

# Molybdenum(0), ruthenium(II), palladium(II), platinum(II), copper(I) and gold(I) complexes of a new methoxy functionalised bis(phosphino)amine: synthesis and structure

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The synthesis, and characterisation, of a new functionalised bis(phosphino)amine  $\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2$  **1** from  $o\text{-H}_2\text{NC}_6\text{H}_4\text{OMe}$  and 2 equiv. of  $\text{Ph}_2\text{PCl}$  in diethyl ether at  $0^\circ\text{C}$  is reported. Oxidation of **1** with either aqueous  $\text{H}_2\text{O}_2$ , elemental  $\text{S}_8$  or grey Se affords the phosphorus(v) compounds  $\text{Ph}_2\text{P(E)N}(o\text{-C}_6\text{H}_4\text{OMe})\text{P(E)Ph}_2$  (E = O **2**; S **3** or Se **4**). Partial oxidation of **1** with 1 equiv. of  $\text{S}_8$  in *n*-hexane affords the mixed P(III)/P(V) species  $\text{Ph}_2\text{P(S)N}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2$  **5** in addition to small amounts of **3**. Reaction of **1** (or **5**) with  $[\text{MX}_2(\text{cod})]$  (M = Pd, Pt; X = Cl or  $\text{CH}_3$ ; cod = cycloocta-1,5-diene) affords either *cis*- $[\text{MX}_2\{\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}]$  (M = Pd, X = Cl **6**; M = Pt, X = Cl **7**; M = Pt, X =  $\text{CH}_3$  **8**) or the neutral five-membered chelate complexes  $[\text{MCl}_2\{\text{Ph}_2\text{P(S)N}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}]$  (M = Pd **9**, M = Pt **10**) in which *P,P*- or *P,S*-chelation respectively was observed. Likewise reaction of  $[\text{Mo}(\text{CO})_4(\text{nbd})]$  (nbd = norbornadiene) or  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  with **1** gave *cis*- $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}]$  **11** or  $[\text{Cu}\{\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}_2]\text{PF}_6$  **12**. Chloro-bridge cleavage and arene elimination of  $[\{\text{RuCl}_2(p\text{-cym})\}_2]$  (*p*-cym = *p*-cymene) with **1** (1 : 2 metal : ligand ratio) affords, in good yield, the octahedral bis chelate ruthenium(II) complex *trans*- $[\text{RuCl}_2\{\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}_2]$  **13**. In contrast, reaction of **1** with two equiv. of  $[\text{AuCl}(\text{tht})]$  (tht = tetrahydrothiophene) gave the dinuclear complex  $[(\text{ClAu})\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2(\text{AuCl})]$  **14** in which the bis(phosphino)amine *P,P*-bridges two {AuCl} metal fragments. All new compounds have been characterised by a combination of multinuclear NMR [ $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{195}\text{Pt}\{^1\text{H}\}$ ], IR spectroscopy and elemental analyses. The molecular structures of six representative examples have been determined by single-crystal X-ray crystallography.

## Introduction

There is immense interest in the development of new phosphorus(III) ligands for various applications principally those of homogeneous metal-catalysed reactions. Functionalisation of for example, tertiary phosphines<sup>1</sup> and to a considerably lesser extent, tertiary phosphites<sup>2</sup> can provide an excellent strategy for finely regulating stereoelectronic properties. Moreover the incorporation of highly polar functional groups<sup>3</sup> or fluoros “ponytails”<sup>4</sup> into a phosphorus(III) ligand structure can dramatically increase the solubility of the resulting ligands and their corresponding complexes in aqueous and fluorous solvents respectively. We have initiated a programme directed towards the functionalisation of phosphinoamines,  $\text{R}_2\text{PN}(\text{H})\text{R}'$  and recently described the facile synthesis of two new ligands bearing an *ortho* keto group located on the secondary amine R' moiety.<sup>5</sup> Furthermore platinum(II) and rhodium(III) complexes of these ligands were shown to undergo smooth intramolecular  $\text{C}_{\text{sp}^2}\text{-H}$  bond activation affording extremely rare examples of five-membered M–P–N–C–C metallacycles.<sup>5</sup> A longer ongoing aim of our work is modification of the exocyclic R groups bound to phosphorus. In contrast the chemistry of “short-bite” ligands<sup>6</sup> including bis(phosphino)amines<sup>7,8</sup> has been reasonably well documented although pendant *O*-donor functionalised derivatives remain sparse. The inclusion of ether groups into tertiary phosphines is one popular choice as illustrated by several very recent reports.<sup>9</sup> Particular interest in these systems originates from the observation that they can behave,

upon co-ordination, as hemilabile ligands in which the P<sup>III</sup> centre is firmly anchored to the metal whilst there exists a weak M–O interaction which can readily be cleaved by substrates *e.g.* in a homogeneous catalytic reaction.<sup>10</sup>

Herein we describe the synthesis of a new methoxy functionalised bis(phosphino)amine and present some of its co-ordination chemistry with selected transition-metals. The structures of all new compounds have been elucidated by a combination of multinuclear NMR spectroscopy, IR spectroscopy, elemental analyses and, in several instances, by X-ray crystallography.

## Experimental

### General

All reactions were performed under nitrogen unless otherwise stated. The starting materials  $[\text{MCl}_2(\text{cod})]$  (M = Pd, Pt),<sup>11,12</sup>  $[\text{Pt}(\text{CH}_3)_2(\text{cod})]$ ,<sup>13</sup>  $[\text{AuCl}(\text{tht})]$ ,<sup>14</sup>  $[\{\text{Ru}(p\text{-cym})\text{Cl}_2\}_2]$  (*p*-cym = *p*-cymene)<sup>15</sup> and  $[\text{RuCl}_2(\text{dmsO})_4]$ <sup>16</sup> were prepared according to previous reported procedures. The compounds  $o\text{-H}_2\text{NC}_6\text{H}_4\text{OMe}$ ,  $\text{Ph}_2\text{PCl}$ ,  $[\text{Mo}(\text{CO})_4(\text{nbd})]$  and  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  were purchased from Aldrich Chemical Co and used directly, with the exception of  $o\text{-H}_2\text{NC}_6\text{H}_4\text{OMe}$  and  $\text{Ph}_2\text{PCl}$  which were distilled prior to use.

