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*

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The synthesis, and characterisation, of a new functionalised bis(phosphino)amine $Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$ **1** from $o\text{-}H_2NC_6H_4OMe$ 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 $Ph_2P(E)N(o\text{-}C_6H_4OMe)P(E)Ph_2$ (E = 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 $Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2$ **5** in addition to small amounts of **3**. Reaction of **1** (or **5**) with $[MX_2(cod)]$ (M = Pd, Pt; X = Cl or CH_3; cod = cycloocta-1,5-diene) affords either *cis*-$[MX_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$ (M = Pd, X = Cl **6**; M = Pt, X = Cl **7**; M = Pt, X = CH_3 **8**) or the neutral five-membered chelate complexes $[MCl_2\{Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2\}]$ (M = Pd **9**, M = Pt **10**) in which *P,P*- or *P,S*-chelation respectively was observed. Likewise reaction of $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) or $[Cu(MeCN)_4]PF_6$ with **1** gave *cis*-$[Mo(CO)_4\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$ **11** or $[Cu\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}_2]PF_6$ **12**. Chloro-bridge cleavage and arene elimination of $[\{RuCl_2(p\text{-cym})\}_2]$ (*p*-cym = *p*-cymene) with **1** (1 : 2 metal : ligand ratio) affords, in good yield, the octahedral bis chelate ruthenium(II) complex *trans*-$[RuCl_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}_2]$ **13**. In contrast, reaction of **1** with two equiv. of [AuCl(tht)] (tht = tetrahydrothiophene) gave the dinuclear complex $[(ClAu)Ph_2PN(o\text{-}C_6H_4OMe)PPh_2(AuCl)]$ **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 [^1H, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$], 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[1] and to a considerably lesser extent, tertiary phosphites[2] can provide an excellent strategy for finely regulating stereoelectronic properties. Moreover the incorporation of highly polar functional groups[3] 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, $R_2PN(H)R'$ 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 C_{sp^2}–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" ligands[6] 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 $[MCl_2(cod)]$ (M = Pd, Pt),[11,12] $[Pt(CH_3)_2(cod)]$,[13] [AuCl(tht)],[14] $[\{Ru(p\text{-cym})Cl_2\}_2]$ (*p*-cym = *p*-cymene)[15] and $[RuCl_2(dmso)_4]$[16] were prepared according to previous reported procedures. The compounds $o\text{-}H_2NC_6H_4OMe$, Ph_2PCl, $[Mo(CO)_4(nbd)]$ and $[Cu(MeCN)_4]PF_6$ were purchased from Aldrich Chemical Co and used directly, with the exception of $o\text{-}H_2NC_6H_4OMe$ and Ph_2PCl which were distilled prior to use.

Infrared spectra were recorded as KBr pellets in the range 4000–220 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

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shifts (δ) in ppm to high frequency of $SiMe_4$ and coupling constants (J) in Hz, $^{31}P\{^1H\}$ NMR spectra (36.2 MHz) were recorded on a JEOL FX90Q spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz and $^{195}Pt\{^1H\}$ 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). All 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.

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

Preparations

$Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$, 1. A solution of Ph_2PCl (5.02 g, 22.8 mmol) in Et_2O (20 cm^3) was added dropwise over 45 min to a solution of o-$H_2NC_6H_4OMe$ (1.40 g, 11.4 mmol) and NEt_3 (2.35 g, 23.2 mmol) in Et_2O (50 cm^3) at 0 °C. The resulting white suspension was stirred for 18 h, the solvent evaporated to dryness and degassed distilled water (100 cm^3) added. The solid was collected by suction filtration, washed with n-hexane (50 cm^3), absolute EtOH (2 × 50 cm^3) and dried *in vacuo*. Yield: 3.57 g, 64%. Selected IR: 2829 ν_{CH}(OMe) cm^{-1}.

