

Synthesis and Late Transition Metal Complexes of the Heterofunctional Phosphane *o*-Ph₂PNHC₆H₄P(S)Ph₂

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The difunctional ligand *o*-Ph₂PNHC₆H₄P(S)Ph₂ (PS) has been prepared by treatment of the lithium amide salt of 2-(diphenylthiophosphanyl)aniline {2-[Ph₂P(S)]C₆H₄NH₂} with Ph₂PCl. The new ligand was oxidised to give the mixed chalcogen species Ph₂P(E)NHC₆H₄P(S)Ph₂, by treatment with H₂O₂ (where E = O) or aerial oxidation by recrystallisation from MeOH, and by reaction with Se₈ (where E = Se) in warm toluene. The complexes [MCl(η³-C₃H₅)(PS)] (M = Pt or Pd), *cis*-[PtCl₂(PS)(PMe₂Ph)], [(AuCl)(PS)], *cis*-[MCl₂(PS)₂] (M = Pt or Pd), *cis*-[PtMe₂(PS)₂] and *trans*-[PtMeCl(PS)₂] have been synthesised by reaction of either [Pt(μ-Cl)(μ-η²:η¹-C₃H₅)₄], [Pd(μ-Cl)(η³-C₃H₅)₂], [(PtCl(μ-Cl)(PMe₂Ph))₂], [AuCl(tht)] (tht = tetrahydrothiophene), [PdCl₂(cod)] or [PtX₂(cod)] (X = Me or Cl; cod = cycloocta-1,5-diene) with (PS). In all these complexes the ligand (PS) is monodentate *P*-bound. Chloride abstraction from [MCl(η³-C₃H₅)(PS)] (M = Pt or Pd), *cis*-[PtCl₂(PS)(PMe₂Ph)], *cis*-[PtCl₂(PS)₂] and *trans*-[PtMeCl(PS)₂], using Ag[ClO₄], gave the monocationic

[M(η³-C₃H₅)(PS)][ClO₄] (M = Pt or Pd), *cis*-[PtCl(PS)(PMe₂Ph)][ClO₄], *trans*-[PtMe(PS)₂][ClO₄] or dicationic [Pt(PS)₂][ClO₄]₂ compounds in which the ligand (PS) is κ²-*P,S*-bound. All compounds described here have been characterised by a combination of ³¹P{¹H} and ¹H NMR spectroscopy, microanalyses, FAB mass spectrometry and IR spectroscopy. The molecular structures of [AuCl(Ph₂PNHC₆H₄P(S)Ph₂-P)] in which there is an intramolecular hydrogen-bonding interaction between the amine proton and the sulfur atom of the thiophosphoryl group and *trans*-[Pt(Ph₂PNHC₆H₄P(S)Ph₂-κ²-*P,S*)₂][ClO₄]₂·CH₂Cl₂·2H₂O in which the perchlorate counterions are associated by hydrogen-bonding interactions to the amine protons of the κ²-*P,S* ligands have been determined by single-crystal X-ray diffraction.

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Introduction

There are numerous examples in the literature of ligands containing both phosphorus and sulfur donor atoms. Meek and co-workers described the preparation of [*o*-(methylthio)phenyl]diphenylphosphane^[1] – a ligand with an aromatic backbone which chelates to form five-membered C₂PSM rings.^[1,2] Rigo and Bressan prepared a series of P–S donor ligands (Ph₂PCH₂CH₂SR) (R = Me, Et and Ph) by the addition of the appropriate chloro derivative RS(CH₂)₂Cl to sodium diphenylphosphide in liquid ammonia.^[3] The methylene-bridged ligand Ph₂PCH₂SMe was found to exhibit both monodentate *P*-bound and bidentate bridging coordination modes.^[4,5] Other phosphane–thioether-based ligands have also been explored^[6–9] as have phosphane–thiolate,^[10–13] phosphane–thioformamide,^[14] phosphane–thiophene,^[15–17] phosphane–sulfoxide,^[18] phosphane–sulfide^[19–21] and phosphane–amino-phosphane–sulfide ligands including Ph₂PNHP(S)Ph₂,^[22] Ph₂PNPhP(S)Ph₂,^[23] in addition to the methylene-, ethylene-, and –[CH₂]₃–backboned bis(phosphane–mono-

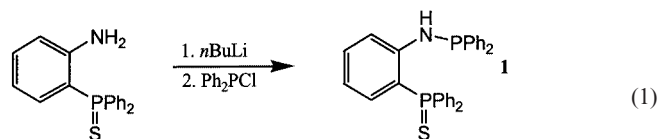
sulfides) Ph₂PCH₂P(S)Ph₂,^[24,25] Ph₂PCH₂CH₂P(S)Ph₂,^[25] and Ph₂PCH₂CH₂CH₂P(S)Ph₂,^[26] respectively. A logical extension to investigations into the reactivity of Ph₂PNHC₆H₄PPh₂^[27,28] is the chemistry of the monochalcogens Ph₂P(E)NHC₆H₄PPh₂ or Ph₂PNHC₆H₄P(E)Ph₂ (E = O, S or Se). We anticipated that these molecules would exhibit a variety of coordination modes, notably as monodentate phosphorus donors and as bidentate phosphorus–chalcogen donor ligands resulting in the formation of seven-membered metallacycles. The nitrogen atom presents a further site to be explored if deprotonation is possible. To further understand the chemistry of these molecules we have synthesised Ph₂PNHC₆H₄P(S)Ph₂ and investigated its reactivity towards Au^I, Pt^{II}, and Pd^{II}. In addition, we have prepared the mixed chalcogen compounds Ph₂P(O)NHC₆H₄P(S)Ph₂ and Ph₂P(Se)NHC₆H₄P(S)Ph₂.

Results and Discussion

Preparation and Characterisation of Ph₂PNHC₆H₄P(S)Ph₂

Treatment of 2-[diphenyl(thio)phosphanyl]aniline with *n*BuLi, at –78 °C in diethyl ether, followed by reaction with Ph₂PCl, gave **1** in good to excellent yields (71–85%) [Equation (1)].

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Attempted preparation of the oxo and seleno analogues Ph₂PNHC₆H₄P(E)Ph₂ (E = O, Se) under the same conditions resulted in re-isolation of the Ph₂P(O)C₆H₄NH₂ starting material and the formation of a complex mixture, respectively. Since the synthesis of the oxo and seleno ligands by the addition of Ph₂PCl to the lithium salt of the appropriate aniline proved unsuccessful, an alternative synthesis was sought. A second possible route to monochalcogen compounds of Ph₂PNHC₆H₄PPh₂ is by selective oxidation. This route has been applied to the synthesis of Ph₂PNHP(E)Ph₂ (E = O, S and Se).^[22,29] A series of experiments involving the reaction of Ph₂PNHC₆H₄PPh₂^[27] with a slightly less than stoichiometric quantity of the appropriate chalcogen or aqueous H₂O₂ in various solvent systems at 0 °C gave poor results. These reactions usually resulted in the precipitation of the dichalcogen compounds Ph₂P(E)NHC₆H₄P(E)Ph₂,^[28] while lesser amounts of starting material and both mixed P^{III},P^V species Ph₂P(E)NHC₆H₄PPh₂ and Ph₂PNHC₆H₄P(E)Ph₂ remain in solution. Separation of these mixtures was not attempted. Ph₂PNHC₆H₄P(S)Ph₂ (**1**) was isolated as a colourless solid and displays similar solubilities and the same sensitivity to air or light as Ph₂PNHC₆H₄PPh₂. The ³¹P{¹H} NMR spectrum (in CDCl₃) of **1** displays two single resonances at δ(P_A) = 28.2 ppm and δ(P_X) = 39.6 ppm {the starting material 2-[diphenyl(thio)phosphanyl]aniline has δ(P) = 39.6 ppm} for the -NHPPH₂ and -P(S)Ph₂ groups, respectively; the ⁴J(³¹P_A-³¹P_X) coupling was not resolved. The ¹H NMR spectrum (in CDCl₃) showed the amine proton as a doublet at δ(H) = 5.68 ppm [²J(³¹P-¹H) = 9 Hz]. From the IR spectrum we can identify ν(N-H), ν(P-N) and ν(P=S) at $\tilde{\nu}$ = 3223, 896 and 634 cm⁻¹, respectively. Microanalytical data were within specified limits and the positive-ion FAB mass spectrum gave the expected parent-ion peak at *m/z* = 494 with appropriate isotope distribution and fragmentation patterns.

