

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

Kirsty G. Gaw,^a Martin B. Smith^{*a} and Alexandra M. Z. Slawin^b

^a Department of Chemistry, Loughborough University, Loughborough, Leics, UK LE11 3TU.
E-mail: m.b.smith@lboro.ac.uk

^b School of Chemistry, University of St. Andrews, St Andrews, Fife, UK KY16 9ST

Received (in Cambridge, UK) 22nd February 2000, Accepted 21st March 2000

Published on the Web 22nd May 2000

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 Ph_2PCl in diethyl ether at 0°C is reported. Oxidation of **1** with either aqueous H_2O_2 , elemental S_8 or grey Se affords the phosphorus(v) compounds $\text{Ph}_2\text{P(E)N}(o\text{-C}_6\text{H}_4\text{OMe})\text{P(E)Ph}_2$ ($\text{E} = \text{O}$ **2**; S **3** or Se **4**). Partial oxidation of **1** with 1 equiv. of 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 $[\text{MX}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}$ or CH_3 ; $\text{cod} = \text{cycloocta-1,5-diene}$) affords either *cis*- $[\text{MX}_2\{\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}]$ ($\text{M} = \text{Pd}, \text{X} = \text{Cl}$ **6**; $\text{M} = \text{Pt}, \text{X} = \text{Cl}$ **7**; $\text{M} = \text{Pt}, \text{X} = \text{CH}_3$ **8**) or the neutral five-membered chelate complexes $[\text{MCl}_2\{\text{Ph}_2\text{P(S)N}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2\}]$ ($\text{M} = \text{Pd}$ **9**, $\text{M} = \text{Pt}$ **10**) in which *P,P*- or *P,S*-chelation respectively was observed. Likewise reaction of $[\text{Mo}(\text{CO})_4(\text{nbd})]$ ($\text{nbd} = \text{norbornadiene}$) 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 $[\{\text{RuCl}_2(p\text{-cym})\}_2]$ ($p\text{-cym} = p\text{-cymene}$) 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 $[\text{AuCl}(\text{tht})]$ ($\text{tht} = \text{tetrahydrothiophene}$) 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 $\{\text{AuCl}\}$ metal fragments. All new compounds have been characterised by a combination of multinuclear NMR [^1H , $^{31}\text{P}\{^1\text{H}\}$ 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 phosphines¹ and to a considerably lesser extent, tertiary phosphites² can provide an excellent strategy for finely regulating stereoelectronic properties. Moreover the incorporation of highly polar functional groups³ or fluorous “ponytails”⁴ 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.⁵ 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.⁵ A longer ongoing aim of our work is modification of the exocyclic R groups bound to phosphorus. In contrast the chemistry of “short-bite” ligands⁶ including bis(phosphino)amines^{7,8} 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.⁹ Particular interest in these systems originates from the observation that they can behave,

upon co-ordination, as hemilabile ligands in which the P^{III} 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.¹⁰

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 $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$),^{11,12} $[\text{Pt}(\text{CH}_3)_2(\text{cod})]$,¹³ $[\text{AuCl}(\text{tht})]$,¹⁴ $[\{\text{Ru}(p\text{-cym})\text{Cl}_2\}_2]$ ($p\text{-cym} = p\text{-cymene}$)¹⁵ and $[\text{RuCl}_2(\text{dmsO})_4]$ ¹⁶ were prepared according to previous reported procedures. The compounds $o\text{-H}_2\text{NC}_6\text{H}_4\text{OMe}$, Ph_2PCl , $[\text{Mo}(\text{CO})_4(\text{nbd})]$ 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 Ph_2PCl 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. ^1H NMR spectra (250 MHz) were recorded on a Bruker AC250 FT spectrometer with chemical

shifts (δ) in ppm to high frequency of SiMe₄ and coupling constants (J) in Hz, ³¹P{¹H} NMR spectra (36.2 MHz) were recorded on a JEOL FX90Q spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H₃PO₄ and coupling constants (J) in Hz and ¹⁹⁵Pt{¹H} NMR spectra (53.7 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with δ referenced to external H₂PtCl₆ (in D₂O/HCl). All spectra were measured in CDCl₃ 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

