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New palladacyclic complexes with pyridylphosphine ligands: crystal structures of [Pd(Azb)(Ph_2POCH_2Py-P,N)][PF_6] and [Pd(Phpy)(Ph_2PNHPy-P,N)][PF_6]

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Abstract

The synthesis of palladacyclic derivatives with the hybrid pyridylphosphine ligands $Py(CH_2)OPPh_2$ (**a**) and $PyNHPPh_2$ (**b**) in a neutral P,N-chelating coordination mode has been achieved. Treatment of selected chloride-bridged cyclometallated precursors $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ [C^N = 2-pyridinin-phenyl **Phpy**, **I**-compounds; 7,8-benzoquinolyl **Bzq**, **II**-compounds; phenylazophenyl **Azb**, **III**-compounds or 2-(2-oxazolinyl)phenyl **Phox**, **IV**-compounds] with **a** or **b** in the presence of stoichiometric KPF_6 gave the mononuclear derivatives **Ia**–**IVa** and **Ib**–**IVb**. The crystal structures of compounds [Pd(Azb)(Ph_2POCH_2Py-P,N)][PF_6] (**IIIa**) and [Pd(Phpy)(Ph_2PNHPy-P,N)][PF_6] (**Ib**) have been determined. The new palladacyclopentadiene precursor $[Pd\{C_4COOMe_4\}(CH_3CN)_2]$ (**V**) has been prepared starting from the polymeric complex $[Pd\{C_4COOMe_4\}]_n$. Its usefulness in the preparation of new derivatives has been tested by means of the straightforward reaction with ligands (**a**) or (**b**) to give mononuclear compounds $[Pd\{C_4(COOMe)_4\}(Ph_2POCH_2Py$-P,N)] (**Va**) and $[Pd\{C_4(COOMe)_4\}(Ph_2PNHPy$-P,N)] (**Vb**). The reactions of hydroxo-bridged precursors $[Pd(C\hat{}N)(\mu\text{-}OH)]_2$ or $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ with $PyNHPPh_2$ afforded mononuclear complexes **Ic**–**Vc** ($PyNPPh_2^-$ = **c** ligand) in which a less common anionic P,N-binding mode is forced as a result of ligand deprotonation. The new complexes were characterised by partial elemental analyses and spectroscopic methods (IR, FAB, ^1H and $^{31}P\{^1H\}$ NMR).

Keywords: Pyridylphosphine ligands; Palladacycles; Hydroxo-complexes; Crystal structures

1. Introduction

The considerable attention received by hybrid ligands containing both a soft phosphine donor atom and a hard functionality [1–4] comes from their versatile coordination behaviour [5,6] and its potential hemilability [3,4], that make their complexes useful as the foundation for molecule-based sensors [7–9], as well as good precursors in catalytic processes [4,10–16]. An important group of ligands with these characteristics are pyridylphosphines [2,17,18], that have found widespread applications in homogeneous catalysis [19]. Thus, 2-(diphenylphosphino)pyridine (Ph_2Ppy) has attracted continuous research in this field due to its ability to coordinate trasition metals as P-monodentate, N-monodentate or P,N-bridging, generating complexes with different properties and applications [17]. The P,N-chelating coordination mode is quite less common as a consequence of ring strain, and related ligands containing organic spacer groups have been developed in order to increase the distance between P and N donor sites [20 and references therein], allowing

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in this way the preparation of new mononuclear complexes. In this sense, ligands such as $Py(CH_2)_nOPPh_2$(n = 1–3) [21], $Py(CH_2)_nNHPPh_2$ (n = 0,1) [20,22,23] and others related that include a hydrazine backbone [24] or N-substitution [23] have recently been described. In addition to their intrinsic interest regarding coordination properties [20], the modification in alkyl chain length and the functionalisation of pyridylphosphines have permitted the tuning of both bite angle and electronic properties of the ligands, leading in some cases to enhancement in catalytic reactivity [21,25–29].

We have recently been interested in the synthesis of some Ni and Pd organometallic derivatives containing N,P-ligands, either with a bis-pentafluorophenyl [30], palladacyclopentadiene [31] or *ortho*-metallated backbone [32,33]. In the last example we have employed selected di-μ-hydroxo-complexes [34] as precursors in the preparation of new compounds when ligand deprotonation was required. Thus, stronger basic treatments were avoided, reaffirming the unique characteristics of such hydroxo-complexes as starting materials by means of simple acid–base reaction with protic electrophiles [35–39]. In this sense, we have also described the synthesis of the binuclear complex $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ [40] and its use in the preparation on new palladacyclopentadiene derivatives that have shown interesting catalytic properties. To date just a few crystal structures of palladacyclopentadiene compounds are known, and the most common starting materials employed to access them are $Pd(dba)_2$, $[Pd(CH_3CN)_2\text{-}(dmbd)_2]$ (dmbd = dimethyl-2-butynedioate) [41], or the less soluble polymeric complex $[Pd\{C_4COOMe_4\}]_n$, sometimes inconvenient [42]. The new precursor $[Pd\{C_4(COOMe)_4\}(CH_3CN)_2]$ (**V**) that we present here, together with the above mentioned hydroxo-complex, allows the enlargement of the field providing new synthetic routes to prepare palladacyclopentadiene derivatives.

In this paper, we mainly report the synthesis and characterisation of new palladacycles that contain the ligands $Py(CH_2)OPPh_2$ and $PyNHPPh_2$ acting as neutral P,N-chelating. A series of new complexes with the less usual anionic $[PyNPPh_2]^-$ ligand has also been prepared using the appropriated hydroxo-complexes as precursors under clean and mild conditions of reaction.

