Flexible κ^4-PNN`O-tetradentate ligands: synthesis, complexation and structural studies†

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The three-step synthesis of new, air-stable, PNN`O-tetradentate ligands **3a·HH–3c·HH** by Schiff base condensation of the 1º amines **2a**–**2c** with 2-$Ph_2PC_6H_4(CHO)$ in refluxing EtOH is described. The racemic ligand **3d·HH**, isolated in 79% yield, was successfully prepared from 2-$C_6H_4(OH)\{C(O)NHCH_2CH(Me)NH_2\}$ **2d** and 2-$Ph_2PC_6H_4(CHO)$ in absolute EtOH. Upon careful choice of metal precursor, ligands **3a·HH–3d·HH** display various coordination modes. Reaction of **3a·HH** with AuCl(tht) (1:1 molar ratio) affords AuCl(**3a·HH**), **4a**, in which κ^1-P-complexation of the functionalised ligand is observed. In contrast, reaction of **3a·HH** (or **3d·HH**) with MCl_2(cod) (M = Pt, Pd) affords MCl_2(**3a·HH**) (M = Pt, **5a**; M = Pd, **5b**) or MCl_2(**3d·HH**) (M = Pt, **5c**; M = Pd, **5d**) in which ligand chelation is achieved using both P and imine N donor atoms. Moreover κ^2-P,N-chelation was also observed when **3a·HH–3c·HH** were separately allowed to react with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in CH_2Cl_2 affording new cationic η^3-allyl complexes $[Pd(\eta^3\text{-}C_3H_5)$(**3a·HH–3c·HH**)]Cl, **6a**–**6c**. Two neutral (methyl)chloropalladium(II) complexes, **7a**/**7c**, were isolated in high yields from **3a·HH** or **3c·HH** and $Pd(CH_3)Cl$(cod). Elimination of cod and single methyl protonation from $Pt(CH_3)_2$(cod) with 1 equiv. of **3a·HH**, **3b·HH** or **3d·HH** in toluene, at room temperature, afforded square-planar complexes $Pt(CH_3)$(κ^3-**3a·H**/**3b·H**/**3d·H**), **8a**/**8b**/**8d**, containing monoanionic κ^3-PNN`-tridentate ligands. The $\kappa^3$-PNN`-tridentate mode was likewise observed for $Pd(CH_3)$(**3a·H**/**3c·H**), **10a**/**10c**, upon treatment of a methanolic solution of $Pd(CH_3)Cl$(**3a·HH**/**3c·HH**) with ^{t}BuOK. Similarly the monohapto (allyl)Pd^{II} compounds $Pd(CH_2CH{=}CH_2)$(**3a·HH–3c·HH**), **9a**–**9c**, were obtained cleanly from **6a**–**6c** and ^{t}BuOK *via* an $\eta^3 \rightarrow \eta^1$ allyl isomerisation. Both amide and phenolic protons in **5a**–**5d** were smoothly deprotonated, with base, to give the κ^4-PNN`O`-tetradentate complexes **11a**/**11b** and **11d**/**11e** containing the dianionic ligands **3a**$^{2-}$/**3d**$^{2-}$ respectively. The Ni^{II} complexes **11c** and **11f** were synthesised directly from $NiCl_2{\cdot}6H_2O$, **3a·HH** (or **3d·HH**) and ^{t}BuOK in CH_3OH. All new compounds were characterised by multinuclear NMR, FT–IR, mass spectrometry and microanalysis. Single crystal X-ray studies have been undertaken on the compounds **3a·HH**, **3c·HH**, **4a**, **7c**, **8a**, **8b**, **8d** and **11a–11d**.

Introduction

Significant developments in functionalised phosphine chemistry[1] continue to play a crucial role in understanding how these versatile ligands coordinate to metals, influence metal reactivity (stereoelectronic properties) and find applications in, for example, homogeneous catalysis. The marriage of two different donor atoms, one a soft P^{III} centre and the other typically N[2] or O[3], has led to a wealth of tertiary phosphines being studied of which hemilabile ligands[4] are a notable class. Whilst many functionalised tertiary phosphines have been shown to act as bidentate ligands[5], few literature examples of tridentate PNO systems are known.[6] In contrast, tetradentate ligands with two (or more) donor types, including tetradentate π radical ligands[7], have attracted considerable interest for their radioimaging/radiotherapeutic[8], liquid crystalline[9] and phosphorescent properties[10] and applications in catalysis (including asymmetric variations).[11] Within this family of ligands the most popular examples of donor set combinations are those comprising N_2O_2[12] and P_2N_2[13] atoms whereas unsymmetrical systems *e.g.* PNN`N`` are either uncommon[14], or in the case of the PNN`O donor motif, extremely rare.[15] Barandov and Abram[16] recently described the synthesis of two new pentadentate Schiff base ligands containing a rare $PN_2O_2$ donor set. Herein we describe the synthesis of a series of tetradentate $\kappa^4$-PNN`O ligands and a stepwise survey of their coordination capabilities towards selected transition-metal centres. Our studies have revealed

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these flexible κ^4-PNN`O ligands adopt numerous ligation modes and afford new examples of chelate stabilised amido[2b] and amido/phenoxo metal(II) complexes. All new compounds have been structurally verified both in solution and the solid-state.

Experimental

Materials

All reactions were carried out under aerobic conditions, with the exception of ligands **3a·HH–3d·HH** whose syntheses were conducted under an atmosphere of dry, oxygen-free, nitrogen. All solvents were distilled prior to use. The compounds **1a**,[17] **2a**,[17] **2d**,[18] 2-$Ph_2PC_6H_4(CHO)$,[19] AuCl(tht) (tht = tetrahydrothiophene),[20] MCl_2(cod) (M = Pt, Pd; cod = cycloocta-1,5-diene),[21] $Pd(CH_3)Cl(cod)$[22] and $Pt(CH_3)_2(cod)$[23] were all prepared according to published procedures. All other reagents were purchased from commercial suppliers.

Instrumentation

FT–IR spectra were recorded as KBr pellets over the range 4000–400 cm^{-1} using a Perkin-Elmer system 2000 FT spectrometer. The ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded either on Bruker AC250 or DPX-400 FT spectrometers with chemical shifts (δ) reported relative to external TMS or H_3PO_4. All NMR spectra (250 or 400 MHz) were recorded in $CDCl_3$ solutions unless otherwise stated. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

X-ray crystallography

Suitable crystals were grown by vapour diffusion of Et_2O into either a $CDCl_3/CH_2Cl_2$ (for **4a**), CH_2Cl_2/CH_3OH (for **7c**·CH_2Cl_2) or $CDCl_3$ solution (for **8b**·$1.5C_7H_8$, **11b**·$0.5CHCl_3$·$0.5Et_2O$, **11c** and **11d**·$CHCl_3$). Slow evaporation of an EtOH (for **3a·HH**·EtOH), $CHCl_3$ (for **3c·HH**·$0.5CHCl_3$) or CH_2Cl_2/Et_2O solution (for **11a**·MeOH) afforded X-ray quality crystals. Suitable crystals of **8a**·$CHCl_3$ (and **8d**·$2C_7H_8$) were obtained from a C_7H_8 solution of **3a·HH** (or **3d·HH**) and $Pt(CH_3)_2$(cod). All measurements were made on a Bruker AXS SMART 1000 CCD area-detector diffractometer, at 150 K, using graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å) and narrow frame exposures (0.3º) in ω. Cell parameters were refined from the observed (ω) angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for **7c**·CH_2Cl_2 and **11d**·$CHCl_3$) and refined on F^2 values for all unique data by full-matrix least-squares (Table 1). All non-hydrogen atoms were refined anisotropically. Programs used were Bruker AXS SMART and SAINT for diffractometer control and frame integration,[24] Bruker SHELXTL for structure solution, refinement and molecular graphics,[25] and local programs.

For **3c·HH**·$0.5CHCl_3$, the $CHCl_3$ molecule was disordered over an inversion centre. For **8b**·$1.5C_7H_8$, point atom modelling was attempted for the C_7H_8 molecules but no suitable disorder model could be established. The Platon Squeeze procedure was therefore successfully applied.[26] For **8d**·$2C_7H_8$, one of the C_7H_8 molecules was disordered and successfully modelled. In **11b**·$0.5CHCl_3$·$0.5Et_2O$, the highly disordered Et_2O molecule was modelled using the Platon Squeeze procedure. For the chiral structures the absolute structure parameters were: **4a,** x = 0.555(6), twinned by inversion; **11d,** x = −0.025(8), single enantiomer, well determined.

Preparation of *1,2*-(OH)C_6H_4{NHC(O)CH_2N=CH-$C_6H_4PPh_2$} (3a·HH). A suspension of **2a** (0.307 g, 1.848 mmol) and 2-$Ph_2PC_6H_4(CHO)$ (0.556 g, 1.915 mmol) in absolute EtOH (30 ml) was refluxed, under a N_2 atmosphere, for *ca.* 4 h. After cooling to r.t., the volume was reduced to *ca*. 10 ml under reduced pressure and the solid collected by suction filtration. The solid was washed with a small portion of EtOH and dried *in vacuo*. Yield: 0.498 g, 61%. Selected data: ^{31}P: –8.1 ppm. ^1H: 9.86 (s, 1H), 9.41 (s, 1H), 8.61 (d, $^4J_{PH}$ 4.0, 1H), 7.77–6.85 (m, 18H), 4.32 (s, 2H) ppm. FT–IR: 3304, 1655 cm^{-1}. EI–MS: *m/z* 438 [M^+]. Anal. (%) Calcd. for $C_{27}H_{23}N_2O_2P$: C, 73.95; H, 5.30; N, 6.39. Found: C, 73.39; H, 5.25; N, 6.33. Compounds **3b·HH** and **3c·HH** were similarly prepared in 65% and 76% yields respectively. Selected data for **3b·HH**: ^{31}P: –11.4 ppm. ^1H: 9.54 (s, 1H), 8.83 (s, 1H), 8.04–6.86 (m, 18H), 4.64 (s, 2H), 4.28 (s, 2H) ppm. FT–IR: 3371, 3269 (NH, OH), 1673 (CO amide I), 1534 (CO amide II) cm^{-1}. EI–MS: *m/z* 452 [M^+]. Anal. (%) Calcd. for $C_{28}H_{25}N_2O_2P$·$0.5H_2O$: C, 72.86; H, 5.69; N, 6.07. Found: C, 72.69; H, 5.61; N, 5.83. Selected data for **3c·HH**: ^{31}P: –8.8 ppm. ^1H: 9.39 (d, $^4J_{PH}$ 3.8, 1H), 8.58 (m, 1H), 7.77–6.77 (m, 18H), 5.83 (s, 1H), 4.25 (s, 2H) ppm. FT–IR: 3249, 3145, 1659, 1649 cm^{-1}. EI–MS: *m/z* 438 [M^+]. Anal. (%) Calcd. for $C_{27}H_{23}N_2O_2P$·C_2H_5OH: C, 71.88; H, 6.28; N, 6.05. Found: C, 71.88; H, 5.84; N, 5.78.