Ph₂PN(*o*-C₆H₄OMe)PPh₂, 1. A solution of Ph₂PCl (5.02 g, 22.8 mmol) in Et₂O (20 cm³) was added dropwise over 45 min to a solution of *o*-H₂NC₆H₄OMe (1.40 g, 11.4 mmol) and NEt₃ (2.35 g, 23.2 mmol) in Et₂O (50 cm³) at 0 °C. The resulting white suspension was stirred for 18 h, the solvent evaporated to dryness and degassed distilled water (100 cm³) added. The solid was collected by suction filtration, washed with *n*-hexane (50 cm³), absolute EtOH (2 × 50 cm³) and dried *in vacuo*. Yield: 3.57 g, 64%. Selected IR: 2829 $\nu_{\text{CH}}(\text{OMe})$ cm⁻¹.

Ph₂P(O)N(*o*-C₆H₄OMe)P(O)Ph₂, 2. A thf (10 cm³) solution of **1** (0.250 g, 0.509 mmol) and aqueous H₂O₂ (30% w/w, 0.1 cm³) 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 $\nu_{\text{CH}}(\text{OMe})$; 1221, 1210 ν_{PO} cm⁻¹.

Ph₂P(S)N(*o*-C₆H₄OMe)P(S)Ph₂, 3. To the solids **1** (0.250 g, 0.509 mmol) and S₈ (0.038 g, 1.19 mmol) was added thf (20 cm³) and this was refluxed for *ca.* 18 h. The volume was concentrated *in vacuo* to *ca.* 1–2 cm³ and addition of *n*-hexane (20 cm³) gave **3** as a white solid which was collected by suction filtration. Yield: 0.262 g, 92%. Selected IR: 2840 $\nu_{\text{CH}}(\text{OMe})$; 611 ν_{PS} cm⁻¹.

In a similar manner Ph₂P(Se)N(*o*-C₆H₄OMe)P(Se)Ph₂ **4** was synthesised from **1** and grey Se. Yield: 0.278 g, 84%. Selected IR: 2834 $\nu_{\text{CH}}(\text{OMe})$; 571 ν_{PSe} cm⁻¹. Slow diffusion of light petroleum (bp 60–80 °C) into a CDCl₃/CH₂Cl₂ solution of **4** over 72 h gave crystals suitable for X-ray crystallography.

Ph₂P(S)N(*o*-C₆H₄OMe)PPh₂, 5. A mixture of **1** (0.250 g, 0.509 mmol) and S₈ (0.016 g, 0.499 mmol) in *n*-hexane (10 cm³) 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 ³¹P{¹H} 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 $\nu_{\text{CH}}(\text{OMe})$; 667, 629, 613 ν_{PS} cm⁻¹.

[PdCl₂{Ph₂PN(*o*-C₆H₄OMe)PPh₂}]₂, 6. A solution of [PdCl₂(cod)] (0.049 g, 0.172 mmol) and **1** (0.086 g, 0.175 mmol) in CH₂Cl₂ (10 cm³) was stirred for *ca.* 1.5 h. The volume was concentrated to *ca.* 1–2 cm³ by evaporation under reduced pressure and addition of diethyl ether (20 cm³) 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 ν_{PdCl} cm⁻¹. Slow diffusion of diethyl ether into a CH₂Cl₂ solution of **6** over 72 h gave crystals suitable for X-ray crystallography.

In a similar manner [PtCl₂{Ph₂PN(*o*-C₆H₄OMe)PPh₂}] **7** (98%) was prepared. Selected IR: 2835 $\nu_{\text{CH}}(\text{OMe})$; 313, 291 ν_{PtCl} cm⁻¹.

[Pt(CH₃)₂{Ph₂PN(*o*-C₆H₄OMe)PPh₂}]₂, 8. To a solution of [Pt(CH₃)₂(cod)] (0.050 g, 0.150 mmol) in toluene (10 cm³) was added **1** (0.068 g, 0.138 mmol) and the solution stirred for 10 min. The volume was concentrated to *ca.* 1–2 cm³ by evaporation under reduced pressure and addition of diethyl ether (10 cm³) and light petroleum (bp 60–80 °C, 10 cm³) gave a white solid **8**. The product was collected by suction filtration and dried *in vacuo*. Yield: 0.086 g, 80%. Selected IR: 2837 $\nu_{\text{CH}}(\text{OMe})$ cm⁻¹.