2. Experimental

2.1. General remarks

C, H and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a Perkin–Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR data (^1H, ^{13}C, ^{31}P) were recorded on Bruker Avance 200, 300 and 400 spectrometers. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in positive mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-keV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000. Conductance measurements were performed with a Crison 525 conductimeter (in acetone solutions, 5×10^{-4} M). TG and DTG curves were recorded on a TA Instruments SDT 2960 thermobalance using an atmosphere of pure nitrogen (50 cm^3 min^{-1}) All the solvents were dried by conventional methods.

The cyclometallated precursors $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ and $[Pd(C\hat{}N)(\mu\text{-}OH)]_2$[C^N = 2-pyridinin-phenyl (Phpy or **I**), 7,8-benzoquinolyl (Bzq or **II**), phenylazophenyl (Azb or **III**), and 2-(2-oxazolinyl)phenyl (Phox or **IV**)] were prepared as described in the literature [34,43,44]. The palladacyclopentadiene precursors $[Pd\{C_4COOMe_4\}]_n$ [42] and $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ [40] and the pyridylphosphine ligands $Py(CH_2)OPPh_2$ [21] and $PyNHPPh_2$ [20] were synthesised according to reported procedures.

2.2. Preparation of $[Pd\{C_4(COOMe)_4\}(CH_3CN)_2]$ (**V**)

An acetonitrile (5 ml) solution of the precursor $[Pd\{C_4(COOMe)_4\}]_n$ (0.100 g, 0.256 mmol) was vigorously stirred for 15 min, and then concentrated under reduced pressure to half of the initial volume. The addition of diethyl ether caused the formation of a yellow solid that was filtered off, washed with ether and air dried. Yield: 102.9 mg (85%). *Anal*. Calc. for $C_{16}H_{18}N_2O_8Pd$: C, 40.6; H, 3.8; N, 5.9. Found: C, 40.3; H, 3.6; N, 6.0%. IR (nujol mull cm^{-1}): ν(C≡N) 2322s, 2292s; ν(C=O) 1710vs, 1548s. ^1H NMR [$CDCl_3$]: δ 2.09 (s, 6H, CH_3CN), 3.66 (s, 6H, COOMe), 3.74 (s, 6H, COOMe). $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 2.2 (CH_3CN), 51.5 ($COOCH_3$).

2.3. Synthesis of complexes $[Pd(C\hat{}N)(Ph_2POCH_2Py\text{-}P,N][PF_6]$[C^N = 2-pyridinin-phenyl (**Ia**), 7,8-benzoquinolyl (**IIa**), phenylazophenyl (**IIIa**) and 2-(2-oxazolinyl)phenyl (**IVa**)]

The new complexes were obtained by treating $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ with 2-(diphenylphosphinyl)oxymethylpyridine in molar ratio 1:2, using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane solution (10 ml) of the corresponding precursor $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ (60 mg) was added the stoi-

chiometric amount of a THF solution of 2-(diphenylphosphinyl)oxymethylpyridine and solid KPF_6. After stirring for 30 min at room temperature, the KCl was filtered and then the solution concentrated under reduced pressure to half volume. Addition of diethyl ether caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dichloromethane–diethylether.

[Pd(Phpy)(Ph_2POCH_2Py-*P,N*)][PF_6] (**Ia**). Yield: 109.0 mg (77%). *Anal*. Calc. for $C_{29}H_{24}F_6N_2OP_2Pd$: C, 49.8; H, 3.5; N, 4.0. Found: C, 50.0; H, 3.6; N, 4.1%. FT-IR (nujol mull cm^{-1}): ν(C═N) 1604vs, 1570s; $\nu(PF_6)$ 840vs. ^1H NMR [$(CD_3)_2CO$]: δ 5.55 (d, 2H, OCH_2, $J_{PH}=18.4$), 6.72 (m, 2H, aromatics), 7.13 (m, 1H, aromatics), 7.59 (m, 7H, aromatics), 7.93 (m, 7H, aromatics), 8.23 (m, 4H, aromatics), 9.14 (d, br, 1H, H^6 pyridine). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 129.5 (s, Ph_2POCH_2Py), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 553 ($M^+ - PF_6$).

[Pd(Bzq)(Ph_2POCH_2Py-*P,N*)][PF_6] (**IIa**). Yield: 92.1 mg (68%). *Anal*. Calc. for $C_{31}H_{24}F_6N_2OP_2Pd$: C, 51.5; H, 3.3; N, 3.9. Found: C, 51.6; H, 3.5; N, 4.0%. FT-IR (nujol mull cm^{-1}): ν(C═N) 1606vs, 1568s; $\nu(PF_6)$ 840vs. ^1H NMR [$(CD_3)_2CO$]: δ 5.65 (d, 2H, OCH_2, $J_{PH}=19.6$), 6.85 (m, 1H, aromatics), 7.14 (m, 1H, aromatics), 7.65 (m, 7H, aromatics), 7.96 (m, 9H, aromatics), 8.30 (m, 1H, aromatics), 8.53 (m, br, 1H, aromatic), 8.77 (d, H^2 Bzq, $J_{HH}=16.0$ Hz), 9.27 (d, 1H, H^6 pyridine, $J_{HH}=10.4$ Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 130.3 (s, Ph_2POCH_2Py), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 577 ($M^+ - PF_6$).

[Pd(Azb)(Ph_2POCH_2Py-*P,N*)][PF_6] (**IIIa**). Yield: 93.0 mg (69%). *Anal*. Calc. for $C_{30}H_{25}F_6N_3OP_2Pd$: C, 49.6; H, 3.5; N, 5.8. Found: C, 49.6; H, 3.5; N, 5.9%. FT-IR (nujol mull cm^{-1}): ν(C═N) 1610vs, 1578s; $\nu(PF_6)$ 844vs. ^1H NMR [$(CD_3)_2CO$]: δ 5.69 (d, 2H, OCH_2, $J_{PH}=20.2$), 6.68 (m, 1H, aromatics), 6.99 (m, 1H, aromatics), 7.25–7.73 (m, 12H, aromatics), 7.91 (m, 6H, aromatics), 8.14 (m, 2H, aromatics), 8.62 (d, 1H, H^6 pyridine, $J_{HH}=10.4$ Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 129.0 (s, Ph_2POCH_2Py), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 580 ($M^+ - PF_6$).