Infrared spectra were recorded as KBr pellets in the range  $4000\text{--}220\text{ cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier-transform spectrometer.  $^1\text{H}$  NMR spectra (250 MHz) were recorded on a Bruker AC250 FT spectrometer with chemical

shifts ( $\delta$ ) in ppm to high frequency of SiMe<sub>4</sub> and coupling constants ( $J$ ) in Hz, <sup>31</sup>P{<sup>1</sup>H} NMR spectra (36.2 MHz) were recorded on a JEOL FX90Q spectrometer with chemical shifts ( $\delta$ ) in ppm to high frequency of 85% H<sub>3</sub>PO<sub>4</sub> and coupling constants ( $J$ ) in Hz and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra (53.7 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with  $\delta$  referenced to external H<sub>2</sub>PtCl<sub>6</sub> (in D<sub>2</sub>O/HCl). All spectra were measured in CDCl<sub>3</sub> unless otherwise stated. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Precious metal salts were provided on loan by Johnson Matthey plc.

## Preparations

**Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>, 1.** A solution of Ph<sub>2</sub>PCl (5.02 g, 22.8 mmol) in Et<sub>2</sub>O (20 cm<sup>3</sup>) was added dropwise over 45 min to a solution of *o*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OMe (1.40 g, 11.4 mmol) and NEt<sub>3</sub> (2.35 g, 23.2 mmol) in Et<sub>2</sub>O (50 cm<sup>3</sup>) at 0 °C. The resulting white suspension was stirred for 18 h, the solvent evaporated to dryness and degassed distilled water (100 cm<sup>3</sup>) added. The solid was collected by suction filtration, washed with *n*-hexane (50 cm<sup>3</sup>), absolute EtOH (2 × 50 cm<sup>3</sup>) and dried *in vacuo*. Yield: 3.57 g, 64%. Selected IR: 2829  $\nu_{\text{CH(OMe)}}$  cm<sup>-1</sup>.

**Ph<sub>2</sub>P(O)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)P(O)Ph<sub>2</sub>, 2.** A thf (10 cm<sup>3</sup>) solution of **1** (0.250 g, 0.509 mmol) and aqueous H<sub>2</sub>O<sub>2</sub> (30% w/w, 0.1 cm<sup>3</sup>) was stirred for 18 h. The solution was evaporated to dryness under reduced pressure to give **2** as a white solid. Yield: 0.170 g, 64%. Selected IR: 2835  $\nu_{\text{CH(OMe)}}$ ; 1221, 1210  $\nu_{\text{PO}}$  cm<sup>-1</sup>.

**Ph<sub>2</sub>P(S)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)P(S)Ph<sub>2</sub>, 3.** To the solids **1** (0.250 g, 0.509 mmol) and S<sub>8</sub> (0.038 g, 1.19 mmol) was added thf (20 cm<sup>3</sup>) and this was refluxed for *ca.* 18 h. The volume was concentrated *in vacuo* to *ca.* 1–2 cm<sup>3</sup> and addition of *n*-hexane (20 cm<sup>3</sup>) gave **3** as a white solid which was collected by suction filtration. Yield: 0.262 g, 92%. Selected IR: 2840  $\nu_{\text{CH(OMe)}}$ ; 611  $\nu_{\text{PS}}$  cm<sup>-1</sup>.

In a similar manner Ph<sub>2</sub>P(Se)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)P(Se)Ph<sub>2</sub> **4** was synthesised from **1** and grey Se. Yield: 0.278 g, 84%. Selected IR: 2834  $\nu_{\text{CH(OMe)}}$ ; 571  $\nu_{\text{PSe}}$  cm<sup>-1</sup>. Slow diffusion of light petroleum (bp 60–80 °C) into a CDCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution of **4** over 72 h gave crystals suitable for X-ray crystallography.

**Ph<sub>2</sub>P(S)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>, 5.** A mixture of **1** (0.250 g, 0.509 mmol) and S<sub>8</sub> (0.016 g, 0.499 mmol) in *n*-hexane (10 cm<sup>3</sup>) were refluxed for 6 h. After allowing the mixture to cool to room temperature the white solid was collected by suction filtration and dried *in vacuo*. Examination of the solid by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy revealed the major species (*ca.* 90%) to be **5** in addition to small amounts of the disulfide **3** (*ca.* 10%). Selected IR: 2831  $\nu_{\text{CH(OMe)}}$ ; 667, 629, 613  $\nu_{\text{PS}}$  cm<sup>-1</sup>.

**[PdCl<sub>2</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>, 6.** A solution of [PdCl<sub>2</sub>(cod)] (0.049 g, 0.172 mmol) and **1** (0.086 g, 0.175 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was stirred for *ca.* 1.5 h. The volume was concentrated to *ca.* 1–2 cm<sup>3</sup> by evaporation under reduced pressure and addition of diethyl ether (20 cm<sup>3</sup>) gave a yellow solid **6**. The product was collected by suction filtration and dried *in vacuo*. Yield: 0.110 g, 94%. Selected IR: 312, 288  $\nu_{\text{PdCl}}$  cm<sup>-1</sup>. Slow diffusion of diethyl ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of **6** over 72 h gave crystals suitable for X-ray crystallography.

In a similar manner [PtCl<sub>2</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}] **7** (98%) was prepared. Selected IR: 2835  $\nu_{\text{CH(OMe)}}$ ; 313, 291  $\nu_{\text{PtCl}}$  cm<sup>-1</sup>.

**[Pt(CH<sub>3</sub>)<sub>2</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>, 8.** To a solution of [Pt(CH<sub>3</sub>)<sub>2</sub>(cod)] (0.050 g, 0.150 mmol) in toluene (10 cm<sup>3</sup>) was added **1** (0.068 g, 0.138 mmol) and the solution stirred for 10 min. The volume was concentrated to *ca.* 1–2 cm<sup>3</sup> by evaporation under reduced pressure and addition of diethyl ether (10 cm<sup>3</sup>) and light petroleum (bp 60–80 °C, 10 cm<sup>3</sup>) gave a white solid **8**. The product was collected by suction filtration and dried *in vacuo*. Yield: 0.086 g, 80%. Selected IR: 2837  $\nu_{\text{CH(OMe)}}$  cm<sup>-1</sup>.

**[PtCl<sub>2</sub>{Ph<sub>2</sub>P(S)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>, 10.** To the solids **5** (0.100 g, 0.191 mmol) and [PtCl<sub>2</sub>(cod)] (0.064 g, 0.171 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>). After stirring for 30 min the volume was concentrated to *ca.* 1 cm<sup>3</sup> and diethyl ether (20 cm<sup>3</sup>) added. The pale yellow solid was collected by suction filtration and dried *in vacuo*. Yield: 0.132 g, 97%. Selected IR: 2838  $\nu_{\text{CH(OMe)}}$ ; 328, 300  $\nu_{\text{PtCl}}$  cm<sup>-1</sup>. Slow diffusion of diethyl ether into a CDCl<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution of **10** over several days gave crystals suitable for X-ray crystallography.