[PtCl₂{Ph₂P(S)N(*o*-C₆H₄OMe)PPh₂}]₂, 10. To the solids **5** (0.100 g, 0.191 mmol) and [PtCl₂(cod)] (0.064 g, 0.171 mmol) was added CH₂Cl₂ (20 cm³). After stirring for 30 min the volume was concentrated to *ca.* 1 cm³ and diethyl ether (20 cm³) added. The pale yellow solid was collected by suction filtration and dried *in vacuo*. Yield: 0.132 g, 97%. Selected IR: 2838 $\nu_{\text{CH}}(\text{OMe})$; 328, 300 ν_{PtCl} cm⁻¹. Slow diffusion of diethyl ether into a CDCl₃/CH₂Cl₂ solution of **10** over several days gave crystals suitable for X-ray crystallography.

In a similar manner [PdCl₂{Ph₂P(S)N(*o*-C₆H₄OMe)PPh₂}] **9** was also prepared (73%). Selected IR: 2834 $\nu_{\text{CH}}(\text{OMe})$; 316, 289 ν_{PdCl} cm⁻¹.

[Mo(CO)₄{Ph₂PN(*o*-C₆H₄OMe)PPh₂}]₂, 11. To a solution of [Mo(CO)₄(nbd)] (0.100 g, 0.333 mmol) in CH₂Cl₂ (20 cm³) 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 cm³. Addition of light petroleum (bp 60–80 °C, 20 cm³) 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 $\nu_{\text{CH}}(\text{OMe})$; 2021, 1922, 1907, 1863 ν_{CO} cm⁻¹. Slow diffusion of light petroleum into a CDCl₃ solution of **11** over 72 h gave crystals suitable for X-ray crystallography.

[Cu{Ph₂PN(*o*-C₆H₄OMe)PPh₂}]₂PF₆, 12. To a solution of [Cu(CH₃CN)₄]PF₆ (0.071 g, 0.191 mmol) in CH₂Cl₂ (20 cm³) 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 cm³ and addition of diethyl ether (15 cm³) gave **12** as a white solid. Yield: 0.195 g, 86%. Selected IR: 2836 $\nu_{\text{CH}}(\text{OMe})$ cm⁻¹. Slow diffusion of diethyl ether into a CDCl₃ solution of **12** over 72 h gave crystals suitable for X-ray crystallography.

[RuCl₂{Ph₂PN(*o*-C₆H₄OMe)PPh₂}]₂, 13. To the solids [{Ru(*p*-cym)Cl₂}]₂ (0.020 g, 0.033 mmol) and **1** (0.064 g, 0.130 mmol) was added CDCl₃ (1 cm³) 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 CDCl₃ (0.5 cm³) and dried *in vacuo*. Yield: 0.067 g, 89%. Selected IR: 2829 $\nu_{\text{CH}}(\text{OMe})$ cm⁻¹. Alternatively **13** was prepared in lower yield (33%) from [RuCl₂(dmso)₄] and 2 equiv. of **1**. Suitable crystals of **13** for X-ray crystallography were obtained by allowing a CDCl₃ solution of [{Ru(*p*-cym)Cl₂}]₂ and **1** to stand for several days.

[AuCl₂{Ph₂PN(*o*-C₆H₄OMe)PPh₂}]₂, 14. To the solids [AuCl(tht)] (0.030 g, 0.092 mmol) and **1** (0.023 g, 0.047 mmol) was added CDCl₃ (2 cm³). The solution was examined by ³¹P{¹H} NMR spectroscopy and showed the only phosphorus species to be **14**. Addition of diethyl ether (15 cm³) gave **14** as a white solid. Yield: 0.044 g, 94%. Selected IR: 2835 $\nu_{\text{CH}}(\text{OMe})$; 326 ν_{AuCl} cm⁻¹.