[Pd(Phox)(Ph_2POCH_2Py-*P,N*)][PF_6] (**IVa**). Yield: 83.4 mg (58%). *Anal*. Calc. for $C_{27}H_{24}F_6N_2O_2P_2Pd$: C, 46.9; H, 3.5; N, 4.0. Found: C, 47.1; H, 3.6; N, 4.2%. FT-IR (nujol mull cm^{-1}): ν(C═N) 1634vs, 1606s, 1588s; $\nu(PF_6)$ 840vs. ^1H NMR [$(CD_3)_2CO$]: δ 4.13 (t, 2H, Phox, $J_{HH}=9.4$ Hz), 4.94 (t, 2H, Phox, $J_{HH}=9.4$ Hz), 5.39 (d, 2H, OCH_2, $J_{PH}=20.4$), 6.61 (m, 1H, aromatics), 6.89 (m, 1H, aromatics), 7.14 (t, 1H, aromatic), 7.47 (m, 1H, aromatic), 7.78 (m, 12H, aromatics), 8.27 (m, 1H, aromatics), 9.20 (d, 1H, H^6 pyridine, $J_{HH}=10.1$ Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 131.1 (s, Ph_2POCH_2Py), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 545 ($M^+ - PF_6$).

*2.4. Preparation of [Pd{C_4(COOMe)$_4$}(Ph_2POCH_2Py-P,N)] (**Va**)*

To an acetone (5 ml) solution of the precursor [Pd{$C_4(COOMe)_4$}$(CH_3CN)_2$] (0.07 g, 0.15 mmol) was added the stoichiometric amount of a THF solution of 2-(diphenylphosphinyl)oxymethylpyridine. The reaction was stirred at room temperature for 30 min, and then the solvent was partially evaporated under reduced pressure. The addition of diethyl ether caused the formation of a yellow crude, that was obtained as a solid after recrystallisation from dichloromethane–hexane. Yield: 72.2 mg (71%). *Anal*. Calc. for $C_{30}H_{28}NO_9PPd$: C, 52.7; H, 4.1; N, 2.1. Found: C, 52.8; H, 4.3; N, 2.2%. FT-IR (nujol mull cm^{-1}): ν(C═O) 1714vs; ν(C═N) 1606s. ^1H NMR [$(CD_3)_2CO$]: δ 3.37 (s, 3H, COOMe), 3.49 (s, 3H, COOMe), 3,53 (s, 3H, COOMe), 3.70 (s, 3H, COOMe), 5.50 (d, 2H, OCH_2, $J_{PH}=20.0$), 7.13–7.90 (m, 13H, aromatics), 9.26 (s, br, 1H, H^6 pyridine). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 116.3 (s, Ph_2POCH_2Py). FAB-MS (positive mode) *m/z*: 684 (M^+).

*2.5. Synthesis of complexes [Pd(C^N)(Ph_2PNHPy-P,N)][PF_6] [C^N=2-pyridinin-phenyl (**Ib**), 7,8-benzoquinolyl (**IIb**), phenylazophenyl (**IIIb**) and 2-(2-oxazolinyl)phenyl (**IVb**)]*

The new complexes were obtained by treating [Pd(C^N)(μ-Cl)]$_2$ with 2-(diphenylphosphinoamino)pyridine in molar ratio 1:2, using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane solution (10 ml) of the corresponding precursor [Pd(C^N)(μ-Cl)]$_2$ (60 mg) was added the stoichiometric amount of solid 2-(diphenylphosphinoamino)pyridine and KPF_6. After stirring for 30 min at room temperature, the KCl was filtered and then the solution concentrated under reduced pressure to half volume. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dichloromethane–hexane.

[Pd(Phpy)(Ph_2PNHPy-P,N)][PF_6] (**Ib**). Yield: 102.5 mg (74%). *Anal*. Calc. for $C_{28}H_{23}F_6N_3P_2Pd$: C, 49.2; H, 3.4; N, 6.1. Found: C, 49.3; H, 3.4; N, 6.2%. FT-IR (nujol mull cm^{-1}): ν(NH) 3336s; ν(C═N) 1616vs, 1574s; ν(PN) 896s; $\nu(PF_6)$ 840vs. ^1H NMR [$(CD_3)_2CO$]: δ 7.02 (m, 5H, aromatics), 7.59–8.06 (m, 14H, aromatics and NH), 8.24 (m, 2H, aromatics), 8.51 (d, 1H, H^2 Ph*py*, $J_{HH}=5.6$ Hz), 8.78 (d, 1H, H^6 pyridine, $J_{HH}=6.0$ Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 84.2 (s, Ph_2PNHpy), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 538 ($M^+ - PF_6$).

[Pd(Bzq)(Ph_2PNHPy-P,N)][PF_6] (**IIb**). Yield: 99.5 mg (75%). *Anal*. Calc. for $C_{30}H_{23}F_6N_3P_2Pd$: C, 50.9; H, 3.3; N, 5.9. Found: C, 51.0; H, 3.4; N, 6.0%. FT-IR (nujol mull cm^{-1}): ν(NH) 3340s; ν(C═N) 1612vs; ν(PN) 906s; $\nu(PF_6)$ 844vs. ^1H NMR

[$(CD_3)_2CO$]: δ 7.28 (m, 4H, aromatics), 7.55–7.73 (m, 8H, aromatics and NH), 7.89–8.11 (m, 8H, aromatics), 8.75 (m, 2H, aromatics), 9.21 (d, 1H, H^6 pyridine, J_{HH} = 6.0 Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 84.9 (s, Ph_2PNHpy), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 562 ($M^+ - PF_6$).