Preparation of *1,2*-(OH)C_6H_4{C(O)NHCH_2CH(Me)N=CH-$C_6H_4PPh_2$} (3d·HH). A mixture of **2d** (0.326 g, 1.678 mmol) and 2-$Ph_2PC_6H_4(CHO)$ (0.505 g, 1.740 mmol) in absolute EtOH (40 ml) was stirred for *ca*. 24 h. The solvent was evaporated to *ca*. 10 ml and **3d·HH** isolated by suction filtration and dried *in vacuo*. Yield: 0.618 g, 79%. Selected data: ^{31}P: –7.8 ppm. ^1H: 12.56 (s, 1H), 8.53 (d, $^4J_{PH}$ 3.8, 1H), 7.75–6.71 (m, 19H), 3.70 (m, 1H), 3.53 (m, 1H), 3.24 (m, 1H), 0.93 (d, $^3J_{HH}$ 6.4, 3H) ppm. FT–IR: 3240, 1641, 1630 cm^{-1}. ES–MS: *m/z* 467 [M^+]. Anal. (%) Calcd. for $C_{29}H_{27}N_2O_2P$: C, 74.65; H, 5.85; N, 6.01. Found: C, 74.92; H, 5.64; N, 6.34.

Preparation of *1,2*-(OH)C_6H_4{NHC(O)CH_2N=CH-$C_6H_4PPh_2AuCl$} (4a). AuCl(tht) (0.0056 g, 0.0175 mmol) was dissolved in CH_2Cl_2 (10 ml) and **3a·HH** (0.079 g, 0.0180 mmol) added to afford a colourless solution. After stirring the solution for 45 min, the volume was reduced to *ca*. 1–2 ml and diethyl ether (20 ml) and petroleum ether (b.p 60–80 °C,

10 ml) added to give **4a** which was collected by filtration and dried *in vacuo*. Yield: 0.107 g, 91%. Selected data: ^{31}P: 29.2 ppm. ^{1}H: 8.82 (s, 1H), 8.68 (s, 1H), 7.94 (s, 1H), 7.69–6.78 (m, 18H), 4.36 (s, 2H) ppm. FT–IR: 3294, 1655 cm^{-1}. ES–MS: *m/z* 635 [M–Cl]. Anal. (%) Calcd. for $C_{27}H_{23}AuClN_2O_2P$: C, 48.33; H, 3.46; N, 4.18. Found: C, 48.51; H, 3.54; N, 3.71.

Preparation of *1,2*-(OH)C$_6$H$_4${NHC(O)CH$_2$N=CH-C$_6$H$_4$PPh$_2$PtCl$_2$} (5a). To a CH_2Cl_2 (20 ml) solution of $PtCl_2$(cod) (0.090 g, 0.241 mmol) was added **3a·HH** (0.104 g, 0.237 mmol) to give a yellow solution. After stirring the solution for 15 min, the volume was reduced under vacuum to *ca*. 1–2 ml and addition of diethyl ether (25 ml) afforded a yellow solid. The solid was collected by suction filtration and dried *in vacuo*. Yield: 0.150 g, 89%. Compound **5b** (91%) was similarly prepared from $PdCl_2$(cod) and **3a·HH**. Selected data for **5a**: ^{31}P ($CDCl_3$/CH_3OH): 10.7 ppm, $^{1}J_{PtP}$ 3492 Hz; 3.0 ppm, $^{1}J_{PtP}$ 3324 Hz. FT–IR: 3258, 1670, 1632 cm^{-1}. ES–MS: *m/z* 669 [M–Cl]. Anal. (%) Calcd. for $C_{27}H_{23}N_2O_2PPtCl_2$: C, 46.03; H, 3.30; N, 3.98. Found: C, 45.95; H, 3.28; N, 3.43. Selected data for **5b**: ^{31}P ($CDCl_3$/CH_3OH): 38.2 ppm. ^{1}H: 10.30 (s, 1H), 10.01 (s, 1H), 8.74 (s, 1H), 8.12–6.79 (m, 18H), 5.37 (s, 2H) ppm. FT–IR: 3324, 3258, 1698, 1645 cm^{-1}. MALDI–MS: *m/z* 580 [M–Cl]. Anal. (%) Calcd. for $C_{27}H_{23}N_2O_2PPdCl_2$: C, 52.66; H, 3.77; N, 4.55. Found: C, 52.54; H, 3.72; N, 4.33. Compounds **5c** (99%) and **5d** (92%) were similarly prepared from **3d·HH** and the appropriate MCl_2(cod). Selected data for **5c**: ^{31}P [$CDCl_3$/$(CD_3)_2SO$]: 6.1 ppm, $^{1}J_{PtP}$ 3799 Hz. ^{1}H: 12.18 (s, 1H), 8.41 (s, 1H), 8.37 (d, $^{4}J_{PH}$ 7.3, 1H), 7.70–6.66 (m, 18H), 5.64 (m, 1H), 4.05 (m, 1H), 3.16 (m, 1H), 0.78 (d, $^{3}J_{HH}$ 6.8, 3H) ppm. FT–IR: 3295, 1640 cm^{-1}. ES–MS: *m/z* 697 [M–Cl]. Anal. (%) Calcd. for $C_{29}H_{27}N_2O_2PPtCl_2$: C, 47.55; H, 3.72; N, 3.83. Found: C, 47.78; H, 3.78; N, 4.21. Selected data for **5d**: ^{31}P [$CDCl_3$/$(CD_3)_2SO$]: 32.9 ppm. ^{1}H: 12.30 (s, 1H), 8.50 (d, $^{4}J_{PH}$ 6.2, 1H), 8.23–6.74 (m, 19H), 5.59 (m, 1H), 4.15 (m, 1H), 3.18 (m, 1H), 0.69 (d, $^{3}J_{HH}$ 6.8, 3H) ppm. FT–IR: 3269, 1639 cm^{-1}. ES–MS: *m/z* 571 [M–2Cl–H$^+$]. Anal. (%) Calcd. for $C_{29}H_{27}N_2O_2PPdCl_2$: C, 54.09; H, 4.24; N, 4.35. Found: C, 53.86; H, 4.28; N, 4.33.

Preparation of [*1,2*-(OH)C$_6$H$_4${NHC(O)CH$_2$N=CH-C$_6$H$_4$PPh$_2$Pd(η^3-C$_3$H$_5$)}]Cl (6a). To a solution of [PdCl(η^3-C_3H_5)]$_2$ (0.037 g, 0.101 mmol) in CH_2Cl_2 (5 ml) was added **3a·HH** (0.091 g, 0.208 mmol) to afford a yellow solution. After stirring for 1 h the solution was concentrated under reduced pressure to *ca*. 1–2 ml and diethyl ether (10 ml) added. The yellow solid was collected and dried *in vacuo*. Yield: 0.107 g, 85%. Compounds **6b** (96%) and **6c** (84%) were prepared in a related manner. Selected data for **6a**: ^{31}P: 24.3 ppm. ^{1}H: 11.66 (s, 1H), 9.20 (s, 1H), 8.74 (s, 1H), 7.84–6.85 (m, 18H), 5.83 (q, 1H), 5.41 (s, 2H), 4.00 (br), 3.07 (br) ppm. FT–IR: 3214, 3145, 1654 cm^{-1}. ES–MS: *m/z* 585 [M–Cl]. Anal. (%) Calcd. for $C_{30}H_{28}N_2O_2PPdCl$: C, 57.98; H, 4.55; N, 4.51. Found: C, 57.46; H, 4.56; N, 4.52. Selected data for **6b**: ^{31}P: 24.2 ppm. ^{1}H: 10.31 (s, 1H), 8.84 (s, 1H), 7.85–7.12 (m, 19H), 5.82 (q, 1H), 5.44 (s, 2H), 4.61 (s, 2H), 4.06 (br), 3.03 (br) ppm. FT–IR: 3394, 1684 cm^{-1}. ES–MS: *m/z* 599 [M–Cl]. Anal. (%) Calcd. for $C_{31}H_{30}N_2O_2PPdCl{\cdot}0.5H_2O$: C, 57.77; H, 4.86; N, 4.35. Found: C, 57.64; H, 4.84; N, 4.23. Selected data for **6c**: ^{31}P: 24.2 ppm. ^{1}H: 10.56 (s, 1H), 8.57 (s, 1H), 7.82–6.74 (m, 19H), 5.70 (q, 1H), 5.09 (s, 2H), 3.90 (br), 2.90 (br) ppm. FT–IR: 3240, 3196, 3141, 1674 cm^{-1}. ES–MS: *m/z* 585 [M–Cl]. Anal. (%) Calcd. for $C_{30}H_{28}N_2O_2PPdCl{\cdot}1.5H_2O$: C, 55.56; H, 4.83; N, 4.32. Found: C, 55.53; H, 4.68; N, 4.03.