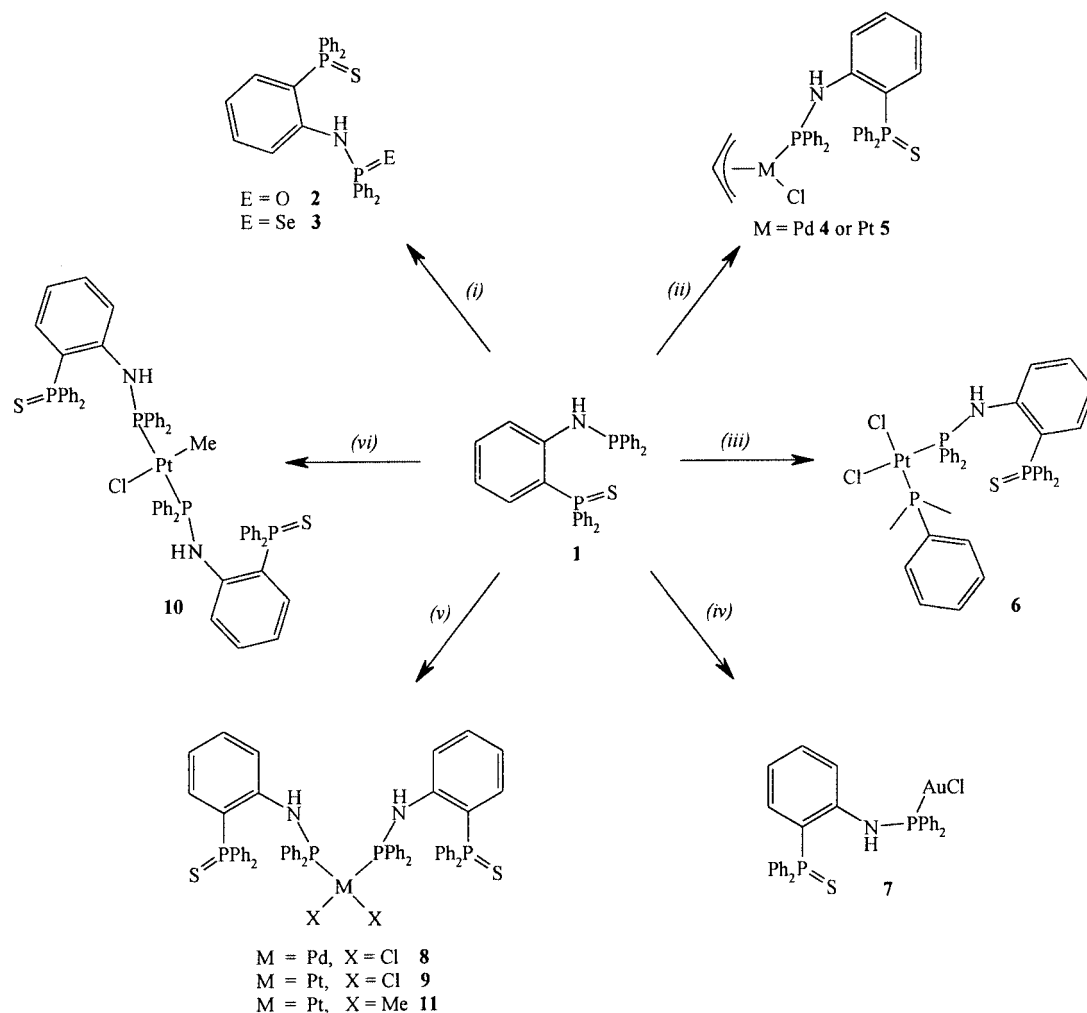
Synthesis of Ph₂P(E)NHC₆H₄P(S)Ph₂

The syntheses of the mixed chalcogen species are straightforward (Scheme 1). The mixed sulfur,oxygen species Ph₂P(O)NHC₆H₄P(S)Ph₂ (**2**) is prepared in 90% yield by the dropwise addition of aqueous hydrogen peroxide to a THF solution of **1**. The sulfur,oxygen species **2** was also isolated after recrystallisation in air of **1** from MeOH (59%). Warming **1** with a stoichiometric amount of elemental selenium in toluene at 60 °C followed by filtration of the warm solution, concentration and storage at below 0 °C gives the mixed S,Se species Ph₂P(Se)NHC₆H₄P(S)Ph₂ (**3**) in good yield (85%). Synthesis and characterisation of the disulfide has been reported elsewhere.^[28] The mixed chalcogen spe-

cies **2** and **3** are air- and moisture-tolerant colourless solids and in common with **1** display two sharp single resonances in their ³¹P{¹H} NMR spectra (Table 1) with no observable ⁴J(³¹P_A-³¹P_X) couplings in addition to amine proton resonances as broad doublets at δ(H) = 8.66 ppm [²J(³¹P-¹H) = 10 Hz] (**2**) and δ(H) = 8.34 ppm [²J(³¹P-¹H) = 8 Hz] (**3**). The infrared spectra of compounds **1** and **2** are consistent with the proposed structures and show bands attributable to ν(P=O) at $\tilde{\nu}$ = 1212 cm⁻¹ (**2**) and ν(P=Se) at $\tilde{\nu}$ = 548 cm⁻¹ (**3**) as well as the anticipated ν(N-H), ν(P-N) and ν(P=S) bands (see Exp. Sect.).

Monodentate Coordination Chemistry of Ph₂PNHC₆H₄P(S)Ph₂

Treatment of suspensions of the di- and tetranuclear species [Pd(μ-Cl)(η³-C₃H₅)]₂ and [Pt(μ-Cl)(μ-η²:η¹-C₃H₅)]₄ (in toluene and THF, respectively) with **1**, results in bridge cleavage to give the mononuclear complexes [MCl(η³-C₃H₅)(Ph₂PNHC₆H₄P(S)Ph₂-P)] [where M = Pd (**4**) (83%) or Pt (**5**) (88%)] (Scheme 1). The ³¹P{¹H} NMR (CDCl₃) spectra of **4** and **5** show the -NHPPH₂ resonances at δ(P) = 55.3 (**4**) and 51.0 ppm [¹J(¹⁹⁵Pt-³¹P) 4946 Hz] (**5**) and the pendent -P(S)Ph₂ group resonances at δ(P) = 39.8 (**4**) and 39.9 ppm (**5**) which are similar to that of the "free" ligand. The unsymmetrical mixed-ligand complex *cis*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}(PMe₂Ph)] (**6**) was prepared by chloride bridge cleavage of the platinum(II) dimer [{PtCl(μ-Cl)(PMe₂Ph)}₂] with **1** in CH₂Cl₂ (Scheme 1). The ³¹P{¹H} NMR (CDCl₃) spectrum of **6** reveals a small phosphorus-phosphorus coupling constant (18 Hz), indicative of a structure with a *cis* arrangement of monodentate phosphane ligands. Two of the three unique phosphorus environments display large Pt-P couplings δ(P) = -16.3 ppm [¹J(¹⁹⁵Pt-³¹P) = 3436 Hz] assigned to the PMe₂Ph group and δ(P) = 32.6 ppm [¹J(¹⁹⁵Pt-³¹P) = 4100 Hz] to the -NHPPH₂ group of **1**. Furthermore, the chemical shift of the pendent -P(S)Ph₂ group [δ(P) = 39.4 ppm] is similar to that observed for **1** and displays no platinum satellites indicating no interaction of the -P(S)Ph₂ moiety with the platinum centre. Evidence in support of the structural assignment of **6** is found in the IR spectrum showing two distinct ν(Pt-Cl) stretches at $\tilde{\nu}$ = 317 and 291 cm⁻¹ consistent with *cis*-PtCl₂ geometry. The reaction between [{PtCl(μ-Cl)(PMe₂Ph)}₂] and **1** was found to be somewhat sensitive to the reaction conditions as out of a total of five subsequent preparations of **6**, twice we found the isolated material to consist of an approximate 1:1 mixture of *cis* and *trans* isomers. Examination of the ³¹P{¹H} NMR spectrum (in CDCl₃) of the isolated product showed the resonances of **6** and additional lines which display a large ²J(³¹P-³¹P) coupling constant of 535 Hz indicative of a structure with a *trans* arrangement of phosphane ligands. As expected, two of the three distinct phosphorus environments display ¹J(¹⁹⁵Pt-³¹P) couplings that are characteristically smaller than those previously observed for the *cis* isomer **6**. The doublet centred at δ(P) = -6.9 ppm [¹J(¹⁹⁵Pt-³¹P) = 2531 Hz] is assigned to the coordinated PMe₂Ph group and the doublet at δ(P) = 46.1 ppm [¹J(¹⁹⁵Pt-³¹P) = 2715 Hz]



