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The co-ordination chemistry of 2-(diphenylphosphinoamino)pyridine †

Stephen M. Aucott, Alexandra M. Z. Slawin and J. Derek Woollins*

Department of Chemistry, University of St Andrews, St Andrews, Fife, UK KY16 9ST.
E-mail: j.d.woollins@st-andrews.ac.uk

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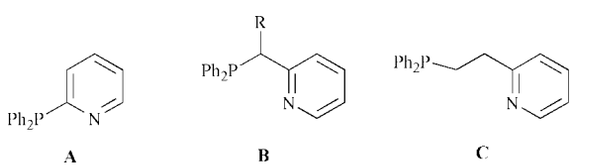
2-(Diphenylphosphinoamino)pyridine, dppap [Ph_2PNHpy], and over 40 illustrative examples of its complexes have been prepared. Monodentate, bidentate and bridging co-ordination of the neutral (and bidentate deprotonated ligand) has been demonstrated in a range of palladium, platinum and gold complexes. Ten demonstrative examples have been characterised by single crystal X-ray diffraction. Ph_2PNHpy exists as hydrogen-bonded dimer pairs; *cis*-[$PtCl(Ph_2PNHpy$-*P*,*N*){Ph_2PNHpy-*P*}]Cl packs in hydrogen-bonded infinite chains; *cis*-[$Pt(Ph_2PNpy$-*P*,*N*)$_2$] and *cis*-[$Pd(Ph_2PNpy$-*P*,*N*)$_2$] are isomorphous. The structures of *cis*-[$Pd(Ph_2PNHpy$-*P*,*N*)$_2$][BF_4]$_2$, [$AuCl(Ph_2PNHpy$-*P*)], [$Pt(C_8H_{12}OMe)(Ph_2PNpy$-*P*,*N*)]·$H_2O$ illustrating hydrogen-bonding, *cis*-[$PtCl(Ph_2PNHpy$-*P*,*N*)(PMe_3)]Cl, *cis*-[$PtCl(Ph_2PNpy$-*P*,*N*)(PMe_3)] and *cis*-[$PtCl(Ph_2PNHpy$-*P*,*N*)(P($OPh)_3$)]Cl are also reported.

The co-ordination chemistry of pyridylphosphine ligands has extensively been studied [1–3] but most research has been focused upon the chemistry of 2-(diphenylphosphino)pyridine **A**; much of the interest is due to the willingness of 2-(diphenylphosphino)pyridine to act as a bidentate ligand containing both hard (nitrogen) and soft (phosphorus) donor atoms. Simple Ph_2Ppy chelate complexes are unstable because of ring strain and, as such, uncommon compared to complexes containing monodentate P bound or bidentate P, N bridging Ph_2Ppy ligands. This rigid short-bite ligand has been used to assemble homo- and hetero-binuclear complexes possessing metal–metal bonds which themselves have unusual reactivities. Numerous other ligand systems which utilise the same donor set as Ph_2Ppy but which contain organic spacer groups between the phosphorus and pyridyl nitrogen donor sites are known and include $Ph_2PCH(R)py$ (where R = H,[4–6] CH_2OEt,[7,8] or PPh_2[9–13] **B**) and $Ph_2PCH_2CH_2py$[14–22] **C** (Fig. 1).

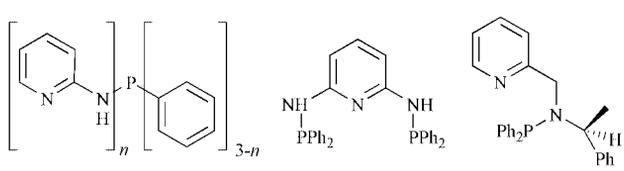
Surprisingly, considering the comparative ease of phosphorus–nitrogen bond forming reactions compared to those in which phosphorus-carbon bonds are formed, relatively few examples of pyridylphosphines in which the donor atoms are separated by amino groups are known, examples include **D**,[23] **E**,[23,24] **F**,[23] **G**,[25,26] and **H**[27] (Fig. 2). In addition the 4-methyl and 6-methyl substituted pyridyl analogues of **D** have been reported.[28] We have resynthesized **D** 2-(diphenylphosphinoamino)pyridine (dppap) **1** as we were interested to see what differences the secondary amine spacer group between the phosphorus and nitrogen donor sites would have on the co-ordination chemistry of **1** and whether the added flexibility would favour simple chelation over bridging or monodentate P bound co-ordination modes compared to that of 2-(diphenylphosphino)pyridine. During our investigation we have studied the reactions of dppap with [AuCl(tht)] (tht = tetrahydrothiophene) and a number of complexes of Pt^{II} and Pd^{II} and have observed three, possibly four, distinct modes of co-ordination. The products from these reactions have been characterised principally by multi-element NMR spectroscopy and X-ray crystallography.

† Electronic supplementary information (ESI) available: FAB MS and IR data for the ligands and complexes. See http://www.rsc.org/suppdata/dt/b0/b003294h/



A **B** **C**

Fig. 1 Examples of phosphinopyridines.



D (n = 1)
E (n = 2)
F (n = 3)

G **H**

Fig. 2 Examples of phosphinoaminopyridines.

Experimental

General

Unless otherwise stated, operations were carried out under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The complexes [AuCl(tht)],[29] [MCl_2(cod)] (M = Pt or Pd; X = Cl, Br, or I; cod = cycloocta-1,5-diene),[30,31] [PtMeX(cod)] (M = Cl or Me),[32] [{Pt(μ-OMe)($C_8H_{12}OMe$)}$_2$][33] and [{PtCl(μ-Cl)(PMe_2Ph)}$_2$][34] were prepared using literature procedures. Complexes of the type *cis*-[$MCl_2(PR_3)_2$] (M = Pt or Pd) were prepared by the addition of stoichiometric quantities of the appropriate free phosphine or phosphite to [MCl_2(cod)] (M = Pd or Pt). Chlorodiphenylphosphine (Strem) was distilled prior to use. 2-Aminopyridine (99% purity), Et_3N (99% purity), 2,6-dimethylpyridine (99% purity), Ag[BF_4] (98% purity), Ag[ClO_4] (99.9% purity), ^{t}BuOK (95% purity) and HBF_4·OEt_2 (85% in diethyl ether) were purchased from Aldrich; H_2O_2 (Fisher, 30 wt.% in water) and reagent grade KBr and NaI (Fisons) were all used without further purification. Infrared spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrmeter, ^{1}H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with δ referenced to

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external $SiMe_4$ and ^{31}P-{^1H} NMR spectra (36.2 or 101.3 MHz) either on a JEOL FX90Q or Bruker AC250 spectrometer with δ referenced to external H_3PO_4. Microanalyses were performed by the Loughborough University service and fast atom bombardment (FAB) mass spectra by the Swansea Mass Spectrometer service. All compounds gave satisfactory positive-ion FAB mass spectra, details of which are included in the supplementary information. We are grateful to Johnson Matthey PLC for the loan of precious metal salts.

Preparations

Ph_2PNHpy 1. Neat chlorodiphenylphosphine (13.5 cm^3, 16.6 g, 75.2 mmol) was added dropwise over 15 min to a solution of 2-aminopyridine (7.07 g, 75.2 mmol) and Et_3N (10.8 cm^3, 7.84 g, 77.48 mmol) in thf (250 cm^3) at 0 °C. The mixture was slowly warmed to room temperature and stirred for 24 h after which time it was filtered to remove precipitated triethylamine hydrochloride. The precipitate was washed with thf (2 × 50 cm^3). The washings and the filtrate were combined and taken to dryness under reduced pressure leaving a pale yellow oil which on cooling spontaneously crystallised. The material was removed from the flask and washed with MeOH (100 cm^3) then diethyl ether (2 × 75 cm^3) and dried *in vacuo*. Yield 16.3 g, 78%. Found (Calc. for $C_{17}H_{15}N_2P$): C 72.99 (73.37), H 5.44 (5.43), N 9.97 (10.07)%. ^1H NMR ($CDCl_3$): δ 7.97 (d, 1 H, py C[6]H), 7.45 (m, 3 H, aromatics) 7.34 (m, 8 H, aromatics), 7.04 (br d, 1 H, aromatic), 6.66 (m, 1 H, aromatic) and 5.71 (d, 1 H, $^2J(^{31}P–^1H)$ 8.4 Hz, NH). Selected IR data (KBr): 3121 ν(N–H), 1601 ν(py C=N) and 920 cm^{-1} ν(P–N).

$Ph_2P(O)NHpy$ 2. Aqueous H_2O_2 (30% w/w, 2.0 cm^3, 17.64 mmol) was added dropwise over 5 min to a solution of Ph_2PNHpy **1** (2.5 g, 8.50 mmol) in thf (20 cm^3) and the mixture stirred for 30 min and then taken to dryness. The crude product was dissolved in hot CH_2Cl_2 (100 cm^3), dried over anhydrous $MgSO_4$ and filtered while hot. The filtrate was concentrated to *ca.* 20 cm^3 and stored at −4 °C for 2 h during which time a white crystalline solid was deposited. The colourless crystals **2** were collected by suction filtration, washed with CH_2Cl_2 (10 cm^3) and dried *in vacuo*. Yield 2.13 g, 81%. Found (Calc. for $C_{17}H_{15}N_2OP$): C 69.31 (69.38), H 5.10 (5.14), N 9.51 (9.52)%. ^1H NMR ($CDCl_3$): δ 7.89 (m, 5 H, aromatics and NH), 7.45 (m, 8 H, aromatics), 7.00 (br d, 1 H, aromatic) and 6.74 (m, 1 H, aromatic). Selected IR data (KBr): 3201 ν(N–H), 1599 ν(py C=N), 1196 ν(P=O) and 950 cm^{-1} ν(P–N).

$Ph_2P(E)NHpy$ (E = S 3 or Se 4). These compounds were prepared by the same general procedure. Ph_2PNHpy **1** (1.00 g, 3.59 mmol) and a stoichiometric quantity of the appropriate chalcogen were heated to reflux in toluene (20 cm^3) for 20–30 min. The reaction mixture was taken to dryness and the residue taken up in CH_2Cl_2 then filtered through a Celite plug. The filtrate was again taken to dryness and the pale yellow solid recrystallised from the minimum of hot toluene and stored at −4 °C to give **3** and **4** as colourless crystalline solids. **3**: yield 0.97 g, 87%. Found (Calc. for $C_{17}H_{15}N_2PS$): C 65.32 (65.97), H 4.80 (4.87), N 8.97 (9.03)%. ^1H NMR ($CDCl_3$): δ 8.03 (m, 4 H, aromatics), 7.85 (d, 1 H, $^2J(^{31}P–^1H)$ 5.1 Hz, NH), 7.45 (m, 8 H, aromatics), 6.93 (br d, 1 H, aromatic) and 6.71 (m, 1 H, aromatic). Selected IR data (KBr): 1599 ν(py C=N), 941 ν(P–N) and 642 cm^{-1} ν(P=S). **4**: yield 1.07 g, 83%. Found (Calc. for $C_{17}H_{15}N_2PSe$): C 56.73 (57.16), H 4.20 (4.23), N 7.57 (7.84)%.^1H NMR ($CDCl_3$): δ 8.04 (m, 4 H, aromatics), 7.84 (d, 1 H, $^2J(^{31}P–^1H)$ 5.3 Hz, NH), 7.45 (m, 8 H, aromatics), 6.92 (br d, 1 H, aromatic) and 6.73 (m, 1 H, aromatic). Selected IR data (KBr): 1598 ν(py C=N), 941 ν(P–N) and 550 cm^{-1} ν(P=Se).

***cis*-[PtCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]Cl 5.** [$PtCl_2$(cod)] (0.095 g, 0.254 mmol) was suspended in MeCN (5 cm^3). To the stirred suspension was added Ph_2PNHpy **1** (0.143 g, 0.514 mmol) as a solid in one go. The mixture was heated until complete solution was achieved and on cooling to room temperature a white solid was deposited. The product was collected by suction filtration, washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*. Yield 0.21 g, 96%. Found (Calc. for $C_{34}H_{30}Cl_2N_4P_2Pt$): C 48.75 (49.65), H 3.32 (3.68), N 6.83 (6.81)%. ^1H NMR ($CDCl_3$): δ 11.26 (br m, 1 H, NH), 8.24 (br d, 2 H, py C[6]H), 7.70 (br d, 4 H, aromatics), 7.49 (m, 13 H, aromatics and NH), 7.30 (m, 8 H, aromatics) and 6.93 (m, 2 H, aromatics). Selected IR data (KBr): 2708 ν(N–H), 1615, 1596 ν(py C=N) and 905 cm^{-1} ν(P–N).

***cis*-[PtX(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]X (X = Br 6 or I 7).** A suspension of *cis*-[PtCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]Cl **5** (0.040 g, 0.049 mmol) and KBr or NaI (0.60 mmol) was heated to reflux in acetone (10 cm^3) for 2 h. After cooling to room temperature the solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2 (3 × 10 cm^3). The extracts were combined and filtered through a small plug of Celite. The filtrate was evaporated to *ca.* 8 cm^3 and diethyl ether (25 cm^3) added to precipitate the product. The bromide and the iodide were isolated as cream and pale yellow solids respectively. **6**: yield 0.033 g, 75%. Found (Calc. for $C_{34}H_{30}Br_2N_4P_2Pt$): C 45.48 (44.88), H 3.47 (3.33), N 6.75 (6.16)%. Selected IR data (KBr): 3052 ν(N–H), 1618, 1586 ν(py C=N) and 902 cm^{-1} ν(P–N). **7**: yield 0.038 g, 78%. Found (Calc. for $C_{34}H_{30}I_2N_4P_2Pt$): C 40.28 (40.62), H 3.13 (3.01), N 5.82 (5.57)%. Selected IR data (KBr): 3052 ν(N–H), 1616, 1587 ν(py C=N) and 899 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]Cl 8.** This was prepared in the same way as the platinum complex **5** using [$PdCl_2$(cod)] (0.085 g, 0.298 mmol) and Ph_2PNHpy **1** (0.168 g, 0.604 mmol) to give a pale yellow product. Yield 0.22 g, 98%. Found (Calc. for $C_{34}H_{30}Cl_2N_4P_2Pd$): C 54.95 (55.64), H 3.53 (4.12), N 6.86 (7.63)%. ^1H NMR ($CDCl_3$): δ 8.12 (br m, 2 H, py C[6]H), 7.46 (br m, 18 H, aromatics and NH), 7.21 (m, 10 H, aromatics) and 6.79 (m, 2 H, aromatics). Selected IR data (KBr): 2709 ν(N–H), 1611, 1597 ν(py C=N) and 907 cm^{-1} ν(P–N).

***cis*-[PdX(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]X (X = Br 9 or I 10).** These compounds were prepared in the same way as their platinum analogues **5** and **6** using *cis*-[PdCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]Cl **8** (0.040 g, 0.055 mmol) and KBr or NaI (0.70 mmol). The bromide and the iodide were isolated as pale yellow and yellow solids respectively. **9**: yield 0.033 g, 73%. Found (Calc. for $C_{34}H_{30}Br_2N_4P_2Pd$): C 49.02 (49.63), H 3.32 (3.67), N 6.83 (6.81)%. Selected IR data (KBr): 3052 ν(N–H), 1617, 1594 ν(py C=N) and 905 cm^{-1} ν(P–N). **10**: yield 0.036 g, 72%. Found (Calc. for $C_{34}H_{30}I_2N_4P_2Pt$): C 45.22 (44.54), H 3.55 (3.30), N 6.23 (6.11)%. Selected IR data (KBr): 3079 ν(N–H), 1619, 1589 ν(py C=N) and 905 cm^{-1} ν(P–N).

***cis*-[Pt(Ph_2PNpy-*P*,*N*)$_2$] 11.** A stirred solution of *cis*-[PtCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]Cl **5** (0.130 g, 0.158 mmol) in MeOH (2 cm^3) was treated with solid ^{t}BuOK (0.037 g, 0.330 mmol) causing the immediate precipitation of a yellow solid. After stirring for 10 min the product was filtered off, washed with MeOH (2 × 2 cm^3) and diethyl ether (2 × 1 cm^3) and dried *in vacuo*. Yield 0.096 g, 81%. Found (Calc. for $C_{34}H_{28}N_4P_2Pt$): C 53.75 (54.48), H 3.45 (3.76), N 7.20 (7.47)%. ^1H NMR ($CDCl_3$): δ 7.78 (m, 2 H, py C[6]H), 7.30 (m, 14 H, aromatics), 7.07 (m, 8 H, aromatics), 6.98 (br d, 2 H, aromatics) and 6.26 (m, 2 H, aromatics). Selected IR data (KBr): 1609, ν(py C=N) and 936 cm^{-1} ν(P–N).

***cis*-[Pd(Ph_2PNpy-*P*,*N*)$_2$] 12.** This was prepared in the same way as the platinum complex **11** using **8** (0.120 g, 0.164 mmol) and ^{t}BuOK (0.038 g, 0.339 mmol) to give a bright yellow

product. Yield 0.082 g, 76%. Found (Calc. for $C_{34}H_{28}N_4P_2Pd$): C 60.97 (61.78), H 4.17 (4.27), N 8.20 (8.48)%. ^{1}H NMR ($CDCl_3$): δ 7.77 (m, 2 H, py C[6]H), 7.31 (m, 14 H, aromatics), 7.10 (m, 8 H, aromatics), 6.90 (br d, 2 H, aromatics) and 6.31 (m, 2 H, aromatics). Selected IR data (KBr): 1604, ν(py C=N) and 942 cm^{-1} ν(P–N).