Preparation of *1,2*-(OH)C$_6$H$_4${NHC(O)CH$_2$N=CH-C$_6$H$_4$PPh$_2$Pd(CH$_3$)Cl} (7a). To a solution of Pd(CH_3)Cl(cod) (0.050 g, 0.189 mmol) in CH_2Cl_2 (10 ml) was added **3a·HH** (0.086 g, 0.196 mmol) to give an initial pale yellow solution whereupon, after a few minutes, a colourless solid **7a** deposited. After stirring for 25 min, the volume was concentrated under reduced pressure to *ca*. 2 ml and diethyl ether (20 ml) added. The solid was collected and dried *in vacuo*. Yield: 0.097 g, 87%. Compound **7c** (91%) was likewise prepared. Selected data for **7a**: ^{31}P [$CDCl_3$/CH_3OH/$(CH_3)_2SO$]: 39.3 ppm. ^{1}H [$(CD_3)_2SO$]: 9.68 (s, 1H), 9.32 (s, 1H), 8.37 (s, 1H), 7.66–6.54 (m, 18H), 4.85 (s, 2H), 0.00 (d, $^{3}J_{PH}$ 3.2, 3H) ppm. FT–IR: 3242, 1650, 1628 cm^{-1}. ES–MS: *m/z* 559 [M–Cl]. Anal. (%) Calcd. for $C_{28}H_{26}N_2O_2PPdCl$: C, 56.48; H, 4.41; N, 4.71. Found: C, 56.14; H, 4.48; N, 4.68. Selected data for **7c**: ^{31}P: 38.0 ppm. ^{1}H: 10.29 (s, 1H), 8.25 (s, 1H), 7.53–6.71 (m, 18H), 6.39 (s, 1H), 4.88 (s, 2H), 0.53 (d, $^{3}J_{PH}$ 4.0, 3H) ppm. FT–IR: 3245, 3204, 3153, 1656, 1608 cm^{-1}. ES–MS: *m/z* 559 [M–Cl]. Anal. (%) Calcd. for $C_{28}H_{26}N_2O_2PPd{\cdot}0.75CH_2Cl_2$: C, 52.39; H, 4.21; N, 4.25. Found: C, 52.38; H, 4.24; N, 4.03.

Preparation of *1,2*-(OH)C$_6$H$_4${NC(O)CH$_2$N=CH-C$_6$H$_4$PPh$_2$Pt(CH$_3$)} (8a). To the solids Pt$(CH_3)_2$(cod) (0.040 g, 0.120 mmol) and **3a·HH** (0.053 g, 0.121 mmol) was added toluene (2 ml) to afford a yellow solution. After standing for 2 d, a yellow crystalline solid formed which was collected and dried. Yield: 0.072 g, 92%. The κ^3-PNN`-tridentate complexes **8b** (62%) and **8d** (84%) were prepared similarly. Selected data for **8a**: ^{31}P: 13.7 ppm, $^{1}J_{PtP}$ 3865 Hz. ^{1}H: 8.43 ($^{3}J_{PtH}$ 43.8, 1H), 7.57–6.72 (m, 18H), 4.84 (s, 2H), 0.00 ($^{2}J_{PtH}$ 72.8, 3H) ppm. FT–IR: 2926, 1636, 1605, 1574 cm^{-1}. ES–MS: *m/z* 646 [M$^+$]. Anal. (%) Calcd. for $C_{28}H_{25}N_2O_2PPt{\cdot}CHCl_3$: C, 45.42; H, 3.42; N, 3.65. Found: C, 45.46; H, 3.27; N, 3.43. Selected data for **8b**: ^{31}P: 13.6 ppm, $^{1}J_{PtP}$ 3809 Hz. ^{1}H: 8.63 ($^{3}J_{PtH}$ 43.2, 1H), 7.71–7.06 (m, 18H), 4.98 (s, 2H), 4.87 (d, $^{2}J_{HH}$ 11.0, 1H), 4.47 (d, $^{2}J_{HH}$ 11.0, 1H), 3.99 (br, 1H), 0.00 ($^{2}J_{PtH}$ 72.0, 3H) ppm. FT–IR: 3384, 3292, 1639, 1602, 1585, 1570 cm^{-1}. ES–MS: *m/z* 662 [M$^+$]. Anal. (%) Calcd. for $C_{29}H_{27}N_2O_2PPt$: C, 52.64; H, 4.12; N, 4.24. Found: C, 52.58; H, 4.08; N, 3.81. Selected data for **8d**: ^{31}P: 14.4 ppm, $^{1}J_{PtP}$ 3834 Hz. ^{1}H: 12.60 (s, 1H), 8.62 ($^{3}J_{PtH}$ 42.4, 1H), 8.35 (dd, 1H), 7.62–6.49 (m, 17H), 4.15 (ddd, 1H), 4.03 (m, 1H), 3.64 (dd, 1H), 1.33 (d, $^{3}J_{HH}$ 6.8, 3H), 0.01 ($^{2}J_{PtH}$ 75.2, 3H) ppm. FT–IR: 1618, 1555 cm^{-1}. ES–MS: *m/z* 676 [M$^+$]. Anal. (%) Calcd. for $C_{30}H_{29}N_2O_2PPt{\cdot}2C_7H_8$: C, 61.45; H, 5.29; N, 3.26. Found: C, 61.57; H, 5.25; N, 3.52.

Preparation of *1,2*-(OH)C$_6$H$_4${NC(O)CH$_2$N=CH-C$_6$H$_4$PPh$_2$Pd(η^1-CH$_2$CH=CH$_2$)} (9a).

To a CH_3OH (2 ml) solution of **6a** (0.051 g, 0.0821 mmol) was added ^{t}BuOK (0.012 g, 0.107 mmol) with immediate formation of a yellow solid. The suspension was stirred for 30 min, and the solid **9a** collected by suction filtration and dried. Yield: 0.041 g, 85%. The η^1-allylpalladium(II) complexes **9b** (51%) and **9c** (51%) were prepared similarly. Selected data for **9a**: ^{31}P: 32.4 ppm. ^{1}H: 8.33 (s, 1H), 8.27 (s, 1H), 7.64–6.85 (m, 18H), 5.39 (m, 1H, =CH), 4.72 (s, 2H), 4.40 (d, 1H, $=CH_2$), 4.16 (d, 1H, $=CH_2$), 1.83 (m, 2H, $-CH_2Pd$) ppm. FT–IR: 3268, 1642, 1605, 1556 cm^{-1}. ES–MS: *m/z* 585 [M$^+$]. Anal. (%) Calcd. for $C_{30}H_{27}N_2O_2PPd$: C, 61.59; H, 4.66; N, 4.79. Found: C, 61.46; H, 4.40; N, 4.45. Selected data for **9b**: ^{31}P: 32.6 ppm. ^{1}H: 8.29 (s, 1H), 7.67–7.08 (m, 18H), 5.25 (m, 1H, =CH), 4.73 (m, 2H), 4.64 (m, 2H), 4.58 (s, 1H), 4.18 (d, 1H, $=CH_2$), 3.74 (d, 1H, $=CH_2$), 1.60 (m, 2H, $-CH_2Pd$) ppm. FT–IR: 1648 (CO amide I), 1556 (CO amide II) cm^{-1}. ES–MS: *m/z* 599 [M$^+$]. Anal. (%) Calcd. for $C_{31}H_{29}N_2O_2PPd\cdot1.5H_2O$: C, 59.47; H, 5.16; N, 4.48. Found: C, 59.29; H, 4.71; N, 4.54. Selected data for **9c**: ^{31}P: 31.8 ppm. ^{1}H: 8.37 (s, 1H), 8.33 (s, 1H), 7.67–6.75 (m, 18H), 5.40 (m, 1H, =CH), 4.62 (s, 2H), 4.20 (m, 1H, $=CH_2$), 3.86 (m, 1H, $=CH_2$), 1.70 (m, 2H, $-CH_2Pd$) ppm. FT–IR: 3211, 1646, 1558 cm^{-1}. ES–MS: *m/z* 585 [M$^+$]. Anal. (%) Calcd. for $C_{30}H_{27}N_2O_2PPd$: C, 61.59; H, 4.66; N, 4.79. Found: C, 60.90; H, 4.43; N, 4.44.

Preparation of *1,2*-(OH)C_6H_4{NC(O)CH_2N=CH-$C_6H_4PPh_2Pd(CH_3)$} (10a).

To a CH_3OH (2 ml) solution of **7a** (0.050 g, 0.084 mmol) was added ^{t}BuOK (0.012 g, 0.107 mmol) with immediate formation of a pale pink solid **10a**. The mixture was stirred for 40 min and the solid isolated by suction filtration and dried *in vacuo*. Yield: 0.045 g, 96%. The methylpalladium(II) complex **10c** (74%) was similarly prepared. Selected data for **10a**: ^{31}P: 36.2 ppm. ^{1}H: 8.36 (s, 1H), 8.29 (s, 1H), 7.68–6.82 (m, 18H), 4.77 (s, 2H), 0.00 (d, $^3J_{PH}$ 3.2, 3H) ppm. FT–IR: 2945, 1651, 1594, 1567 cm^{-1}. ES–MS: *m/z* 559 [M$^+$]. Anal. (%) Calcd. for $C_{28}H_{25}N_2O_2PPd$: C, 60.16; H, 4.52; N, 5.01. Found: C, 59.66; H, 4.20; N, 4.89. Selected data for **10c**: ^{31}P: 34.7 ppm. ^{1}H [$CDCl_3$/$(CD_3)_2SO$]: 8.43 (s, 1H), 8.30 (s, 1H), 7.77–6.81 (m, 18H), 4.76 (s, 2H), 0.00 (d, $^3J_{PH}$ 3.2, 3H) ppm. FT–IR: 3384, 3212, 2949, 1646, 1555 cm^{-1}. ES–MS: *m/z* 559 [M$^+$]. Anal. (%) Calcd. for $C_{28}H_{25}N_2O_2PPd\cdot H_2O$: C, 58.29; H, 4.73; N, 4.86. Found: C, 58.27; H, 4.20; N, 4.79.

