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Square-planar metal(II) complexes containing ester functionalised bis(phosphino) amines: Mild P–N methanolysis and C_{arene}–H cyclometallation

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ABSTRACT

The synthesis of three new ester functionalised bis(phosphino)amines $Ph_2PN\{R\}PPh_2$ [R = C_6H_4(3-CO_2Me) **1a**; $C_6H_3(3,5\text{-}CO_2Me)_2$ **1b**; C_6H_4(4-CO_2Me) **1c**] upon stoichiometric reaction of Ph_2PCl and the appropriate $H_2N\{R\}$ in Et_2O is described. Reaction of 1 equiv. of **1a**–**c** with MCl_2(cod) (M = Pt, Pd) in CH_2Cl_2 afforded the dichlorometal(II) complexes $PtCl_2$(**1a**) **2a**, $PtCl_2$(**1b**) **2b**, $PtCl_2$(**1c**) **2c** and $PdCl_2$(**1b**) **2ˋb** respectively. The corresponding dibromo (and diiodo) platinum(II) complexes **3b** (and **4b**) were synthesised, in >80% isolated yields, from $PtBr_2$(cod) or PtI_2(cod). When a suspension of **2b** in MeOH was stirred at r.t. for ca. 16 h the mixed complex cis-$PtCl_2[Ph_2PNH\{R\}](Ph_2POMe)$ **5a** [R = $C_6H_3(3,5\text{-}CO_2Me)_2$] was cleanly generated. Metathesis of **5a** using excess NaBr or NaI in MeOH/acetone afforded cis-$PtBr_2[Ph_2PNH\{R\}](Ph_2POMe)$ **5b** or cis-$PtI_2[Ph_2PNH\{R\}](Ph_2POMe)$ **5c**. Methanolysis of $PtCl_2$(**1a**) **2a** at ambient temperature afforded, in low yield (18%), the regiospecific P,C-orthometallated complex cis-PtCl $[Ph_2PNH\{C_6H_3(3\text{-}CO_2Me)\}](Ph_2POMe)$ **6**. We speculate the C–H activated complex **6** is obtained via initial formation of cis-$PtCl_2[Ph_2PNH\{C_6H_4(3\text{-}CO_2Me)\}](Ph_2POMe)$ **7**. A similar observation was also found using **2c** whereupon examination of the isolated solid, by $^{31}P\{^1H\}$ NMR spectroscopy, revealed formation of three complexes namely orthometallated cis-$PtCl[Ph_2PNH\{C_6H_3(4\text{-}CO_2Me)\}](Ph_2POMe)$ **9**, cis-$PtCl[Ph_2PNH\{C_6H_4(4\text{-}CO_2Me)\}](Ph_2POMe)$ **10** and cis-$PtCl_2(Ph_2POMe)_2$ **8**. All new compounds reported here have been characterised by multinuclear NMR and IR spectroscopy, microanalysis and in six cases by single crystal X-ray crystallography. The X-ray structure of cis-$PtCl[Ph_2PNH\{C_6H_3(3\text{-}CO_2Me)\}](Ph_2POMe)$ **6** revealed selective C–H cycloplatination at the 6-position (as opposed to the 2-position) of the *N*-arene ring.

1. Introduction

Cyclometallated complexes represent an important class of compound widely encountered in modern organometallic and coordination chemistry [1]. Various examples of C–H activated (sp^2 or sp^3) achiral [2,3] or chiral [4] metal complexes have been reported and find numerous applications in areas ranging from organic transformations [3,5], directed self-assembly [6], catalysis [7], chemical sensing [8] and as luminescent materials [9].

Phosphorus based compounds such as tertiary phosphines [10], phosphinites [11], phosphites [12], iminophosphoranes [3,13] and PCP-pincer ligands [14] have widely been studied in a range of C–H activation processes. In contrast trivalent phosphorus ligands bearing one (or more) P–N bonds have recently been shown to undergo sp^2 or sp^3 C–H cyclometallation at Ru, Rh, Ir, Ni, Pd and Pt metal centres affording bidentate [15], tridentate [16] or tetradentate [17] carbometallated complexes. We have demonstrated in previous work that functionalised (phosphino)amines undergo thermally induced orthometallation at Pt^{II} and Rh^{III} metal centres affording rare examples of thermally stable M–P–N–C_{arene}–C_{arene} five-membered metallacycles [15e]. In this work we wished to explore whether chelating bis(phosphino)amines of the type $(Ph_2P)_2N\{R\}$ would themselves undergo C–H metallation, a reaction that has previously been observed for $(Ph_2P)_2CH_2$ [1]. We report here the synthesis of three bis(phosphino)amines bearing one (or two) –CO_2Me groups and a brief survey of their coordination chemistry at Pd^{II} and Pt^{II} metal centres. A general feature of (phosphino)amine chemistry is their air/moisture sensitivity due to the reactive nature of the heterolytic P–N bond [18]. We demonstrate here the selective methanolysis of a P–N bond [19] for some

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of these strained four-membered ester functionalised bis(phosphino)amine complexes and furthermore disclose a facile C–H bond activation under remarkably mild conditions. Six single crystal X-ray structure determinations have been undertaken.

2. Experimental

2.1. Materials

Standard Schlenk techniques were used for the syntheses of ligands **1a**–**c** whilst all other reactions were performed under aerobic conditions using previously distilled solvents unless otherwise stated. The compounds $H_2NC_6H_4(3\text{-}CO_2Me)$, $H_2NC_6H_4(4\text{-}CO_2Me)$ and $H_2NC_6H_3(3,5\text{-}CO_2Me)_2$ were obtained from commercial suppliers and used directly. The complexes $MX_2(cod)$ (M = Pt, Pd; X = Cl, Br, I) were prepared according to literature methods [20].

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets in the range 4000–200 cm^{-1} on a Perkin–Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 or 400 MHz) were recorded on a Bruker AC250 or DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of external $Si(CH_3)_4$ and coupling constants (J) in Hz, $^{31}P\{^1H\}$ NMR spectra (36.2 MHz, 101.3 or 162.0 MHz) were recorded either on a Jeol FX90Q, Bruker AC250 or DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of external 85% H_3PO_4. All $^{195}Pt\{^1H\}$ NMR spectra (53.7 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with δ referenced to external H_2PtCl_6 (in D_2O/HCl). NMR spectra were measured in $CDCl_3$ unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

2.3. Syntheses

*2.3.1. $Ph_2PN\{C_6H_4(3\text{-}CO_2Me)\}PPh_2$ **1a** and bis(phosphino)amines **1b**, **1c***