***cis*-[Pt(Ph$_2$PNHpy-*P*,*N*)$_2$][BF$_4$]$_2$ 13.** To a stirred solution of complex **5** (0.127 g, 0.154 mmol) in CH_2Cl_2 (20 cm^3) was added solid Ag[BF_4] (0.061 g, 0.313 mmol). After stirring for approximately 16 h the precipitated AgCl was filtered off through a small Celite plug, the solution concentrated by evaporation under reduced pressure to *ca.* 2–3 cm^3 and diethyl ether (30 cm^3) added. The cream product was collected by suction filtration, washed with diethyl ether (10 cm^3) and dried *in vacuo*. Yield 0.116 g, 81%. Found (Calc. for $C_{34}H_{30}B_2F_8N_4P_2Pt$: C 44.72 (44.14), H 3.46 (3.27), N 7.01 (6.06)%. ^{1}H NMR (d_6-dmso): δ 8.20 (m, 2 H, NH), 7.99 (m, 2 H, py C[6]H), 7.48 (m, 22 H, aromatics), 7.24 (m, 2 H, aromatics) and 7.14 (br d, 2 H, aromatics). Selected IR data (KBr): 3235 ν(N–H), 1615 ν(py C=N) and 900 cm^{-1} ν(P–N).

***cis*-[Pd(Ph$_2$PNHpy-*P*,*N*)$_2$][BF$_4$]$_2$ 14.** This was prepared in the same way as the platinum complex **13** using **8** (0.122 g, 0.166 mmol) and Ag[BF_4] (0.066 g, 0.339 mmol) to give a cream product. Yield 0.110 g, 79%. Found (Calc. for $C_{34}H_{30}B_2F_8N_4P_2Pd$): C 49.63 (48.81), H 4.16 (3.61), N 8.20 (8.48)%. ^{1}H NMR (d_6-dmso): δ 8.17 (m, 2 H, NH), 7.97 (m, 2 H, py C[6]H), 7.45 (m, 22 H, aromatics), 7.22 (m, 2 H, aromatics) and 7.11 (br d, 2 H, aromatics). Selected IR data (KBr): 3236 ν(N–H), 1615 ν(py C=N) and 900 cm^{-1} ν(P–N).

***cis*-[PtMe(Ph$_2$PNHpy-*P*,*N*){Ph$_2$PNHpy-*P*}]Cl 15.** To a stirred CH_2Cl_2 (2 cm^3) solution of [PtClMe(cod)] (0.102 g, 0.288 mmol) was added Ph_2PNHpy **1** (0.162 g, 0.582 mmol) as a solid in one go. The mixture was stirred for 20 min, filtered through Celite and diethyl ether (40 cm^3) added. The white solid was collected by suction filtration, washed with diethyl ether (3 × 10 cm^3) and dried *in vacuo*. Yield 0.219 g, 95%. Found (Calc. for $C_{35}H_{33}ClN_4P_2Pt$): C 52.49 (52.41), H 4.21 (4.15), N 6.40 (6.98)%. ^{1}H NMR ($CDCl_3$): δ 11.49 (m, 1 H, NH), 8.35 (m, 1 H, py C[6]H), 7.97 (br d, 1 H, py C[6]H), 7.84 (br m, 1 H, NH), 7.45 (m, 22 H, aromatics), 6.69 (m, 2 H, aromatics), 6.19 (m, 2 H, aromatics) and 0.64 (dd, 3 H, ^3J(^{31}P–^{1}H) 4, ^2J(^{195}Pt–^{1}H) 51 Hz, PtMe). Selected IR data (KBr): 2706 ν(N–H), 1614, 1592 ν(py C=N) and 907 cm^{-1} ν(P–N).

***cis*-[PtMe(Ph$_2$PNpy-*P*,*N*){Ph$_2$POMe-*P*}] 16.** A stirred solution of complex **15** (0.112 g, 0.140 mmol) in MeOH (1 cm^3) was treated with solid ^{t}BuOK (0.040 g, 0.352 mmol) and the resultant yellow solution stirred for 90 min. Dropwise addition of distilled water (3 cm^3) to the stirred reaction mixture gave **16** as a pale yellow solid which was collected by suction filtration and dried over phosphorus pentaoxide *in vacuo*. Yield 0.077 g, 78%. Found (Calc. for $C_{31}H_{30}N_2OP_2Pt$): C 52.57 (52.92), H 3.75 (4.30), N 3.61 (3.98)%. ^{1}H NMR ($CDCl_3$): δ 8.14 (m, 1 H, py C[6]H), 7.68 (m, 3 H, aromatics), 7.26 (m, 16 H, aromatics), 6.89 (m, 2 H, aromatics), 6.28 (m, 2 H, aromatics), 3.00 (d, 3 H, ^3J(^{31}P–^{1}H) 8 Hz, OMe) and 0.25 (dd, 3 H, ^3J(^{31}P–^{1}H) 4, ^2J(^{195}Pt–^{1}H) 55 Hz, PtMe). Selected IR data (KBr): 1613 ν(py C=N), 1020 ν(P–OMe) and 937 cm^{-1} ν(P–N).

[AuCl{Ph$_2$PNHpy-*P*}] 17. Ph_2PNHpy **1** (0.094 g, 0.338 mmol) was added as a solid to a stirred CH_2Cl_2 (3 cm^3) solution of [AuCl(tht)] (0.108 g, 0.337 mmol). After stirring for 20 min the solution was filtered through a small Celite plug and diethyl ether (30 cm^3) added. The white solid was collected by suction filtration, washed with diethyl ether (5 × 10 cm^3) and dried *in vacuo*. Yield 0.155 g, 90%. Found (Calc. for $C_{17}H_{15}AuClN_2P$): C 39.99 (39.98), H 2.80 (2.96), N 5.08 (5.49)%. ^{1}H NMR ($CDCl_3$): δ 8.01 (m, 1 H, py C[6]H), 7.76 (m, 3 H, aromatics), 7.48 (m, 9 H, aromatics and NH), 6.89 (m, 1 H, aromatic) and 6.83 (m, 1 H, aromatic). Selected IR data (KBr): 3373 ν(N–H), 1593 ν(py C=N) and 909 cm^{-1} ν(P–N).

[{Au(μ-Ph$_2$PNHpy-*P*,N)}$_2$][ClO$_4$]$_2$ (HT) 18. To a stirred solution of complex **17** (0.125 g, 0.245 mmol) in CH_2Cl_2 (20 cm^3) was added Ag[ClO_4] (0.051 g, 0.247 mmol) in nitromethane (10 cm^3) and the mixture stirred in the dark for 5 h. The precipitated AgCl was filtered off through a small Celite plug, the solution concentrated by evaporation under reduced pressure to *ca.* 4–5 cm^3 and diethyl ether (25 cm^3) added. The white product was collected by suction filtration, washed with diethyl ether (10 cm^3) and dried *in vacuo*. Yield 0.103 g, 71%. Found (Calc. for $C_{17}H_{15}AuClN_2O_4P$): C 34.89 (35.52), H 2.45 (2.63), N 4.40 (4.87)%. ^{1}H NMR ($CDCl_3$): δ 8.10 (m, 2 H, py C[6]H), 7.91–7.16 (m, 24 H, aromatics and NH), 7.05 (br d, 2 H, aromatic) and 6.86 (m, 2 H, aromatic). Selected IR data (KBr): 3204 ν(N–H), 1611 ν(py C=N), 1102, 623 ν(ClO_4) and 924 cm^{-1} ν(P–N).

[Pt(C$_8$H$_{12}$OMe)(Ph$_2$PNpy-*P*,*N*)]·H$_2$O 19. To a stirred suspension of [{Pt(μ-OMe)(C_8H_{12}OMe)}$_2$] (0.150 g, 0.205 mmol) in MeOH (3 cm^3) were added in quick succession the solids Ph_2PNHpy **1** (0.114 g, 0.410 mmol) and ^{t}BuOK (0.046 g, 0.410 mmol) resulting in a pale yellow solution that was stirred for 30 min. Distilled water (*ca.* 12 drops) was added dropwise to the mixture causing a fine pale yellow precipitate to be deposited which was collected by suction filtration, washed with distilled water (2 × 2 cm^3) and dried *in vacuo*. Yield 0.231 g, 92%. Found (Calc. for $C_{26}H_{31}N_2O_2PPt$): C 49.37 (49.60), H 5.09 (4.96), N 4.07 (4.45)%. ^{1}H NMR ($CDCl_3$): δ 7.73 (m, 1 H, py C[6]H), 7.53 (m, 3 H, aromatics) 7.34 (m, 8 H, aromatics), 7.19 (m, 1 H, aromatic), 6.98 (br d, 1 H, aromatic) and expected C_8H_{12}OMe resonances. Selected IR data (KBr): 1607 ν(py C=N) and 941 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PMe$_3$)]Cl 20.** A typical synthesis was performed as follows. Solid Ph_2PNHpy **1** (0.074 g, 0.266 mmol) was added to a stirred suspension of *cis*-[$PtCl_2(PMe_3)_2$] (0.110 g, 0.263 mmol) in CH_2Cl_2 (3 cm^3) giving a clear solution. The mixture was stirred for 10 min and diethyl ether (20 cm^3) slowly added causing a white crystalline solid to be deposited. The crude product **20** was collected by suction filtration, recrystallised from CH_2Cl_2–diethyl ether and dried *in vacuo.* Yield 0.150 g, 92%. Found (Calc. for $C_{20}H_{24}Cl_2N_2P_2Pt$): C 38.87 (38.72), H 3.75 (3.90), N 4.22 (4.52)%. ^{1}H NMR ($CDCl_3$): δ 11.71 (m, 1 H, NH), 9.14 (m, 1 H, py C[6]H), 8.03 (m, 4 H, aromatics), 7.65 (m, 8 H aromatics), 6.92 (m, 1 H, aromatic) and 1.50 (d, 9 H, ^3J(^{195}Pt–^{1}H) 34.3, ^2J(^{31}P–^{1}H) 11.7 Hz, PMe). Selected IR data (KBr): 2642 ν(N–H), 1616 ν(py C=N) and 911 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(PMe$_3$)] 21.** A typical deprotonation was performed as follows. Solid ^{t}BuOK (0.018 g, 0.160 mmol) was added to a stirred solution of complex **20** (0.100 g, 0.161 mmol) in MeOH (1 cm^3) causing a pale yellow solid to be deposited. Distilled water (3–5 drops) was added to complete the precipitation. The product was collected by suction filtration, washed with distilled water (2 × 1 cm^3) and ice cold MeOH (2 × 1 cm^3) and dried over phosphorus pentaoxide *in vacuo.* Yield 0.082 g, 87%. Found (Calc. for $C_{20}H_{23}ClN_2P_2Pt$): C 40.83 (41.14), H 3.37 (3.97), N 4.34 (4.80)%. ^{1}H NMR ($CDCl_3$): δ 8.90 (m, 1 H, py C[6]H), 7.86 (m, 3 H, aromatics), 7.46 (m, 6 H aromatics), 7.29 (m, 2 H, aromatic), 6.99 (m, 1 H, aromatic), 6.33 (m, 1 H, aromatic) and 1.42 (d, 9 H, ^3J(^{195}Pt–^{1}H) 33.7, ^2J(^{31}P–^{1}H) 11.1 Hz, PMe). Selected IR data (KBr): 1608 ν(py C=N) and 940 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PEt$_3$)]Cl 22.** As for complex **20** using Ph$_2$PNHpy **1** (0.064 g, 0.234 mmol) and *cis*-[PtCl$_2$(PEt$_3$)$_2$] (0.117 g, 0.233 mmol) to give a white crystalline product. Yield 0.133 g, 86%. Found (Calc. for $C_{23}H_{30}Cl_2N_2P_2Pt$): C 41.74 (41.70), H 4.27 (4.56), N 3.66 (4.23)%. ^{1}H NMR ($CDCl_3$): δ 11.82 (m, 1 H, NH), 9.20 (m, 1 H, py C[6]H), 8.02 (m, 3 H, aromatics), 7.61 (m, 8 H, aromatics), 7.30 (m, 1 H, aromatic), 6.90 (m, 1 H, aromatic), 1.82 (dq, 6 H, $^2J(^{31}P–^1H)$ 10.0 Hz, PCH_2) and 0.97 (dt, 9 H, Me). Selected IR data (KBr): 2664 ν(N–H), 1615 ν(py C=N) and 912 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(PEt$_3$)] 23.** As for complex **21** using **22** (0.125 g, 0.187 mmol) and ^{t}BuOK (0.021 g, 0.187 mmol). The reaction mixture was diluted with distilled water (20 cm^3) and then extracted with CH_2Cl_2 (2 × 10 cm^3). The extracts were combined and dried over anhydrous $MgSO_4$, the drying agent filtered off and the filtrate evaporated under reduced pressure to *ca*. 1–2 cm^3. Hexane (30 cm^3) was added with stirring to give a pale yellow powder. Yield 0.109 g, 92%. Found (Calc. for $C_{23}H_{29}ClN_2P_2Pt$): C 43.75 (44.13), H 4.32 (4.67), N 3.98 (4.48)%. ^{1}H NMR ($CDCl_3$): δ 8.94 (m, 1 H, py C[6]H), 7.85 (m, 3 H, aromatics), 7.44 (m, 6 H, aromatics), 7.25 (m, 2 H, aromatic), 6.92 (m, 1 H, aromatic), 6.28 (m, 1 H, aromatic), 1.75 (dq, 6 H, $^2J(^{31}P–^1H)$ 10.1 Hz, PCH_2) and 0.89 (dt, 9 H, Me). Selected IR data (KBr): 1612 ν(py C=N) and 943 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(P^{n}Bu$_3$)]Cl 24.** [PtCl$_2$(cod)] (0.105 g, 0.281 mmol) and P^{n}Bu$_3$ (0.14 cm^3, 0.114 g, 0.563 mmol) were stirred in CH_2Cl_2 (5 cm^3) for 10 min. Ph$_2$PNHpy **1** (0.079 g, 0.284 mmol) was added as a solid in one go, giving a pale yellow solution which was stirred for 10 min. Diethyl ether (50 cm^3) was added to give a fine white powder. Recrystallisation from CH_2Cl_2–diethyl ether gave complex **24** as a fine white powder. Yield 0.182 g, 87%. Found (Calc. for $C_{29}H_{42}Cl_2N_2P_2Pt$): C 47.00 (46.65), H 5.52 (5.67), N 3.11 (3.75)%. ^{1}H NMR ($CDCl_3$): δ 11.73 (m, 1 H, NH), 9.20 (1 H, m, py C[6]H), 7.98 (m, 3 H, aromatics), 7.64 (m, 8 H, aromatics), 7.31 (m, 1 H, aromatic), 6.90 (m, 1 H, aromatic) and 1.77–0.73 (m, 27 H, P^{n}Bu). Selected IR data (KBr): 2599 ν(N–H), 1612 ν(py C=N) and 913 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(P^{n}Bu$_3$)] 25.** As for complex **21** using **24** (0.130 g, 0.174 mmol) and ^{t}BuOK (0.020 g, 0.178 mmol) the resulting pale yellow solution was diluted with distilled water (30 cm^3) and extracted with CH_2Cl_2 (2 × 15 cm^3). The extracts were combined and dried over anhydrous $MgSO_4$. The drying agent was filtered off and the filtrate concentrated by evaporation under reduced pressure to *ca*. 2–3 cm^3. Addition of hexane (40 cm^3) followed by slow evaporation over 3 days gave **25** as pale yellow crystals. Yield 0.110 g, 89%. Found (Calc. for $C_{29}H_{41}ClN_2P_2Pt$): C 49.65 (49.05), H 5.39 (5.82), N 3.61 (3.94)%. ^{1}H NMR ($CDCl_3$): δ 8.93 (m, 1 H, py C[6]H), 7.82 (m, 3 H, aromatics), 7.44 (m, 6 H, aromatics), 7.24 (m, 2 H, aromatic), 6.89 (m, 1 H, aromatic), 6.26 (m, 1 H, aromatic) and 1.84–0.72 (m, 27 H, P^{n}Bu). Selected IR data (KBr): 1612 ν(py C=N) and 943 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PMe$_2$Ph)]Cl 26.** As for complex **20** using Ph$_2$PNHpy **1** (0.071 g, 0.255 mmol) and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (0.138 g, 0.254 mmol) to give a white crystalline product. Yield 0.163 g, 94%. Found (Calc. for $C_{25}H_{26}Cl_2N_2P_2Pt$): C 43.71 (44.00), H 3.55 (3.84), N 3.91 (4.10)%. ^{1}H NMR ($CDCl_3$): δ 12.20 (m, 1 H, NH), 9.17 (m, 1 H, py C[6]H), 7.87 (m, 3 H, aromatics), 7.65 (m, 1 H, aromatic), 7.40 (m, 12 H, aromatics), 6.87 (m, 2 H, aromatics) and 1.77 (d, 6 H, $^3J(^{195}Pt–^1H)$ 35.1, $^2J(^{31}P–^1H)$ 11.3 Hz, PMe). Selected IR data (KBr): 2570 ν(N–H), 1616 ν(py C=N) and 916 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(PMe$_2$Ph)] 27.** As for complex **21** using **26** (0.123 g, 0.180 mmol) and ^{t}BuOK (0.020 g, 0.178 mmol) to give a pale yellow powder. Yield 0.098 g, 84%. Found (Calc. for $C_{25}H_{25}ClN_2P_2Pt$): C 46.34 (46.48), H 4.21 (3.90), N 3.84 (4.34)%. δ 8.94 (m, 1 H, py C[6]H), 7.72 (m, 3 H, aromatics), 7.35 (m, 12 H, aromatics), 6.93 (m, 1 H, aromatic), 6.29 (m, 2 H, aromatics) and 1.68 (d, 6 H, $^3J(^{195}Pt–^1H)$ 35.1, $^2J(^{31}P–^1H)$ 10.7 Hz, PMe). Selected IR data (KBr): 1612 ν(py C=N) and 941 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PPh$_2$H)]Cl 28.** As for complex **20** using Ph$_2$PNHpy **1** (0.045 g, 0.162 mmol) and *cis*-[PtCl$_2$(PPh$_2$H)$_2$] (0.102 g, 0.160 mmol) to give a fine white powder. Yield 0.111 g, 95%. Found (Calc. for $C_{29}H_{26}Cl_2N_2P_2Pt$): C 46.85 (47.68), H 3.63 (3.59), N 3.70 (3.83)%. ^{1}H NMR ($CDCl_3$): δ 12.51 (m, 1 H, NH), 9.17 (m, 1 H, py C[6]H), 7.97 (d, 1 H, aromatic), 7.83 (m, 3 H, aromatics), 7.73 (m, 1 H, aromatic), 7.48 (m, 16 H, aromatics), 7.28 (m, 1 H, aromatic), 7.04 (m, 1 H, aromatic), 6.98 (m, 1 H, aromatic), 6.79 (m, 1 H, aromatic) and 5.22 (d, 1 H, $^2J(^{195}Pt–^1H)$ 90.2, $^1J(^{31}P–^1H)$ 395 Hz, PH).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]Cl 29.** As for complex **20** using Ph$_2$PNHpy **1** (0.059 g, 0.212 mmol) and *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.167 g, 0.211 mmol) to give a white crystalline product. Yield 0.158 g, 93%. Found (Calc. for $C_{35}H_{30}Cl_2N_2P_2Pt$): C 51.38 (52.12), H 3.85 (3.75), N 3.22 (3.47)%. ^{1}H NMR ($CDCl_3$): δ 12.03 (m, 1 H, NH), 9.32 (m, 1 H, py C[6]H), 7.93 (d, 1 H, aromatic), 7.72–7.21 (m, 26 H, aromatics) and 6.89 (m, 1 H, aromatic). Selected IR data (KBr): 2578 ν(N–H), 1617 ν(py C=N) and 912 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(PPh$_3$)] 30.** As for complex **21** using **29** (0.173 g, 0.214 mmol) and ^{t}BuOK (0.024 g, 0.214 mmol) to give a pale yellow powder. Yield 0.143 g, 87%. Found (Calc. for $C_{35}H_{29}ClN_2P_2Pt$): C 53.93 (54.59), H 3.32 (3.80), N 3.54 (3.64)%. ^{1}H NMR ($CDCl_3$): δ 9.16 (m, 1 H, py C[6]H), 7.45–7.16 (m, 26 H, aromatics), 6.98 (d, 1 H, aromatic) and 6.30 (m, 1 H, aromatic). Selected IR data (KBr): 1612 ν(py C=N) and 937 cm^{-1} ν(P–N).

