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Synthesis and characterisation of κ^1-*P* and κ^2-*P*,*N* palladium(II) complexes of the open cage water soluble aminophosphine PTN

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Dedicated to Professor Robert J. Angelici in recognition of his outstanding and creative contributions to many important areas of organometallic and coordination chemistry.

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ABSTRACT

New palladium(II) complexes containing the water soluble aminophosphine PTN ligand (PTN = 7-phospha-3,7-dimethyl-1,3,5-triazabicyclo[3.3.1]nonane) in 1:1 and 1:2 ratio Pd/PTN ligand, respectively, were prepared and fully characterised by mono and bidimensional ^{31}P, ^{1}H and ^{13}C NMR techniques showing that PTN can adopt both κ^1-*P* and κ^2-*P*,*N* coordination modes. The complexes with Pd/PTN ratio 1:2 are highly soluble in water at room temperature. Suitable crystals for X-ray structure determination were obtained for the neutral complex κ^2-*P*,*N*-Pd(PTN)$(OAc)_2$ (**1**) and for the monocationic complex [Pd(κ^2-*P*,*N*-PTN)(κ^1-*P*-PTN)Cl][PF_6] (**5**).

1. Introduction

Ligand design for homogeneous catalysts has progressed in the last few years from bidentate diphosphines and diamines to mixed donor atom moieties, such as phosphino ethers, phosphino thioethers and, particularly, aminophosphines [1] and the corresponding complexes were used in hydroformylation, hydrogenation, hydrosilylation and allylic alkylation reactions [2–5]. Pd(II) complexes have found extensive application as catalysts for olefin-CO copolymerisation [6], C–C coupling reactions [7], etc., also bearing P,N bidentate or hemilabile ligands.

Among aminophosphine ligands, the neutral water-soluble phosphine 1-phospha-3,5,7-triazaadamantane (PTA) [8] was successfully used as monodentate ligand for transition metal complexes able to bring about many catalysed processes such as regioselective hydrogenations [9] and hydroformylation [10] of olefins in aqueous media. The open cage aminophosphine 7-phospha-3,7-dimethyl-1,3,5-triazabicyclo[3.3.1]nonane (PTN) [11] can be considered as the P,N-bidentate analogue of PTA, and it was demonstrated that both κ^1-*P* and κ^2-*P*,*N* coordination modes are possible, both in solution and the solid state [12].

Examples of coordination compounds bearing Ph– and Me–P substituted PTNs include Au and Mo complexes either in mono- or bidentate coordination mode, such as [AuCl{κ^1-*P*-PTN(R)}], [AuCl{κ^1-*P*-PTN(Me)}$_2$], [$AuMe_2${κ^2-*P*,*N*-PTN(Me)}][$AuCl_4$] and [$Mo(CO)_4${κ^2-*P*,*N*-PTN(R)}] (R = Me, Ph) reported by Schmidbaur and co-workers [13].

More recently, we have reported the synthesis, spectroscopic and X-ray crystal structural data for Rh(COD) complexes bearing PTN, both as monodentate and chelate ligand [14], and their use as catalysts for olefin hydroformylation in organic and biphasic organic/water solvent systems.

Hereby results on the synthesis, characterisation and solid state structural determination of novel Pd(II)–PTN complexes are presented. The PTN ligand can adopt both coordination modes, mainly depending on the choice of the metal precursor and reaction conditions. X-ray crystal structures of [Pd(κ^2-*P*,*N*-PTN)$(OAc)_2$] and [Pd(κ^2-*P*,*N*-PTN)(κ^1-*P*-PTN)Cl][PF_6] are reported and discussed.

2. Experimental

2.1. General procedures, methods and materials

All syntheses have been performed under a dry nitrogen atmosphere applying standard Schlenk techniques. Solvents have been

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purified by distillation over suitable drying agents and degassed prior to use. 7-Phospha-3,7-dimethyl-1,3,5-triazabicyclo[3.3.1]-nonane PTN [11,13], $NaBAr^F_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) [15] and PdClMe(cod) (COD = 1,5-cyclooctadiene) [16] were prepared according to the literature methods. All other reagents (technical grade) were used as purchased from Aldrich or Fluka, unless otherwise stated. Deuterated solvents for routine NMR measurements were dried over activated molecular sieves. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR spectra were obtained on a Bruker Avance DRX-300 spectrometer (300.13, 75.47 and 121.49 MHz, respectively). Chemicals shifts (δ) are reported in ppm relative to TMS, referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C{^{1}H}NMR) or 85% H_3PO_4 (^{31}P{^{1}H} NMR). Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer at the University of Florence. Infrared spectra were recorded on a FT-IR Perkin–Elmer Spectrum BX instrument. Electrospray mass spectrometry measurements have been carried out at the University of Pisa, Italy, on an Applied Biosystems Sciex API 4000 triple quadrupole mass spectrometer (Sciex Co, Concord, Ontario, Canada) equipped with a Turbo-V Ionspray interface, coupled to a Perkin–Elmer Series 200 Micro dual solvent delivery system and a Perkin–Elmer Series 200 autosampler (Perkin–Elmer, Waltham, MA, USA). The analyses were performed in flow injection mode at 200 μl/min (mobile phase: water/acetonitrile 1:1 containing 0.1% formic acid).