Scheme 1. (i) $H_2O_2(aq)$, THF or Se_8 , C_6H_5Me , 60 °C; (ii) $[Pd(\mu-Cl)(\eta^3-C_3H_5)_2]$, C_6H_5Me or $[Pt(\mu-Cl)(\mu-\eta^2:\eta^1-C_3H_5)_4]$, THF; (iii) $[PtCl_2(\mu-Cl)(PMe_2Ph)_2]$, CH_2Cl_2 ; (iv) $[AuCl(tht)]$, CH_2Cl_2 ; (v) $[MX_2(cod)]$ ($M = Pt$, $X = Cl$ or Me ; $M = Pd$, $X = Cl$), CH_2Cl_2 ; (vi) $[PtClMe(cod)]$, CH_2Cl_2

Table 1. Selected bond lengths [Å] and angles [°] for $[AuCl(Ph_2PNHC_6H_4P(S)Ph_2-P)]$ (**7**)

P(2)–S(2)	1.971(2)	P(2)–C(2)	1.826(5)
C(2)–C(1)	1.409(7)	C(1)–N(1)	1.408(6)
N(1)–P(1)	1.685(4)	P(1)–Au(1)	2.237(2)
Au(1)–Cl(1)	2.269(2)		
S(2)–P(2)–C(2)	114.20(2)	P(2)–C(2)–C(1)	120.00(4)
C(2)–C(1)–N(1)	120.00(4)	C(1)–N(1)–P(1)	126.30(4)
N(1)–P(1)–Au(1)	155.20(2)	P(1)–Au(1)–Cl(1)	177.40(7)

to the coordinated $-NHPPH_2$ group of **1**. The single resonance at $\delta(P) = 41.5$ ppm is assigned to the pendent $-P(S)Ph_2$ group and, although at slightly higher frequency than those observed for either **1** or **6**, remains uncoordinated, as indicated by the absence of platinum satellites. A number of literature studies have focused upon the solution *cis/trans* isomerism of platinum complexes of the type $[PtX_2(PR_3)_2]$ (where $X = Cl, Br$, or I and $R =$ alkyl or aryl groups) and showed, in the main, that the kinetic *cis* isomer was rapidly converted into the thermodynamic *trans* isomer

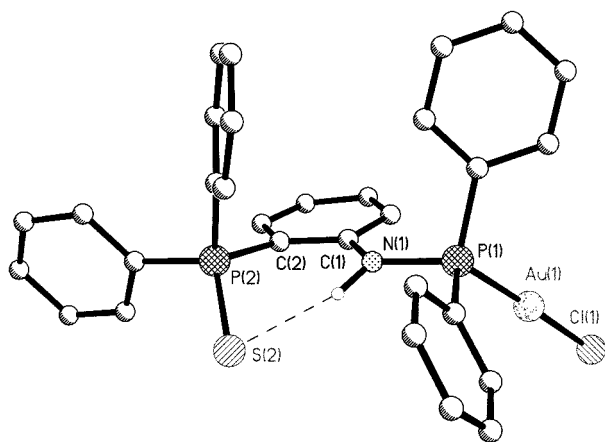
by the addition of a catalytic amount of PR_3 .^[29–32] We found that the addition of a small quantity (ca. 3–5 mg) of **1** to a dichloromethane solution of the *cis/trans* mixture resulted in isomerisation of the *trans* species to give pure *cis* isomer **6** (by $^{31}P\{^1H\}$ NMR). We have previously employed this technique to convert *trans*- $[PtCl_2(HL)(PMe_2Ph)]$ to *cis*- $[PtCl_2(HL)(PMe_2Ph)]$ [where $HL = Ph_2PNHP(O)Ph_2$].^[33] In the absence of added **1** the composition of a CD_2Cl_2 solution of the *cis/trans* mixture remained unchanged after storage for up to six weeks at ambient temperature. Preparation of the pure *trans* isomer was not pursued. Compound **1** reacts cleanly with $[AuCl(tht)]$ in CH_2Cl_2 by displacement of the tht molecule to give $[AuCl\{Ph_2PNHC_6H_4P(S)Ph_2-P\}]$ (**7**) (Scheme 1) as a colourless solid in 83% yield. The complex is slightly sensitive to light when in solution and a grey solid was deposited, presumably gold metal, after only moderate exposure. The ^{31}P NMR spectrum (in $CDCl_3$) shows two single lines at $\delta(P) = 40.1$ and 58.2 ppm assigned to the $-P(S)Ph_2$ group and the gold-coordinated $-NHPPH_2$ group, respectively. Upon coordination, the signal of the phosphorus(III) centre