***cis*-[PtBr(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]Br 31.** As for complex **20** using Ph$_2$PNHpy **1** (0.063 g, 0.226 mmol) and *cis*-[PtBr$_2$(PPh$_3$)$_2$] (0.197 g, 0.224 mmol) in methanol (10 cm^3) to give a white crystalline product. Yield 0.179 g, 89%. Found (Calc. for $C_{35}H_{30}Br_2N_2P_2Pt$): C 47.05 (46.94), H 3.63 (3.38), N 2.91 (3.13)%. Selected IR data (KBr): 2699 ν(N–H), 1616 ν(py C=N) and 911 cm^{-1} ν(P–N).

***cis*-[PtI(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]I 32.** As for complex **20** using Ph$_2$PNHpy **1** (0.059 g, 0.212 mmol) and [PtI$_2$(PPh$_3$)$_2$] (0.205 g, 0.211 mmol) to give a pale yellow crystalline product. Yield 0.190 g, 91%. Found (Calc. for $C_{35}H_{30}I_2N_2P_2Pt$): C 41.53 (42.49), H 3.16 (3.06), N 2.10 (2.83)%. Selected IR data (KBr): 2701 ν(N–H), 1615 ν(py C=N) and 912 cm^{-1} ν(P–N).

***cis*-[PtMe(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]Cl 33.** As for complex **20** using Ph$_2$PNHpy **1** (0.050 g, 0.180 mmol) and *cis*-[PtClMe(PPh$_3$)$_2$] (0.137 g, 0.178 mmol) to give a fine white powder. Yield 0.123 g, 88%. Found (Calc. for $C_{36}H_{33}Cl_2N_2P_2Pt$): C 54.56 (55.00), H 4.20 (4.23), N 3.44 (3.56)%. ^{1}H NMR ($CDCl_3$): δ 11.45 (m, 1 H, NH), 8.46 (m, 1 H, py C[6]H), 8.08 (d, 1 H, aromatic), 7.62 (m, 1 H, aromatic), 7.46–7.21 (m, 25 H, aromatics), 6.79 (m, 1 H, aromatic) and 0.62 (dd, $^2J(^{195}Pt–^1H)$ 49.8 Hz, PtMe). Selected IR data (KBr): 2666 ν(N–H), 1616 ν(py C=N) and 908 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(P(OMe)$_3$)]Cl 34.** As for complex **20** using Ph$_2$PNHpy **1** (0.085 g, 0.305 mmol) and *cis*-

$[PtCl_2(P(OMe)_3)_2]$ (0.137 g, 0.303 mmol) to give a fine white powder. Yield 0.196 g, 97%. Found (Calc. for $C_{20}H_{24}Cl_2N_2O_3P_2Pt$): C 36.68 (35.94), H 3.49 (3.62), N 4.35 (4.19)%. Selected IR data (KBr): 2642 ν(N–H), 1618 ν(py C=N) and 914 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(P(OMe)$_3$)] 35.** As for complex **21** using **34** (0.136 g, 0.203 mmol) and ^{t}BuOK (0.023 g, 0.205 mmol) to give a pale yellow powder. Yield 0.113 g, 88%. Found (Calc. for $C_{20}H_{23}ClN_2O_3P_2Pt$): C 38.13 (38.02), H 3.42 (3.67), N 4.14 (4.43)%. ^{1}H NMR ($CDCl_3$): δ 8.87 (m, 1 H, py C[6]H), 7.84 (m, 3 H, aromatics), 7.50 (m, 6 H, aromatics), 7.40 (m, 2 H, aromatics), 7.07 (d, 1 H, aromatic), 6.34 (m, 1 H, aromatic) and 3.98 (d, 9 H, $^3J(^{31}P–^1H)$ 8.2 Hz, POMe). Selected IR data (KBr): 1615 ν(py C=N) and 944 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(P(OEt)$_3$)]Cl 36.** As for complex **20** using Ph_2PNHpy **1** (0.071 g, 0.255 mmol) and *cis*-$[PtCl_2(P(OEt)_3)_2]$ (0.152 g, 0.254 mmol) to give a fine white powder. Yield 0.143 g, 79%. Found (Calc. for $C_{23}H_{30}Cl_2N_2O_3P_2Pt$): C 38.60 (38.89), H 4.14 (4.26), N 3.76 (3.94)%. ^{1}H NMR ($CDCl_3$): δ 12.25 (m, 1 H, NH), 9.08 (m, 1 H, py C[6]H), 7.91 (m, 3 H, aromatics) 7.72 (m, 1 H, aromatic), 7.52 (m, 8 H, aromatics), 7.30 (m, 1 H, aromatic), 6.92 (m, 1 H, aromatic), 4.06 (dq, 6 H, $^3J(^{31}P–^1H)$ 8.8 Hz, $POCH_2$) and 1.19 (t, 9 H, Me). Selected IR data (KBr): 2590 ν(N–H), 1618 ν(py C=N) and 913 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(P(OEt)$_3$)] 37.** As for complex **21** using **36** (0.164 g, 0.243 mmol) and ^{t}BuOK (0.027 g, 0.241 mmol) to give a pale yellow powder. Yield 0.139 g, 90%. Found (Calc. for $C_{23}H_{29}ClN_2O_3P_2Pt$): C 40.68 (40.99), H 4.15 (4.34), N 4.13 (4.16)%. ^{1}H NMR ($CDCl_3$): δ 8.83 (m, 1 H, py C[6]H), 7.79 (m, 3 H, aromatics), 7.43 (m, 6 H, aromatics), 7.38 (m, 2 H, aromatics), 7.02 (d, 1 H, aromatic), 6.31 (m, 1 H, aromatic), 4.04 (dq, 6 H, $^3J(^{31}P–^1H)$ 8.4 Hz, $POCH_2$) and 1.07 (t, 9 H, Me). Selected IR data (KBr): 1614 ν(py C=N) and 947 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(P(O^{n}Bu)$_3$)]Cl 38.** As for complex **24** using $[PtCl_2(cod)]$ (0.093 g, 0.249 mmol), (0.14 cm^3, 0.130 g, 0.519 mmol) and Ph_2PNHpy **1** (0.070 g, 0.252 mmol) to give **38** as a fine white powder. Yield 0.164 g, 83%. Found (Calc. for $C_{29}H_{42}Cl_2N_2O_3P_2Pt$): C 43.75 (43.84), H 5.35 (5.33), N 3.62 (3.53)%. ^{1}H NMR ($CDCl_3$): δ 10.66 (m, 1 H, NH), 9.15 (m, 1 H, py C[6]H), 7.82 (m, 3 H, aromatics), 7.48 (m, 2 H, aromatics), 7.26 (m, 6 H, aromatics), 6.82 (m, 2 H, aromatics), 3.62 (m, 6 H, $POCH_2$), 1.23 (m, 6 H, CH_2), 1.06 (m, 6 H, CH_2) and 0.74 (t, 9 H, Me). Selected IR data (KBr): 2637 ν(N–H), 1619 ν(py C=N) and 912 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(P(OPh)$_3$)]Cl 39.** As for complex **20** using Ph_2PNHpy **1** (0.054 g, 0.194 mmol) and *cis*-$[PtCl_2(P(OPh)_3)_2]$ (0.171 g, 0.193 mmol) to give a fine white powder. Yield 0.160 g, 97%. Found (Calc. for $C_{35}H_{30}Cl_2N_2O_3P_2Pt$): C 48.98 (49.19), H 3.41 (3.54), N 2.94 (3.28)%. ^{1}H NMR ($CDCl_3$): δ 12.52 (m, 1 H, NH), 9.08 (m, 1 H, py C[6]H), 8.02 (br d, 1 H, aromatic), 7.77 (m, 4 H, aromatics), 7.60 (m, 2 H, aromatics), 7.41 (m, 6 H, aromatics), 7.27–7.21 (m, 8 H, aromatics), 6.91 (br d, 1 H, aromatic) and 6.86–6.81 (m, 6 H, aromatics). Selected IR data (KBr): 2616 ν(N–H), 1619 ν(py C=N) and 916 cm^{-1} ν(P–N).

***cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(P(OPh)$_3$)] 40.** As for complex **21** using **39** (0.173 g, 0.202 mmol) and ^{t}BuOK (0.023 g, 0.205 mmol) to give a pale yellow powder. Yield 0.141 g, 85%. Found (Calc. for $C_{35}H_{29}ClN_2O_3P_2Pt$): C 50.62 (51.39), H 3.37 (3.57), N 2.73 (3.42)%. ^{1}H NMR ($CDCl_3$): δ 8.81 (m, 1 H, py C[6]H), 7.62 (m, 4 H, aromatics), 7.46 (m, 2 H, aromatics), 7.28 (m, 6 H, aromatics), 7.20–7.16 (m, 8 H, aromatics), 6.96 (br d, 1 H, aromatic), 6.89–6.84 (m, 6 H, aromatics) and 6.26 (m, 1 H, aromatic). Selected IR data (KBr): 1614 ν(py C=N) and 932 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNHpy-*P*,*N*)(PMe$_2$Ph)]Cl 41.** As for complex **20** using Ph_2PNHpy **1** (0.102 g, 0.367 mmol) and *cis*-$[PdCl_2(PMe_2Ph)_2]$ (0.165 g, 0.364 mmol) to give a cream crystalline product. Yield 0.192 g, 89%. Found (Calc. for $C_{25}H_{26}Cl_2N_2P_2Pd$): C 50.28 (50.57), H 4.29 (4.41), N 4.03 (4.72)%. ^{1}H NMR ($CDCl_3$): δ 11.91 (m, 1 H, NH), 8.99 (m, 1 H, py C[6]H), 7.87–7.77 (m, 5 H, aromatics), 7.62 (m, 2 H, aromatics), 7.49 (m, 4 H, aromatics), 7.28–7.23 (m, 6 H, aromatics), 6.88 (m, 1 H, aromatic) and 1.79 (d, 6 H, $^2J(^{31}P–^1H)$ 11.6 Hz, PMe). Selected IR data (KBr): 2619 ν(N–H), 1614 ν(py C=N) and 915 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNpy-*P*,*N*)(PMe$_2$Ph)] 42.** As for complex **21** using **41** (0.149 g, 0.251 mmol) and ^{t}BuOK (0.028 g, 0.250 mmol) to give a bright yellow crystalline product. Yield 0.123 g, 88%. Found (Calc. for $C_{25}H_{25}ClN_2P_2Pd$): C 53.65 (53.89), H 4.29 (4.52), N 4.75 (5.03)%. ^{1}H NMR ($CDCl_3$): δ 8.76 (m, 1 H, py C[6]H), 6.69 (m, 4 H, aromatics), 7.48 (m, 2 H, aromatics), 7.40–7.18 (m, 10 H, aromatics), 6.87 (br d, 1 H, aromatic), 6.32 (m, 1 H, aromatic) and 1.63 (d, 6 H, $^2J(^{31}P–^1H)$ 10.7 Hz, PMe). Selected IR data (KBr): 2616 ν(N–H), 1607 ν(py C=N) and 949 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]Cl 43.** As for complex **20** using Ph_2PNHpy **1** (0.065 g, 0.234 mmol) and *cis*-$[PdCl_2(PPh_3)_2]$ (0.162 g, 0.231 mmol) to give a cream crystalline product. Yield 0.159 g, 96%. Found (Calc. for $C_{35}H_{30}Cl_2N_2P_2Pd$): C 58.64 (58.56), H 4.04 (4.21), N 4.15 (3.90)%. ^{1}H NMR ($CDCl_3$): δ 11.25 (m, 1 H, NH), 8.90 (m, 1 H, py C[6]H), 7.95 (m, 1 H, aromatic), 7.75–7.22 (m, 20 H, aromatics), 6.90–6.81 (m, 6 H, aromatics) and 6.66 (m, 1 H, aromatic). Selected IR data (KBr): 2659 ν(N–H), 1612 ν(py C=N) and 913 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNpy-*P*,*N*)(PPh$_3$)] 44.** As for complex **21** using **43** (0.160 g, 0.223 mmol) and ^{t}BuOK (0.025 g, 0.223 mmol) to give a bright yellow product. Yield 0.143 g, 94%. Found (Calc. for $C_{35}H_{29}ClN_2P_2Pd$): C 60.99 (61.69), H 4.19 (4.29), N 4.02 (4.11)%. ^{1}H NMR ($CDCl_3$): δ 8.70 (m, 1 H, py C[6]H) and 7.97–6.59 (m, 28 H, aromatics). Selected IR data (KBr): 1604 ν(py C=N) and 944 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNHpy-*P*,*N*)(P(OMe)$_3$)]Cl 45.** As for complex **20** using Ph_2PNHpy **1** (0.063 g, 0.226 mmol) and *cis*-$[PdCl_2(P(OMe)_3)_2]$ (0.131 g, 0.308 mmol) to give a fine cream powder. Yield 0.170 g, 95%. Found (Calc. for $C_{20}H_{24}Cl_2N_2O_3P_2Pd$): C 42.01 (41.44), H 4.16 (4.17), N 5.16 (4.83)%. Selected IR data (KBr): 2688 ν(N–H), 1614 ν(py C=N) and 914 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNHpy-*P*,*N*)(P(OEt)$_3$)]Cl 46.** As for complex **24** using $[PdCl_2(cod)]$ (0.095 g, 0.333 mmol), $P(OEt)_3$ (0.12 cm^3, 0.116 g, 0.698 mmol) and Ph_2PNHpy **1** (0.093 g, 0.334 mmol) to give **46** as a cream powder. Yield 0.199 g, 96%. Found (Calc. for $C_{23}H_{30}Cl_2N_2O_3P_2Pd$): C 44.67 (44.43), H 4.65 (4.86), N 4.48 (4.51)%. ^{1}H NMR ($CDCl_3$): δ 11.88 (br s, 1 H, NH), 8.88 (m, 1 H, py C[6]H), 7.96–7.80 (m, 4 H, aromatics), 7.70–7.26 (m, 8 H, aromatics), 6.89 (m, 1 H, aromatic), 4.12 (dq, 6 H, $^3J(^{31}P–^1H)$ 9.0 Hz, $POCH_2$) and 1.12 (t, 9 H, Me). Selected IR data (KBr): 2587 ν(N–H), 1614 ν(py C=N) and 914 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph$_2$PNHpy-*P*,*N*)(P(O^{n}Bu)$_3$)]Cl 47.** As for complex **24** using $[PdCl_2(cod)]$ (0.101 g, 0.354 mmol), 90% pure $P(O^nBu)_3$ (0.22 cm^3, 0.199 g, 0.715 mmol) and Ph_2PNHpy **1** (0.099 g, 0.356 mmol) to give **46** as a cream powder. Yield 0.205 g, 82%. Found (Calc. for $C_{29}H_{42}Cl_2N_2O_3P_2Pd$): C 48.75 (49.34), H 5.35 (6.00), N 4.62 (3.97)%. ^{1}H NMR ($CDCl_3$): δ 10.22 (br s,