[Pd(Azb)(Ph$_2$PNHPy-P,N)][PF$_6$] (**IIIb**). Yield: 77.9 mg (59%). *Anal*. Calc. for $C_{29}H_{24}F_6N_4P_2Pd$: C, 49.0; H, 3.4; N, 7.9. Found: C, 49.2; H, 3.5; N, 8.0%. FT-IR (nujol mull cm^{-1}): ν(NH) 3340s; ν(C=N) 1614vs; ν(PN) 906s; $\nu(PF_6)$ 842vs. ^1H NMR [$(CD_3)_2CO$]: δ 6.45 (m, 1H, aromatics), 6.87 (m, 2H, aromatics), 7.24–7.71 (m, 20H, aromatics and NH), 7.97 (d, 1H, H^6 pyridine, J_{HH} = 7.6 Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 83.5 (s, Ph_2PNHpy), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 565 ($M^+ - PF_6$).

[Pd(Phox)(Ph$_2$PNHPy-P,N)][PF$_6$] (**IVb**). Yield: 105.6 mg (75%). *Anal*. Calc. for $C_{26}H_{23}F_6N_3OP_2Pd$: C, 46.2; H, 3.4; N, 6.2. Found: C, 46.4; H, 3.5; N, 6.2%. FT-IR (nujol mull cm^{-1}): ν(NH) 3326s; ν(C=N) 1614vs; ν(PN) 904s; $\nu(PF_6)$ 848vs. ^1H NMR [$(CD_3)_2CO$]: δ 4.52 (t, 2H, Phox, J_{HH} = 9.5 Hz), 5.03 (t, 2H, Phox, J_{HH} = 9.5 Hz), 6.98 (m, 2H, aromatics), 7.15 (m, 2H, aromatics), 7.27 (d, 1H, aromatic, J_{HH} = 8.4 Hz), 7.46 (d, 1H, aromatic, J_{HH} = 7.4 Hz), 7.67 (m, 7H, aromatics and NH), 7.98 (m, 5H, aromatics), 8.49 (d, 1H, H^6 pyridine, J_{HH} = 6.0 Hz). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 82.9 (s, Ph_2PNHpy), −143.7 (m, PF_6). FAB-MS (positive mode) *m/z*: 530 ($M^+ - PF_6$).

2.6. Preparation of [Pd{C$_4$(COOMe)$_4$}(Ph$_2$PNHPy-P,N)] (**Vb**)

To an acetone (5 ml) solution of the precursor [Pd{C_4(COOMe)$_4$}($CH_3CN)_2$] (0.07 g, 0.15 mmol) was added the stoichiometric amount of solid 2-(diphenylphosphinoamino)pyridine. The reaction was stirred at room temperature for 30 min, and then the solvent was partially evaporated under reduced pressure. The addition of diethyl ether caused the formation of a yellow solid, that was filtered off, air dried and recrystallised from dichloromethane–hexane. Yield: 58.8 mg (69%). *Anal*. Calc. for $C_{29}H_{27}N_2O_8PPd$: C, 52.1; H, 4.1; N, 4.2. Found: C, 52.3; H, 4.4; N, 4.3%. FT-IR (nujol mull cm^{-1}): ν(NH) 3236s; ν(C=O) 1704vs; ν(C=N) 1656s; ν(PN) 904s. ^1H NMR [$(CD_3)_2CO$]: δ 2.77 (s, 3H, COOMe), 3.51 (s, 3H, COOMe), 3.56 (s, 3H, COOMe), 3.61 (s, 3H, COOMe), 6.91 (m, 1H, aromatics), 7.01 (m, 1H, aromatics), 7.48–7.89 (m, 11H, aromatics and NH), 8.13 (m, 1H, aromatics), 8.42 (s, br, 1H, H^6 pyridine). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: δ 77.9 (s, Ph_2PNHpy). FAB-MS (positive mode) *m/z*: 669 (M^+).

2.7. Crystal structure determination of [Pd(Azb)(Ph$_2$POCH$_2$Py-P,N)][PF$_6$] (**IIIa**) and [Pd(Phpy)(Ph$_2$PNHPy-P,N)][PF$_6$] (**Ib**)

Crystals of (**IIIa**) (0.25×0.16×0.12 mm^3) and (**Ib**) (0.19×0.13×0.10 mm^3) suitable for X-ray diffraction studies were prepared by slow diffusion of hexane into their dichloromethane solutions, mounted on glass fibre and transferred to an Bruker Smart CCD diffractometer at −173 °C. The crystallographic data are summarised in Table 1. Mo Kα radiation was used (λ = 0.71073 Å). The structures were solved by Patterson methods [45] and refined anisotropically on F^2 [45].

The ranges of *hkl* were $-15 \leqslant h \leqslant 14$, $-12 \leqslant k \leqslant 11$, $-37 \leqslant l \leqslant 37$ for **IIIa**, and $-11 \leqslant h \leqslant 11$, $-18 \leqslant k \leqslant 19$, $-27 \leqslant l \leqslant 28$ for **Ib**. Two molecules were found in the asymmetrical unit of the latter. Hydrogen atoms were introduced in calculated positions.