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 α) radiation (λ = 1.541 78 Å) and ω -scans or a Bruker SMART diffractometer with

graphite-monochromated Mo-K α 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° or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data were integrated using the SAINT¹⁷ program) and for the Rigaku AFC7S data collections by ω -scans over a single quadrant of reciprocal space. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by empirical methods.¹⁸

Structures were solved by direct methods and refined by full matrix least squares against F (TEXSAN¹⁹) or F^2 (SHELXTL²⁰) 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.²¹ All non H-atoms in the structures were refined anisotropically including the 1/2 weight CHCl_3 in **6** and **10**. The additional 1/2 weight CH_2Cl_2 in **6** was refined isotropically. The two protons on the 1/2 weight CH_2Cl_2 in **6** were not located. In **10** the C–H proton on the 1/2 weight CHCl_3 was located. For **13** the C–H protons on the two CHCl_3 solvates were located whilst the C–H protons on the disordered CH_2Cl_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.

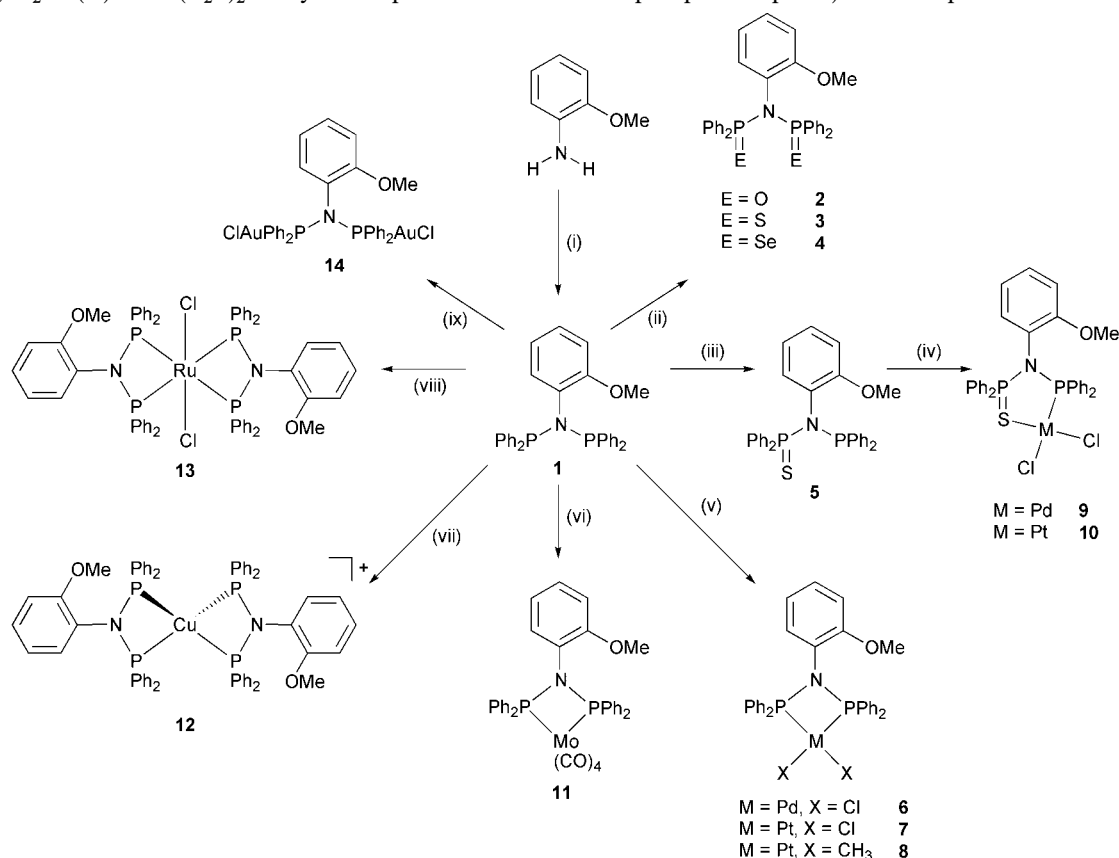
CCDC reference number 440/180. See <http://www.rsc.org/suppdata/nj/b0/b001458n/> for crystallographic files in .cif format.