1 H, NH), 8.89 (m, 1 H, py C[6]H), 7.81 (m, 3 H, aromatic), 7.51–7.14 (m, 9 H, aromatics), 6.75 (m, 1 H, aromatic), 3.54 (m, 6 H, $POCH_2$), 1.22–0.95 (m, 12 H, CH_2CH_2) and 0.72 (t, 9 H, Me). Selected IR data (KBr): 2684 ν(N–H), 1615 ν(py C=N) and 910 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph_2PNHpy-*P*,*N*)($P(OPh)_3$)]Cl 48.** As for complex **20** using Ph_2PNHpy **1** (0.057 g, 0.205 mmol) and *cis*-[$PdCl_2$-($P(OPh)_3$)$_2$] (0.163 g, 0.204 mmol) to give a cream crystalline product. Yield 0.144 g, 92%. Found (Calc. for $C_{35}H_{30}Cl_2N_2O_3P_2Pd$): C 54.65 (54.88), H 3.82 (3.95), N 3.45 (3.66)%. ^{1}H NMR ($CDCl_3$): δ 11.25 (br s, 1 H, NH), 8.90 (m, 1 H, py C[6]H), 7.95 (m, 3 H, aromatic), 7.75–6.22 (m, 18 H, aromatics), 6.90–6.81 (m, 6 H, aromatics) and 6.66 (m, 1 H, aromatic). Selected IR data (KBr): 2664 ν(N–H), 1614 ν(py C=N) and 915 cm^{-1} ν(P–N).

***cis*-[PdCl(Ph_2PNpy-*P*,*N*)($P(OPh)_3$)] 49.** To a CH_2Cl_2 (30 cm^3) solution of complex **48** (0.134 g, 0.175 mmol) was added dropwise a CH_2Cl_2 (DCM) (10 cm^3) solution of Et_3N (0.018 g 0.179 mmol) and the reaction mixture stirred for 1 h. Distilled water (20 cm^3) was added and the DCM layer separated and retained. The water layer was extracted with 10 cm^3 of DCM. The extracts were combined and dried over anhydrous $MgSO_4$. The drying agent was removed by filtration and the filtrate concentrated under reduced pressure to *ca.* 1–2 cm^3. Diethyl ether (40 cm^3) was slowly added to give a bright yellow powder. Yield 0.115 g, 90%. Found (Calc. for $C_{35}H_{29}ClN_2O_3P_2Pd$): C 56.97 (57.62), H 3.91 (4.01), N 3.64 (3.84)%. ^{1}H NMR ($CDCl_3$): δ 8.70 (m, 1 H, py C[6]H), 7.93 (m, 3 H, aromatics), 7.65 (m, 24 H, aromatics) and 6.34 (m, 1 H, aromatic). Selected IR data (KBr): 1610 ν(py C=N) and 930 cm^{-1} ν(P–N).

X-Ray crystallography

Details of the structure determination are given in Table 1. X-Ray diffraction measurements were made at room temperature with graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å) using a Siemens SMART diffractometer (**17**, **19**, **20**, **21** **39**) or with Cu-Kα radiation and a Rigaku AFC7S serial diffractometer (**1**, **5**, **11**, **12**, **14**). For the SMART data, intensity data were collected using 0.3 or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data integrated using the SAINT program) and for the Rigaku AFC7S data collections by ω scans over a single quadrant of reciprocal space. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least squares against F (TEXSAN[35]) or F^2 (SHELXTL[36]) for all data with $I > 3\sigma(I)$.

CCDC reference number 186/2050.

See http://www.rsc.org/suppdata/dt/b0/b003294h/ for crystallographic files in .cif format.

Results and discussion

Synthesis and chalcogen derivatives of dppap

The first reported synthesis of 2-(diphenylphosphinoamino)-pyridine,[23] **1**, and its subsequent use in the preparation of a number of metal complexes was published in 1967 followed by the chalcogen derivatives $Ph_2P(E)NHpy$, E = S **2** and Se **3**, in 1970.[28] The original synthesis of dppap involved slow dropwise addition of Ph_2PCl in diethyl ether to 2-aminopyridine and Et_3N in the same solvent. Our synthesis is essentially the same (eqn. 1): the dropwise addition of neat Ph_2PCl to a thf solution of 2-aminopyridine, containing a small excess of Et_3N as base. The ligand was isolated after work-up as an air and moisture tolerant colourless crystalline solid in good yield (78%). It is readily soluble in chlorinated solvents, acetone, thf and toluene but less soluble in MeOH, diethyl and light petroleum. dppap exhibits a single ^{31}P-{^{1}H} NMR resonance (in $CDCl_3$) at δ(P) 26.4. The ^{1}H NMR spectrum in the same solvent shows the pyridyl C[6] proton as a multiplet at δ(H) 7.97 and the amine proton appears as a broad doublet at δ(H) 5.7 [$^2J(^{31}P–^1H)$ = 8 Hz]. In the IR spectrum we observe a very weak ν(N–H) band, due to intermolecular hydrogen bonding, at 3121 cm^{-1} and two strong bands at 1601 and 920 cm^{-1} assigned to ν(py C=N) of the pyridine ring and ν(P–N) respectively. Microanalytical data were satisfactory and the positive-ion FAB mass spectrum gave the expected parent ion and fragmentation patterns. Crystals of Ph_2PNHpy suitable for X-ray crystallography were obtained by slow evaporation of a concentrated $CDCl_3$ solution (Fig. 3, Table 2). The molecular structure reveals that the P(1)–N(2)–C(2)–N(2) backbone is essentially planar with a mean deviation of 0.03 Å. In addition, the crystal structure also shows that in the solid state the molecule exists as hydrogen bonded dimers. The NH proton of one molecule is hydrogen bonded to the pyridyl nitrogen of a second and the pyridyl nitrogen of the second interacts with the NH proton of the first, leading to a head to tail type arrangement of molecules. The H(2N)···N(1A) distance is 2.04 Å with an intermolecular N(1A)···N(2) separation of 2.289(4) Å and an N(2)–H(2N)···N(1A) angle of 160°.

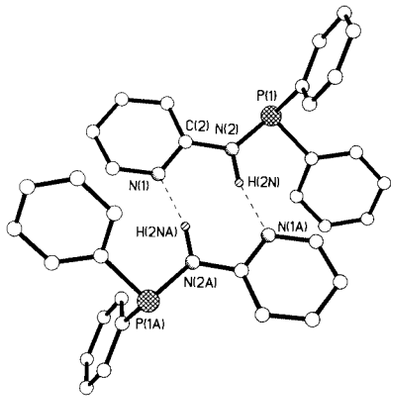
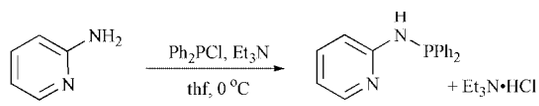


Fig. 3 Crystal structure of Ph_2PNHpy **1** showing the hydrogen-bonded dimer pairs.



(1)

Curiously, the oxide of dppap was not previously reported alongside the thio and seleno analogues. We have found that $Ph_2P(O)NHpy$ **2** can easily be prepared by the addition of a small excess of aqueous H_2O_2 to a thf solution of the phosphorus(III) species. $Ph_2P(S)NHpy$ **3** was prepared according to the literature method[28] by refluxing the ligand with a stoichiometric quantity of sulfur in toluene. The seleno derivative $Ph_2P(Se)NHpy$ **4** was also prepared in the same manner using selenium metal although the published procedure requires the use of the highly toxic potassium selenocyanate. Although compounds **2**-**4** display a number of very similar spectroscopic properties, the strong ν(N–H) band observed in the spectrum of the oxide was not apparent in the spectra of either the thio or seleno analogue. Selected analytical data for $Ph_2P(E)NHpy$ (where E = O **2**, S **3** or Se **4**) are detailed in Table 3.

Mixed dppap co-ordination mode complexes

dppap reacts with [MCl_2(cod)] (M = Pt or Pd) in warm acetonitrile to give the cationic species *cis*-[MCl(Ph_2PNHpy-*P*,*N*)-{Ph_2PNHpy-*P*}]Cl (M = Pt **5** or Pd **8**) in excellent yield, 96 and 98% respectively (Scheme 1). No evidence was found for either

Table 1 Crystal data for the ligand and complexes

	1	**5**	**11**	**12**	**14**	**17**	**19**	**20**	**21**	**39**
Empirical Formula	$C_{17}H_{15}N_2P$	$C_{34}H_{30}Cl_2N_4P_2Pt{\cdot}0.5H_2O$	$C_{34}H_{28}N_4P_2Pt$	$C_{34}H_{28}N_4P_2Pd$	$C_{34}H_{30}B_2F_8N_4P_2Pd$	$C_{17}H_{15}AuClN_2P$	$C_{26}H_{29}N_2OPPt{\cdot}H_2O$	$C_{20}H_{24}Cl_2N_2P_2Pt{\cdot}CHCl_3$	$C_{20}H_{23}ClN_2P_2Pt$	$C_{35}H_{30}Cl_2N_2O_3P_2Pt{\cdot}CH_2Cl_2$
M	278.29	831.59	749.66	660.97	836.59	510.70	629.59	739.71	583.88	939.47
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	*Fdd2* (no. 43)	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a/Å	15.577(1)	11.994(4)	10.526(2)	10.530(2)	24.662(4)	9.42620(10)	9.6006(7)	9.3444(3)	11.3818(2)	11.19290(10)
b/Å	12.190(3)	15.236(3)	12.720(2)	12.715(1)	26.730(3)	18.80220(10)	9.9187(7)	15.4169(5)	13.2084(2)	11.43150(10)
c/Å	8.139(1)	9.839(3)	22.094(1)	22.115(1)	10.728(2)	10.16510(10)	13.3323(9)	19.5595(6)	14.19120(10)	16.5134(3)
α/°		94.12(2)					100.1220(10)			71.7460(10)
β/°	105.156(8)	113.79(2)	97.980(8)	98.097(8)		110.7120(10)	100.3670(10)	102.0410(10)		82.0510(10)
γ/°		90.39(2)					98.1210(10)			73.6220(10)
U/Å^3	1491.7(4)	1639.7(9)	2929.8(8)	2931.4(5)	7072(2)	1685.16(3)	1209.7(2)	2755.8(2)	2133.44(5)	1922.27(4)
Z	4	2	4	4	8	4	2	4	4	2
μ/mm^{-1}	1.541	10.376	9.889	6.371	5.742	8.980	5.891	5.705	6.859	4.048
Reflections measured	2449	5151	4877	4882	1479	7247	5390	22430	9437	8317
Independent reflections	2357	4878	4595	4600	1259	2431	3396	3934	3054	5405
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.050, 0.039	0.038, 0.040	0.025, 0.027	0.032, 0.030	0.039, 0.045	0.0212, 0.0516	0.0204, 0.0444	0.0434, 0.0883	0.0174, 0.0380	0.0262, 0.0616

Table 2 Selected bond lengths (Å) and angles (°) for Ph_2PNHpy **1**

P(1)–N(2)	1.705(3)	N(2)–C(2)	1.374(5)
C(2)–N(1)	1.329(4)	C(2)–C(3)	1.415(5)
C(7)–P(1)–N(2)	103.9(2)	C(13)–P(1)–N(2)	99.6(2)
P(1)–N(2)–C(2)	124.4(2)	C(7)–P(1)–C(13)	101.5(2)
N(2)–C(2)–N(1)	115.7(3)	N(2)–C(2)–C(3)	122.9(4)

Scheme 1 (*i*) Ph_2PNHpy, MeCN; (*ii*) KBr or NaI, acetone; (*iii*) ^{t}BuOK, MeOH; (*iv*) Ag[BF_4], CH_2Cl_2; (*v*) $HBF_4{\cdot}OEt_2$, CH_2Cl_2.

trans bis(ligand)- or mono(bidentate ligand)-palladium(II) or -platinum(II) complexes. By comparison, the Ph_2Ppy equivalents of **5** and **8** *cis*-[MCl(Ph_2Ppy-*P*,*N*){Ph_2Ppy-*P*}]$^+$ (where M = Pt[37] or Pd[38]) were prepared by the addition of one equivalent of halide abstractor to the appropriate *cis*-[MCl_2-{Ph_2Ppy-*P*}$_2$] complex in solution. The ^{31}P-{^{1}H} NMR spectrum (in $CDCl_3$) of **5** shows a broad singlet at δ(P) 51.4 with platinum satellites. The large $^1J(^{195}Pt–^{31}P)$ coupling constant of 3576 Hz is indicative of a *cis* arrangement of phosphines around a platinum(II) centre. Complete assignment of the ^{1}H NMR spectra (in $CDCl_3$) of **5** and **8** is difficult due to the fluxional nature (see below) of these molecules in solution. The expected downfield shifted pyridyl C[6] proton normally observed for complexes containing co-ordinated pyridine groups[12,39] is evident in the ^{1}H NMR spectra at δ(H) 8.24 for **5** and 8.12 for **8** and appears as a multiplet. The spectrum of **5** also displays a very broad resonance at δ(H) 11.2 with an integration which roughly equates to one proton. A D_2O exchange experiment was performed to determine whether this resonance was attributable to the pyridyl C[6] proton(s) or those of the amino groups and it was found to be due to the acidic amine protons. The anticipated high-frequency NH resonance was not apparent in the ^{1}H NMR spectrum of the palladium complex **8**. The line broadening of the amine resonance is most likely due to fluxionality within the molecule;

Table 3 Selected spectroscopic data for $Ph_2P(E)NHpy$, E = O, S or Se

	$\delta(^1H)$			IR(cm^{-1})			
Compound	NH	Aromatics	$\delta(^{31}P)$	P=E	PN	NH	CN(py)
2	—[a]	7.9–6.7	16.8	1196	950	3201	1599
3	7.8(d)[b]	8.1–6.7	51.6	642	941	—	1599
4	7.8(d)[b]	8.1–6.7	47.4[b]	550	941	—	1598

[a] Amine proton resonance obscured by aromatic resonances. [b] $^2J(^{31}P–^1H)$ 5 Hz. [c] $^1J(^{31}P–^{77}Se)$ 783 Hz.

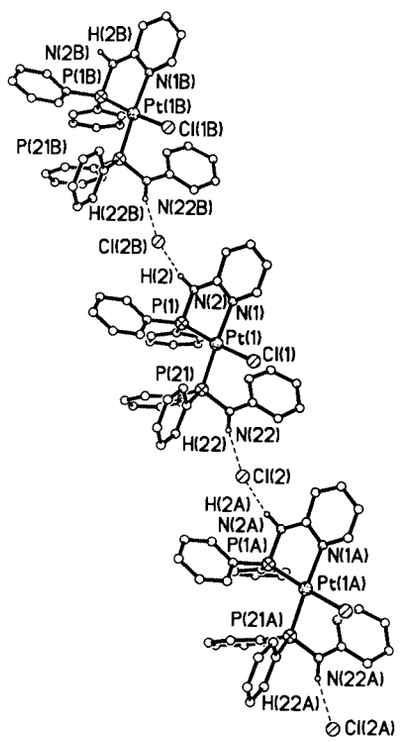


Fig. 4 Crystal structure of *cis*-[PtCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]-Cl **5** showing the hydrogen-bonded infinite chains.

