Reactivity of a cationic square-planar palladium(II) chloro complex containing bis[2-(diphenylphosphino)ethyl]amine: chloro substitutions by anionic ligands and formation of neutral digold(I) compounds possessing linear PAuX fragments. The X-Ray crystal structure of $Au_2[Ph_2P(CH_2)_2N(NO)(CH_2)_2PPh_2]Cl_2$

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The interaction of sodium tetrachloropalladate(II) with the potentially tridentate aminophosphine bis[2-(diphenylphosphino)ethyl]amine (PNHP) in 1 : 1 molar ratio leads to the formation of the four-coordinate complex [Pd(PNHP)Cl]Cl (**1**). Complex **1** undergoes chloro substitution reactions with NaX (X = Br, I), CuCl, $AgNO_3$, the amino acid *N*-acetyl-L-cysteine (AcCysSH) and the tripeptide reduced glutathione (γ-L-Glu-L-Cys-Gly, GSH) affording [Pd(PNHP)X]X′ [X = X′ = Br (**2**), I (**3**), NO_3 (**4**); X = Cl, X′ = $CuCl_2$ (**1a**); X′ = Cl, X = RS = AcCysS (**8**), GS (**9**)]. However, gold(I) induces abstraction of the aminophosphine from the ionic complexes **1** and **2** to produce the neutral compounds $Au_2(PNHP)X_2$ [X = Cl (**5**), Br (**6**)]. The dinuclear complex $Au_2(PN(NO)P)Cl_2$ (**5a**), containing the ligand bis[2-(diphenylphosphino)ethyl]nitrosylamine, was formed by reaction of **4** with gold(I) in the presence of traces of nitrosyl chloride. Addition of one molar equivalent of PNHP to **1** results, by a ring-opening process, in the formation of $[Pd(PNHP)_2]Cl_2$ (**7**) in which the palladium is five-coordinate. The ionic complexes **1**, **2** and **4** were shown by X-ray diffraction to be distorted square-planar and complex **2** has a N–H···Br bond of 2.371 Å with the ligand adopting a boat conformation. The X-ray crystal structure of the novel neutral compound **5a** shows linear P–Au–Cl arrangements with intermolecular Au···Au interactions of 3.0412(9) Å.

Ligands with mixed donor atoms have been the subject of many studies in recent years.[1–5] The higher water solubility of transition metal complexes containing phosphorus-nitrogen-phosphorus ligands compared to those with common phosphines increases their potential application in catalytic transformations.[6] Due to the high trans influence of P, and with an appropriate choice of substituents on both P and N, Pt(II) aminophosphine complexes[7] can bind to the DNA bases guanine and thymine *via* a novel chelate ring-opening mechanism and are cytotoxic to cancer cells. The presence of other ligands such as sulfur-containing molecules can prevent toxic side effects of these complexes under *in vivo* conditions.[8] Palladium(II) complexes such as [pd(triphos)X]X (X = Cl, Br, I) show faster kinetics than platinum(II) complexes by reaction with gold group metals.[9a] For further comparison purposes the study of the chemistry of Pd(II) aminophosphine complexes was considered of interest in this work.

On the other hand, gold(I) compounds with tertiary phosphines have been extensively studied,[9b,c,10] due to the exhibition of anticancer activity for tetrahedral systems and the usefulness of linear compounds in the treatment of rheumatoid arthritis. The aurophilic interactions between linearly coordinated Au(I) centres[11] have the potential to self-assemble superstructures through intermolecular contacts, with the formation of supramolecular aggregates[12] that in several cases are strongly photo-luminescent.[13,14] Although diphosphines such as $Ph_2P(CH_2)_nPPh_2$ (n = 1–8),[15–19] $Ph_2P(CH{=}CH)PPh_2$[20] or $Ph_2P[CH_2(C{=}CH_2)CH_2]PPh_2$[21] have been widely used to form dinuclear gold(I) complexes, aminophosphines have been used much less in gold chemistry.[19,22,23] Since studies on metal complexes containing the linear aminophosphine bis[2-(diphenylphosphino)ethyl]amine (PNHP) are very limited,[24,25] the aim of this work is to report novel reactions of [Pd(PNHP)Cl]Cl with gold group metal compounds,[26] thiols and an excess of PNHP.

Experimental

General procedures

Dichloromethane was redistilled under nitrogen over $CaCl_2$. Diphenylphosphine, palladium chloride and palladium bromide were purchased from Strem Chemicals, potassium *tert*-butoxide, bis(2-chloroethyl)amine hydrochloride, *N*-acetyl-L-methionine, *N*-acetyl-L-cysteine and 2,2′-thiodiethanol were from Aldrich, sodium chloride, bromide and iodide from Panreac, gold metal from S.E.M.P.S.A. and reduced glutathione from Sigma. Solutions of *N*-acetyl-L-methionine, *N*-acetyl-L-cysteine (AcCysSH) and reduced glutathione (GSH) were degassed by bubbling with argon prior to use. THF was dried over Na and freshly distilled before use.

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Microanalyses were performed at the University of Santiago de Compostela. Fast atom bombardment (FAB) mass spectra were obtained in a KRATOS MS 50 spectrometer using 3-nitrobenzyl alcohol as the matrix. Infrared spectra were recorded at ambient temperature as KBr pellets (4000–500 cm^{-1}) and Nujol mulls (500–100 cm^{-1}) on a Mattson Cygnus 100 spectrophotometer. The bands are reported as vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad. Electronic absorption spectra were recorded at 22 °C (40 μM sample concentration, MeOH–H_2O–DMSO 3 : 3 : 2) on a Shimadzu spectrophotometer with temperature control using 1 cm pathlength cells. ^{31}P $\{^1H\}$ NMR spectra were recorded on a Bruker AMX500 spectrometer at 202.46 MHz and a DMX500 NMR spectrometer at 202 MHz. Chemical shifts (δ) are reported relative to external 85% H_3PO_4; s = singlet, d = doublet, t = triplet, J = coupling constant in Hz.

The pH measurements were made using a Corning 240 pH meter equipped with an Aldrich microcombination electrode standardised with buffers at pH 4, 7 and 10. For deuterated and mixed solvents, the pH meter readings are given without correction and are designated as pH* values. Some of the samples used for NMR spectroscopy were kept at room temperature (*ca.* 22 °C) for a few days and were diluted in order to obtain positive electrospray ion mass spectra (ESI-MS) in a Platform II mass spectrometer (Micromass, Manchester, U.K.). Samples (10 to 100 μM) were injected in CD_3OD–D_2O–DMSO-d_6 using an infusion pump with a flow rate of 0.48 mL h^{-1}. A source temperature of 75 °C and a drying gas flow rate of 450 L h^{-1} were found to be suitable parameters for analysis. A potential of 2.8 kV was applied to the probe capillary and a cone voltage of 50 V over 100–1000 Da was used. The quadrupole was scanned at 100 amu s^{-1}. The mass accuracy of all measurements was within 0.1 m/z unit. Conductivities were measured at 25 °C using 10^{-3} M solutions in DMF or CH_3CN on a WTW model LF-3 instrument.

Syntheses

Au(tdg)Cl. Solutions of Au(tdg)Cl[27] (tdg = thiodiglycol = 2,2′-thiodiethanol) were prepared by treating Au (0.25 g, 1.269 mmol) with 2.5 mL HCl (36%) and 1.5 mL HNO_3 (60%) on an oil bath (120 °C), followed by the addition of 2 × 2.5 mL HCl. The solution was then allowed to cool to room temperature. Methanol (10 mL) was then added, the solution was neutralised with $CaCO_3$ and the resultant suspension was filtered. The clear final filtrate containing tetrachloroauric acid was reduced with 2,2′-thiodiethanol (1 mL) until the colour changed from yellow to colourless, to give Au(tdg)Cl *in situ*.

