# Late transition-metal complexes of $[Ph_2P(O)NP(E)Ph_2]^-$ (E = S or Se) with a P,N-hybrid ligand: synthesis and structure

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The unsymmetrical ligands  $[Ph_2P(O)NP(E)Ph_2]^-$  (E = S or Se) adopt a range of ligation modes (O,E-chelate, E-monodentate and as a non-co-ordinating anion) upon reaction with selected late transition-metal tertiary phosphine complexes. Hence treatment of cis-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with K[Ph<sub>2</sub>P(O)NP(E)Ph<sub>2</sub>] in methanol gave the expected six-membered O,E-chelate complexes  $[Pt(PPh_3)_2 \{Ph_2P(O)NP(E)Ph_2-O,E\}]^+$  isolated as their hexafluorophosphate salts. When  $[Pt(Ph_2PC_6H_4NH_2-P,N)_2]Cl_2$  was allowed to react under analogous conditions the monocationic mixed complexes  $[Pt(Ph_2PC_6H_4NH-P,N)(Ph_2PC_6H_4NH_2-P,N)][Ph_2P(O)NP(E)Ph_2]$  were obtained in excellent yields (>90%). Reaction of  $[Pd(Ph_2PC_6H_4NH_2-P,N)_2]Cl_2$  with  $K[Ph_2P(O)NP(S)Ph_2](1:2)$ molar ratio) gave a mixture of three products identified by  ${}^{31}P-{}^{1}H$  NMR as [Pd(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH-P,N)  $(Ph_2PC_6H_4NH_2-P,N)$ ][Ph\_2P(O)NP(S)Ph\_2], [Pd(Ph\_2PC\_6H\_4NH-P,N){Ph\_2P(O)NP(S)Ph\_2-O,S}] (P trans to O) and (Ph\_2PC\_6H\_4NH\_2-P,N)]  $Ph_2PC_6H_4NH_2$ . Alternatively the neutral compound  $[Pd(Ph_2PC_6H_4NH-P,N)]Ph_2P(O)NP(S)Ph_2-O,S]$  was synthesised in moderate yield from  $[PdCl_2(Ph_2PC_6H_4NH_2-P,N)]$  and two equivalents of K[Ph\_2P(O)NP(S)Ph\_2]. Chloride metathesis of  $[Pt(X)Cl(Ph_2PC_6H_4NH_2-P,N)]$  (X = CH<sub>3</sub> or Cl) with K[Ph\_2P(O)NP(E)Ph\_2] gave a series of platinum(II) complexes  $[Pt(X){Ph_2P(O)NP(E)Ph_2-E}(Ph_2PC_6H_4NH_2-P,N)]$  (P trans to E) in which the anion adopts an E-monodentate co-ordination mode. The gold(I) complexes  $[AuCl(PPh_3)]$  and  $[AuCl(Ph_2PC_6H_4NH_2)]$ undergo smooth substitution reactions with  $K[Ph_2P(O)NP(E)Ph_2]$  to give  $[Au\{Ph_2P(O)NP(E)Ph_2-E\}(PPh_3)]$  and  $[Au{Ph_2P(O)NP(E)Ph_2-E}(Ph_2PC_6H_4NH_2)]$  respectively. All new compounds have been characterised by a combination of multinuclear NMR [<sup>1</sup>H, <sup>31</sup>P-{<sup>1</sup>H} and <sup>195</sup>Pt-{<sup>1</sup>H}], IR spectroscopy and elemental analyses. The molecular structures of four examples have been determined by single-crystal X-ray crystallography and furthermore reveal intra- and inter-molecular  $PE \cdots H-N$  hydrogen bonding arrangements. There is also evidence for  $\pi$ -delocalisation within the E–P–N–P–O backbone.

## Introduction

The co-ordination chemistry of  $[R_2P(E)NP(E)R_2]^-$  has of late received much attention principally because of its close association with acetylacetonate (acac).<sup>1</sup> Whereas extensive work has focused on symmetrical systems (E = O, S or Se) there has been considerably less documentation regarding the asymmetrical ligands  $[R_2P(O)NP(E)R_2]^-$  [E = S I; E = Se II] bearing both "hard" and "soft" donor atoms.<sup>1d-f,2-6</sup> Moreover several complexes of  $[R_2P(E)NP(E)R_2]^-$  have found important applications as NMR shift reagents,<sup>7</sup> selective metal extractants<sup>8</sup> and in catalysis.<sup>9</sup> Clearly an appreciation of the co-ordinating capabilities of these ligands towards metals and their subsequent reactivity is important given that complexes of acac (and its analogues) are useful in several metal complex catalysed reactions.<sup>10</sup>

In recent studies we have observed three different binding modes for  $[R_2P(O)NP(E)R_2]^-$  (R = Ph) at various late transition-metal centres (Chart 1, A–C), the most prevalent being O,E-chelation, e.g.  $[PdL_2{Ph_2P(O)NP(E)Ph_2-O,E}]PF_6$ (L = PPh<sub>3</sub>; 2L = Ph\_2PCH\_2CH\_2PPh\_2 or cis-Ph\_2PCH= CHPPh\_2).<sup>1f</sup> The  $[R_2P(O)NP(E)R_2]^-$  anion can also behave as an E-monodentate bound ligand, e.g.  $[Pd(en){Ph_2P(O)-Ph_2P$   $NP(E)Ph_2-E_{2}]$  (en =  $H_2NCH_2CH_2NH_2).^{1e}$  It is tempting to suggest from these sparse examples alone that the  $[R_2P(O)NP(E)R_2]^-$  bonding mode adopted may be influenced by the spectator ligand present within the metal coordination sphere. We therefore were interested to probe what ligation modes would be adopted using a hybrid ligand bearing a P,N-donor set. Numerous studies with  $Ph_2PC_6H_4NH_2$ , incorporating both tertiary phosphine and primary amine functionalities, have been described with several complexes finding important uses in catalysis and as antitumour agents.<sup>11</sup>