$Ph_2P(O)N(o\text{-}C_6H_4OMe)P(O)Ph_2$, 2. A thf (10 cm^3) solution of **1** (0.250 g, 0.509 mmol) and aqueous H_2O_2 (30% w/w, 0.1 cm^3) 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 ν_{CH}(OMe); 1221, 1210 ν_{PO} cm^{-1}.

$Ph_2P(S)N(o\text{-}C_6H_4OMe)P(S)Ph_2$, 3. To the solids **1** (0.250 g, 0.509 mmol) and S_8 (0.038 g, 1.19 mmol) was added thf (20 cm^3) and this was refluxed for *ca.* 18 h. The volume was concentrated *in vacuo* to *ca.* 1–2 cm^3 and addition of n-hexane (20 cm^3) gave **3** as a white solid which was collected by suction filtration. Yield: 0.262 g, 92%. Selected IR: 2840 ν_{CH}(OMe); 611 ν_{PS} cm^{-1}.

In a similar manner $Ph_2P(Se)N(o\text{-}C_6H_4OMe)P(Se)Ph_2$ **4** was synthesised from **1** and grey Se. Yield: 0.278 g, 84%. Selected IR: 2834 ν_{CH}(OMe); 571 ν_{PSe} cm^{-1}. Slow diffusion of light petroleum (bp 60–80 °C) into a $CDCl_3/CH_2Cl_2$ solution of **4** over 72 h gave crystals suitable for X-ray crystallography.

$Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2$, 5. A mixture of **1** (0.250 g, 0.509 mmol) and S_8 (0.016 g, 0.499 mmol) in n-hexane (10 cm^3) 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 $^{31}P\{^1H\}$ 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 ν_{CH}(OMe); 667, 629, 613 ν_{PS} cm^{-1}.

$[PdCl_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$, 6. A solution of $[PdCl_2(cod)]$ (0.049 g, 0.172 mmol) and **1** (0.086 g, 0.175 mmol) in CH_2Cl_2 (10 cm^3) was stirred for *ca.* 1.5 h. The volume was concentrated to *ca.* 1–2 cm^3 by evaporation under reduced pressure and addition of diethyl ether (20 cm^3) 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 CH_2Cl_2 solution of **6** over 72 h gave crystals suitable for X-ray crystallography.

In a similar manner $[PtCl_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$ **7** (98%) was prepared. Selected IR: 2835 ν_{CH}(OMe); 313, 291 ν_{PtCl} cm^{-1}.

$[Pt(CH_3)_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$, 8. To a solution of $[Pt(CH_3)_2(cod)]$ (0.050 g, 0.150 mmol) in toluene (10 cm^3) 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^3 by evaporation under reduced pressure and addition of diethyl ether (10 cm^3) and light petroleum (bp 60–80 °C, 10 cm^3) gave a white solid **8**. The product was collected by suction filtration and dried *in vacuo*. Yield: 0.086 g, 80%. Selected IR: 2837 ν_{CH}(OMe) cm^{-1}.

$[PtCl_2\{Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2\}]$, 10. To the solids **5** (0.100 g, 0.191 mmol) and $[PtCl_2(cod)]$ (0.064 g, 0.171 mmol) was added CH_2Cl_2 (20 cm^3). After stirring for 30 min the volume was concentrated to *ca.* 1 cm^3 and diethyl ether (20 cm^3) added. The pale yellow solid was collected by suction filtration and dried *in vacuo*. Yield: 0.132 g, 97%. Selected IR: 2838 ν_{CH}(OMe); 328, 300 ν_{PtCl} cm^{-1}. Slow diffusion of diethyl ether into a $CDCl_3/CH_2Cl_2$ solution of **10** over several days gave crystals suitable for X-ray crystallography.

In a similar manner $[PdCl_2\{Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2\}]$ **9** was also prepared (73%). Selected IR: 2834 ν_{CH}(OMe); 316, 289 ν_{PdCl} cm^{-1}.