In a similar manner [PdCl<sub>2</sub>{Ph<sub>2</sub>P(S)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}] **9** was also prepared (73%). Selected IR: 2834  $\nu_{\text{CH(OMe)}}$ ; 316, 289  $\nu_{\text{PdCl}}$  cm<sup>-1</sup>.

**[Mo(CO)<sub>4</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>, 11.** To a solution of [Mo(CO)<sub>4</sub>(nbd)] (0.100 g, 0.333 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added **1** (0.163 g, 0.332 mmol) and the resulting solution stirred for *ca.* 2 h. The solution was filtered through a small Celite pad and the volume concentrated *in vacuo* to *ca.* 1–2 cm<sup>3</sup>. Addition of light petroleum (bp 60–80 °C, 20 cm<sup>3</sup>) gave **11**. The mixture was stored at *ca.* 0 °C overnight and the solid collected by suction filtration and dried *in vacuo*. Yield: 0.235 g, 89%. Selected IR: 2835  $\nu_{\text{CH(OMe)}}$ ; 2021, 1922, 1907, 1863  $\nu_{\text{CO}}$  cm<sup>-1</sup>. Slow diffusion of light petroleum into a CDCl<sub>3</sub> solution of **11** over 72 h gave crystals suitable for X-ray crystallography.

**[Cu{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>PF<sub>6</sub>, 12.** To a solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (0.071 g, 0.191 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added **1** (0.187 g, 0.380 mmol) and the resulting solution stirred for *ca.* 2 h. The volume was concentrated *in vacuo* to *ca.* 2 cm<sup>3</sup> and addition of diethyl ether (15 cm<sup>3</sup>) gave **12** as a white solid. Yield: 0.195 g, 86%. Selected IR: 2836  $\nu_{\text{CH(OMe)}}$  cm<sup>-1</sup>. Slow diffusion of diethyl ether into a CDCl<sub>3</sub> solution of **12** over 72 h gave crystals suitable for X-ray crystallography.

**[RuCl<sub>2</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>, 13.** To the solids [Ru(*p*-cym)Cl<sub>2</sub>]<sub>2</sub> (0.020 g, 0.033 mmol) and **1** (0.064 g, 0.130 mmol) was added CDCl<sub>3</sub> (1 cm<sup>3</sup>) to give an immediate dark red solution. After stirring for *ca.* 18 h the dark yellow suspension was filtered, the solid washed with a small portion of CDCl<sub>3</sub> (0.5 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.067 g, 89%. Selected IR: 2829  $\nu_{\text{CH(OMe)}}$  cm<sup>-1</sup>. Alternatively **13** was prepared in lower yield (33%) from [RuCl<sub>2</sub>(dmso)<sub>4</sub>] and 2 equiv. of **1**. Suitable crystals of **13** for X-ray crystallography were obtained by allowing a CDCl<sub>3</sub> solution of [Ru(*p*-cym)Cl<sub>2</sub>]<sub>2</sub> and **1** to stand for several days.

**[AuCl]<sub>2</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}]<sub>2</sub>, 14.** To the solids [AuCl(tht)] (0.030 g, 0.092 mmol) and **1** (0.023 g, 0.047 mmol) was added CDCl<sub>3</sub> (2 cm<sup>3</sup>). The solution was examined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and showed the only phosphorus species to be **14**. Addition of diethyl ether (15 cm<sup>3</sup>) gave **14** as a white solid. Yield: 0.044 g, 94%. Selected IR: 2835  $\nu_{\text{CH(OMe)}}$ ; 326  $\nu_{\text{AuCl}}$  cm<sup>-1</sup>.

## X-Ray crystallography

The crystal structures of compounds **4**, **6** and **10–13** were determined using a Rigaku AFC7S serial diffractometer with graphite-monochromated (Cu-K $\alpha$ ) radiation ( $\lambda = 1.54178 \text{ \AA}$ ) and  $\omega$ -scans or a Bruker SMART diffractometer with

graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Details of the crystal data collections and refinements are given in Table 1. For the SMART data, intensities were collected using  $0.3^\circ$  or  $0.15^\circ$  width  $\omega$  steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data were integrated using the SAINT<sup>17</sup> program) and for the Rigaku AFC7S data collections by  $\omega$ -scans over a single quadrant of reciprocal space. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by empirical methods.<sup>18</sup>

Structures were solved by direct methods and refined by full matrix least squares against  $F$  (TEXSAN<sup>19</sup>) or  $F^2$  (SHELXTL<sup>20</sup>) for all data with  $I > 2\sigma(I)$ . Standard SHELXTL weighting scheme was used for **4**, **6** and **10–12** whilst in the case of **13** the weighting scheme for the Rigaku/TEXSAN was as previously reported.<sup>21</sup> All non H-atoms in the structures were refined anisotropically including the 1/2 weight  $\text{CHCl}_3$  in **6** and **10**. The additional 1/2 weight  $\text{CH}_2\text{Cl}_2$  in **6** was refined isotropically. The two protons on the 1/2 weight  $\text{CH}_2\text{Cl}_2$  in **6** were not located. In **10** the C–H proton on the 1/2 weight  $\text{CHCl}_3$  was located. For **13** the C–H protons on the two  $\text{CHCl}_3$  solvates were located whilst the C–H protons on the disordered  $\text{CH}_2\text{Cl}_2$  were not. All other protons were refined in idealised geometries with a riding model. Refinements converged to residuals given in Table 1. All calculations were made with programs of SHELXTL systems.