2.2. Synthesis of [Pd(κ^2-P,N-PTN)(OAc)$_2$] (**1**)

A solution of PTN (31.50 mg, 0.181 mmol) in dichloromethane (10 ml) was added to a degassed solution of $Pd(OAc)_2$ (40.0 mg, 0.178 mmol) in dichloromethane (12.0 ml) under stirring at room temperature. After 20 min, diethyl ether (6.0 ml) was added to the solution and a brown precipitate was obtained, which was then filtered under nitrogen. The product was finally dried in a stream of nitrogen. Yield 65%. *Anal.* Calc. for $C_{11}H_{22}N_3O_4PPd$: C, 33.24; H, 5.53; N, 10.56. Found: C, 33.00; H, 5.47; N, 10.47%. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.30 (d, $^2J_{HP}$ = 13.5 Hz, 3H, P-CH_3), 1.80 (s, 3H, CH_3-COO), 1.90 (s, 3H, CH_3-COO), 2.34 (s, 3H, N-CH_3), 3.50 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{HP}$ = 8.6 Hz, 2H, P-CH*H*′-N), 3.70 (d, $^2J_{HH}$ = 12.5 Hz, 2H, N-CH*H*′-NCH_3), 3.88 (d, $^2J_{HH}$ = 13.8 Hz, 1H, N-*CH*H′-N), 3.98 (d, $^2J_{HH}$ = 13.8 Hz, 1H, N*CH*H′-N), 4.14 (d, $^2J_{HH}$ = 15.2 Hz, 2H, P-*CH*H′-N), 4.70 (d, $^2J_{HH}$ = 12.5 Hz, 2H, N-*CH*H′-NCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 3.60 (d, $^1J_{CP}$ = 25.7 Hz, P-CH_3), 22.0 (s, *C*H_3-COO), 23.5 (s, *C*H_3-COO), 45.4 (s, N-CH_3), 50.10 (d, $^1J_{CP}$ = 22.8 Hz, P-CHH′-N), 70.00 (d, $^3J_{CP}$ = 9.5 Hz, N-CHH′-NCH_3), 79.90 (d, $^3J_{CP}$ = 5.6 Hz, N-CHH′-N), 176.80 (s, COO), 177.20 (s, COO). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −41.60 (s).

2.3. Synthesis of [Pd(κ^2-P,N-PTN)(Me)Cl] (**2**)

To a degassed solution of PdClMe(cod) (80.0 mg, 0.307 mmol) in dichloromethane (7.0 ml) was added dropwise a solution of PTN (54.0 mg, 0.316 mmol) in dichloromethane (7 ml) over 10 min. The reaction mixture was allowed to stir for 40 min and then evacuated to dryness. The off-white product was re-crystallised from dichloromethane and *n*-pentane. Yield 80%. *Anal.* Calc. for $C_8H_{19}ClN_3PPd$: C, 29.12; H, 5.76; N, 12.73. Found: C, 29.00; H, 5.70; N, 12.69%. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 0.50 (d, $^3J_{HP}$ = 3.4 Hz, 3H, Pd–CH_3), 1.20 (d, $^2J_{HP}$ = 10.8 Hz, 3H, P-CH_3), 2.40 (s, 3H, N-CH_3) 3.60 (dd, $^2J_{HH}$ = 12.5 Hz, $^4J_{HP}$ = 2.0 Hz, 2H, N-CH*H*′-NCH_3), 3.67 (d, $^2J_{HH}$ = 9.2 Hz, 2H, P-CH*H*′-N) 3.88 (br d, $^2J_{HH}$ = 13.4 Hz, 1H, N-CH*H*′-N), 3.95 (d, $^2J_{HH}$ = 9.2 Hz, 2H, P-*CH*H′-N), 3.99 (d, $^2J_{HH}$ = 13.4 Hz, 1H, N-*CH*H′-N), 4.35 (dd, $^2J_{HH}$ = 12.5 Hz, $^4J_{HP}$ = 2.0 Hz, 2H, N-*CH*H′-NCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −7.70 (s, Pd–CH_3), 5.50 (d, $^1J_{CP}$ = 22.7 Hz, P-CH_3), 46.30 (s, N-CH_3), 52.10 (d, $^1J_{CP}$ = 19.7 Hz, P-CHH′-N), 70.70 (d, $^3J_{CP}$ = 10.2 Hz, N-CHH′-NCH_3), 78.30 (d, $^3J_{CP}$ = 3.2 Hz, N-CHH′-N). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −37.00 (s).

2.4. Synthesis of [Pd(κ^2-P, N-PTN)(Me)(CH_3CN)](BAr^F_4) (**3**)

To a degassed solution of **2** (50.0 mg, 0.152 mmol) in a CH_2Cl_2-CH_3CN solvent mixture (25:1, 8.0 ml) was added $NaBAr^F_4$ (141.0 mg, 0.159 mmol). The reaction mixture was allowed to stir for 1.5 h, then the suspension was filtered through celite and the resulting clear solution was concentrated to half of its original volume. On addition of diethyl ether (10 ml) an off-white product precipitated, which was filtered off, washed with cold diethyl ether (2 × 5 ml) and dried in a stream of nitrogen. Yield 65%. *Anal.* Calc. for $C_{42}H_{34}N_4BF_{24}PPd$: C, 42.07; H, 2.85; N, 4.67. Found: C, 42.12; H, 2.90; N, 4.57%. IR (KBr): ν(CN) 2292, 2319 cm^{-1} (w). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 0.40 (d, $^3J_{HP}$ = 2.3 Hz, 3H, Pd–CH_3), 1.30 (d, $^2J_{HP}$ = 11.6 Hz, 3H, P-CH_3), 2.26 (s, 3H, CH_3CN), 2.30 (s, 3H, N-CH_3), 3.70 (m, 2H, P-*CH*H′-N), 3.76 (m, 2H, N-CH*H*′-NCH_3), 3.89 (m, 2H, P-CH*H*′-N), 3.90 (d, $^2J_{HH}$= 13.0 Hz, 1H, N-CH*H*′-N), 4.00 (d, $^2J_{HH}$ = 13.0 Hz, 1H, N-*CH*H′-N), 4.29 (d, $^2J_{HH}$ = 11.2 Hz, 2H, N-*CH*H′-NCH_3), 7.54 (br s, 4H, Ar-H*p*), 7.70 (br s, 8H, Ar-H_o). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −6.20 (s, Pd–CH_3), 2.85 (s, *C*H_3-CN), 5.20 (d, $^1J_{CP}$ = 25.5 HZ, P-CH_3), 46.00 (s, N-CH_3), 51.10 (d, $^1J_{CP}$ = 21.7 Hz, P-CHH′-N), 70.30 (d, $^3J_{CP}$ = 10.7 Hz, N-CHH′-NCH_3), 78.50 (d, $^3J_{CP}$ = 3.6 Hz, N-CHH′-N), 117.50 (s, Ar-C_p), 119.20 (s, CN), 124.60 (q, $^1J_{CF}$ = 272.5 Hz, CF_3), 128.90 (q, $^2J_{CF}$ = 30.7 Hz, *C*-CF_3), 134.80 (s, Ar-C_o), 161.80 (non-binomial q, $^1J_{CB}$ = 49.8 Hz, Ar-C_i). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −35.00 (s).