Herein we report the first examples of  $Pd^{II}_{-}$ ,  $Pt^{II}_{-}$  and  $Au^{I}Ph_{2}PC_{6}H_{4}NH_{2}$  complexes with  $[Ph_{2}P(O)NP(E)Ph_{2}]^{-}$  including their synthesis and characterisation. Furthermore we demonstrate a range of bonding modes for  $[Ph_{2}P-(O)NP(E)Ph_{2}]^{-}$  including O,E-chelation, E-monodendate and the first example of  $[Ph_{2}P(O)NP(E)Ph_{2}]^{-}$  acting as a non-coordinating anion (D). The crystal structures of

 $\begin{array}{l} [Pt(Ph_2PC_6H_4NH-P,N)(Ph_2PC_6H_4NH_2-P,N)][Ph_2P(O)NP-(Se)Ph_2], & [Pd(Ph_2PC_6H_4NH-P,N)\{Ph_2P(O)NP(S)Ph_2-O,S\}], \\ [Pt(CH_3)\{Ph_2P(O)NP(S)Ph_2-S\}(Ph_2PC_6H_4NH_2-P,N)] & and \\ [Au\{Ph_2P(O)NP(S)Ph_2-S\}(Ph_2PC_6H_4NH_2)] & have been determined. \end{array}$ 

## Experimental

## General procedures

All reactions were carried out in air using previously distilled or HPLC grade solvents. The ligands  $[Ph_2P(O)NP(E)Ph_2]^ (E = S \text{ or } Se)^4$  were prepared according to a literature method as were  $[AuCl(Ph_2PC_6H_4NH_2)]^{11b}$  and  $[M(X)Cl-(Ph_2PC_6H_4NH_2-P,N)]$  (M = Pt or Pd, X = Me or Cl).<sup>11c</sup> The complexes  $[M(Ph_2PC_6H_4NH_2-P,N)_2]Cl_2$ , *cis*-[PtCl\_2(PPh\_3)\_2] and  $[AuCl(PPh_3)]$  were prepared from  $[MCl_2(cod)]$  (M = Pd, Pt; cod = cycloocta-1,5-diene) or [AuCl(tht)] (tht = tetrahydrothiophene) and the appropriate stoichiometry of tertiary phosphine in CH<sub>2</sub>Cl<sub>2</sub>.

Infrared spectra were recorded as KBr pellets in the range 4000–200 cm<sup>-1</sup> on a Perkin–Elmer System 2000 Fouriertransform spectrometer, <sup>1</sup>H NMR spectra (250 MHz) 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 NMR 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.

#### Syntheses

[Pt(PPh<sub>3</sub>)<sub>2</sub>{Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>-O,S}]PF<sub>6</sub>, **1.** To the solids cis-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.071 g, 0.0898 mmol) and K[Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>] (0.047 g, 0.0997 mmol) was added CH<sub>3</sub>OH (2.5 cm<sup>3</sup>). After stirring for 150 min, the solution was filtered and [NH<sub>4</sub>][PF<sub>6</sub>] (0.043 g) in CH<sub>3</sub>OH (minimum volume) added. The white solid was collected by suction filtration and dried *in vacuo*. Yield: 0.101 g, 87%. IR: 575 ( $\nu_{ps}$ ). <sup>1</sup>H NMR: δ 7.67–7.06 (arom. H). In a similar manner [Pt(PPh<sub>3</sub>)<sub>2</sub>{Ph<sub>2</sub>P(O)NP(Se)Ph<sub>2</sub>-O,Se}]PF<sub>6</sub> **2** was prepared (90%). IR: 547 ( $\nu_{pse}$ ). <sup>1</sup>H NMR: δ 7.73–7.05 (arom. H).

[Pt(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH-*P*,*N*)(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-*P*,*N*)][Ph<sub>2</sub>P(O)-NP(S)Ph<sub>2</sub>], 3. To the solids [Pt(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-*P*,*N*)<sub>2</sub>]Cl<sub>2</sub> (0.052 g, 0.0634 mmol) and K[Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>] (0.063 g, 0.134 mmol) was added CH<sub>3</sub>OH (1 cm<sup>3</sup>). The resulting bright yellow suspension was stirred for *ca*. 1 h. The solid was collected by suction filtration, washed with CH<sub>3</sub>OH (*ca*. 0.5 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.074 g, 99%. IR: 3666 (v<sub>OH</sub>), 3386, 3341, 3221 (v<sub>NH</sub>), 594 (v<sub>PS</sub>). <sup>1</sup>H NMR:  $\delta$  8.08–6.58 (arom. H, NH, NH<sub>2</sub>). The CH<sub>3</sub>OH filtrate was examined by <sup>31</sup>P-{<sup>1</sup>H} NMR and showed Ph<sub>2</sub>P(O)NHP(S)Ph<sub>2</sub> as the only phosphorus containing species present.

In a similar manner the following complex was prepared:  $[Pt(Ph_2PC_6H_4NH-P,N)(Ph_2PC_6H_4NH_2-P,N)][Ph_2P(O)NP (Se)Ph_2]$  4 (92%), IR: 3665 ( $v_{OH}$ ), 3388, 3334, 3221 ( $v_{NH}$ ), 552 ( $v_{PSe}$ ). <sup>1</sup>H NMR:  $\delta$  8.08–6.61 (arom. H, NH, NH<sub>2</sub>). Slow diffusion of CH<sub>3</sub>OH into a CDCl<sub>3</sub> solution of 4 over the course of several days gave crystals suitable for X-ray crystallography. The reaction of I with  $[Pd(Ph_2PC_6H_4NH_2-P,N)_2]Cl_2$  under analogous conditions gave a mixture of three phosphorus containing species:  $[Pd(Ph_2PC_6H_4NH-P,N)(Ph_2PC_6H_4NH_2-P,N)]$   $\begin{array}{l} P,N)][Ph_2P(O)NP(S)Ph_2] \ \, \textbf{5}, \ \, [Pd(Ph_2PC_6H_4NH-P,N)\{Ph_2P-(O)NP(S)Ph_2-O,S\}] \ \, \textbf{6} \ \, \text{and} \ \, Ph_2PC_6H_4NH_2 \, . \end{array}$ 

