 912 (for **7a** and **7b**, respectively) uma assigned to the [M−ClO$_4$] fragments.

5. Crystal structures of 7a and 7b

Suitable crystals were grown by slowly evaporating chloroform/ *n*-hexane solutions of **7a** and **7b**. The molecular structures are illustrated in Figs. 7 and 8. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The crystal structure comprises one cation, one ClO$_4^-$ anion and, in the crystal of **7b**, a disordered chloroform molecule per asymmetric unit. The palladium atom is bonded to the C(1) carbon atom of the metallated ring and to the three phosphorus atoms P(1), P(2) and P(3), of the triphos ligand. A fifth interaction to the N(1) nitrogen completes the coordination sphere about the palladium atom.

The Pd(1)–N(1) distance of 2.410(3) and 2.448(3) Å for **7a** and **7b**, respectively, is somewhat longer than the values of 2.338(3) Å, reported recently by us in a similar complex with a triphos ligand [29], and of 2.23(2) Å found in an authentic penta-coordinated palladium(II) complex [58]. However, the Pd–N bond length is shorter than the weak interactions in the range 2.576(4)–2.805(5) Å found in other five-coordinated complexes of palladium [59–64]. The τ parameter, an index of trigonality [65] as a general descriptor of five-co-ordinate molecules, is 0.63 and 0.42, for complexes **7a** and **7b**, respectively, nearly half-way between the trigonal-bipyramidal (τ = 1) and the square pyramidal (τ = 0) geometry; therefore, coordination around the palladium atom may be viewed as a distorted trigonal-bipyramid, with the Pd(1), N(1), P(1) and P(3) atoms in the equatorial plane and the metallated carbon atom and the central phosphorus atom at the apical position, or alternatively it may be regarded as square pyramidal with the Pd(1), C(1), P(1), P(2) and P(3) atoms in the basal plane and the nitrogen at the apical position (see Tables 3–5).

The Pd(1)–C(1) bond distance [2.067(3) and 2.059(3) Å, for **7a** and **7b**, respectively], and the Pd(1)–P(1), Pd(1)–P(2) and Pd(1)–P(3) bond lengths [2.305(1), 2.313(1) and 2.329(1) Å for **7a** and 2.320(1), 2.323(1) and 2.297(1) Å for **7b**] were in agreement with those found in related Pd(II) complexes [23,29,66].

Intramolecular π–π stacking was observed between the heterocyclic ring and the phenyl ring of the central phosphorus atom. Additionally intermolecular π–π interactions were also observed between the pyridazine rings of two centrosymmetrically related cations of **7b** (Fig. 9 and Table 6).

Hydrogen bonding between the N(2)–H(31) hydrogen and O(1) oxygen atom of the perchlorate anion was found in complex **7b** [[N(2)–H(31), 0.74(6) Å; O(1)···H(31), 2.57(6) Å; **N(2)**–H(31)···**O(1)**, 3.188(8) Å, 142(6)°].

6. 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.
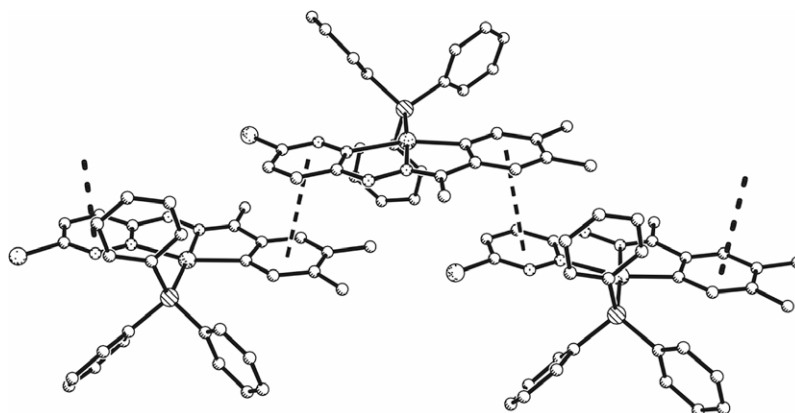
Fig. 6. Intermolecular π,π-stacking interactions in the crystal of **3b**. Dashed lines link ring cneters involved in each stacking interaction.

6.1. General procedures

Solvents were purified by standard methods [67]. Chemicals were reagent grade. The phosphines PPh$_3$, Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb), (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (triphos) were purchased from Aldrich and Ph$_2$P(CH$_2$)$_2$AsPh$_2$ (arphos) was purchased from Alfa. Microanalyses were carried out using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometers. NMR spectra were obtained as CDCl$_3$, CD$_3$SOCD$_3$ or CD$_3$COCD$_3$ solutions and referenced to SiMe$_4$ (^{1}H, ^{13}C–{^{1}H}) or 85% H$_3$PO$_4$ ^{31}P–{^{1}H}) and were recorded on a Bruker AC-300F or a Bruker AC-500F 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) or 3-mercapto-1,2-pro-panediol (1-thioglycerol) were used as the matrix The ESI mass spectra were recorded using a QSTAR Elite mass spectrometer, using acetonitrile or dichloromethane/ethanol as solvents. Conductivity measurements were made on a CRISON GLP 32 conductivi-meter using 10^{-3} mol dm^{-3} solutions in dry acetonitrile or dimethylformamide.