To a stirred suspension of $H_2N\{C_6H_4(3\text{-}CO_2Me)\}$ (0.840 g, 5.56 mmol) in NEt_3 (2.559 g, 25.3 mmol) and Et_2O (100 mL) was added Ph_2PCl (2.800 g, 12.7 mmol) in Et_2O (20 mL) dropwise over 20 min whilst the temperature was maintained at approx. 0 °C. The mixture was stirred at ambient temperature for ~7 d and the solvent evaporated to dryness under reduced pressure. After addition of degassed distilled water (70 mL), the solid was collected by suction filtration and washed with hexane (50 mL) and absolute EtOH (50 mL) to afford **1a**. Yield: 2.493 g, 85%. Selected data for **1a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 69.0 ppm. ^1H NMR: δ 7.64–6.83 (m, 24H, arom. H), 3.74 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1722 cm^{-1}. FAB–MS: *m/z* 519 [M^+]. Found C, 72.57; H, 5.27; N, 2.62. $C_{32}H_{27}NO_2P_2\cdot 0.5H_2O$ (528.5) requires C, 72.71; H, 5.35; N, 2.65%. In a similar manner $Ph_2PN\{C_6H_3(3,5\text{-}CO_2Me)_2\}PPh_2$ (**1b**) and $Ph_2PN\{C_6H_4(4\text{-}CO_2Me)\}PPh_2$ (**1c**) were prepared in 82% and 58% isolated yields respectively. Selected data for **1b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 69.0 ppm. ^1H NMR: δ 7.89–7.24 (m, 23H, arom. H), 3.74 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1727 cm^{-1}. FAB–MS: *m/z* 578 [M^+]. Found C, 69.63; H, 5.06; N, 2.53. $C_{34}H_{29}NO_4P_2\cdot 0.5H_2O$ (586.6) requires C, 69.62; H, 5.17; N, 2.39%. Selected data for **1c**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 68.5 ppm. ^1H NMR: δ 7.66–6.77 (m, 24H, arom. H), 3.83 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1717 cm^{-1}. FAB–MS: *m/z* 536 [M + O]. Found C, 72.65; H, 5.41; N, 2.63. $C_{32}H_{27}NO_2P_2\cdot 0.5H_2O$ (528.5) requires C, 72.71; H, 5.35; N, 2.65%.

*2.3.2. $PtCl_2$(**1a**) **2a** and complexes **2b**, **2c**, **2ˋb**, **3b**, **4b***

To a CH_2Cl_2 (10 mL) solution of $PtCl_2(cod)$ (0.095 g, 0.254 mmol) was added **1a** (0.132 g, 0.254 mmol) as a solid in one portion. The pale yellow solution was stirred for 20 min and the volume concentrated to ~1 mL under reduced pressure. Addition of Et_2O (30 mL) gave a solid which was collected by suction filtration, washed with Et_2O (10 mL) and dried in vacuo. Yield: 0.191 g, 96%. Selected data for **2a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.4 ppm, $^1J_{PtP}$ 3334 Hz. ^1H NMR: δ 7.90–6.67 (m, 24H, arom. H), 3.75 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1724, ν_{PtCl} 314, 292 cm^{-1}. Found C, 49.19; H, 3.59; N, 1.53%. $C_{32}H_{27}NO_2P_2PtCl_2$ (785.5) requires C, 48.93; H, 3.47; N, 1.78%. In a similar manner the following dihalometal(II) complexes were synthesised using $PtCl_2(cod)$ (for **2b**, **2c**), $PdCl_2(cod)$ (for **2ˋb**), $PtBr_2(cod)$ (for **3b**) or $PtI_2(cod)$ (for **4b**): Selected data for **2b** (99% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 22.5 ppm, $^1J_{PtP}$ 3339 Hz. ^1H NMR: δ 8.39–7.35 (m, 23H, arom. H), 3.78 (s, 6H, CO_2Me). ^{195}Pt NMR: −4056 ppm. FT–IR: ν_{CO} 1733, 1720, ν_{PtCl} 307, 290 cm^{-1}. Found C, 48.16; H, 3.61; N, 1.63%. $C_{34}H_{29}NO_4P_2PtCl_2$ (843.5) requires C, 48.41; H, 3.47 N, 1.66%. Selected data for **2c** (86% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.3 ppm, $^1J_{PtP}$ 3330 Hz. ^1H NMR: δ 7.88–6.57 (m, 24H, arom. H), 3.83 (s, 3H, CO_2Me). FT–IR: ν_{CO} 1721, ν_{PtCl} 307, 290 cm^{-1}. Found C, 48.98; H, 3.55; N, 1.92%. $C_{32}H_{27}NO_2P_2PtCl_2$ (785.5) requires C, 48.93; H, 3.47; N, 1.78%. Selected data for **2ˋb** (91% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.1 ppm. ^1H NMR: δ 8.38–7.44 (m, 23H, arom. H), 3.79 (s, 6H, CO_2Me). FT–IR: ν_{CO} 1733, 1720, ν_{PdCl} 314, 296 cm^{-1}. Found C, 53.71; H, 4.04; N, 1.83%. $C_{34}H_{29}NO_4P_2PdCl_2$ (754.8) requires C, 54.10; H, 3.88; N, 1.86%. Selected data for **3b** (89% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.3 ppm, $^1J_{PtP}$ 3260 Hz. ^1H NMR: δ 8.37–7.37 (m, 23H, arom. H), 3.78 (s, 6H, CO_2Me). FT–IR: ν_{CO} 1733, 1721 cm^{-1}. Found C, 44.01; H, 3.32; N, 1.36%. $C_{34}H_{29}NO_4P_2PtBr_2$ (932.4) requires C, 43.79; H, 3.14; N, 1.50%. Selected data for **4b** (85% isolated yield): $^{31}P\{^1H\}$ NMR ($CDCl_3$): 17.4 ppm, $^1J_{PtP}$ 3066 Hz. ^1H NMR: δ 8.30–7.32 (m, 23H, arom. H), 3.74 (s, 6H, CO_2Me). FT–IR: ν_{CO} 1728 cm^{-1}. Found C, 39.42; H, 2.78; N, 1.30%. $C_{34}H_{29}NO_4P_2PtI_2$ (1026.4) requires C, 39.78; H, 2.85; N, 1.36%.

*2.3.3. cis-$PtCl_2[Ph_2PNH\{C_6H_3(3,5\text{-}CO_2Me)_2\}](Ph_2POMe)$ **5a** and complexes **5b**, **5c**, **5d***