[Pd(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH-*P*,*N*){Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>-*O*,*S*}], 6. To a suspension of [PdCl<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-*P*,*N*)] (0.030 g, 0.066 mmol) in CH<sub>3</sub>OH (1 cm<sup>3</sup>) was added solid K[Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>] (0.064 g, 0.136 mmol). The yellow solid dissolved to give an orange solution whereupon an orange solid formed within *ca*. 1–2 min. The mixture was stirred for 1 h and the product collected by suction filtration, washed with CH<sub>3</sub>OH (*ca*. 0.5 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.026 g, 48%. FAB<sup>+</sup> MS: *m/z* 815 (M<sup>+</sup>). IR: 3378 ( $v_{NH}$ ), 576 ( $v_{PS}$ ). <sup>1</sup>H NMR: δ 7.91–6.28 (arom. H, NH). Slow diffusion of CH<sub>3</sub>OH into a CDCl<sub>3</sub> solution of **6** over the course of several days gave crystals suitable for X-ray crystallography.

[Pt(CH<sub>3</sub>){Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>-S}(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-P,N)], 7. To a suspension of [Pt(CH<sub>3</sub>)Cl(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-P,N)] (0.041 g, 0.0784 mmol) in CH<sub>3</sub>OH (1 cm<sup>3</sup>) was added solid K[Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>] (0.041 g, 0.0869 mmol). After stirring the mixture for 1 h, the product was collected by suction filtration, washed with a small portion of CH<sub>3</sub>OH (*ca.* 0.5 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.057 g, 79%. FAB<sup>+</sup>MS: *m/z* 920 (M<sup>+</sup>). IR: 3291, 3262 ( $\nu_{NH}$ ), 571 ( $\nu_{PS}$ ). <sup>1</sup>H NMR: δ 7.68–6.93 (arom. H), 6.51 [NH<sub>2</sub>, <sup>2</sup>J(PtH) 28.8 Hz], 0.01 [CH<sub>3</sub>, <sup>2</sup>J(PtH) 75.0 Hz, <sup>3</sup>J(PH) 3.5 Hz]. Slow diffusion of CH<sub>3</sub>OH into a CDCl<sub>3</sub> solution of 7 over the course of several days gave crystals suitable for X-ray crystallography.

In a similar manner the following complexes were prepared:  $[Pt(CH_3){Ph_2P(O)NP(Se)Ph_2-Se}(Ph_2PC_6H_4NH_2-P,N)]$  8 (80%), FAB<sup>+</sup>MS: m/z 967 (M<sup>+</sup>). IR: 3289 ( $v_{NH}$ ), 537 ( $v_{PSe}$ ). <sup>1</sup>H NMR:  $\delta$  7.98–6.93 (arom. H), 6.45 [NH<sub>2</sub>, <sup>2</sup>J(PtH) 28.8 Hz], -0.1 [CH<sub>3</sub>, <sup>2</sup>J(PtH) 74.8 Hz, <sup>3</sup>J(PH) 3.5 Hz]. [PtCl{Ph\_2P-(O)NP(S)Ph\_2-S}(Ph\_2PC\_6H\_4NH\_2-P,N)] 9 (99%), FAB<sup>+</sup>MS: m/z 940 (M<sup>+</sup>). IR: 3442 ( $v_{NH}$ ), 570 ( $v_{PS}$ ), 298 ( $v_{PtCl}$ ). <sup>1</sup>H NMR:  $\delta$ 8.40–7.12 (arom. H, NH<sub>2</sub>). [PtCl{Ph\_2P(O)NP(Se)Ph\_2-Se}(Ph\_2PC\_6H\_4NH\_2-P,N)] 10 (95%), FAB<sup>+</sup>MS: m/z 987 (M<sup>+</sup>). IR: 3442 ( $v_{NH}$ ), 537 ( $v_{PSe}$ ), 297 ( $v_{PtCl}$ ). <sup>1</sup>H NMR:  $\delta$  8.13–7.14 (arom. H, NH<sub>2</sub>).

[Au{Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>-S}(PPh<sub>3</sub>)], 11. To a suspension of [AuCl(PPh<sub>3</sub>)] (0.034 g, 0.0687 mmol) in CH<sub>3</sub>OH (0.5 cm<sup>3</sup>) was added solid K[Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>] (0.033 g, 0.0670 mmol). The suspension dissolved and after *ca*. 5 min a white solid formed. The mixture was stirred for 20 min, the product collected by suction filtration, washed with a small portion of CH<sub>3</sub>OH (*ca*. 0.5 cm<sup>3</sup>) and dried *in vacuo*. Compounds 11 (and 12) may be recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O-light petroleum (bp 60-80 °C). Yield: 0.044 g, 69%. IR: 564 ( $v_{PS}$ ). <sup>1</sup>H NMR:  $\delta$ 8.04-7.01 (arom. H).

In a similar manner the following complexes were prepared: [Au{Ph<sub>2</sub>P(O)NP(Se)Ph<sub>2</sub>-Se}(PPh<sub>3</sub>)] **12** (80%), IR: 553 ( $\nu_{PSe}$ ). <sup>1</sup>H NMR:  $\delta$  8.10–7.03 (arom. H). [Au{Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>-S}(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)] **13** (91%), IR: 3424, 3298, 3168 ( $\nu_{NH}$ ), 561 ( $\nu_{PS}$ ). <sup>1</sup>H NMR:  $\delta$  8.09–6.37 (arom. H), 4.64 (NH<sub>2</sub>). [Au{Ph<sub>2</sub>P(O)NP(Se)Ph<sub>2</sub>-Se}(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)] **14** (93%), IR: 3416, 3295, 3155 ( $\nu_{NH}$ ), 557 ( $\nu_{PSe}$ ). <sup>1</sup>H NMR:  $\delta$  8.05–6.46 (arom. H), 4.67 (NH<sub>2</sub>).