6.2. Syntheses

6.2.1. Preparation of 3,4-(Me)$_2$C$_6$H$_3$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$] (a)

A mixture of 2-hydrazino-4-(trifluoromethyl)pyrimidine (0.476 g, 2.67 mmol), 3,4-dimethylacetophenone (0.389 g, 2.63 mmol) and 0.1 cm^3 of acetic acid in 50 cm^3 of ethanol was stirred for 4 h at room temperature (r.t.). The yellow precipitate formed was filtered off and dried in air. Yield 0.673 g, 83%. Anal. Calc. for C$_{15}$H$_{15}$N$_4$F$_3$: C, 58.4; H, 4.2; N, 18.2. Found: C, 58.3; H,4.1; N, 18.4%. IR: ν(C=N) 1585s, ν(N–H) 3229s cm^{-1}. RMN ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 8.75 [d, 1H, H11, ^{3}J(H10H11) = 4.9], 8.48 [s, 1H, NH], 7.63 [s, br 1H, H2, ^{4}J(H2H6) = 1.8], 7.53 [dd, 1H, H6, ^{3}J(H6H5) = 7.9, ^{4}J(H2H6) = 1.8], 7.15 [d, 1H, H5, ^{3}J(H5H6) = 7.9], 7.05 [d, 1H, H10, ^{3}J(H10H11) = 4.9], 2.34 2.31, 2.29 [s 3H; s 3H; s3H, Me(C=N), Me^a, Me^b].

Compound **b** was prepared similarly from 3-chlororo-6-hydra-zinpyridazine as a white solid.

6.2.2. 3,4-(Me)$_2$C$_6$H$_3$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$) (b)

Yield 0.441 g, 61%. Anal. Calc. for C$_{14}$H$_{15}$N$_4$Cl: C, 61.2; H, 5.5; N, 20.4. Found: C, 61.1; H, 5.7; N, 20.1%. IR: ν(C=N) 1612sh, ν(C=N) 3236sh cm^{-1}. RMN ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): 8.49 [s, br 1H, NH], 7.67 y 7.38 [2d, 2H, H11, H12, ^{3}J (H10H11) = 9.3], 7.54 [s, br 1H, H2, ^{4}J(H2H6) = 1.7], 7.48 [dd, 1H, H6, ^{3}J(H5H6) = 7.9,
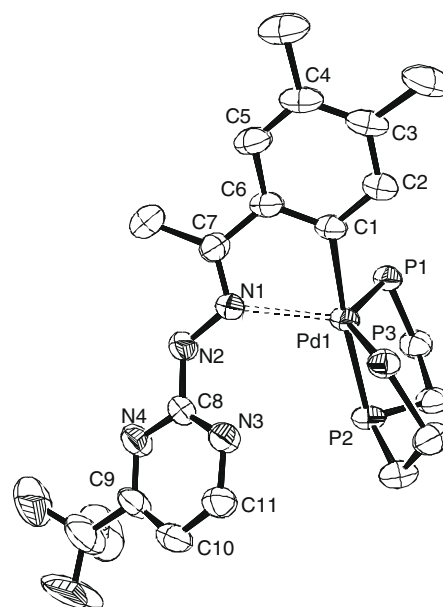
Fig. 7. Cation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$]}-{(PPh$_2$CH$_2$-CH$_2$)$_2$PPh-*P,P,P*}][ClO$_4$] (**7a**) with labelling scheme. Hydrogen and phenyl ring atoms have been omitted for clarity.

^{4}J(H2H6) = 1.7], 7.17 [d, 1H, H5, ^{3}J(H5H6) = 7.9], 2.33, 2.31 [s, 3H; br 6H, Me(C=N), Me^a, Me^b].

6.2.3. Preparation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)-C$_4$H$_2$N$_2$]}(OAc)] (1a)

Method 1: A pressure tube containing 3,4-(Me)$_2$C$_6$H$_3$C(Me)= NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$] (**a**) (138 mg, 0.450 mmol), palladium(II) acetate (101 mg, 0.450 mmol) and 20 cm^3 of dry toluene was sealed under argon. The resulting mixture was heated at 60 °C for 24 h. After cooling to r.t. the solution was filtered to give a red solid. Yield 0.145 g, 68%. Anal. Calc. for C$_{17}$H$_{17}$N$_4$O$_2$PdF$_3$: C, 43.2; H, 3.6; N, 11.8. Found: C, 43.3; H, 3.5; N, 11.7%. IR: ν(C=N) 1547m, ν (N–H) 3268m. ν_{as}(COO) 1434s, ν_s(COO) 1300 m cm^{-1}. RMN ^{1}H (300 MHz, CD$_3$SOCD$_3$, δ ppm, J Hz): 11.97 [s, 1H, NH], 8.19 [d, 1H, H11, ^{3}J(H10H11) = 5.7], 6.79 [s, 1H, H2], 6.55 [s, 1H, H5], 6.32 [d, 1H, H10], 2.20, 2.11, 2.07 [s, 3H; br 6H, Me(C=N), Me^a, Me^b], 1.89 [s, 3H, OAc]. FAB-MS: *m/z* = 413 [(L-H)Pd]$^+$. Specific molar conductivity, Λ_m = 6.46 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

Method 2: A pressure tube containing 3,4-(Me)$_2$C$_6$H$_3$C(Me)= NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$] (**a**) (152 mg, 0.490 mmol), palladium(II)
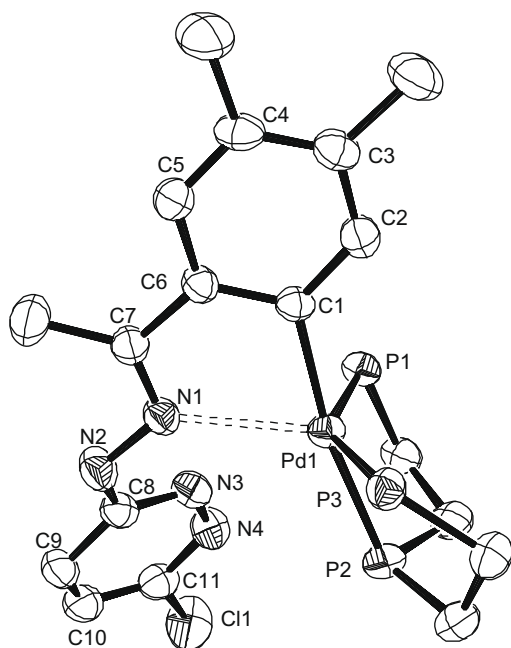
Fig. 8. Cation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$)} {(PPh$_2$CH$_2$-CH$_2$)$_2$PPh-*P,P,P*}][ClO$_4$] (**7b**) with labelling scheme. Hydrogen and phenyl ring atoms have been omitted for clarity.