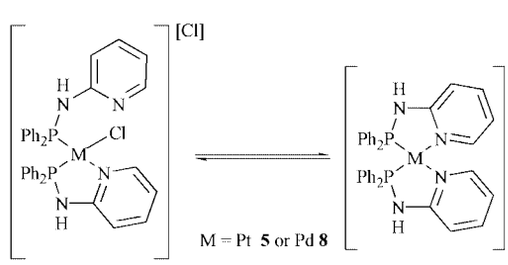
also hydrogen bonding to the counter ion may contribute to this effect. The expected free *ν*(N–H) in the IR spectra were not observed but the presence of strong broad bands at 2708 **5** and 2709 cm^{-1} **8** are characteristic of strong hydrogen-bonding interactions between the amine protons and the chloride counter ions, causing a significant reduction in the NH stretching frequency. Also contained within the IR spectrum are two bands [1615 and 1596 **5**, 1611 and 1597 cm^{-1} **8**] both of which correspond to pyridine ring *ν*(C=N) vibrations. The first band has significantly been shifted (to higher wavenumber by 11–14 cm^{-1});[7,12,39] the second is comparable with that of the "free" ligand value (1601 cm^{-1}) accounting for the chelating and 'dangling' ligands respectively. The positive-ion FAB mass spectra gave two clusters of peaks at *m*/*z* 750/1 and 786/7 for **5** and 698 and 663 for **8** which correspond to $[M - Cl]^+$ and $[M - 2Cl]^{2+}$ and micro analytical data were in good agreement with calculated values. The crystal structure of *cis*-[PtCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}]Cl **5** (Fig. 4, Table 4) shows that the molecule is square planar at platinum [maximum deviations from Pt(1)–Cl(1)–P(21)–N(1)–P(1) mean plane 0.2 Å below for Cl(1) and 0.14 Å above for P(21)] with distortions from idealised square-planar geometry at the metal due to the bulk of the phosphine groups and to the bite angle of the chelating ligand [P(21)–Pt(1)–P(1) 99.18(8), P(1)–Pt(1)–N(1) 82.9(2)°]. The five-membered Pt(1)–P(1)–N(2)–C(2)–N(1) ring is planar with a mean deviation of only 0.03 Å. The P(21)–N(22)–C(22) bond angle [123.7(6)°]

Table 4 Selected bond lengths (Å) and angles (°) for *cis*-[PtCl(Ph_2PNHpy-*P*,*N*){Ph_2PNHpy-*P*}Cl **5**

Pt(1)–P(1)	2.219(2)	Pt(1)–P(21)	2.252(2)
P(1)–N(2)	1.689(7)	P(21)–N(22)	1.686(6)
N(2)–C(2)	1.360(1)	N(22)–C(22)	1.380(1)
C(2)–N(1)	1.350(1)	C(22)–N(21)	1.330(1)
N(1)–Pt(1)	2.109(2)	Pt(1)–Cl(1)	2.345(2)
P(1)–Pt(1)–P(21)	99.18(8)	N(1)–Pt(1)–Cl(1)	92.0(2)
P(1)–Pt(1)–Cl(1)	172.79(7)	P(21)–Pt(1)–N(1)	176.5(2)
P(1)–Pt(1)–N(1)	82.9(2)	P(21)–Pt(1)–Cl(1)	86.20(8)
P(1)–N(2)–C(2)	120.2(6)	P(21)–N(22)–C(22)	123.7(6)
N(2)–C(2)–N(1)	118.0(7)	N(22)–C(22)–N(21)	117.1(7)

of the monodentate P bound ligand is very similar to that observed for the "free" ligand [124.4(2)°] and is marginally reduced upon chelation [120.2(6)°]. A small reduction in the P–N bond length [dppap P–N length, 1.705(3) Å] is displayed upon co-ordination to the platinum centre but no significant difference is observed between monodentate [1.686(6) Å] and bidentate [1.689(7) Å] ligand co-ordination modes. Although chelation causes no obvious change in P–N bond length the N(2)–C(2) and C(2)–N(1) bonds of the bidentate ligand are contracted and elongated by approximately 0.02 Å respectively. The Pt(1) and unbound pyridyl nitrogen N(21)···Pt distance of 3.06 Å does not rule out the proposed fluxional behaviour of the molecule. The structure also confirms the cationic nature of **5** and reveals that the chloride counter ion Cl(2) is involved in hydrogen-bonding interactions with two NH protons and acts as a bridge between adjacent molecules. The first is with an NH proton of a monodentate P bound ligand [H(22)···Cl(2) 2.34, Cl(2)···N(22) 3.223(7) Å, N(22)–H(22)···Cl(2) 160.6°]. The second interaction is with an NH proton of a chelating ligand on an adjacent molecule [H(2A)···Cl(2) 2.16, Cl(2)···N(2A) 3.111(7) Å, N(2A)–H(2A)···Cl(2) 169.1°] a consequence of which is the chain like packing of molecules in the crystal lattice. The solid state hydrogen bonding also explains the absence of free *ν*(N–H) bands corroborating the IR spectral assignment.

Clearly the $^{31}P-\{^1H\}$ NMR data for complex **5** contradict the solid state structure which should (if this species persists in solution) give an AX type spectrum. The broad phosphorus resonance is indicative of an intramolecular fluxional process (eqn. 2) which means that δ(P) is intermediate between values



(2)

observed for monodentate P bound and bidentate P–N bound structures. This type of behaviour has been observed in

a number of platinum(II) systems containing ligands having both phosphorus and nitrogen donor sites.[13,40] Habtemariam and Sadler[41] found that in solution (D_2O, pH 8.6) *cis*-[PtCl(Ph$_2$P(CH$_2$)$_2$NMe$_2$-*P*,*N*){Ph$_2$P(CH$_2$)$_2$NMe$_2$-*P*}]Cl (ring opened form) was in equilibrium with *cis*-[Pt{Ph$_2$P(CH$_2$)$_2$NMe$_2$-*P*,*N*}$_2$]Cl$_2$ (ring closed form). Their ^{31}P and ^{195}Pt NMR studies gave spectra with very broad peaks, which they suggested was due to a possible exchange reaction between the two species. Balch and co-workers[42] observed, by variable temperature ^{31}P-{^{1}H} NMR, a rapid exchange between *cis*-[PtI$_2${Ph$_2$Ppy-*P*}$_2$] and the chelated form *cis*-[PtI{Ph$_2$Ppy-*P*}(Ph$_2$Ppy-*P*,*N*)]I in dichloromethane. Their work showed that ionic dissociation is favoured at low temperatures. A variable temperature ^{31}P-{^{1}H} NMR study of *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*){Ph$_2$PNHpy-*P*}]Cl **5** in CD_2Cl_2 down to 183 K did not reveal any spectral changes. The bromo and iodo derivatives *cis*-[MX(Ph$_2$PNHpy-*P*,*N*){Ph$_2$PNHpy-*P*}]X (M = Pt, X = Br **6** or I **7**; M = Pd, X = Br **9** or I **10**) can be prepared by metathesis with an excess of the appropriate halide ion in refluxing acetone (Scheme 1). The complexes display IR and mass spectral data comparable to those of their chloro analogues; the ^{31}P-{^{1}H} NMR δ values (in dmso/C_6D_6) are closer to those observed for the dicationic species **13** and **14** suggesting that in solution the bis-chelate dicationic form is favoured.

Neutral bis-bidentate complexes of dppap

The first, and to the best of our knowledge only reported example of a complex containing the [Ph$_2$PNpy]$^-$ ligand is *trans*-[Ni(Ph$_2$PNpy-*P*,*N*)$_2$][43] prepared in 20% yield by the addition of phenyllithium to a thf solution of dppap followed by [NiBr$_2$(thf)$_2$]. We have found that deprotonation is possible under much milder conditions. Treatment of the dichloro species **5** and **8** with two equivalents of ^{t}BuOK in methanol leads to (Scheme 1) deprotonation of the dppap ligands giving neutral species *cis*-[M(Ph$_2$PNpy-*P*,*N*)$_2$] (M = Pt **11** or Pd **12**). Both the palladium and the platinum complexes display sharp single ^{31}P-{^{1}H} NMR resonances that occur at significantly higher frequencies than those of their starting materials, [δ(P) 63.0 **11** and 84.5 **12** , *cf.* 51.4 **5** and 71.4 **8**] since deprotonation results in the formation of stable, non-fluxional bis-chelate complexes (the chelate-ring effect).[44] Furthermore, the ^1J(^{195}Pt–^{31}P) coupling constant of **11** (3334 Hz) is considerably smaller than that of **5** (3576 Hz). The ^{1}H NMR spectra of **11** and **12** confirm the absence of any amine protons and the pyridyl C[6] protons are observed as multiplets at δ(H) 7.77 and are significantly shifted downfield from the remaining aromatic resonances. The IR spectra also lend evidence to support the proposed structure including the absence of any ν(N–H) bands and only one pyridyl ν(C=N) band occurring at slightly higher wavenumber [1609 **11** and 1604 cm^{-1} **12**] than for the "free" ligand [1601 cm^{-1} **1**]. Deprotonation of the amino group causes an increase in P–N bond order and shifts the ν(PN) to higher frequency compared to that of free dppap. This phenomenon has been observed in a number of related ligand systems containing PNP,[45,46] PNP(E) (E = O,[47–51] S or Se[52]), and (E)PNP(E) (E = O,[53–57] S[58–64] or Se[64–67]) backbones, where electron delocalisation upon deprotonation occurs over the three four or five atom backbone. Lengthening of the P=E and shortening of the P–N bonds is the net result. This effect is much less pronounced with P–N–py systems and only small changes in bond angles and lengths occur in the P–N–C–N backbone as a consequence of deprotonation (see below). In the platinum complex **11** deprotonation is accompanied by an increase in ν(PN) from 920 to 936 cm^{-1} and in the palladium complex **12** to 942 cm^{-1}. Microanalytical and mass spectral data were satisfactory for both complexes. The molecular structures of the platinum complex **11** and its palladium analogue **12** (Fig. 5, Table 5) display *cis* geometry with respect to the phosphorus atoms and are square planar at metal. Each complex consists of two chemically equivalent M–P–N–C–N rings, which, upon crystallographic examination, are found to contain subtle geometrical differences. The five-membered rings in the platinum complex **11** are slightly distorted from planar with P(1) lying 0.17 Å below the Pt(1)–P(1)–N(2)–C(2)–N(1) mean plane and P(2) lying 0.14 Å above the Pt(1)–P(2)–N(22)–C(22)–N(21) mean plane. The angle between these planes is 14°. The five-membered, PdPCN$_2$ rings of complex **12** exhibit similar deviations from planarity. The pyridyl nitrogens N(1) and N(21) lie 0.34 Å above and 0.28 Å below the Pd(1)–P(1)–N(2)–C(2)–N(1) and Pd(1)–P(2)–N(22)–C(22)–N(21) mean planes respectively and are inclined by *ca.* 12° to their respective five-membered rings. The P–N bond lengths are not significantly different, P(1)–N(2) and P(2)–N(22) [1.640(5), 1.644(5) Å for **11** and 1.638(3), 1.645(3) Å for **12**] but shorter than those observed for **5** [1.686(6) and 1.689(7) Å] and much shorter than in free dppap [1.705(3) Å]. A significantly larger contraction of the N(2)–C(2), N(22)–C(22) [1.332(7), 1.333(7) Å for **11** and 1.331(5), 1.341(5) Å for **12**] and elongation of the C(2)–N(1), C(22)–N(21) [1.390(7), 1.380(7) Å for **11** and 1.381(4), 1.374(5) Å for **12**] bonds is observed compared to those of the neutral chelating ligand in **5** [N(2)–C(2) 1.360(1) and C(2)–N(1) 1.350(1) Å]. The P–N–C bond angles [114.0(4) and 113.8(4)° for **11**, 114.7(3) and 114.5(3)° for **12**] are considerably smaller than those of either the "free" ligand **1** [124.4(2)°] or the chelating

Table 5 Selected bond lengths (Å) and angles (°) for complexes **11** and **12**

	11	**12**
M–P(1)	2.243(2)	2.247(1)
M–P(2)	2.234(1)	2.244(1)
P(1)–N(2)	1.640(5)	1.638(3)
P(2)–N(22)	1.644(5)	1.645(3)
N(2)–C(2)	1.322(7)	1.331(5)
N(22)–C(22)	1.333(7)	1.341(5)
C(2)–N(1)	1.390(7)	1.381(4)
C(22)–N(21)	1.380(7)	1.374(5)
N(1)–M	2.112(4)	2.119(3)
N(21)–M	2.112(4)	2.118(3)
P(1)–M–P(2)	105.68(5)	104.62(4)
N(1)–M–N(21)	97.7(1)	98.9(1)
P(1)–M–N(21)	169.1(1)	168.99(9)
P(2)–M–N(1)	172.8(1)	173.13(9)
P(1)–M–N(1)	79.0(1)	78.89(8)
P(2)–M–N(21)	78.7(1)	78.80(9)
M–P(1)–N(2)	104.5(2)	103.5(1)
M–P(2)–N(22)	105.5(2)	104.7(1)
P(1)–N(2)–C(2)	113.8(4)	114.7(3)
P(2)–N(22)–C(22)	114.0(4)	114.5(3)
N(2)–C(2)–N(1)	122.2(5)	121.1(4)
N(22)–C(22)–N(21)	121.6(5)	121.3(3)

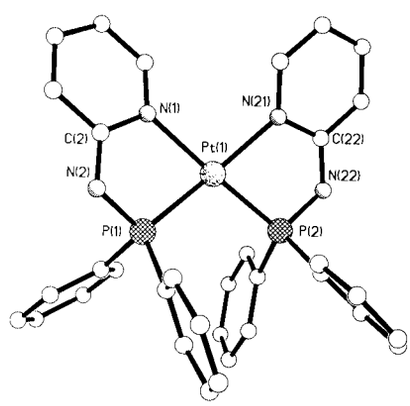


Fig. 5 Crystal structure of *cis*-[Pt(Ph$_2$PNpy-*P*,*N*)$_2$] **11**; *cis*-[Pd(Ph$_2$PNpy-*P*,*N*)$_2$] **12** is isomorphous and is not illustrated.

ligand of complex **5** [120.2(6)°]. This contraction in bond angle upon deprotonation is also observed in related systems containing other P–N–P fragments in their backbones.[45–67]

Dicationic bis-bidentate complexes of dppap

We have also found (Scheme 1) that chloride abstraction from *cis*-[MCl(Ph$_2$PNHpy-*P*,*N*){Ph$_2$PNHpy-*P*}]Cl (M = Pt **5** or Pd **8**) with Ag[BF$_4$] in dichloromethane affords the dicationic species *cis*-[M(Ph$_2$PNHpy-*P*,*N*)$_2$][BF$_4$]$_2$ (M = Pt **13** or Pd **14**). In addition, complexes **13** and **14** were easily prepared by treatment of *cis*-[M(Ph$_2$PNpy-*P*,*N*)$_2$] (M = Pt **11** or Pd **12**) with a small excess of HBF$_4$·OEt$_2$ in dichloromethane. Compounds **13** and **14** were isolated as cream solids in good yield (81 and 79% respectively) and display the expected spectral and analytical properties. The platinum complex displayed a sharp single resonance with platinum satellites in the ^{31}P-{^{1}H} NMR spectrum (in d$_6$-dmso) [δ(P) 64.1, ^1J(^{195}Pt–^{31}P) 3475 Hz]. Similarly, the palladium complex gave a sharp singlet at δ(P) 88.0. The ^{1}H NMR spectra (in d$_6$-dmso) of the two complexes clearly showed the NH proton resonances as multiplets at δ(H) 8.20 (**13**) and 8.17 (**14**) and the pyridyl C[6] proton resonances as multiplets at δ(H) 7.99 (**13**) and 7.97 (**14**). The IR spectra displayed broad ν(N–H) bands at 3235 cm^{-1}. This shift to higher wavenumber, compared to that of *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*){Ph$_2$PNHpy-*P*}]Cl **5** [ν(N–H) 2666 cm^{-1}], is because of the much weaker hydrogen bonding between the amine protons and the [BF$_4$]$^-$ anions. Additional bands for both **13** and **14** at *ca.* 900 cm^{-1} [ν(P–N)], and single bands at higher wavenumber than that of free dppap, at 1615 cm^{-1} [ν(py C=N)], indicative of protonated ligand and pyridyl co-ordination respectively, were in evidence. Microanalytical data were satisfactory and the positive ion FAB mass spectra gave, for both complexes, the expected [M − 2BF$_4$]$^{2+}$ parent ion with appropriate isotope distribution and fragmentation patterns. The structure of *cis*-[Pd(Ph$_2$PNHpy-*P*,*N*)$_2$][BF$_4$]$_2$ **14** (Fig. 6, Table 6) reveals it to be a four-co-ordinate species with *cis* geometry and is square planar at palladium. In addition the molecule possesses crystallographic twofold symmetry, the palladium atom is located on the twofold axis. The small bite angle of the ligand causes considerable distortions from idealised square planar geometry. The *trans* P–Pd–N [167.6(2)°] axes are less than 180° and the *cis* P–Pd–P [101.9(1)°] and N–Pd–N [98.3(5)°] angles exceed 90°. The five-membered rings of **14** are slightly puckered with the amine nitrogen N(1) lying 0.2 Å above the Pd(1)–P(1)–N(2)–C(2)–N(1) mean plane. The angle between the planes defined by the two rings is 21°. The P(1)–N(2)–C(2) angle is 119.1(6)° whilst the P(1)–N(2), N(2)–C(2) and C(2)–N(1) distances are 1.677(7), 1.39(1) and 1.33(1) Å respectively. The P(1)–N(2)–C(2) angle and the P(1)–N(2) distance are as expected for protonated chelating ligands, however a small increase (the converse of previously discussed examples) in the N(2)–C(2) distance is exhibited. In addition, the elongation of the C(2)–N(1) bond (also evident in previous examples) does not occur. The crystal structure also shows that the NH protons are hydrogen bonded to the [BF$_4$]$^-$ counter ions [H(2)···F(3) 2.24, F(3)···N(2) 2.95(1), N(2)–H(2)···F(3) 163.0°].