Crystals of 13 suitable for X-ray crystallography were obtained by slow evaporation of a  $CH_3OH-CDCl_3$  solution over *ca.* 2 months.

Microanalytical and selected spectroscopic data are given in Tables 1 and 2.

#### X-Ray crystallography

The crystal structures of compounds 4, 6, 7 and 13 were obtained using a Bruker SMART diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Details of the crystal data collections and refinements are

	Analysis (%)	Analysis (%)			
Compound	С	Н	N		
1	55.05 (55.55)	3.80 (3.90)	1.00 (1.10)		
2	53.45 (53.60)	3.65 (3.75)	1.00 (1.05)		
3 <sup><i>a</i></sup>	60.15 (60.70)	4.35 (4.45)	3.40 (3.50)		
$4^{a}$	58.10 (58.40)	3.85 (4.30)	3.20 (3.40)		
6	61.20 (61.90)	4.00 (4.35)	3.55 (3.45)		
7	55.95 (56.15)	4.20 (4.30)	3.05 (3.05)		
8	52.60 (53.40)	3.95 (4.05)	2.85 (2.90)		
9	53.25 (53.65)	3.65 (3.85)	3.20 (3.00)		
10	50.70 (51.10)	3.45 (3.70)	3.00 (2.85)		
11	56.20 (56.55)	3.95 (3.95)	1.20 (1.55)		
12	53.20 (53.75)	3.50 (3.75)	1.10 (1.50)		
13	55.35 (55.65)	3.75 (4.00)	3.25 (3.10)		
14	52.75 (52.90)	3.60 (3.80)	3.30 (2.95)		

given in Table 3. 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>12</sup> program). Structures were solved by direct methods and refined by full matrix least squares against  $F^2$  of all data using SHELXTL software.<sup>13a</sup> Absorption corrections were performed on the basis of multiple equivalent reflections using the SADABS program.<sup>13b</sup>

Table 2Selected NMR data ( $\delta$  in ppm, J in Hz) for compounds 1–14

All non H-atoms in the structures were refined anisotropically including the solvent in 4 although the protons were not located on this 1/2 weight CH<sub>3</sub>OH. In 7 the 1/4 weight CHCl<sub>3</sub> was refined isotropically. All N–H H atoms were located and refined isotropically. All other protons were refined in idealised geometries with a riding model. Refinements converged to the residuals given in Table 3. All calculations were made with programs of SHELXTL systems.

CCDC reference number 440/116. See http://www.rsc.org/ suppdata/nj/1999/777/ for crystallographic files in .cif format.

## **Results and discussion**

The reaction of  $[PtCl_2L_2]$  (L = tertiary phosphine) with the symmetrical anions  $[R'_2P(E)NP(E)R'_2]^-$  (R' = Ph or OPh; E = S or Se) has been shown to give  $[Pt{R'_2P(E)NP(E)R'_2}-$ E,E'}L<sub>2</sub>]<sup>+</sup>.<sup>14'</sup> We find that transmetallation of  $K[Ph_2P(O)NP(E)Ph_2]$  (E = S I; E = Se II) with cis- $[PtCl_2(PPh_3)_2]$  (ca. 1:1 molar ratio) in methanol likewise affords the O,E-chelate cationic complexes [Pt{Ph<sub>2</sub>P-(O)NP(E)Ph<sub>2</sub>-O,E}(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (E = S 1; E = Se 2), isolated as their hexafluorophosphate salts. Compounds 1 and 2 are akin to the known palladium(II) salts  $[Pd{Ph_2P(O)NP(E)Ph_2 O_{E}(PPh_{3})_{2}]PF_{6}$ .<sup>1f</sup> The spectroscopic and analytical data for these platinum(II) complexes are unremarkable (Tables 1, 2 and Experimental section). As expected the magnitude of  ${}^{1}J(PtP)$  is reduced by *ca*. 400 Hz [3246 Hz for 1 (P *trans* to S); 3207 Hz for 2 (P trans to Se)] in comparison with cis- $[PtCl_2(PPh_3)_2]$  [<sup>1</sup>J(PtP) 3673 Hz] but increased by ca. 350

Compound	$\delta(\mathrm{PR}_3)^a$	J(PtP)	$\delta(\mathbf{P_E})^b$	$J(PtP_E)$	$\delta(P_0)$	J(PP)	J(PSe)	$\delta(\mathrm{Pt})$
1	21.0	3246	28.6	72	32.8	20		-4298
	8.8 <sup>c</sup>	4020						
2	20.3	3207	16.6	84	34.2	18	477	-4342
	$7.0^{c}$	4025						
3	27.5	3123	38.2		14.2			-4497
4	27.4	3136	26.0		14.3		651	-4491
5	$44.7^{d}$		34.8		12.8			
6	53.6		32.0		27.3			
7	26.9	4219	18.2	96	15.6	6.6		-4291
8	26.7	4170	14.2	97	16.6	6.0	525	-4319
9	23.5	3501	29.5	66	17.3	9.0		-3748
10	23.3	3448	15.5	75	18.4	8.5	518	-3783
11	37.3		27.4		12.1			
12	37.9		14.9		12.7		462	
13	25.2		27.0		12.2			
14	25.8		14.5		13.0		467	
<sup><i>a</i></sup> $PR_3 = Ph_2PC_6I$	H <sub>4</sub> NH <sub>2</sub> or PPh <sub>3</sub>	$b^{b} E = S$ or Se.	<sup>c</sup> P trans to O	$[no J(PtP_0) cou$	pling observed	(36.2 MHz)]. d	Sample also con	ntained 6 and

Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>.