Preparation of *1,2*-(O)C_6H_4{NC(O)CH_2N=CH-$C_6H_4PPh_2Pt$} (11a).

Method 1. A CH_3OH (3 ml) solution of **5a** (0.101 g, 0.143 mmol) was treated with ^{t}BuOK (0.044 g, 0.392 mmol). The orange/red suspension was stirred for 40 min, filtered and washed with a small portion of CH_3OH. Yield: 0.079 g, 88%. Compound **11b** was prepared similarly in quantitative yield whereas **11c** was prepared (in 91% yield) from $NiCl_2\cdot6H_2O$, ^{t}BuOK and **3a·HH**. Selected data for **11a**: ^{31}P: 8.0 ppm, $^1J_{PtP}$ 3371 Hz. ^{1}H: 8.38 ($^3J_{PtH}$ 99.6, 1H), 8.34 (d, 1H), 7.80–6.63 (m, 17H), 5.13 ppm ($^3J_{PtH}$ 15.8, 2H). FT–IR: 1628 (CO), 1609 cm^{-1}. ES–MS: *m/z* 632 [M$^+$]. Anal. (%) Calcd. for $C_{27}H_{21}N_2O_2PPt$: C, 51.35; H, 3.36; N, 4.44. Found: C, 50.82; H, 3.17; N, 4.78. Selected data for **11b**: ^{31}P: 21.3 ppm. ^{1}H: 8.18 (d, 1H), 8.05 (s, 1H), 7.70–6.68 (m, 17H), 5.03 ppm (s, 2H). FT–IR: 1642 (CO), 1616 cm^{-1}. ES–MS: *m/z* 543 [M$^+$]. Anal. (%) Calcd. for $C_{27}H_{21}N_2O_2PPd$: C, 59.73; H, 3.91; N, 5.16. Found: C, 59.53; H, 3.83; N, 5.85. Selected data for **11c**: ^{31}P: 19.7 ppm. ^{1}H: 8.17 (d, 1H), 8.03 (s, 1H), 7.74–6.46 (m, 17H), 4.59 ppm (s, 2H). FT–IR: 1634 (CO), 1608 cm^{-1}. ES–MS: *m/z* 495 [M$^+$]. Anal. (%) Calcd. for $C_{27}H_{21}N_2O_2PNi\cdot CH_2Cl_2$: C, 57.97; H, 4.00; N, 4.83. Found: C, 57.84; H, 3.80; N, 4.90.

Method 2. To a CH_2Cl_2 (5 ml) solution of $Pd(OAc)_2$ (0.025 g, 0.111 mmol) was added **3a·HH** (0.050 g, 0.114 mmol) to give a deep red solution. The solution was stirred for 45 min, the volume reduced to *ca*. 1–2 ml and addition of diethyl ether (20 ml) gave **11b** which was collected by suction filtration and dried *in vacuo*. Yield: 0.056 g, 93%.

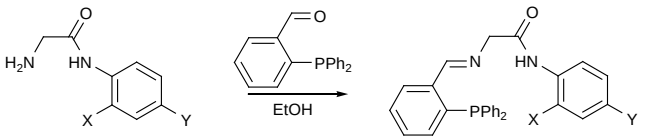
The complexes **11d–11f** (78, 83 and 80% yields respectively) were prepared using the same procedure as for **11a–11c**. Selected data for **11d**: ^{31}P: 10.4 ppm, $^1J_{PtP}$ 3378 Hz. ^{1}H: 8.58 ($^3J_{PtH}$ 95.2, 1H), 8.32 (dd, 1H), 7.73–6.48 (m, 17H), 4.11 (m, 1H), 3.89 (ddd, 1H), 3.60 (dd, 1H), 1.39 (d, $^3J_{HH}$ 6.6, 3H) ppm. FT–IR: 1598, 1566, 1526 cm^{-1}. ES–MS: *m/z* 660 [M$^+$]. Anal. (%) Calcd. for $C_{29}H_{25}N_2O_2PPt\cdot CHCl_3$: C, 46.25; H, 3.37; N, 3.60. Found: C, 46.29; H, 3.32; N, 3.53. Selected data for **11e**: ^{31}P: 24.3 ppm. ^{1}H: 8.27 (s, 1H), 8.24 (dd, 1H), 7.70–6.44 (m, 17H), 4.07 (m, 1H), 3.84 (ddd, 1H), 3.51 (dd, 1H), 1.32 (d, $^3J_{HH}$ 6.5, 3H) ppm. FT–IR: 1595, 1563, 1525 cm^{-1}. ES–MS: *m/z* 571 [M$^+$]. Anal. (%) Calcd. for $C_{29}H_{25}N_2O_2PPd$: C, 61.00; H, 4.42; N, 4.91. Found: C, 60.36; H, 4.45; N, 4.65. Selected data for **11f**: ^{31}P: 22.7 ppm. ^{1}H: 8.13 (m, 2H), 7.83–6.09 (m, 17H), 3.84 (m, 1H), 3.72 (ddd, 1H), 3.39 (dd, 1H), 1.51 (d, $^3J_{HH}$ 6.4, 3H) ppm. FT–IR: 1597, 1569, 1522 cm^{-1}. FAB–MS: *m/z* 523 [M$^+$]. Anal. (%) Calcd. for $C_{29}H_{25}N_2O_2PNi\cdot CHCl_3$: C, 56.07; H, 4.09; N, 4.36. Found: C, 55.51; H, 4.01; N, 4.12.

Results and discussion

Ligand Syntheses

The new unsymmetric ligands **3a·HH**–**3c·HH** were synthesised from **2a**–**2c** (Scheme 1) using a previous literature method for the synthesis of ligands with N_2O_2[17,27a] and N_3O[27b] donor sets. Reaction of the aminoalcohols $RC_6H_4NH_2$ (R = 2-OH, 4-OH or 2-CH_2OH) with carbobenzyloxyglycine and a slight excess of DCC in THF for 4 h gave **1a**–**1c** in high yields. Treatment of **1a**–**1c** with Pd/C (10%) and cyclohexene in refluxing EtOH gave, after filtration and evaporation of the solvent, the 1º amines **2a**–**2c** (characterising data for **1b, 1c**, **2b** and **2c** provided in the ESI). Using a well established route[14d,14e,16,28,29e] for synthesising phosphinoimines, reaction of **2a**–**2c** with 2-$Ph_2PC_6H_4$(CHO) in refluxing EtOH gave, after workup, the tetradentate ligands **3a·HH**–**3c·HH** in good yields (61–76%). This synthetic approach was also used to prepare **3d·HH** from 2-C_6H_4(OH){C(O)NHCH$_2$CH(Me)NH$_2$} **2d**[18] and 2-$Ph_2PC_6H_4$(CHO) in EtOH at ambient temperature (Scheme 2). Compounds **3a·HH**–**3d·HH** were obtained as off-white solids, soluble in a range of common organic

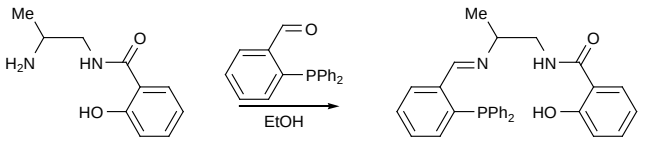
solvents. The spectroscopic data confirm Schiff base condensation, with formation of a CH=N bond, since new ^{31}P signals were observed at δ(P) –8 ppm [*c.f.* δ(P) –11.2 ppm for 2-$Ph_2PC_6H_4$(CHO)]. Furthermore the ^{1}H NMR spectra, in all four cases, show a distinct C*H*=N resonance in the range δ(H) 8.58–8.83 ppm and a singlet in the region δ(H) 4.25–4.32 ppm for the methylene group (CH_2N). Compounds **3a·HH**–**3d·HH** adopt an *E*- (anti-) configuration as previously observed for other phosphinoimine ligand systems[14a] and based on single crystal X-ray studies for **3a·HH** and **3c·HH** (*vide infra*).