Table 3
Intermolecular π–π stacking parameters for **2b** using the program PLATON [69].

Parameter	Plane 2/pyridazine	Plane 3/plane 3
d(c1–c2) (Å/α °)	3.69/0.0	3.69/0.0
d($^\perp$c1–P(2)) (Å/β °)	3.61/11.6	3.61/11.7
d($^\perp$c2–P(1)) (Å/γ °)	3.61/11.6	3.61/10.7

Table 4
Intermolecular π–π stacking parameters for **3a** using the program PLATON.

Parameter	Plane 2/pyrimidine	Plane 3/plane 3
d(c1–c2) (Å/α °)	3.69/8.3	3.62/0.0
d($^\perp$c1–P(2)) (Å/β °)	3.58/5.9	3.59/7.2
d($^\perp$c2–P(1)) (Å/γ °)	3.67/14.2	3.59/7.2

Table 5
Intermolecular π–π stacking parameters for **3b** using the program PLATON.

Parameter	Cyclometallated phenyl/pyridazine
d(c1–c2) (Å/α °)	3.66/4.1
d($^\perp$c1–P(2)) (Å/β °)	3.56/16.8
d($^\perp$c2–P(1)) (Å/γ °)	3.51/13.4

acetate (112 mg, 0.490 mmol) and 20 cm^3 of dry dichloromethane was sealed under argon. The resulting mixture was stirred for 24 h at r.t. and the solvent removed under vacuum to give a red solid. Yield 0.188 g, 81%.

Complex **1b** was prepared similarly as a yellow solid.

6.2.4. [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$)}(OAc)] (1b)

Yield: method 1, 0.092 g, 43%; method 2, 0.099 g, 46%. IR: ν (C=N) 1588 m, ν(N–H) 3111sh, ν$_{as}$(COO) 1497 m, ν$_s$(COO) 1421s cm^{-1}. Anal. Calc. for C$_{16}$H$_{17}$N$_4$O$_2$PdCl: C, 43.7; H, 3.9; N, 12.8. Found: C, 43.5; H, 3.6; N, 12.7%. RMN ^{1}H (300 MHz, CD$_3$SOCD$_3$, δ ppm, *J* Hz): 10.3 [br, 1H, NH], 7.14 [s, 1H, H2], 6.90 y 6.77 [d, 2H,
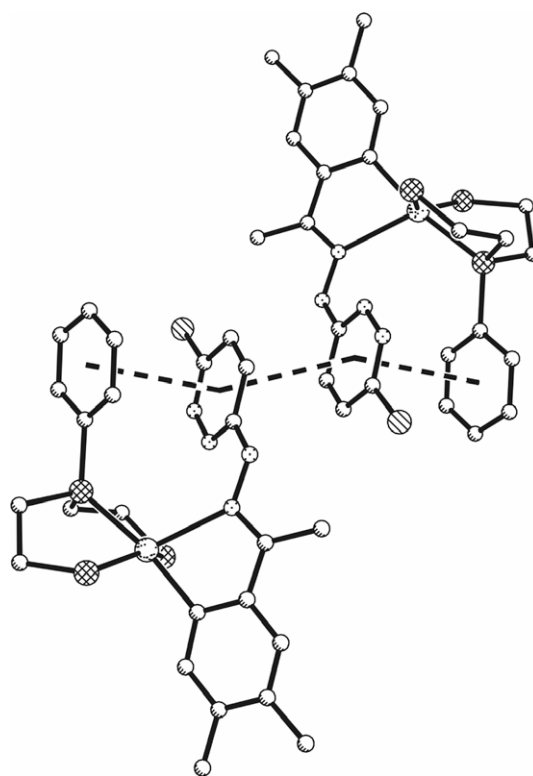

Fig. 9. Inter- and intramolecular π,π-stacking interactions in the crystal of **7b**. Dashed lines link ring centers involved in each stacking interaction. Terminal phosphine phenyl rings have been omitted for clarity.

H10; d, 2H, H11, ^{3}*J*(H10H11) = 9.6], 6.70 [s, 1H, H5], 2.19 [s, 3H, Me(C=N)], 2.07 [s, 6H, Me^a, Me^b], 1.90 [s, 3H, OAc]. FAB-MS: *m/z* = 382 uma [(L-H)Pd]$^+$. ESI-MS: *m/z* = 440.0 [M]$^+$. Specific molar conductivity, Λ_m = 5.96 ohm^{-1} cm^2 mol^{-1} (in dimethylformamide).

6.2.5. Preparation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)-C$_4$H$_2$N$_2$)}(Cl)] (2a)

A stirred solution of palladium(II) chloride (133.2 mg, 0.7510 mmol) and lithium chloride (863.9 mg, 1.502 mmol) in methanol (50 cm^3) was treated with 3,4-(Me)$_2$C$_6$-H$_3$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$N$_2$] (**a**) (237 mg, 0.770 mmol) and sodium acetate (43 mg, 0.80 mmol). The mixture was stirred at r.t. for 24 h. The yellow precipitate formed was filtered off, and dried in air. Yield 0.310 g, 92%. Anal. Calc. for C$_{15}$H$_{14}$N$_4$ClPdF$_3$: C, 40.1; H, 12.5; N, 3.2. Found: C, 40.4; H, 12.3; N, 3.1%. IR: ν(C=N) 1570s, ν (N–H) 3281w cm^{-1}. RMN ^{1}H (300 MHz, CD$_3$SOCD$_3$, δ ppm, *J* Hz): 8.44 [d, 1H, H11, ^{3}*J*(H10H11) = 5.4], 7.30 [d, 1H, H10], 7.00 [s, 1H, H2], 6.82 [s, 1H, H5], 2.31 [s, 3H, Me(C=N)], 2.12 [s, 6H, Me^a, Me^b]. FAB-MS: *m/z* = 413 [(L-H)Pd]$^+$. Specific molar conductivity, Λ_m = 17.09 ohm^{-1} cm^2 mol^{-1} (in dimethylformamide).