2.8. Synthesis of complexes [Pd(C^N)(Ph$_2$PNPy-P,N)][C^N = 2-pyridinin-phenyl (**Ic**), 7,8-benzoquinolyl (**IIc**), phenylazophenyl (**IIIc**) and 2-(2-oxazolinyl)phenyl (**IVc**)]

The new complexes were obtained by treating [Pd(C^N)(μ-OH)]$_2$ with 2-(diphenylphosphinoamino)pyridine in molar ratio 1:2, using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane solution (10 ml) of the corresponding precursor [Pd(C^N)(μ-OH)]$_2$ (60 mg) was added the stoichiometric amount of solid 2-(diphenylphosphinoamino)pyridine. After stirring for 30 min at room temperature, the solution was concentrated under reduced pressure to half volume. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dichloromethane–hexane.

[Pd(Phpy)(Ph$_2$PNPy-P,N)] (**Ic**). Yield: 92.9 mg (80%). *Anal*. Calc. for $C_{28}H_{22}N_3PPd$: C, 62.5; H, 4.1; N, 7.8. Found: C, 62.6; H, 4.4; N, 8.0%. FT-IR (nujol mull cm^{-1}): ν(C=N) 1598vs, 1578s; ν(P–N) 934s. ^1H NMR [$CDCl_3$]: δ 6.26 (m, 1H, aromatics),6.82 (m, 1H, aromatics),7.02 (m, 1H, aromatics), 7.06 (m, 1H, aromatics), 7.13 (m, 1H, aromatics), 7.24–7.46 (m, 8H, aromatics), 7.60 (m, 1H, aromatics), 7.77 (m, 1H, aromatics), 7.90 (m, 6H, aromatics), 8.51 (d, 1H, H^6 pyridine). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 89.1 (s, Ph_2PNpy). FAB-MS (positive mode) *m/z*: 537 (M^+).

[Pd(Bzq)(Ph$_2$PNPy-P,N)] (**IIc**). Yield: 98.3 mg (88%). *Anal*. Calc. for $C_{30}H_{22}N_3PPd$: C, 64.1; H, 3.9; N, 7.5. Found: C, 64.0; H, 3.9; N, 7.4%. FT-IR (nujol mull cm^{-1}): ν(C=N) 1602vs; ν(P–N) 942s. ^1H NMR [$CDCl_3$]: δ 6.26 (m, 1H, aromatics), 6.90 (m, 1H, aromatics), 7.12 (m, 1H, aromatics), 7.22–7.34 (m, 8H, aromatics), 7.46 (m, 1H, aromatics), 7.54 (m, 2H, aromatics), 7.71 (m, 1H, aromatics), 7.90 (m, 5H, aromatics), 8.28

Table 1
Crystal data and structure refinement details for compounds **IIIa** and **Ib**

	IIIa	**Ib**
Empirical formula	$C_{30}H_{25}F_6N_3OP_2Pd$	$C_{28}H_{23}F_6N_3P_2Pd$
Formula weight	725.87	683.83
Temperature (K)	100(2)	100(2)
Absorption coefficient (mm^{-1})	0.821	0.888
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.3185(7)	8.6055(4)
b (Å)	9.0996(6)	14.8741(7)
c (Å)	28.3540(19)	21.6614(11)
α (°)	90	96.35(1)
β (°)	97.5450(10)	91.61(1)
γ (°)	90	105.40(1)
V ($Å^3$)	2895.0(3)	2651.9(2)
Z	4	4
D_{calc} (Mg m^{-3})	1.665	1.713
$F(000)$	1456	1368
Reflections collected	32565	30989
Independent reflections (R_{int})	6691 (0.220)	11840 (0.0205)
Parameters	388	721
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
R_1[a]	0.0374	0.0347
wR^2[b]	0.0805	0.0806
S[c]	1.241	0.975
Maximum, minimum $\Delta\rho$ (e $Å^{-3}$)	0.795, −0.506	0.599, −0.611

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$ for reflections with $I > 2\sigma I$.
[b] $wR_2 = \left\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right\}^{1/2}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.
[c] $S = \left\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\right\}^{1/2}$; n is the number of reflections and p, the total number of parameters refined.

(m, 1H, aromatics), 8.89 (m, 1H, H^6 pyridine). $^{31}P^1H$ NMR [$CDCl_3$]: δ 89.6 (s, Ph_2PNpy). FAB-MS (positive mode) m/z: 561 (M^+).

[Pd(Azb)(Ph$_2$PNPy-P,N)] (**IIIc**). Yield: 84.6 mg (76%). *Anal.* Calc. for $C_{29}H_{23}N_4PPd$: C, 61.7; H, 4.1; N, 9.9. Found: C, 61.7; H, 4.0; N, 9.7%. FT-IR (nujol mull cm^{-1}): ν(C═N) 1604vs; ν(P–N) 940s. ^1H NMR [$CDCl_3$]: δ 5.90 (m, 1H, aromatics), 6.93 (m, 3H, aromatics), 7.16 (m, 3H, aromatics), 7.32–7.46 (m, 9H, aromatics), 7.61 (m, 2H, aromatics), 7.83 (m, 4H, aromatics), 8.00 (d, 1H, H^6 pyridine, $J_{HH} = 7.5$Hz). $^{31}P^1H$ NMR [$CDCl_3$]: δ 87.0 (s, Ph_2PNpy). FAB-MS (positive mode) m/z: 564 (M^+).

[Pd(Phox)(Ph$_2$PNPy-P,N)] (**IVc**). Yield: 90.8 mg (77%). *Anal.* Calc. for $C_{26}H_{22}F_6N_3OPPd$: C, 58.9; H, 4.2; N, 7.9. Found: C, 59.0; H, 4.3; N, 8.1%. FT-IR (nujol mull cm^{-1}): ν(C═N) 1604vs; ν(P–N) 942s. ^1H NMR [$CDCl_3$]: δ 4.16 (t, 2H, Phox, $J_{HH} = 9.4$ Hz), 4.70 (t, 2H, Phox, $J_{HH} = 9.4$ Hz), 6.24 (m, 1H, aromatics), 6.89 (m, 3H, aromatics), 7.03 (m, 4H, aromatics), 7.13–7.44 (m, 7H, aromatics), 7.97 (m, 3H, aromatics). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 84.7 (s, Ph $_2$ PNpy). FAB-MS (positive mode) m/z: 529 (M^+).