X = OH, Y = H **2a**
X = CH_2OH, Y = H **2b**
X = H, Y = OH **2c**

X = OH, Y = H **3a·HH**
X = CH_2OH, Y = H **3b·HH**
X = H, Y = OH **3c·HH**

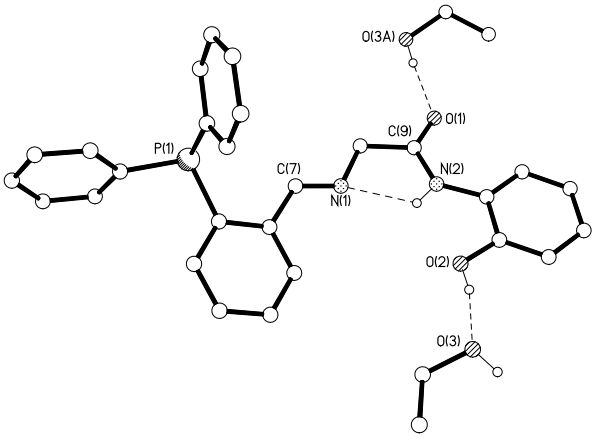
Scheme 1



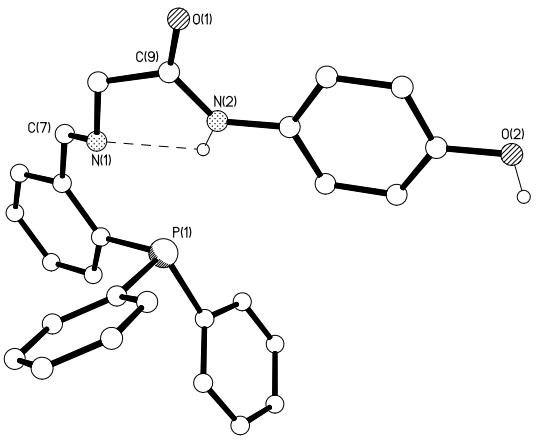
2d **3d·HH**

Scheme 2

The X-ray structures of **3a·HH**·EtOH [Fig. 1(a)] and **3c·HH**·0.5$CHCl_3$ [Fig. 1(b)] have been determined. In both **3a·HH** and **3c·HH** the geometry around P(1) is distorted tetrahedral with C–P–C angles in the range 101.03(8)–104.08(8)°. The most distinct structural difference between these isomeric ligands is the relative orientation of the Ph_2P– unit with respect to the N(1)/N(2)/O(2) donor atoms. In **3a·HH** the Ph_2P– group points away from N(1)/N(2)/O(2) yet in **3c·HH** this group faces both the N(1)/N(2) donor atoms. Free rotation about C(7)–C(aryl) is plausible thus predisposing all four donor atoms (for **3a·HH**) in the same plane when bound in a tetradentate fashion. Various H-bonding interactions in **3a·HH** and **3c·HH** exist including, common to both structures, an intramolecular N(1)···H(2)–N(2) H-bond [N(1)···N(2) 2.638(2) Å, N(1)···H(2)–N(2) 117.0(17)° for **3a·HH**; N(1)···N(2) 2.688(2) Å, N(1)···H(2)–N(2) 116.6(16)° for **3c·HH**]. Furthermore, additional intermolecular H-bonding to an EtOH solvate [O(1)···O(3A) 2.6846(19) Å, O(1)···H(3B)–O(3A) 172(3)° and O(2)···O(3) 2.598(2) Å, O(2)–H(2A)···O(3) 167(3)°] is evident in **3a·HH**. Compound **3c·HH** forms chains along the *c* direction *via* intermolecular H-bonding [O(2)···O(1A) 2.694(2) Å, O(2)–H(2A)···O(1A) 158(3)°] between adjacent molecules (see ESI for further details).



(a)

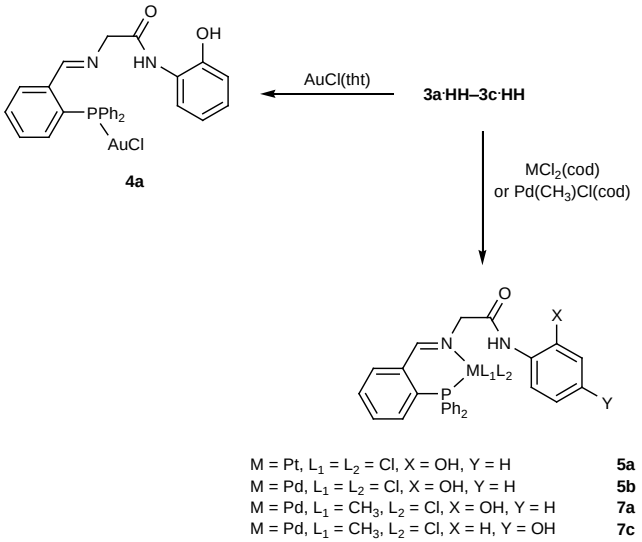


(b)

Fig. 1 Molecular structures of (a) **3a·HH**·EtOH and (b) **3c·HH**·0.5$CHCl_3$. The disordered $CHCl_3$ and all hydrogen atoms except those on N(2), O(2), O(3) and O(3A) are removed for clarity. Symmetry operator A = –x + 1, y + $^1/_2$, –z + $^5/_2$.

Coordination studies

The reactivity of **3a·HH**–**3d·HH** towards linear and square-planar metal centres was explored in order to evaluate their flexibility and coordination potential. Classical κ^1-P-coordination was achieved upon stoichiometric reaction of **3a·HH** with AuCl(tht) in CH_2Cl_2 affording **4a** in 91% yield (Scheme 3). The downfield shift of δ(P) 29.2 ppm [in addition to a minor (*ca.* 5%) species identified as AuCl{2-$Ph_2PC_6H_4$(CHO)}, δ(P) 32.2 ppm, presumably arising from hydrolysis of the imine bond] clearly support *P*-coordination of **3a·HH**.



Scheme 3

The X-ray structure of **4a** (Fig. 2, Table 2) shows typical Au–P [2.2283(10) Å], Au–Cl [2.2714(12) Å] and Cl–Au–P [179.61(6)°] parameters consistent with a near linear geometry around Au(I). Upon coordination, the conformation of **3a·HH**, with respect to the NN`O- group, remains unaltered. Furthermore there persists a strong intramolecular N(1)···H(2)–N(2) H-bond [N(1)···N(2) 2.592(5) Å, N(1)···H(2)–N(2) 116°] and neighbouring molecules form chains (see ESI) along the *a* direction through O–H···O intermolecular H-bonds [O(2)···O(1A) 2.661(4) Å, O(2)–H(2A)···O(1A) 143°].

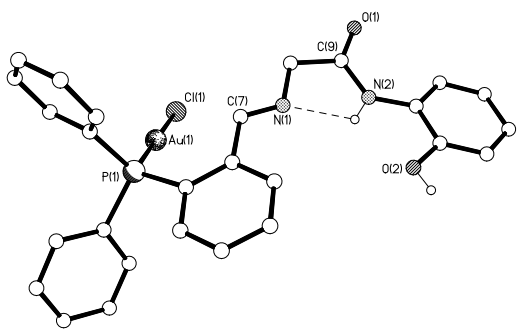
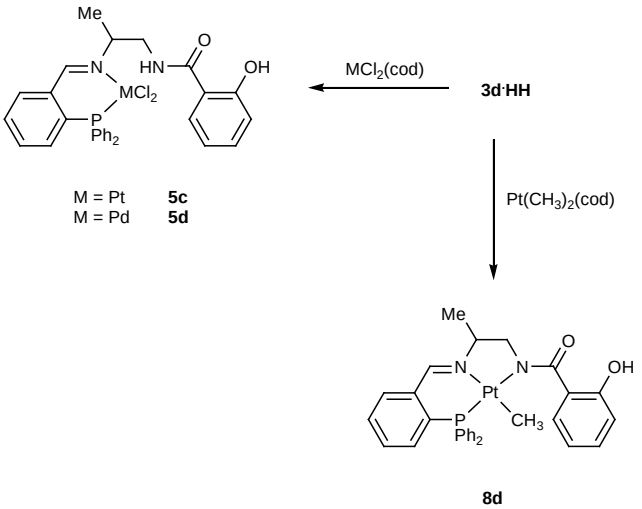
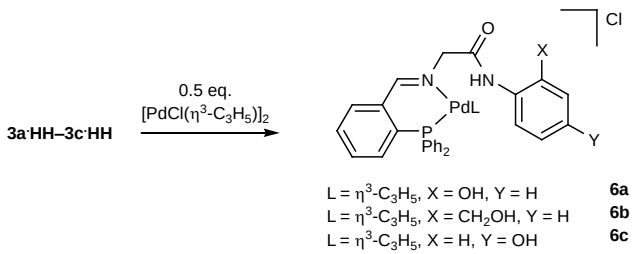


Fig. 2 Molecular structure of **4a**. All hydrogen atoms except those on N(2) and O(2) are removed for clarity.

Phosphinoimines are well known to form late transition-metal chelate complexes using both P and imine N-donor atoms.[29] Furthermore Pd^{II} iminophosphine complexes have been used in a range of catalytic applications highlighting the versatility of these ligand systems.[6f,30] In order to probe the coordination behaviour of ligands **3a·HH**–**3d·HH** treatment of MCl_2(cod) (M = Pt, Pd) with one equiv. of **3a·HH** (or **3d·HH**) afforded the chelate complexes **5a**, **5b** (or **5c**, **5d**) (Scheme's 3 & 4). Mononuclear cationic [Pd(η^3-C_3H_5)(**3a·HH**–**3c·HH**)]Cl (**6a**–**6c**) and neutral Pd(CH_3)Cl(**3a·HH**/**3c·HH**) (**7a**,**7c**) complexes were readily prepared from [PdCl(η^3-C_3H_5)]$_2$ and Pd(CH_3)Cl(cod) (Scheme's 3 & 5). In all complexes, κ^2-P,N-chelation was deduced from downfield phosphorus chemical shifts [δ(P) 38.2 ppm (for **5b**); *ca*. 24 ppm (for **6a**–**6c**); *ca*. 38 ppm (for **7a**, **7c**)]. For **5a**, in $CDCl_3$/CH_3OH solution, two species at δ(P) 10.7 ppm, $^1J_{PtP}$ 3492 Hz and 3.0 ppm, $^1J_{PtP}$ 3324 Hz were observed, tentatively assigned neutral and cationic structures, the later presumably involving NH/OH coordination.



Scheme 4



Scheme 5

The X-ray structure of **7c**·CH_2Cl_2 (Fig. 3, Table 2) shows the phosphinoimine κ^2-P,N-donor atoms to chelate the palladium(II) centre with six-membered ring formation. The methyl group lies *trans* to N with Pd–P, Pd–N, Pd–C and Pd–Cl bond lengths similar to those in previous reported compounds.[6j] In **7c**·CH_2Cl_2 the "Pd(CH_3)Cl" fragment is hinged about P(1)···N(1)/C(7) with P(1)–C(1)–C(6)–C(7) lying essentially flat (within ±0.032 Å). The Pd(1) metal atom resides out of the basal plane of the P(1), N(1), Cl(1) and C(28) donor substituents by 0.027 Å. An intermolecular O(1`)···H(2A)–O(2) [O(1`)···O(2) 2.696(3) Å and O(1`)···H(2A)–O(2) 178(4)°; symmetry operator ' = x, –y + $^1/_2$, z – $^1/_2$] H-bond links molecules into chains along the *c* direction (see ESI) and there also exists an intramolecular N(2)–H(2)···Cl(1) [N(2)···Cl(1) 3.131(2) Å and

N(2)–H(2)···Cl(1) 166(3)°] H-bond. From the solid state structure it is possible to envisage how **3c·HH** could further function as a tridentate ligand.