2.5. Synthesis of trans-[Pd(κ^1-P-PTN)$_2$Cl$_2$] (**4**)

To a degassed solution of Pd(cod)Cl_2 (145.0 mg, 0.510 mmol) in dichloromethane (40 ml) was added PTN (180.0 mg, 1.040 mmol) and the resulting reaction mixture was allowed to stir for 1 h at room temperature. The volume of the solution was then reduced to 7 ml under nitrogen stream and diethyl ether (10 ml) was added. The solid product obtained was filtered off, washed with diethyl ether and dried in a stream of nitrogen, obtaining a yellow microcrystalline compound. Yield 79%. *Anal.* Calc. for $C_{14}H_{32}Cl_2N_6P_2Pd$: C, 32.12; H, 6.11; N, 16.05. Found: C, 32.10; H, 6.01; N, 15.98%. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.20 (pseudo t, $^2J_{HP}$+$^4J_{HP}$ = 2.2 Hz, 6H, P-CH_3), 2.30 (s, 6H, N-CH_3), 3.20 (d, $^2J_{HH}$ = 14.2 Hz, 4H, N-CH*H*′-NCH_3), 3.54 (d, $^2J_{HH}$ = 10.8 Hz, 4H, P-CH*H*′-N), 3.82 (d, $^2J_{HH}$ = 13.5 Hz, 2H, N-CH*H*′-N), 3.94 (d, $^2J_{HH}$ = 13.5 Hz, 2H, N-*CH*H′-N), 3.97 (d, $^2J_{HH}$ = 10.8 Hz, 4H, P-*CH*H′-N), 4.50 (d, $^2J_{HH}$ = 14.2 Hz, 4H, N-*CH*H′-NCH_3). ^{1}H NMR (D_2O, 25 °C): δ 1.54 (dd, $^2J_{HP}$ = 11.0 Hz, $^4J_{HP}$ = 2.1 HZ, 6H, P-CH_3), 2.37 (s, 6H, N-CH_3), 3.72 (d, $^2J_{HH}$ = 11.3 Hz, 4H, P-CH*H*′-N), 3.80 (d, $^2J_{HH}$ = 15.0 Hz, 4H, N-CH*H*′-NCH_3), 3.98 (AB, $^2J_{HH}$ = 14.9 Hz, 4H, N-CH*H*′-N), 4.14 (AB, d, $^2J_{HH}$= 15.0 Hz, 4H, N-*CH*H′-NCH_3), 4.16 (d, $^2J_{HH}$ = 11.3 Hz, 4H, P-*CH*H′-N). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 15.30 (t, $^1J_{CP}$ = 7.8 HZ, P-CH_3), 38.70 (s, N-CH_3), 49.90 (t, $^1J_{CP}$+$^3J_{CP}$ = 12.5 Hz, P-CHH′-N), 70.50 (t, $^3J_{CP}$ = 7.8 Hz, N-CHH′-NCH_3), 75.80 (s, N-CHH′-N). ^{13}C{^{1}H} NMR (D_2O, 25 °C): δ 12.05 (d, $^1J_{CP}$ = 20.2 Hz, P-CH_3), 42.4 (s, N-CH_3), 51.50 (d, $^1J_{CP}$ = 23.3 Hz, P-CHH′-N), 68.10 (d, $^3J_{CP}$ = 11.1 Hz, N-CHH′-NCH_3), 75.82 (s, N-CHH′-N). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −49.00 (s). ^{31}P{^{1}H} NMR (D_2O, 25 °C): δ −31.20 (s). ESI-MS: *m*/*z* 489 (M^+- Cl), 454 (M^+−2Cl).

2.6. Synthesis of [Pd(κ^2-P,N-PTN)(κ^1-P-PTN)Cl](PF_6) (**5**)

To a degassed solution of **4** (90.0 mg, 0.172 mmol) in dichloromethane (20 ml) was added $AgPF_6$ (90.0 mg, 0.205 mmol). The

resulting suspension was allowed to stir in a aluminium foil-covered Schlenk tube at room temperature for 1 h. Afterwards, the suspension was filtered through celite and the clear solution was concentrated to half of its original volume. Diethyl ether (15 ml) was added, precipitating a pale yellow semi-crystalline compound, which was filtered off, washed with additional diethyl ether (10 ml) and dried under vacuum. Yield 63%. *Anal.* Calc. for $C_{14}H_{32}ClF_6N_6P_3Pd$: C, 26.57; H, 5.06; N, 13.27. Found: C, 26.47; H, 4.99; N, 13.24%. ^{1}H NMR (CD_3COCD_3, 25 °C): δ 1.60 (br s, 3H, P-CH_3), 1.80 (br s, 3H, P-CH_3), 2.40 (br s, 3H, N-CH_3) 2.60 (br s, 3H, N-CH_3), 3.67–4.50 (m, 20H, P-CH*H*′-NCH_3 + P-*CH*H′-NCH_3 + N-CH*H*′-NCH_3 + N-*CH*H′-NCH_3 + N-CH*H*′-N + N-*CH*H′-N). ^{13}C{^{1}H} NMR (CD_3COCD_3, 25 °C): δ 7.40 (br s, P-CH_3), 16.90 (br s, P-CH_3), 38.10 (br s, N-CH_3), 46.40 (br s, N-CH_3), 50.90 (br s, P-CHH′-N), 54.30 (br s, P-CHH′-N), 68.60 (br s, N-CHH′-NCH_3), 69.30 (br s, N-CHH′-NCH_3), 78.40 (br s, N-CHH′-N). ^{31}P{^{1}H} NMR (CD_3COCD_3, 25 °C): δ −25.00 (br s, P (*trans* N)), −45.60 (br s, P (*trans* Cl)), −144.3 (sept, $^1J_{PF}$ = 708 Hz, PF_6).

