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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