is shifted to higher frequency by 30 ppm relative to the that of the “free” ligand. The IR spectrum (KBr) of **7** shows that the $\nu(\text{N}-\text{H})$ band at $\tilde{\nu} = 3109 \text{ cm}^{-1}$ has undergone a large shift to lower frequency compared to that of **1** [$\nu(\text{N}-\text{H})$ at $\tilde{\nu} = 3223 \text{ cm}^{-1}$] which suggests that the amine proton may be involved in intra/intermolecular hydrogen bonding. Crystals of X-ray quality were grown by layering a CH₂Cl₂ solution of **7** with diethyl ether. The crystal structure of [AuCl{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**7**) along with selected bond lengths and angles (Table 1) is shown in Figure 1 and reveals an intramolecular hydrogen-bonding interaction between the S(2) atom and the amine hydrogen atom H(1n) of N(1) [H(1n)⋯S(2) 2.36 Å, S(2)⋯N(1) 3.25 Å, N(1)–H(1n)⋯S(2) 158°], corroborating the IR evidence. The molecule has a near planar P(2)–C(2)–C(1)–N(1)–P(1) backbone [maximum deviation from the mean plane 0.1 Å for P(1)]. The P(1)–Au(1)–Cl(1) angle is approximately linear [177.40(7)°] and is “anti” with respect to the amine proton H(1n) which appears to be a consequence of the previously discussed hydrogen-bonding interaction. The addition of 2 equiv. of **1** to a CH₂Cl₂ solution of [PdCl₂(cod)] gave a pale-yellow precipitate after only 5 min of stirring. The product, characterised as *cis*-[PdCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**8**), was recovered in near quantitative yield (97%). The extreme insolubility of this material in all common organic solvents prevented measurement of its ³¹P{¹H}, ¹H NMR and mass spectra. Structural and geometrical assignments therefore, are based solely on microanalytical and IR data, the former was in excellent agreement with the proposed formulation, the latter showing two bands at $\tilde{\nu} = 318$ and 298 cm^{-1} for $\nu(\text{Pd}-\text{Cl})$, consistent with *cis*-PdCl₂ geometry. The $\nu(\text{NH})$ stretch at $\tilde{\nu} = 3106 \text{ cm}^{-1}$ like that of [AuCl{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**7**) occurs at a much lower frequency than in the “free” ligand [$\nu(\text{NH})$ at $\tilde{\nu} = 3223 \text{ cm}^{-1}$]. This suggests that the amine protons of *cis*-[PdCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**8**) are involved in hydrogen-bonding interactions similar to those observed in complex **7**, which may account for the insolubility of **8**. In contrast, the preparation of the platinum analogue *cis*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**9**) under the same reaction conditions gave a pale-yellow solution that showed no sign of precipitation even after prolonged stirring. The product was precipitated by the addition of diethyl ether and isolated after recrystallisation from CH₂Cl₂/diethyl ether as a colourless solid in 88% yield (Scheme 1). Once dry, **9** displayed limited solubility in CHCl₃ but was readily soluble in CH₂Cl₂. The ³¹P{¹H} NMR spectrum (in CD₂Cl₂) of *cis*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}] showed two distinct phosphorus environments at $\delta(\text{P}) = 37.6 \text{ ppm}$ [$J(^{195}\text{Pt}-^{31}\text{P}) = 4103$] and $\delta(\text{P}) = 40.6 \text{ ppm}$, corresponding to the coordinated phosphorus(III) centres and the “dangling” phosphorus(V) moieties, respectively. The large $J(^{195}\text{Pt}-^{31}\text{P}_\text{A})$ coupling constant of 4103 Hz is in good agreement with a *cis* disposition of ligands (i.e. P *trans* to Cl). In addition, no platinum satellites were observed for the uncoordinated phosphorus(V) groups, also, the chemical shift of the pendent –P(S)Ph₂ group is similar to that found

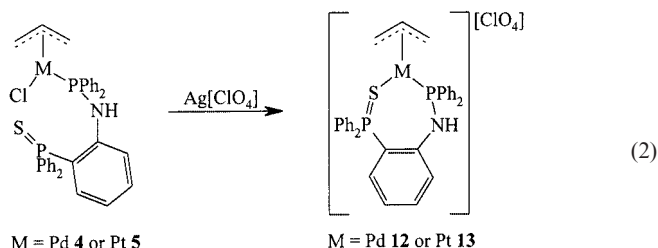
in **1** [$\delta(\text{P}) = 39.6 \text{ ppm}$] implying no interaction with the metal centre. The ³¹P{¹H} NMR spectrum of **9** also showed that the isolated product (from three separate syntheses) was consistently contaminated with an impurity (ca. 4–5%) observed as two singlets at $\delta(\text{P}) = 40.2$ and 40.8 ppm thought to be *trans*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}]₂; positive assignment of the impurity resonances to the appropriate phosphorus(III) and -(V) centres is impossible as no obvious platinum satellites were observed for either peak. Further evidence in support of the neutral nonchelating *cis* structure comes from the IR spectrum (KBr) which shows two $\nu(\text{Pt}-\text{Cl})$ stretches at $\tilde{\nu} = 311$ and 290 cm^{-1} , consistent with a *cis*-PtCl₂ geometry. The 2:1 molar ratio reaction of **1** with a CH₂Cl₂ solution of [PtClMe(cod)] results in the deposition of a colourless solid and near-quantitative recovery (98%) of the surprisingly insoluble complex *trans*-[PtClMe{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**10**). As for **8**, the insolubility of **10** in common organic solvents prevents measurement of its NMR or mass spectra, hence only infrared and microanalytical data are available. Elemental analysis confirms that the isolated material has been correctly formulated as [PtMeCl{Ph₂PNHC₆H₄P(S)Ph₂-P}]. The assignment of *trans* geometry to complex **10** is based purely upon the product obtained, **15**, using **10** as starting material (see below). Reaction of 2 equiv. of **1** with [PtMe₂(cod)] in CH₂Cl₂ produces an off-white powder, characterised as the dimethyl derivative *cis*-[PtMe₂{Ph₂PNHC₆H₄P(S)Ph₂-P}] (**11**), as is evident from the ³¹P{¹H} NMR spectrum (in CDCl₃) where the much smaller $J(^{195}\text{Pt}-^{31}\text{P})$ coupling constant of 2059 Hz is concordant with *cis* (P *trans* to CH₃) geometry. The coordinated –NHPPH₂ and “dangling” –P(S)Ph₂ group resonances occur at $\delta(\text{P}) = 55.3$ and 39.6 ppm , respectively. The ¹H NMR (CDCl₃) spectrum displays the amine protons as a broad multiplet at $\delta(\text{H}) = 8.1 \text{ ppm}$ and the PtMe₂ moiety at $\delta(\text{H}) = 0.20 \text{ ppm}$ as a double doublet, flanked by ¹⁹⁵Pt satellites [$^2J(^{195}\text{Pt}-^1\text{H}) = 72 \text{ Hz}$]. In all of the above complexes (**4**–**11**) the IR spectra (KBr) provide additional evidence of coordination through P only showing strong $\nu(\text{P}=\text{S})$ absorption at $\tilde{\nu} \approx 632\text{--}634 \text{ cm}^{-1}$ [“free” ligand $\nu(\text{P}=\text{S})$ at $\tilde{\nu} = 634 \text{ cm}^{-1}$] which is characteristic of no interaction between the –P(S)Ph₂ group and the metal centre.

Bidentate Coordination Chemistry of Ph₂PNHC₆H₄P-(S)Ph₂

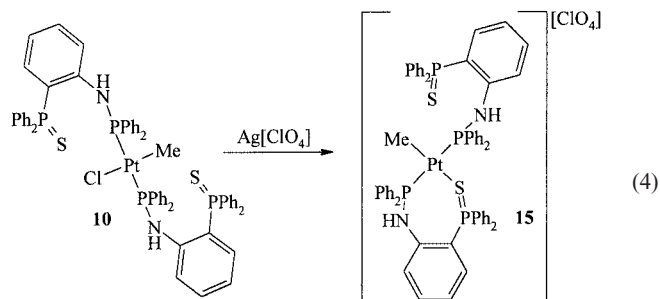
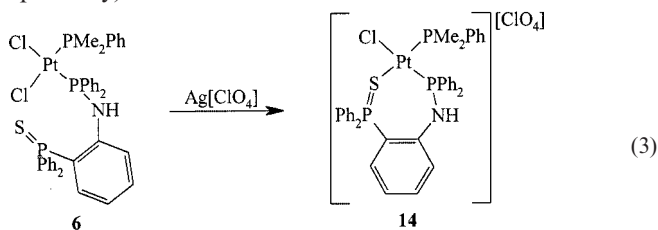
We have previously reported that chelation of the potentially bidentate mixed P^{III},P^V P,O ligand Ph₂PNHP(O)Ph₂^[34] the P,N ligand Ph₂PNHpy,^[35] and the unsymmetric P,P' ligand Ph₂PNHC₆H₄PPh₂^[27] can be induced by the use of halide abstractors such as Ag[BF₄] and Ag[ClO₄] in CH₂Cl₂. This preparative technique has been extended with good results to bring about the chelation of monodentate Ph₂PNHC₆H₄P(S)Ph₂ (**1**) resulting in the formation of cationic species containing seven-membered P–N–C–C–P–S–M rings. Smooth conversion of the neutral (allyl)Pd^{II} (**4**) and –Pt^{II} (**5**) complexes to the cationic “ring-closed” complexes [Pd(η³-C₃H₅){Ph₂PNHC₆H₄P-(S)Ph₂-κ²-P,S}][ClO₄] (**12**) and [Pt(η³-C₃H₅)-

Figure 1. Crystal structure of $[\text{AuCl}(\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-P})]$ (**7**)

$\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}\kappa^2\text{-P,S}\}[\text{ClO}_4]$ (**13**) [Equation (2)] was achieved by the addition of a small excess of $\text{Ag}[\text{ClO}_4]$ to CH_2Cl_2 solutions of **3** and **4**.



