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New κ^3-PNN′- and κ^4-PNN′O-polydentate ligands: Synthesis, coordination and structural studies

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ABSTRACT

The three-step synthesis of new mixed P/N/N′/O-donor ligands $C_6H_3(OH)\{2\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}(4\text{-}CH_3)$ **3a·HH** and $C_6H_4(OH)\{3\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}$ **3b·HH**, by Schiff base condensation of the 1° amines $C_6H_3(OH)\{2\text{-}NHC(O)CH_2NH_2\}(4\text{-}CH_3)$ **2a** or $C_6H_4(OH)\{3\text{-}NHC(O)CH_2NH_2\}$ **2b** with $C_6H_4(CHO)(2\text{-}PPh_2)$ in refluxing EtOH, is described. Reaction of 1 equiv. of **3a·HH** or **3b·HH** with $MCl_2(cod)$ (M = Pt, Pd; cod = cycloocta-1,5-diene) affords the κ^2-PN-chelate complexes MCl_2(**3a·HH**) (M = Pd **4a**; M = Pt **4b**) and MCl_2(**3b·HH**) (M = Pt **4c**). The dichlorometal(II) complexes **4d** and **4e**, bearing instead a pendant 4-phenolic group, were similarly prepared (in >90% yield). Chloro-bridge cleavage of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ with **3a·HH** or **3b·HH** gave the monocationic κ^2-PN-chelate complexes $[Pd(\eta^3\text{-}C_3H_5)$(**3a·HH**)]Cl **5a** or $[Pd(\eta^3\text{-}C_3H_5)$(**3b·HH**)]Cl **5b**, respectively. Elimination of cod, and single CH_3 protonation, from $Pt(CH_3)_2(cod)$ upon reaction with 1 equiv. of **3a·HH** or **3b·HH** in C_7H_8 at room temperature afforded the neutral complexes $C_6H_3(OH)\{2\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt(CH_3)\}(4\text{-}CH_3)$ **6a** and $C_6H_4(OH)\{3\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt(CH_3)\}$ **6b**, respectively bearing a monoanionic (**3a·H**$^-$ or **3b·H**$^-$) κ^3-PNN′-tridentate ligand. Amide and phenol deprotonation were readily achieved, using KO^{t}Bu as base, to give high yields of the κ^4-PNN′O-tetradentate complexes $C_6H_3(O)\{2\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pd\}(4\text{-}CH_3)$ **7a** and $C_6H_3(O)\{2\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt\}(4\text{-}CH_3)$ **7b** bearing the dianionic ligand **3a**$^{2-}$. All new compounds have been characterised by multinuclear NMR, FTIR, mass spectroscopy and microanalysis. Single crystal X-ray studies have been performed on compounds **1b**·1.5CH_2Cl_2, **3b·HH**·0.5Et_2O, **6b**·$CHCl_3$ and **7b**·0.5Et_2O.

1. Introduction

Organometallic and coordination complexes of tridentate and tetradentate ligands continue to attract wide interest for the diverse ligating capabilities, sensing, magnetic and luminescent properties and catalytic applications. Various donor atom combinations have been documented in the literature and, in many cases, contain at least one phosphorus donor centre. A range of different donor atom combinations have been reported for tridentate ligands including amongst others: P_2B [1], P_2C [2], P_2Si [3], P_2N [4], P_2O [5], PC_2 [6], PN_2 [7], PNO [8], PNS [8c] and PS_2 [9]. Furthermore, while examples of symmetric tetradentate systems are relatively common and include, for example, P_2N_2 [10], O_2N_2 [11] or S_2N_2 [12], nonsymmetric tetradentate ligands are considerably more unusual and include P_3C [13], P_3Si [14], P_3N [15], PN_3 [16], PN_2O [17] and As_2PN [18]. Herein we describe the synthesis of two new potentially tetradentate ligands bearing a PNN′O donor set combination. We demonstrate, given the correct spatial donor atom orientation, that all four donor centres can readily coordinate to a square-planar metal(II) centre. All new compounds are structurally supported by a combination of spectroscopic and crystallographic techniques.

2. Experimental

2.1. Materials

Standard Schlenk techniques were used for the synthesis of $C_6H_3(OH)\{2\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}(4\text{-}CH_3)$ **3a·HH** and $C_6H_4(OH)\{3\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}$ **3b·HH** whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. The compounds $C_6H_4(CHO)(2\text{-}PPh_2)$ [19], $MCl_2(cod)$ (M = Pt, Pd; cod = cycloocta-1,5-diene) [20] and $Pt(CH_3)_2(cod)$ [21] were all prepared according to known procedures. All other chemicals were obtained from commercial sources and used directly without further purification.

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets on either a Perkin–Elmer System 2000 (4000–400 cm^{-1} range) or a Spectrum 100S

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(4000–250 cm^{-1} range) Fourier-Transform spectrometer. ^1H NMR spectra (400 MHz) were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $Si(CH_3)_4$ and coupling constants (J) in Hz. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4. NMR spectra were measured in $CDCl_3$ or $(CD_3)_2SO$ at 298 K. Elemental analyses (Perkin–Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Mass spectra were recorded within the Department of Chemistry at Loughborough University and by the EPSRC National Mass Spectrometry Service at Swansea University. Compounds **4a** and **4b** were analysed (Thermofisher LTQ Orbitrap XL instrument) by nano-electrospray (nano-ESI) in a positive ionisation mode using CH_2Cl_2 as primary solvent.