Au(tdg)Br. The same procedure was used to prepare solutions of [Au(tdg)Br][28] by treating a concentrated solution of $HAuCl_4$ with KBr (1.3 g, 10.96 mmol) in Et_2O–H_2O (3 : 1, 20 mL). The organic phase was extracted with Et_2O.

PNHP. Bis[2-(diphenylphosphino)ethyl]amine (PNHP) was prepared as an air-stable hydrochloride (PNHP·HCl) using a modification of a literature method.[29,30] Diphenylphosphine (14 mL, 15.0 g, 80.4 mmol) was added to a suspension of potassium *tert*-butoxide (23.4 g, 208.5 mmol) in dry THF (450 mL) under argon. The resulting deep red solution was stirred for 20 min and bis(2-chloroethyl)amine hydrochloride (7.1 g, 40.0 mmol) was added as a powder. The mixture was heated at reflux for 28 h at 80 °C and after that a 1 M solution of HCl (*ca.* 100 mL) was added. After removing the solvents a white solid precipitated and was dried *in vacuo*. It was recrystallised from CH_2Cl_2–Et_2O and washed with CH_3CN. Yield: 60%, mp 155 °C. Calcd for $C_{28}H_{30}NP_2Cl$ (PNHP·HCl): C, 70.4; H, 6.3; N, 2.9. Found: C, 70.1; H, 6.4; N, 3.0%. ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P − 22.7s. IR ν_{max}/cm^{-1} (N–H) 3300. MS (FAB): 442 (M^+, 100%).

[Pd(PNHP)X]X [X = Cl (1), Br (2), I (3)]. A suspension of PdX_2 (X = Cl, 0.0743 g, 0.4188 mmol; X = Br, 0.1115 g, 0.4188 mmol) and NaX (X = Cl, 0.0489 g, 0.8376 mmol; X = Br, 0.1724 g, 1.6752 mmol) in H_2O (15 mL) was heated on a water bath (80 °C) until a clear solution was obtained. This was allowed to cool to room temperature. For the synthesis of **3** NaI (0.2511 g, 1.6752 mmol) was added as a powder to an aqueous solution of Na_2PdCl_4 (0.4188 mmol). A solution of PNHP·HCl (0.2000 g, 0.4188 mmol) in CH_2Cl_2 (15 mL) was added dropwise. The resultant solutions were stirred for 15 h at room temperature and after that the organic phase was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed *in vacuo* to leave a yellow (**1** and **2**) or dark red (**3**) solid. Solids were recrystallised from CH_2Cl_2–*n*-hexane (**1** and **3**) or CH_2Cl_2–acetone (**2**) solutions. Crystals suitable for X-ray diffraction were obtained for **1** from a CD_3OD–D_2O–DMSO-d_6 solution and for **2** from a CH_2Cl_2–acetone solution.

1: Yield: 90%, mp 172 °C. Found: C, 52.4; H, 4.8; N, 2.2. $C_{28}H_{31}NOP_2PdCl_2$ (**1**·H_2O) requires: C, 52.7; H, 4.9; N, 2.3%. IR ν_{max}/cm^{-1} (Pd–Cl) 312s. MS (FAB): m/z 582 (M^+ − Cl, 100%); 547 (M^+ − 2Cl, 8%). ESI-MS (+): m/z 582 ([Pd(PNHP)Cl]$^+$). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 34.6s. Λ (CH_3CN or DMF) = 47.2 or 22.8 ohm^{-1} cm^2 mol^{-1}. UV λ/nm (ε/M^{-1} cm^{-1}) 356 (2,700), 290 (3,750).

2: Yield: 74%, mp 175 °C. Found: C, 46.1; H, 4.2; N, 1.9. $C_{28}H_{31}NOP_2PdBr_2$ (**2**·H_2O) requires: C, 46.3; H, 4.3; N, 1.9%. IR ν_{max}/cm^{-1} (Pd–Br) 254s. MS (FAB): m/z 626 (M^+ − Br, 77%); 547 (M^+ − 2Br, 8%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P = 36.0s. Λ (CH_3CN or DMF) = 64.6 or 70.8 ohm^{-1} cm^2 mol^{-1}.

3: Yield: 71%, mp 239 °C. Found: C, 40.9; H, 3.8; N, 1.7. $C_{28}H_{31}NOP_2PdI_2$ (**3**·H_2O) requires: C, 40.9; H, 3.8; N, 1.7%. IR ν_{max}/cm^{-1} (Pd–I) 190s. MS (FAB): m/z 673 (M^+ − I, 100%); 547 (M^+ − 2I, 10%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P = 37.9s. Λ (CH_3CN or DMF) = 116.8 or 85.8 ohm^{-1} cm^2 mol^{-1}.

[Pd(PNHP)Cl][$CuCl_2$] (1a). CuCl (0.0192 g, 0.1939 mmol) was added as a solid to a solution of [Pd(PNHP)Cl]Cl·H_2O (0.1200 g, 0.1886 mmol) in dry CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 16 h under nitrogen. The resultant solution was filtered, the volume of the filtrate was reduced and Et_2O was added to precipitate the brown-greenish complex, which was isolated by filtration and dried *in vacuo*. Yield: 45%, mp 150 °C (dec.). Found: C, 45.1; H, 4.3; N, 1.9. $C_{28}H_{31}NOP_2PdCuCl_3$ (**1a**·H_2O) requires: C, 45.6; H, 4.3; N, 1.9%. IR ν_{max}/cm^{-1} (Pd–Cl) 314s; (Cu–Cl) 296w. MS (FAB): m/z 582 (M^+ − $CuCl_2$, 34%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 36.6s. Λ(CH_3CN) = 67.1 ohm^{-1} cm^2 mol^{-1}.

[Pd(PNHP)(ONO_2)](NO_3) (4). To a solution of [Pd(PNHP)Cl]Cl·H_2O (0.1500 g, 0.2357 mmol) in $CHCl_3$ (18 mL), a solution of $AgNO_3$ (0.0906 g, 0.5333 mmol) in MeOH (20 mL) was added dropwise and immediately a white precipitate of AgCl was formed. The reaction mixture was kept for 20 h, protected from light, then filtered and the solvents removed from the filtrate *in vacuo*. The yellow-greenish solid was recrystallised from CH_2Cl_2–*n*-hexane. Crystals suitable for X-ray diffraction were obtained from a solution of the complex in $CDCl_3$. Yield: 87%, mp 177 °C (dec.). Found: C, 49.6; H, 4.9; N, 5.8. $C_{29}H_{33}N_3O_7P_2Pd$ (**4**·CH_3OH) requires: C, 49.4; H, 4.7; N, 5.9%. IR ν_{max}/cm^{-1} (Pd–O) 346w; $(N–O)_{ionic\ nitrate}$ 1340, 841m; $(N–O)_{asym}$ 1384vs, 1272m; $(N–O)_{sym}$ 1027w. MS (FAB): m/z 609 (M^+ − NO_3, 41%); 547 (M^+ − $2NO_3$, 100%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 36.3s. Λ(CH_3CN or DMF) = 182.3 or 111.9 ohm^{-1} cm^2 mol^{-1}.