$[Mo(CO)_4\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$, 11. To a solution of $[Mo(CO)_4(nbd)]$ (0.100 g, 0.333 mmol) in CH_2Cl_2 (20 cm^3) 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^3. Addition of light petroleum (bp 60–80 °C, 20 cm^3) 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 ν_{CH}(OMe); 2021, 1922, 1907, 1863 ν_{CO} cm^{-1}. Slow diffusion of light petroleum into a $CDCl_3$ solution of **11** over 72 h gave crystals suitable for X-ray crystallography.

$[Cu\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}_2]PF_6$, 12. To a solution of $[Cu(CH_3CN)_4]PF_6$ (0.071 g, 0.191 mmol) in CH_2Cl_2 (20 cm^3) 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^3 and addition of diethyl ether (15 cm^3) gave **12** as a white solid. Yield: 0.195 g, 86%. Selected IR: 2836 ν_{CH}(OMe) cm^{-1}. Slow diffusion of diethyl ether into a $CDCl_3$ solution of **12** over 72 h gave crystals suitable for X-ray crystallography.

$[RuCl_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}_2]$, 13. To the solids $[\{Ru(p\text{-}cym)Cl_2\}_2]$ (0.020 g, 0.033 mmol) and **1** (0.064 g, 0.130 mmol) was added $CDCl_3$ (1 cm^3) 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 $CDCl_3$ (0.5 cm^3) and dried *in vacuo*. Yield: 0.067 g, 89%. Selected IR: 2829 ν_{CH}(OMe) cm^{-1}. Alternatively **13** was prepared in lower yield (33%) from $[RuCl_2(dmso)_4]$ and 2 equiv. of **1**. Suitable crystals of **13** for X-ray crystallography were obtained by allowing a $CDCl_3$ solution of $[\{Ru(p\text{-}cym)Cl_2\}_2]$ and **1** to stand for several days.

$[\{AuCl\}_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}]$, 14. To the solids $[AuCl(tht)]$ (0.030 g, 0.092 mmol) and **1** (0.023 g, 0.047 mmol) was added $CDCl_3$ (2 cm^3). The solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy and showed the only phosphorus species to be **14**. Addition of diethyl ether (15 cm^3) gave **14** as a white solid. Yield: 0.044 g, 94%. Selected IR: 2835 ν_{CH}(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-Kα) radiation (λ = 1.541 78 Å) and ω-scans or a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). 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 SAINT[17] 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]