2.3. Syntheses

2.3.1. Preparation of $C_6H_3(OH)\{2\text{-}NHC(O)CH_2NHCO_2Bz\}(4\text{-}CH_3)$ (**1a**) and $C_6H_4(OH)\{3\text{-}NHC(O)CH_2NHCO_2Bz\}$ (**1b**)

To a THF (100 mL) solution of carbobenzyloxyglycine (5.054 g, 0.024 mol) was added, in quick succession, $C_6H_3(OH)(2\text{-}NH_2)(4\text{-}CH_3)$ (2.980 g, 0.024 mol) and dicyclohexylcarbodiimide, DCC (5.346 g, 0.026 mol). The solution was stirred for approx. 4 h during which time a white solid formed. The solid was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The THF solvent was replaced by ethyl acetate (100 mL) and petroleum ether (b.p 40–60 °C, 100 mL) to afford **1a** which was collected by suction filtration and dried *in vacuo*. Yield: 5.544 g, 73%. Selected data: ^1H [$(CD_3)_2SO$]: 9.65 (s, 1H), 9.08 (s, 1H), 7.73–6.72 (m, 8H), 5.08 (s, 2H), 3.85 (d, 2H), 2.19 (s, 3H) ppm. FTIR: 3344, 3286, 3258, 1721, 1659 cm^{-1}. FTMS: *m/z* 315 [M+H]. *Anal.* Calc. for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.78; N, 8.91. Found: C, 65.00; H, 5.89; N, 9.35%. Similarly, $C_6H_4(OH)\{3\text{-}NHC(O)CH_2NH\text{-}CO_2Bz\}$ **1b** was prepared in 68% yield. Selected data: ^1H [$(CD_3)_2SO$]: 9.84 (s, 1H), 9.40 (s, 1H), 7.55–6.94 (m, 9H), 6.45 (dd, 1H), 5.06 (s, 2H), 3.79 (d, 2H) ppm. FTIR: 3392, 3313, 3224, 1704, 1692, 1674 cm^{-1}. FTMS: *m/z* 301 [M+H]. *Anal.* Calc. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.38; N, 9.33. Found: C, 64.18; H, 5.64; N, 9.33%.

2.3.2. Preparation of $C_6H_3(OH)\{2\text{-}NHC(O)CH_2NH_2\}(4\text{-}CH_3)$ (**2a**) and $C_6H_4(OH)\{3\text{-}NHC(O)CH_2NH_2\}$ (**2b**)

A mixture of **1a** (1.002 g, 3.19 mmol), Pd (10% on C) (0.268 g), EtOH (50 mL) and cyclohexene (2.5 mL) was refluxed for 15 min. After cooling, the mixture was filtered and the solution evaporated to dryness under reduced pressure to afford **2a**. Yield: 0.502 g, 87%. Selected data: ^1H [$(CD_3)_2SO$]: 7.81 (d, 1H), 6.56–6.46m, 2H), 3.03 (s, 2H), 1.99 (s, 3H) ppm. FTIR: 3421, 3352, 3255, 3060, 3028, 1648 cm^{-1}. ESMS: *m/z* 181 [M+H]. *Anal.* Calc. for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.73; N, 15.55. Found: C, 60.19; H, 6.84; N, 15.53%. The related compound $C_6H_4(OH)\{3\text{-}NHC(O)CH_2NH_2\}$ **2b** was also prepared (91% isolated yield). Selected data: ^1H [$(CD_3)_2SO$]: 9.65 (br, 1H), 7.23–6.43 (m, 4H), 3.23 (s, 2H) ppm. FTIR: 3345, 3331, 3296, 1673 cm^{-1}. ESMS: *m/z* 167 [M+H]. *Anal.* Calc. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.08; N, 16.86. Found: C, 58.21; H, 6.37; N, 16.09%.

2.3.3. Preparation of $C_6H_3(OH)\{2\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}(4\text{-}CH_3)$ (**3a**·**HH**) and $C_6H_4(OH)\{3\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}$ (**3b**·**HH**)

A suspension of **2a** (0.399 g, 2.21 mmol) and $C_6H_4(CHO)(2\text{-}PPh_2)$ (0.667 g, 2.30 mmol) in absolute EtOH (40 mL) was refluxed, under a N_2 atmosphere, for approx. 4 h. After cooling to r.t., the volume was reduced to ~10 mL under reduced pressure, cooled to 0 °C and the solid collected by suction filtration. The solid **3a**·**HH** was washed with a small portion of EtOH and dried *in vacuo*. Yield: 0.608 g, 61%. Selected data: ^{31}P [$(CD_3)_2SO$]: –9.6 ppm. ^1H: 9.78 (s, 1H), 9.16 (s, 1H), 8.54 (d, 1H), 7.72–6.84 (m, 18H), 4.24 (s, 2H), 2.15 (s, 3H) ppm. FTIR: 3314, 1654 cm^{-1}. ESMS: *m/z* 453 [M+H]. *Anal.* Calc. for $C_{28}H_{25}N_2O_2P$: C, 74.31; H, 5.58; N, 6.19. Found: C, 74.05; H, 5.49; N, 6.11%. Similarly $C_6H_4(OH)\{3\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2\}$ **3b**·**HH** was prepared in 53% isolated yield. Selected data: ^{31}P [$(CD_3)_2SO$]: –13.6 ppm. ^1H: 9.82 (d, 1H), 9.43 (s, 1H), 8.84 (d, 1H), 8.02–6.90 (m, 16H), 6.49 (ddd, 1H), 4.23 (s, 2H) ppm. FTIR: 3243, 3104, 1661 cm^{-1}. EIMS: *m/z* 438 [M]. *Anal.* Calc. for $C_{27}H_{23}N_2O_2P$: C, 73.95; H, 5.30; N, 6.39. Found: C, 73.79; H, 5.29; N, 6.45%.