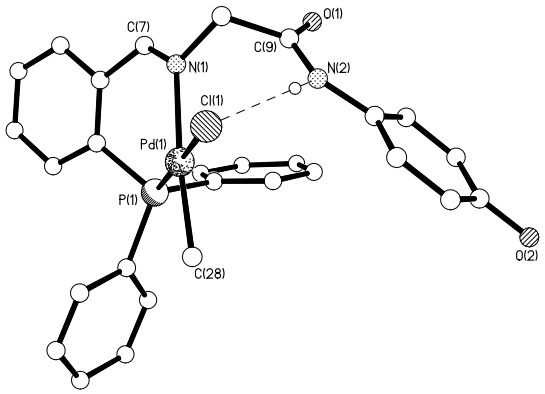
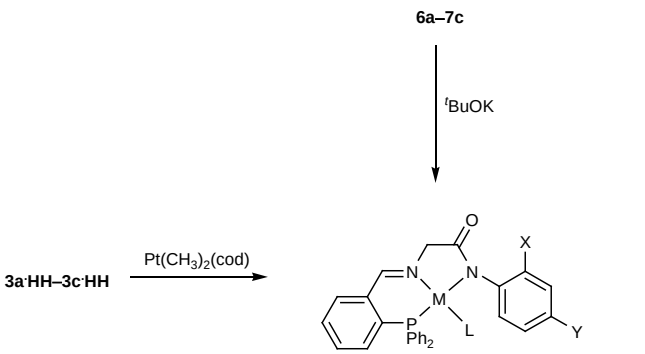


Fig. 3 Molecular structure of **7c**. The CH_2Cl_2 solvent of crystallisation and all hydrogen atoms except on N(2) are removed for clarity.



M = Pt, L = CH_3, X = OH, Y = H	**8a**
M = Pt, L = CH_3, X = CH_2OH, Y = H	**8b**
M = Pd, L = η^1-C_3H_5, X = OH, Y = H	**9a**
M = Pd, L = η^1-C_3H_5, X = CH_2OH, Y = H	**9b**
M = Pd, L = η^1-C_3H_5, X = H, Y = OH	**9c**
M = Pd, L = CH_3, X = OH, Y = H	**10a**
M = Pd, L = CH_3, X = H, Y = OH	**10c**

Scheme 6

In order to verify whether ligands **3a·HH**–**3d·HH** could function as κ^3-PNN`-tridentate ligands it was necessary to find a synthetic method which would permit single deprotonation of the NH amide group. Klein *et al*[31] demonstrated the secondary amide phosphine 2-$Ph_2PC_6H_4(NHR)$ smoothly reacts with $Co(CH_3)\{P(CH_3)_3\}_4$ to afford a five-coordinate Co^I complex accompanied by CH_4 elimination. When $Pt(CH_3)_2$(cod) was employed instead, we reasoned the P,N_{imine} group would displace the cod ligand and position the coordinated ligand for methyl protonation/elimination by the NH amide hydrogen (the OH group could function similarly). Satisfyingly, in toluene this reaction proceeds cleanly to give **8a** (and **8b**, **8d**) in high yields as yellow, air-stable solids (Scheme's 4 & 6) which were fully characterised by NMR, FT–IR, ES–MS and microanalyses. In the $^{31}P\{^1H\}$ NMR spectra of **8a**, **8b** and **8d**, clean ^{31}P resonances were observed around δ(P) 13 ppm [$^1J_{PtP}$ 3800–3870 Hz]. The ^1H NMR spectra clearly show retention of one methyl group [δ(H) *ca.* 0.00 ppm, $^2J_{PtH}$ *ca.* 73 Hz] and was further corroborated by single crystal X-ray structure determinations of **8a** (Fig. 4), **8b** (Fig. 5) and **8d** (Fig. 6).

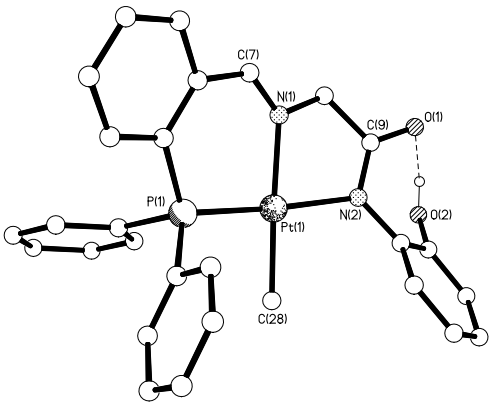


Fig. 4 Molecular structure of **8a** showing the intramolecular O–H···O H-bond. The $CHCl_3$ solvent of crystallisation is removed for clarity.

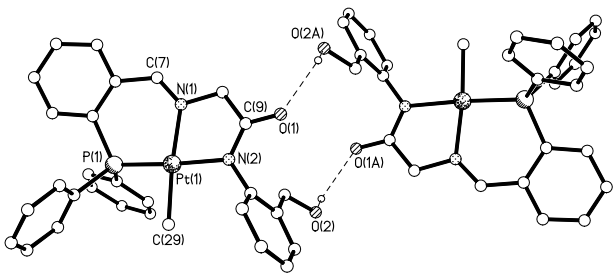


Fig. 5 Molecular structure of **8b** showing the H-bonded dimer pair formation. The C_7H_8 solvent of crystallisation is removed for clarity.

The complexes **8a**, **8b** and **8d** display an essentially square-planar environment around the platinum centre with bond angles in the range 80.31(13)–95.45(9)° (Table 2). The Pt–N(1) and Pt–N(2) bond lengths vary slightly whilst the Pt–P and Pt–C bond distances are similar.[14a] Furthermore, trigonal planar geometries around N(1) and N(2) can be inferred from bond angles (*ca.* ∑ 360°) at both nitrogen centres in accord with amide functional groups. In **8a**, the Pt(1)–N(1)–C(7)–C(6)–C(1) ring is essentially flat (within ±0.09 Å) with P(1) lying 0.39 Å out of this plane whereas in **8b** the N(1)–C(7)–C(6)–C(1)–P(1) ring is essentially flat (within ±0.07 Å) with Pt(1) lying 0.37 Å out of this plane. For the five-membered ring in **8a**, N(1) lies 0.38 Å out of the plane with respect to Pt(1)–N(2)–C(9)–C(8) which is essentially flat (within ±0.004 Å) and this feature remains for **8b**. For **8d**, the N(2)–Pt(1)–N(1)–C(8) is co-planar (within

±0.006 Å) with C(10) out of this plane by 0.68 Å resulting in an envelope conformation. The two compounds **8a** and **8b**, differing only by an extra methylene group, give rise to disparate intramolecular and intermolecular O···H–O H-bonding motifs. In **8a** and **8d** there is an intramolecular O(1)···H(2)–O(2) H-bond [O(1)···O(2) 2.543(5) Å, O(1)···H(2)–O(2) 151° for **8a**; O(1)···O(2) 2.509(5) Å, O(1)···H(2)–O(2) 160(6)° for **8d**]. For **8b**, dimer pairs are formed through intermolecular O···H–O H-bonding [O(1A)···O(2) 2.758(5) Å, O(1A)···H(2)–O(2) 127°; symmetry operator A = –x+1, –y+1, –z+1] generating an $R^2_2(16)$ ring motif. The effect of amide deprotonation and complexation has clearly reduced the potential for any further H-bonding.

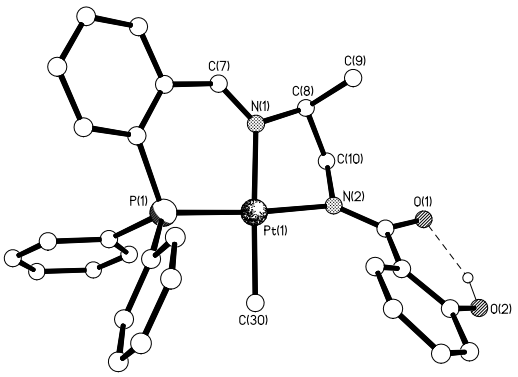
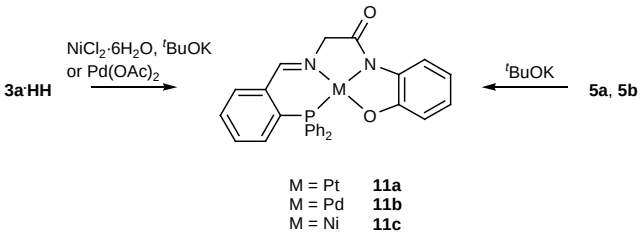


Fig. 6 Molecular structure of **8d**. The C_7H_8 solvent is removed for clarity.