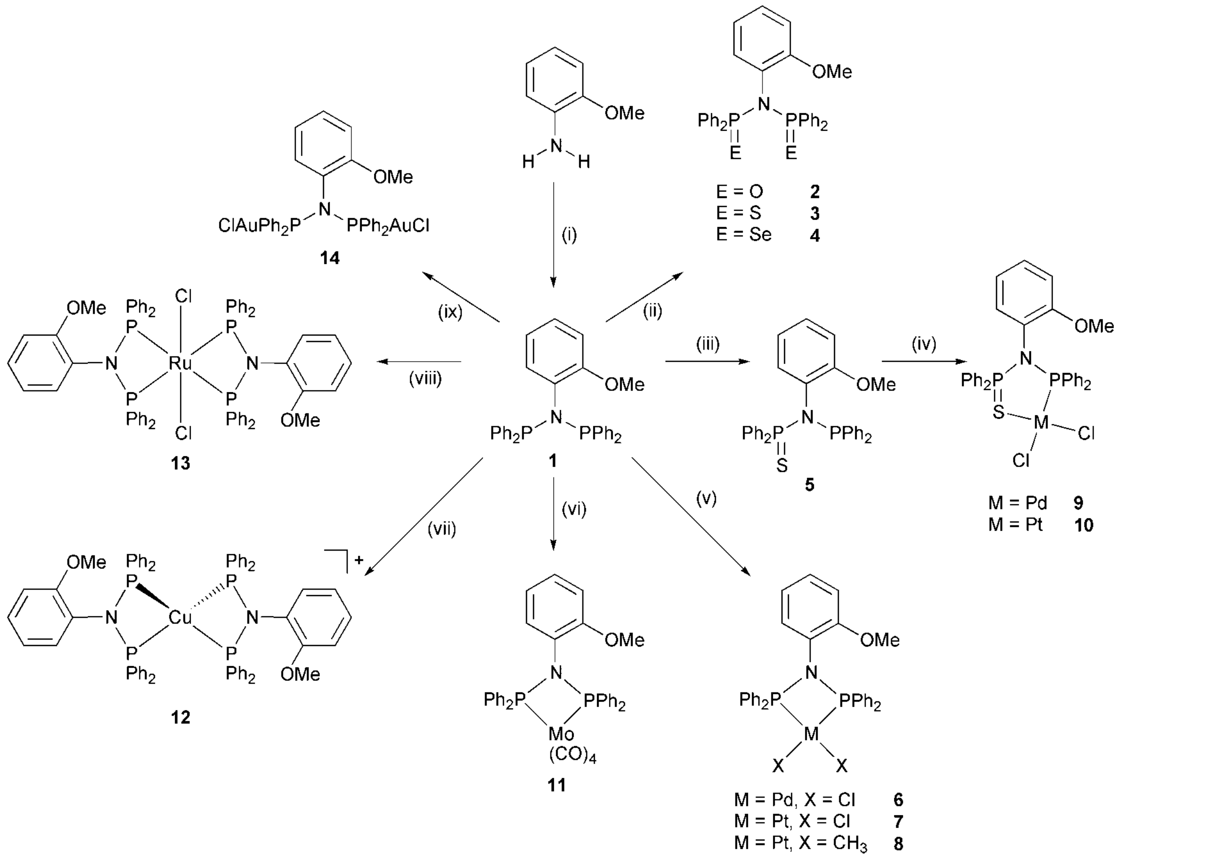
Structures were solved by direct methods and refined by full matrix least squares against F (TEXSAN[19]) or F^2 (SHELXTL[20]) for all data with $I > 2\sigma(I)$. Standard SHELXTL weighting scheme was used for **4**, **6** and **10**–**12** whilst in the case of **13** the weighting scheme for the Rigaku/TEXSAN 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 $R_2PN(H)R'$ or $(R_2P)_2NR'$ 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 $Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$ **1** (Scheme 1) by treatment of commercially available Ph_2PCl with $o\text{-}H_2NC_6H_4OMe$ proceeded smoothly in diethyl ether and gave, after workup, a white solid in 64% yield. Attempts to prepare the mono(phosphino)amine $Ph_2PNH(o\text{-}C_6H_4OMe)$ 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 $^{31}P\{^1H\}$ NMR spectrum of **1** showed a single resonance at δ(P) 65.6 (Table 2) similar to that previously observed for the unsubstituted ligand $Ph_2PN(C_6H_5)PPh_2$ [δ(P) 68.8[6]] 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 $Ph_2P(O)N(o\text{-}C_6H_4OMe)P(O)Ph_2$ **2** and $Ph_2P(O)PPh_2$. 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** [δ(P) 26.0] there is a negligible change in ^{31}P chemical shift upon oxidation [δ(P) 67.9 for **3**, δ(P) 65.8 for **4**] and furthermore, in the case of **4** there is an associated ^1J(PSe) of 783 Hz. We also found that, using conditions identical to those described by Cavell and co-workers[7] for the synthesis of $Ph_2P(E)N(Ph)PPh_2$ (E = S or Se), we were able to prepare $Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2$ **5**. However in our hands we were unable to obtain **5** analytically pure although $^{31}P\{^1H\}$ 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) $[MCl_2(cod)]$ (M = Pd or Pt); (v) $[MX_2(cod)]$ (M = Pd or Pt, X = Cl or CH_3); (vi) $[Mo(CO)_4(nbd)]$; (vii) $[Cu(CH_3CN)_4]PF_6$; (viii) $[\{Ru(p\text{-cym})Cl_2\}_2]$; (ix) 2 equiv. [AuCl(tht)].