2.3.4. Preparation of $C_6H_3(OH)\{2\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2PdCl_2\}(4\text{-}CH_3)$ (**4a**), $C_6H_3(OH)\{2\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2PtCl_2\}(4\text{-}CH_3)$ (**4b**), $C_6H_4(OH)\{3\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2PtCl_2\}$ (**4c**), $C_6H_4(OH)\{4\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2PdCl_2\}$ (**4d**) and $C_6H_4(OH)\{4\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2PtCl_2\}$ (**4e**)

To a CH_2Cl_2 (20 mL) solution of $PdCl_2(cod)$ (0.064 g, 0.22 mmol) was added **3a**·**HH** (0.101 g, 0.22 mmol) to give a yellow solution. After stirring the solution for 15 min a yellow solid formed and the volume then reduced under vacuum to ~1–2 mL. Addition of diethyl ether (25 mL) further aided precipitation. The solid **4a** was collected by suction filtration and dried *in vacuo*. Yield: 0.136 g, 96%. Compounds **4b**–**4e** were prepared similarly using either $PtCl_2(cod)$ or $PdCl_2(cod)$. Selected data for **4a**: ^{31}P [$(CD_3)_2SO$]: 33.1 ppm. FTIR: 3318, 3261, 1701, 1644, 1625, 1594 cm^{-1}. FTMS + p NSI: *m/z* 557 [M−2HCl+H^+]. *Anal.* Calc. for $C_{28}H_{25}N_2O_2PPdCl_2$: C, 53.39; H, 4.01; N, 4.45. Found: C, 53.51; H, 4.21; N, 4.13%. Selected data for **4b** (90% yield): ^{31}P [$(CD_3)_2SO$]: 9.1 ppm, $^1J_{PtP}$ 3476 Hz; 3.8 ppm, $^1J_{PtP}$ 3753 Hz; 1.4 ppm, $^1J_{PtP}$ 3230 Hz. FTIR: 3389, 3266, 1667, 1631, 1596 cm^{-1}. FTMS + p NSI: *m/z* 683 [M–Cl]. *Anal.* Calc. for $C_{28}H_{25}N_2O_2PPtCl_2{\cdot}Et_2O$: C, 48.49; H, 4.46; N, 3.54. Found: C, 49.09; H, 3.81; N, 4.03%. Selected data for **4c** (97% yield): ^{31}P [$(CD_3)_2SO$]: 8.8 ppm, $^1J_{PtP}$ 3479 Hz; 4.0 ppm, $^1J_{PtP}$ 3771 Hz; 1.5 ppm, $^1J_{PtP}$ 3204 Hz. FTIR: 3349, 3203, 1662, 1635, 1592 cm^{-1}. *Anal.* Calc. for $C_{27}H_{23}N_2O_2PPtCl_2{\cdot}0.5Et_2O$: C, 46.97; H, 3.81; N, 3.78. Found: C, 46.71; H, 3.51; N, 3.92%. Selected data for **4d** (93% yield): ^{31}P [$(CD_3)_2SO$]: 37.9 ppm. FTIR: 3406, 1668, 1644, 1598 cm^{-1}. ESMS: *m/z* 581 [M–Cl]. *Anal.* Calc. for $C_{27}H_{23}N_2O_2PPdCl_2{\cdot}0.25CH_2Cl_2$: C, 51.37; H, 3.73; N, 4.40. Found: C, 51.23; H, 3.81; N, 4.07%. Selected data for **4e** (94% yield): ^{31}P [$(CD_3)_2SO$]: 9.8 ppm, $^1J_{PtP}$ 3487 Hz; 1.8 ppm, $^1J_{PtP}$ 3952 Hz. FTIR: 3210, 1670, 1636, 1593 cm^{-1}. ESMS: *m/z* 669 [M–Cl]. *Anal.* Calc. for $C_{27}H_{23}N_2O_2PPtCl_2$: C, 46.03; H, 3.30; N, 3.98. Found: C, 46.09; H, 3.76; N, 3.83%.

2.3.5. Preparation of $[C_6H_3(OH)\{2\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2Pd(\eta^3\text{-}C_3H_5)\}(4\text{-}CH_3)]Cl$ (**5a**) and $[C_6H_4(OH)\{3\text{-}NHC(O)CH_2N{=}CHC_6H_4PPh_2Pd(\eta^3\text{-}C_3H_5)\}]Cl$ (**5b**)

To a solution of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ (0.037 g, 0.10 mmol) in CH_2Cl_2 (5 mL) was added **3a**·**HH** (0.092 g, 0.20 mmol) to afford a yellow solution. After stirring for 1 h the solution was concentrated under reduced pressure to ~1–2 mL and diethyl ether (10 mL) added. The yellow solid **5a** was collected and dried *in vacuo*. Yield: 0.113 g, 88%. Selected data for **5a**: ^{31}P ($CDCl_3$): 24.3 ppm. ^1H: 8.88 (s, 1H), 8.71 (s, 1H), 7.81–6.87 (m, 18H), 5.80 (q, 1H), 5.40 (s, 2H), 4.00 (br), 3.07 (br), 2.24 (s, 3H) ppm. FTIR: 3434, 3222, 3160, 1656, 1629 cm^{-1}. ESMS: *m/z* 599 [M–Cl]. *Anal.* Calc. for $C_{31}H_{30}N_2O_2PPdCl$: C, 58.68; H, 4.78; N, 4.42. Found: C, 58.34; H, 4.79; N, 4.44%. Selected data for **5b** (96% yield): ^{31}P ($CDCl_3$): 24.0 ppm. ^1H: 8.58 (s, 1H), 8.33 (s, 1H), 7.77–6.47 (m, 19H), 5.68 (q, 1H), 5.13 (s, 2H), 3.88 (br), 2.81 (br) ppm. FTIR: 3378, 3248, 3196, 3140, 1683, 1633, 1608 cm^{-1}. ESMS: *m/z* 585 [M–Cl]. *Anal.* Calc. for $C_{30}H_{28}N_2O_2PPdCl{\cdot}0.25CH_2Cl_2$: C, 56.53; H, 4.48; N, 4.36. Found: C, 56.20; H, 4.49; N, 3.93%.