A suspension of **2b** (0.218 g, 0.258 mmol) in MeOH (60 mL) was stirred at ambient temperature for approx. 16 h. The solid was filtered under reduced pressure, washed with MeOH (8 mL) and dried in vacuo. Yield: 0.178 g, 79%. Selected data for **5a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 81.4 ppm, $^1J_{PtP}$ 4332 Hz; 30.1 ppm, $^1J_{PtP}$ 3960 Hz; $^2J_{PP}$ 16 Hz ^1H NMR: δ 8.33 (d, $^2J_{PH}$ 10.5 Hz, 1H, NH), 8.06–7.33 (m, 23H, arom. H), 3.80 (s, 6H, CO_2Me), and 2.81 (d, $^3J_{PH}$ 11.5 Hz, 3H, OMe). ^{195}Pt NMR: −4315 ppm. FT–IR (KBr): ν_{NH} 3239, ν_{CO} 1732, 1725, ν_{PtCl} 316, 284 cm^{-1}. Found C, 48.00; H, 3.61; N, 1.58. $C_{35}H_{33}NO_5P_2PtCl_2$ (875.6) requires C, 48.01; H, 3.81; N, 1.60%. The platinum(II) complexes **5b** (98% isolated yield) and **5c** (96% isolated yield) were synthesised by metathesis of **5a** with either NaBr or NaI in MeOH/acetone. Selected data for **5b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 80.6 ppm, $^1J_{PtP}$ 4268 Hz; 30.6 ppm, $^1J_{PtP}$ 3934 Hz; $^2J_{PP}$ 21 Hz. ^1H NMR: δ 8.15 (d, $^2J_{PH}$ 10.6 Hz, 1H, NH), 8.08–7.32 (m, 23H, arom. H), 3.81 (s, 6H, CO_2Me) and 2.80 (d, $^3J_{PH}$ 11.6 Hz, 3H, OMe). ^{195}Pt NMR: −4556 ppm. FT–IR (KBr): ν_{NH} 3233, ν_{CO} 1726 cm^{-1}. FAB–MS: *m/z* 884 [M–Br]. Found C, 42.73; H, 3.11; N, 1.31. $C_{35}H_{33}NO_5P_2PtBr_2\cdot 0.25CH_2Cl_2$ (985.7) requires C, 42.95; H, 3.40; N, 1.42%. Selected data for **5c**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 80.4 ppm, $^1J_{PtP}$ 4110 Hz; 29.9 ppm, $^1J_{PtP}$ 3789 Hz; $^2J_{PP}$ 9 Hz. ^1H NMR: δ 8.08–7.32 (m, 24H, arom. H and NH), 3.81 (s, 6H, CO_2Me) and 2.79 (d, $^3J_{PH}$ 11.3 Hz, 3H, OMe). ^{195}Pt NMR: −5074 ppm. FT–IR (KBr): ν_{NH} 3194, ν_{CO} 1725 cm^{-1}. FAB–MS: *m/z* 931 [M–I]. Found C, 40.06; H, 3.27; N, 1.25. $C_{35}H_{33}NO_5P_2PtI_2$ (1058.5) requires C, 39.71; H, 3.15; N, 1.32%. Selected data for **5d**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 108.2, 50.8 ppm, $^{2}J_{PP}$ 24 Hz. ^{1}H NMR: δ 8.36 (d, $^{2}J_{PH}$ 12.3 Hz, 1H, NH), 8.02–7.32 (m, 23H, arom. H), 3.76 (s, 6H, CO_2Me), and 2.76 (d, $^{3}J_{PH}$ 11.3 Hz, 3H, OMe). FT–IR (KBr): ν_{NH} 3205, ν_{CO} 1732, 1726, ν_{PdCl} 317, 285 cm^{-1}. An analytically pure sample of **5d** could not be obtained.

2.3.4. *cis-PtCl[P,C-Ph$_2$PNH{C$_6$H$_3$(3-CO$_2$Me)}](Ph$_2$POMe)* **6**

A suspension of **2a** (0.099 g, 0.126 mmol) in MeOH (15 mL) was stirred at ambient temperature for 27 h. Unreacted starting material was removed by suction filtration and the solid washed with a small portion of MeOH (5 mL) to give **2a** (0.072 g recovered). The methanol filtrate was left to slowly concentrate over 14 d yielding a small crop of pale yellow crystals. Yield: 0.018 g, 18%. Selected data for **6**: ^{31}P{^{1}H} NMR ($CDCl_3$): 117.3 ppm, $^{1}J_{PtP}$ 2292 Hz; 71.7 ppm, $^{1}J_{PtP}$ 4421 Hz; $^{2}J_{PP}$ 20 Hz. ^{1}H NMR: δ 8.39–7.29 (m, 23H, arom. H), 4.73 (d, $^{2}J_{PH}$ 2.7 Hz, $^{3}J_{PtH}$ 86 Hz, 1H, NH), 3.76 (s, 3H, CO_2Me) and 2.85 (d, $^{3}J_{PH}$ 11.1 Hz, 3H, OMe). FT–IR (KBr): ν_{OH} 3413, ν_{NH} 3310, ν_{CO} 1696 cm^{-1}. Found C, 49.95; H, 3.88; N, 1.86. $C_{33}H_{30}NO_3P_2PtCl \cdot CH_3OH$ (813.1) requires C, 50.22; H, 4.22; N, 1.72%.

2.3.5. *cis-PtCl[P,C-Ph$_2$PNH{C$_6$H$_3$(4-CO$_2$Me)}](Ph$_2$POMe)* **9**

A suspension of **2c** (0.032 g, 0.041 mmol) was heated under reflux in MeOH (15 mL) for 16 h. The solvent was removed in vacuo and the resulting residue examined by ^{31}P{^{1}H} NMR spectroscopy. The residue was resuspended in MeOH (15 mL) and heated under reflux for a further 68 h. The solvent was removed in vacuo, CH_2Cl_2 (1 mL) added and an off-white solid (0.035 g) isolated by precipitation with Et_2O (30 mL). Three Pt^{II} complexes were observed, the major species present were identified as **9** and **10** along with a trace amount of **8**. Selected spectroscopic data for **9**: ^{31}P{^{1}H} NMR ($CDCl_3$): 117.5 ppm, $^{1}J_{PtP}$ 2314 Hz; 72.7 ppm, $^{1}J_{PtP}$ 4434 Hz; $^{2}J_{PP}$ 17.6 Hz. ^{1}H NMR: δ 8.94 (dt, $^{2}J_{PH}$ 7.7 Hz, $^{3}J_{PtH}$ 41 Hz, 1H, arom. H), 4.91 (d, $^{2}J_{PH}$ 3.2 Hz, $^{3}J_{PtH}$ 86 Hz, 1H, NH), 3.73 (s, 3H, CO_2Me) and 2.87 (d, $^{3}J_{PH}$ 11.2 Hz, 3H, OMe). Selected spectroscopic data for **10**: ^{31}P{^{1}H} NMR ($CDCl_3$): 80.9 ppm, $^{1}J_{PtP}$ 4337 Hz; 28.7 ppm, $^{1}J_{PtP}$ 3950 Hz; $^{2}J_{PP}$ 13.2 Hz. ^{1}H NMR: δ 8.29 (d, $^{2}J_{PH}$ 10.6 Hz, 1H, NH), 3.72 (s, 3H, CO_2Me) and 2.77 (d, $^{3}J_{PH}$ 11.6 Hz, 3H, OMe).

2.4. *X-ray crystallography*

Crystals of **2a**·0.75$CHCl_3$, suitable for X-ray crystallography, were grown over several days by allowing Et_2O to diffuse slowly into a $CDCl_3$ solution. Suitable crystals of **4b** were prepared upon vapour diffusion of diethyl ether into a $CDCl_3$ solution of PtI_2(cod) and Ph_2PN{C_6H_4(3-CO_2Me)}PPh_2 over the course of several days. Suitable crystals of **5a**·$CHCl_3$ or **5c**·CH_2Cl_2 were obtained by slow diffusion of Et_2O into a $CDCl_3$/CH_2Cl_2 (for **5a**) or CH_2Cl_2 (for **5c**) solution whereas crystals of **6** were obtained upon allowing a CH_3OH filtrate to stand. Crystals of **9**·$CHCl_3$·CH_3OH were grown by allowing CH_3OH to diffuse slowly into a $CDCl_3$ solution of a mixture of **8**–**10**.