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

Compound	**4**	**6**	**10**	**11**	**12**	**13**
Empirical formula	$C_{31}H_{27}NOP_2Se_2$	$C_{32}H_{28.50}Cl_{4.50}NOP_2Pd$	$C_{31.50}H_{27.50}Cl_{3.50}NOP_2PtS$	$C_{35}H_{27}MoNO_5P_2$	$C_{62}H_{54}CuF_6N_2O_2P_5$	$C_{65}H_{58}N_2O_2P_4Cl_{10}Ru$
M	649.40	770.92	849.21	699.46	1191.46	1478.68
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	15.7749(3)	11.8731(3)	15.0814(6)	9.0732(1)	11.1500(2)	12.587(6)
b/Å	18.8326(3)	14.3704(3)	9.2086(4)	18.9395(2)	30.8735(4)	14.127(5)
c/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)
V/Å^3	5790.2(2)	3636.3(2)	3435.6(2)	3289.8(1)	5923.1(2)	1708(2)
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293
Space group	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	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 [*R*(int) = 0.1059]	8551 [*R*(int) = 0.0374]	4931 [*R*(int) = 0.0283]	4677 [*R*(int) = 0.0173]	13 891 [*R*(int) = 0.0718]	6016 [*R*(int) = 0.020]
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0336, *wR*2 = 0.0611	*R*1 = 0.0559, *wR*2 = 0.1564	*R*1 = 0.0261, *wR*2 = 0.0752	*R*1 = 0.0209, *wR*2 = 0.0563	*R*1 = 0.0578, *wR*2 = 0.1269	*R*1 = 0.087, *wR*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]	*J*(PSe)	*J*(PtP)	*J*(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] OCH_3 resonance. [c] Sample also contained small amounts of **3**. [d] 1 : 2 : 1 triplet. [e] Pt–CH_3, *δ* 0.80, *J*(PtH) 73.7, *J*(PH) 12.8 Hz. [f] ^1J(PtP), ^2J(PtP) respectively. [g] $\omega_{1/2}$ 110 Hz. $[PF_6]^-$ counter ion centered at *δ*(P) −144. [h] Measured in $CDCl_3/CH_3OH$.

$^{31}P\{^1H\}$ NMR spectrum which showed two well separated doublets at *δ*(P) 53.7 (P^{III}) and 73.5 (P^V) with a ^2J(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 $[MX_2(cod)]$ (M = Pd, Pt; X = Cl, CH_3; cod = cycloocta-1,5-diene) in CH_2Cl_2 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**

	Analysis (%)		
Compound	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 $0.5CHCl_3$ 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 OCH_3 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 $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 gave the d^{10} cationic copper complex $[Cu\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}_2]PF_6$ **12** whereas reaction of **1** with $[\{Ru(p\text{-cym})Cl_2\}_2]$ gave the octahedral ruthenium(II) complex $[RuCl_2\{Ph_2PN(o\text{-}C_6H_4OMe)PPh_2\}_2]$ **13**. Independently we also prepared **13** from $[RuCl_2(dmso)_4]$ and 2 equiv. of **1** albeit in reduced yield (33%). The *trans* isomer of **13** was isolated as indicated by one singlet in the ^{31}P NMR spectrum at *δ*(P) 77.7. In contrast we find that when **1** was reacted with the d^{10} 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.* $RN(PX_2)_2$, R = alkyl; X = alkoxy, F] have previously been used in the preparation of heterobimetallic complexes.[22] Jones *et al.*