*2.3.6. Preparation of $C_6H_3(OH)\{2\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt(CH_3)\}(4\text{-}CH_3)$ (**6a**), $C_6H_4(OH)\{3\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt(CH_3)\}$ (**6b**) and $C_6H_4(OH)\{4\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt(CH_3)\}$ (**6c**)*

To the solids $Pt(CH_3)_2(cod)$ (0.039 g, 0.12 mmol) and **3a**·**HH** (0.054 g, 0.12 mmol) was added toluene (1 mL) to afford an initial yellow solution which later turned orange. After standing for approx. 2 d, a yellow crystalline solid **6a** formed which was collected by suction filtration, washed with petroleum ether (b.p. 60–80, 5 mL) and dried. Yield: 0.050 g, 65%. The κ^3-PNN′-tridentate complexes **6b** (84% yield) and **6c** (86% yield) were prepared similarly. Selected data for **6a**: ^{31}P ($CDCl_3$): 13.3 ppm, ^1J(PtP) 3852 Hz. ^1H: 8.40 (^3J(PtH) 43.9, s, 1H), 7.57–6.66 (m, 17H), 4.80 (s, 2H), 2.08 (s, 3H), 0.00 (^2J(PtH) 71.5 Hz, d, 3H) ppm. FTIR: 3422, 1636, 1616, 1590, 1568 cm^{-1}. ESMS: *m/z* 662 [M]. *Anal.* Calc. for $C_{29}H_{27}N_2O_2PPt$: C, 52.64; H, 4.12; N, 4.24. Found: C, 52.09; H, 4.12; N, 4.12%. Selected data for **6b**: ^{31}P [$(CD_3)_2SO$]: 12.3 ppm, ^1J(PtP) 3736 Hz. ^1H: 9.22 (s, 1H), 9.06 (^3J(PtH) 41.0, s, 1H), 8.09–6.44 (m, 18H), 4.91 (s, 2H), 0.00 (^2J(PtH) 70 Hz, d, 3H) ppm. FTIR: 3368, 3230, 1635, 1611, 1567 cm^{-1}. ESMS: *m/z* 648 [M]. *Anal.* Calc. for $C_{28}H_{25}N_2O_2PPt{\cdot}0.75C_7H_8$: C, 55.72; H, 4.37; N, 3.92. Found: C, 55.37; H, 4.39; N, 4.06%. Selected data for **6c**: ^{31}P [$(CD_3)_2SO$]: 12.2 ppm, ^1J(PtP) 3689 Hz. ^1H: 9.07 (s, 1H), 8.11–6.75 (m, 18H, arom. H), 4.91 (s, 2H), 0.00 (^2J(PtH) 72.0 Hz, d, 3H) ppm. FTIR: 1628, 1573 cm^{-1}. ESMS: *m/z* 648 [M+H]. *Anal.* Calc. for $C_{28}H_{25}N_2O_2PPt$: C, 51.93; H, 3.90; N, 4.33. Found: C, 51.64; H, 3.72; N, 3.77%.

*2.3.7. Preparation of $C_6H_3(O)\{2\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pd\}(4\text{-}CH_3)$ (**7a**) and $C_6H_3(O)\{2\text{-}NC(O)CH_2N{=}CHC_6H_4PPh_2Pt\}(4\text{-}CH_3)$ (**7b**)*

A yellow CH_3OH (2 mL, HPLC grade) suspension of **4a** (0.099 g, 0.16 mmol) was treated with ^{t}BuOK (0.040 g, 0.36 mmol). The resulting purple suspension was stirred for 1 h, the solid **7a** collected by filtration and washed with a small portion of CH_3OH. Yield: quantitative. Compound **7b** was prepared similarly in 92% yield. Both **7a** and **7b** could be recrystallised from CH_2Cl_2/Et_2O/hexanes. Selected data for **7a**: ^{31}P ($CDCl_3$): 20.3 ppm. ^1H: 7.97 (s, 1H), 7.93 (s, 1H), 7.64–7.34 (m, 14H), 6.48 (d, 2H), 4.96 (s, 2H), 2.16 (s, 3H) ppm. FTIR: 1640 (CO), 1606, 1583 cm^{-1}. ESMS: *m/z* 557 [M]. *Anal.* Calc. for $C_{28}H_{23}N_2O_2PPd{\cdot}H_2O$: C, 58.49; H, 4.39; N, 4.87. Found: C, 58.36; H, 4.08; N, 4.82%. Selected data for **7b**: ^{31}P ($CDCl_3$): 6.9 ppm, ^1J(PtP) 3374 Hz. ^1H: 8.25, ^3J(PtH) 97.1 Hz (s, 1H), 8.07 (d, 1H), 7.71–6.50 (m, 16H), 5.03 (s, 2H), 2.21 (s, 3H) ppm. FTIR: 1635 (CO), 1610, 1587 cm^{-1}. ESMS: *m/z* 647 [M]. *Anal.* Calc. for $C_{28}H_{23}N_2O_2PPt$: C, 52.09; H, 3.60; N, 4.34. Found: C, 51.96; H, 3.74; N, 3.99%.

2.4. X-ray crystallography

Slow evaporation of a THF/Et_2O solution of **1b** gave suitable crystals whereas crystals of **3b**·**HH** were obtained by vapour diffusion of Et_2O into a CH_2Cl_2/EtOH solution. For **6b** and **7b**, suitable crystals were obtained by vapour diffusion of Et_2O into a $CHCl_3$/MeOH (or CH_2Cl_2) solution. Details of the data collection parameters and crystal data for **1b**·$1.5CH_2Cl_2$, **3b**·**HH**·$0.5Et_2O$, **6b**·$CHCl_3$ and **7b**·$0.5Et_2O$ are given in Table 1. Measurements for **3b**·**HH**·$0.5Et_2O$, **6b**·$CHCl_3$ and **7b**·$0.5Et_2O$ were made on a Bruker SMART 1000 (Apex II for **1b**·$1.5CH_2Cl_2$) CCD diffractometer using graphite monochromated radiation from a sealed tube Mo Kα source. Narrow frame ω-scans were employed and intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in a riding model with U_{eq} set to 1.2 U_{eq} of the carrier atom (1.5 U_{eq} for methyl hydrogen) except for N*H* and O*H* coordinates in **1b**·$1.5CH_2Cl_2$ and **3b**·**HH**·$0.5Et_2O$ which were freely refined. In each structure the solvent of crystallisation was badly disordered and modelled by the Platon Squeeze procedure [22]. In **3b**·**HH**·$0.5Et_2O$, disorder in one of the phenyl rings [C(22)–C(27)] was modelled with restraints on geometry and displacement parameters; major component occupancy = 58.4(11)%. In **7b**·$0.5Et_2O$, the hydrogen atoms in the CH_3 groups [C(28) and C(56)] were disordered (50/50). Programs used included Bruker AXS APEX II and SMART [23] for diffractometer control and SAINT for frame integration [24], Bruker SHELXTL [25] for

Table 1
Crystallographic data for **1b**·$1.5CH_2Cl_2$, **3b**·**HH**·$0.5OEt_2$, **6b**·$CHCl_3$ and **7b**·$0.5OEt_2$.