The products **12** and **13** were isolated in excellent yields (92 and 95%, respectively) as cream-coloured solids. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for complexes **12** and **13** are of the AX type and show two sharp doublets at $\delta(\text{P}^{\text{III}}) = 69.5$ ppm and $\delta(\text{P}^{\text{V}}) = 46.4$ ppm for **12** and $\delta(\text{P}^{\text{III}}) = 58.3$ ppm and $\delta(\text{P}^{\text{V}}) = 45.6$ ppm for **13** which occur at higher frequency than their monodentate *P*-bound parent compounds. Indicative of chelating ligand behaviour are the small $^2J(\text{P}^{\text{III}}\text{-P}^{\text{V}})$ couplings of 16 (**12**) and 13 Hz (**13**), the corresponding platinum satellites for compound **13** are particularly diagnostic and show a large $^1J(^{195}\text{Pt}\text{-P}^{\text{III}})$ coupling of 4720 Hz and a much smaller $^2J(^{195}\text{Pt}\text{-P}^{\text{V}})$ coupling of 123 Hz. The complexes *cis*- $[\text{PtCl}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}\kappa^2\text{-P,S}\}(\text{PMe}_2\text{Ph})][\text{ClO}_4]$ (**14**) and *trans*- $[\text{PtMe}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-P}\}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}\kappa^2\text{-P,S}\}][\text{ClO}_4]$ (**15**) were prepared from *cis*- $[\text{PtCl}_2\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-P}\}(\text{PMe}_2\text{Ph})]$ (**6**) and *trans*- $[\text{PtMeCl}\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-P}\}_2]$ (**10**) in an identical manner to complexes **12** and **13** [Equations (3) and (4), respectively).



Both compounds were precipitated by the addition of diethyl ether and isolated as cream-coloured or colourless solids in 95 (**14**) and 82% (**15**) yields and are readily soluble in CH_2Cl_2 and MeOH but less so in CHCl_3 . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **14** reveals a small $^2J(^{31}\text{P}\text{-}^{31}\text{P})$ coupling of 15 Hz, confirming that *cis* geometry was retained upon chelation. The low-frequency double doublet at $\delta(\text{P}) = -4.4$ ppm [$^1J(^{195}\text{Pt}\text{-}^{31}\text{P}) = 3390$ Hz] is assigned to the PMe_2Ph ligand and displays two P-P couplings, the previously mentioned $^2J(^{31}\text{P}\text{-}^{31}\text{P})$ *cis* coupling and a $^3J(^{31}\text{P}\text{-}^{31}\text{P})$ *trans* coupling of 9 Hz. The $-\text{NHPPH}_2$ group P resonance appears as a doublet at $\delta(\text{P}) = 40.5$ ppm [$^1J(^{195}\text{Pt}\text{-}^{31}\text{P}) = 3821$ Hz] and displays only the *cis* $^2J(^{31}\text{P}\text{-}^{31}\text{P})$ coupling. The high-frequency resonance at $\delta(\text{P}) = 43.6$ ppm appears as a doublet and is assigned to the coordinated $-\text{P}(\text{S})\text{Ph}_2$ group by virtue of the small $^2J(^{195}\text{Pt}\text{-}^{31}\text{P})$ coupling of 47 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2) of **15** shows four unique phosphorus environments. The first resonance at $\delta(\text{P}) = 43.1$ ppm, assigned to the pendant $-\text{P}(\text{S})\text{Ph}_2$ group, appears as a singlet with no platinum satellites which is consistent with noncoordinating behaviour. The double doublet resonance at $\delta(\text{P}) = 44.7$ ppm, assigned to the coordinated $-\text{P}(\text{S})\text{Ph}_2$ group of the chelating ligand, shows two distinct $^3J(^{31}\text{P}\text{-}^{31}\text{P})$ couplings of 3 and 11 Hz in addition to platinum satellites with a small $^2J(^{195}\text{Pt}\text{-}^{31}\text{P})$ coupling of 70 Hz. The doublet at $\delta(\text{P}) = 59.2$ ppm, assigned to the $-\text{NHPPH}_2$ group of the nonchelating ligand, is coupled to the coordinated P^{V} centre [$^3J(^{31}\text{P}\text{-}^{31}\text{P}) = 11$ Hz] and displays a small $^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$ coupling of 3192 Hz which is characteristic of mutual *trans* phosphane geometry. The high-frequency resonance at $\delta(\text{P}) = 64.4$ ppm is assigned to the $-\text{NHPPH}_2$ group of the chelating ligand as chelation has previously been observed to cause a shift to higher frequency in both the P^{III} and P^{V} centres, cf. the conversions of $[\text{MCl}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-P}\}]$ [where $\text{M} = \text{Pd}$ (**4**) or Pt (**5**)] to $[\text{M}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2\text{-}\kappa^2\text{-P,S}\}][\text{ClO}_4]$ [where $\text{M} = \text{Pd}$ (**12**) or Pt (**13**)]. The phosphorus atom of this group is *cis*-coupled to the coordinated $-\text{P}(\text{S})\text{Ph}_2$ group as suggested by the small $^3J(^{31}\text{P}\text{-}^{31}\text{P})$ *cis* coupling of 3 Hz. The $^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$ coupling of 3225 Hz is also consistent with *trans* geometry as is the absence of any typically small (ca. 2000 Hz) phosphorus *trans* to methyl couplings. Contrary to expectation there is no resolvable *trans* $^2J(^{31}\text{P}\text{-}^{31}\text{P})$ coupling, which we would expect to be of the order of ca. 500 Hz in magnitude. ($^{31}\text{P}\text{-}^{31}\text{P}$) COSY ex-