Au_2(PNHP)X_2 [X = Cl (5), Br (6)]. A solution of NaOH (0.0126 g, 0.3150 mmol) in H_2O (1.5 mL) was added to a solution of PNHP·HCl (0.1500 g, 0.3141 mmol) in CH_2Cl_2

(15 mL) and the mixture was stirred for 4 h. The organic phase was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and filtered. To the filtrate another solution of Au(tdg)X (0.1237 g of Au, 0.6282 mmol) in CH_3OH (X = Cl) or Et_2O (X = Br), prepared as described above, was added dropwise and the mixture was stirred for 15 h. Solvents were removed *in vacuo* and a colourless oil appeared. It was stirred with water, affording a white solid that was isolated by filtration, dried *in vacuo* and recrystallised from CH_2Cl_2–Et_2O (X = Cl) or CH_2Cl_2–*n*-hexane (X = Br).

5: Yield: 53%, mp 169 °C. Found: C, 37.3; H, 3.3; N, 1.5. $C_{28}H_{29}NP_2Au_2Cl_2$ requires: C, 37.1; H, 3.2; N, 1.5%. IR ν_{max}/cm^{-1} (Au–Cl) 326vs,b. MS (FAB): *m*/*z* 870 ($M^+ - Cl$, 100%); 638 ($M^+ - Au - 2Cl$, 13%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 22.0s. $\Lambda(CH_3CN) = 8.4$ ohm^{-1} cm^2 mol^{-1}.

6: Yield: 59%, mp 200 °C (dec.). Found: C, 32.2; H, 3.2; N, 1.3. $C_{28}H_{33}NO_2P_2Au_2Br_2$ [(**6**)·$2H_2O$] requires: C, 32.6; H, 3.2; N, 1.3%. IR ν_{max}/cm^{-1} (Au–Br) 230w. MS (FAB): *m*/*z* 914 ($M^+ - Br$, 100%); 638 ($M^+ - Au - 2Br$, 7%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 25.8s. $\Lambda(CH_3CN) = 15.2$ ohm^{-1} cm^2 mol^{-1}.

Au_2[PN(NO)P]Cl_2 (5a). To a solution of [Pd(PNHP)-(ONO_2)](NO_3)·CH_3OH (0.0134 g, 0.0190 mmol) in $CDCl_3$ (1.0 mL) a solution of Au(tdg)Cl (0.0037 g of Au, 0.0190 mmol) in CH_3OH (~1.0 mL), prepared as described above, was added and the mixture was allowed to react for 24 h. Further additions of Au(I) to complete 3 equiv. were done after the same time interval. Colourless crystals suitable for X-ray diffraction were obtained after the solution had stood at ambient temperature for 3 months. ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 25.5 [1P, s, P^B], 24.6 [1P, s, $P^{B'}$].

[$Pd(PNHP)_2$]Cl_2 (7). A suspension of $PdCl_2$ (0.0557 g, 0.3141 mmol) and NaCl (0.0367 g, 0.6283 mmol) in H_2O (10 mL) was heated on a water bath (80 °C) until a clear solution was obtained. This was allowed to cool to room temperature and a solution of PNHP·HCl (0.3000 g, 0.6283 mmol) in CH_2Cl_2 (15 mL) was added dropwise. The resultant solution was stirred for 1 h at room temperature, the organic phase was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed from the filtrate *in vacuo* to leave a crystalline yellow solid. Yield: 85%, mp 130 °C. Found: C, 56.7; H, 5.2; N, 2.4. $C_{58}H_{62}N_2P_4PdCl_6$ [(**7**)·$2CH_2Cl_2$)] requires: C, 56.6; H, 5.1; N, 2.3%. IR ν_{max}/cm^{-1} (M–P) 367sh, 345m, 317s,b. MS (FAB): *m*/*z* 988 ($M^+ - 2Cl$, 12%); 561 ($M^+ - 2Cl - 2C_2H_4PPh_2$, 9%); 547 ($M^+ - 2Cl -$ PNHP, 84%). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ_P 45.2 [2P, d, $^2J(P^A,P^B) = \sim 23.0$ Hz, P^A], 15.4 [1P, t, $^2J(P^A,P^B) = \sim 23.0$ Hz, P^B], −22.8 [1P, s, P^C].

[Pd(PNHP)(SR)]Cl [RSH = AcCysSH (8), GSH = (9)]. To a suspension of **1**·H_2O (0.0100 g, 0.0157 mmol) in CD_3OD (0.3 mL) a solution of AcCysSH (0.0026 g, 0.0160 mmol) or GSH (0.0049 g, 0.0160 mmol) in D_2O (0.3 mL) was added slowly and the colour of the solution turned from light to dark yellow. The reaction mixture was left for 18 h and after that DMSO-d_6 (0.2 mL) was added, the pH was measured and ^{31}P $\{^1H\}$ NMR spectra were recorded. Another molar equivalent of AcCysSH (0.0026 g, 0.0160 mmol) or GSH (0.0049 g, 0.0160 mmol) in D_2O (0.1 mL) was added and the same procedure was repeated.

8: ESI-MS (+): *m*/*z* 709.4 ([Pd(PNHP)(AcCysS)]$^+$). ^{31}P $\{^1H\}$ NMR (CD_3OD–D_2O–DMSO-d_6, pH* ~ 2.1): δ_P 39.8s. UV λ/nm (ε/M^{-1} cm^{-1}) 300 (14,750), 450 (780).

9: ESI-MS (+): *m*/*z* 853.4 ([Pd(PNHP)(GS)]$^+$). ^{31}P $\{^1H\}$ NMR (CD_3OD–D_2O–DMSO-d_6, pH* ~ 2.9): δ_P 40.1 [1P, s, P^A], 40.0 [1P, s, $P^{A'}$]. UV λ/nm (ε/M^{-1} cm^{-1}) 300 (15,650), 450 (900).

Titrations

Titration of Na_2PdCl_4 and Au_2(PNHP)Cl_2 (5) with PNHP·HCl. To a solution of Na_2PdCl_4 in H_2O, prepared *in situ* as described in the synthesis of complex **1**, and to a solution of Au_2(PNHP)Cl_2 (**5**) in $CDCl_3$ solutions of PNHP·HCl in $CDCl_3$ were added reaching different stoichiometric ratios. The ^{31}P $\{^1H\}$ NMR spectrum of the organic layer was recorded after every addition.

Titration of [Pd(PNHP)Cl]Cl (1) with $AgNO_3$. A solution of $AgNO_3$ in CD_3OD was added slowly to a solution of [Pd(PNHP)Cl]Cl·H_2O in $CDCl_3$ and the mixture (1 : 1 stoichiometric ratio) was left for 12 h in the absence of light. After removing the AgCl precipitate, the ^{31}P $\{^1H\}$ NMR spectrum was recorded. This procedure was repeated after addition of 2 and 3 equiv. of $AgNO_3$.

Titration of [Pd(PNHP)X]X [X = Cl (1), Br (2), I (3), NO_3 (4)] and [$Pd(PNHP)_2$]Cl_2 (7) with Au(I). Solutions of Au(tdg)X in CH_3OH, prepared as described above, were added dropwise to a solution of **1**, **2**, **4** or **7** in $CDCl_3$ and after 12 h the ^{31}P $\{^1H\}$ NMR spectrum was recorded. Further additions to complete 2 and 3 molar equiv. of Au(I) were done after the same time interval. A similar procedure was followed for the titration of complex **3** by addition of AuI as a solid.