2.7. Synthesis of trans-[Pd(κ^1-P-PTN)$_2$(Me)Cl] (**6**)

To a degassed solution of PdClMe(cod) (161.4 mg, 0.610 mmol) in dichloromethane (15 ml) was added a solution of PTN (210.8 mg, 1.220 mmol) in dichloromethane (7 ml). The resulting clear mixture was allowed to stir at room temperature for 30 min, followed by concentration to a small volume (5 ml). Upon addition of diethyl ether (10 ml) the product precipitated as an off-white compound, which was filtered off, washed with fresh diethyl ether (2 × 5 ml) and then dried in a stream of nitrogen. Yield 75%. *Anal.* Calc. for $C_{15}H_{35}ClN_6P_2Pd$: C, 35.82; H, 6.96; N, 16.70. Found: C, 35.77; H, 6.89; N, 16.65%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.20 (t, $^3J_{HP}$ = 6.6 Hz, 3H, Pd–CH_3) 1.20 (pseudo t, $^2J_{HP}$+$^4J_{HP}$ = 1.8 Hz, 6H, P-CH_3), 2.10 (s, 6H, N-CH_3) 3.34 (d, $^2J_{HH}$ = 14.7 Hz, 4H, N-CH*H*′-NCH_3) 3.50 (d, $^2J_{HH}$ = 10.8 Hz, 4H, P-CH*H*′-N), 3.84 (d, $^2J_{HH}$ = 13.4 Hz, 2H, N-CH*H*′-N), 3.92 (d, $^2J_{HH}$ = 10.8 Hz, 4H, P-*CH*H′-N), 3.96 (d, $^2J_{HH}$ = 13.4 Hz, 2H, N-*CH*H′-N), 4.35 (d, $^2J_{HH}$ = 14.7 Hz, 4H, N-*CH*H′-NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ −8.40 (t, $^2J_{CP}$ = 5.3 Hz, Pd–CH_3), 16.90 (t, $^1J_{CP}$ = 5.2 Hz, P-CH_3), 38.30 (s, N-CH_3), 50.90 (t, $^1J_{CP}$ = 8.2 Hz, P-CHH′-N), 70.70 (t, $^3J_{CP}$ = 5.3 Hz, N-CHH′-NCH_3), 75.90 (s, N-CHH′-N). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ −49.15 (s).

2.8. Synthesis of trans-[Pd(κ^1-P-PTN)$_2$(Me)](BAr$^F_4$) (**7**)

To a degassed solution of **6** (73.0 mg, 0.140 mmol) in dichloromethane (15 ml) was added $NaBAr^F_4$ (135.0 mg, 0.150 mmol). The reaction mixture was allowed to stir under nitrogen at room temperature for 1 h, followed by filtration through celite. The solution obtained was concentrated to dryness and diethyl ether (5 ml) was added to the yellow residue. The suspension was stirred for 10 minutes and then the product was filtered off under nitrogen, washed with diethyl ether (5 ml) and dried in a stream of nitrogen. Yield 80%. *Anal.* Calc. for $C_{47}H_{47}BF_{24}N_6P_2Pd$: C, 42.43; H, 3.53; N, 6.31. Found: C, 42.39; H, 3.49; N, 6.28%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.27 (t, $^3J_{HP}$ = 7.0 Hz, 3H, Pd–CH_3), 1.18 (pseudo t, $^2J_{HP}$ + $^4J_{HP}$ = 2.7 Hz, 6H, P-CH_3), 2.30 (s, 6H, N-CH_3), 3.58 (d, $^2J_{HH}$ = 15.0 HZ, 4H, P-CH*H*′-N), 3.63 (d, $^2J_{HH}$ = 10.8 Hz, 4H, N-CH*H*′-NCH_3), 3.75–3.97 (m, 8H, N-CH*H*′-N + N-*CH*H′-N + P-*CH*H′-N), 4.02 (d, $^2J_{HH}$ = 10.8 HZ, 4H, N-*CH*H′-NCH_3), 7.55 (s, 4H, Ar-H_p) 7.72 (s, 8H, Ar-H_o). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ −5.20 (br s, Pd–CH_3), 10.50 (br s, P-CH_3), 45.30 (s, N-CH_3), 52.00 (t, $^1J_{CP}$ = 7.9 Hz, P-CHH′-N), 70.50 (br s, N-CHH′-NCH_3), 77.90 (s, N-CHH′-N), 117.5 (s, Ar-C_p), 124.50 (q, $^1J_{CF}$ = 272.5 Hz, CF_3), 128.90 (q, $^2J_{CF}$ = 31.0 Hz, *C*-CF_3), 134.80 (s, Ar-C_o), 161.70 (non-binomial q, $^1J_{CB}$ = 49.8 Hz, Ar-C_i). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ −53.15 (s).

2.9. X-ray crystal structure determinations

Single crystals of **1** and **5** were obtained upon slow evaporation of the corresponding CH_2Cl_2 solutions at room temperature. Diffraction data were collected at room temperature on an Enraf Nonius CAD4 automatic diffractometer with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. Unit cell parameters were determined from least-squares refinement of the setting angles of 25 carefully centred reflections. Crystal data and data collection details are reported in Table 1. Atomic scattering factors were taken from crystallographic tables [17]. The structures were solved by direct methods and refined by full-matrix F^2 refinement. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced in their calculated positions, with thermal parameters 20% larger than those of the adjacent carbon atoms. All the calculations were performed on a PC using the WINGX package [18] with SIR-97 [19], SHELX-97 [20] and ORTEP-3 programs [21] (see Scheme 1).

3. Results and discussion

3.1. Synthesis and characterisation of Pd–PTN complexes

Novel palladium(II) complexes containing the water soluble PTN ligand were prepared by reaction of the $Pd(OAc)_2$, $Pd(cod)Cl_2$ and PdMe(cod)Cl with either an equimolar amount of PTN (Scheme 2) or with 2 equiv. (Scheme 3), respectively.[1] All complexes were characterised in solution by standard NMR techniques and the relevant data are summarised in Table 2. The complexes are generally formed at room temperature immediately after the addition of the ligand to the dichloromethane solution of the palladium precursor and were isolated as moderately air-stable solids.

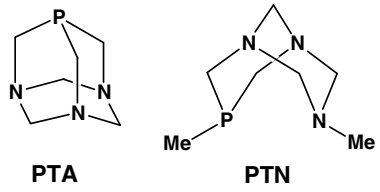
Starting from the palladium precursor $Pd(OAc)_2$, the reaction with 1 equiv. of PTN in dichloromethane afforded $Pd(PTN)(OAc)_2$ (**1**). Upon slow evaporation of a dichloromethane solution of **1**, brown crystals suitable for X-ray crystallographic analysis were isolated and the solid state structure confirmed the presence of two monodentate acetate ligands and PTN behaving as bidentate P,N-chelate (vide infra). In solution (CD_2Cl_2), **1** is characterised by a singlet at −41.60 in the ^{31}P{^{1}H} spectrum. Of diagnostic relevance were found to be the ^{1}H signals corresponding to the CH_3-P (1.30 d, $^2J_{HP}$ 13.5 Hz) and CH_3-N groups (2.34 s) belonging to coordinated PTN, and the ^{13}C{^{1}H} values at 3.60 (d, $^1J_{CP}$ 25.7 Hz, CH_3-P) and 45.4 ppm (s, CH_3-N). The acetate ligands gave resonances at 1.80 and 1.90 (s, ^{1}H) and 176.8, 177.20 (s, ^{13}C{^{1}H}), suggesting that the κ^2-*P,N* behaviour of PTN is maintained in solution. Complex **1** dissolved readily in water (377 mg/ml at 25 °C), however NMR spectra in D_2O indicated major decomposition to occur in this solvent.