Complex **2b** was synthesized following a similar procedure as a yellow solid.

6.2.6. [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$)}(Cl)] (2b)

Yield 0.296 g, 95%. Anal. Calc. for C$_{14}$H$_{14}$N$_4$Cl$_2$Pd: C, 40.5; H, 3.4; N, 13.5. Found: C, 40.4; H, 3.3; N, 13.2%. IR: ν(C=N) 1540 m, ν(N–H) 3241sh cm^{-1}. RMN ^{1}H (300 MHz, CD$_3$SOCD$_3$, δ ppm, *J* Hz): 7.60 y 7.25 [d, 2H, H10; d, 2H, H11, ^{3}*J*(H10H11) = 9.6], 7.07 [s, 1H, H2], 6.78 [s, 1H, H5], 2.27 [s, 3H, Me(C=N)], 2.11 [s, 6H, Me^a, Me^b]. FAB-MS: *m/z* = 382 [(L-H)Pd]$^+$. Specific molar conductivity, Λ_m = 17.21 ohm^{-1} cm^2 mol^{-1} (in dimethylformamide).

Table 6
Intermolecular π–π stacking parameters for **7a** and **7b** using the program PLATON.

Parameter	7a	7b	7b
	Pyrimidine ring/phosphine phenyl	Pyridazine ring/phosphine phenyl	Pyrazine ring/pyrazine ring
$d(c1–c2)$ (Å/α)	3.52/12.7	3.56/14.7	3.76/0.0
$d(^\perp c1–P(2))$ (Å)	3.37/3.8	3.21/12.5	3.36/26.7
$d(^\perp c2–P(1))$ (Å)	3.51/16.4	3.48/25.6	3.36/26.7

6.2.7. Preparation of [Pd{3,4-(Me)₂C₆H₂C(Me)=NN(H)[3′-(CF₃)C₄H₂-N₂]}(PPh₃)]-[CF₃SO₃] (3a)

Silver trifluoromethanesulfonate (46 mg, 0.18 mmol) was added to a suspension of **2a** (35 mg, 0.079 mmol) in acetone (15 cm³). The resulting mixture was stirred for 4 h and filtered through celite to remove the AgCl precipitate formed. PPh₃ (18.6 mg, 0.071 mmol) was added to the filtrate and the resulting orange solution was stirred for another 2 h. The solvent was removed to give a red solid which was recrystallized from chloroform/hexane. Yield 35.1 mg, 60%. Anal. Calc. for $C_{34}H_{29}N_4PdO_3PF_6S$: C, 49.6; H, 3.9; N, 8.3. Found: C, 49.7; H, 3.8; N, 8.2%. IR: ν(C=N) 1534s, ν(N–H) 3215m, ν(CF₃SO₃) 1250s. RMN ¹H (300 MHz, CDCl₃, δ ppm, J Hz): 11.8 [br, 1H, NH, (DMSO-d^6)], 6.94 [s, 1H, H2], 6.53 [d, 1H, H11, ³J(H10H11) = 5.7], 6.19 [d, 1H, H10], 5.69 [d, 1H, H5, ⁴J(PH5) = 5.1], 2.53 [s, 3H, Me(C=N)], 2.09 [s, 3H, Meᵇ], 1.65 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CDCl₃, δ ppm, J Hz): 37.90 s. ESI-MS: m/z = 675.1 [M–CF₃SO₃]⁺. Specific molar conductivity, $Λ_m$ = 181 ohm⁻¹ cm² mol⁻¹ (in acetonitrile).

Compound **3b** was prepared similarly, but recrystallized from dichloromethane/hexane, as a yellow solid.

6.2.8. [Pd{3,4-(Me)₂C₆H₂C(Me)=NN(H)(4′-ClC₄H₂N₂)}(PPh₃)][CF₃SO₃] (3b)

Yield 30.9 mg, 55%. Anal. Calc. for $C_{33}H_{29}N_4ClPdO_3PF_3S$: C, 50.1; H, 3.7; N, 7.1. Found: C, 49.9; H, 3.8; N, 7.2%. IR: ν(C=N) 1562m, ν(N–H) 3285m, ν(CF₃SO₃) 1306 cm⁻¹. RMN ¹H (300 MHz, CDCl₃, δ ppm, J Hz): 11.52 [d, 1H, NH, ⁴J(PH) = 5.4], 7.18 [d, 1H, H10 or H11, ³J(H10H11) = 9.6], 6.80 [s, 1H, H2], 5.76 [d, 1H, H5, J(PH5) = 4.8], 2.50 [s, 3H, Me(C=N)], 2.18 [s, 3H, Meᵇ], 2.07 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CDCl₃, δ ppm, J Hz): 40.61s. FAB-MS: m/z = 643 [M–CF₃SO₃]⁺. Specific molar conductivity, $Λ_m$ = 109.6 ohm⁻¹ cm² mol⁻¹ (in acetonitrile).