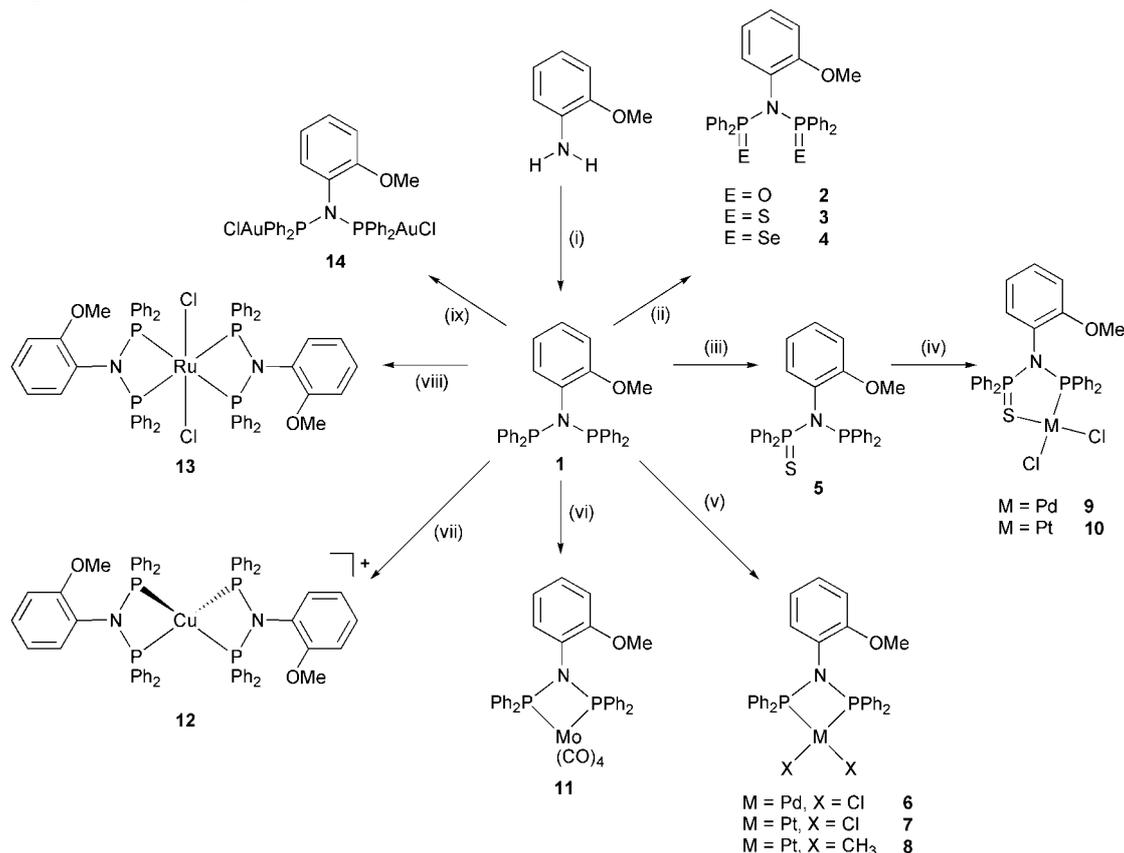
CCDC reference number 440/180. See <http://www.rsc.org/suppdata/nj/b0/b001458n/> for crystallographic files in .cif format.

## Results and discussion

The aminolysis of chlorophosphines is an efficient method for preparing  $\text{R}_2\text{PN}(\text{H})\text{R}'$  or  $(\text{R}_2\text{P})_2\text{NR}'$  yet this procedure has

not widely been exploited, in part possibly because of the associated instability of the P–N bonds in these ligands. The synthesis of the new ligand  $\text{Ph}_2\text{PN}(\text{o}-\text{C}_6\text{H}_4\text{OMe})\text{PPh}_2$  **1** (Scheme 1) by treatment of commercially available  $\text{Ph}_2\text{PCL}$  with  $\text{o}-\text{H}_2\text{NC}_6\text{H}_4\text{OMe}$  proceeded smoothly in diethyl ether and gave, after workup, a white solid in 64% yield. Attempts to prepare the mono(phosphino)amine  $\text{Ph}_2\text{PNH}(\text{o}-\text{C}_6\text{H}_4\text{OMe})$  using a 1 : 1 stoichiometry, gave under the experimental conditions used here, only **1** after workup albeit in reduced yield. We have also successfully used this procedure for the synthesis of other functionalised ligands and these will be reported in due course. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** showed a single resonance at  $\delta(\text{P})$  65.6 (Table 2) similar to that previously observed for the unsubstituted ligand  $\text{Ph}_2\text{PN}(\text{C}_6\text{H}_5)\text{PPh}_2$  [ $\delta(\text{P})$  68.8<sup>6</sup>] indicating marginal chemical shift change as a consequence of introducing an *o*-methoxy group. Solutions of **1** in  $\text{CDCl}_3$ , prepared under anaerobic conditions, are unstable and decompose gradually over *ca.* 5 d to give  $\text{Ph}_2\text{P}(\text{O})\text{N}(\text{o}-\text{C}_6\text{H}_4\text{OMe})\text{P}(\text{O})\text{Ph}_2$  **2** and  $\text{Ph}_2\text{P}(\text{O})\text{PPh}_2$ . Other pertinent spectroscopic and analytical data are given in Tables 2 and 3 and the Experimental section.

Oxidation of **1** with either aqueous  $\text{H}_2\text{O}_2$ , elemental sulfur or grey selenium gave the corresponding phosphorus(v) derivatives **2–4** whose structures were elucidated by analytical (Table 3), spectroscopic (Table 2) and furthermore, in the case of **4**, by X-ray crystallography. With the exception of **2** [ $\delta(\text{P})$  26.0] there is a negligible change in  $^{31}\text{P}$  chemical shift upon oxidation [ $\delta(\text{P})$  67.9 for **3**,  $\delta(\text{P})$  65.8 for **4**] and furthermore, in the case of **4** there is an associated  $^1\text{J}(\text{PSe})$  of 783 Hz. We also found that, using conditions identical to those described by Cavell and co-workers<sup>7</sup> for the synthesis of  $\text{Ph}_2\text{P}(\text{E})\text{N}(\text{Ph})\text{PPh}_2$  (E = S or Se), we were able to prepare  $\text{Ph}_2\text{P}(\text{S})\text{N}(\text{o}-\text{C}_6\text{H}_4\text{OMe})\text{PPh}_2$  **5**. However in our hands we were unable to obtain **5** analytically pure although  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy revealed the only other phosphorus containing species present was **3** (in *ca.* 10% by integration of the two phosphorus species). This compound was identified by its



**Scheme 1** (i)  $\text{Ph}_2\text{PCL}$ ,  $\text{Et}_2\text{O}$ ; (ii)  $\text{H}_2\text{O}_2$  or  $\text{S}_8$  or grey Se; (iii) 1 equiv.  $\text{S}_8$ ; (iv)  $[\text{MCl}_2(\text{cod})]$  (M = Pd or Pt); (v)  $[\text{MX}_2(\text{cod})]$  (M = Pd or Pt, X = Cl or  $\text{CH}_3$ ); (vi)  $[\text{Mo}(\text{CO})_4(\text{mbd})]$ ; (vii)  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ ; (viii)  $[\{\text{Ru}(\text{p-cym})\text{Cl}_2\}_2]$ ; (ix) 2 equiv.  $[\text{AuCl}(\text{tth})]$ .