*2.9. Preparation of [Pd{C$_4$(COOMe)$_4$}(Ph$_2$PNPy-P,N)][NBu$_4$] (**Vc**)*

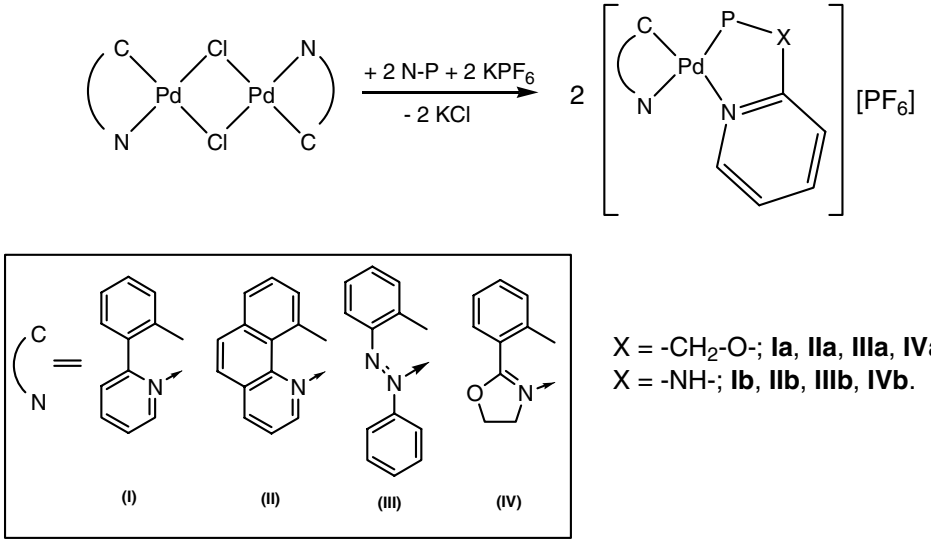
To an acetone (15 ml) solution of the precursor $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ (0.06 g, 0.05 mmol) was added the stoichiometric amount of solid 2-(diphenylphosphinoamino)pyridine. The reaction was stirred at room temperature for 60 min, and then the solvent was partially evaporated under reduced pressure. The addition of diethyl ether caused the formation of a yellow solid, that was filtered off, air dried and recrystallised from dichloromethane–hexane. Yield: 57.1 mg (68%). *Anal.* Calc. for $C_{45}H_{62}N_3O_8PPd$: C, 59.4; H, 6.9; N, 4.6. Found: C, 59.4; H, 6.9; N, 4.7%. FT-IR (nujol mull cm^{-1}): ν(C═O) 1718s; ν(C═N) 1602vs. ν(P–N) 933s ^1H NMR [$CDCl_3$]: δ 1.01 (t, 12H, NBu_4), 1.41 (m, 8H, NBu_4), 1.65 (m, 8H, NBu_4), 3.47 (m, 20H, NBu_4 + COOMe), 6.31 (m, 1H, aromatics), 6.91 (m, 1H, aromatics), 6.87–7.38 (m, 11H, aromatics), 7.76 (s, br, 1H, H^6 pyridine). $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 85.3 (s, Ph_2PNpy). FAB-MS (negative mode) m/z: 667 (M^-).

3. Results and discussion

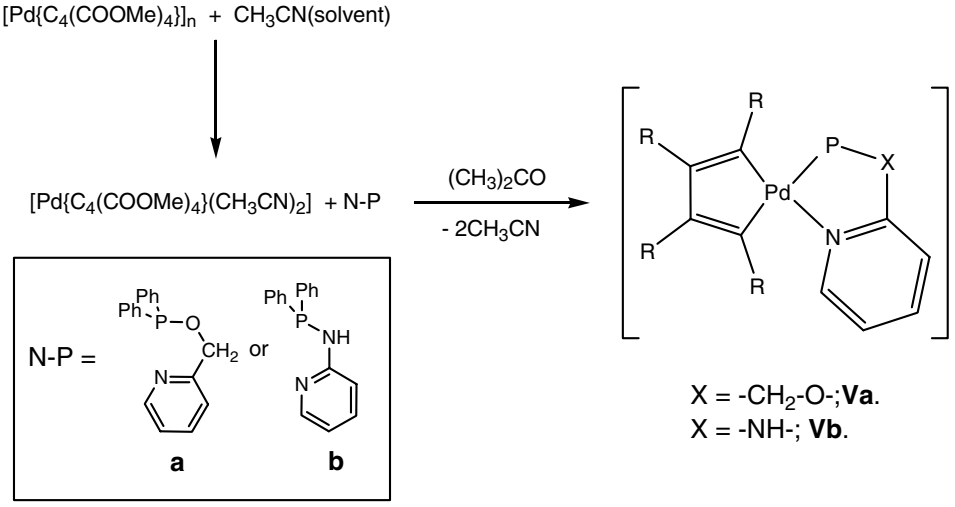
In dichloromethane, the chloro-bridged cyclometallated dimers [{Pd(μ-Cl)(C^N)}$_2$][C^N = 2-pyridinin-phenyl **I**, 7,8-benzoquinolyl **II**, phenylazophenyl **III** and 2-(2-oxazolinyl)phenyl **IV**] react with ligands **a** or **b** in the presence of stoichiometric KPF_6 under the smooth conditions described in Section 2, to afford the white compounds [Pd(C^N)(Ph_2POCH_2Py-P,N][PF_6] (**Ia**–**IVa**) or [Pd(C^N)(Ph_2PNHPy-P,N)][PF_6] (**Ib**–**IVb**), in which a rigid P,N-chelation of the ligands is induced (Scheme 1). Measurements of their molar conductivity in acetone solutions indicate that all the complexes behave as 1:1 electrolytes [46], in accordance with the proposed formulae. The new palladium complexes are air-stable and their IR spectra show the characteristic absorptions of the PF6 − anion at ca. 840 and 558 cm^{-1}, together with two bands in the 1632–1568 cm^{-1} region, attributed to the C═N stretching vibrations of the P,N-ligands and the corresponding cyclometallated backbone. The ν(C═N) band that appears at higher wavenumber can be assigned to the P,N-pyridine ring involved in a chelating coordination mode. As expected on the analogy of previously reported data [20 and references therein], this band is shifted with regard to the free ligands (1601 cm^{-1}). The IR spectra of compounds **Ib**–**IVb** also display ν(P–N) bands around 900 cm^{-1} characteristic of –NH protonated ligand, and a sharp strong ν(N–H) absorption at ≈3330 cm^{-1} that suggest little hydrogen-bonding interaction between the amine protons and the $[PF_6]^-$ anion.