6.2.9. Preparation of [Pd{3,4-(Me)₂C₆H₂C(Me)=NN[3′-(CF₃)C₄H₂N₂]}(PPh₃)] (4a)

A stirred solution of compound **3a** (30 mg, 0.036 mmol) in methanol, 50 cm³, was treated with sodium acetate (3.3 mg, 0.040 mmol). The mixture was stirred at room temperature for 15 h. The solvent removed to give a red solid which was recrystallized from dichloromethane/hexane, filtered off, and dried in air. Yield 8.3 mg, 34%. Anal. Calc. for $C_{33}H_{28}N_4PdPF_3$: C, 58.7; H, 4.2; N, 8.3. Found: C, 58.6; H, 4.2; N, 8.2%. IR: ν(C=N) 1547s cm⁻¹. RMN ¹H (300 MHz, CDCl₃, δ ppm, J Hz): 6.74 [s, 1H, H2]; 5.75 [d, 1H, H5, ⁴J(PH5) = 4.8]; 5.70 [d, 1H, H11, ³J(H10H11) = 5.7]; 2.53 [s, 3H, Me(C=N)], 2.05 [s, 3H, Meᵇ]; 1.58 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CDCl₃, δ ppm, J Hz): 39.40 s. ESI-MS: m/z = 674.1 [M]⁺. Specific molar conductivity, $Λ_m$ = 8.41 ohm⁻¹ cm² mol⁻¹ (in acetonitrile).

Compound **4b** was obtained following a similar procedure as a red solid.

6.2.10. [Pd{3,4-(Me)₂C₆H₂C(Me)=NN[3′-(CF₃)C₄H₂N₂]}(PPh₃)] (4b)

Yield 13.4 mg, 58%. Anal. Calc. for $C_{32}H_{28}N_4PdClP$: C, 59.9; H, 4.4; N, 8.7. Found: C, 59.6; H, 4.2; N, 8.7%. IR: ν(C=N) 1603 m cm⁻¹. RMN ¹H (300 MHz, CDCl₃, δ ppm, J Hz): 6.62 [s, 1H, H2]; 5.63 [d, 1H, H5, ⁴J(PH5) = 3.6]; 2.31 [s, 3H, Me(C=N)], 2.09 [s, 3H, Meᵇ], 1.57 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CDCl₃, δ ppm, J Hz): 38.54 s. ESI-MS: m/z = 641.1 [M+H]⁺. Specific molar conductivity, $Λ_m$ = 1.36 ohm⁻¹ cm² mol⁻¹ (in acetonitrile).

6.2.11. Preparation of [Pd{3,4-(Me)₂C₆H₂C(Me)=NN(H)[3′-(CF₃)C₄H₂-N₂]}(PPh₂(CH₂)₂As-Ph₂)][ClO₄] (5a)

Silver trifluoromethanesulfonate (21.6 mg, 0.0840 mmol) was added to a solution of **2a** (30.9 mg, 0.0688 mmol) in acetone (15 cm³). The resulting mixture was stirred for 4 h and filtered through cellite to remove the AgCl precipitate formed. Ph₂P(CH₂)₂AsPh₂ (26.2 mg, 0.0592 mmol) was then added to the filtrate and the solution stirred for another 2 h, after which an excess of sodium perchlorate was added. The mixture was stirred for a further 1 h and a pink complex precipitated out by addition of water, filtered off and dried in vacuo. Yield 56.0 mg, 99%. Anal. Calc. for $C_{41}H_{38}N_4PdO_4PF_3ClAs$: C, 51.5; H, 4.0; N, 5.8. Found: C, 51.6; H, 4.1; N, 5.1%. IR: ν(C=N) 1548m, ν(N–H) 3185m, ν(ClO₄) 1380s cm⁻¹. RMN ¹H (300 MHz, CDCl₃, δ ppm, J Hz): 6.59 [s, 1H, H2], 6.09, 6.04 [d, 1H, d, 1H, ³J(H10H11) = 5.8, H10, H11], 5.83 [d, 1H, H5, ⁴J(PH5) = 4.5], 2.22 [s, 3H, Me(C=N)], 2.15 [s, 3H, Meᵇ], 2.03 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CDCl₃, δ ppm, J Hz): 21.63 [s]. FAB-MS: m/z = 855. [M–ClO₄]⁺. Specific molar conductivity, $Λ_m$ = 109.5 ohm⁻¹ cm² mol⁻¹ (in acetonitrile).

6.2.12. Preparation of [{Pd{3,4-(Me)₂C₆H₂C(Me)=NN(H)[3′-(CF₃)C₄-H₂N₂]}}₂(μ-PPh₂(CH₂)₄PPh₂)][CF₃SO₃]₂ (6a)

Silver trifluoromethanesulfonate (42.3 mg, 0.164 mmol) was added to a solution of **2a** (50.7 mg, 0.112 mmol) in acetone (15 cm³). The resulting mixture was stirred for 4 h, and filtered through celite to remove the AgCl precipitate. Ph₂P(CH₂)₄PPh₂ (26.2 mg, 0.0592 mmol) was added to the filtrate and the resulting solution stirred for another 2 h. The solvent removed to give a yellow solid which was recrystallized from dichloromethane/hexane, filtered off, and dried in air. Yield 63.4 mg, 73%. Anal. Calc. $C_{60}H_{56}N_8Pd_2O_6P_2F_{12}S_2$: C, 46.4; H, 3.6; N, 7.2. Found: C, 46.5; H, 3.5; N, 7.1%. IR: ν(C=N) 1532m, ν(N–H) 3308 m, ν(CF₃SO₃) 1750s cm⁻¹. RMN ¹H (300 MHz, CDCl₃, δ ppm, J Hz): 11.5 [br, 1H, NH], 6.69 [s, 1H, H2], 6.50 [d, 1H, H10, ³J(H10H11) = 5.7], 6.35, [d, 1H, H11], 5.86 [d, 1H, H5, ⁴J(PH5) = 5.4], 2.51 [s, 3H, Me(C=N)], 2.18 [s, 3H, Meᵇ], 2.04 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CDCl₃, δ ppm, J Hz): 26.82 [s]. FAB-MS: m/z = 841 [(L–H)Pd(dppb)+H]⁺, 1253 uma [M–2CF₃SO₃]⁺. Specific molar conductivity, $Λ_m$ = 269 ohm⁻¹ cm² mol⁻¹ (in acetonitrile).