Details of the crystal data for **2a**·0.75$CHCl_3$, **4b**, **5a**·$CHCl_3$, **5c**·CH_2Cl_2, **6** and **9**·$CHCl_3$·CH_3OH along with a summary of data collection parameters are given in Table 1. Measurements for **2a**·0.75$CHCl_3$ and **5a**·$CHCl_3$ were determined using a Rigaku AFC7S diffractometer with graphite-monochromated (Mo-K_α) radiation (λ = 0.71073 Å) and ω scans. Empirical absorption corrections (DIFABS) [21] were applied. The structures were solved by the heavy-atom method [22] and all of the non-hydrogen atoms refined anisotropically. The H on N(1) in **5a**·$CHCl_3$ was located from a ΔF map and allowed to refine isotropically with no distance restraint. All other H atoms were idealised and fixed (C–H 0.95 Å). No additional constraints or restraints were applied. Refinement was by full-matrix least-squares methods. Calculations were performed using TEXSAN [23].

Data were collected (for **4b** and **6**) using a Nonius κ CCD area detector diffractometer mounted at the window of a rotating molybdenum anode. Ω scans were employed such that 95% of the unique data were recorded at least once. Data collection and processing were carried out using the programs COLLECT [24], DENZO [25], and maXus [26] and an empirical absorption correction was applied using SORTAV [27]. The structures were solved via direct methods [28] and refined by full-matrix least-squares [29] on F^2.

Table 1
Crystallographic data for **2a**·0.75$CHCl_3$, **4b**, **5a**·$CHCl_3$, **5c**·CH_2Cl_2, **6** and **9**·$CHCl_3$·CH_3OH.

Compound	**2a**·0.75$CHCl_3$	**4b**	**5a**·$CHCl_3$	**5c**·CH_2Cl_2	**6**	**9**·$CHCl_3$·CH_3OH
Empirical Formula	$C_{32.75}H_{27.75}Cl_{4.25}NO_2P_2Pt$	$C_{32}H_{27}I_2NO_2P_2Pt$	$C_{36}H_{34}Cl_5NO_5P_2Pt$	$C_{36}H_{35}Cl_2I_2NO_5P_2Pt$	$C_{33}H_{30}ClNO_3P_2Pt$	$C_{35}H_{35}Cl_4NO_4P_2Pt$
Formula weight	875.00	968.38	994.92	1143.38	781.06	932.47
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P-1$	$P2_1/c$	$P2_1/c$
a [Å]	8.792(4)	9.2343(18)	9.2043(3)	9.583(4)	10.647(2)	13.6757(5)
b [Å]	25.034(4)	19.414(4)	15.2574(5)	15.294(6)	17.517(4)	11.7451(4)
c [Å]	16.521(4)	18.236(4)	27.4992(9)	15.682(7)	16.715(3)	23.2206(16)
α [°]				113.982(7)		
β [°]	98.34(2)	97.67(3)	92.6590(10)	105.088(4)	105.06(3)	105.299(7)
γ [°]				97.402(5)		
Volume [$Å^3$]	3597.8(19)	3239.9(11)	3857.7(2)	1954.4(14)	3010.3(10)	3597.6(3)
Z	4	4	4	2	4	4
λ	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T/K	293(2)	150(2)	293(2)	93(2)	150(2)	100(2)
Density (calc.) [Mg/m^3]	1.615	1.985	1.713	1.943	1.723	1.722
Absorption coeff. [mm^{-1}]	4.334	6.364	4.109	5.429	4.892	4.326
Crystal habit and colour	Plate; colourless	Needle; yellow	Tablet; colourless	Prism; yellow	Plate; colourless	Plate; colourless
Crystal size [mm^3]	0.70 × 0.30 × 0.14	0.22 × 0.04 × 0.04	0.20 × 0.10 × 0.08	0.10 × 0.05 × 0.03	0.40 × 0.10 × 0.03	0.04 × 0.03 × 0.01
θ range [°]	2.62–25.00	3.06–27.50	1.48–23.25	2.26–25.34	3.01–27.47	3.09–27.48
Reflections collected	6786	29,864	16,528	12,433	34,591	33,376
Independent reflections	6349	7387	5527	6891	6881	8243
	[R_{int} = 0.0442]	[R_{int} = 0.0610]	[R_{int} = 0.0301]	[R_{int} = 0.0719]	[R_{int} = 0.0603]	[R_{int} = 0.0498]
Completeness (%)	99.9	99.4	99.7	96.6	99.7	99.9
No. of parameters	399	363	456	449	373	430
Final R^{a}, R_w^{b}	0.059, 0.157	0.035, 0.063	0.033, 0.073	0.076, 0.184	0.036, 0.108	0.037, 0.091

[a] $R = \sum||F_o|-|F_c||/\sum|F_o|$.

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

Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated using a riding model.

Data were collected (for **5c**·CH_2Cl_2) using a Rigaku 007 generator with a Mercury detector on Mo radiation.

The crystallographic data collection for **9**·$CHCl_3$·CH_3OH was performed using a Rigaku AFC12 Kappa 3-circle CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) controlled by the CrystalClear-SM Expert 2.0 [30] software package and an Oxford Cryosystem N_2 open flow cryostat at 100(2) K. The data were processed and semi-empirical absorption corrections were applied using FS_PROCESS [31] in CrystalClear-SM Expert 2.0. The structures were solved by charge flipping and refined by full-matrix least-square procedures on F^2 using SUPERFLIP [32] and SHELXL-97 [33] respectively. All non-hydrogen atoms were refined anisotropically and H-atoms were refined isotropically at calculated positions using a riding model.

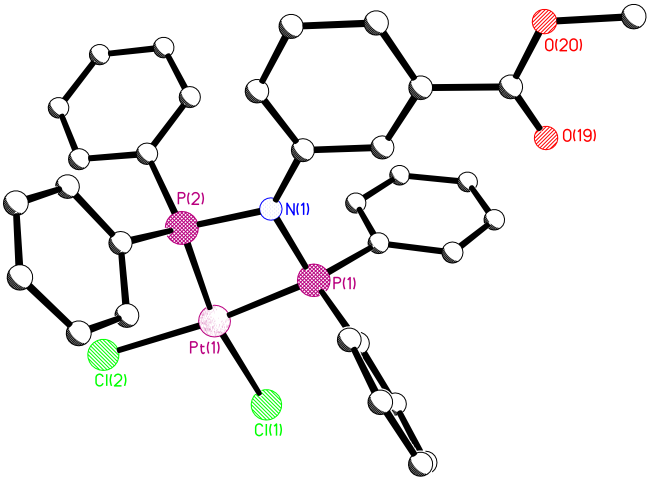
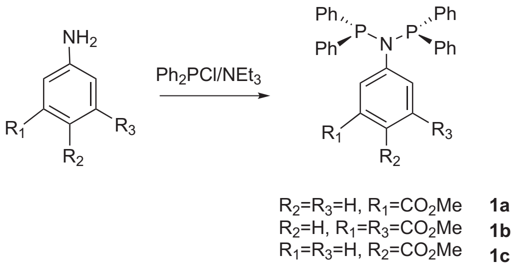


Fig. 1. X-ray structure of **2a**. The $CHCl_3$ solvent of crystallisation and all hydrogen atoms have been removed for clarity.