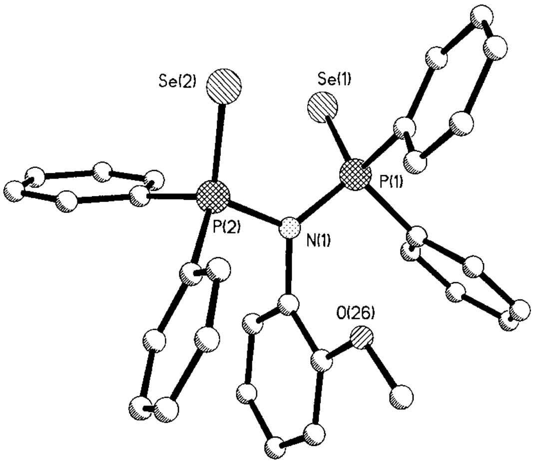


Fig. 1 Crystal structure of **4**.

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(I) and gold(III) complexes with bidentate 1,2-$\{Ph_2PN(H)\}_2C_6H_4$ and 3,4-$\{Ph_2PN(H)\}_2MeC_6H_3$ 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 $\{Ph_2P(Se)\}_2NH$ [2.085(1) and 2.101(1) Å], $C_6H_4\{NHP(Se)Ph_2\}_2$ [2.081(6) and 2.107(5) Å] and $\{Ph_2P(Se)NPPh_2\}_2$ [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 $\{Ph_2P(Se)\}_2NH$ [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 [124.77(10)°] is smaller than that found in $\{Ph_2P(Se)\}_2NH$ [132.3(2)°].[24]

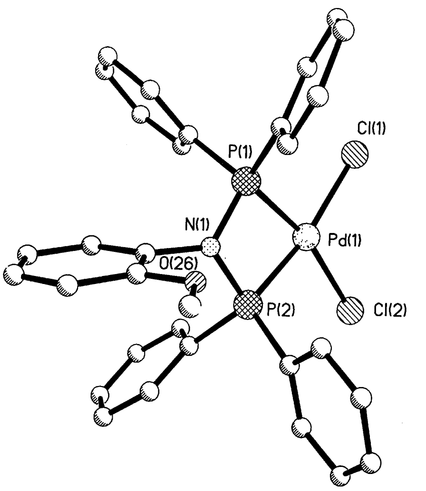


Fig. 2 Crystal structure of **6** (solvent molecules omitted for clarity).

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)		

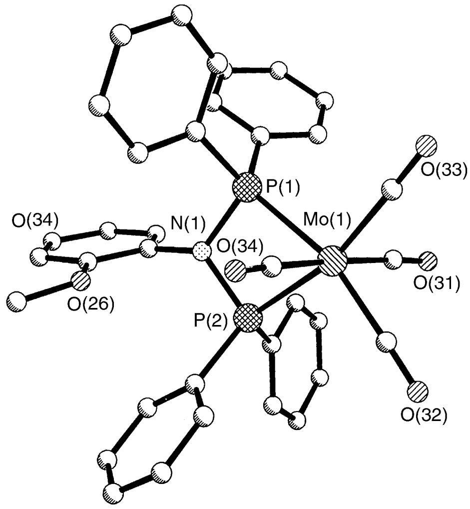


Fig. 3 Crystal structure of **11**.

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)

The crystal structure of **6** (Fig. 2, Table 5) entails a *cis* disposed $Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$ 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_2N 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 $R_2PN(R)PR_2$ ligands span two metal centres, as in $[Pd_2Cl_2\{PhN\{P(OPh)_2\}_2\}_2]$ and $[Pd_2\{MeN\{P(OPh)_2\}_2\}_3]$, the P–N–P angle is enlarged and falls in the range 113–120°.[29] 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 $Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$ ligand and four terminal carbon monoxide ligands. The four-membered