Compound	**1b**·$1.5CH_2Cl_2$	**3b**·**HH**·$0.5OEt_2$	**6b**·$0.5OEt_2$	**7b**·$0.5OEt_2$
Empirical formula	$C_{16}H_{16}N_2O_4{\cdot}1.5CH_2Cl_2$	$C_{27}H_{24}N_2O_2P{\cdot}0.5OEt_2$	$C_{28}H_{25}N_2O_2PPt{\cdot}CHCl_3$	$C_{28}H_{23}N_2O_2PPt{\cdot}0.5OEt_2$
Formula weight	427.70	476.51	766.93	682.60
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	*Fdd*2	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	17.772(5)	8.5606(13)	10.1906(6)	11.8789(4)
b (Å)	77.05(2)	10.0060(15)	16.8627(10)	14.6793(5)
c (Å)	4.7521(12)	16.348(2)	17.5250(10)	15.8954(5)
α (°)		87.437(2)		82.1451(5)
β (°)		76.095(2)	97.3012(10)	76.8028(5)
γ (°)		71.080(2)		85.4477(5)
V (Å^3)	6507(3)	1285.0(3)	2987.1(3)	2669.89(15)
Z	16	2	4	4
λ	0.71073	0.71073	0.71073	0.71073
T (K)	150(2)	150(2)	150(2)	150(2)
D_{calc} [mg m^3]	1.746	1.232	1.705	1.698
Absorption coefficient (mm^{-1})	0.594	0.137	5.048	5.347
Crystal habit and colour	plate, pale yellow	rod, colourless	tablet, yellow	block, red
Crystal size (mm^3)	0.42 × 0.14 × 0.03	0.99 × 0.08 × 0.04	0.11 × 0.10 × 0.04	0.36 × 0.35 × 0.11
θ Range (°)	2.35–25.00	2.15–27.50	1.68–29.01	1.81–28.96
Reflections collected	2864	10909	25926	23700
Independent reflections	1618 [R_{int} = 0.0335]	5654 [R_{int} = 0.0283]	7213 [R_{int} = 0.0508]	12353 [R_{int} = 0.0177]
Reflections with $F^2 > 2\sigma(F^2)$	1286	3498	4830	10504
Completeness (%)	99.6	99.0	100.0	99.3
Number of parameters	208	341	309	613
Final R^a, $R_w{}^b$	0.0634, 0.1805	0.0548, 0.1451	0.0355, 0.0707	0.0207, 0.0537

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

structure solution, refinement, and molecular graphics and local programs.