Reactions of dppap with [PtMeX(cod)] (where X = Me or Cl)

Reaction of two equivalents of complex **1** with [PtMe$_2$(cod)] gives a mixture of products. ^{31}P-{^{1}H} NMR shows three singlet resonances; δ(P) 26.4 corresponding to unchanged ligand, δ(P) 54.3 [^1J(^{195}Pt–^{31}P) 2090 Hz] to [PtMe$_2${Ph$_2$PNHpy-*P*}$_2$] and δ(P) 70.7 [^1J(^{195}Pt–^{31}P) 2178 Hz] to [PtMe$_2$(Ph$_2$PNHpy-*P*,*N*)]. The observed difference in chemical shift of these two complexes is also evident in *cf.* **5** and **13** where increased δ(P) values were obtained upon chelation (the chelate ring effect).[44] The relative intensities of the signals indicates that the expected complex [PtMe$_2${Ph$_2$PNHpy-*P*}$_2$] constitutes approximately

Table 6 Selected bond lengths (Å) and angles (°) for *cis*-[Pd(Ph$_2$PNHpy-*P*,*N*)$_2$][BF$_4$]$_2$ **14**

Pd(1)–P(1)	2.234(2)	C(2)–N(1)	1.33(1)
P(1)–N(2)	1.677(7)	N(1)–Pd(1)	2.084(9)
N(2)–C(2)	1.39(1)		
P(1)–Pd(1)–P(1A)	101.9(1)	N(1)–Pd(1)–N(1A)	98.3(5)
P(1)–Pd(1)–N(1A)	167.6(2)	P(1)–N(2)–C(2)	119.1(6)
P(1)–Pd(1)–N(1)	81.2(2)	C(2)–N(1)–Pd(1)	119.8(7)
N(2)–C(2)–N(1)	114.2(8)		

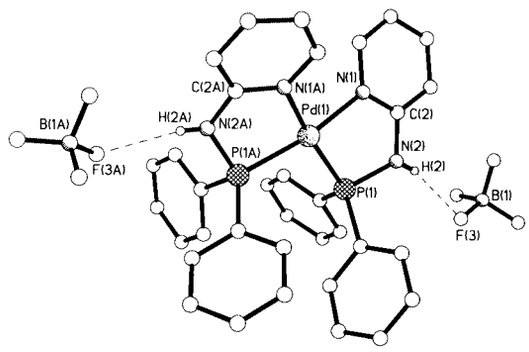
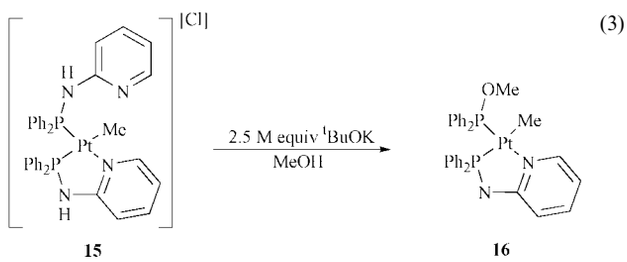


Fig. 6 Crystal structure of *cis*-[Pd(Ph$_2$PNHpy-*P*,*N*)$_2$][BF$_4$]$_2$ **14**.

70% of the isolated material. The positive-ion FAB mass spectrum gave parent ion peaks which coincide with the proposed species observed in the ^{31}P-{^{1}H} NMR spectrum. Slow dropwise addition of a CH$_2$Cl$_2$ solution of **1** to a solution of [PtMe$_2$(cod)] in the same solvent gave by ^{31}P-{^{1}H} NMR [PtMe$_2$(Ph$_2$PNHpy-*P*,*N*)] exclusively. All attempts to isolate this material from the reaction mixture failed due to its extremely high solubility in all common solvents. The preparation of [PtMe$_2${Ph$_2$PNHpy-*P*}$_2$] as a pure solid was abandoned due to constant contamination with unchanged ligand and the mono(bidentate ligand) species. By comparison, the addition of two equivalents of solid Ph$_2$PNHpy **1** to a dichloromethane solution of [PtClMe(cod)] gave a single product, characterised as *cis*-[PtMe(Ph$_2$PNHpy-*P*,*N*){Ph$_2$PNHpy-*P*}]Cl **15**, in 95% yield. The Ph$_2$Ppy equivalent of **15** *cis*-[PtMe(Ph$_2$Ppy-*P*,*N*){Ph$_2$Ppy-*P*}][BF$_4$] was prepared by the addition of a halide abstractor to *cis*-[PtClMe{Ph$_2$Ppy-*P*}$_2$] in solution and the product has crystallographically been characterised.[68] There is good ^{31}P-{^{1}H} NMR evidence for the structural assignment of **15**. The complex displays a well resolved AX type ^{31}P-{^{1}H} NMR spectrum, with a low frequency resonance at δ(P) 38.4 [^1J(^{195}Pt-^{31}P$_A$) 3948 Hz] assigned to monodentate P bound ligand *trans* to pyridyl nitrogen of the chelating ligand. The observed large *trans* P–Pt–N(py) coupling constant [3948 Hz] is much greater than that observed for *cis*-[Pt(PPh$_3$)$_2$(py)$_2$][ClO$_4$]$_2$[69] [3276 Hz] but is in fairly good agreement with that of *cis*-[PtMe(Ph$_2$Ppy-*P*,*N*){Ph$_2$Ppy-*P*}]-[BF$_4$][68] [4226 Hz]. The high frequency resonance occurs at δ(P) 84.2 [^1J(^{195}Pt–^{31}P$_X$) 2019 Hz] assigned to the PN chelating ligand and displays a typical *trans* P–Pt–Me coupling constant. The small ^2J(^{31}P$_A$–^{31}P$_X$) coupling constant of 11 Hz is indicative of a mutual *cis* arrangement of phosphines around the metal. Further evidence is provided by the ^{1}H NMR spectrum (in CDCl$_3$) which shows a broad peak at δ(H) 11.5 and a multiplet at δ(H) 8.3 assigned respectively to the amine and the pyridyl C[6] protons of the chelating ligand. Two broad doublets δ(H) 7.8 and 8.0 have been tentatively assigned to the amine and pyridyl C[6] protons respectively of the 'dangling' P bound ligand. The methyl group resonance appears as a double doublet at δ(H) 0.64 [^3J(^{31}P–^{1}H) 4, ^2J(^{195}Pt–^{1}H) 51 Hz]. The IR spectrum of **15** is very similar to those of **5** and **8** with respect to the absence of the expected free ν(N–H) band. The lack of which, considering the structural similarities of **5** and

15, is almost certainly due to the same type of solid state hydrogen bonding observed in the crystal structure of **5**. This assumption is supported by the broad ν(N–H) band at 2706 cm^{-1} which, as discussed earlier, is characteristic of strongly hydrogen-bonded NH protons. Also, there are two bands at 1614 and 1592 cm^{-1} assigned as the ν(C=N) of the pyridine ring, indicative of two dppap co-ordination modes, bidentate PN and 'dangling' P bound. The absence of a ν(Pt–Cl) stretch is also consistent with the proposed structure. Microanalytical data were in good agreement with calculated values and the positive ion FAB mass spectrum showed a peak at *m/z* 766 which corresponds to $[PtMe(Ph_2PNHpy)_2]^+$. No attempt to synthesize mono(bidentate ligand) complexes from [PtClMe(cod)] was made. Reaction of **15** with 2.5 molar equivalents of ^{t}BuOK in methanol leads to Ph_2P–N bond cleavage of one of the dppap ligands and deprotonation of the other to give, in 78% yield, the unexpected platinum(II) species *cis*-$[PtMe(Ph_2PNpy\text{-}P,N)\{Ph_2POMe\text{-}P\}]$ **16** (eqn. 3). The AX ^{31}P-{^{1}H} NMR



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spectrum (in $CDCl_3$) of **16** shows a high-frequency resonance at δ(P) 100.6 [$^1J(^{195}Pt–^{31}P)$ 4447 Hz], which we have assigned as the co-ordinated Ph_2POMe. Although comparison of the previously mentioned Ph_2POMe δ(P) and *J* values found for **16** to those observed for *cis*-$[PtCl_2(Ph_2POMe)_2]$, δ(P) 85.6 [$^1J(^{195}Pt–^{31}P)$ 4175 Hz],[70] is not entirely valid it highlights the high frequency resonances and the large *J* values associated with platinum(II) methyl diphenylphosphinite complexes. The lower frequency resonance occurs at δ(P) 90.0 [$^1J(^{195}Pt–^{31}P)$ 1950 Hz], and is assigned to the deprotonated chelating ligand. The small coupling constant [1950 Hz] is similar to that of complex **15** [2019 Hz], establishing that the chelating ligand *trans* P–Pt–Me geometry of **15** persists in **16**. Additional evidence in support of the proposed retention of *cis* geometry is the small $^2J(^{31}P_A–^{31}P_X)$ coupling constant of 8 Hz, a value consistent with a *cis* configuration of ligands. The ^{1}H NMR spectrum of **16** supports the proposed structural assignment. The absence of amine proton resonances and the presence of the anticipated pyridyl C[6] proton multiplet at δ(H) 8.1 are in accord with the structure, but, most significant, is the doublet resonance of the P–OMe methyl group that integrates to three protons at δ(H) 3.0 [$^3J(^{31}P–^1H)$ 8 Hz] . The three methyl protons in common with complex **15** occur as a double doublet at δ(H) 0.25 [$^3J(^{31}P–^1H)$ 4, $^2J(^{195}Pt–^1H)$ 55 Hz]. Supporting IR data include only one pyridyl ν(CN) band [1613 cm^{-1}] in contrast to two [1614 and 1592 cm^{-1}] observed for complex **15** and the ν(PN) band [937 cm^{-1}] at higher energy than those of **15** [907 cm^{-1}], which is indicative of deprotonation. Microanalytical data were satisfactory and the positive-ion FAB mass spectrum gave the expected parent ion for $[PtMe(Ph_2PNpy)(Ph_2POMe)]^+$ at *m/z* = 704 and isotope distribution patterns.

Although the synthesis of complex **16**, *via* methanolysis of a Ph_2P–N bond, is rather unusual, a number of similar Ph_2P–N bond cleavage reactions have been observed. Krishnamurthy and co-workers[71] recently reported the facile P–N bond cleavage in unsymmetrical diphosphazene complexes of palladium(II) giving products of the type $[PdCl_2\{PhP(NH^iPr)R\}(Ph_2POMe)]$ (where R = OC_6H_4Br-4 or $OC_6H_3Me_2$-3,5). Browning and Farrar[72] reported a similar reaction in the dicationic platinum(II) complex $[Pt(dppma)_2]^{2+}$ [dppma = bis(diphenylphosphino)methylamine, $Ph_2PN(Me)PPh_2$], yielding $[Pt\{Ph_2PN(Me)PPh_2\}(Ph_2PNHMe)(Ph_2POMe)]^{2+}$. In addition to the above examples of ring opening reactions, recent publications from our group have demonstrated that methanolysis of Ph_2P–N bonds in complexes bearing monodentate phosphines can be induced by prolonged reflux in methanol[49] or *via* the reaction of four equivalents of $Ph_2PNHP(O)Ph_2$ with the cyclometallated dimer $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}o\text{-}C,N)\}_2]$ in methanol at ambient temperature yielding $[PdCl\{Ph_2PNP(O)Ph_2\text{-}P,O\}(Ph_2POMe)]$.[48]

Table 7 Selected bond lengths (Å) and angles (°) for $[AuCl(Ph_2PNHpy\text{-}P)]$ **17**

Cl(1)–Au(1)	2.2813(12)	Au(1)–P(1)	2.2187(11)
P(1)–N(2)	1.687(4)	N(2)–C(2)	1.399(7)
C(2)–N(1)	1.336(6)		
Cl(1)–Au(1)–P(1)	177.14(5)	Au(1)–P(1)–N(2)	114.3(2)
P(1)–N(2)–C(2)	121.7(3)	N(2)–C(2)–N(1)	116.0(4)

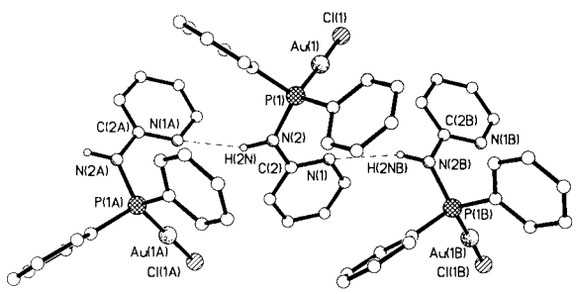


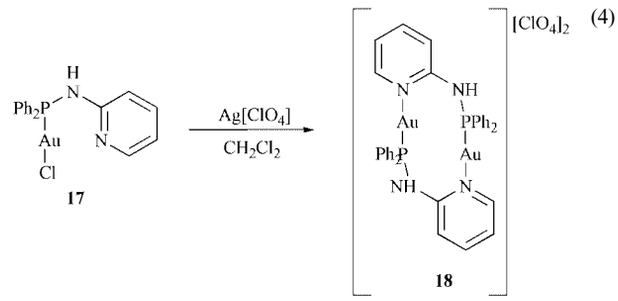
Fig. 7 Crystal structure of $[AuCl\{Ph_2PNHpy\text{-}P\}]$ **17** showing the hydrogen-bonded infinite chains.

Gold complexes of dppap

The reaction of dppap with [AuCl(tht)] proceeds by the displacement of tht to give the anticipated product $[AuCl\{Ph_2PNHpy\text{-}P\}]$ **17** in excellent yield (90%). The complex exhibits the expected spectroscopic and analytical properties. It showed a single sharp resonance in the ^{31}P-{^{1}H} NMR spectrum (in $CDCl_3$) at δ(P) 55.4 and the ^{1}H NMR spectrum in the same solvent showed the pyridyl C[6] proton as a multiplet at δ(H) 8.01 and that the amine proton was obscured by the aromatic resonances. From the IR spectrum we can identify a strong ν(N–H) band at 3373 cm^{-1}; in contrast to previously discussed complexes where strong hydrogen-bonding interactions have broadened and shifted this band to a much lower frequency. We can also identify ν(P–N) at 909 cm^{-1} and ν(py C=N) at 1593 cm^{-1} which is at lower wavenumber than the "free" ligand vibration (1601 cm^{-1}) which suggests that there is little, if any, interaction between the pyridyl nitrogen and the gold atom. Suitable crystals of **17** were grown by slow diffusion of diethyl ether into a dichloromethane solution.

The crystal structure (Fig. 7, Table 7) confirmed the absence of any interaction between the gold and pyridyl nitrogen atoms; the Au(1)···N(1) distance is 3.23 Å. The Cl(1)–Au(1)–P(1) angle at 177.14(5)° is unremarkable and the P(1)–N(2)–C(2) angle of 121.7(3)° is as expected for a monodentate P bound ligand. The P(1)–N(2) and C(2)–N(1) distances of 1.687(4) and 1.336(6) Å are as anticipated. A long distance intermolecular hydrogen-bonding interaction between the NH proton H(2N) and the pyridyl nitrogen N(1A) of adjacent molecules is evident. The H(2N)···N(1A) distance of 2.06 Å and the N(2)–H(2N)···N(1A) angle of 139° may be compared with those in **1** [H(2N)···N(1A) 2.04 Å] and [N(2)–H(2N)···N(1A) 160°].

Treatment of **17** in dichloromethane with solid $Ag[ClO_4]$ gave after work-up a white powder which we have characterised as $[\{Au(\mu\text{-}Ph_2PNHpy\text{-}P,N)\}_2][ClO_4]_2$ (HT) **18** (HT = head to

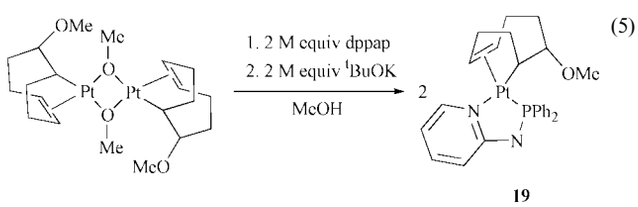


(4)

tail), eqn. (4). The complex displays a sharp single resonance in the ^{31}P-{^{1}H} NMR (in CH_2Cl_2–C_6D_6) at δ(P) 62.7, a shift to higher frequency of 7 ppm relative to the starting material **16**. The ^{1}H NMR was particularly uninformative but the IR spectrum showed a higher energy pyridyl ν(C=N) band at 1611 cm^{-1} compared to 1592 cm^{-1} for **15** which is indicative of co-ordinating behaviour. The positive-ion FAB mass spectrum gave evidence for the formation of the bimetallic species showing a peak at *m*/*z* 951 which corresponds to [{Au(μ-Ph_2PNHpy-*P*,*N*)}$_2$]$^{2+}$. Attempts to grow crystals of **18** from MeOH–Et_2O and CH_2Cl_2–Et_2O solvent systems resulted in complete decomposition and isolation of crystalline Au[ClO_4].