By reaction of [Pd(cod)(Me)Cl] with 1 equiv. of PTN, the corresponding complex [PdMe(κ^2-*P,N*-PTN)Cl] (**2**) was isolated. The ^{1}H NMR signal due to Pd-Me shows as a doublet at 0.50 ppm with a coupling constant $^3J_{HP}$ of 13.4 Hz, as expected for a *cis* Me–Pd–P geometry. Chelate behaviour of PTN can be inferred from the signals belonging to CH_3-P (1.20 d, $^2J_{HP}$ 10.8 Hz) and CH_3-N groups (2.40 s). Also the ^{13}C{^{1}H} NMR spectral data for **2** are quite comparable with those of **1**, with signals at 5.50 (d, $^1J_{CP}$ 22.7 Hz, CH_3-P) and 46.30 ppm (s, CH_3-N). Subsequent treatment of **2** with $NaBAr^F_4$ as halide scavenger in a mixture of dichloromethane and acetonitrile, afforded the monocationic complex [Pd(κ^2 − *P,N*−PTN)(Me)(CH_3CN)][BAr$^F_4$] (**3**). Coordination of acetonitrile to Pd

[1] The reaction between $Pd(cod)Cl_2$ and PTN (1:1 ratio) in CH_2Cl_2 gave an insoluble precipitate preventing characterisation by standard techniques.

Table 1
Crystallographic data and structure refinement details for compounds **1** and **5**

	1	**5**
Empirical formula	$C_{11}H_{22}N_3O_4PPd$	$C_{14}H_{32}ClF_6N_6P_3Pd$
Formula weight	397.69	633.22
Temperature (K)	293(2)	293(2)
Wavelength (Mo Kα) (Å)	0.71073	
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.682(9)	9.716(5)
b (Å)	12.329(2)	9.748(5)
c (Å)	13.320(4)	14.448(5)
α (°)	90.00	71.321(5)
β (°)	113.370(4)	72.814(5)
γ (°)	90.00	78.516(5)
V (Å^3)	1610.3(15)	1230.3(10)
Z	4	2
D_{calc} (g cm^{-3})	1.640	1.709
Absorption coefficient (mm^{-1})	1.267	1.118
F(000)	808	640
Crystal size (mm)	0.75 × 0.50 × 0.42	0.35 × 0.35 × 0.30
Theta range for data collection (°)	2.08–26.99	2.73–24.98
Index range	$-13 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 17$
Reflections collected	3496	4316
Independent reflections	3496	4316
Refinement method	full-matrix least-square on F^2	
Data/restraints/parameter	3496/0/185	4316/0/284
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0284$, $wR_2 = 0.0747$	$R_1 = 0.0470$, $wR_2 = 0.1218$
R indices (all data)	$R_1 = 0.0359$, $wR_2 = 0.0769$	$R_1 = 0.0628$, $wR_2 = 0.1322$
Goodness-of-fit on F^2	1.045	1.039
Largest difference peak and hole (e Å^{-3})	0.081 and −0.848	0.925 and −0.588



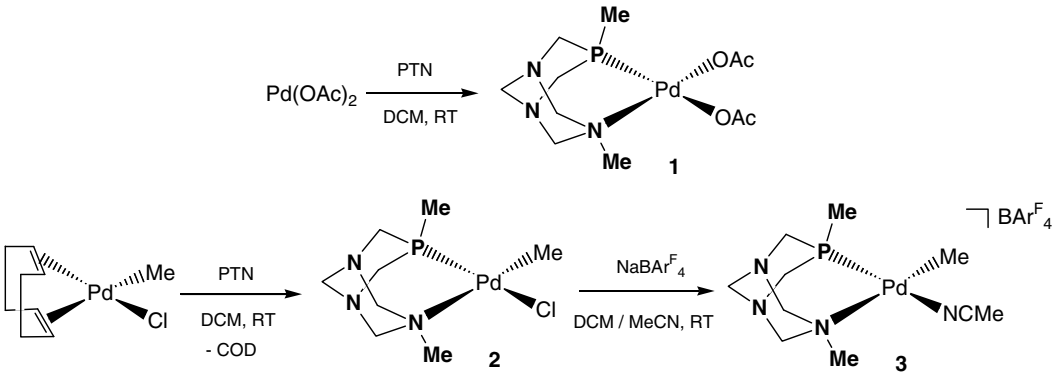
Scheme 1.

was ascertained from the presence of ^{1}H singlet at 2.26 and IR stretching bands at 2292 and 2319 cm^{-1} [22].