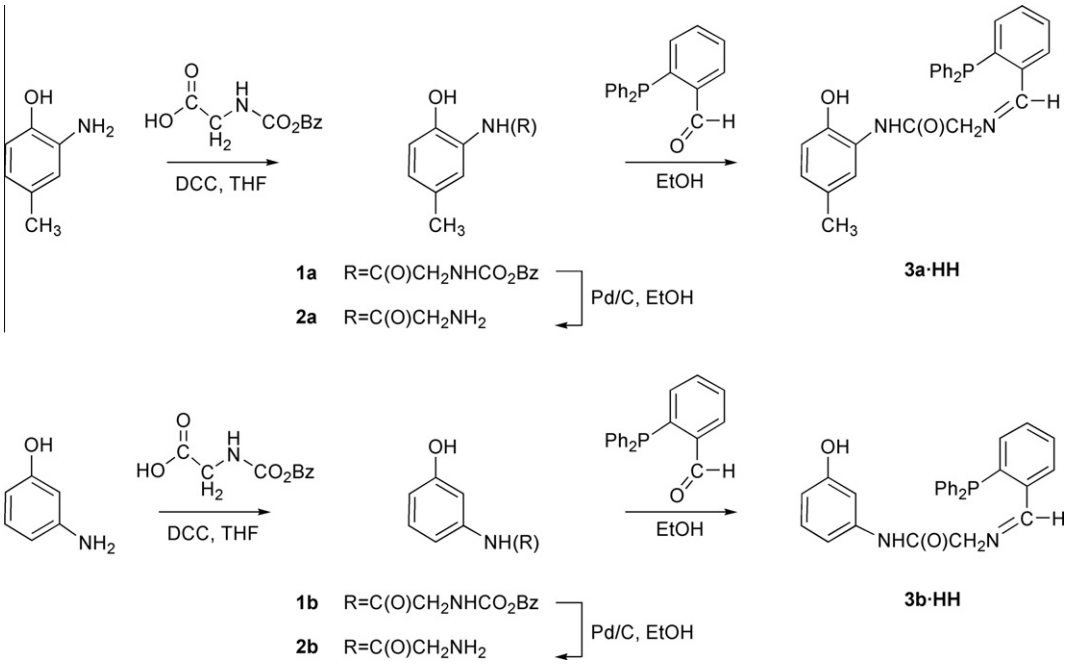
3. Results and discussion

3.1. Ligand synthesis

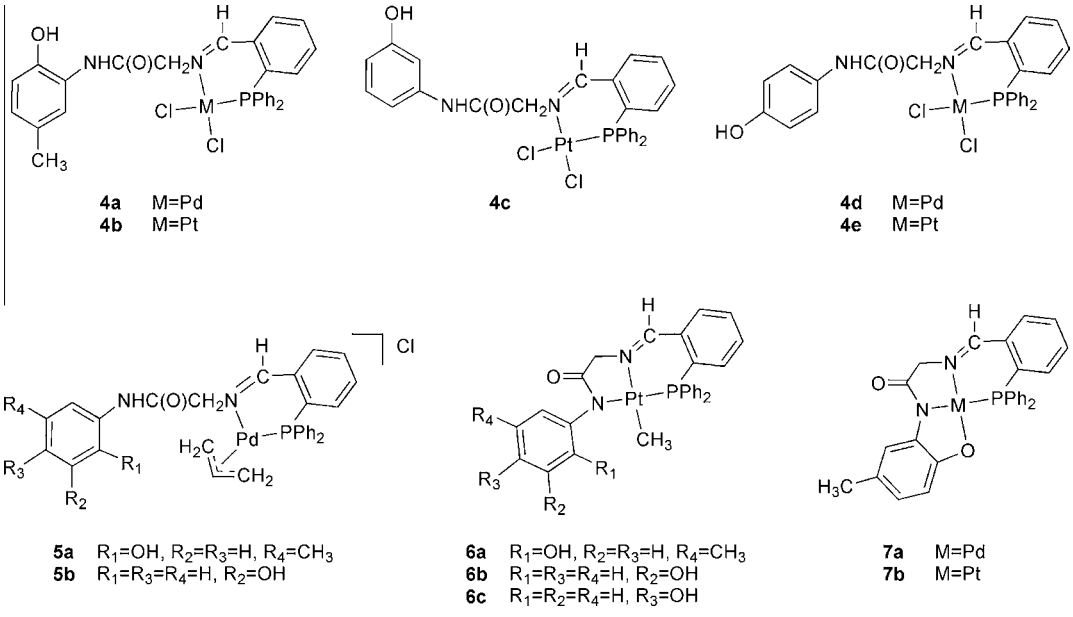
The nonsymmetric ligands **3a**·**HH** and **3b**·**HH** (Scheme 1) were synthesised, starting from commercially available 2-amino-4-methylphenol or 3-aminophenol, using an adapted method for the synthesis of ligands with N_2O_2 and N_3O donor sets [26]. Hence reaction of the appropriate aminophenol with carbobenzyloxyglycine and a slight excess of DCC in THF for 4 h gave **1a** or **1b** in 73% and 68% yields, respectively. Hydrogenolysis of **1a** or **1b** with Pd/C (10%) and cyclohexene in refluxing EtOH afforded the primary amines **2a** and **2b**. Characterising data for **1a**–**2b** are given in Section 2.

The X-ray structure of **1b**·1.5CH_2Cl_2 has been determined (Fig. 1) and confirms the successful incorporation of the {3-NHC(O)CH_2NHCO_2Bz} group. A 2-dimensional structure (SI-FIG1) propagating in the *ac* plane was obtained through a combination of strong (amino)NH···O(amide) [N(1)···O(2') 2.777(5) Å, N(1)–H(1A)···O(2') 156(5)°; N(2)···O(3'') 2.901(6) Å, N(2)–H(2)···O(3'') 149(5)°] and (hydroxyl)O–H···O(amide) [O(1)···O(3''') 2.870(5) Å, O(1)–H(1)···O(3''') 162(7)°; symmetry operators ′ = $z + ¼$; $x - ¼$, $-y + ¼$, $z - ¼$; '' = x, y, $z + 1$, ''' = $x + ¼$, $-y + ¼$] intermolecular H-bonding interactions.

Schiff base condensation of **2a** or **2b** with C_6H_4(CHO)(2-PPh_2) in refluxing EtOH gave, after simple workup, the phosphino(imines) **3a**·**HH** or **3b**·**HH** in 61% and 53% yields, respectively. Schiff base



Scheme 1. Preparation of **1a**–**2b**, **3a**·**HH** and **3b**·**HH**.



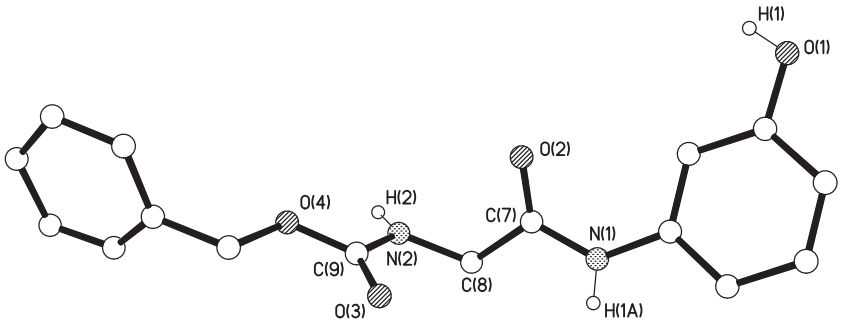


Fig. 1. X-ray structure of **1b**. The CH_2Cl_2 solvent of crystallisation and all hydrogen atoms except those on N(1), N(2) and O(1) have been removed for clarity.

condensation was readily ascertained by ^{31}P and ^{1}NMR spectroscopy. Compounds **3a**·**HH** and **3b**·**HH** adopt an *E*-(*anti*-)configuration as previously found for other phosphino(imines) [16a,17a,27] and further supported, in the case of **3b**·**HH**, by a single crystal X-ray study. The X-ray structure of **3b**·**HH**·0.5OEt_2 (Fig. 2) has been determined with the geometry around P(1) being essentially distorted tetrahedral with C–P–C angles in the range 101.08(11)°–103.30(11)°. The P(1) group faces both the N(1)/N(2) donor atoms in contrast to our previous work [17a] in which, for the 2-positioned –OH isomer, the O(2)/N(1)/N(2) groups point away from the $-PPh_2$ substituent. Various H-bonding interactions exist including an intramolecular N(1)···H(2)–N(2) H-bond [N(1)···N(2) 2.668(2) Å, N(1)···H(2)–N(2) 117(2)°] and an intermolecular O(1)···H(2A')–O(2') [O(1)···O(2') 2.687(2) Å, O(1)···H(2A') O(2') 176(3)°; symmetry operator ′ = $-x$+3, $-y$ + 1, $-z$ + 1] H-bond linking molecules into head-to-tail dimer pairs (SIFIG2) with an $R_2^2(16)$ motif [28]. Intermolecular O···H−O hydrogen bonded 1D-chains were previously observed by us when the phenolic group is located in the 4-position [17a].