3. Results and discussion

3.1. Ligand synthesis

The synthesis of a range of ester functionalised bis(phosphino)amines followed a similar experimental protocol to that previously reported by ourselves [15e,34c] and others [34a,34b,34d]. Hence the new bis(phosphino)amines **1a**–**c** were prepared by straightforward condensation of Ph_2PCl and the appropriate primary amine with NEt_3 as base (Eqn. (1)). Compounds **1a**–**c** exhibited a single $^{31}P\{^1H\}$ NMR resonance (in $CDCl_3$) at ~δ(P) 69 in accordance with other known examples [34a,34c]. In their ^1H NMR spectra the methyl protons resonate around δ(H) 3.8 whereas the FT–IR spectra (pressed KBr discs) displayed strong absorptions in the range 1727–1717 cm^{-1} (CO stretch) and 927–891 cm^{-1} (PN stretch). The positive-ion FAB mass spectra gave the anticipated parent ions for all three ligands with an additional [M + O] ion observed for the 3- and 4-isomeric bis(phosphino)amines.

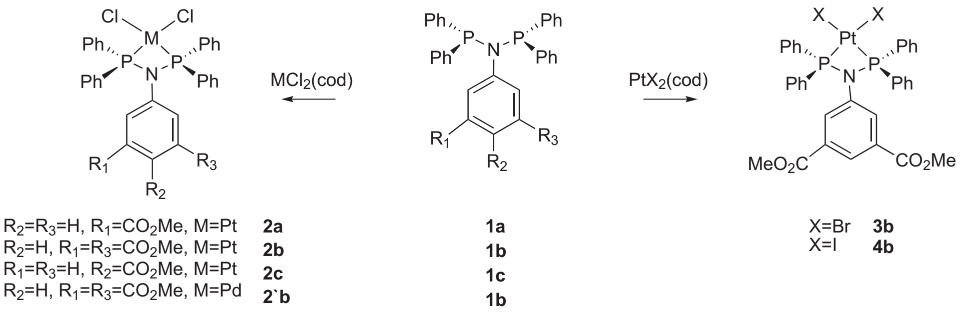


3.2. Coordination studies

Reaction of **1a**–**c** with $PtCl_2(cod)$ proceeded smoothly, with facile displacement of cod, to give the P,P′-chelate complexes **2a**–**c** in excellent yield (typically ~90%) according to Scheme 1. The $^{31}P\{^1H\}$ NMR spectra (in $CDCl_3$) showed singlets at δ(P) 21 with $^1J_{PtP}$ coupling constants of ~3300 Hz consistent with the phosphorus ligand trans to chloride [34a,34c,34d]. In the FT–IR spectra bands attributed to ν_{CO}, ν_{PN} and ν_{PtCl} were observed for all three complexes (see Experimental Section for characterising data). The dibromo- **3b** and diiodoplatinum(II) **4b** analogues were prepared from 1 equiv. of **1b** and $PtBr_2(cod)$ or $PtI_2(cod)$ respectively. Furthermore the dichloropalladium(II) complex **2`b** was prepared from $PdCl_2(cod)$. A reduction in the magnitude of the $^1J_{PtP}$ coupling constants from approx. 3300 Hz in the chlorides **2a**–**c** to 3260 Hz (for **3b**) and 3066 Hz (for **4b**) is consistent with the observation of increasing trans influence of the halide ligand on going from Cl > Br > I. Other selected characterising data is given in the Experimental Section.

Compound **2a**·$0.75CHCl_3$ was characterised by X-ray crystallography and the molecular structure shown in Fig. 1 with selected bond lengths and angles given in Table 2. The geometry around the platinum centre is distorted square-planar as reflected by the bond angles [P(1)–Pt(1)–P(2) 72.68(11), P(2)–Pt(1)–Cl(2) 98.80(12), Cl(1)–Pt(1)–Cl(2) 91.32(13), P(1)–Pt(1)–Cl(1) 97.34(12)°] which agree with previous literature values [34a,34c]. The four-membered PtP_2N ring is essentially planar while the Pt–P/P–N distances compare well with those of known $PtCl_2[Ph_2PN\{R\}PPh_2]$ compounds [34a,34c]. Finally the Pt–Cl bond lengths [2.346(3) Å and 2.349(3) Å] are typical for a P-donor centre trans to a chloride ligand.

The X-ray structure of **4b** is shown in Fig. 2 (Table 3) and the metric parameters are broadly as expected. Only two other crystallographic examples of analogous complexes with short-bite P–N–P ligands have been reported [35].



Scheme 1. Synthesis of compounds **2a**–**4b**.

Table 2
Selected bond lengths and angles for **2a**·0.75CHCl$_3$.

Bond length/Å	
Pt(1)–P(1)	2.192(3)
Pt(1)–P(2)	2.209(3)
Pt(1)–Cl(1)	2.346(3)
Pt(1)–Cl(2)	2.349(3)
P(1)–N(1)	1.721(8)
N(1)–P(2)	1.706(9)
C(19)–O(19)	1.185(16)
C(19)–O(20)	1.300(15)
Bond angle/°	
P(1)–Pt(1)–P(2)	72.68(11)
P(1)–Pt(1)–Cl(1)	97.34(12)
P(2)–Pt(1)–Cl(1)	169.71(12)
P(1)–Pt(1)–Cl(2)	170.70(11)
P(2)–Pt(1)–Cl(2)	98.80(12)
Cl(1)–Pt(1)–Cl(2)	91.32(13)
Pt(1)–P(1)–N(1)	94.2(3)
P(1)–N(1)–P(2)	99.1(5)
N(1)–P(2)–Pt(1)	94.0(3)

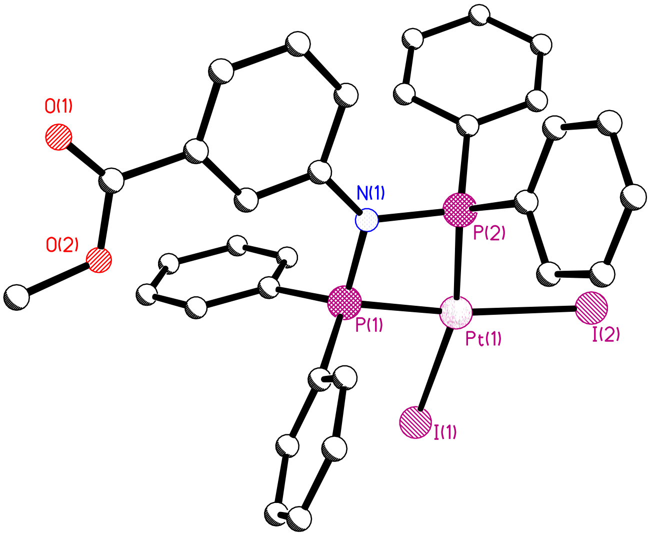
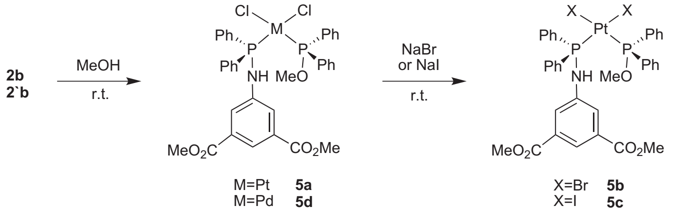


Fig. 2. X-ray structure of **4b**. All hydrogen atoms have been removed for clarity.

Table 3
Selected bond lengths and angles for **4b**.