Table 3Details of the X-ray data collections and refinements for  $4 \cdot 0.5$ CH3OH,  $6, 7 \cdot 0.25$ CHCl3 and 13

Compound	<b>4</b> · 0.5CH <sub>3</sub> OH	6	$7 \cdot 0.25 \text{CHCl}_3$	13
Empirical formula	CcoHcoNoOP, PtSe · 0.5CHoOH	C.,H.,N.OP.PdS	CtaHaaNaOPaPtS: 0.25CHCla	C.,H.,AuN,OP,S
 М	1243.99	815.09	949.66	906.66
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	13.3168(6)	9.8531(3)	10.7499(3)	9.0446(3)
b/Å	13.4648(6)	13.4561(4)	13.9705(4)	11.5989(3)
c/Å	18.2628(8)	15.5289(5)	16.7686(4)	19.1145(6)
$\alpha/^{\circ}$	109.01(1)	102.9820(10)	112.0190(10)	91.8030(10)
₿/°	96.1290(10)	94.7740(10)	99.4310(10)	95.2790(10)
$\nu/^{\circ}$	113.8590(10)	110.6100(10)	98.6350(10)	104.4790(10)
$V/Å^3$	2721.6(2)	1847.9(1)	2240.6(1)	1930.2(1)
T/K	293(2)	293(2)	293(2)	293(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2	2
$\mu/\text{mm}^{-1}$	3.409	0.725	3.362	4.024
Reflections collected	12436	8374	11568	6880
Independent reflections	7564[R(int) = 0.0369]	5236[R(int) = 0.0378]	6429[R(int) = 0.0439]	5133[R(int) = 0.0299]
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0359, wR2 = 0.0824	R1 = 0.0490, wR2 = 0.1157	R1 = 0.0438, wR2 = 0.0994	R1 = 0.0413, wR2 = 0.1006

Hz when P is disposed *trans* to O (4020 Hz for 1; 4025 Hz for 2).

When  $[Pt(Ph_2PC_6H_4NH_2-P,N)_2]Cl_2$  [prepared from  $[PtCl_2(cod)]$  (cod = cycloocta-1,5-diene) and 2 equivalents of  $Ph_2PC_6H_4NH_2$  was allowed to react in a 1:2 molar ratio with I (or II) in methanol under similar conditions, the bright solids [Pt(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH-P,N)(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>vellow P,N][Ph<sub>2</sub>P(O)NP(E)Ph<sub>2</sub>] (E = S 3; E = Se 4) were obtained in excellent yields (>90%). The  ${}^{31}P{-}{}^{1}H$  NMR spectra of 3 (and 4) both show a single  $\delta(P)$  resonance at *ca*.  $\delta$  27 with a  $^{1}J(PtP)$  of 3123 Hz (for 3) and 3136 Hz (for 4). It has previously been reported<sup>11j</sup> that  $[Pt(Ph_2PC_6H_4NH_2-P,N)_2]Cl_2$ undergoes double deprotonation with base to give the neutral bis(amido) complex  $[Pt(Ph_2PC_6H_4NH-P,N)_2]$  with a negligible change in  $\delta(P)$  but a reduction in <sup>1</sup>J(PtP) from 3343 to 3032 Hz respectively. The differences in  ${}^{1}J(PtP)$  reflect the trans influence of an amine versus amido ligand. The observed  ${}^{1}J(PtP)$  values of ca. 3130 Hz for 3 (and 4) suggest that one co-ordinated Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> ligand has been deprotonated. Hence the co-ordination sphere around the platinum(II) centre embraces a chelating  $Ph_2PC_6H_4NH_2$  and  $[Ph_2PC_6H_4NH]^$ ligand, the latter deprotonated by [Ph<sub>2</sub>P(O)NP(E)Ph<sub>2</sub>]<sup>-</sup> Indeed upon examination of the methanolic filtrate by  $\frac{31}{9}$ - $\{^{1}H\}$  NMR, only the protonated phosphorus(v) compounds Ph<sub>2</sub>P(O)NHP(E)Ph<sub>2</sub> were observed whose NMR data match those previously reported.<sup>4</sup> The counterion in 3 (and 4) is the  $[Ph_2P(O)NP(E)Ph_2]^-$  anion whose similarity in  $\delta(P)$  with that reported for I and II supports a non-co-ordinating role [further corroborated by the absence of any J(PtP)].<sup>4</sup>



In the crystal structure of **4** (Table 4 and Fig. 1) the platinum(II) centre is *cis* co-ordinated by two P,N-didentate ligands arranged in a slightly distorted square planar geometry  $[N(2)-Pt(1)-P(1) \ 83.3(2), \ N(20)-Pt(1)-P(2) \ 84.6(2), \ N(2)-Pt(1)-N(20) \ 89.5(2), \ P(1)-Pt(1)-P(2) \ 102.61(6)^{\circ}]$ . The two

Pt(1

N(20

Se(3)

P(3)

P(1)

N(2)

**Fig. 1** Crystal structure of  $[Pt(Ph_2PC_6H_4NH-P,N)(Ph_2PC_6H_4NH_2-P,N)][Ph_2P(O)NP(Se)Ph_2] \cdot 0.5CH_3OH 4$  (C–H hydrogen atoms and solvent molecule omitted for clarity).