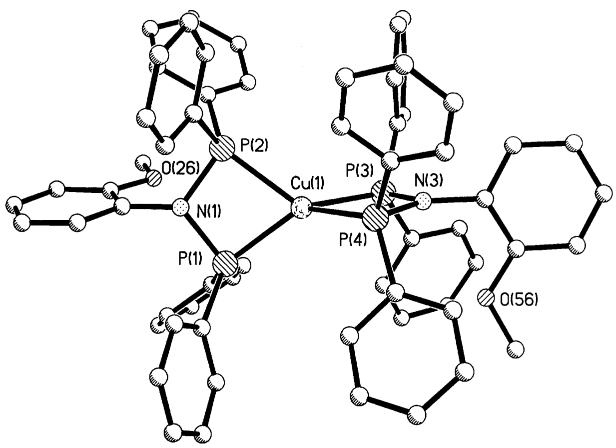


Fig. 4 Crystal structure of **12** (PF_6^- counter ion omitted for clarity).

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)

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)

MoP_2N ring is essentially planar and the Mo–P/P–N distances compare well with those of $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ [Mo–P 2.484(2), 2.476(2) Å; P–N range 1.701(4)–1.716(3) Å][30] and $[Mo(CO)_4\{EtNP(OC_6H_4Br\text{-}4)\}_3]$ [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 2.4880(5) Å] in **11** are slightly longer than found in $[Mo(CO)_4\{PhNP(OC_6H_5)_2\}_2]$ [Mo–P 2.440(2), 2.427(2) Å] indicating **1** is a poorer π-acceptor ligand than $PhN\{P(OC_6H_5)_2\}_2$.[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**.

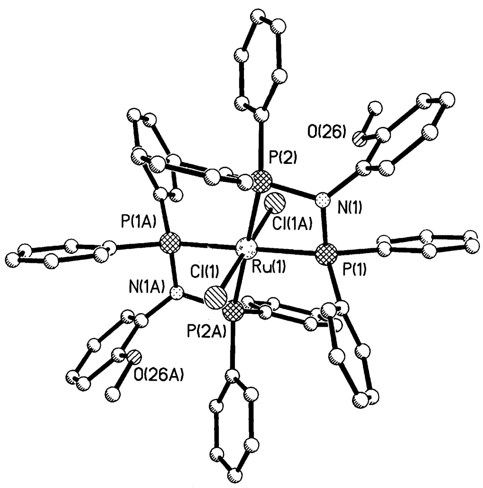


Fig. 5 Crystal structure of **13** (solvent molecules omitted for clarity).

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)		

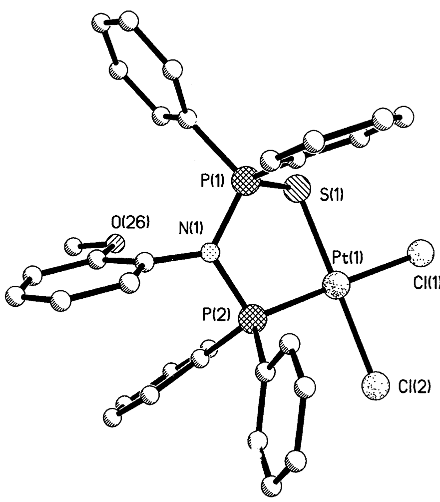


Fig. 6 Crystal structure of **10** (solvent molecule omitted for clarity).

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 $Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$ 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_2N 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 $Ph_2PN(o\text{-}C_6H_4OMe)PPh_2$ ligands disposed in a *trans* configuration. Within the four-membered RuP_2N 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 $[Ru(\eta^5\text{-}C_5H_5)Cl\{(Ph_2P)_2NH\}]$ [2.2777(10), 2.2813(10); 2.4607(10) and 1.692(3), 1.694(3) Å respectively].[33] Within the RuP_2N 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 $Ph_2P(S)N(o\text{-}C_6H_4OMe)PPh_2$ 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 $[PtCl_2\{Ph_2P(S)N(Ph)PPh_2\}]$.[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

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