**Table 1** Crystallographic data for compounds **4**, **6** and **10–13**

Compound	<b>4</b>	<b>6</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>
Empirical formula	C <sub>31</sub> H <sub>27</sub> NOP <sub>2</sub> Se <sub>2</sub>	C <sub>32</sub> H <sub>28.50</sub> Cl <sub>4.50</sub> NOP <sub>2</sub> Pd	C <sub>31.50</sub> H <sub>27.50</sub> Cl <sub>3.50</sub> NOP <sub>2</sub> PtS	C <sub>35</sub> H <sub>27</sub> MoNO <sub>5</sub> P <sub>2</sub>	C <sub>62</sub> H <sub>54</sub> CuF <sub>6</sub> N <sub>2</sub> O <sub>2</sub> P <sub>5</sub>	C <sub>65</sub> H <sub>58</sub> N <sub>2</sub> O <sub>2</sub> P <sub>4</sub> Cl <sub>10</sub> Ru
<i>M</i>	649.40	770.92	849.21	699.46	1191.46	1478.68
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
<i>a</i> /Å	15.7749(3)	11.8731(3)	15.0814(6)	9.0732(1)	11.1500(2)	12.587(6)
<i>b</i> /Å	18.8326(3)	14.3704(3)	9.2086(4)	18.9395(2)	30.8735(4)	14.127(5)
<i>c</i> /Å	19.4901(4)	21.5491(5)	25.0051(9)	19.2823(1)	17.2571(3)	11.423(6)
$\alpha$ /°						92.14(4)
$\beta$ /°		98.502(1)	98.384(1)	96.862(1)	94.393(1)	112.82(4)
$\gamma$ /°						111.20(3)
<i>V</i> /Å <sup>3</sup>	5790.2(2)	3636.3(2)	3435.6(2)	3289.8(1)	5923.1(2)	1708(2)
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)	293(2)	293
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P1</i>
<i>Z</i>	8	4	4	4	4	1 <sup>a</sup>
$\mu$ /mm <sup>-1</sup>	2.689	0.954	4.536	0.538	0.567	0.757
Reflections collected	33 146	22 016	14 656	13 779	35 606	6314
Independent reflections	6966	8551	4931	4677	13 891	6016
	[ <i>R</i> (int) = 0.1059]	[ <i>R</i> (int) = 0.0374]	[ <i>R</i> (int) = 0.0283]	[ <i>R</i> (int) = 0.0173]	[ <i>R</i> (int) = 0.0718]	[ <i>R</i> (int) = 0.020]
Final <i>R</i> indices	<i>R</i> 1 = 0.0336, <i>wR</i> 2 = 0.0611	<i>R</i> 1 = 0.0559, <i>wR</i> 2 = 0.1564	<i>R</i> 1 = 0.0261, <i>wR</i> 2 = 0.0752	<i>R</i> 1 = 0.0209, <i>wR</i> 2 = 0.0563	<i>R</i> 1 = 0.0578, <i>wR</i> 2 = 0.1269	<i>R</i> 1 = 0.087, <i>wR</i> 2 = 0.119

<sup>a</sup> Molecule disposed about a centre of symmetry located on the ruthenium.**Table 2** Selected NMR data for compounds **1–14**

Compound	$\delta$ (P)	$\delta$ (P <sub>E</sub> ) <sup>a</sup>	<i>J</i> (PSe)	<i>J</i> (PtP)	<i>J</i> (PP)	$\delta$ (Pt)	$\delta$ (H) <sup>b</sup>
<b>1</b>	65.6						3.82
<b>2</b>		26.0					3.51
<b>3</b>		67.9					3.24
<b>4</b>		65.8	783				3.20
<b>5</b> <sup>c</sup>	53.7	73.5			103.5		
<b>6</b>	37.9						2.85
<b>7</b>	22.6			3343		−4082 <sup>d</sup>	2.82
<b>8</b>	52.0			1607		−4170 <sup>d</sup>	2.69 <sup>e</sup>
<b>9</b>	78.6	105.7			61.6		2.70
<b>10</b>	73.4	73.4		3884, 110 <sup>f</sup>	57.0		2.72
<b>11</b>	92.4						2.51
<b>12</b>	89.1 <sup>g</sup>						2.68
<b>13</b>	77.7 <sup>h</sup>						2.63
<b>14</b>	84.9						2.96

<sup>a</sup> E = O, S or Se. <sup>b</sup> OCH<sub>3</sub> resonance. <sup>c</sup> Sample also contained small amounts of **3**. <sup>d</sup> 1 : 2 : 1 triplet. <sup>e</sup> Pt–CH<sub>3</sub>,  $\delta$  0.80, *J*(PtH) 73.7, *J*(PH) 12.8 Hz. <sup>f</sup> <sup>1</sup>*J*(PtP), <sup>2</sup>*J*(PtP) respectively. <sup>g</sup>  $\omega_{1/2}$  110 Hz. [PF<sub>6</sub>]<sup>−</sup> counter ion centered at  $\delta$ (P) −144. <sup>h</sup> Measured in CDCl<sub>3</sub>/CH<sub>3</sub>OH.

<sup>31</sup>P{<sup>1</sup>H} NMR spectrum which showed two well separated doublets at  $\delta$ (P) 53.7 (P<sup>III</sup>) and 73.5 (P<sup>V</sup>) with a <sup>2</sup>*J*(PP) of ca. 104 Hz.

The co-ordination chemistry of **1** with various transition-metal centres has been explored (Scheme 1). Hence reaction of **1** (or **5**) with [MX<sub>2</sub>(cod)] (M = Pd, Pt; X = Cl, CH<sub>3</sub>; cod = cycloocta-1,5-diene) in CH<sub>2</sub>Cl<sub>2</sub> gave the corresponding metal(II) complexes **6–10** in good to high yields (ca. 90%).

**Table 3** Microanalytical data<sup>a</sup> for compounds **1–4** and **6–14**

Compound	Analysis (%)		
	C	H	N
<b>1</b>	75.50(75.80)	5.50(5.50)	2.05(2.80)
<b>2</b>	70.80(71.10)	5.10(5.20)	2.60(2.70)
<b>3</b>	66.40(67.00)	4.75(4.90)	2.45(2.50)
<b>4</b>	57.10(57.30)	4.10(4.20)	1.85(2.20)
<b>6</b>	56.20(55.70)	4.20(4.10)	1.90(2.10)
<b>7</b>	49.45(49.20)	3.60(3.60)	1.75(1.80)
<b>8</b>	55.00(55.30)	4.55(4.65)	1.90(1.95)
<b>9</b>	52.60(53.10)	3.85(3.90)	1.60(2.00)
<b>10</b> <sup>b</sup>	44.70(44.55)	3.25(3.25)	1.45(1.65)
<b>11</b>	60.50(60.10)	4.25(3.90)	1.75(2.00)
<b>12</b>	62.10(62.50)	4.90(4.60)	2.70(2.40)
<b>13</b>	63.75(64.45)	4.60(4.70)	2.40(2.45)
<b>14</b>	38.45(38.95)	2.70(2.85)	1.35(1.45)

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Contains 0.5CHCl<sub>3</sub> as solvate.