The ^{1}H NMR spectra show the corresponding aromatic signals of the cyclometallated ligands, with a typical doublet resonance attributed to the pyridyl C [6] proton in the 7.97–9.27 ppm region, shifted downfield from the rest aromatic resonances. In both series the lowest field values for this proton is shown by the Phpy derivative, whereas Bzq complexes present the highest one. The $^{31}P\{^1H\}$ NMR spectra of the mononuclear complexes confirm their cationic nature and the absence of any fluxional process, and consist of a $[PF_6]^-$ septuplet centered at −143.7 ppm together with sharp singlets with chemical shifts in the usual range of Pd(II)-bound phosphorus atom. There are not marked differences in chemical shift on varying the cyclometallated ligand (**a** compounds 129.0–131.1 ppm; **b** compounds 82.9–84.9 ppm). The FAB mass spectrometry displays the expected fragments corresponding to $[M^+ - PF_6]$, in accordance with reported data for related compounds [20,21].

On the other hand, recrystallisation of [Pd{C_4(COOMe)$_4$}]$_n$ from acetonitrile affords in good yield a novel complex with satisfactory microanalytical data for [Pd{C_4COOMe_4}(CH_3CN)$_2$] (**V**). The incorporation of acetonitrile was substantiated by the presence of IR absorption bands of strong intensity at 2322 and 2292 cm^{-1}, and further confirmed by NMR data, as shown in Section 2. The results of a thermogravimetric analysis of **V** in nitrogen display a weight loss at ca. 115 °C of about 17% of the total weight, that corresponds to liberation of two CH_3CN molecules. In acetone, the new precursor **V** reacts with ligands **a** or **b** (molar ratio 1:1) under mild conditions to give the corresponding neutral square-planar complexes **Va** and **Vb** shown in Scheme 2. The new palladium complexes are air-stable yellow solids that show negligible molar conductance. The IR spectra of these complexes show a very strong bands [ν(CO)] at ≈1705 cm^{-1} characteristic of the carboxylate groups [31,42] together with the above mentioned absorbances that confirm the presence of the pyridylphosphine ligands.



Scheme 1.



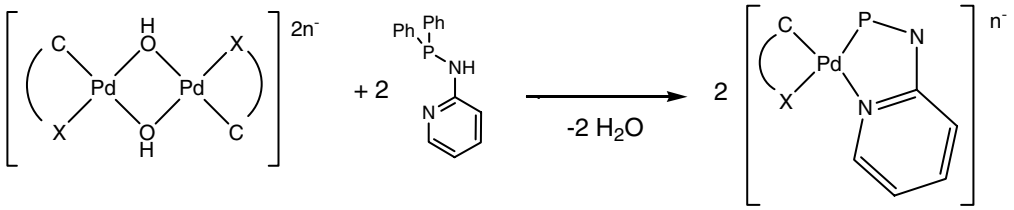
Scheme 2.

The ^{1}H NMR spectra also display the aromatic signals of the neutral ligands, with the typical low field resonance of H^{6} as outstanding feature, together with the characteristic four resonances of asymmetric palladacyclopentadiene compounds that correspond to the different methoxycarbonyl groups [41]. As expected, complexes **Va** and **Vb** bearing a palladacyclopentadiene backbone present the highest field $^{31}P\{^{1}H\}$ NMR signals in its respective series. This variation is in agreement with our previous results found when comparing the same cyclometallated systems with iminophosphine ligands [31,32].

In order to prepare new complexes with the anionic $[PyNPPh_2]^-$ ligand **c**, the di-μ-hydroxo-complexes $[\{Pd(\mu\text{-}OH)(C\hat{}N)\}_2]$ and $[Pd_2\{C_4(COOMe)_4\}_2(\mu\text{-}OH)_2][NBu_4]_2$ were employed as precursors in reactions with $PyNHPPh_2$. A few examples of compounds containing **c** have been described [20,47], involving in their preparation treatment with ^{t}BuOK/MeOH. The recognised basicity of such precursors and its usefulness in previous synthetic work prompt us to perform the reactions shown in Scheme 3 to obtain **Ic**–**Vc** with satisfactory microanalytical and FAB mass spectrometry data. The loss of both *ν*(NH) and *ν*(OH) bands in the IR spectra of new compounds with regards to those of the starting materials, together with the expected ^{1}H NMR data, confirmed that the proposed reactions took place. An increase in P–N bond order and consequent shifting of the *ν*(PN) absorption to higher frequencies has been observed in P–N-py systems upon deprotonation. In our compounds **Ic**–**Vc**, a significant shift of ca. 35 cm^{-1} in the *ν*(PN) band is detected in comparison with related **Ib**–**Vb** complexes. Deprotonation of the amino group also involves displacement of singlet resonances in the $^{31}P\{^{1}H\}$ NMR spectra, that now appear in the range 84.7–89.1 ppm.