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

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			-
Pt(1)-N(2)	2.008(5)	Se(3)-P(3)	2.140(2)
Pt(1)-N(20)	2.108(5)	P(3)–N(3)	1.572(6)
Pt(1) - P(1)	2.239(2)	N(3)-P(4)	1.563(6)
Pt(1) - P(2)	2.241(2)	P(4)-O(4)	1.520(5)
$\begin{array}{l} N(2)-Pt(1)-N(20)\\ N(2)-Pt(1)-P(1)\\ N(20)-Pt(1)-P(1)\\ N(2)-Pt(1)-P(2)\\ N(20)-Pt(1)-P(2) \end{array}$	89.5(2) 83.3(2) 172.7(2) 174.0(2) 84.6(2)	P(1)-Pt(1)-P(2) Se(3)-N(3)-P(3) P(3)-N(3)-P(4) N(3)-P(4)-O(4)	102.61(6) 119.6(2) 149.9(4) 120.5(3)

five-membered Pt-P-C-C-N metallacycles embody a P,Nchelating  $Ph_2PC_6H_4NH_2$  ligand and a deprotonated  $[Ph_2PC_6H_4NH]^-$  ligand. The Pt(1)-P(1), Pt(1)-P(2), Pt(1)-N(2) and Pt(1)-N(20) bond lengths are comparable to those reported in the bis-homoleptic species  $[Pt{Ph_2PC_6H_4NH_2}$ - $P,N_{2}^{2^{+}}$  and  $[Pt{Ph_2PC_6H_4NH-P,N}_2].^{11l,11m}$ The  $[Ph_2P(O)NP(Se)Ph_2]^-$  anion is involved in hydrogen bonding with the NH protons of the cis co-ordinated ligands  $H(20B) \cdots O(4)$  146°]. This effectively twists the O(4)-P(4)-N(3)-P(3)-Se(3) fragment to adopt a syn conformation thereby forcing the O...Se donor atoms closer together  $(O \cdots Se \text{ contact } 4.15 \text{ Å})$ . In contrast  $Ph_2P(Se)NHP(Se)Ph_2$  has an approximate anti disposition of the two selenium atoms with the molecules associated by N-H···Se hydrogen bonds to form dimer pairs.<sup>15</sup> Within the uncomplexed anion, the P(3)-N(3)-P(4) angle is substantially enlarged [149.9(4)°] with respect to when [Ph<sub>2</sub>P(O)NP(E)Ph<sub>2</sub>]<sup>-</sup> adopts a O,E-chelating, E-bridging or E-monodentate bonding mode.<sup>1d-f,2-6</sup> To the best of our knowledge this represents the first crystal structure of a  $[Ph_2P(O)NP(Se)Ph_2]^-$  anion with a transitionmetal complex cation. The potassium ion in K[Ph<sub>2</sub>P(S)NP(S)Ph<sub>2</sub>] can readily be exchanged by other cations as earlier documented.<sup>16</sup> Interestingly the P-N-P angle in  $[Ph_2P(S)NP(S)Ph_2]^-$  varies markedly from 128.6(2)° (for K<sup>+</sup>) to 180° [for N(PPh\_3)<sub>2</sub><sup>+</sup>].

The analogous reaction of [Pd(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-P,N)<sub>2</sub>]Cl<sub>2</sub> with I was also studied. A dark orange solid was isolated whose <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum revealed one predominant P(O)NP(S)Ph<sub>2</sub>] 5. In addition two minor species were also present and identified as the neutral compound  $[Pd(Ph_2PC_6 H_4NH-P,N$ {Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>-O,S}] 6 and free Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>- $NH_2$  [ $\delta(P)$  – 19.7]. Independently 6 was isolated in modest yield from [PdCl<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-P,N)] and two equivalents of K[Ph<sub>2</sub>P(O)NP(S)Ph<sub>2</sub>]. The  $[Ph_2P(O)NP(S)Ph_2]^-$  anion acts as an O,E-chelating ligand whereas the second equivalent presumably behaves as a base since examination of the filtrate by  ${}^{31}P-{}^{1}H$  NMR reveals only the neutral species Ph<sub>2</sub>P(O)NHP(S)Ph<sub>2</sub>. In accordance with the structure depicted, the  ${}^{31}P-{}^{1}H$  NMR spectrum of 6 shows three single resonances at  $\delta(P)$  53.6, 32.0 and 27.3 consistent with three inequivalent nuclei and only one isomer present in CDCl<sub>3</sub> solution. The downfield shift at  $\delta$  53.6 corresponds to the P(III) centre within the five-membered M-P-C-C-N chelate ring. The other <sup>31</sup>P chemical shifts are indicative of O,S-chelation and similar to those reported elsewhere.1f,4

To confirm the structure of compound **6** and to establish unambiguously which isomer was formed we carried out a single crystal X-ray diffraction study (Fig. 2, Table 5). This reveals that two anionic ligands are co-ordinated in a didentate mode around the palladium centre [maximum deviation of 0.06 Å for Pd out of the plane of its four substituents] with O(2) trans to P(3) of the chelating amido ligand. The S(1)– P(1)–N(1)–P(2)–O(2) fragment is approximately planar and is hinged with respect to the co-ordination plane [*i.e.* along the S(1)···O(2) vector] by 39°. Within the S(1)–P(1)–N(1)–P(2)–

0(4)

P(4)

N(3



Fig. 2 Crystal structure of  $[Pd(Ph_2PC_6H_4NH-P,N){Ph_2P(O)-NP(S)Ph_2-O,S}]$  6 (C–H hydrogen atoms omitted for clarity).