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 $\text{Ph}_2\text{PN}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2$ **1** (Scheme 1) by treatment of commercially available Ph_2PCl with $o\text{-H}_2\text{NC}_6\text{H}_4\text{OMe}$ proceeded smoothly in diethyl ether and gave, after workup, a white solid in 64% yield. Attempts to prepare the mono(phosphino)amine $\text{Ph}_2\text{PNH}(o\text{-C}_6\text{H}_4\text{OMe})$ 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 $\text{Ph}_2\text{PN}(\text{C}_6\text{H}_5)\text{PPh}_2$ [$\delta(\text{P})$ 68.8⁶] indicating marginal chemical shift change as a consequence of introducing an *o*-methoxy group. Solutions of **1** in CDCl_3 , prepared under anaerobic conditions, are unstable and decompose gradually over *ca.* 5 d to give $\text{Ph}_2\text{P}(\text{O})\text{N}(o\text{-C}_6\text{H}_4\text{OMe})\text{P}(\text{O})\text{Ph}_2$ **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 H_2O_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}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-workers⁷ for the synthesis of $\text{Ph}_2\text{P}(\text{E})\text{N}(\text{Ph})\text{PPh}_2$ ($\text{E} = \text{S}$ or Se), we were able to prepare $\text{Ph}_2\text{P}(\text{S})\text{N}(o\text{-C}_6\text{H}_4\text{OMe})\text{PPh}_2$ **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) Ph_2PCl , Et_2O ; (ii) H_2O_2 or S_8 or grey Se; (iii) 1 equiv. S_8 ; (iv) $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}$ or Pt); (v) $[\text{MX}_2(\text{cod})]$ ($\text{M} = \text{Pd}$ or Pt , $\text{X} = \text{Cl}$ or 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. $[\text{AuCl}(\text{tbt})]$.

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

Compound	4	6	10	11	12	13
Empirical formula	C ₃₁ H ₂₇ NOP ₂ Se ₂	C ₃₂ H _{28.50} Cl _{4.50} NOP ₂ Pd	C _{31.50} H _{27.50} Cl _{3.50} NOP ₂ PtS	C ₃₅ H ₂₇ MoNO ₅ P ₂	C ₆₂ H ₅₄ CuF ₆ N ₂ O ₂ P ₅	C ₆₅ H ₅₈ N ₂ O ₂ P ₄ Cl ₁₀ 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)
α /°						92.14(4)
β /°		98.502(1)	98.384(1)	96.862(1)	94.393(1)	112.82(4)
γ /°						111.20(3)
<i>V</i> /Å ³	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>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P1</i>
<i>Z</i>	8	4	4	4	4	1 ^a
μ /mm ^{−1}	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)	[<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>I</i> > 2 σ (<i>I</i>)]	<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

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

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

^a E = O, S or Se. ^b OCH₃ resonance. ^c Sample also contained small amounts of **3**. ^d 1 : 2 : 1 triplet. ^e Pt–CH₃, δ 0.80, *J*(PtH) 73.7, *J*(PH) 12.8 Hz. ^f ¹*J*(PtP), ²*J*(PtP) respectively. ^g $\omega_{1/2}$ 110 Hz. [PF₆][−] counter ion centered at δ (P) −144. ^h Measured in CDCl₃/CH₃OH.

³¹P{¹H} NMR spectrum which showed two well separated doublets at δ (P) 53.7 (P^{III}) and 73.5 (P^V) with a ²*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 [MX₂(cod)] (M = Pd, Pt; X = Cl, CH₃; cod = cycloocta-1,5-diene) in CH₂Cl₂ gave the corresponding metal(II) complexes **6–10** in good to high yields (*ca.* 90%).

Table 3 Microanalytical data^a for compounds **1–4** and **6–14**

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

^a Calculated values in parentheses. ^b Contains 0.5CHCl₃ as solvate.