The molybdenum(0) complex **11** was prepared in a similar manner by displacement of nbd from [Mo(CO)<sub>4</sub>(nbd)] (nbd = norbornadiene) with 1 equiv. of **1**. In the complexes **6–8** an upfield shift in  $\delta$ (P) of between 10 and 40 ppm was observed whereas for **11**, a downfield shift in  $\delta$ (P) of ca. 25 ppm was noted (Table 2). In the <sup>1</sup>H NMR spectra of **6–11** the OCH<sub>3</sub> group was shifted to lower field by ca. 1 ppm with respect to the free ligand **1**. The isolated dichlorometal(II) complexes **6** and **7** have a *cis* configuration since two distinct M–Cl stretches were observed in their IR spectra. For **11** four strong carbonyl absorptions in the region 2021–1863 cm<sup>-1</sup> are characteristic of a Group 6 *cis* tetracarbonyl metal complex. Reaction of two equiv. of **1** with [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> gave the d<sup>10</sup> cationic copper complex [Cu{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}<sub>2</sub>]PF<sub>6</sub> whereas reaction of **1** with [{Ru(*p*-cym)Cl<sub>2</sub>}<sub>2</sub>] gave the octahedral ruthenium(II) complex [RuCl<sub>2</sub>{Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub>}<sub>2</sub>] **13**. Independently we also prepared **13** from [RuCl<sub>2</sub>(dmso)<sub>4</sub>] and 2 equiv. of **1** albeit in reduced yield (33%). The *trans* isomer of **13** was isolated as indicated by one singlet in the <sup>31</sup>P NMR spectrum at  $\delta$ (P) 77.7. In contrast we find that when **1** was reacted with the d<sup>10</sup> starting material [AuCl(tht)] (tht = tetrahydrothiophene) the binuclear species **14** was obtained in 94% yield. Here **1** bridges two {AuCl} metal fragments. The downfield shift [ $\delta$ (P) 84.9] and the observation of one Au–Cl stretch at 326 cm<sup>-1</sup> in the infrared spectrum were in accord with complexation of **1**. Ligands of this P–N–P class [*i.e.* RN(PX<sub>2</sub>)<sub>2</sub>, R = alkyl; X = alkoxy, F] have previously been used in the preparation of heterobimetallic complexes.<sup>22</sup> Jones *et al.*

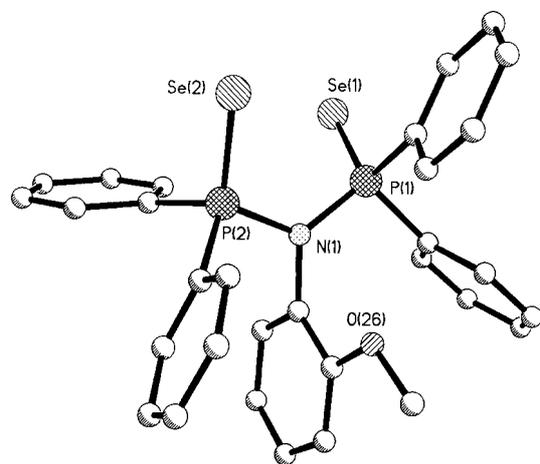


Fig. 1 Crystal structure of 4.

Table 4 Selected bond distances (Å) and angles (°) for compound 4

P(1)–Se(1)	2.1056(6)	P(1)–N(1)	1.727(2)
P(2)–Se(2)	2.0936(7)	N(1)–P(2)	1.725(2)
Se(1)–P(1)–N(1)	116.08(6)	N(1)–P(2)–Se(2)	114.80(7)
P(1)–N(1)–P(2)	124.77(10)		

recently described some unusual dinuclear gold(i) and gold(III) complexes with bidentate 1,2- $\{\text{Ph}_2\text{PN}(\text{H})\}_2\text{C}_6\text{H}_4$  and 3,4- $\{\text{Ph}_2\text{PN}(\text{H})\}_2\text{MeC}_6\text{H}_3$  ligands.<sup>23</sup>

The crystal structure of 4 (Fig. 1, Table 4) is broadly as anticipated. The P=Se bond lengths [2.1056(6) and 2.0936(7) Å] are similar to those observed for  $\{\text{Ph}_2\text{P}(\text{Se})\}_2\text{NH}$  [2.085(1) and 2.101(1) Å],  $\text{C}_6\text{H}_4\{\text{NHP}(\text{Se})\text{Ph}_2\}_2$  [2.081(6) and 2.107(5) Å] and  $\{\text{Ph}_2\text{P}(\text{Se})\text{NPPH}_2\}_2$  [2.120(2) and 2.122(2) Å].<sup>24–26</sup> Furthermore the P–N bond lengths [1.727(2) and 1.725(2) Å] are marginally longer than those in  $\{\text{Ph}_2\text{P}(\text{Se})\}_2\text{NH}$  [1.678(4) and 1.686(3) Å] which exists in the solid state as a N–H···Se hydrogen bonded dimer pair.<sup>24</sup> The P–N–P angle

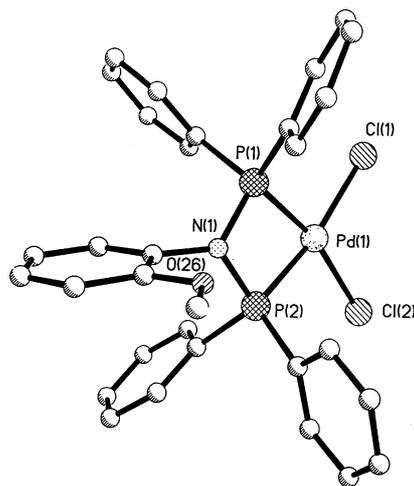


Fig. 2 Crystal structure of 6 (solvent molecules omitted for clarity).