Bond length/Å	
Pt(1)–P(1)	2.2100(13)
Pt(1)–P(2)	2.2105(13)
Pt(1)–I(1)	2.6380(6)
Pt(1)–I(2)	2.6544(7)
P(1)–N(1)	1.715(4)
N(1)–P(2)	1.709(4)
C(19)–O(1)	1.206(5)
C(19)–O(2)	1.333(5)
Bond angle/°	
P(1)–Pt(1)–P(2)	72.89(4)
P(1)–Pt(1)–I(1)	92.54(3)
P(2)–Pt(1)–I(1)	164.95(3)
P(1)–Pt(1)–I(2)	170.26(3)
P(2)–Pt(1)–I(2)	97.71(3)
I(1)–Pt(1)–I(2)	96.995(12)
Pt(1)–P(1)–N(1)	93.41(12)
P(1)–N(1)–P(2)	100.15(18)
N(1)–P(2)–Pt(1)	93.55(12)



Scheme 2. Synthesis of compounds **5a**–**5d**.

Examples of P–C bond cleavage in coordinated phosphines are known and this reaction can be performed using either base [36] or a low molecular weight alcohol [37,38]. This feature has also been observed [19,34b,39] for P–N bond(s), in both free and complexed (phosphino)amines, which are susceptible to attack by MeOH. We find, using **2b** in the first instance, a clean and selective bond cleavage of one P–N bond affording the mixed platinum(II) species **5a** (Scheme 2). When a suspension of **2b** was stirred for 16 h in MeOH a colourless solid **5a** was isolated in 79% yield and has been fully characterised. The ^{31}P{^{1}H} NMR spectrum of **5a** showed two doublets, each with associated ^{195}Pt satellites, indicative of inequivalent phosphorus environments. The downfield resonance at δ(P) 81.1 is assigned to the coordinated Ph$_2$POMe and the upfield resonance at δ(P) 30.0 assigned [19a,34b] to the ligated monodentate (phosphino)amine Ph$_2$PNH{R} [R = C$_6$H$_3$(3,5-CO$_2$Me)$_2$]. A small $^2J_{PP}$ coupling constant of 13 Hz implies a mutually cis arrangement of both coordinated ligands. In the ^{1}H NMR spectrum the expected resonances for the aromatic and ester groups were observed in addition to a doublet at δ(H) 8.33 ($^2J_{PH}$ 12 Hz) which was assigned to the amine proton and a doublet at δ(H) 2.8 ($^3J_{PH}$ 12 Hz) for the Ph$_2$POMe [37]. The FT–IR spectrum showed two absorptions in the ν_{PtCl} region providing further support for a cis configuration and a weak band at 3239 cm^{-1} consistent with the presence of a –NH group. This reaction, although relatively uncommon, has previously been observed for other P–N–P type systems [19c,35b,39]. It has been shown in this work, using Ph$_2$PN{3,5-C$_6$H$_3$(CO$_2$Me)$_2$}PPh$_2$, mild conditions (MeOH/r.t.) are sufficient. Stirring a MeOH suspension of **2`b** for 16 h gave the mixed palladium complex cis-PdCl$_2$[Ph$_2$PNH{C$_6$H$_3$(3,5-CO$_2$Me)$_2$}](Ph$_2$POMe) **5d** along with some cis-PdCl$_2$(Ph$_2$POMe)$_2$ and unreacted **2`b**. ^{31}P{^{1}H} NMR spectroscopy revealed **5d** to be the major species present (~80%) in the crude solid and displayed the expected AX pattern. Prolonged reflux times only increased the amount of cis-PdCl$_2$(Ph$_2$POMe)$_2$ resulting from a second P–N cleavage.

The molecular structure of **5a**·CHCl$_3$ (Fig. 3, Table 4), as determined by X-ray crystallography, showed the platinum to be in a slightly distorted square-planar environment with the coordination sphere occupied by two chloride and two monodentate phosphorus ligands Ph$_2$POMe and Ph$_2$PNH{C$_6$H$_3$(3,5-CO$_2$Me)$_2$} in a cis configuration. The Pt–Cl bond lengths [2.3704(16) Å and 2.3500(14) Å] and Pt–P [2.2517(14) Å and 2.2209(15) Å] compare well with literature values e.g. cis-PtCl$_2$[*S*-Ph$_2$PNH{C(H)(Me)(Ph)}](Ph$_2$POMe) [2.374(2) Å and 2.356(2) Å for Pt–Cl and 2.214(3) and 2.244(2) Å for Pt–P] [39]. The structural parameters of the Ph$_2$POMe ligand are also similar to those found in related complexes containing this group. The P(1)–N(1) bond length [1.679(5) Å] is shorter than the accepted value for a P–N single bond implying partial double bond character. There is also an intramolecular hydrogen bond between a metal bound chloride ligand and the N–H hydrogen [N(1)...Cl(1) 3.032(5) Å; H(1N)...Cl(1) 2.25(4) Å; N(1)–H(1N)...Cl(1) 138(5)°] [35b].

Attempts to prepare cis-PtX$_2$[Ph$_2$PNH{C$_6$H$_3$(3,5-CO$_2$Me)$_2$}](Ph$_2$POMe) (X = Br **5b** or I 5**c**) by stirring a MeOH suspension of **3b**

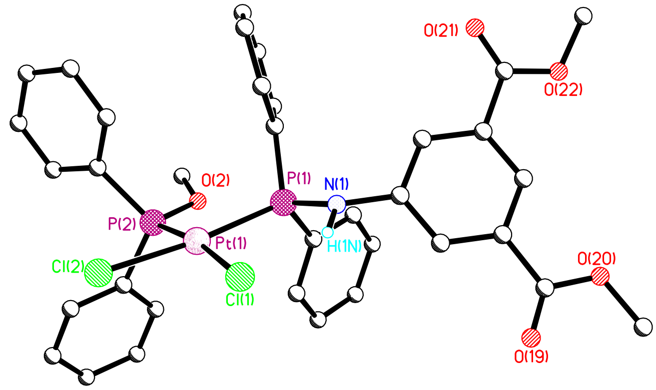


Fig. 3. X-ray structure of **5a**. The $CHCl_3$ solvent of crystallisation and all hydrogen atoms except on N(1) have been removed for clarity.

Table 4
Selected bond lengths and angles for **5a**·$CHCl_3$ and **5c**·CH_2Cl_2.

Bond length/Å	**5a**·$CHCl_3$ (X = Cl)	**5c**·CH_2Cl_2 (X = I)
Pt(1)–P(1)	2.2517(14)	2.281(3)
Pt(1)–P(2)	2.2209(15)	2.228(3)
Pt(1)–X(1)	2.3704(16)	2.6781(11)
Pt(1)–X(2)	2.3500(14)	2.6598(12)
P(1)–N(1)	1.679(5)	1.679(9)
P(2)–O(2)	1.602(4)	1.590(8)
C(19)–O(19)	1.203(7)	1.206(15)
C(19)–O(20)	1.330(7)	1.297(14)
C(21)–O(21)	1.181(8)	1.203(14)
C(21)–O(22)	1.311(8)	1.355(14)
Bond angle/°		
P(1)–Pt(1)–P(2)	94.03(5)	92.56(11)
P(1)–Pt(1)–X(1)	92.94(5)	94.53(8)
P(2)–Pt(1)–X(1)	171.49(6)	170.96(8)
P(1)–Pt(1)–X(2)	173.98(6)	175.26(7)
P(2)–Pt(1)–X(2)	85.96(5)	87.00(9)
X(1)–Pt(1)–X(2)	87.63(6)	86.39(4)
Pt(1)–P(1)–N(1)	108.99(17)	108.6(4)
O(2)–P(2)–Pt(1)	110.53(15)	109.3(3)

or **4b** gave predominantly unreacted starting materials. Refluxing these solutions produced mainly cis-$PtX_2(Ph_2POMe)_2$ (X = Br or I) instead and little spectroscopic evidence for the mixed compounds **5b**/**5c**. However clean metathesis of **5a** with NaBr (or NaI) in $(CH_3)_2CO$/MeOH afforded the desired complexes **5b** and **5c** in excellent yields. Characterising data for these compounds are given in the Experimental Section.