Bridge cleavage reactions of dppap

The rapid sequential addition of two equivalents of Ph_2PNHpy **1** followed by ^{t}BuOK to a suspension of [{Pt(μ-OMe)(C_8H_{12}-OMe)}$_2$] in methanol resulted in methoxy bridge cleavage of the platinum(II) dimer, eqn. (5). Obtaining the product (which was



(5)

first isolated as a pale yellow oil) as a solid proved troublesome. Precipitation (of a pale yellow solid) was finally achieved by dropwise addition of distilled water to a methanol solution of **19**. Examination of this material by ^{31}P-{^{1}H} NMR (in $CDCl_3$) showed that a single phosphorus-containing product had been isolated, characterised as [Pt(C_8H_{12}OMe)(Ph_2PNpy-*P*,*N*)] **19**. The ^{31}P-{^{1}H} NMR displays a single resonance at δ(P) 63.2 which is very similar to δ(P) 63.0 observed for *cis*-[Pt(Ph_2PNpy-*P*,*N*)$_2$] **11**. The large ^{1}J(^{195}Pt–^{31}P) of 4087 Hz enabled us to establish which isomer had been synthesized, *i.e.* phosphorus *trans* to the olefin portion of C_8H_{12}OMe, as P *trans* to Pt–C bonds have typical ^{1}J(^{195}Pt–^{31}P) values of 2000 Hz. The ^{1}H NMR spectrum gave the expected C_8H_{12}OMe resonances and also confirmed that the ligand was deprotonated. Assignment of the IR spectrum was difficult but we were able to identify ν(py C=N) at 1607 cm^{-1} and ν(P–N) at 941 cm^{-1} which are consistent with deprotonated chelating ligand behaviour and also very close to those found for complex **11** [ν(py C=N) 1609, ν(P–N) 936 cm^{-1}]. Micro analytical data were satisfactory and the positive-ion FAB mass spectrum gave the expected parent ion peak. The crystal structure of **19** (Fig. 8, Table 8) shows that the complex is approximately square planar at platinum with the predicted phosphorus *trans* to olefin geometry. The five-membered Pt(1)–P(1)–N(2)–C(2)–N(1) ring is planar with a mean deviation of only 0.01 Å. The bond lengths and angles of the ring are very similar to those observed in the $PtPCN_2$ rings of *cis*-[Pt(Ph_2PNpy-*P*,*N*)$_2$] **11**, most notably the contracted P(1)–N(2)–C(2) angle [115.3(3)°] and the reduced P(1)–N(2) distance [1.647(3) Å]. The crystal structure clearly established the presence of water molecules in the lattice and their bridging

Table 8 Selected bond lengths (Å) and angles (°) for [Pt(C_8H_{12}OMe)-(Ph_2PNpy-*P*,*N*)]·H_2O **19**

Pt(1)–P(1)	2.2233(11)	Pt(1)–N(1)	2.132(3)
Pt(1)–C(23)	2.064(4)	P(1)–N(2)	1.647(3)
Pt(1)–C(19)	2.261(4)	N(2)–C(2)	1.354(5)
Pt(1)–C(20)	2.290(5)	C(2)–N(1)	1.380(5)
P(1)–Pt(1)–N(1)	79.77(9)	N(1)–Pt(1)–C(20)	103.6(2)
P(1)–Pt(1)–C(23)	96.43(13)	C(23)–Pt(1)–C(19)	87.8(2)
P(1)–Pt(1)–C(19)	155.68(14)	C(23)–Pt(1)–C(20)	80.2(2)
P(1)–Pt(1)–C(20)	169.13(14)	Pt(1)–P(1)–N(2)	106.97(13)
N(1)–Pt(1)–C(23)	176.2(2)	P(1)–N(2)–C(2)	115.3(3)
N(1)–Pt(1)–C(19)	95.4(2)	N(2)–C(2)–N(1)	121.4(4)

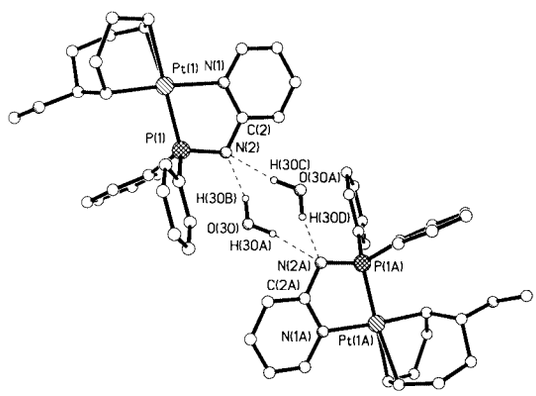
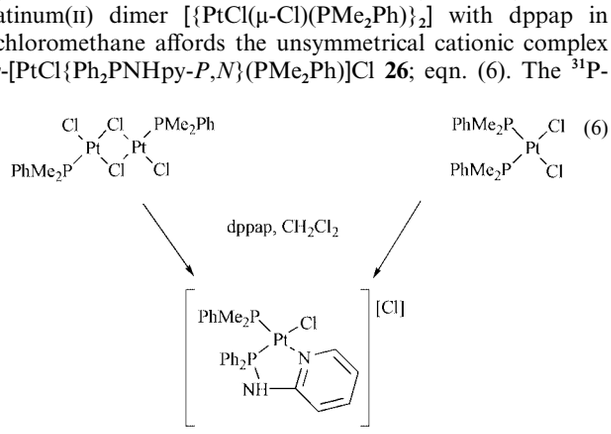


Fig. 8 Crystal structure of [Pt(C_8H_{12}OMe)(Ph_2PNpy-*P*,*N*)]·H_2O **19** illustrating the hydrogen-bonding.

role in dimer formation. The pseudo-eight membered ring is symmetric and displays two distinct pairs of hydrogen bonds [H(30A)···N(2) 2.14, N(2)···O(30) 3.11 Å, O(30)–H(30A)···N(2) 167° and H(30B)···N(2A) 2.01, N(2A)···O(30) 2.95 Å, O(30)–H(30b)···N(2A) 162°]. The six-membered O_2H_4 ring is inclined by *ca* 76° to the co-ordination plane.

The synthesis of the mixed ligand complex *cis*-[PtMe-(Ph_2PNpy-*P*,*N*){Ph_2POMe-*P*}] **16**, discussed above, represents a rather unusual reaction. A more established route to complexes of the type [$MCl_2(PR_3)(PR'_3)$] is *via* a redistribution reaction and a number of mixed phosphine ligand complexes of platinum(II) and palladium(II) have previously been reported.[73,74] We found that chloride bridge cleavage of the platinum(II) dimer [{PtCl(μ-Cl)(PMe_2Ph)}$_2$] with dppap in dichloromethane affords the unsymmetrical cationic complex *cis*-[PtCl{Ph_2PNHpy-*P*,*N*}(PMe_2Ph)]Cl **26**; eqn. (6). The ^{31}P-



(6)

{^{1}H} NMR spectrum (in $CDCl_3$) of **26** is an AX type with platinum satellites, and reveals a small phosphorus–phosphorus coupling constant indicative of a structure with a mutual *cis* arrangement of phosphine ligands. The chemical shift of the P–N ligand, δ(P) 62.2, and the sharp spectral lines suggest bidentate co-ordination behaviour with no fluxionality. This is

substantiated upon examination of the ^{1}H NMR spectrum which shows the amine proton as a broad multiplet at δ(H) 12.22 and the pyridyl C[6] proton as a multiplet at δ(H) 9.17 both significantly shifted to higher frequency than those observed for the "free" ligand [δ(H) 7.97 C[6]H and 5.71 NH **1**], which are also consistent with chelating behaviour. The cationic nature of the complex is exemplified by the very broad ν(N–H) band at 2570 cm^{-1} in the IR spectrum, which is characteristic of strong hydrogen bonding, in this case with the chloride counter ion.

Cationic mixed ligand complexes of Pt^{II} and Pd^{II}

We also found that complex **26** was the sole product formed upon reaction of dppap with *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] in dichloromethane (eqn. 6) confirmed by ^{31}P-{^{1}H} NMR. The crude product was precipitated by the addition of diethyl ether to the reaction mixture but recrystallisation from dichloromethane–diethyl ether was necessary to remove residual PMe$_2$Ph, evidenced by its characteristic odours and line broadening in the ^{31}P-{^{1}H} NMR spectrum. The reaction proceeds rapidly by substitution of PMe$_2$Ph and halide, presumably as a consequence of the chelate ring effect. This substitution reaction was generally applied in the synthesis of a range of unsymmetrical cationic mixed ligand platinum and palladium complexes of the type *cis*-[MX′(Ph$_2$PNHpy-*P*,*N*)(PR$_3$)]X (M = Pt, X' = X = Cl, PR$_3$ = PMe$_3$ **20**, PEt$_3$ **22**, P^{n}Bu$_3$ **24**, PMe$_2$Ph **26**, PPh$_2$H **28** or PPh$_3$ **29**; X′ = X = Br **31** or I **32**, PR$_3$ = PPh$_3$); X′ = Me, X = Cl, Pr$_3$ = PPh$_3$; **33**, X′ = X = Cl, PR$_3$ = P(OMe)$_3$ **34**, P(OEt)$_3$ **36**, P(O^{n}Bu)$_3$ **38** or P(OPh)$_3$ **39**; M = Pd, X′ = X = Cl, PR$_3$ = PMe$_2$Ph **41**, PPh$_3$ **43**, P(OMe)$_3$ **45**, P(OEt)$_3$ **46**, P(O^{n}Bu)$_3$) **47** or P(OPh)$_3$ **48**). Of the complexes listed above the majority were synthesized using solutions of solid [MCl$_2$(PR$_3$)$_2$] (M = Pt or Pd) type materials. The formation and isolation in good to excellent yield (82–96%) of complexes **24**, **38**, **46** and **47** by addition of dppap to quickly prepared dichloromethane solutions of [MCl$_2$(cod)] (M = Pt or Pd) and the appropriate phosphorus ligand clearly demonstrates that precursor isolation and purification is not necessary. All of the complexes displayed similar spectroscopic properties to those described for compound **26**, *i.e.* AX type ^{31}P-{^{1}H} NMR spectra with small ^{2}J(^{31}P$_A$–^{31}P$_X$) coupling constants. High frequency pyridyl C[6]H and amine proton resonances as well as broad ν(NH) bands were in evidence in the ^{1}H NMR and IR spectra respectively. As well as the characterising data described above the ^{1}H NMR spectrum of *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)-(PPh$_2$H)]Cl **28** displays a doublet at δ(H) 5.22 with platinum satellites [^1J(^{195}Pt–^{1}H) 90 Hz] due to the PPh$_2$H proton as well a ^1J(^{31}P–^{1}H) of 395 Hz in the non-decoupled ^{31}P NMR. Also the IR spectrum contains a band at 2319 cm^{-1} which is characteristic of ν(P-H). The chloro **29**, bromo **31** and iodo **32** analogues of *cis*-[PtX(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]X were prepared in an identical manner from the relevant [PtX$_2$(PPh$_3$)$_2$] (X = Cl, Br or I) starting material. However, we also found that **31** and **32** could be prepared from the chloro analogue **29** by metathesis with a large excess of the appropriate halide ion in refluxing acetone, a procedure which should be applicable, but was not extended to other chloro-complexes. Poorly resolved ^{31}P-{^{1}H} NMR spectra were obtained for complexes **31** and **32** when run in CDCl$_3$ due to rapid halide exchange with the solvent. The CDCl$_3$ solutions of **31** and **32** were left to stand for 1 week and then re-examined by ^{31}P-{^{1}H} NMR had undergone 100% conversion into the corresponding chloro-complexes. Positive ion FAB mass spectral and micro analytical data were consistent with the proposed structural assignments of **31** and **32**. The addition of a stoichiometric quantity of dppap to a dichloromethane solution of *cis*-[PtClMe(PPh$_3$)$_2$] gave the anticipated product *cis*-[PtMe(Ph$_2$PNHpy-*P*,*N*)(PPh$_3$)]Cl **33**, in 88% yield. The expected AX type ^{31}P-{^{1}H} NMR spectrum in CDCl$_3$ is displayed, and shows a high-frequency resonance at δ(P) 82.3

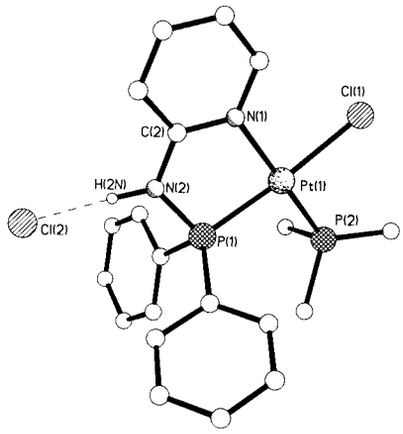


Fig. 9 Crystal structure of *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PMe$_3$)]Cl **20**.

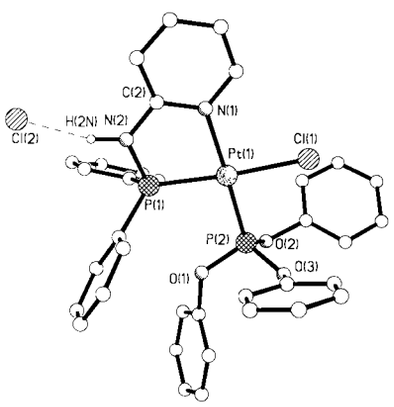


Fig. 10 Crystal structure of *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(P(OPh)$_3$)]Cl **39**.

[^1J(^{195}Pt–^{31}P) 2013 Hz], assigned to the chelating PN ligand with the phosphorus donor atom as suggested by the magnitude of the coupling constant lying *trans* to the Pt–C bond. The lower frequency resonance at δ(P) 16.7 [^1J(^{195}Pt–^{31}P$_A$) 3948 Hz] displays a large platinum–phosphorus coupling constant that is identical to the value observed for complex **15** [^1J(^{195}Pt–^{31}P$_A$) 3948 Hz] which has the same *cis* R$_3$P–Pt–N(py) geometry. The ^{1}H NMR (CDCl$_3$) spectrum of **33** shows the methyl protons as a double doublet with platinum satellites at δ(H) 0.62 [^2J(^{195}Pt–^{1}H) 50 Hz]. The platinum complexes **36**, **38** and **39**, which have co-ordinated triethyl, tributyl and triphenyl phosphite groups respectively, all display the characteristically large coupling constants expected for these ligands. Most of the products were isolated as analytically pure crystalline solids after one or two recrystallisations from dichloromethane–diethyl ether. The one exception was *cis*-[PtCl{Ph$_2$PNHpy-*P*,*N*}(PMe$_3$)]Cl **20**, which was stirred overnight in a thf–dichloromethane mixture with elemental sulfur which effected oxidation of the residual PMe$_3$ allowing its removal from the complex. The crystal structures of **20** and **39** (Figs. 9 and 10 and Table 9) show the anticipated *cis* geometry of phosphorus atoms and reveal square-planar geometry at platinum [maximum deviations from Pt(1)–P(1)–P(2)–Cl(1)–N(1) mean plane 0.4 Pt(1) and 0.01 Å Pt(1) for **20** and **39** respectively]. A small difference is observed in the planarity of the Pt(1)–P(1)–N(2)–C(2)–N(1) five-membered rings. The ring of **20** is near planar with a mean deviation of only 0.05 Å, whilst that of **39** is slightly more distorted with maximum deviations of 0.09 Å above and below the mean plane for P(1) and N(2) respectively. The P(2) and Cl(1) substituents of both complexes lie significantly below the previously specified mean ring plane by 0.28 P(2) and 0.16 Å Cl(1) for **20** and 0.26 P(2) and 0.24 Å Cl(1) for **39**. Interestingly, in these cases the pyridyl plane is only

Table 9 Selected bond lengths (Å) and angles (°) for complexes **20** and **39**

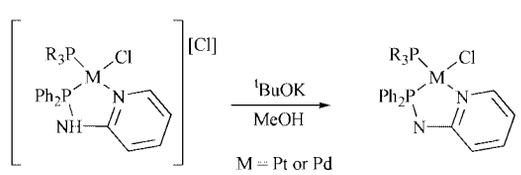
	20	**30**
Pt(1)–P(1)	2.216(2)	2.2338(13)
Pt(1)–P(2)	2.258(3)	2.2113(12)
Pt(1)–N(1)	2.129(7)	2.117(4)
Pt(1)–Cl(1)	2.358(2)	2.3459(14)
P(1)–N(2)	1.681(7)	1.681(4)
N(2)–C(2)	1.376(10)	1.374(6)
C(2)–N(1)	1.337(9)	1.353(6)
P(1)–Pt(1)–P(2)	97.27(8)	96.03(5)
N(1)–Pt(1)–Cl(1)	91.9(2)	92.77(11)
P(1)–Pt(1)–N(1)	82.6(2)	82.50(11)
P(2)–Pt(1)–Cl(1)	88.29(9)	88.69(5)
P(1)–Pt(1)–Cl(1)	174.44(8)	175.27(5)
P(2)–Pt(1)–N(1)	176.9(2)	178.14(12)
Pt(1)–P(1)–N(2)	101.3(2)	100.7(2)
P(1)–N(2)–C(2)	119.8(5)	120.1(3)
N(2)–C(2)–N(1)	118.5(7)	118.0(4)
C(2)–N(1)–Pt(1)	116.8(5)	117.0(3)

inclined by *ca.* 5° to the $MPCN_2$ ring plane. The bond lengths and angles of **20** and **39** are very similar to those displayed by the previously discussed platinum(II) complex **5**. Another feature of **20** and **39** common to **5** is the cationic nature of the complexes and the hydrogen-bonding interaction between the amine proton H(2N) and the chloride counter ion Cl(2) [H(2N)···Cl(2) 2.14, Cl(2)···N(2) 3.01 Å, N(2)–H(2N)···Cl(2) 167° for complex **20** and H(2N)···Cl(2) 2.11, Cl(2)···N(2) 3.06 Å, N(2)–H(2N)···Cl(2) 161° for **39**].