Table 5 Selected bond distances (Å) and angles (°) for compound 6

Pd(1)–Cl(1)	2.369(2)	Pd(1)–P(2)	2.2078(13)
Pd(1)–Cl(2)	2.353(2)	P(1)–N(1)	1.701(4)
Pd(1)–P(1)	2.2196(13)	N(1)–P(2)	1.714(4)
Cl(1)–Pd(1)–Cl(2)	96.36(6)	P(1)–Pd(1)–P(2)	71.99(5)
Cl(1)–Pd(1)–P(1)	96.88(5)	Pd(1)–P(1)–N(1)	94.30(14)
Cl(1)–Pd(1)–P(2)	168.87(6)	P(1)–N(1)–P(2)	99.3(2)
Cl(2)–Pd(1)–P(2)	94.73(6)	N(1)–P(2)–Pd(1)	94.34(14)
Cl(2)–Pd(1)–P(1)	166.46(6)		

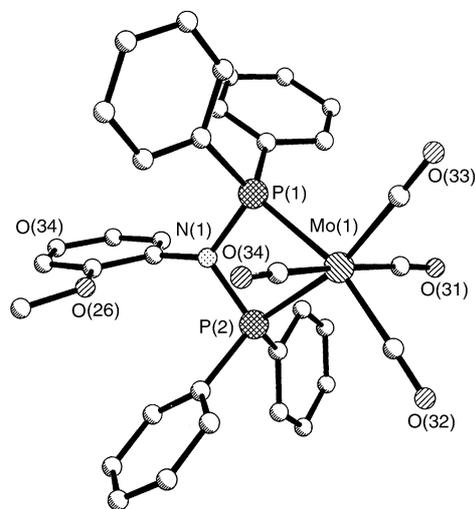


Fig. 3 Crystal structure of 11.

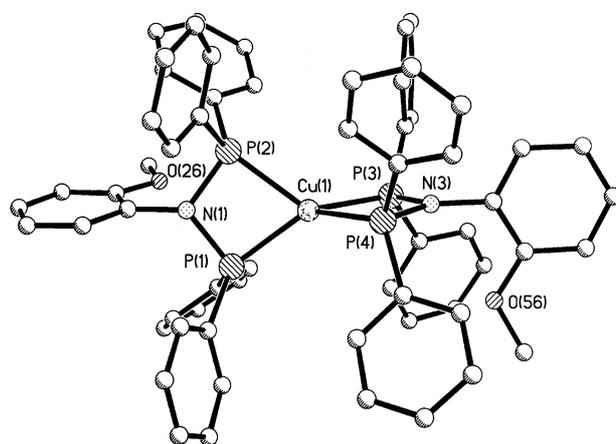
Table 6 Selected bond distances (Å) and angles (°) for compound 11

Mo(1)–P(1)	2.5102(5)	P(1)–N(1)	1.729(2)
Mo(1)–P(2)	2.4880(5)	N(1)–P(2)	1.729(2)
Mo(1)–C range	1.998(2)–2.045(2)		
Mo(1)–P(1)–N(1)	94.49(5)	P(1)–Mo(1)–P(2)	65.78(2)
Mo(1)–P(2)–N(1)	95.29(5)	P(1)–N(1)–P(2)	103.43(8)

[124.77(10)°] is smaller than that found in  $\{\text{Ph}_2\text{P}(\text{Se})\}_2\text{NH}$  [132.3(2)°].<sup>24</sup>

The crystal structure of 6 (Fig. 2, Table 5) entails a *cis*-disposed  $\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2$  and two chloride ligands around a palladium centre. The geometry is best described as distorted square-planar as reflected by the bond angles [P(1)–Pd(1)–P(2) 71.99(5), P(2)–Pd(1)–Cl(2) 94.73(6), Cl(1)–Pd(1)–Cl(2) 96.36(6), P(1)–Pd(1)–Cl(1) 96.88(5)°]. The Pd(1) is 0.04 Å below the plane of its four substituents and the PdP<sub>2</sub>N ring is essentially planar. The Pd–Cl and Pd–P bond lengths are all normal<sup>27,28</sup> whilst the P–N distances [1.701(4) and 1.714(4) Å] may indicate some partial double bond character. As a consequence of *P,P*-chelation the P(1)–N(1)–P(2) angle is 99.3(2)° but in contrast, when  $\text{R}_2\text{PN}(\text{R})\text{PR}_2$  ligands span two metal centres, as in  $[\text{Pd}_2\text{Cl}_2\{\text{PhN}\{\text{P}(\text{OPh})_2\}_2\}_2]$  and  $[\text{Pd}_2\{\text{MeN}\{\text{P}(\text{OPh})_2\}_2\}_3]$ , the P–N–P angle is enlarged and falls in the range 113–120°.<sup>29</sup> There is no Pd(1)···O(26) interaction (5.3 Å).

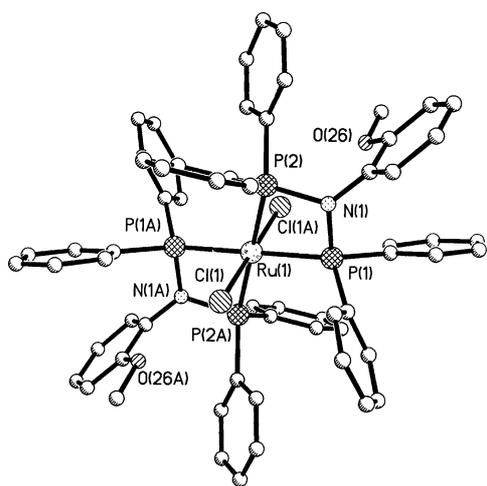
The crystal structure of 11 (Fig. 3, Table 6) shows that the geometry around the molybdenum is distorted octahedral with a *cis*-chelating  $\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2$  ligand and four terminal carbon monoxide ligands. The four-membered

Fig. 4 Crystal structure of 12 ( $\text{PF}_6^-$  counter ion omitted for clarity).

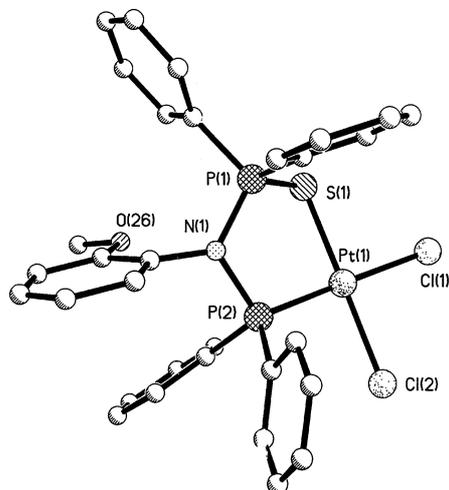
**Table 7** Selected bond distances (Å) and angles (°) for compound **12**