Crystallography

Table 1 summarises the crystal data, data collection, structural solution and refinement parameters for complexes **1**·H_2O, **2**·$(CH_3)_2CO$, **4**·H_2O·CH_3OH and **5a**. A colourless plate of **1**·H_2O, a yellow block of **2**·$(CH_3)_2CO$, a yellow tablet of **4**·H_2O·CH_3OH and a colourless block of **5a** were mounted on glass fibers and used for data collection. A SMART APEX CCD area detector was used for **1**·H_2O and a Stoe Stadi4 four-circle diffractometer equipped with an Oxford Cryosystem variable temperature device for the other complexes. Graphite monochromated Mo-K_α radiation was used for **1**·H_2O, **2**·$(CH_3)_2CO$ and **5a**, and Cu-K_α radiation was used for data collection of **4**·H_2O·CH_3OH. A SADABS[31] or psi-scan[32] absorption correction was made for **1**·H_2O and **5a**, respectively, while it was optimised numerically for **2**·$(CH_3)_2CO$ and **4**·H_2O·CH_3OH.

The structures of **1**·H_2O, **4**·H_2O·CH_3OH and **5a** were solved by direct methods, using the progam SHELXS-97[33] (**1**·H_2O and **5a**) and SIR92[34] (**4**·H_2O·CH_3OH), and by Patterson methods (DIRDIF)[35] for **2**·$(CH_3)_2CO$. The structures were refined by full-matrix least-squares techniques on F^2 using the program SHELXL-97.[36] Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model, except for **1**·H_2O for which a mixed model was used. Hydrogen atoms of water molecules were not included for **1**·H_2O and **4**·H_2O·CH_3OH.

CCDC reference numbers 181546–181549. See http://www.rsc.org/spdata/nj/b1/b109675n/ for crystallographic data in CIF or other electronic format.

Results and discussion

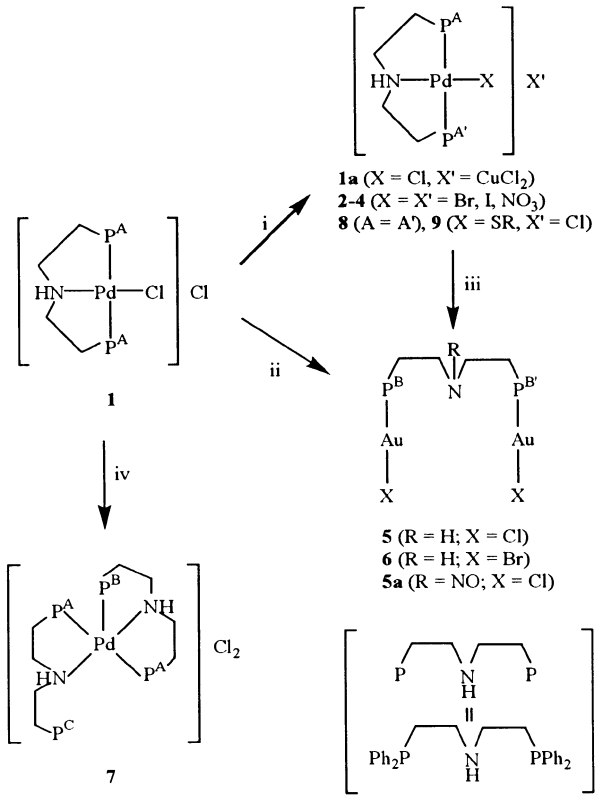
Syntheses

Treatment of a solution of PNHP·HCl in dichloromethane with sodium hydroxide in a 1 : 1 stoichiometric ratio led to the free amine. Scheme 1 shows the complexes prepared in this work with their phosphorus atoms labelled.

By reaction of an aqueous solutions of PdX_4^{2-} with the hydrochloride salt of PNHP dissolved in dichloromethane,

Table 1 Summary of crystal parameters, data collection and refinement for **1**·H_2O, **2**·$(CH_3)_2CO$, **4**·H_2O·CH_3OH and **5a**

	1·H_2O	**2**·$(CH_3)_2CO$	**4**·H_2O·CH_3OH	**5a**
Empirical formula	$C_{28}H_{31}Cl_2NP_2OPd$	$C_{31}H_{35}Br_2NP_2OPd$	$C_{29}H_{35}N_3P_2O_8Pd$	$C_{28}H_{28}Cl_2N_2P_2OAu_2$
Formula weight/g mol^{-1}	636.78	765.76	721.94	935.30
T/K	100(2)	150(2)	220(2)	293(2)
λ/Å	0.71073 (Mo)	0.71073 (Mo)	1.54178 (Cu)	0.71073 (Mo)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	20.245(3)	11.722(4)	8.044(5)	14.120(3)
b/Å	15.725(2)	12.209(4)	12.719(5)	12.871(3)
c/Å	17.788(2)	12.640(4)	15.492(7)	16.849(3)
α/°	90	114.823(13)	76.89(3)	90.00
β/°	104.492(2)	101.696(19)	82.59(4)	109.72(3)
γ/°	90	98.816(17)	89.47(4)	90.00
U/Å^3	5482.8(12)	1548.8(8)	1530.6(13)	2882.5(10)
Z	8	2	2	4
Calcd density/Mg m^{-3}	1.543	1.642	1.566	2.155
μ/mm^{-1}	1.011	3.307	6.343	10.489
Reflec. collected	36 343	6158	6923	5066
Indep. reflect.	11 191	5495	5034	5066
R_{int}	0.1300	0.0833	0.0272	0.000
R_1 (final)	0.0580	0.0466	0.0733	0.0515
wR_2 (final)	0.1342	0.1104	0.2161	0.0966



(i) X = Cl, X' = $CuCl_2$: **1** + CuCl (**1a**); X = X' = Br, I, NO_3: **1** + 2NaX (**2**, **3**), **1** + 2$AgNO_3$ (**4**); X = SR, X' = Cl: **1** + RSH [RSH = AcCysSH (**8**), GSH (**9**)]
(ii) **1** + 2Au(tdg)Cl (**5**)
(iii) **2** + 2Au(tdg)Br (**6**), **4** + 3Au(tdg)Cl (**5a**)
(iv) **1** + PNHP (**7**)

Scheme 1 Reactivity of [Pd(PNHP)Cl]Cl (**1**) to form ionic (**1a**, **2**–**4**, **7**–**9**) and neutral (**5**) complexes. Reaction between **2** or **4** and Au(tdg)Cl to form **5a**.

complexes **1**–**3** and **7** were obtained as solids from the organic phase.[26] This procedure constitutes a slight variation of a literature method.[24b] A metathesis reaction of complex **1** with **2** equiv. of NaX (X = Br, I) also led to compounds **2** and **3**, respectively. The addition of CuCl, $AgNO_3$ and AcCysSH or GSH to solutions of complex **1** in $CHCl_3$ or CD_3OD did not cause any ring-opening;[26] compounds [Pd(PNHP)Cl][$CuCl_2$] (**1a**), [Pd(PNHP)(ONO_2)]NO_3 (**4**) and [Pd(PNHP)(AcCysS)]Cl (**8**) or [Pd(PNHP)(GS)]Cl (**9**), respectively, were obtained. Complexes **5** and **6** were prepared as solids by reaction of the free amine with **2** equiv. of Au(tdg)X (X = Cl, Br). Both complexes can also be obtained by reaction of gold(I) with the hydrochloride form of the ligand, but in lower yields. Attempts to prepare Au_2(PNHP)I_2 were unsuccessful. Likewise, complexes [Pd(PNHP)$_2$]X_2 (X = Br, I) could not be prepared.