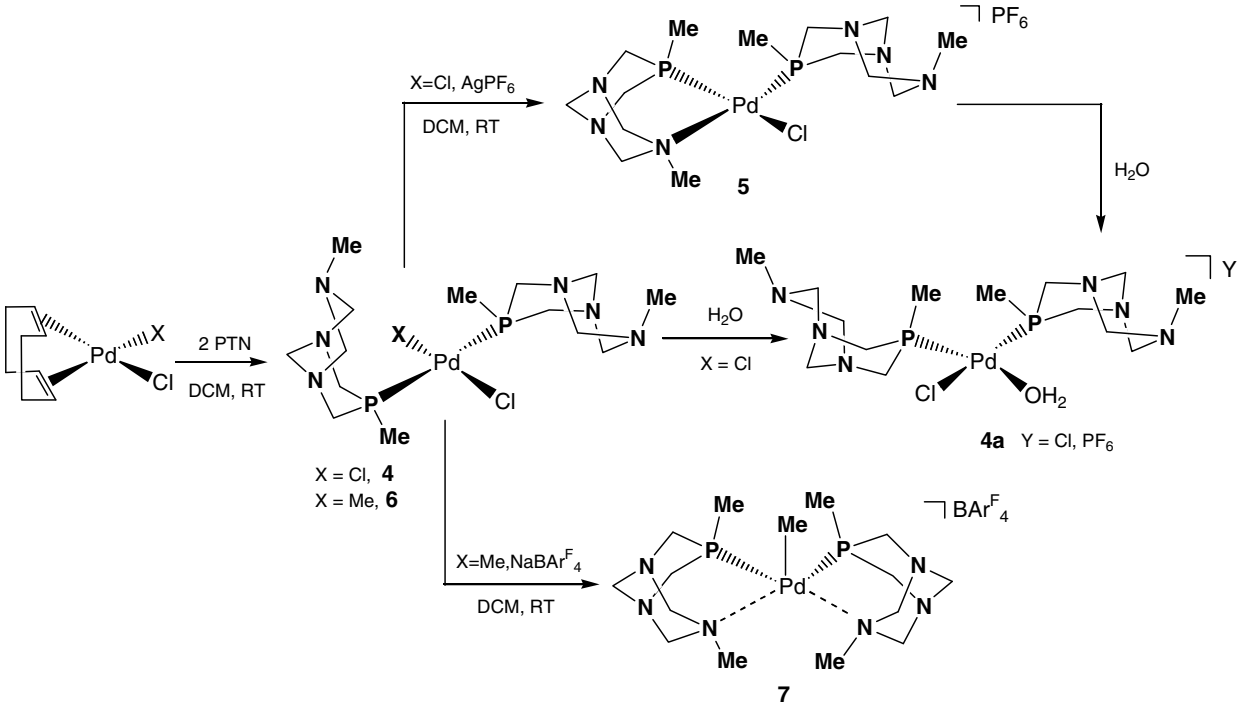
The solvent is likely to replace the chloride anion in **2** without disrupting the κ^2-*P,N* coordination, as deduced from the ^{1}H NMR value for Pd–Me (0.40 d, $^3J_{HP}$ 12.3 Hz) and the negligible position shift for the aminophosphine CH_3-P (1.30 d, $^2J_{HP}$ 11.6 Hz) and CH_3-N groups (2.30 s). $^{13}C\{^1H\}$ data are in line with this attribution (Table 2). The trend in ^{31}P chemical shift variation upon passing from acetate *trans* to P to chloride to acetonitrile is downfield as expected (Table 2).

A second family of palladium(II) complexes was prepared by reaction of the same Pd(II) precursors with 2 equiv. of PTN. Starting from *cis*-[Pd(cod)Cl_2] complex *trans*-[Pd(κ^1-*P*-PTN)$_2$$Cl_2$] (**4**) was obtained. The correct attribution of the geometry came from the close inspection of the $^{13}C\{^1H\}$ data, especially for the P-CH_3 signal that is now present as pseudo-triplet (15.30 ppm, $^1J_{CP}$+$^3J_{CP}$ = 7.8 Hz) and N-CH_3 (38.70 s), indicative of κ^1-*P* coordination of PTN [14]. By contrast, little effect on the proton signals for these groups was observed (Table 2). Further evidence for the presence of two coordinated PTN molecules in **4** came from ESI-MS analysis showing a peak at m/z 489 corresponding to the [M−Cl] molecular peak. Chloride lability can be due to the analysis conditions (MeCN/H_2O) and is reflected in the very high water solubility. The most significant changes in NMR from CD_2Cl_2 to D_2O were found for the P-CH_3 group, with the change in the ^{1}H NMR from a pseudo-triplet to a doublet of doublets at 1.54 (dd, $^2J_{HP}$ = 11.0 Hz, $^4J_{HP}$ = 2.1 Hz) and in the ^{13}C spectrum from triplet to doublet (12.05 d, $^1J_{CP}$ = 20.2 Hz). Moreover, the $^{31}P\{^1H\}$ singlet shifted from *ca.* −49 to −31 ppm, likely due to *trans* → *cis* rearrangement and chloride displacement by water with formation of a cationic putative species *cis*-[Pd(κ^1-*P*-PTN)$_2$Cl(H_2O)]Cl (**4a**) whose isolation however was not attempted.

Complex **4** undergoes neat chloride abstraction when treated with an equimolar amount of $AgPF_6$ and the moderately water soluble [S_{H_2O}(25 °C) = 6.47 mg/ml], monocationic pale yellow complex [Pd(PTN)$_2$Cl][PF_6] (**5**) was isolated. In acetone-d_6, **5** shows two broad bands in the $^{31}P\{^1H\}$ NMR spectrum, at *ca.* −25 (κ^1-*P*) and −45 ppm (κ^2-*P,N*), denoting the presence of two inequivalent *cis*-disposed phosphorus nuclei. By slow evaporation of a dichloromethane solution of **5**, well-formed yellow crystals were isolated and the solid state X-ray crystal structure of **5** determined as [Pd(κ^2-*P,N*-PTN)(κ^1-*P*-PTN)Cl][PF_6] featuring both coordination modes possible for PTN. $^{31}P\{^1H\}$ NMR spectrum in D_2O shows a broad singlet at *ca.* −30 ppm while the ^{1}H spectrum is characterised by signals superimposable to those of **4a**, suggesting a hemilabile behaviour for the κ^2-*P,N* ligand under these conditions. Double halide abstraction from **4** with a known excess (2.5 equiv.) of $AgPF_6$ in dichloromethane was also attempted. Initially an orange precipitate is formed immediately upon mixing of the reagents, however it was observed to decompose quickly even if stored at low temperature under a protecting nitrogen atmosphere, hence preventing characterisation.

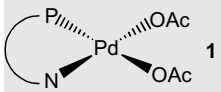
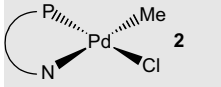
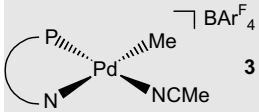
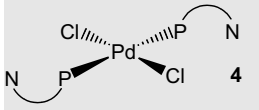
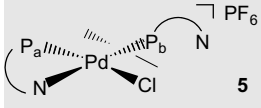
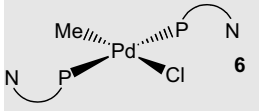
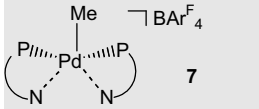


Scheme 2. Synthesis of palladium complexes **1**–**3** with Pd:PTN ratio 1:1.



Scheme 3. Synthesis of palladium complexes **4**–**7** with Pd:PTN ratio 1:2.