Compound **6b** was obtained following a similar procedure as a yellow solid, but using silver perchlorate instead of silver trifluoromethanesulfonate.

6.2.13. [{Pd{3,4-(Me)₂C₆H₂C(Me)=NN(H)(4′-ClC₄H₂N₂)}}₂ (μ-PPh₂(CH₂)₄PPh₂)][ClO₄]₂ (6b)

Yield 54.3 mg, 70%. Anal. Calc. for $C_{56}H_{56}N_8Pd_2O_8P_2Cl_4$: C, 48.5; H, 4.1; N, 8.1. Found: C, 48.6; H, 4.2; N, 8.2%. IR: ν(C=N) 1601m, ν(N–H) 3263 m, ν(ClO₄) 1100s cm⁻¹. RMN ¹H (300 MHz, CD₃SOCD₃, δ ppm, J Hz): 7.19 [d, 1H, H10 H11, ³J(H10H11) = 9.6], 6.91 [s, 1H, H2], 5.57 [d, 1H, H5, ⁴J(PH5) = 4.2], 2.37 [s, 3H, Me(C=N)], 1.99 [s, 3H, Meᵇ], 1.50 [s, 3H, Meᵃ]. RMN ³¹P–{¹H} (121.49 MHz, CD₃SOCD₃, δ ppm, J Hz): 31.03 s. MS-FAB: m/z = 758.9

[{(L-H)Pd}$_2$]H$^+$, 1185 uma [M−2ClO$_4$]$^+$. Specific molar conductivity, Λ_m = 101.5 ohm^{-1} cm^2 mol^{-1} (in dimethylformamide).

Compound **8b** was obtained as a yellow solid following a similar procedure to the one used for **6a**, but using a complex/phosphine 3:1 molar ratio.

6.2.14. [{Pd[3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4′ClC$_4$H$_2$N$_2$)]}$_3${μ_3-(PPh$_2$-CH$_2$CH$_2$)$_2$PPh}] [CF$_3$SO$_3$]$_3$ (8b)

Yield 74.9 mg, 63%. Anal. Calc. for C$_{79}$H$_{75}$N$_{12}$Pd$_3$O$_9$Cl$_3$P$_3$F$_9$S$_3$: C, 44.7; H, 3.6; N, 7.8. Found: C, 44.6; H, 3.5; N, 7.9%. IR: v(C=N) 1601m, v (N−H) 3311 m, v(CF$_3$SO$_3$) 1254s cm^{-1}. RMN ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): 11.35 [d, 2H, NH, ^4J(PH) = 5.1], *11.14* [d, 1H, N*H*, ^4J(P*H*) = 5.1], 5.19 [d, 2H, H5, ^4J(PH5) = 4.8], *4.53* [d, 1H, *H5*, ^4J(P*H5*) = 4.5], 2.40 [s, 6H, Me(C=N)], *2.32* [s, 3H, *Me*(C=N)], 2.05 [s, 6H, Me^a], *1.98* [s, 3H, *Me^a*], 1.50 [s, 6H, Me^b], *1.23* [s, 3H, *Me^b*]. ^{31}P–{^{1}H} NMR (121.49 MHz, CDCl$_3$, δ ppm) 27.52 d, *24.71t*, J(PP) = 21.0. Data in italics are for the cyclometallated fragment bonded to the central phosphorus atom. MS-FAB: m/z = 913 uma [(L-H)Pd(trifos)]$^+$. ESI-MS: m/z = 1972.1 [M−CF$_3$SO$_3$]$^+$. Specific molar conductivity, Λ_m = 304 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

6.2.15. Preparation of [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)[3′-(CF$_3$)C$_4$H$_2$-N$_2$]}{(PPh$_2$CH$_2$ CH$_2$)$_2$PPh-P,P,P}][ClO$_4$] (7a)

(PPh$_2$CH$_2$CH$_2$)$_2$)PPh (54.8 mg, 0.103 mmol) was added to a suspension of **2a** (50.0 mg, 0.111 mmol) in acetone (20 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 yellow complex precipitated out by addition of water filtered off and chromatographed on a column packed with silica gel. Elution with dichloromethane–ethanol 1% afforded the desired product as a yellow solid. Yield 29.1 mg, 27%. Anal. Calc. for C$_{49}$H$_{47}$N$_4$PdO$_4$P$_3$ClF$_3$: C, 56.2; H, 4.5; N, 5.3. Found: C, 56.6; H, 4.2; N, 5.1%. IR: v(C=N) 1584m, v(N−H) 3250 m, v(ClO$_4$) 1099s cm^{-1}. RMN ^{1}H (300 MHz, CDCl$_3$, δ ppm, J Hz): 7.97 [d, 1H, H10, ^3J(H10H11) = 4.5], 7.90 [s, br, 1H, NH], 6.57 [d, 1H, H11], 5.56 [d, 1H, H5, ^4J(PH5) = 8.31], 2.12 [s, 3H, Me(C=N)], 2.08 [s, 3H, Me^b], 1.51 [s, 3H, Me^a]. RMN ^{31}P–{^{1}H} (121.49 MHz, CDCl$_3$, δ ppm, J Hz): 87.78 [t, 1P, P, ^2J(PP) = 69.6], 42.75 d. ESI-MS: m/z = 947.2 [M−ClO$_4$]$^+$. Specific molar conductivity, Λ_m = 92.4 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

Compound **7b** was obtained following a similar procedure, as yellow solid.