The molecular structure of **5c**·CH_2Cl_2 (Fig. 4, Table 4), as determined by X-ray crystallography, showed the platinum to be in a slightly distorted square-planar environment with the coordination sphere occupied by two iodides, Ph_2POMe and $Ph_2PNH\{C_6H_3(3,5\text{-}CO_2Me)_2\}$ ligands bound in a cis configuration. Similar to **5a**, there is also an intramolecular hydrogen bond between a metal bound iodide ligand and the N–H hydrogen [N(1)…I(1) 3.283(10) Å; H(1N)…I(1) 2.41(7) Å; N(1)–H(1N)…I(1) 149(10)°].

When the same procedure was extended to **2a** and **2c**, high recovery of the unreacted platinum(II) starting materials was observed. However upon leaving a MeOH filtrate of **2a** to stand for ~2 weeks a small crop of pale yellow crystals (18% isolated yield) were obtained and shown, by single crystal X-ray crystallography, to be the cyclometallated platinum(II) complex cis-PtCl[$Ph_2PNH\{C_6H_3(3\text{-}CO_2Me)\}$]($Ph_2POMe$) **6** (Eqn. (2)). The $^{31}P\{^1H\}$ NMR spectrum of **6** showed two doublets at δ(P) 117.3 and 71.7 with a $^1J_{PtP}$ of 2292 and 4421 Hz respectively. The upfield resonance at δ(P) 71.7 indicates the phosphorus is within a five-membered chelate ring and the $^1J_{PtP}$ suggests the phosphorus is trans to chloride. In contrast, for the resonance at δ(P) 117.3, the small $^1J_{PtP}$ suggests the phosphorus is trans to a high trans influence ligand, in this case an orthometallated arene group [15e]. The small $^2J_{PP}$ coupling of 20 Hz suggests that these phosphorus ligands are mutually cis. The ^1H NMR spectra showed, in addition to the anticipated aromatic, NH and – CO_2Me resonances, a doublet at δ(H) 2.85 ($^2J_{PH}$ 11.1 Hz) assigned to the Ph_2POMe methyl protons. The FT–IR spectrum showed one absorption assigned to ν_{PtCl} with an additional band at 3310 cm^{-1} (ν_{NH}) supporting cleavage and protonation of a single P–N bond. Bands assigned to ν_{CO} and ν_{PN} were observed at 1696 cm^{-1} and 923 cm^{-1} respectively. When **2a** was heated under reflux in MeOH for 16 h three major compounds were identified by ^{31}P NMR including cycloplatinated **6**, **7** [δ(P) 81.0, $^1J_{PtP}$ 4342 Hz; 29.3, $^1J_{PtP}$ 3950 Hz, $^2J_{PP}$ 17.6 Hz] and cis-$PtCl_2(PPh_2OMe)_2$ **8** [δ(P) 85.5, $^1J_{PtP}$ 4179 Hz].

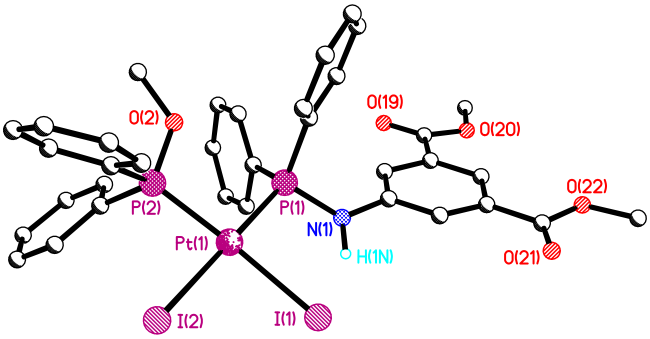
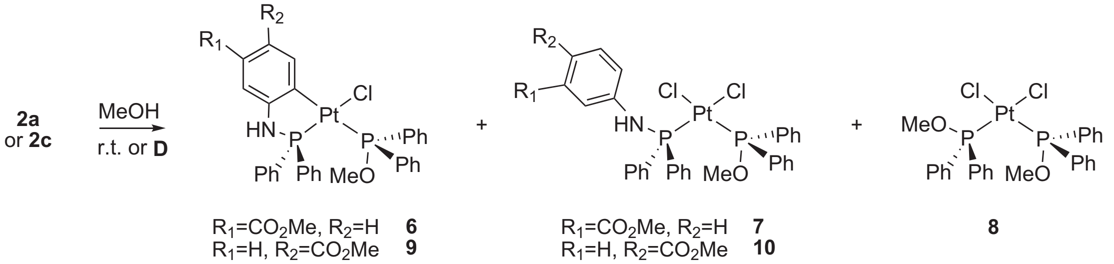
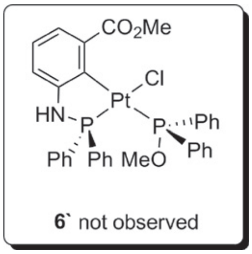


Fig. 4. X-ray structure of **5c**. The CH_2Cl_2 solvent of crystallisation and all hydrogen atoms except on N(1) have been removed for clarity.





6` not observed

Since the exact structure of **6** could not be readily ascertained from NMR spectroscopy alone, i.e. the data could not allow for accurately distinguishing between which regioisomer [2-(**6`**) or 6-positioned (**6**)] had formed, a single crystal X-ray analysis was undertaken. This confirmed that platination had occurred specifically at the less sterically hindered 6-position [40] on the *N*-arene ring of $Ph_2PNH\{C_6H_3(3\text{-}CO_2Me)\}$. The X-ray structure of **6** (Fig. 5, Table 5) revealed an approximate square-planar coordination of the platinum [P(1)–Pt(1)–C(1) 83.08(11), Cl(1)–Pt(1)–C(1) 93.20(11), Cl(1)–Pt(1)–P(2) 86.57(4), P(2)–Pt(1)–P(1) 96.97(4)°] within the five-membered chelate ring. The two phosphorus ligands adopt a cis configuration with typical Pt–P [2.1951(11) and 2.2855(10) Å] bond lengths. The observation of different Pt–P bond distances clearly reflect the different trans ligands present.