Crystals suitable for X-ray diffraction of Au_2(PN(NO)P)Cl_2 (**5a**) were afforded by slow evaporation of a $CDCl_3$–CH_3OH solution containing a mixture of **4** and Au(tdg)Cl in a 1 : 3 stoichiometric ratio. The formation of this dinuclear compound with the nitrosylaminophosphine ligand can be explained by the presence in the Au(I) solution of traces of nitrosyl chloride coming from the *aqua regia* used for digestion of gold.

Compounds **1**, **1a**, **2**, **3** and **6** gave satisfactory microanalyses for hydrates, while **4** and **7** were isolated as methanol and dichloromethane solvates, respectively.

Characterization

Molar conductivities. Complexes **1**, **1a** and **2** do not behave as conductors in 10^{-3} M CH_3CN solutions,[37] which could be due to ion pair formation.

^{31}P {^{1}H} NMR spectroscopy of the complexes. The ^{31}P {^{1}H} NMR spectra for complexes **1**, **1a**, **2**, **3** and **4** (Table 2) showed a singlet in agreement with symmetry equivalent phosphorus atoms (P^A) of the aminophosphine. These resonances are shifted downfield from that of the free ligand (coordination shifts, $\Delta\delta$, 57.3, 59.3, 58.7, 60.6 and 59.0 respectively), as expected for chelated ligands.[38] The NMR data are therefore consistent with the formation of distorted square-planar complexes where the palladium is bound to the three donor atoms of PNHP and to one halide or nitrate (**4**). Similar structures were previously found in solution for analogous complexes with bis[2-(diphenylphosphino)ethyl]phenylphosphine (triphos).[26,39–42]

Complex **7** showed three signals: a singlet at δ – 22.8 (P^C), a triplet centred at δ 15.4 (P^B) and a doublet centred at δ 45.2 (P^A), the coupling constant $^2J(P^A,P^B)$ being *ca.* 23.0 Hz. On

Table 2 $^{31}P\ \{^1H\}$ NMR data for complexes and reactions

	δ (P^A)	δ (P^B)
1[a]	34.6(s)	
1 + $AgNO_3$[b]	37.9(s)	
1 + 2 $AgNO_3$[b]	40.1(s)	
1 + 1 Au(tdg)Cl[c]	34.1(s)	21.9(s)
1 + 2 Au(tdg)Cl[c]		21.8(s)
1 + 3 Au(tdg)Cl[c]		21.8(s)
1a[a]	36.6(s)	
2[a]	36.0(s)	
2 + 1 Au(tdg)Cl[d]	36.5(s)	24.0(s)
2 + 2 Au(tdg)Cl[d]		24.0(s)
2 + 3 Au(tdg)Cl[d]		24.0(s)
3[a]	37.9(s)	
3 + 1 AuI[a]	36.7(s)	
3 + 2 AuI[a]	36.7(s)	
3 + 3 AuI[a]	36.7(s)	
4[a]	36.3(s)	
4 + 1 Au(tdg)Cl[c]	33.9(s)	22.0(s)
4 + 2 Au(tdg)Cl[c]	33.8(s)	22.0(s)
4 + 3 Au(tdg)Cl[c]		22.0(s)
5[a]		22.0(s)
5a[e]		25.5(s)[f]
6[d]		25.8(s)
7[a]	45.2(d)[g]	15.4(t)[g]
7 + 1 Au(tdg)Cl[c]	33.9(s)	22.1(s)
7 + 2 Au(tdg)Cl[c]	33.6(s)	22.0(s)
7 + 3 Au(tdg)Cl[c]	33.5(s)	22.0(s)
7 + 4 Au(tdg)Cl[c]		22.0(s)
1[h,i]	36.0(s)	
1 + 2 AcMet[h]	37.9(s)	
1 + 1 AcCysSH[h]	37.4(s)	
	39.7(s)	
1 + 2 AcCysSH (**8**)[h]	39.8(s)	
1 + 1 GSH[h]	37.4(s)	
	40.0(s)/39.9(s)	
1 + 2 GSH (**9**)[h]	40.1(s)/40.0(s)	

[a] Spectrum in $CDCl_3$. [b] Spectrum in $CDCl_3$–CD_3OD. [c] Spectrum in $CDCl_3$–CH_3OH. [d] Spectrum in $CDCl_3$–Et_2O. [e] Spectrum in $CDCl_3$–CD_2Cl_2. [f] $\delta(P^B) = 24.6$(s). [g] $^2J(P^A,P^B) = \sim 23.0$ Hz, $\delta(P^C) = -22.8$(s). [h] Spectrum in CD_3OD–D_2O–DMSO-d_6. [i] −pH* ~ 7.4.

the basis of the multiplicity and the integration (1 : 1 : 2) the $^{31}P\ \{^1H\}$ NMR data suggest the formation of a five-coordinate complex with the two aminophosphines arranged around the palladium in a square pyramidal structure[24b] (Scheme 1). Attempts to isolate the analogous bromide and iodide complexes led to $^{31}P\ \{^1H\}$ NMR spectra characteristic of mixtures of [Pd(PNHP)X]X and $[Pd(PNHP)_2]X_2$.

Complexes **5** and **6** $[Au_2(PNHP)X_2]$ showed only one resonance in the $^{31}P\ \{^1H\}$ NMR spectrum at δ 22.0 and 25.8, respectively, indicating that both phosphorus atoms of the linear P–Au–X fragments are equivalent.[19,27c] However, the $^{31}P\ \{^1H\}$ NMR spectrum of $Au_2[PN(NO)P]Cl_2$ (**5a**) showed two very close resonances: a singlet at δ 25.5 and another peak at δ 24.6, indicating inequivalent phosphorus atoms.

Reactions with biologically relevant molecules. The $^{31}P\ \{^1H\}$ NMR spectrum of a CD_3OD–D_2O–DMSO-d_6 solution containing complex [Pd(PNHP)Cl]Cl (**1**) and AcCysSH or GSH in a 1 : 1 molar ratio at pH* *ca.* 2.2 or 2.9, respectively, showed, besides a small signal due to unreacted complex **1**, other resonance at δ 39.7 or δ 40.0 and 39.9 indicating the formation of new species. With the addition of another molar equivalent of the biomolecule the former peak was the only signal present in the spectra, confirming that AcCysSH or GSH displaces the chloride ligand from $[Pd(PNHP)Cl]^+$ to afford the new thiolate complexes [Pd(PNHP)(SR)]Cl [SR = AcCysS (**8**), GS (**9**)] (Scheme 1). The two signals in the spectrum of **9** around 40 ppm seem to indicate the non-equivalence of the phosphorus atoms, probably due to the chiral α-CH of the glutathione.

Similar reactions between S-containing molecules and monofunctional platinum chloride complexes such as $[Pt(dien)Cl]^+$[43] or $[Pt(terpy)Cl]^+$[44] (dien = diethylenetriammine, terpy = 2,2′,6′,2″-terpyridine) have been reported. However, the triphos complex $[Pt(triphos)Cl]^+$ did not react with thiols.[26] It was necessary to replace the chloride ligand by a good leaving group such as nitrate to prepare the thiolate complexes or the acetylmethionine derivative. Complex **1** as well as $[Pt(terpy)Cl]^+$ did not react with the amino acid *N*-acetyl-L-methionine.[44]

Reactions with excess ligand. A solution of Na_2PdCl_4 in H_2O was titrated with PNHP·HCl ($CDCl_3$) in different molar ratios. The appearance in the spectrum of a singlet at δ 34.7 after the addition of 0.25 molar equiv. of the ligand indicated formation of complex **1** (Scheme 1). When 1.0 molar equiv. of PNHP was added no new signals appeared in the spectrum. Subsequent additions of aminophosphine gave rise to three new signals: a doublet at δ 45.3, a triplet at δ 15.3 and a singlet at δ −22.5, which coexist with the singlet due to complex **1**. When the metal : ligand ratio was 1 : 2, the three new signals were the only resonances in the spectrum. The presence of these signals is consistent with the formation of complex **7** (*vide supra*).