6.2.16. [Pd{3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4′-ClC$_4$H$_2$N$_2$)}{(PPh$_2$CH$_2$CH$_2$)$_2$PPh-P,P,P}] [ClO$_4$] (7b)

Yield 62.7 mg, 60%. Anal. Calc. for C$_{48}$H$_{47}$N$_4$PdCl$_2$O$_4$P$_3$: C, 56.8; H, 4.7; N, 5.6. Found: C, 56.5; H, 4.5; N, 5.8%. IR: v(C=N) 1589m, v(N−H) 3115m, v(ClO$_4$) 1099 scm^{-1}. RMN ^{1}H (500 MHz, CDCl$_3$, δ ppm, J Hz): 9.35 [s, br, 1H, NH], 6.94, 6.50 [d, 1H, H10, H11, ^3J(H10H11) = 9.3], 5.66 [d, 1H, H5, ^4J(PH5) = 8.5], 2.18 [s, 3H, Me(C=N)], 2.08 [s, 3H, Me^b], 1.51 [s, 3H, Me^a]. RMN ^{31}P–{^{1}H} (121.49 MHz, CDCl$_3$, δ ppm, J Hz): 87.89 [t, 1P, P, ^2J(PP) = 70.2], 42.42 (d). FAB-MS: m/z = 912 [M−ClO$_4$]$^+$. Specific molar conductivity, Λ_m = 99.0 ohm^{-1} cm^2 mol^{-1} (in dimethylformamide).

6.2.17. X-ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Bruker Smart 1K CCD and a Bruker X8 Apex **7b** diffractometers using graphite-monochromated Mo Kα radiation. All the measured reflections were corrected for Lorentz and polarization 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–N*H* hydrogens which were located in a differ-

ence Fourier map) and refined in riding mode. The Cl(1), Cl(2) and Cl(3) chlorine atoms of the chloroform solvent molecule in the crystal of **3a** were disordered and, consequently, refined in two complementary positions with occupancies of 60% and 40%. The S(1), C(33), F(1) and oxygen, atoms of the trifluoromethanesulfonate ion in complex **3b** were found to be disordered over two positions (with occupancies of approximately 63% and 37%). Disorder was also present in the CF3 group of **7a** which F(1), F(2) and F(3) fluorine atoms were refined in complementary positions (occupancies of 70% and 30%). The refinement was carried out taking into account both components. Refinement converged with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [68].

7. Supplementary material

CCDC 705890, 705891, 705892, 705893 and 705894 contain the supplementary crystallographic data for **2b**, **3a**, **3b**, **7a** and **7b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] I. Omae, in: Organometallic Intramolecular-Coordination Compounds, Elsevier Science, Amsterdam–New York, 1986.
[2] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 571 (1984) 250.
[3] G.R. Newkome, W.E. Puckett, W.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[4] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[5] M. Pfeffer, Recl. Trav. Chim. Pyas-Bas 109 (1990) 567.
[6] J. Vicente, I. Saura-Llamas, Comment Inorg. Chem. 28 (2007) 29.
[7] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527.
[8] J. Djukic, A. Hijazi, H.D. Flack, G. Bernardinelli, Chem. Soc. Rev. 37 (2007) 406.
[9] I. Omae, Coor. Chem. Rev. 248 (2004) 995.
[10] M. Pfeffer, J.P. Sutter, M.A. Rottevel, A. de Cian, J. Fischer, Tetrahedron 48 (1992) 2427.
[11] A.D. Ryabov, R. van Eldik, G. Le Borgne, M. Pfeffer, Organometallics 12 (1993) 1386.
[12] B.S. Wild, Coord. Chem. Rev. 166 (1997) 291.
[13] S.Y.M. Chooi, P.H. Leung, C.C. Lim, K.F. Mok, G.H. Quek, K.Y. Sim, M.K. Tan, Tetrahedron: Asymmetry 3 (1992) 529.
[14] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 17 (1992) 215.
[15] C. Navarro-Ranninger, I. López solera, J. Rodríguez, J.L. García-Ruano, P.R. Raithby, J.R. Masaguer, C. Alonso, J. Med. Chem. 36 (1993) 3795.
[16] C. Navarro-Ranninger, I. López-Solera, V.M. Gonzalez, J.M. Pérez, A. Alvarez-Valdés, A. Martin, P.R. Raithby, J.R. Masaguer, C. Alonso, Inorg. Chem. 35 (1996) 5181.
[17] A. Bose, C.H. Saha, J. Mol. Catal. 49 (1989) 271.
[18] M. López-Torres, A. Fernández, J.J. Fernández, S. Castro-Juiz, A. Suárez, J.M. Vilay, M.T. Pereira, Organometallics 20 (2001) 1350.
[19] A. Gómez-Quiroga, C. Navarro-Ranninger, Coord. Chem. Rev. 248 (2004) 119.
[20] I. Omae, J. Organomet. Chem. 692 (2007) 2608–2632.
[21] A. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. La Deda, D. Pucci, Coor. Chem. Rev. 250 (2006) 1373.
[22] P.A. Chase, R.J.M. Klein-Gebbink, G. van Koten, J. Organomet. Chem. 298 (2004) 4016.
[23] J.M. Vila, M.T. Pereira, J.M. Ortigueira, J.J. Fernández, A. Fernández, M. López-Torres, H. Adams, Organometallics 18 (1999) 5484.
[24] J.M. Vila, M. Gayoso, M.T. Pereira, M. López-Torres, J.J. Fernández, A. Fernández, J.M. Ortigueira, J. Organomet. Chem. (1997) 171.
[25] J.M. Vila, M.T. Pereira, J.M. Ortigueira, D. Lata, M. López-Torres, J.J. Fernández, A. Fernández, H. Adams, J. Organomet. Chem. 566 (1998) 93.
[26] A. Fernández, J.J. Fernández, M. López-Torres, A. Suárez, J.M. Ortigueira, J.M. Vila, H. Adams, J. Organomet. Chem. 612 (2000) 85.
[27] A. Fernández, P. Uría, J.J. Fernández, M. López-Torres, A. Suárez, D. Vázquez-García, M.T. Pereira, J.M. Vila, J. Organomet. Chem. 620 (2001) 8.
[28] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, J.M. Vila, J. Organomet. Chem. 690 (2005) 3669.