periments and re-recording of the spectrum at higher field do not shed any light on this anomaly. It is also worth noting the absence of $^2J(^{31}\text{P}-^{31}\text{P})$ *trans* coupling between the two coordinated chemically inequivalent $-\text{NHPPh}_2$ groups. The ^1H NMR spectrum of **15** (in CD_2Cl_2) is consistent with the proposed structure and shows two multiplets at $\delta(\text{H}) = 8.62$ ppm [$^3J(^{195}\text{Pt}-^1\text{H}) = 34$ Hz] and $\delta(\text{H}) = 5.78$ ppm [$^3J(^{195}\text{Pt}-^1\text{H}) = 54$ Hz], assigned to the *P*-bound and the κ^2 -*P,S*-bound ligand amine protons, respectively, with platinum satellites. The expected Pt–Me proton resonance appears as a broad pseudotriplet at $\delta(\text{H}) = -0.20$ ppm with typical $^2J(^{195}\text{Pt}-^1\text{H})$ and $^3J(^{31}\text{P}-^1\text{H})$ couplings of 76 and 15 Hz, respectively. The IR spectrum is diagnostic and shows two $\nu(\text{N}-\text{H})$ bands at $\tilde{\nu} = 3190$ and 3144 cm^{-1} and two $\nu(\text{P}=\text{S})$ bands at $\tilde{\nu} = 632$ and 622 cm^{-1} , corresponding to pendant and coordinated $-\text{P}(\text{S})\text{Ph}_2$ groups, respectively. In addition, the $\nu(\text{P}-\text{N})$ band at $\tilde{\nu} = 916$ cm^{-1} shows a prominent shoulder at $\tilde{\nu} = 925$ cm^{-1} which is also compatible with two ligand environments. Treatment of *cis*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-*P*}]₂ (**9**) with 2 equiv. of Ag[ClO₄] in CH₂Cl₂ resulted in abstraction of both chloride ligands and the formation of the dicationic bis(chelate) species *cis*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -*P,S*}]₂[ClO₄]₂ (**16**) isolated as an off-white microcrystalline solid in 88% yield. The isolated product, despite repeated recrystallisation, was consistently contaminated with an impurity (ca. 5%), observed as two triplets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta(\text{P}) = 42.9$ and 55.3 ppm [$^1J(^{195}\text{Pt}-^{31}\text{P}) = 2596$ Hz], which was thought to be the *trans* isomer of **16**, formed from the suspected *trans*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-*P*}]₂ impurity in **9**. The complex is readily soluble in CH₂Cl₂ and MeOH but sparingly so in CHCl₃. The ^{31}P NMR spectrum (in CD_2Cl_2) of the platinum complex **16** shows two sets of resonances at $\delta(\text{P}) = 48.8$ ppm [$^1J(^{195}\text{Pt}-^{31}\text{P}_\text{X}) = 3649$ Hz] and $\delta(\text{P}) = 45.3$ ppm [$^2J(^{195}\text{Pt}-^{31}\text{P}_\text{A}) = 38$ Hz], corresponding to the coordinated phosphorus(III) and phosphorus(V) groups, respectively. Once again, chelation results in a shift of signals relative to those of the neutral species *cis*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-*P*}]₂ (**9**) [$\delta(\text{P}^\text{III}) = 37.6$ ppm and $\delta(\text{P}^\text{V}) = 40.6$ ppm]. The $^1J(^{195}\text{Pt}-^{31}\text{P}^\text{III})$ coupling is decreased by over 450 Hz to 3649 Hz relative to that of **9** but is still consistent with the proposed *cis* geometry. Further evidence of ligand chelation is the now apparent small $J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ coupling constant of 5 Hz. It is unclear whether the observed $J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ coupling of 5 Hz is *cis* or *trans* in origin or a combination of both as the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of *cis*-[PtCl{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -*P,S*}(PMe₂Ph)][ClO₄] (**14**) (see above), which has a single PtP₂C₂SN ring, and, as such, no *trans*-P–Pt–S–P grouping, contain no such coupling. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of *trans*-[PtMe{Ph₂PNHC₆H₄P(S)Ph₂-*P*}{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -*P,S*}] [ClO₄] (**15**) shows two distinct *cis* $^3J(^{31}\text{P}_\text{A}-^{31}\text{P}_\text{X})$ couplings (see above). The IR spectrum supports the bis(chelate) structure, most notably by the observed shift to lower wavenumber of the $\nu(\text{P}=\text{S})$ band [623 cm^{-1} vs. 634 cm^{-1} found in **9**] which is a trend also observed in all of the previously described κ^2 -*P,S* chelate com-

plexes (**12**–**15**). An attempt to grow crystals of *cis*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -*P,S*}]₂[ClO₄]₂ (**16**), suitable for X-ray crystallographic analysis by layering a CH₂Cl₂ solution with diethyl ether, resulted in crystallisation of the *trans* isomer. A $^{31}\text{P}\{^1\text{H}\}$ NMR study of CD_2Cl_2 and $\text{CD}_2\text{Cl}_2/\text{Et}_2\text{O}$ solutions of **16** over a six week period showed that the *cis/trans* ratio of the compound, i.e. 95:5, remained constant and allowed us to discount the occurrence of slow *cis*-to-*trans* isomerism. The structure of *trans*-**16** (Figure 2) along with its core geometry (Figure 3) are displayed with selected bond lengths and angles (Table 2). The crystal structure of *trans*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -

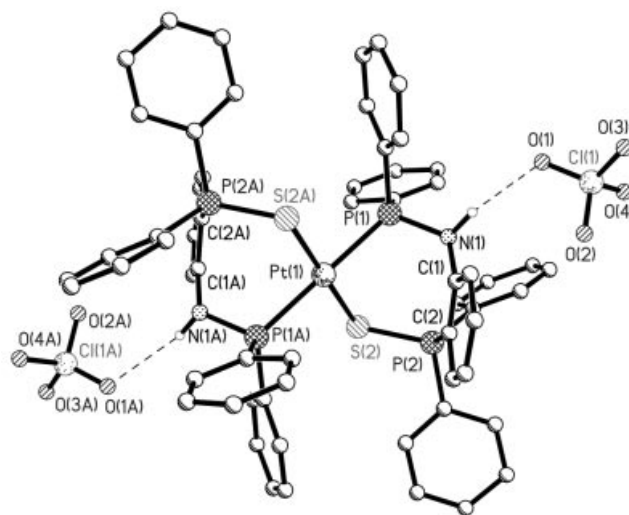


Figure 2. Crystal structure of *trans*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂-*P,S*}]₂[ClO₄]₂·CH₂Cl₂·2H₂O; the CH₂Cl₂ and water molecules are omitted for clarity

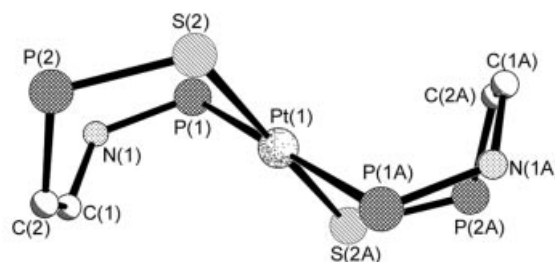


Figure 3. Core geometry of *trans*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂-*P,S*}]₂[ClO₄]₂

Table 2. Selected bond lengths [Å] and angles [°] for *trans*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂-*P,S*}]₂[ClO₄]₂·CH₂Cl₂·2H₂O

Pt(1)–S(2)	2.2432(14)	S(2)–P(2)	2.027(2)
P(2)–C(2)	1.794(6)	C(2)–C(1)	1.405(8)
C(1)–N(1)	1.428(7)	N(1)–P(1)	1.671(5)
P(1)–Pt(1)	2.3325(13)		
P(1)–Pt(1)–P(1A)	180.0	S(2)–Pt(1)–S(2A)	180.0
P(1)–Pt(1)–S(2)	90.71(5)	P(1)–Pt(1)–S(2A)	89.29(5)
S(2)–P(2)–C(2)	111.3(2)	Pt(1)–S(2)–P(2)	108.18(7)
C(2)–C(1)–N(1)	120.5(5)	P(2)–C(2)–C(1)	121.1(4)
N(1)–P(1)–Pt(1)	110.1(2)	C(1)–N(1)–P(1)	123.5(4)

$P,S\}_{2}[ClO_4]_2$ reveals that the molecule possesses a crystallographic centre of symmetry through the platinum atom and that one CH_2Cl_2 and two H_2O molecules (not shown for clarity) per molecule of complex are present. Near-perfect square-planar geometry at the metal centre is evident, presumably because of the lack of strain imposed at the platinum centre by the seven-membered rings. The two seven-membered PtP_2C_2NS metallacycles adopt a conformation best described as pseudo-boat form. Each ring consists of three distinct planes of atoms, $[P(1), N(1), S(2), P(2)]$, $[P(2)-C(2)-C(1)-N(1)]$ and $[P(1)-Pt(1)-S(2)]$. The angle between $[P(1), N(1), S(2), P(2)]$ and $[P(2)-C(2)-C(1)-N(1)]$ is approximately 119° whilst that between $[P(1), N(1), S(2), P(2)]$ and $[P(1)-Pt(1)-S(2)]$ is 56° . The dicationic nature of the complex is highlighted by the presence of two disordered $[ClO_4]^-$ counterions which are involved in hydrogen-bonding interactions with the two amine protons $[H(1n)\cdots O(2) 2.27(7) \text{ \AA}, O(1)\cdots N(1) 3.03(1) \text{ \AA}, N(1)-H(1n)\cdots O(1) 134(7)^\circ]$. Reaction of the near insoluble palladium complex **8** with $Ag[ClO_4]$ in a CH_2Cl_2 /MeOH solvent mixture gave, after removal of the deposited $AgCl$ and precipitation of the product with diethyl ether, a yellow solid. Examination of this material by $^{31}P\{^1H\}$ NMR (in CD_2Cl_2) showed that multiple products had been formed. No further attempt was made to prepare *cis*- $[Pd\{Ph_2PNHC_6H_4P(S)Ph_2-k^2-P,S\}_2][ClO_4]_2$.