Table 2
Selected ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR data for **1**–**7**, in CD_2Cl_2 unless stated

Complex	^{1}H (δ, ppm; J_{HP}, HZ)	$^{13}C\{^{1}H\}$ (δ, ppm; J_{CP}, HZ)	$^{31}P\{^{1}H\}$(δ, ppm)
 **1**	1.30 (d, 13.5, P-CH_3); 2.34 (s, 3H, N-CH_3); 1.80, 1.90 (s, 6H, CH_3-COO).	3.60 (d, 25.7, P-CH_3); 22.0, 23.5 (s, CH_3-COO); 45.4 (s, N-CH_3); 176.80, 177.20 (s, COO)	−41.60s
 **2**	0.50 (d, 3.4, Pd–CH_3), 1.20 (d, 10.8 Hz, P-CH_3), 2.40 (s, N-CH_3)	−7.70 (s, Pd–CH_3), 5.50 (d, 22.7, P-CH_3), 46.30 (s, N-CH_3)	−37.00s
 **3**	0.40 (d, 2.3, Pd–CH_3), 1.30 (d, 11.6, P-CH_3), 2.26 (s, CH_3CN), 2.30 (s, N-CH_3)	−6.20 (s, Pd–CH_3), 2.85 (s, CH_3-CN), 5.20 (d, 25.5, P-CH_3), 46.00 (s, N-CH_3)	−35.00s
 **4**	1.20 (pseudo t, 2.2, P-CH_3), 2.30 (s, N-CH_3).[a] 1.54 (dd, 11.0, 2.1 P-CH_3), 2.37 (s, N-CH_3).[b]	15.30 (pseudo t, 7.8, P-CH_3), 38.70 (s, N-CH_3).[a] 12.05(d, 20.2, P-CH_3), 42.4 (s, N-CH_3).[b]	−49.00s[a] −31.20s[b]
 **5**	1.60 (br s, P-CH_3), 1.80 (br s, P-CH_3), 2.40 (br s, N-CH_3) 2.60 (br s, N-CH_3).[c]	7.40 (br s, P-CH_3), 16.90 (br s, P-CH_3), 38.10 (br s, N-CH_3), 46.40 (br s, N-CH_3).[c]	−25.00s (P_a), −45.60s(P_b)
 **6**	0.20 (t, 6.6, Pd–CH_3) 1.20 (pseudo t, 1.8, P-CH_3), 2.10 (s, N-CH_3).[d]	−8.40 (pseudo t, 5.3, Pd–CH_3), 16.90 (t, 5.2, P-CH_3), 38.30 (s, N-CH_3).[d]	−49.15s
 **7**	0.27 (t, 7.0, Pd–CH_3), 1.18 (pseudo t, 2.7, P-CH_3), 2.30 (s, N-CH_3).[d]	−5.20 (br s, Pd–CH_3), 10.50 (br s, P-CH_3), 45.30 (s, N-CH_3).[d]	−53.15s

[a] In CD_2Cl_2.
[b] In D_2O.
[c] In acetone-d_6.
[d] In $CDCl_3$.

By reaction of PdMe(cod)Cl with 2 equiv. of PTN, the off-white complex *trans*-[PdMe(κ^1-*P*-PTN)$_2$Cl] (**6**) was obtained. Similarly to **4**, NMR data suggest that the two PTN ligands are *trans* to each other, as from the $^{31}P\{^1H\}$ NMR singlet at $\delta = -49$ ppm and $^{13}C\{^1H\}$ triplet for the methyl group bound to palladium (0.20 ppm, $^3J_{HP}$ 6.6 Hz). Subsequent treatment of complex **6** with 1 equiv. of $NaBAr^F_4$ as halide scavenger in dichloromethane, afforded the monocationic complex *trans*-[PdMe(κ^1-*P*, *N*-PTN)$_2$][BAr^F_4] (**7**), yellow and highly insoluble in water as expected from the presence of BAr^F_4 counter ion. The NMR data collected in $CDCl_3$ (Table 2) suggest a highly fluxional situation intermediate between κ^1-*P* and κ^2-*P,N* behaviour for PTN (Scheme 3). Addition of acetonitrile to a solution of **7** in CH_2Cl_2 in order to stabilise the complex by solvent coordination failed as evidenced by the absence of the ^1H NMR signal corresponding to coordinated MeCN.

3.2. X-ray crystal structures of [Pd(κ^2-P,N-PTN)(OAc)$_2$] (**1**) and [Pd(κ^2-P,N-PTN)(κ^1-P-PTN)Cl](PF$_6$) (**5**)

The coordination geometry of palladium in compound **1** is best described as square-planar, with one PTN-ligand coordinating to the metal atom in the κ^2-*P,N* mode and occupying thus two *cis*-coordination sites at the metal centre. An ORTEP drawing of the molecular structure is shown in Fig. 1, while selected bond distances and angles are reported in Table 3.

The coordination sphere around palladium is completed by two carboxylate oxygen atoms stemming from two acetate units. The palladium atom deviates from the coordination plane, which is defined by the atoms N(1), P(1), O(1) and O(3) of 0.0344(9) Å in the direction of O(2). The *P,N* ligand coordinates in its most abundant conformation, which corresponds to the *exo*/*exo* form [13]. Most importantly, unlike related symmetrical Rh [14] and Au [13] complexes, no disorder of the P(1), N(1)-donor sites was observed, due to the fact that both carboxylic oxygen atoms O(2) and O(4) of the coordinating acetate moieties point to the same spatial direction and prevent thus a *pseudo* C2 symmetry of the molecule. The coordinating PTN-ligand, which is almost symmetrically disposed with respect to the mirror plane defined by the atoms N(1), C(6) and P(1), shows a significant deviation of C(1) of 0.1298(39) Å from the symmetry plane in direction of C(5). The P(1)–Pd(1)–N(1) bite angle of 86.56(7)° is in the range of related metal complexes, which exhibit a κ^2-*P,N* coordination mode of this ligand [13,14].

Since the coordinating phosphorus atom P(1) exerts a much higher *trans influence* compared to the coordinating nitrogen atom N(1), the acetate unit *trans* to the phosphorus donor atom is weaker bonded to the metal centre compared to that *trans* to the nitrogen atom N(1), which is supported by the different bond length of the corresponding Pd–O(acetate) bonds of 2.037(2) Å (Pd(1)–O(1)) and of 2.103(2) Å (Pd(1)–O(3)). All four acetate oxygen atoms are co-involved in the formation of a complex web of hydrogen bonds. The shortest intermolecular distances found for all four acetate oxygen atoms are reported in Table 2.