The molybdenum(0) complex **11** was prepared in a similar manner by displacement of nbd from [Mo(CO)₄(nbd)] (nbd = norbornadiene) with 1 equiv. of **1**. In the complexes **6–8** an upfield shift in δ (P) of between 10 and 40 ppm was observed whereas for **11**, a downfield shift in δ (P) of *ca.* 25 ppm was noted (Table 2). In the ¹H NMR spectra of **6–11** the OCH₃ 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^{−1} are characteristic of a Group 6 *cis* tetracarbonyl metal complex. Reaction of two equiv. of **1** with [Cu(CH₃CN)₄]PF₆ in CH₂Cl₂ gave the d¹⁰ cationic copper complex [Cu{Ph₂PN(*o*-C₆H₄OMe)PPh₂}₂]PF₆ **12** whereas reaction of **1** with [{Ru(*p*-cym)Cl₂}₂] gave the octahedral ruthenium(II) complex [RuCl₂{Ph₂PN(*o*-C₆H₄OMe)PPh₂}₂] **13**. Independently we also prepared **13** from [RuCl₂(dmsO)₄] and 2 equiv. of **1** albeit in reduced yield (33%). The *trans* isomer of **13** was isolated as indicated by one singlet in the ³¹P NMR spectrum at δ (P) 77.7. In contrast we find that when **1** was reacted with the d¹⁰ 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 [δ (P) 84.9] and the observation of one Au–Cl stretch at 326 cm^{−1} in the infrared spectrum were in accord with complexation of **1**. Ligands of this P–N–P class [*i.e.* RN(PX₂)₂, R = alkyl; X = alkoxy, F] have previously been used in the preparation of heterobimetallic complexes.²² Jones *et al.*

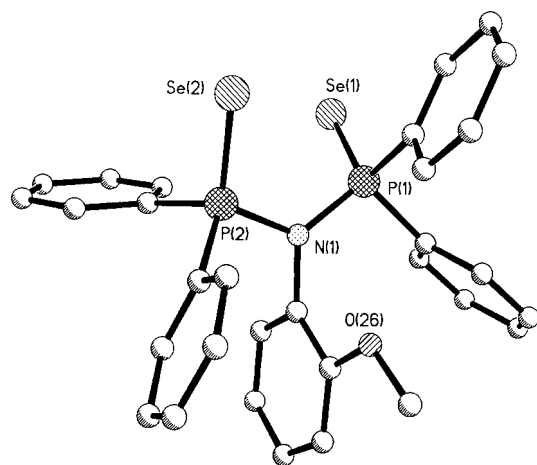


Fig. 1 Crystal structure of 4.

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(II) 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.²³

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].^{24–26} 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.²⁴ The P–N–P angle

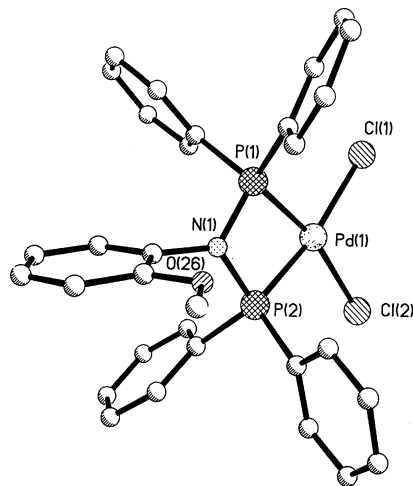


Fig. 2 Crystal structure of 6 (solvent molecules omitted for clarity).

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)		

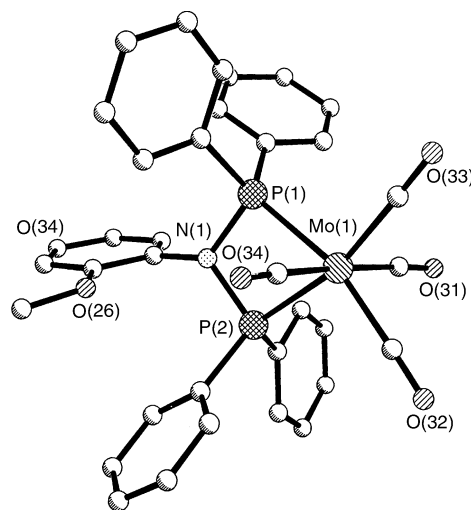


Fig. 3 Crystal structure of 11.