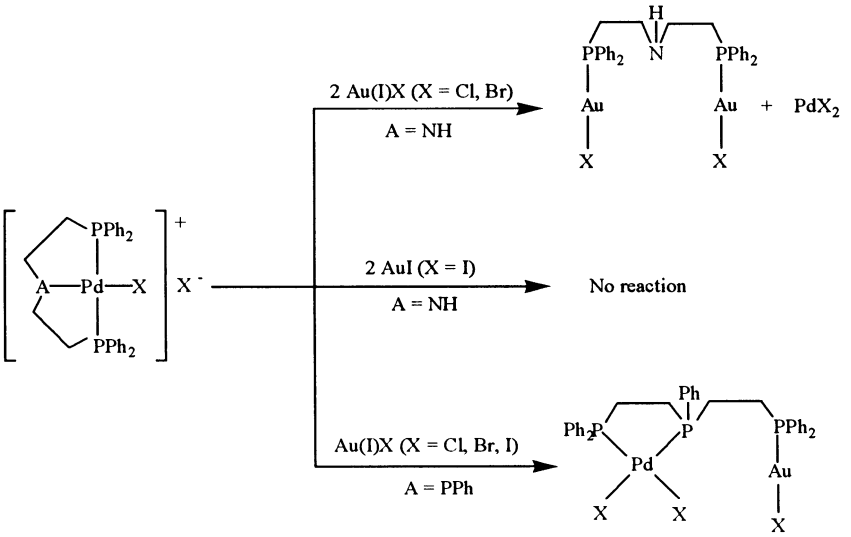
Ligand exchange reactions were observed by titration of $Au_2(PNHP)Cl_2$ with aminophosphine. Addition of 0.5 equiv. of PNHP to a $CDCl_3$ solution of complex **5** leads to a broadening of the signal at δ 22.0 and the appearance of a new signal at δ 33.8, indicating the existence of two different gold-phosphorus environments. With a 1 : 1 stoichiometric ratio the spectrum shows only one signal at δ 33.7, consistent with one type of phosphorus atom in a likely annular structure. Subsequent additions of the aminophosphine result in a broadening of this signal.

Reactions with metal salts. By addition of 1 equiv. of $AgNO_3$ in $CDCl_3$–CD_3OD to complex **1** the signal at δ 34.6 shifts downfield to δ 37.9. A single signal at δ 40.1 appears when the second equivalent is added. This indicates the replacement in complex **1** of the chloride counterion and the ligand by nitrate with formation of complex **4** (Scheme 1). Similar results were previously observed for analogous triphos compounds,[41] indicating that $AgNO_3$ does not induce any chelate ring-opening.

The $^{31}P\ \{^1H\}$ NMR spectrum of a mixture containing [Pd(PNHP)X]X (**1**, **2**) and Au(tdg)X (X = Cl, Br) in $CDCl_3$–MeOH and $CDCl_3$–Et_2O, respectively, in a 1 : 1 stoichiometric ratio showed two singlets with very similar intensities at δ 34.1 and 21.9 (X = Cl) and δ 36.5 and 24.0 (X = Br). Further additions of **2** or **3** equiv. of Au(I) showed in both cases the disappearance of the signal at lower field assigned to complexes **1** (X = Cl) and **2** (X = Br). The signal around δ 23.0 was assigned to the linear P–Au–X fragments[45] in the neutral dinuclear complexes $Au_2(PNHP)X_2$ [X = Cl (**5**), Br (**6**)]. With the first addition, Au(I) abstracts the aminophosphine from the palladium complex, which coexists in solution with the neutral dinuclear species [eqn. (1a)]. An excess of Au(I) leads to complexes **5** or **6** as the only aminophosphine derivatives [eqn. (1b)].

$$2\ [Pd(PNHP)X]X + 2\ Au(tdg)X \rightarrow [Pd(PNHP)X]X + Au_2(PNHP)X_2 + Pd(tdg)_2X_2 \quad (1a)$$

$$[Pd(PNHP)X]X + 2\ Au(tdg)X \rightarrow Au_2(PNHP)X_2 + Pd(tdg)_2X_2 \quad (1b)$$



Scheme 2 Abstraction of PNHP from [Pd(PNHP)X]X (X = Cl, Br) and ring-opening of [Pd(P_3)X]X [X = Cl, Br, I; P_3 = PhP(CH_2CH_2-PPh_2)$_2$] induced by Au(I)X.

A different behaviour was observed for the analogous triphos complex [Pd(triphos)Cl]Cl, which forms the heterobimetallic compound PdAu(triphos)Cl_3 by interaction with Au(I)[26] *via* ring-opening (Scheme 2). However, in both cases when starting from the square-planar ionic complexes [Pd(L)Cl]Cl (L = PNHP, triphos) neutral species containing linear gold(I) were obtained.

Similar results as for **1** and **2** were found when [Pd(PNHP)(ONO_2)](NO_3) (**4**) was titrated with Au(I) (Table 1). After the first addition of Au(tdg)Cl a mixture containing complexes **4** and **5** was observed. Further additions of Au(I) leads to complex **5** as the only aminophosphine compound formed. However, the reaction of [Pd(PNHP)I]I (**3**) with AuI did not cause any change in the ^{31}P $\{^1H\}$ NMR spectrum, indicating that gold(I) iodide does not abstract the aminophosphine from **3** and consequently complex Au_2(PNHP)I_2 was not formed.

The ^{31}P $\{^1H]$ NMR spectrum of a mixture containing [Pd(PNHP)$_2$]Cl_2 (**7**) and Au(tdg)Cl in $CDCl_3$–MeOH in a 1 : 1 stoichiometric ratio showed a singlet at δ 33.9 corresponding to complex **1** and a very small signal at δ 22.1 assigned to the dinuclear complex **5** (Table 1). When 4 equiv. of Au(I) were added the dinuclear complex **5** was the only aminophosphine compound observed [eqn. (1c)].

$$[Pd(PNHP)_2]Cl_2 + 4\ Au(tdg)Cl \rightarrow 2\ Au_2(PNHP)Cl_2 + [Pd(tdg)_4]Cl_2 \qquad (1c)$$

Mass spectrometry. In the FAB mass spectra of complexes [Pd(PNHP)X]X′ the most intense peak corresponds to the fragment [$M^+ - X'$], this pattern of fragmentation being analogous to that found for similar triphos complexes.[26] For [Pd(PNHP)(ONO_2)](NO_3) (**4**) a peak at m/z 547 due to the loss of both nitrate ligand and counterion exhibits an abundance of 100%. The presence of a peak at m/z 988 for [Pd(PNHP)$_2$]Cl_2 (**7**) confirms the formation of [Pd(PNHP)$_2$]$^{2+}$ as was previously observed for [M(triphos)$_2$][$SnPh_2Cl_3$]$_2$ complexes.[46] The most abundant peak for Au_2(PNHP)X_2 complexes corresponds to the Au_2(PNHP)X fragments. The ESI-MS (+) for **8** and **9** reveal the presence of [Pd(PNHP)(SR)]$^+$ ions.