The crystal structure of the monocationic palladium complex **5** shows a square-planar coordinated palladium atom with a κ^2-*P,N* and a κ^1-*P* coordinating PTN ligand. One PF_6^- counter-ion compensates the positive charge of the palladium atom. An ORTEP drawing of the molecular structure is shown in Fig. 2, while selected bond distances and angles are reported in Table 3.

Table 3
Selected bond length (Å) and bond angles (°) for **1** and **5**

	1	5
Pd(1)–Cl(1)		2.380(2)
Pd(1)–P(1)	2.187(1)	2.231(2)
Pd(1)–P(2)		2.256(2)
Pd(1)–N(1)	2.109(2)	2.205(4)
Pd(1)–O(1)	2.037(2)	
Pd(1)–O(3)	2.103(2)	
P(1)–Pd(1)–N(1)	86.56(7)	83.57(13)
P(2)–Pd(1)–N(1)		176.57(13)
P(1)–Pd(1)–Cl(1)		167.40(6)
O(1)–Pd(1)–O(3)	88.26(9)	
Most significant intermolecular distances (Å) for **1** and **5**		
O(1)···H(5B)	2.385	
O(2)···H(7B)	2.634	
O(3)···H(4)	2.455	
O(4)···H(11)	2.712	
Pd(1)···N(4)		3.142(5)
P(1)···N(1)	2.946(3)	2.956(5)
P(2)···N(4)		2.867(5)
Cl(1)···H(5)		2.781
F(2)···H(12)		2.620
F(3)···H(6A)		2.624
F(3)···H(8C)		2.607
F(4)···H(7A)		2.563
F(5)···H(1C)		2.623

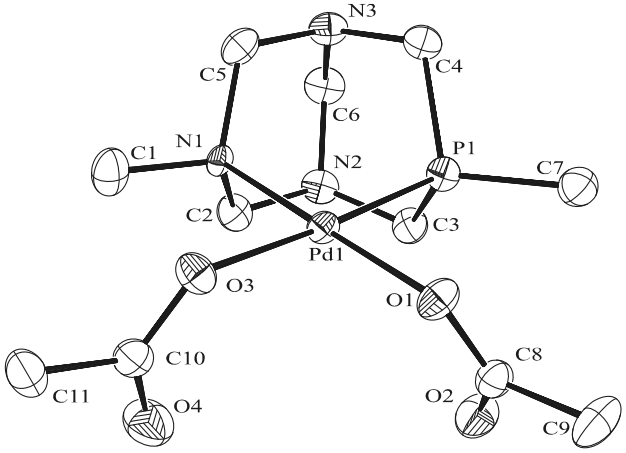


Fig. 1. ORTEP plot of **1**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are shown at the 30% probability level.

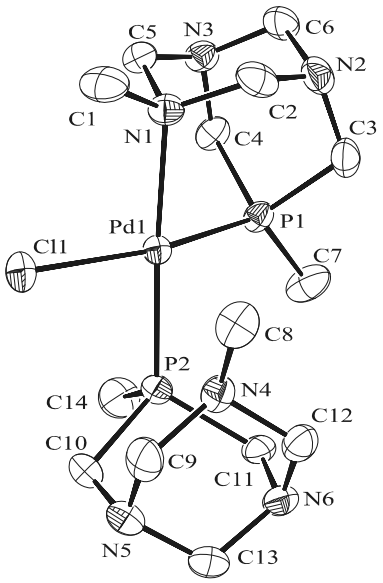


Fig. 2. ORTEP plot of **5**. Hydrogen atoms and the counter-ion PF_6 are omitted for clarity and thermal ellipsoids are shown at the 30% probability level.

The fourth coordination site is occupied by a chloride atom, which is located *trans* to the phosphorus atom (P1) of the κ^2-*P,N* coordinating PTN unit. As a consequence the phosphorus donor atom P(2) of the κ^1-*P* coordinating PTN unit coordinates *trans* to the nitrogen atom N(1) of the κ^2-*P,N* PTN unit. The palladium atom deviates from the coordination plane, which is defined by the atoms N(1), P(1), P(2) and Cl(1) of 0.1004(14) Å in direction of the non-coordinating nitrogen atom N(4). The intra-molecular Pd(1)···N(4) distance of 3.142(5) Å, is only slightly shorter than the sum of the van der Waals radii of palladium and nitrogen (3.170 Å) and thus only a very weak interaction may exist. The κ^1-*P* coordinating ligand is orientated almost orthogonally with respect to the coordination plane, showing the Cl(1)–Pd(1)–P(2)–N(4) torsion angle of 77.67(10)°, which is comparable to the value found for RhCl(COD)(κ^1-*P*-PTN) (82.38(8)°) [14]. The N(1)–Pd(1)–P(1) bite angle of 83.57(13)° is slightly smaller than that found for compound **1** (86.56(7)°), which is due to the shorter Pd(1)–P(1) and Pd(1)–N(1) bond length found for the latter compound and not to significantly different intra-molecular P(1)···N(1) distances, which are 2.946(3) and 2.956(5) Å for **1** and **5**, respectively. The κ^1-*P* coordinating PTN unit in compound **5** exhibits an intra-molecular P(2)···N(4) distance of 2.867(5) Å, which is significantly longer compared to the value found for the κ^2-*P,N* coordinated ligand, evidencing the occurrence of a ring strain of the ligand upon its coordination to the metal atom [14]. As far as intermolecular hydrogen bonds are concerned the chloride as well as fluorine atoms build up a complex web of hydrogen bonding interactions (Table 3).

4. Conclusions

New palladium(II) complexes bearing the water soluble aminophosphine PTN in 1:1 and 1:2 metal-to-ligand ratio were prepared and fully characterised by conventional spectroscopic methods and by X-ray diffraction analysis in the case of complexes **1** and **5**. In the case of κ^2,P,N coordination, hemilabile behaviour was observed when dissolving complex **5** in water, in line with the long Pd–N bond length in the corresponding X-ray crystal structure indicating a highly tensioned cage in such bidentate coordination to the metal. The Pd–PTN complexes described in this study show good solubility in water and are expected to be active species for bringing about palladium-catalysed C–C coupling reactions in water or water-biphasic conditions [23]. Attempts to explore these pathways are currently under scrutiny in our laboratory and will be reported in due time.

5. Supplementary material

CCDC 655262 and 662952 contain the supplementary crystallographic data for **1** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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