[29] M. López-Torres, A. Fernández, J.J. Fernández, A. Suárez, M.T. Pereira, J.M. Ortigueira, J.M. Vila, H. Adams, Inorg. Chem. 40 (2001) 4583.
[30] W. Lu, M.C.W. Chan, N. Zhu, C. Che, C. Li, Z. Hui, J. Am. Chem. Soc. 126 (2004) 7639.
[31] M. Nonoyama, C. Sugiura, Polyhedron 1 (1982) 179.
[32] G. Garcia-Herbosa, A. Muñoz, D. Miguel, S. Garcia-Granda, Organometallics 13 (1994) 1775.
[33] G. García-Herbosa, N.G. Conelly, A. Muñoz, J.V. Cuevas, A.G. Orpen, S.D. Politzer, Organometallics 20 (2001) 3223.
[34] M.S. Muñoz, B. García, S. Ibeas, F.J. Hoyuelos, I. Peñacoba, A.M. Navarro, J.M. Leal, New J. Chem. 28 (2004) 1450–1456.
[35] M. Ghedini, I. Aiello, A. Crispini, M. La Deda, Dalton Trans. (2004) 1386.
[36] H. Masui, Coord. Chem. Rev. 219 (2001) 957.
[37] A. Crispini, M. Ghedini, J. Chem. Soc., Dalton Trans. (1997) 75.
[38] R.M. Ceder, M. Gómez, J. Sales, J. Organomet. Chem. 361 (1989) 391.
[39] C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J.H. Rodríguez-Ramos, J.R. Masaguer, J.L. García-Ruano, Organometallics 12 (1993) 4104.
[40] A. Capapé, M. Crespo, J. Granell, M. Font. Bardía, J. Solans, Dalton Trans. (2007) 2030.
[41] A. Castiñeiras, A.G. Sicilia-Zafra, J.M. González-Pérez, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, Inorg. Chem. 41 (2002) 6956.
[42] K. Molčanov, M. Ćurić, D. Babić, B. Kojić-Prodić, J. Organomet. Chem. 692 (2007) 3874.
[43] H. Onoue, I. Moritani, J. Organomet. Chem. 43 (1972) 431.
[44] H. Onoue, K. Minami, K. Nakagawa, Bull. Chem. Soc. Jpn. 43 (1970) 3480.
[45] K. Nakamoto, IR and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley and Sons, New York, 1997.
[46] F. Ortega-Jimenez, E. Gómez, O. Sharma, M.C. Ortega-Alfaro, R.A. Toscazo, C. Alvarez-Toledano, Z. Anorg. Allg. Chem. 628 (2002) 2002.
[47] J. Vicente, J.A. Abad, J. Gil-Rubio, P.G. Jones, E. Bembenek, Organometallics 12 (1993) 4151.
[48] F. Neve, A. Crispín, C. Di Pietro, S. Campagna, Organometallics 21 (2002) 3511.
[49] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.
[50] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, New J. Chem. 26 (2002) 398.

[51] J.M. Vila, E. Gayoso, M.T. Pereira, J.M. Ortigueira, G. Alberdi, M. Mariño, R. Alvarez, A. Fernández, Eur. J. Inorg. Chem. (2004) 2937.
[52] P.S. Pregosin, R.W. Kuntz, 31P and 13C NMR of transition metal phosphine complexes, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR 16, Springer, Berlin, 1979.
[53] J. Albert, M. Gómez, J. Granell, J. Sales, Organometallics 9 (1990) 1405.
[54] R. Bosque, J. Granell, J. Sales, M. Font-Bardía, X. Soláns, J. Organomet. Chem. 453 (1993) 147.
[55] J. Albert, J. Granell, J. Sales, M. Font-Bardía, X. Soláns, Organometallics 14 (1995) 1393.
[56] J. Bravo, C. Cativiela, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 650 (2002) 157.
[57] S.W. Lai, T.C. Cheung, M.C.W. Chang, K.K. Cheung, S.M. Peng, C.M. Che, Inorg. Chem. 39 (2000) 255.
[58] F. Cecconi, C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci, J. Chem. Soc., Dalton Trans. (1989) 211.
[59] J. Granell, D. Sainz, J. Sales, X. Solans, M. Font-Altaba, J. Chem. Soc., Dalton Trans. (1986) 1785.
[60] J. Granell, J. Sales, J. Vilarrasa, J.P. Declercq, G. Germain, C. Miravilles, X. Soláns, J. Chem. Soc., Dalton Trans. (1983) 2441.
[61] Z. Taira, S. Yamazaki, Bull. Chem. Soc. Jpn. 59 (1986) 649.
[62] L.A. Villanueva, K. Abboud, J.M. Boncella, Organometallics 10 (1991) 2969.
[63] D. Onggo, D.C. Craig, A.D. Rae, H.A. Goodwin, Aust. J. Chem. 44 (1991) 219.
[64] O. Schlager, K. Wieghardt, B. Nuber, Inorg. Chem. 34 (1995) 6449.
[65] (a) $\tau = (\beta - \alpha)/60$; where $(\beta - \alpha)$ is the difference of in-plane trans bond angles.;
(b) A.W. Addison, T.N. Rao, J. Reedijk, J. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[66] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, Eur. J. Inorg. Chem. (2002) 2389.
[67] D.D. Perrin, W.L.F. Armarego, D.L. Perrin, Purification of Laboratory Chemicals, 3rd ed., Pergamon, London, 1998.
[68] G. M Sheldrick, SHELX-97, An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.
[69] A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, University of Utrecht, The Netherlands, 2001.