Refluxing $PtCl_2[Ph_2PN\{C_6H_4(4\text{-}CO_2Me)\}PPh_2]$ **2c** in MeOH for 16 h gave a 1:1 mixture of the orthometallated complex $PtCl[Ph_2PNH\{C_6H_3(4\text{-}CO_2Me)\}](Ph_2POMe)$ **9** [δ(P) 117.5, $^1J_{PtP}$ 2314 Hz; 72.7, $^1J_{PtP}$ 4434 Hz, $^2J_{PP}$ 17.6 Hz] and cis-$PtCl[Ph_2PNH\{C_6H_4(4\text{-}CO_2Me)\}](Ph_2POMe)$ **10** [δ(P) 80.9, $^1J_{PtP}$ 4337 Hz; 28.7, $^1J_{PtP}$ 3950 Hz, $^2J_{PP}$ 13.2 Hz] as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. Further refluxing (up to 68 h) in MeOH favoured formation of **9** over **10** (4:1 ratio) as judged by $^{31}P\{^1H\}$ NMR in addition to a small amount of cis-$PtCl_2(PPh_2OMe)_2$ **8** [δ(P) 85.6, $^1J_{PtP}$ 4175 Hz] presumably as a consequence of P–N cleavage of the platinum(II) bound (phosphino)amine. The ^1H NMR spectrum confirmed the presence of –NH [δ(H) 4.91 ($^2J_{PH}$ 3.2 Hz, $^3J_{PtH}$ 86 Hz) and 8.29 ($^2J_{PH}$ 10.6 Hz)], –CO_2Me [δ(H) 3.73 and 3.72] and OMe [δ(H) 2.87 ($^3J_{PH}$ 11.6 Hz) and 2.77 ($^3J_{PH}$ 11.2 Hz)] groups in **9** and **10** respectively. Although P–N bond cleavage using higher boiling linear alcohols has not been attempted in our work, Urriolabeitia and co-workers have shown that related mixed platinum(II) complexes can be synthesised [39].

The X-ray structure of **9** (Fig. 6, Table 5) revealed similar metric parameters to **6** including an approximate square-planar coordination of the platinum [P(1)–Pt(1)–C(1) 83.00(14), Cl(1)–Pt(1)–C(1) 92.69(14), Cl(1)–Pt(1)–P(2) 88.05(4), P(2)–Pt(1)–P(1) 96.17(4)°] within the five-membered chelate ring. Likewise the two phosphorus ligands in **9** adopt a cis configuration with typical Pt–P [2.1935(12) and 2.2916(12) Å] bond lengths. Dimer pairs are formed through intermolecular H-bonding with CH_3OH [N(1)...O(1S) 2.997(6) Å; H(1)...O(1S) 2.14 Å; N(1)–H(1)...O(1S) 163° and O(1S)...O(1) 2.830(7) Å; H(1S1)...O(1) 2.04(2) Å; O(1S)–H(1S1)...O(1)

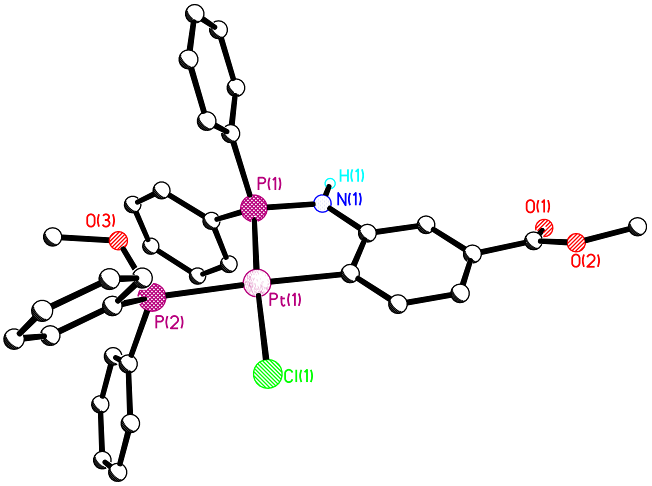


Fig. 5. X-ray structure of **6**. All hydrogen atoms except on N(1) have been removed for clarity.

Table 5
Selected bond lengths and angles for **6** and **9**·$CHCl_3$·CH_3OH.

Bond length/Å	**6**	**9**·$CHCl_3$·CH_3OH
Pt(1)–P(1)	2.1951(11)	2.1935(12)
Pt(1)–P(2)	2.2855(10)	2.2916(12)
Pt(1)–Cl(1)	2.3590(11)	2.3652(11)
Pt(1)–C(1)	2.062(3)	2.075(4)
P(1)–N(1)	1.663(3)	1.671(4)
P(2)–O(3)	1.606(3)	1.611(3)
C(X)–O(1)	1.211(5)[a]	1.232(6)[b]
C(X)–O(2)	1.331(5)[a]	1.328(7)[b]
Bond angle/°		
P(1)–Pt(1)–P(2)	96.97(4)	96.17(4)
P(1)–Pt(1)–Cl(1)	174.84(3)	173.01(4)
P(2)–Pt(1)–Cl(1)	86.57(4)	88.05(4)
P(1)–Pt(1)–C(1)	83.08(11)	83.00(14)
P(2)–Pt(1)–C(1)	176.98(10)	178.74(14)
Cl(1)–Pt(1)–C(1)	93.20(11)	92.69(14)
Pt(1)–P(1)–N(1)	103.94(12)	104.29(15)
Pt(1)–P(2)–O(3)	109.90(10)	109.55(13)

[a] X = C(5).
[b] X = C(7).

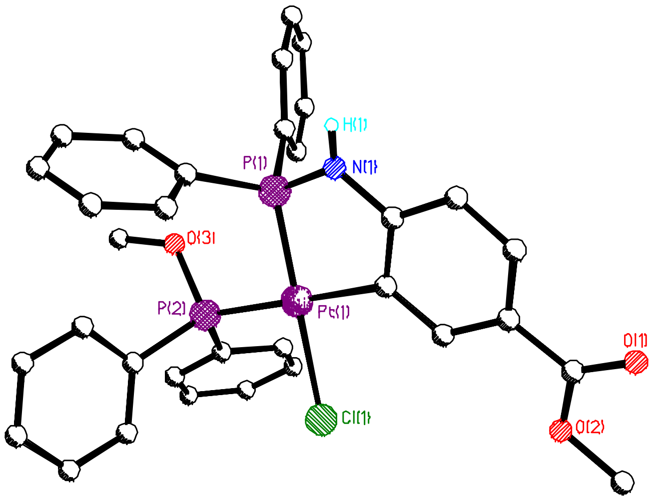


Fig. 6. X-ray structure of **9**. The $CHCl_3$ and CH_3OH solvents of crystallisation and all hydrogen atoms except on N(1) have been removed for clarity.

157(5)°] generating 20-membered rings. Crystallographic examples of mononuclear M–P–N–C_{arene}–C_{arene} metallacycles, bearing a P,C-metallated (phosphino)amine, are relatively uncommon [15].

4. Conclusions

In summary, we have shown new functionalised bis(phosphino)amines can readily be prepared and display typical coordination properties towards late transition-metal centres. The reactivity of the P–N bond is demonstrated by the ease of cleavage of a strained four-membered M–P–N–P ring upon stirring suspensions of these complexes in MeOH. This non-optimised route may provide access to various mixed platinum(II) complexes containing $R_2PNH\{R\}$ and R_2POR ligands. We also observed formation of two orthometallated species under very mild conditions. Further studies are in progress and will be reported in due course.

Acknowledgements

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Appendix A. Supplementary material

CCDC 216325, 843540–843543, 849491; contains a complete set of X-ray crystallographic structural data for compounds **2a**·0.75$CHCl_3$, **4b**, **5a**·$CHCl_3$, **5c**·CH_2Cl_2, **6** and **9**·$CHCl_3$·CH_3OH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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