Anionic Bidentate Coordination Chemistry of $Ph_2PNHC_6H_4P(S)Ph_2$

Previous work has demonstrated that metal complexes constructed using ligands bearing phosphanylamine groups can be easily deprotonated using a relatively mild base, e.g. Et_3N or the metal alkoxide $tBuOK$, to afford neutral chelate ring metallacycles.^[29,30] Upon reaction of complexes **8** and **9** with $tBuOK$ in MeOH a rapid change in colour is observed. Bright-yellow and bright-orange solids were isolated from the platinum and palladium reactions, respectively. Although the positive-ion FAB MS data gave promising results, i.e. showed isotope profiles at $m/z = 1091/2$ for palladium and 1180 for platinum corresponding to $[M\{Ph_2PNC_6H_4P(S)Ph_2-k^2-P,S\}_2]^+$, supporting evidence was poor. In particular, $^{31}P\{^1H\}$ NMR evidence showed that multiple products had been formed. Attempts to isolate single products from the mixtures were not successful. Substitution of $tBuOK$ for the milder base Et_3N failed as no reaction was observed even at reflux in MeOH.

Conclusion

We have shown that the mixed P^{III},P^V ligand $Ph_2PNHC_6H_4P(S)Ph_2$ (**1**) can be prepared by treating the lithium amide salt of $Ph_2P(S)C_6H_4NH_2$ with Ph_2PCl and that this ligand has the potential to ligate in a number of bonding modes. Apart from behaving as a typical unidentate *P*-bonded ligand, participation of the $P=S$ function can be induced by removal from a metal complex of a chloride ligand using a halide abstractor. Further studies are cur-

rently in progress into additional coordination modes of this ligand.

Experimental Section

General: Unless otherwise stated, manipulations were performed under oxygen-free dinitrogen using predried solvents and standard Schlenk techniques. 2-[Diphenyl(thio)phosphanyl]aniline was prepared by the addition of a stoichiometric quantity of elemental sulfur to a toluene solution of 2-(diphenylphosphanyl)aniline. The complexes $[Pd(\mu-Cl)(\eta^3-C_3H_5)]_2$,^[36] $[Pt(\mu-Cl)(\mu-\eta^2:\eta^1-C_3H_5)]_4$,^[37] $[PtCl(\mu-Cl)(PMe_2Ph)]_2$,^[38] $[MX(Y)(cod)]$ ($M = Pt$ or Pd ; $X, Y = Me, Cl, Br$ or I ; $cod = cycloocta-1,5$ -diene),^[39–32] or $[AuCl(tht)]$ ^[33] ($tht = tetrahydrothiophene$) were prepared according to literature procedures. *n*BuLi (Lancaster) was titrated against diphenylacetic acid just prior to use. Aqueous H_2O_2 (30% w/w, Fluka) and $Ag[ClO_4]$ (99% purity, Aldrich) were obtained commercially and used without further purification. Infrared spectra were recorded as KBr pellets in the range 4000 – 220 cm^{-1} with a Perkin–Elmer system 2000 Fourier transform spectrometer, 1H NMR spectra (250 or 270 MHz) either with a Bruker AC250 FT or a JEOL GSX270 spectrometer with δ referenced to external $SiMe_4$ and $^{31}P\{^1H\}$ NMR spectra (36.2, 101.3 or 109.4 MHz) either with a JEOL FX90Q, a Bruker AC250 FT, or a JEOL GSX270 spectrometer with δ referenced to external H_3PO_4 . Microanalyses were performed by the St Andrews University School of Chemistry Service. Precious metal salts were provided on loan by Johnson Matthey plc.

$Ph_2PNHC_6H_4P(S)Ph_2$ (1**):** A solution of 2.43 m *n*BuLi (4.0 mL, 9.72 mmol) in hexane was added dropwise over a period of 10 min to a cooled (-78°C cardice/acetone), stirred suspension of 2-[diphenyl(thio)phosphanyl]aniline (3.00 g, 9.70 mmol) in dry, degassed diethyl ether (200 mL). The mixture was stirred at -78°C for 1 h, warmed to room temperature and stirred for a further 3 h giving a white suspension in a dark orange solution. The reaction mixture was cooled once more to -78°C (cardice/acetone) and neat chlorodiphenylphosphane (1.75 mL, 2.15 g, 9.74 mmol) was added dropwise over 5 min. The white suspension in a pale yellow solution was stirred at -78°C for 30 min, warmed to room temperature, stirred for 3 h and then stripped of solvent in vacuo. The pale brown oily solid was then triturated with dry MeOH (30 mL) at 0°C for 10 min. The colourless solid was collected by suction filtration, washed with ice-cold MeOH ($2 \times 10 \text{ mL}$) and dried overnight in vacuo. Yield: 4.07 g, 85%. 1H NMR ($CDCl_3$): $\delta = 7.75$ – 7.66 (m, 4 H, aromatics), 7.56 – 7.16 (m, 18 H, aromatics), 6.71 – 6.59 (m, 2 H, aromatics), 5.68 [br. d, $^2J(^{31}P-^1H) = 9 \text{ Hz}$, 1 H, NH] ppm. FAB⁺ MS: $m/z = 494 [M]^+$. Selected IR data (KBr): $\tilde{\nu} = 3223$ [br, $\nu(N-H)$], 896 [vs, $\nu(P-N)$], 634 [vs, $\nu(P=S)$] cm^{-1} .

$Ph_2P(O)NHC_6H_4P(S)Ph_2$ (2**). Method A:** To a stirred THF (25 mL) solution of **1** (0.480 g, 0.973 mmol) was added aqueous hydrogen peroxide (30% w/w, 0.2 mL, 1.76 mmol) dropwise over a 10 min period. The mixture was stirred for 10 min, then concentrated to dryness, giving an off-white oily residue. The residue was taken up in CH_2Cl_2 and dried with anhydrous $MgSO_4$. Filtration to remove the drying agent, followed by concentration of the filtrate to dryness, and recrystallisation from a minimum of hot toluene gave **2** as a colourless crystalline solid. The product was collected by suction filtration, washed with toluene ($2 \times 5 \text{ mL}$) and dried in vacuo. Yield: 0.445 g, 90%. 1H NMR ($CDCl_3$): $\delta = 8.66$ [br. d, $^2J(^{31}P-^1H) = 10 \text{ Hz}$, 1 H, NH], 7.78 – 7.69 (m, 4 H, aromatics), 7.57 – 7.24 (m, 18 H, aromatics), 6.77 – 6.79 (m, 2 H, aromatics)

ppm. FAB⁺ MS: m/z = 510 [M]⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3117 [w, v(N–H)], 1212 [s, v(P=O)], 924 [s, v(P–N)], 632 [vs, v(P=S)] cm^{−1}. **Method B:** Ph₂PNHC₆H₄P(S)Ph₄ (**1**) (0.536 g, 1.086 mmol) was dissolved in boiling MeOH (30 mL) and the hot solution was first cooled to room temperature and then stored at 4 °C overnight to give **2** as a colourless powder, which was collected by suction filtration, washed with ice-cold MeOH (2 × 10 mL), and dried overnight in vacuo. Yield: 0.324 g, 59%. ³¹P{¹H} NMR (CDCl₃) and microanalytical data are similar to those of the material generated by Method A.