O(2) ring there is evidence for electron delocalisation with long P–S and short P–N bond distances. The P–O bond length in **6** is 1.502(4) Å which can be compared to those observed in the non-co-ordinating but strongly PO···H–N hydrogen bonded Ph<sub>2</sub>P(O)NHP(S)Ph<sub>2</sub> [1.491(4) and 1.514(4) Å].<sup>3</sup>

Reaction of  $[Pt(X)Cl(Ph_2PC_6H_4NH_2-P,N)]$  with I (or II) (2:1 molar ratio) in methanol gave instead the platinum(II)  $[Pt(X){Ph_2P(O)NP(E)Ph_2-E}(Ph_2PC_6H_4NH_2$ complexes P,N] [X = CH<sub>3</sub>, E = S 7; X = CH<sub>3</sub>, E = Se 8; X = Cl, E = S 9; X = Cl, E = Se 10]. The spectroscopic and microanalytical data (see Table 1 and 2, Experimental section) reinforce in all cases the formation of a single isomer in which  $[Ph_2P(O)NP(E)Ph_2]^-$  is monodentate bound through the soft E-donor centre. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectra for 7 and 8 show a small downfield shift of ca. 5 ppm for the co-ordinated Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> ligand and a reduced <sup>1</sup>J(PtP) of ca. 500 Hz relative to  $[Pt(CH_3)Cl(Ph_2PC_6H_4NH_2-P,N)]$  [ $\delta(P)$  20.6, <sup>1</sup>J(PtP) 4716 Hz]. For compounds 9 and 10, there is a very small downfield shift of ca. 1 ppm for the co-ordinated Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> ligand and a reduced <sup>1</sup>J(PtP) of ca. 400 Hz relative to  $[PtCl_2(Ph_2PC_6H_4NH_2-P,N)][\delta(P) 22.2, ^1J(PtP)]$ 3906 Hz, recorded in (CH<sub>3</sub>)<sub>2</sub>SO-(CD<sub>3</sub>)<sub>2</sub>SO]. The PO group was typically observed around  $\delta(P)$  15–18 indicative of a "dangling" phosphorus(v) moiety. No evidence for isomerisation (e.g. to III) was observed even after allowing CDCl<sub>3</sub> solutions of 7 (or 8) to stand for up to 14 d. Addition of concentrated HCl to a CDCl<sub>3</sub> solution of 8 and monitoring the reaction by <sup>31</sup>P-{<sup>1</sup>H} NMR revealed the formation of  $[PtCl_2(Ph_2PC_6H_4NH_2-P,N)]$  and  $Ph_2P(O)NHP(S)Ph_2$ . No attempts to test for methane formation were pursued. Unlike the reaction of I with [PdCl<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-P,N)] to give 6 the chelating amine proton in 9 and 10 has not undergone deprotonation and no evidence for species such as  $[PtCl(Ph_2PC_6H_4NH-P,N){Ph_2P(O)NP(E)Ph_2-E}]^$ or  $[Pt(Ph_2PC_6H_4NH-P,N]{Ph_2P(O)NP(E)Ph_2-O,E}]$  was observed by <sup>31</sup>P-{<sup>1</sup>H} NMR spectroscopy. Compounds 7 and 8 are the first examples of organometallic complexes of

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

Pd(1)-N(26)	2.003(5)	S(1)-P(1)	2.027(2)
Pd(1)–O(2)	2.096(4)	P(1)-N(1)	1.598(5)
Pd(1)-P(3)	2.220(2)	N(1) - P(2)	1.602(5)
Pd(1)–S(1)	2.350(2)	P(2)–O(2)	1.502(4)
N(26)-Pd(1)-O(2)	86.1(2)	Pd(1)-S(1)-P(1)	104.56(7)
N(26)-Pd(1)-P(3)	83.4(2)	S(1)-P(1)-N(1)	118.3(2)
O(2) - Pd(1) - P(3)	169.42(12)	P(1)-N(1)-P(2)	127.8(3)
N(26) - Pd(1) - S(1)	172.5(2)	N(1)-P(2)-O(2)	117.7(2)
O(2) - Pd(1) - S(1)	97.52(12)	P(2) - O(2) - Pd(1)	128.4(2)
P(3)-Pd(1)-S(1)	93.06(5)		



Ph2P(O)NPh2PE-Au-L

$L = PPh_3, E = S$	11
L = PPh <sub>3</sub> , E = Se	12
$L = Ph_2PC_6H_4NH_2$ , $E = S$	13
$L = Ph_2PC_6H_4NH_2, E = Se$	14

 $[Ph_2P(O)NP(E)Ph_2]^-$  in which the ligand adopts a E-unidentate co-ordination mode.

The molecular structure of 7 has also been determined (Fig. 3, Table 6). The platinum metal centre has a distorted square planar co-ordination geometry with angles about the metal centre of C(50)-Pt(1)-S(2) 82.6(2), N(14)-Pt(1)-P(1) 84.3(2), C(50)-Pt(1)-P(1) 92.9(3) and N(14)-Pt(1)-S(2) 100.2(2)°. Furthermore the arrangement of the ligands around the metal is such that the methyl group is *trans* to the amino group of the



**Fig. 3** Crystal structure of  $[Pt(CH_3){Ph_2P(O)NP(S)Ph_2-S}(Ph_2PC_6H_4NH_2-P,N)] \cdot 0.25CHCl_3$  7 (C-H hydrogen atoms and solvent molecule omitted for clarity).

Table 6 Selected bond distances (Å) and angles (°) for compounds 7 and 13  $\,$ 

	7 (M = Pt)	13 (M = Au)
M(1)–P(1)	2.197(2)	2.286(2)
M(1) - S(2)	2.372(2)	2.319(2)
S(2) - P(2)	2.030(3)	2.065(3)
P(2) - N(2)	1.574(6)	1.579(6)
N(2)–P(3)	1.589(6)	1.615(7)
P(3)–O(3)	1.492(5)	1.507(5)
Pt(1)-C(50)	2.063(8)	
Pt(1)-N(14)	2.153(6)	
P(1)-M(1)-S(2)	175.41(7)	167.80(6)
M(1)-S(2)-P(2)	112.75(10)	108.18(9)
S(2) - P(2) - N(2)	120.5(3)	119.4(3)
P(2)-N(2)-P(3)	135.5(4)	132.3(4)
N(2)-P(3)-O(3)	119.1(4)	119.7(3)
C(50) - Pt(1) - S(2)	82.6(2)	
N(14) - Pt(1) - P(1)	84.3(2)	
C(50) - Pt(1) - P(1)	92.9(3)	
N(14) - Pt(1) - S(2)	100.2(2)	
C(50) - Pt(1) - N(14)	176.8(3)	