3.2. Coordination studies

The reactivity of **3a**·**HH** and **3b**·**HH** towards Pd^{II} and Pt^{II} square planar metal centres was briefly investigated in order to ascertain the geometric flexibility of both new ligands. Phosphino(imines) are well known ligands which coordinate in a κ^2-PN-chelating manner at various transition metal centres [27]. Treatment of **3a**·**HH** or **3b**·**HH** with MCl_2(cod) (M = Pt, Pd) afforded the κ^2-PN-chelate complexes MCl_2(**3a**·**HH**) (M = Pd **4a**; M = Pt **4b**) and MCl_2(**3b**·**HH**) (M = Pt **4c**) in excellent yields (>90%). For NMR comparison purposes, the isomeric 4-phenol positioned metal(II) complexes **4d** and **4e** were also prepared. Furthermore we successfully synthesised the mononuclear cationic complexes [Pd(η^3-C_3H_5)(**3a**·**HH**)]Cl **5a** and [Pd(η^3-C_3H_5)(**3b**·**HH**)]Cl **5b** from the room temperature reaction of [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ and **3a**·**HH** or **3b**·**HH** in CH_2Cl_2. The $^{31}P\{^1H\}$ NMR spectra of **4a**, **4d**, **5a** and **5b** all showed downfield phosphorus chemical shifts [δ(P) 33.1; 37.9; 24.3 and 24.0 ppm, respectively]. For **4b**, **4c** and **4e**, in $(CD_3)_2SO$ solution, three Pt^{II} species were observed with $^1J_{PtP}$ coupling constants typically in the range of 3204–3952 Hz suggesting possible coordination of one or both the NH/OH donor groups and formation of cationic platinum(II) species in highly polar DMSO solvent media. Other characterising data are given in Section 2.

Reaction of **3a**·**HH** or **3b**·**HH** with $Pt(CH_3)_2$(cod) in C_7H_8 at ambient temperature gave the neutral κ^3-PNN′-tridentate complexes **6a** and **6b** in 65% and 84% yields, respectively. In the $^{31}P\{^1H\}$ NMR spectra a single ^{31}P resonance was observed at δ(P) 13.3 (**6a**) and 13.2 (**6b**) ppm with $^1J_{PtP}$ of approx. 3800 Hz. The ^{1}H NMR spectra clearly confirmed the presence of one methyl bound ligand and was further supported by the single crystal X-ray structure determination of **6b**·$CHCl_3$ (Fig. 3).

Complex **6b** displayed an essentially square-planar geometry around the Pt^{II} centre with bond angles in the range 81.07(15)°–95.13(11)° (Table 2). The Pt(1)–N(1)–C(8)–C(7)–C(2)–P(1) six-membered ring is essentially flat with Pt(1) and N(1) lying 0.456 Å and 0.161 Å, respectively out of the plane defined by atoms C(8), C(7), C(2) and P(1). For the five-membered ring, C(9) and N(1) are 0.025 Å and 0.024 Å, respectively out of the plane defined by atoms Pt(1), N(1), C(9), C(10) and N(2). Dimer pairs are formed through intermolecular O···H–O H-bonding [O(1)···O(2A) 2.636(5) Å, O(1)···H(2A)–O(2A) 174°; symmetry operator A = $-x$ + 1, $-y$, $-z$] generating an $R_2^2(16)$ ring motif [28].

Reaction of **4a** or **4b** with ^{t}BuOK, in CH_3OH, gave the neutral complexes **7a** and **7b** in which κ^4-PNN′O-tetradendate coordination of **3a**$^{2-}$ has occurred. For **7b**, the $^{31}P\{^1H\}$ NMR spectrum showed a reduction (~500 Hz) in $^1J_{PtP}$ coupling relative to the κ^3-PNN′-tridentate coordination observed in **6a**. The X-ray structure of **7b**·0.5Et_2O has been determined (Fig. 4 and SIFIG3) with selected bond lengths and angles given in Table 3. There are two molecules with very similar conformations in the asymmetric unit. The Pt–P, Pt–N and Pt–O bond lengths are all broadly as anticipated [17a,29]. Consistent with κ^4-PNN′O-tetradendate coordination is the presence of one six- (PtPCCCN) and two five-membered (PtNCCN and PtNCCO) chelate rings. The three metallocyclic conformations in **7b** can be described as follows: the Pt(1)–N(1)–

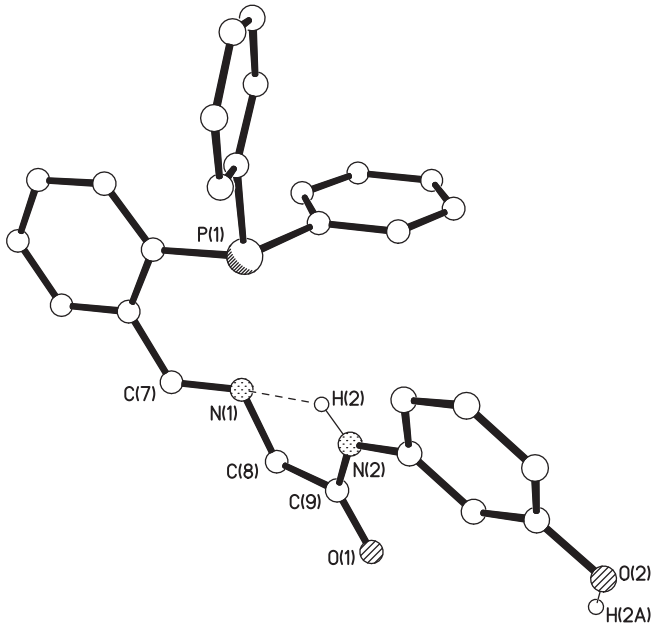


Fig. 2. X-ray structure of **3b**·**HH**. The Et_2O solvent of crystallisation and all hydrogen atoms except those on N(2) and O(2) have been removed for clarity.