Electronic absorption spectroscopy. Complexes **8** and **9** absorb at higher wavelengths [*ca.* 450 (~850 M^{-1} cm^{-1}) and 300 nm (~15,000 M^{-1} cm^{-1})] compared to **1**. The broad band in the visible region is probably due to spin allowed transitions in square-planar palladium(II) complexes, while the intense band in the ultraviolet is a charge transfer in nature.[47]

Infrared spectroscopy. A broad band between 3400 and 3500 cm^{-1} assignable to the N–H vibration[48,49] was observed in the near infrared spectra (4000–500 cm^{-1}) of complexes **1**–**7**. This band, present at 3300 cm^{-1} in the IR spectrum of the free amine, is shifted to higher energy as a result of the complexation. Bands corresponding to the ν(N–O) vibrations for complex **4**, as well as a shoulder at 1340 cm^{-1} characteristic for uncoordinated nitrate, were in agreement with the presence of both nitrate ligand and counterion. The far infrared spectra (500–100 cm^{-1}) of **1**–**3** and **1a** showed strong bands assigned to Pd–X stretchs corresponding to terminal bonds.[50a] For **1a** a weak band at 296 cm^{-1} due to ν(Cu–Cl) of the linear $CuCl_2^-$ group was also observed.[50b] The terminal Au–X stretches[51,52] for **5** and **6** appeared as very strong and weak bands at 326 and 230 cm^{-1}, respectively.

Crystallography

Perspective views of the molecular structures and numbering schemes of complexes **1**·H_2O, **2**·$(CH_3)_2CO$, **4**·H_2O·CH_3OH and **5a** are shown in Figs. 1 and 2. Selected bond lengths and angles are listed in Tables 3 and 4. Walther *et al.*[25] previously reported the crystal structure of the chloro complex, solved at 293 K in space group $P2_1/n$, there showing the unit cell with $Z = 2$.

Palladium(II) exhibits a distorted square-planar geometry in complexes **1**, **2** and **4**. The aminophosphine is a tridentate chelate ligand bound through the two P atoms and the nitrogen (PNP), the fourth coordination position is occupied by a halide (**1** and **2**) or nitrate (**4**), which acts as a monodentate ligand. The other halide or nitrate is a counteranion. The complexes are isostructural with [Ni(PNHP)Cl]Cl and show analogous structures to [Pd(triphos)X]X (X = Cl, Br, I).[39,42,53] The Pd–N bond lengths [2.061(5) average and 2.070(5) Å for **1** and **2**, respectively] are essentially the same as the literature value of 2.041 Å[54] and not significantly different from that found in [Pd(COOMe){2-($CHPPh_2$)-6-(CH_2PPh_2)pyridine}][55] where the PNP ligand forms two chelate rings around Pd(II). As expected, the weaker *trans* influence of the Pd–O bond compared to Pd–X[41] leads to a Pd–N bond distance for **4** [2.021(7) Å] shorter than in the halide complexes **1** or **2**. However, the greater size and *trans* influence of bromide than chloride causes a very

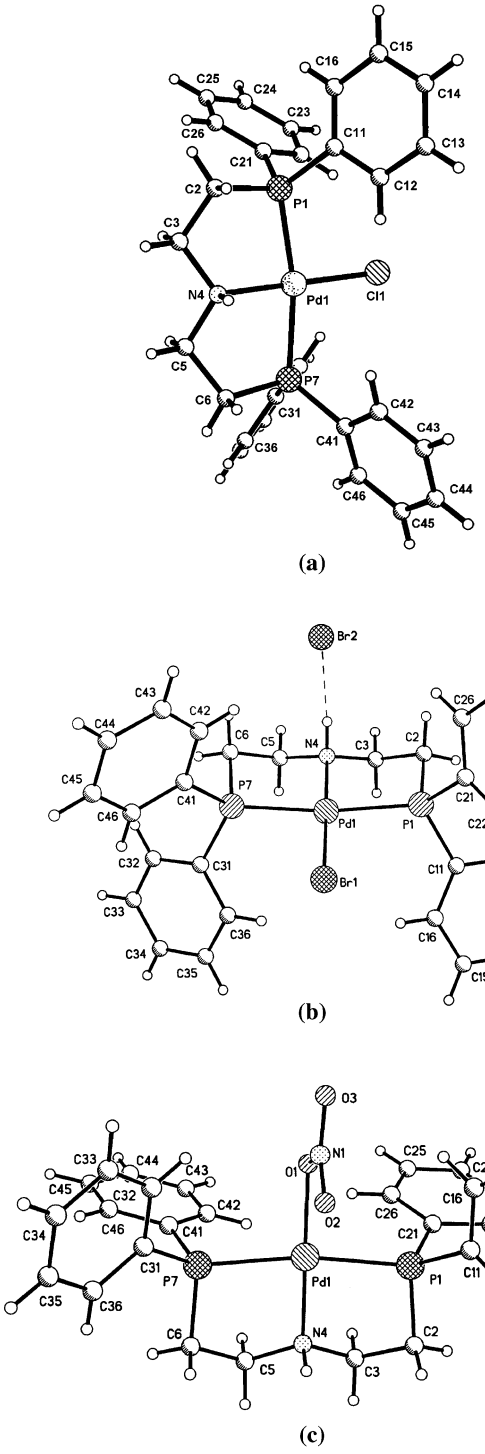


Fig. 1 ORTEP diagram for: (a) one of the cations $[Pd(PNHP)Cl]^+$ of **1** in the asymmetric unit [cation A: Pd(1), Cl(1); cation C: Pd(2), Cl(2)], (b) [Pd(PNHP)Br]Br (**2**) and (c) cation $[Pd(PNHP)(ONO_2)]^+$ of **4**.

slight increase in the Pd–N bond length from **1** to **2**. On the other hand the smaller *trans* influence of the nitrogen over the phosphorus[56] produces Pd–X bond lengths in **1** and **2** [Pd–Cl = 2.3051(2) average and Pd–Br = 2.418(1) Å, respectively] shorter than those for triphos complexes[26,53] and the usual literature values.[54] The Pd–O bond length of **4**, 2.041(6) Å, is also shorter than the same distance for $[Pd(triphos)(ONO_2)](NO_3)$ [2.127(4) Å].[41] The Pd–P distances for **1** are in the expected range for other similarly arranged Pd(II) compounds.[55]

The P–Pd–N and P–Pd–X angles for **1**, **2** and **4**, below and above 90°, respectively, show the distorted square-planar environment at palladium. This distortion is also reflected in the values of the angles P–Pd–P and N–Pd–X, all of which are less than 180°. However, this distortion is not greater in **4** than in **1** or **2**, probably due to the disposition of the nitrate plane almost perpendicular to the coordination plane, reducing the steric hindrance around the metal.

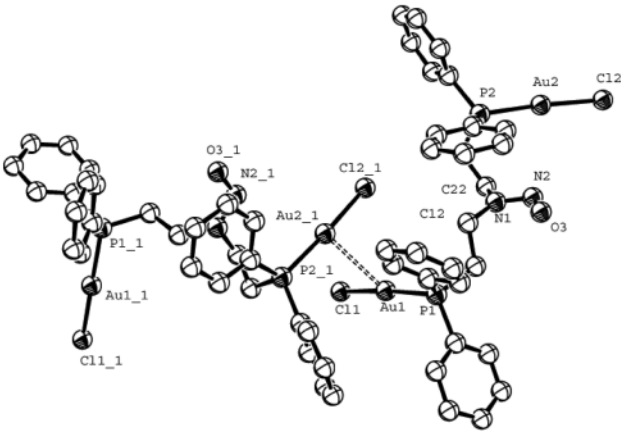


Fig. 2 ORTEP diagram for **5a**.