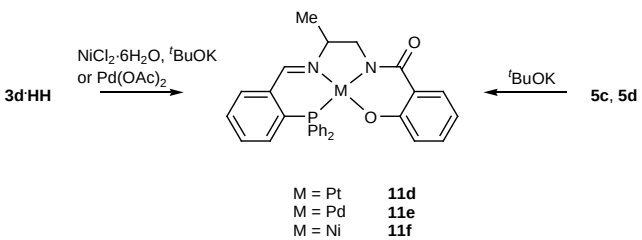
Two further studies were undertaken regarding the formation of **8a** and **8b** from $Pt(CH_3)_2$(cod). Firstly, in solution by $^{31}P\{^1H\}$ NMR spectroscopy, could we possibly observe the intermediate formation of $Pt(CH_3)_2$(**3a·HH**) **8a`** and, secondly, could a second methane elimination be thermally induced? *In situ* monitoring of a 1:1 mixture of $Pt(CH_3)_2$(cod)/**3a·HH** in toluene/C_6D_6 revealed the immediate formation of two new species at δ(P) 24.8 ppm [$^1J_{PtP}$ 1905 Hz] and δ(P) 25.2 ppm [$^1J_{PtP}$ 1831 Hz]. For both speices, the magnitude of $^1J_{PtP}$ was indicative of κ^2-P,N-chelation with *trans* coordinated methyl ligands. We believe restricted rotation about the amide bond leads to these two species which are *E*/*Z*-conformational isomers.[14a] Over *ca.* 2 h the intensity of these phosphorus signals diminishes as a new signal at δ(P) appears corresponding to the formation of **8a** in solution. When **8b** was refluxed in toluene under N_2 for 68h only the starting compound was isolated, clearly indicating that a second methane protonation by the benzylalcohol group is extremely slow. Likewise, **8a** in refluxing toluene for 24 h showed no evidence, by $^{31}P\{^1H\}$ NMR spectroscopy, of *O*-coordination despite the more acidic phenolic substituent.

Alternatively, κ^3-PNN`-tridentate ligation could be induced by reacting **6a–6c**, **7a** or **7c** with ^{t}BuOK in CH_3OH at room temperature (Scheme 6). These clean transformations afforded the compounds **9a**–**9c**, **10a** and **10c** in good to excellent isolated yields (51–96%). Very few examples of tridentate[28,32], and fewer still of didentate[33], ligands have been shown to stabilise soft metal centres towards η^1-allyl coordination. Upon complexation, there was a small change in δ(P) of *ca.* 5–10 ppm for **9a**–**9c**. However the most significant insight was provided by new, sharp ^1H resonances for all five protons on the η^1-allyl ligand, clearly supporting monohapto coordination. The solution stability of **10a** towards internal protonation by the OH group was also investigated since Pd compounds are often more reactive than their Pt counterparts. $^{31}P\{^1H\}$ NMR monitoring of a CD_2Cl_2 solution of **10a** over several days at r.t. afforded a mixture of phosphorus containing compounds including **11b** (*vide infra*).



Scheme 7

Having established three distinct binding modes for these ligands, we were interested to see whether they could function as κ^4-tetradentate ligands using all four donor atoms (P, N/N` and O). Complexed ligands with either an *ortho* –OH or –CH_2OH group would be anticipated to use the *O*-donor in bonding to a single metal centre with concomitant formation of a five- or six-membered chelate ring. Accordingly reaction of **5a**, **5b**, bearing the more acidic phenolic group, in CH_3OH with ^{t}BuOK gave the neutral compounds **11a** and **11b**. The nickel complex **11c** was obtained directly from $NiCl_2·6H_2O$, **3a·HH** and ^{t}BuOK in CH_3OH (Scheme 7). Compounds **11d**–**11f** were prepared cleanly using an identical approach to those described for **11a**–**11c** (Scheme 8). Upon *N*,*O*-chelation, there is a marked reduction in $^1J_{PtP}$ for **11a** (3371 Hz) and **11d** (3378 Hz) in comparison to the κ^3-PNN`-tridentate compounds **8a** (3865 Hz) and **8d** (3834 Hz). Sharp ^{31}P resonances at δ(P) 19.7 ppm (for **11c**) and 22.7 ppm (for **11f**) are indicative of square-planar, diamagnetic species. Alternatively **11b** could be prepared, in one-step, by reaction of $Pd(OAc)_2$ and **3a·HH** in CH_2Cl_2.



Scheme 8

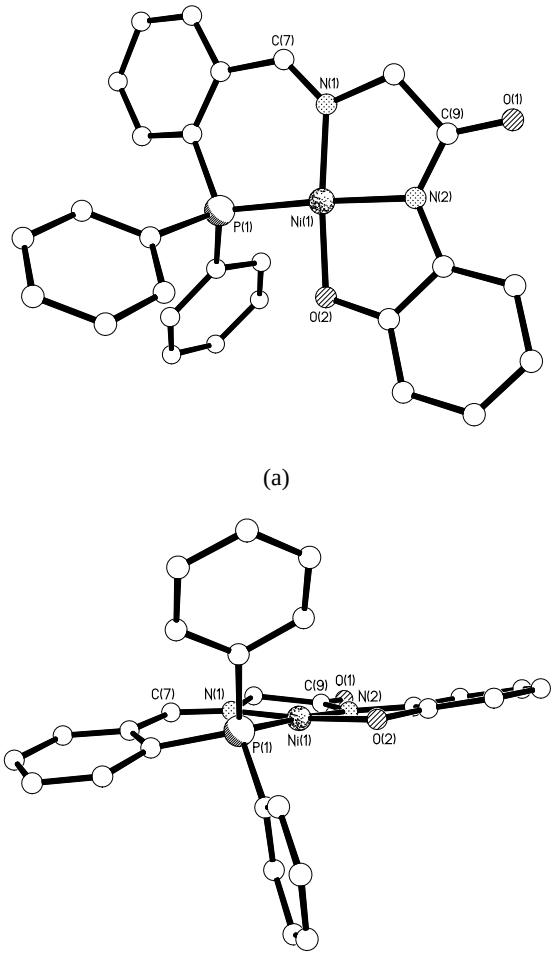


Fig. 7 Molecular structure of (a) **11c** (compounds **11a** and **11b** isomorphous) (b) side-on view showing the ring conformations in **11c**.

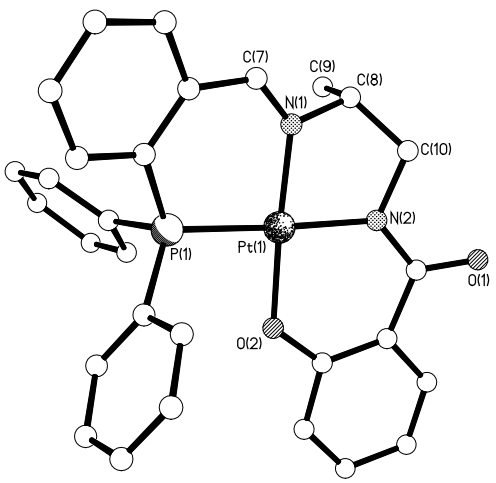


Fig. 8 Molecular structure of **11d**. The $CHCl_3$ solvent is removed for clarity.

The X-ray structures of the Pt, Pd and Ni complexes **11a**–**11c** and **11d** have each been determined (Fig's 7, 8 and ESI; Table 2). In compounds **11a**–**11c** tetradentate κ^4-PNN`O-complexation has clearly resulted with formation of one six-(M–P–C–C–C–N) and two five-membered (M–N–C–C–N and M–N–C–C–O) chelate rings. As an illustration, the three ring conformations in **11c** are described as follows: the Ni(1)–N(1)–C(7)–C(6)–C(1) part of the ring is essentially flat (within ±0.05 Å) with P(1) lying 0.30 Å out of this plane, whereas both five-membered rings are effectively planar [within ±0.04 Å for Ni(1)–N(2)–C(10)–C(15)–O(2) and ±0.07 Å for Ni(1)–N(1)–C(8)–C(9)–N(2)]. Within this series the M–P, M–N and M–O bond lengths follow the expected trend on going from Pt > Pd > Ni. In **11a** the Pt(1)–N(1) [1.977(3) Å] and Pt(1)–N(2) [2.000(3) Å] distances are similar, the later compares favourably with previous Pt–N_{amide} bond lengths [2.035(6) Å and 2.067(5) Å].[13i] The Pd–O bond lengths for the two independent molecules in **11b** [2.001(5) Å and 1.997(5) Å] are similar to those in $Pd(OPh)_2(bpy)$ [1.996(7) Å][34] but significantly shorter than found in Pd{κ^2-P,N-2-$Ph_2PC_6H_4(CH_2NMe_2)$}Cl(OPh) (P *trans* to O, 2.088(5) Å *vs.* P(1) *trans* to N(1) in **11b**].[35] Crystallographically characterised examples with this combination of donor atoms around the central Ni^{II}, Pd^{II} or Pt^{II} are extremely sparse.[15,36–38] As far as we are aware only one Ni^{II} complex containing a κ^4-PNN`O tetradentate ligand has been crystallographically reported[15] and shows similar Ni–P and Ni–O distances to those found in **11c** [2.1553(5) and 1.8405(12) Å respectively]. For **11a**, there is an O–H···O intermolecular H-bond [O(2)···O(3) 2.775(4) Å, O(2)···H(3)–O(3) 174°] to a CH_3OH solvate molecule.

Conclusions

In summary, we have developed an efficient, simple, procedure to four new PNN`O-functionalised tertiary phosphines and shown these ligands can adopt a range of coordination modes, including tetradentate ligation, at different transition-metal centres with either linear or square-planar geometries. Further studies are in progress and will be reported in due course.

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Table 1 Details of the X-ray data collections and refinements for compounds **3a·HH**·EtOH, **3c·HH**·0.5$CHCl_3$, **4a**, **7c**·CH_2Cl_2, **8a**·$CHCl_3$, **8b**·1.5C_7H_8, **8d**·2C_7H_8, **11a**·CH_3OH, **11b**·0.5$CHCl_3$·0.5Et_2O, **11c** and **11d**·$CHCl_3$.