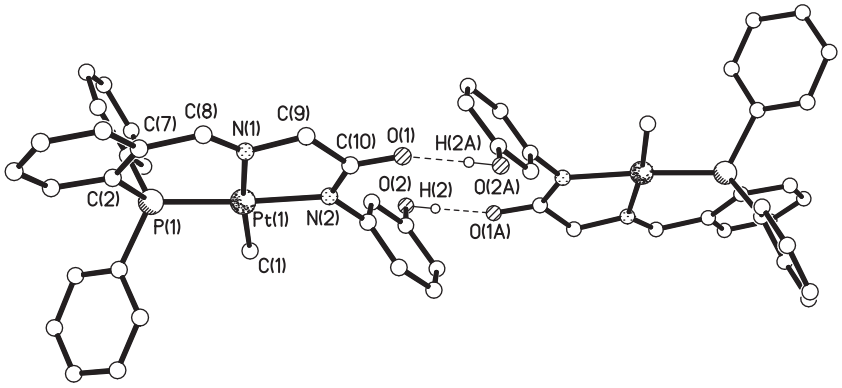


Fig. 3. X-ray structure of **6b**. The $CHCl_3$ solvent of crystallisation and all hydrogen atoms except those on O(2) and O(2A) have been removed for clarity.

Table 2
Selected bond lengths and angles for **6b**·$CHCl_3$.

Bond length (Å)	
Pt(1)–P(1)	2.1828(13)
Pt(1)–N(1)	2.059(4)
Pt(1)–N(2)	2.062(4)
Pt(1)–C(1)	2.055(5)
C(8)–N(1)	1.283(6)
C(10)–O(1)	1.257(5)
Bond angle (°)	
P(1)–Pt(1)–C(1)	91.24(15)
P(1)–Pt(1)–N(1)	95.13(11)
P(1)–Pt(1)–N(2)	175.86(10)
N(1)–Pt(1)–C(1)	173.36(18)
N(1)–Pt(1)–N(2)	81.07(14)
N(2)–Pt(1)–C(1)	92.61(17)

Table 3
Selected bond lengths and angles for **7b**·0.5OEt_2.[a]

Bond length (Å)	
Pt(1)–P(1)	2.2259(6) [2.2263(7)]
Pt(1)–N(1)	1.974(2) [1.972(2)]
Pt(1)–N(2)	1.989(2) [1.995(2)]
Pt(1)–O(2)	2.0010(17) [2.0103(19)]
C(7)–N(1)	1.285(3) [1.288(4)]
C(9)–O(1)	1.234(3) [1.228(3)]
Bond angle (°)	
P(1)–Pt(1)–O(2)	97.95(5) [97.42(5)]
P(1)–Pt(1)–N(1)	95.13(6) [95.60(7)]
P(1)–Pt(1)–N(2)	177.71(6) [179.01(7)]
N(1)–Pt(1)–O(2)	166.49(8) [166.92(8)]
N(1)–Pt(1)–N(2)	83.42(8) [84.22(10)]
N(2)–Pt(1)–O(2)	83.40(8) [82.74(9)]

[a] Equivalent parameters for the second independent molecule are given in square parentheses.

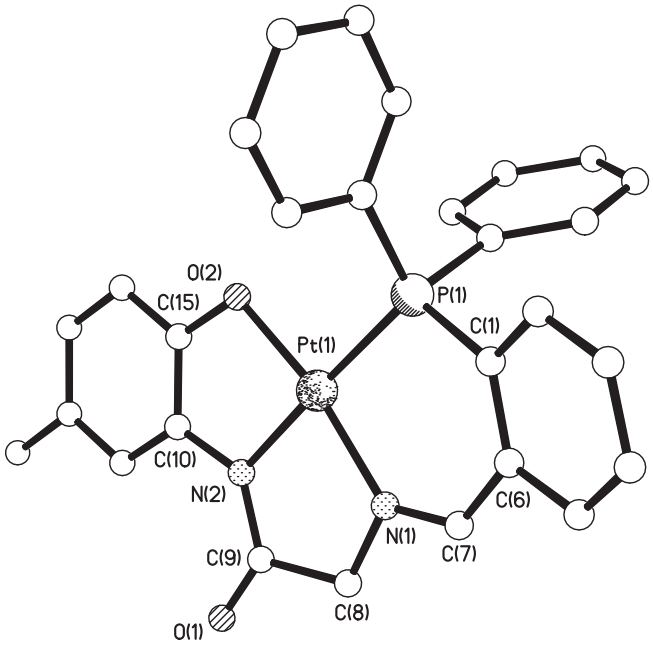


Fig. 4. X-ray structure of **7b**. The Et_2O solvent of crystallisation and all hydrogen atoms have been removed for clarity.

C(7)–C(6)–C(1)–P(1) ring is essentially flat with P(1) lying 0.40 Å [or 0.27 Å for P(2)] out of the plane defined by atoms Pt(1), N(1), C(7), C(6) and C(1), whereas both five-membered rings are effectively planar [within 0.06 Å for Pt(1)–N(1)–C(8)–C(9)–N(2) and 0.005 Å for Pt(1)–N(2)–C(10)–C(15)–O(2) for mol. 1; 0.06 Å and 0.008 Å for mol. 2].

4. Conclusions

In summary, we have shown that new multifunctionalised phosphino(imines) containing predisposed NH/OH groups can be prepared and shown to adopt various ligation modes at square planar metal centres such as Pt^{II} and Pd^{II}.

Acknowledgements

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Appendix A. Supplementary material

CCDC 833456, 833457, 833458 and 833459 contain the supplementary crystallographic data for **1b**·1.5CH_2Cl_2, **3b**·**HH**·0.5Et_2O, **6b**·$CHCl_3$ and **7b**·0.5Et_2O, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.045.

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