Fig. 4 Crystal structure of (a)  $[Au{Ph_2P(O)NP(S)Ph_2-S}(Ph_2PC_6H_4NH_2)]$  13 (C-H hydrogen atoms omitted for clarity), (b) intermolecular hydrogen bonding in 13.

chelating  $Ph_2PC_6H_4NH_2$  ligand. The Pt(1)-P(1) distance of 2.197(2) Å in 7 is similar to that in  $[PtCl_2(Ph_2PC_6H_4NH_2-P,N)][2.188(1) Å]$  whereas the Pt(1)-N(14) distance of 2.153(6) Å is longer than that in  $[PtCl_2(Ph_2PC_6H_4NH_2-P,N)][2.048(4)$ Å] reflecting the difference in *trans* influence of a methyl *vs.* chloride ligand.<sup>17</sup> The  $[Ph_2P(O)NP(S)Ph_2]^-$  anion is bound through the soft S-donor atom as would be anticipated on the basis of the hard–soft acid–base (HSAB) principle whereas the "dangling" PO group is involved in intramolecular H-bonding with the neighbouring amino N–H proton  $[N(14)\cdots O(3) 2.73, H(14)\cdots O(3) 1.77 Å, N(14)-H(14)\cdots O(3) 171°]$ . Examples of metal complexes with an E-monodentate  $[Ph_2P(O)NP(E)Ph_2]^-$  ligand are confined to  $[Pd(en)-\{Ph_2P(O)NP(E)Ph_2-E\}_2]$  and  $[Au\{Ph_2PNHP(O)Ph_2\}\{Ph_2-P(O)NP(E)Ph_2-E\}]$  (E = S or Se).<sup>1e</sup>

The chloride substitution reaction of [AuCl(L)] (L = PPh<sub>3</sub> or Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>) with one equivalent of I (or II) in methanol at room temperature affords the white solids  $[Au{Ph_2P(O)NP(E)Ph_2-E}(L)]$  [E = S, L = PPh<sub>3</sub> 11; E = Se, L = PPh<sub>3</sub> 12; E = S, L = Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> 13; E = Se, L = Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> 14] in high yields (69–93%). The composition of 11–14 was readily confirmed by spectroscopic and microanalytical data. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectra are in agreement with the proposed structures for 11–14 with resonances for the co-ordinated tertiary phosphine at  $\delta(P)$  ca. 37 (for 11 and 12) and ca. 25 (for 13 and 14). In all cases there is a small downfield shift of ca. 5 ppm with respect to  $\delta(P)$  for [AuCl(L)] [ $\delta$ 33.4 (L = PPh<sub>3</sub>); 21.0 (L = Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)]. In addition  $\delta(P_0)$  was typically observed around  $\delta$  12 suggesting the absence of any phosphoryl interaction with the metal centre whereas  $\delta(P_E)$  were indicative of E-monodentate co-ordination modes. Furthermore in the <sup>1</sup>H NMR spectrum of **13** and **14** the amine resonance is similar to that observed in [AuCl(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)] [ $\delta$ (H) 4.4] consistent with only P-ligation of the hybrid ligand. The absence of  $v_{AuCl}$  at 327 cm<sup>-1</sup> for [AuCl(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)] and 329 cm<sup>-1</sup> for [AuCl(Ph<sub>3</sub>)] provides further strong evidence for the formation of the metathesised compounds **11–14**.

The molecular structure of 13 (Fig. 4a, Table 6) shows the gold(I) centre to be co-ordinated by the PIII donor atom of  $Ph_2PC_6H_4NH_2$  and the S donor atom of  $[Ph_2P (O)NP(S)Ph_2]^-$  in a slightly distorted linear geometry [P(1)-Au(1)-S(2) 167.80(6)°]. The Au(1)-P(1) distance [2.286(2) Å] is slightly longer than that in  $[Au(Ph_2PC_6H_4NH_2)(C_4H_8S)]$ - $CIO_4$  [2.261(2) Å]<sup>11b</sup> and  $[AuI(Ph_2PC_6H_4NH_2)]$  [2.260(4) Å].<sup>11d</sup> The Au(1)– $\overline{S}(2)$  distance [2.319(2) Å] in 13 is similar to that in  $[Au(HL){Ph_2P(O)NP(S)Ph_2-S}]$  [HL = P(3)-O(3) backbone, the bond lengths and angles reflect some degree of delocalisation. The P(2)-N(2)-P(3) angle in 13 [132.3(4)°] is comparable to that reported in  $[Au(HL){Ph_2P(O)NP(S)Ph_2-S}]$  [134.8(6)°].<sup>1e</sup> The non-coordinated amine group is involved in intermolecular hydrogen bonding (Fig. 4b) linking molecules of 13 into onedimensional chains  $[N(14) \cdots O(3A) 3.04 \text{ \AA}, H(14) \cdots O(3A) 2.09$ Å, N(14)–H(14)···O(3A) 163°].

## Conclusion

It has been demonstrated that  $[Ph_2P(O)NP(E)Ph_2]^-$  forms a variety of mixed Pd<sup>II</sup>, Pt<sup>II</sup> and Au<sup>I</sup> complexes containing Ph\_2PC\_6H\_4NH\_2 (or PPh\_3) ligands. Furthermore [Pt-(CH\_3){Ph\_2P(O)NP(E)Ph\_2-E}(Ph\_2PC\_6H\_4NH\_2-P,N)] (E = S or Se) are the first examples of organometallic complexes with E-monodentate  $[Ph_2P(O)NP(E)Ph_2]^-$  ligands.

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