In contrast to its rapid reaction with *cis*-$[MCl_2(PR_3)_2]$ (M = Pt or Pd) dppap is unreactive towards *trans*-$[MCl_2(PCy_3)_2]$ (M = Pt or Pd) even after prolonged reflux in thf. Examination of the reaction mixture after 48 h at reflux showed the presence of only *trans*-$[MCl_2(PCy_3)_2]$ (M = Pt or Pd) and dppap. We can only assume that the inertness of the *trans* complexes is due to steric bulk of the PCy_3 ligands, which is great enough to prevent approach of the dppap molecule to the metal centre.

Neutral mixed ligand complexes of Pt^{II} and Pd^{II}

Using the same synthetic approach used to generate the neutral bis-chelate complexes **11** and **12** neutral species of the type *cis*-[MCl(Ph$_2$PNpy-*P*,*N*)(PR$_3$)] (M = Pt, PR$_3$ = PMe$_3$ **21**, PEt$_3$ **23**, P^{n}Bu$_3$ **25**, PMe$_2$Ph **27**, PPh$_3$ **30**, P(OMe)$_3$ **35**, P(OEt)$_3$ **37** or P(OPh)$_3$ **40**; M = Pd, PR$_3$ = PMe$_2$Ph **42** or PPh$_3$ **44**) were easily prepared by the addition of a stoichiometric quantity of ^{t}BuOK to a methanol solution of the corresponding protonated cationic species, eqn. (7). The neutral species



(7)

cis-[PtCl(Ph$_2$PNpy-*P*,*N*)(PMe$_3$)] **21** was prepared using this method and isolated as a pale yellow solid in 87% yield. The ^{31}P-{^{1}H} NMR spectrum (in $CDCl_3$) of **21** is, as expected, an AX type with platinum satellites.

Although the spectrum is very similar to that of its precursor *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PMe$_3$)]Cl **20**, comparison of the two spectra reveals significant differences. In common with **20** [$^2J(^{31}P_A–^{31}P_X) = 18$ Hz], the ^{31}P-{^{1}H} NMR spectrum of **21** reveals a small but slightly reduced $^2J(P_A–P_X)$ coupling constant of 14 Hz which is characteristic of a mutual *cis* arrangement of phosphine ligands. The deprotonated $[Ph_2PNpy]^-$ ligand of **21** displays a high-frequency resonance at δ(P) 65.2 [$^1J(^{195}Pt–^{31}P)$ 3542 Hz], a shift to higher frequency of approximately 3 ppm and a significantly reduced, by 237 Hz, $^1J(^{195}Pt–^{31}P)$ coupling constant relative to **20**. The low-frequency resonance assigned to the co-ordinated PMe_3 group of **21** at δ(P) −27.9 [$^1J(^{195}Pt–^{31}P)$ 3239 Hz] is also changed relative to **20** but to a lesser extent. A small shift of 0.6 ppm to lower frequency occurs in conjunction with an increase of 125 Hz in $^1J(^{195}Pt–^{31}P)$ coupling constant. The shifts in δ(P) to higher or lower frequency and the accompanying increase/reduction in *J* values that occur upon conversion of **20** into **21** represent a trend common to all deprotonated species (see Table 11).

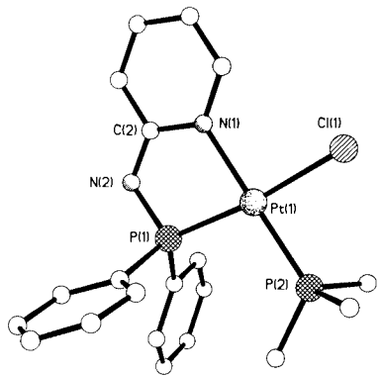


Fig. 11 Crystal structure of *cis*-[PtCl(Ph$_2$PNpy-*P*,*N*)(PMe$_3$)] **21**.

Not all of the cationic species described above behaved predictably under deprotonating conditions. A dichloromethane solution of *cis*-[PtCl(Ph$_2$PNHpy-*P*,*N*)(PPh$_2$H)]Cl **28**, when treated with a stoichiometric quantity of Et_3N, initially gave the expected yellow solution but with prolonged stirring a white solid was deposited. The extreme insolubility of this material prevented measurement of its NMR or mass spectra, hence only IR and microanalytical data are available. The IR spectrum is very similar to that of the starting material **28**, and suggests that the dppap ligand is still protonated with ν(P–N) 903 cm^{-1} and hydrogen bonded to a chloride counter ion as evidenced by the broad ν(N–H) band at 2675 cm^{-1} which along with the absence of a ν(P–H) band could mean that a bimetallic phosphido bridged species has been formed. Microanalytical data were in close but not perfect agreement with the above formulation. Further work and characterisation is needed fully to understand this reaction. Several unsuccessful attempts to synthesize *cis*-[PdCl(Ph$_2$PNpy-*P*,*N*)(P(OPh)$_3$)] **49** using ^{t}BuOK in methanol were made. Examination of reaction residues by ^{31}P-{^{1}H} NMR (in $CDCl_3$) showed multiple products and the presence of a significant quantity of starting material. Furthermore, a gradual darkening of the NMR sample (from bright orange to black) over the course of 1 hour was observed. The degraded NMR sample was re-examined and showed additional peaks not observed for the fresh sample. The impurities and the eventual blackening of the NMR sample are thought to stem from the formation, followed by rapid decomposition, of unstable palladium alkoxy species. The presence of unchanged starting material in reaction residues suggests the possibility that two molecules of base have reacted with one molecule of starting material resulting first in the desired deprotonation and secondly in abstraction and replacement of the chloride ligand with $[^tBuO]^-$ or $[MeO]^-$. Attempted deprotonation reactions of palladium P(OMe)$_3$ **45**, P(OEt)$_3$ **46** and P(O^{n}Bu)$_3$ **47** derivatives using the same method gave similar results to those observed for the palladium P(OPh)$_3$ **48** complex. We found that the dropwise addition of a solution of Et_3N to a dilute dichloromethane solution of **48** gave after work-up only the anticipated deprotonated product **49** as a bright yellow powder in 90% yield. Application of the same mild conditions to the deprotonation of complexes **46** and **47** gave comparable results to those obtained using ^{t}BuOK in

methanol, and complex **45**, due to poor solubility, remained unchanged. Similar reactions conducted using stoichiometric quantities of the hindered, non-co-ordinating base 2,6-dimethylpyridine instead of Et_3N showed, by ^{31}P-{^1H} NMR (in $CDCl_3$), that decomposition had not occurred. Additionally, NMR samples left to stand over 48 hours showed no obvious sign of darkening. The ^{31}P-{^1H} NMR spectra of reaction mixtures using **46** and **47** displayed two sets of AX type resonances corresponding to unchanged starting material and possibly the expected product. Curiously, the addition of a large excess of 2,6-dimethylpyridine to NMR samples containing both protonated and deprotonated species failed to push the reaction to completion and caused only minimal changes in solution composition. No further attempts at synthesizing compounds of the type *cis*-[PdCl(Ph_2PNpy-*P*,*N*)-($P(OR)_3$)] were made. An example of this type of complex was also crystallograpically characterised. The crystal structure of **21** (Fig. 11, Table 10) shows that the *cis* geometry of complex

Table 10 Selected bond lengths (Å) and angles (°) for complex **21**

Pt(1)–P(1)	2.2136(11)	Pt(1)–P(2)	2.2537(14)
Pt(1)–N(1)	2.091(4)	Pt(1)–Cl(1)	2.3811(14)
P(1)–N(2)	1.638(4)	N(2)–C(2)	1.329(6)
C(2)–N(1)	1.377(6)		
P(1)–Pt(1)–P(2)	100.06(5)	N(1)–Pt(1)–Cl(1)	93.17(12)
P(1)–Pt(1)–N(1)	79.69(11)	P(2)–Pt(1)–Cl(1)	87.06(5)
P(1)–Pt(1)–Cl(1)	172.85(5)	P(2)–Pt(1)–N(1)	176.44(11)
Pt(1)–P(1)–N(2)	105.80(2)	P(1)–N(2)–C(2)	115.20(3)
N(2)–C(2)–N(1)	121.10(4)	C(2)–N(1)–Pt(1)	116.70(3)

Table 11 ^{31}P-{^1H}[a] NMR data for complexes **1**–**4**

Compound	Chemical shifts (ppm)		Coupling constants/Hz		
	$\delta(P_A)$ [dppap]	$\delta(P_X)$ [PX_3]	^1J(Pt–P_{dppap})	^1J(Pt–P_X)	^2J(P_{dppap}–P_X)
1 Ph_2PNHpy	26.4	—	—	—	—
2 $Ph_2P(O)NHpy$[b]	16.8	—	—	—	—
3 $Ph_2P(S)NHpy$	51.6	—	—	—	—
4 $Ph_2P(Se)NHpy$	47.4 [783][c]	—	—	—	—
5 *cis*-[PtCl(HL)(HL-*P*)]Cl	51.4	—	3576	—	—
6 *cis*-[PtBr(HL)(HL-*P*)]Br[d]	62.1	—	3559	—	—
7 *cis*-[PtI(HL(HL-*P*)]I[d]	62.3	—	3541	—	—
8 *cis*-[PdCl(HL)(HL-*P*)]Cl	71.4	—	—	—	—
9 *cis*-[PdBr(HL)(HL-*P*)]Br[d]	83.7	—	—	—	—
10 *cis*-[PdI(HL)(HL)-*P*)]I[d]	83.3	—	—	—	—
11 *cis*-[Pt($L)_2$]	63.0	—	3334	—	—
12 *cis*-[Pd($L)_2$]	84.5	—	—	—	—
13 *cis*-[Pt($HL)_2$][BF_4]$_2$[e]	64.1	—	3475	—	—
14 *cis*-[Pd($HL)_2$][BF_4]$_2$[e]	88.0	—	—	—	—
15 *cis*-[PtMe(HL)(HL-*P*)Cl[f]	38.4, 84.2	—	3948, 2019	—	11
16 *cis*-[PtMe(L)(Ph_2POMe)][f]	90.0	100.6	1950	4447	8
17 [AuCl(HL-*P*)]	55.4	—	—	—	—
18 [{Au(μ-HL)}$_2$][ClO_4]$_2$ (HT)[g]	62.7	—	—	—	—
19 [Pt(C_8H_{12}OMe)(L)]·H_2O	63.2	—	4087	—	—
20 *cis*-[PtCl(HL)(PMe_3)]Cl	62.3	−27.3	3779	3114	18
21 *cis*-[PtCl(L)(PMe_3)]	65.2	−27.9	3542	3239	14
22 *cis*-[PtCl(HL)(PEt_3)]Cl	61.7	4.3	3816	3123	17
23 *cis*-[PtCl(L)(PEt_3)]	64.7	3.3	3589	3246	13
24 *cis*-[PtCl(HL)(P^nBu_3)]Cl	61.5	−3.3	3840	3106	16
25 *cis*-[PtCl(L)(P^nBu_3)]	64.7	−4.4	3603	3251	12
26 *cis*-[PtCl(HL)(PMe_2Ph)]Cl	62.2	−21.3	3750	3198	15
27 *cis*-[PtCl(L)(PMe_2Ph)]	64.8	−20.2	3502	3337	12
28 *cis*-[PtCl(HL)(PPh_2H)]Cl	62.1	−16.9[h]	3513	3271	16
29 *cis*-[PtCl(HL)(PPh_3)]Cl	63.7	6.8	3754	3361	14
30 *cis*-[PtCl(L)(PPh_3)]	66.4	10.3	3493	3486	9
31 *cis*-[PtBr(HL)(PPh_3)]Br	—	—	—	—	—
32 *cis*-[PtI(HL)(PPh_3)I	—	—	—	—	—
33 *cis*-[PtMe(HL)(PPh_3)]Cl	82.3	16.7	2013	3948	10
34 *cis*-[PtCl(HL)(P{OMe}$_3$)]Cl	—	—	—	—	—
35 *cis*-[PtCl(L)($P(OMe)_3$)]	54.9	71.6	3847	5371	18
36 *cis*-[PtCl(HL)($P(OEt)_3$)]Cl	62.4	68.0	3691	5382	17
37 *cis*-[PtCl(L)($P(OEt)_3$]	64.3	82.8	3385	5560	13
38 *cis*-[PtCl(HL)($P(O^nBu)_3$)]Cl[i]	62.5	67.8	3691	5371	18
39 *cis*-[PtCl(HL)($P(OPh)_3$)]Cl	61.4	63.9	3552	6461	14
40 *cis*-[PtCl(L)($P(OPh)_3$)]	66.5	74.7	3285	5955	13
41 *cis*-[PdCl(HL)(PMe_2Ph)]Cl[j]	86.1	1.9	—	—	6
42 *cis*-[PdCl(L)(PMe_2Ph)][j]	91.8	−0.2	—	—	4
43 *cis*-[PdCl(HL)(PPh_3)]Cl[j]	88.8	29.9	—	—	3
44 *cis*-[PdCl(L)(PPh_3)][j]	93.6	29.6	—	—	n.o[k]
45 *cis*-[PdCl(HL)($P(OMe)_3$)]Cl	—	—	—	—	—
46 *cis*-[PdCl(HL)($P(OEt)_3$)]Cl	84.6	93.5	—	—	22
47 *cis*-[PdCl(HL)($P(O^nBu)_3$)]Cl[i]	76.7	56.2	—	—	44
48 *cis*-[PdCl(HL)($P(OPh)_3$)]Cl[j]	88.1	89.3	—	—	26
49 *cis*-[PdCl(L)($P(OPh)_3$)]	91.6	99.1	—	—	20

[a] Spectra (36.2 MHz) measured in $CDCl_3$ unless otherwise stated. [b] Spectrum (36.2 MHz) measured in CDCl–dmso. [c] ^1J(^{31}P–^{77}Se) coupling constant. HL = Ph_2PNHpy **1**, L = [Ph_2PNpy]$^-$. Co-ordination is bidentate in most cases. Monodentate Ph_2PNHpy-*P* ligands are denoted by HL-*P*. [d] Spectrum (36.2 MHz) measured in dmso–C_6D_6. [e] Spectrum (36.2 MHz) measured in d_6-dmso. [f] Spectrum (101.3 MHz) measured in $CDCl_3$. [g] Spectrum (36.2 MHz) measured in CH_2Cl_2–C_6D_6. [h] ^1J(P–H) 395 Hz. [i] Spectrum (36.2 MHz) measured in $CDCl_3$–MeOH. [j] Spectrum (101.3 MHz) measured in $CDCl_3$. [k] Not observed.

20 remains unchanged upon deprotonation and reveals approximately square-planar geometry at platinum [maximum deviations from Pt(1)–P(1)–P(2)–Cl(1)–N(1) mean plane 0.22 Å below for Cl(1) and 0.35 Å below for P(2)]. The Pt(1)–P(1)–N(2)–C(2)–N(1) five-membered ring is essentially planar with a mean deviation of only 0.06 Å. The bond lengths and angles of **21** are very similar to those displayed by the previously discussed platinum(II) complex **11** which also contains deprotonated chelating dppap ligands, but are significantly different to those of the cationic species **20**. Most notable among these differences are the contracted P(1)–N(2) [1.638(4) Å] and N(2)–C(2) [1.329(6) Å] and the elongated C(2)–N(1) [1.377(6) Å] bond lengths compared to those of **20** [1.681(7), 1.376(10) and 1.337(9) Å] respectively. Another salient feature of **21** is the contraction of the P(1)–N(2)–C(2) bond angle from 119.8(5)° in **20** to 115.20(3)°. The crystal structure also highlights, by the absence of counter ions, the neutral nature of the complex.

In this work we have demonstrated that the dppap ligand exhibits a variety of co-ordination modes including monodentate P bound and bidentate PN bound. We have also shown that the co-ordinated dppap ligand can be deprotonated and stabilised by incorporation into a metallacycle further extending the range of complexes available. Methanolysis of the P–N bond in dppap under basic reaction conditions leading to a platinum-bound Ph_2POMe ligand has also been observed. Further work on the catalytic behaviour of systems containing this ligand is in progress.

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