Cu(1)–P(1)	2.3010(12)	P(1)–N(1)	1.719(3)
Cu(1)–P(2)	2.3268(12)	N(1)–P(2)	1.717(3)
Cu(1)–P(3)	2.2944(12)	P(3)–N(3)	1.705(3)
Cu(1)–P(4)	2.3330(12)	N(3)–P(4)	1.720(3)
P(1)–Cu(1)–P(2)	73.19(4)	Cu(1)–P(1)–N(1)	90.21(11)
P(1)–Cu(1)–P(3)	132.12(5)	Cu(1)–P(2)–N(1)	89.41(11)
P(1)–Cu(1)–P(4)	132.18(5)	Cu(1)–P(3)–N(3)	90.75(12)
P(2)–Cu(1)–P(3)	130.06(5)	Cu(1)–P(4)–N(3)	89.08(12)
P(2)–Cu(1)–P(4)	126.16(5)	P(1)–N(1)–P(2)	106.8(2)
P(3)–Cu(1)–P(4)	73.06(4)	P(3)–N(3)–P(4)	107.1(2)

MoP<sub>2</sub>N ring is essentially planar and the Mo–P/P–N distances compare well with those of [Mo<sub>2</sub>(CO)<sub>8</sub>{μ-*cis*-[PhNP(OC<sub>6</sub>H<sub>4</sub>Me-*p*)]<sub>2</sub>}<sub>2</sub>] [Mo–P 2.484(2), 2.476(2) Å; P–N range 1.701(4)–1.716(3) Å]<sup>30</sup> and [Mo(CO)<sub>4</sub>{EtNP(OC<sub>6</sub>H<sub>4</sub>Br-4)}<sub>3</sub>] [average Mo–P 2.452(5) Å; P–N *ca.* 1.70(1) Å].<sup>31</sup> In contrast the observed Mo–P bond lengths [2.5102(5) and

**Fig. 5** Crystal structure of **13** (solvent molecules omitted for clarity).**Table 8** Selected bond distances (Å) and angles (°) for compound **13**

Ru(1)–Cl(1)	2.416(3)	P(1)–N(1)	1.714(7)
Ru(1)–P(1)	2.348(3)	N(1)–P(2)	1.754(8)
Ru(1)–P(2)	2.2332(2)	P(1)–Ru(1)–P(2)	69.84(9)
Cl(1)–Ru(1)–P(1)	88.49(9)	P(1)–Ru(1)–P(2A)	110.16(9)
Cl(1)–Ru(1)–P(2)	87.89(9)	Ru(1)–P(1)–N(1)	94.8(3)
Cl(1)–Ru(1)–P(1A)	91.51(9)	N(1)–P(2)–Ru(1)	94.2(2)
Cl(1)–Ru(1)–P(2A)	92.11(9)		
P(1)–N(1)–P(2)	101.2(4)		

**Fig. 6** Crystal structure of **10** (solvent molecule omitted for clarity).**Table 9** Selected bond distances (Å) and angles (°) for compound **10**

Pt(1)–Cl(1)	2.3515(12)	S(1)–P(1)	2.010(2)
Pt(1)–Cl(2)	2.3164(13)	P(1)–N(1)	1.688(4)
Pt(1)–S(1)	2.2948(12)	N(1)–P(2)	1.735(4)
Pt(1)–P(2)	2.2029(12)		
Cl(1)–Pt(1)–Cl(2)	89.76(5)	P(2)–Pt(1)–S(1)	92.53(14)
Cl(1)–Pt(1)–S(1)	88.46(5)	Pt(1)–S(1)–P(1)	97.43(6)
Cl(1)–Pt(1)–P(2)	178.73(5)	S(1)–P(1)–N(1)	108.52(14)
Cl(2)–Pt(1)–P(2)	89.20(4)	P(1)–N(1)–P(2)	116.2(2)
Cl(2)–Pt(1)–S(1)	175.45(4)	N(1)–P(2)–Pt(1)	108.70(13)

2.4880(5) Å] in **11** are slightly longer than found in [Mo(CO)<sub>4</sub>{PhNP(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>] [Mo–P 2.440(2), 2.427(2) Å] indicating **1** is a poorer π-acceptor ligand than PhN{P(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>.<sup>32</sup> The P–N–P angle in **11** [103.43(8)°] differs by approximately ±3° with respect to that found in complexes **6** and **12**.

The crystal structure of the cationic complex **12** (Fig. 4, Table 7) confirms a markedly distorted tetrahedral geometry of the copper(i) metal centre with the co-ordination sphere occupied by two chelating Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub> ligands. The Cu–P bond distances are normal [2.2944(12)–2.3330(12) Å] whilst the P–N bond lengths [1.705(3)–1.719(3) Å] are similar to those found in **4**. Both CuP<sub>2</sub>N rings are essentially planar and orthogonal to each other. Within both metallorings, the P–N–P angles [106.8(2) and 107.1(2)°] are slightly enlarged with respect to that found in **11**.

The crystal structure of **13** (Fig. 5, Table 8) shows the ruthenium(ii) centre to be essentially octahedral with two chloride and two Ph<sub>2</sub>PN(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub> ligands disposed in a *trans* configuration. Within the four-membered RuP<sub>2</sub>N ring the considerable ring strain is reflected by an acute P(1)–Ru(1)–P(2) angle of 69.84(9)°. The Ru–P, Ru–Cl and P–N distances in **13** are slightly shorter than those in the ruthenium(ii) complex [Ru(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Cl{(Ph<sub>2</sub>P)<sub>2</sub>NH}] [2.2777(10), 2.2813(10); 2.4607(10) and 1.692(3), 1.694(3) Å respectively].<sup>33</sup> Within the RuP<sub>2</sub>N metallacycle the P–N–P angle of 101.2(4)° is somewhat enlarged with respect to that of **6** but contracted in comparison to **11** and **12**.

The crystal structure of **10** (Fig. 6, Table 9) shows a monomeric chelated metal complex with a square-planar environment comprising a central platinum centre, a *P,S*-bound Ph<sub>2</sub>P(S)N(*o*-C<sub>6</sub>H<sub>4</sub>OMe)PPh<sub>2</sub> ligand and a *cis* disposition of two chloride ligands. The Pt is 0.05 Å below the plane of the four donor substituents. Within the Pt–S–P–N–P five-membered metallacycle S(1) shows a maximum deviation [0.33 Å] out of the plane. The Pt(1)–Cl(1) bond length [2.3515(2) Å] is larger than that of Pt(1)–Cl(2) [2.3164(13) Å] and as anticipated for the different *trans* influences of phosphorus *vs.* sulfur donor atoms. The P–S and P–N bond distances and angles are comparable to those reported by Cavell and co-workers for [PtCl<sub>2</sub>{Ph<sub>2</sub>P(S)N(Ph)PPh<sub>2</sub>}].<sup>7</sup>

## Conclusion

In conclusion, we have shown the facile synthesis of a new bis(phosphino)amine and its co-ordination chemistry with a range of transition-metals. Further studies are in progress and will be reported in due course.

## Acknowledgements

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