The nitrate ligand has trigonal planar geometry with slightly distorted O–N–O angles [125.6(1), 119.7(9) and 114.7(1)°]. The coordination is also reflected in the larger N–O distance for the oxygen bound to palladium(II) [1.344(1) Å] compared to those for the uncoordinated oxygen atoms [1.195(1) and 1.228(1) Å]. This is a consequence of the decrease in the nitrogen–oxygen bond order.

Due to the free rotation about the C–C bonds in the ethylene chains of the ligand complex **2** seems to adopt a boat conformation. [Fig. 1(b)] that was not observed for **1** and **4** [Fig. 1(a) and (c)]. Complex **2** shows N–H···Br hydrogen bonds of 2.371 Å, involving the Br counteranion.[57] This short interaction is not observed in **1** or **4** (N–H···Cl *ca.* 7.184 Å or N–H···O *ca.* 6.211 Å).

The X-ray crystal structure of $Au_2[PN(NO)P]Cl_2$ (**5a**) corresponds to a neutral dinuclear complex where the gold atoms are bridged by the aminophosphine through the two P atoms, the nitrogen being uncoordinated.[15–21] Au(I) completes its coordination with a chlorine atom resulting in linear P–Au–Cl fragments. As far as we know this is the first X-ray crystal structure containing the difunctional ligand $(NO)N(CH_2CH_2PPh_2)_2$ [PN(NO)P], which has a nitrosyl group on the nitrogen. On the basis of the $^{31}P\{^1H\}$ NMR data previously discussed for complexes **5**, **5a** and **6**, an identical structure can be proposed for all 3 complexes in the solid state with the only difference due to the nitrosyl substituent on the nitrogen for **5a**.

Complex **5a** has a gauche-skew conformation regarding the relative orientation of the two Ph_2PAuCl groups at the central nitrogen atom. This conformation allows for a short intermolecular Au···Au contact of 3.041(9) Å almost perpendicular to the axis determined by the linear P–Au–Cl fragments and could be responsible for a potential luminescent activity.[58] Such a gold(I)–gold(I) interaction observed between adjacent molecules of **5a** is in the range characteristic of attractive aurophilic bonds.[11a,b,23,59–61] This value is analogous to the intermolecular Au···Au distance (3.048 Å) found in the trinuclear complex $Au_3(tripod)Br_3$ [tripod = 1,1,1-tris(diphenylphosphinomethyl)-ethane] containing P–Au–Br linear fragments[62a], shorter than the intramolecular interaction in $Au_2(dppm)Cl_2$ (3.351 Å)[15] and close to the intramolecular Au···Au distance (3.091 Å) for $Au_3(tripod)Cl_3$.[62b] The Au–P and Au–Cl bond lengths are very close to those found in other complexes with linear and tripodal phosphines.[16–18,20,21,62a] The shortening of the Au–P bond compared to the Au–Cl bond may be attributed to some metal-to-ligand d_π-d_π back bonding.[11,15,18,62b,c]

Table 3 Selected distances (Å) and angles (°) for complexes **1**·H_2O, **2**·$(CH_3)_2CO$ and **4**·H_2O·CH_3OH

	1·H_2O		**2**·$(CH_3)_2CO$	**4**·H_2O·CH_3OH
Pd(1)–P(1A)	2.2973(2)	Pd(1)–P(7)	2.299(2)	2.316(2)
Pd(1)–P(7A)	2.3060(2)	Pd(1)–P(1)	2.301(2)	2.308(2)
Pd(2)–P(1C)	2.3021(2)			
Pd(2)–P(7C)	2.3172(2)			
Pd(1)–N(4A)	2.065(5)	Pd(1)–N(4)	2.070(5)	2.021(7)
Pd(2)–N(4C)	2.056(5)			
Pd(1)–Cl(1)	2.3082(2)	Pd(1)–Br(1)	2.418(1)	—
Pd(2)–Cl(2)	2.3019(2)	Pd(1)–O(1)	—	2.041(6)
P(1A)–Pd(1)–P(7A)	168.37(7)	P(7)–Pd(1)–P(1)	168.76(6)	167.34(8)
P(1C)–Pd(2)–P(7C)	168.86(7)			
N(4A)–Pd(1)–P(1A)	84.41(2)	N(4)–Pd(1)–P(1)	84.27(2)	84.17(2)
N(4A)–Pd(1)–P(7A)	84.43(2)	N(4)–Pd(1)–P(7)	84.51(2)	84.51(2)
N(4C)–Pd(2)–P(1C)	84.37(2)			
N(4C)–Pd(2)–P(7C)	84.73(2)			
P(1A)–Pd(1)–Cl(1)	95.26(6)	P(7)–Pd(1)–Br(1)	94.87(5)	—
P(7A)–Pd(1)–Cl(1)	96.12(6)	P(1)–Pd(1)–Br(1)	96.37(5)	
P(1C)–Pd(2)–Cl(2)	94.04(6)	P(1)–Pd(1)–O(1)	—	95.31(2)
P(7C)–Pd(2)–Cl(2)	96.94(7)	P(7)–Pd(1)–O(1)		95.73(2)
N(4A)–Pd(1)–Cl(1)	175.76(2)	N(4)–Pd(1)–Br(1)	177.39(1)	—
N(4C)–Pd(2)–Cl(2)	177.40(2)	N(4)–Pd(1)–O(1)	—	177.2(3)
		O(2)–N(1)–O(3)		125.6(1)
		O(2)–N(1)–O(1)		119.7(9)
		O(3)–N(1)–O(1)		114.7(1)

Table 4 Selected distances (Å) and angles (°) for complex **5a**

Au(1)–P(1)	2.236(3)	Au(1)–Au(2)_1	3.0412(9)
Au(2)–P(2)	2.243(4)	N(1)–N(2)	1.338(2)
Au(1)–Cl(1)	2.308(4)	N(2)–O(3)	1.193(2)
Au(2)–Cl(2)	2.295(4)	Cl(1)–Au(1)–Au(2)_1	73.44(9)
P(1)–Au(1)–Cl(1)	171.82(2)	Cl(2)_1–Au(2)_1–Au(1)	87.19(2)
P(2)–Au(2)–Cl(2)	176.20(2)	C(22)–N(1)–N(2)	113.1(2)
P(1)–Au(1)–Au(2)_1	114.56(9)	C(12)–N(1)–N(2)	124.8(2)
P(2)_1–Au(2)_1–Au(1)	95.50(9)	C(22)–N(1)–C(12)	122.0(2)
N(1)–N(2)–O(3)	111.6(2)		

The N–N distance [1.338(2) Å] is characteristic of a single bond while the N–O bond length [1.193(2) Å] is very close to the shortest N–O distance found in the coordinated nitrate ligand of **4** [1.195(1) Å]. This value is therefore indicative of a bond order greater than one.

Conclusion

The ionic square-planar complex [Pd(PNHP)Cl]Cl undergoes chloro substitution reactions by interaction with NaX (X = Br, I), CuCl, $AgNO_3$ and the thiols AcCysSH and GSH. The bromo counteranion in [Pd(PNHP)Br]Br, where PNHP adopts a boat conformation, acts as a better hydrogen-bonding acceptor site for N–H than chloride or nitrate. The formation of Pd(II) thiolate adducts increases the aqueous solubility and may be useful for biological studies. Gold(I) abstracts the aminophosphine from [Pd(PNHP)X]X (X = Cl, Br, NO_3) to form neutral digold(I) compounds. The crystal structure of Au_2[PN(NO)P]Cl_2 shows the presence of aurophilic intermolecular interactions between linear P–Au–Cl fragments, which could generate luminescent activity.

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