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)°].²⁴

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 PdP₂N ring is essentially planar. The Pd–Cl and Pd–P bond lengths are all normal^{27,28} 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°. 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

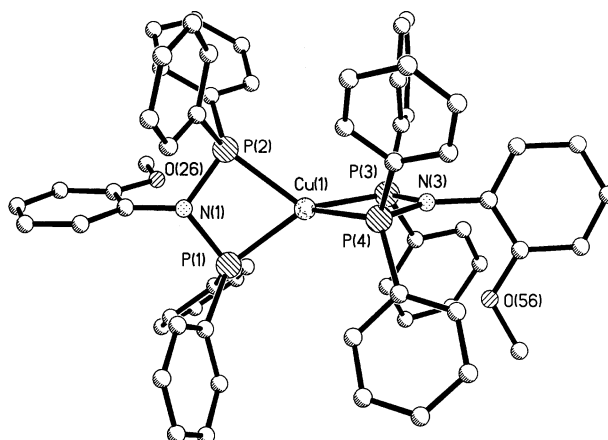
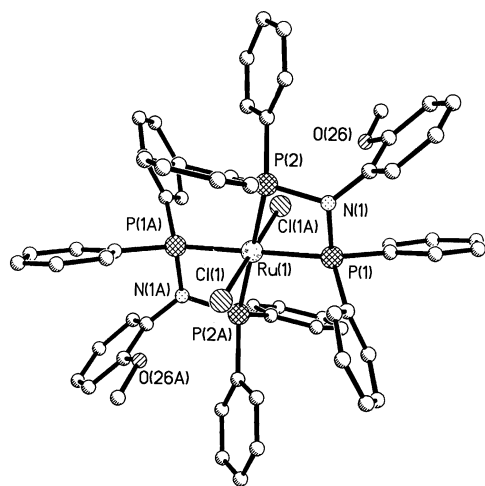


Fig. 4 Crystal structure of 12 (PF_6^- counter ion omitted for clarity).

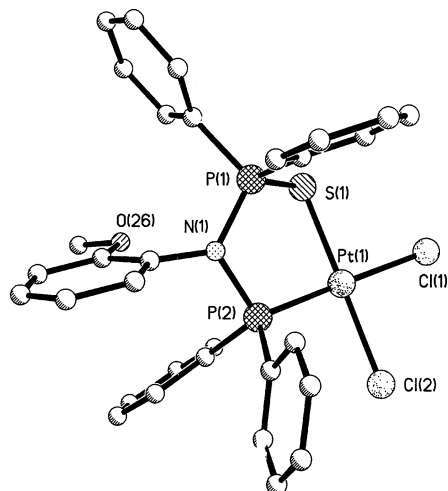
Table 7 Selected bond distances (Å) and angles (°) for compound **12**

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)

MoP₂N ring is essentially planar and the Mo–P/P–N distances compare well with those of [Mo₂(CO)₈{μ-*cis*-[PhNP(OC₆H₄Me-*p*)]₂}] [Mo–P 2.484(2), 2.476(2) Å; P–N range 1.701(4)–1.716(3) Å]³⁰ and [Mo(CO)₄{EtNP(OC₆H₄Br-4)}₃] [average Mo–P 2.452(5) Å; P–N *ca.* 1.70(1) Å].³¹ 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)		
Cl(1)–Ru(1)–P(1)	88.49(9)	P(1)–Ru(1)–P(2)	69.84(9)
Cl(1)–Ru(1)–P(2)	87.89(9)	P(1)–Ru(1)–P(2A)	110.16(9)
Cl(1)–Ru(1)–P(1A)	91.51(9)	Ru(1)–P(1)–N(1)	94.8(3)
Cl(1)–Ru(1)–P(2A)	92.11(9)	N(1)–P(2)–Ru(1)	94.2(2)
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)₄{PhNP(OC₆H₅)₂}₂] [Mo–P 2.440(2), 2.427(2) Å] indicating **1** is a poorer π-acceptor ligand than PhN{P(OC₆H₅)₂}₂.³² 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 Ph₂PN(*o*-C₆H₄OMe)PPh₂ 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 CuP₂N 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 Ph₂PN(*o*-C₆H₄OMe)PPh₂ ligands disposed in a *trans* configuration. Within the four-membered RuP₂N 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(η⁵-C₅H₅)Cl{(Ph₂P)₂NH}] [2.2777(10), 2.2813(10); 2.4607(10) and 1.692(3), 1.694(3) Å respectively].³³ Within the RuP₂N 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 Ph₂P(S)N(*o*-C₆H₄OMe)PPh₂ 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 [PtCl₂{Ph₂P(S)N(Ph)PPh₂}].⁷

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

We should like to thank the EPSRC for a studentship (K.G.G), Infineum UK Ltd for financial support, and Johnson Matthey plc for the generous loan of precious metal salts.

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