3.1. X-ray structures of *IIIa* and *Ib*

Selected bond distances and angles are presented in Table 2. To the best of our knowledge (Cambridge Structural Database V. 5.24 with February, April and July 2003 updates), the X-ray data of **IIIa** (Fig. 1) represents the first description of a crystal structure in which the 2-(diphenylphosphinyl)oxymethylpyridine ligand appears coordinated to a metal centre. The bite angle of this ligand coordinated to palladium in **IIIa** is 91.16(6)°. The coordination around the metal centre is



Scheme 3.

Table 2
Selected bond lengths (Å), angles (°) and torsion angles (°)

Bond length (Å)/angle/torsion angle (°)	IIIa	Ib
Pd(1)–C(1)	1.998(3)	2.002(3)
Pd(1)–N(1)	2.110(2)	2.094(2)
Pd(1)–N(2)	2.138(2)	2.129(2)
Pd(1)–P(1)	2.2329(7)	2.2137(7)
C(1)–Pd(1)–N(1)	78.91(10)	81.20(10)
C(1)–Pd(1)–N(2)	166.93(9)	171.05(9)
C(1)–Pd(1)–P(1	94.64(8)	98.03(8)
N(1)–Pd(1)–N(2)	96.41(8)	100.52(9)
N(1)–Pd(1)–P(1)	171.13(6)	170.02(6)
N(2)–Pd(1)–P(1)	91.16(6)	81.78(6)

tetrahedrally distorted with improper torsion angles of −4.44° for P(1)–C(1)–N(1)–Pd(1) and −8.25° for N(2)–N(1)–C(1)–Pd(1) [48]. In accordance with the classification from Allen and Taylor [49], the six-membered ring defined by the palladium atom and the chelating P,N-ligand show a distorted *sofa* conformation. The torsion angles in the complex do not conform to the ideal of around 20°.

A slight tetrahedral distortion of the planar palladium environment is observed in **Ib** (Fig. 2), with improper torsion angles of −6.92° for P(1)–C(1)–N(1)–Pd(1) and −5.72° for N(2)–N(1)–C(1)–Pd(1) (mean angles of the two complexes in the the asymmetrical unit) [48]. The small bite angle of the ligand is similar to that found in related compounds, and other trends reported for palladium complexes in comparison with the free ligand are also followed [20]. Thus, a little reduction in the P–N length [1.696(2) Å; free ligand 1.705(3) Å] and P(1)–N(3)–C(16) angle [119.06(18)°; free ligand 124.4(2)°] is observed, together with a small elongation in N(3)–C(16) length [1.385(3) Å; free ligand 1.374(5) Å]. In our complex is also detected an elongation in N(2)–C(16) length [1.345(3) Å; free ligand 1.329(4) Å]. The absence of solid state hydrogen bonding between the NH proton and PF_6 counter ion is confirmed by N–F distances over 3.6 Å, in agreement with the interpretation of the IR spectra.

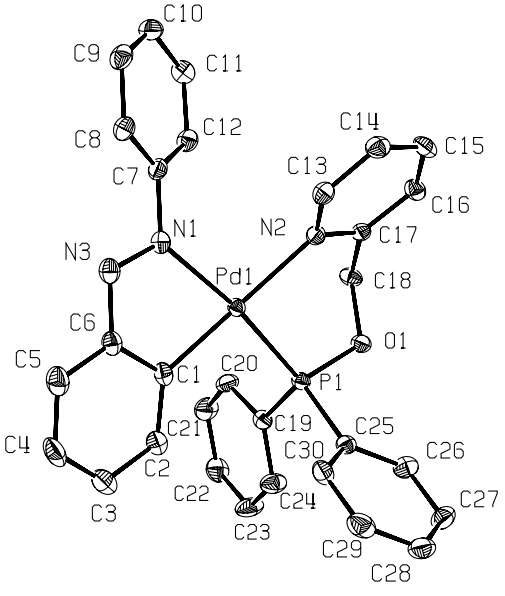


Fig. 1. Structure of the $[Pd(Azb)(Ph_2POCH_2Py\text{-}P,N)]^+$ cation in the single crystal structure of **IIIa**. All hydrogen atoms have been omitted for clarity.

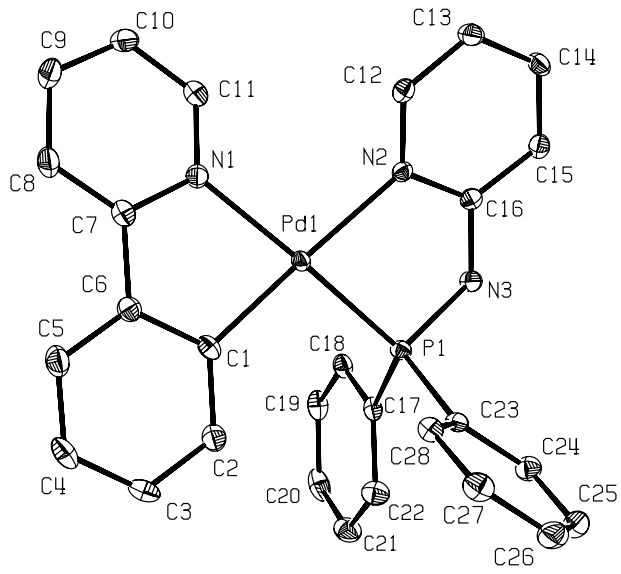


Fig. 2. ORTEP diagram of one of the two independent molecules present in the asymmetry unit of **Ib**. For clarity, all hydrogen atoms have been omitted.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 235179 (**IIIa**), 235180 (**Ib**) Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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