Compound	**3a·HH**·EtOH	**3c·HH**·0.5$CHCl_3$	**4a**	**7c**·CH_2Cl_2	**8a**·$CHCl_3$	**8b**·1.5C_7H_8
Formula	$C_{29}H_{29}N_2O_3P$	$C_{27.5}H_{23.5}Cl_{1.5}N_2O_2P$	$C_{27}H_{23}AuClN_2O_2P$	$C_{29}H_{28}Cl_3N_2O_2PPd$	$C_{29}H_{26}Cl_3N_2O_2PPt$	$C_{39.5}H_{39}N_2O_2PPt$
M	484.51	498.13	670.86	680.25	766.93	799.79
Crystal dimensions	0.79 x 0.16 x 0.06	0.61 x 0.26 x 0.10	0.24 x 0.19 x 0.15	0.31 x 0.20 x 0.18	0.65 x 0.15 x 0.09	0.24 x 0.19 x 0.06
Colour, habit	Lath, colourless	Lath, colourless	Block, colourless	Block, colourless	Rod, yellow	Block, yellow
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	11.0184(8)	18.7587(11)	7.3440(6)	13.6159(6)	9.1632(14)	11.8821(10)
b/Å	18.5035(13)	8.3781(5)	16.0841(13)	13.2505(6)	11.944(2)	14.1839(12)
c/Å	12.7514(9)	17.3155(10)	21.1068(17)	16.1783(7)	14.872(2)	21.8916(18)
α/°					99.169(3)	
β/°	95.4000(13)	114.6476(9)		95.7566(8)	103.818(2)	103.7463(13)
γ/°					112.534(2)	
V/Å^3	2588.2(3)	2473.4(3)	2493.2(3)	2904.1(2)	1401.7(4)	3583.8(5)
Z	4	4	4	4	2	4
μ/mm^{-1}	0.139	0.301	6.099	1.000	5.379	3.995
θ range/°	1.86–27.50	2.36–27.50	1.59–28.97	1.99–29.00	1.92–28.92	1.73–28.87
Measured reflections	22131	20748	21675	25451	12247	30189
Independent reflections	5901	5646	5974	7080	6407	8575
Observed reflections ($F^2 > 2\sigma$)	4303	4273	5330	5579	5961	6516
Goodness of fit on F^2	1.019	1.040	1.050	1.060	1.082	0.951
R_{int}	0.0272	0.0270	0.0382	0.0301	0.0251	0.0490
$R[F^2 > 2\sigma(F^2)]$[a]	0.0442	0.0428	0.0269	0.0320	0.0328	0.0374
$wR2$ [all data][b]	0.1176	0.1175	0.0572	0.0707	0.0872	0.0904
Largest difference map features/eÅ^3	0.611, –0.474	0.636, –0.443	1.177, –0.967	0.679, –0.879	2.698, –2.572	1.949, –2.115

Table 1 Contd

Compound	**8d**·2C_7H_8	**11a**·CH_3OH	**11b**·0.5$CHCl_3$·0.5Et_2O	**11c**	**11d**·$CHCl_3$
Formula	$C_{44}H_{45}N_2O_2PPt$	$C_{28}H_{25}N_2O_3PPt$	$C_{29.5}H_{26.5}Cl_{1.5}N_2O_{2.5}PPd$	$C_{27}H_{21}N_2NiO_2P$	$C_{30}H_{26}Cl_3N_2O_2PPt$
M	859.88	663.56	639.57	495.14	778.94
Crystal dimensions	0.33 x 0.32 x 0.14	0.51 x 0.26 x 0.03	0.16 x 0.08 x 0.05	0.32 x 0.13 x 0. 11	0.53 x 0.13 x 0.10
Colour, habit	Block, yellow	Plate, orange	Block, orange	Block, red	Plate, yellow
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$Pna2_1$
a/Å	14.8590(8)	8.5258(4)	14.2900(9)	8.9313(4)	18.5242(8)
b/Å	15.6070(8)	9.3993(4)	24.1029(16)	11.5187(6)	17.4935(8)
c/Å	16.2867(9)	15.6457(7)	17.0697(11)	11.5474(6)	9.2080(4)
α/°		91.4448(7)		73.327(2)	
β/°	95.8849(9)	100.6844(7)	110.6250(13)	84.831(2)	
γ/°		108.3565(7)		70.061(2)	
V/Å^3	3757.1(3)	1164.66(9)	5502.5(6)	1069.76(9)	2983.9(2)
Z	4	2	8	2	4
μ/mm^{-1}	3.817	6.128	0.911	1.011	5.055
θ range/°	1.77–29.05	2.29–28.96	1.60–25.00	1.84–29.10	1.60–27.49
Measured reflections	29318	10164	39875	9613	25028
Independent reflections	9048	5347	9684	4986	6745
Observed reflections ($F^2 > 2\sigma$)	6720	5037	5908	4309	5392
Goodness of fit on F^2	1.061	1.044	0.940	1.046	1.070
R_{int}	0.0378	0.0268	0.0860	0.0132	0.0350
$R[F^2 > 2\sigma(F^2)]$[a]	0.0322	0.0230	0.0626	0.0291	0.0324
$wR2$ [all data][b]	0.0653	0.0582	0.1643	0.0776	0.0752
Largest difference map features/eÅ^3	1.051, –1.060	1.358, –1.814	0.969, –1.281	0.368, –0.260	1.956, –1.482

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond distances and angles for compounds **3a·HH**·EtOH, **3c·HH**·0.5$CHCl_3$, **4a**, **7c**·CH_2Cl_2, **8a**·$CHCl_3$, **8b**·1.5C_7H_8, **8d**·2C_7H_8, **11a**·CH_3OH, **11b**·0.5$CHCl_3$·0.5Et_2O, **11c** and **11d**·$CHCl_3$.

Bond length (Å)	**3a·HH**·EtOH	**3c·HH**·0.5$CHCl_3$	**4a** (M = Au)	**7c**·CH_2Cl_2 (M = Pd)	**8a**·$CHCl_3$ (M = Pt)	**8b**·1.5C_7H_8 (M = Pt)	**8d**·2C_7H_8 (M = Pt)
M(1)–P(1)			2.2283(10)	2.1983(6)	2.1795(12)	2.1842(10)	2.1889(10)
M(1)–Cl(1)			2.2714(12)	2.4062(6)			
M(1)–C_{methyl}				2.031(3)	2.044(5)	2.052(4)	2.061(4)
M(1)–N(1)				2.1899(19)	2.050(4)	2.061(3)	2.077(3)
M(1)–N(2)					2.090(4)	2.075(3)	2.070(3)
M(1)–O(1)							
C(7)–N(1)	1.254(2)	1.266(2)	1.249(5)	1.281(3)	1.279(6)	1.274(5)	1.275(5)
C(9)–O(1)	1.229(2)	1.234(2)	1.220(5)	1.236(3)	1.257(6)	1.260(5)	
C(11)–O(1)							1.275(4)
Bond angle (°)							
Cl(1)–M(1)–P(1)			179.61(6)	177.18(2)			
Cl(1)–M(1)–N(1)				93.33(5)			
Cl(1)–M(1)–C_{methyl}				87.53(8)			
P(1)–M(1)–C_{methyl}				91.15(8)	89.05(14)	90.54(14)	89.38(11)
N(1)–M(1)–C_{methyl}				174.39(11)	174.77(17)	173.98(16)	172.59(14)
N(2)–M(1)–C_{methyl}					95.44(17)	92.97(17)	94.90(14)
N(1)–M(1)–P(1)				88.23(5)	95.26(11)	95.45(9)	95.27(9)
N(2)–M(1)–P(1)					173.78(11)	176.45(10)	175.43(9)
N(1)–M(1)–N(2)					80.48(14)	81.04(13)	80.31(13)
O(2)–M(1)–P(1)							
O(2)–M(1)–N(1)							
O(2)–M(1)–N(2)							

Table 2 Contd

Bond length (Å)	**11a**·CH_3OH (M = Pt)	**11b**·0.5$CHCl_3$·0.5Et_2O (M = Pd)[a]	**11c** (M = Ni)	**11d**·$CHCl_3$ (M = Pt)
M(1)–P(1)	2.2368(8)	2.2494(18) [2.2403(19)]	2.1553(5)	2.2187(16)
M(1)–Cl(1)				
M(1)–C_{methyl}				
M(1)–N(1)	1.977(3)	1.982(6) [1.968(6)]	1.8659(14)	1.973(5)
M(1)–N(2)	2.000(3)	1.957(5) [1.960(6)]	1.8528(14)	2.006(5)
M(1)–O(1)	2.008(2)	2.001(5) [1.997(5)]	1.8405(12)	1.974(5)
C(7)–N(1)	1.291(4)	1.289(8) [1.287(9)]	1.285(2)	1.287(8)
C(9)–O(1)	1.227(4)	1.246(7) [1.226(8)]	1.235(2)	
C(11)–O(1)				1.262(7)
Bond angle (°)				
Cl(1)–M(1)–P(1)				
Cl(1)–M(1)–N(1)				
Cl(1)–M(1)–C_{methyl}				
P(1)–M(1)–C_{methyl}				
N(1)–M(1)–C_{methyl}				
N(2)–M(1)–C_{methyl}				
N(1)–M(1)–P(1)	95.34(8)	94.50(16) [96.07(18)]	96.70(5)	93.75(16)
N(2)–M(1)–P(1)	178.58(7)	174.70(16) [178.85(17)]	176.78(5)	177.18(16)
N(1)–M(1)–N(2)	83.36(11)	83.8(2) [83.7(2)]	86.20(6)	83.4(2)
O(2)–M(1)–P(1)	98.56(6)	98.18(13) [96.97(14)]	90.24(4)	89.19(14)
O(2)–M(1)–N(1)	166.11(10)	167.2(2) [166.7(2)]	172.19(6)	176.9(2)
O(2)–M(1)–N(2)	82.75(9)	83.7(2) [83.2(2)]	86.95(6)	93.6(2)

[a] Two independent molecules in the asymmetric unit. Equivalent parameters for the second molecule are given in parentheses.