Ph₂P(Se)NHC₆H₄P(S)Ph₂ (3): Elemental selenium (0.085 g, 1.076 mmol) and **1** (0.534 g, 1.072 mmol) were stirred in warm (60 °C) toluene (20 mL) for 30 min. The solution was filtered through Celite while still warm to remove a trace amount of unchanged selenium. The Celite was washed with warm (60 °C) toluene (2 × 10 mL). The filtrate and washings were combined and reduced in volume to ca. 15 mL, and the resulting colourless solid was collected by suction filtration, washed with toluene (2 × 5 mL) and ice-cold diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 0.524 g, 85%. ¹H NMR (CDCl₃): δ = 8.34 [br. d, ²J(³¹P–¹H) = 8 Hz, 1 H, NH], 7.79–7.68 (m, 4 H, aromatics), 7.63–7.24 (m, 18 H, aromatics), 6.85 (m, 1 H, aromatic), 6.77–6.67 (m, 1 H, aromatic) ppm. FAB⁺ MS: m/z = 573 [M]⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3098 [s, v(N–H)], 925 [vs, v(P–N)], 631 [s, v(P=S)], 548 [vs, v(P=Se)] cm^{−1}.

[PdCl(η^3 -C₃H₅){Ph₂PNHC₆H₄P(S)Ph₂-P}] (4): To a stirred toluene (15 mL) suspension of [Pd(μ -Cl)(η^3 -C₃H₅)₂] (0.115 g, 0.316 mmol) was added in one portion solid **1** (0.312 g, 0.632 mmol). The mixture was stirred for 3 h to give a light, cream-coloured precipitate. The solvent volume was reduced in vacuo to ca. 5 mL and light petroleum ether (40–60 °C) (20 mL) was added to further precipitate the product, which was collected by suction filtration, washed with light petroleum ether (40–60 °C) (2 × 15 mL), and dried in vacuo. Yield: 0.354 g, 83%. ¹H NMR (CDCl₃): δ = 8.02 (s, 1 H, NH), 7.81–7.24 (m, 22 H, aromatics), 6.82–6.73 (m, 2 H, aromatic), 5.36 (m, 1 H, allyl), 4.64 (m, 1 H, allyl), 3.59 (m, 1 H, allyl), 3.04 (m, 1 H, allyl), 2.39 (m, 1 H, allyl) ppm. FAB⁺ MS: m/z = 676 [M]⁺, 641 [M – Cl]⁺, 600 [M – Cl – C₃H₅]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3144 [br, v(N–H)], 912 [m, v(P–N)], 632 [m, v(P=S)] cm^{−1}.

[PtCl(η^3 -C₃H₅){Ph₂PNHC₆H₄P(S)Ph₂-P}] (5): To a stirred THF (20 mL) suspension of [Pt(μ -Cl)(μ - η^2 : η^1 -C₃H₅)₄] (0.153 g, 0.141 mmol) was added in one portion solid **1** (0.280 g, 0.568 mmol). The mixture was stirred for 6 h to give a dirty yellow solution that was filtered through a Celite plug to remove a small quantity of dark insoluble material. The resulting very pale yellow solution was reduced in vacuo to ca. 4–5 mL, and light petroleum ether (40–60 °C) (25 mL) was added to precipitate the product as a cream-coloured powder, which was collected by suction filtration, washed with light petroleum ether (40–60 °C) (2 × 10 mL), and dried in vacuo. Yield: 0.379 g, 88%. ¹H NMR (CDCl₃): δ = 8.07 [s, ³J(¹⁹⁵Pt–¹H) = 47 Hz, 1 H, NH], 7.80–7.19 (m, 22 H, aromatics), 6.78–6.71 (m, 2 H, aromatic), 4.76 (m, 1 H, allyl), 4.28 (m, 1 H, allyl), 2.92 (m, 2 H, allyl) 1.87 [m, ³J(¹⁹⁵Pt–¹H) = 78 Hz, 1 H, allyl] ppm. FAB⁺ MS: m/z = 765 [M]⁺, 730 [M – Cl]⁺, 689 [M – Cl – C₃H₅]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3142 [br, v(N–H)], 912 [s, v(P–N)], 634 [s, v(P=S)], 298 [w, v(Pt–Cl)] cm^{−1}.

cis-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}(PMe₂Ph)] (6): To a stirred CH₂Cl₂ (25 mL) solution of [PtCl(μ -Cl)(PMe₂Ph)]₂ (0.126 g, 0.156 mmol) was added dropwise over 10 min a CH₂Cl₂ (20 mL) solution of **1** (0.154 g, 0.312 mmol). The resulting pale yellow solu-

tion was stirred for 30 min and then concentrated under reduced pressure to ca. 1–2 mL, and addition of petroleum ether (60–80 °C) precipitated an off-white solid. The product was collected by suction filtration, washed with petroleum ether (60–80 °C) (3 × 10 mL) and dried in vacuo. Yield: 0.246 g, 88%. ¹H NMR (CDCl₃): δ = 8.47 (m, 1 H, NH), 7.90 (m, 1 H, aromatic), 7.83 (m, 22 H, aromatics), 6.82–6.68 (m, 2 H, aromatics) and 1.46 [d, ²J(³¹P–¹H) = 11, ³J(¹⁹⁵Pt–¹H) = 35 Hz, 6 H, PMe] ppm. FAB⁺ MS: m/z = 898 [M]⁺, 862 [M – Cl]⁺, 827 [M – 2 Cl]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3143 [w, v(N–H)], 912 [s, v(P–N)], 634 [m, v(P=S)], 317 (w) + 291 (w) [v(PtCl)] cm^{−1}.

[AuCl{Ph₂PNHC₆H₄P(S)Ph₂-P}] (7): To a stirred solution of [AuCl(tht)] (0.045 g, 0.140 mmol) in CH₂Cl₂ (4 mL) was added **1** (0.070 g, 0.142 mmol) as a solid in one portion. The mixture was stirred for 1 h and filtered through a Celite plug to remove a small amount of grey insoluble material. Diethyl ether (35 mL) was added slowly until a white solid precipitated. The product was collected by suction filtration, washed with diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 0.085 g, 83%. ¹H NMR (CDCl₃): δ = 8.00 [br. d, ²J(³¹P–¹H) = 3 Hz, 1 H, NH], 7.71–7.29 (m, 21 H, aromatics), 7.14 (m, 1 H, aromatic), 6.95 (m, 1 H, aromatic) and 6.71 (m, 1 H, aromatic) ppm. FAB⁺ MS: m/z = 726 [M]⁺, 691/692 [M – Cl]⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3109 [m, v(N–H)], 927 [m, v(P–N)], 632 [s, v(P=S)], 339 [w, v(Au–Cl)] cm^{−1}.

cis-[PdCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}]₂ (8): To a stirred solution of [PdCl₂(cod)] (0.078 g, 0.273 mmol) in CH₂Cl₂ (2.5 mL) was added **1** (0.273 g, 0.553 mmol) as a solid in one portion. The resulting clear pale yellow solution was stirred for 10 min, and the pale yellow precipitate was collected by suction filtration, washed with CH₂Cl₂ (2 × 2 mL) and diethyl ether (3 × 10 mL), and dried in vacuo. Yield: 0.309 g, 97%. Selected IR data (KBr): $\tilde{\nu}$ = 3108 [br, v(N–H)], 919 [vs, v(P–N)], 632 [vs, v(P=S)], 318 (w) + 298 (w) [v(Pd–Cl)] cm^{−1}.

cis-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}]₂ (9): This compound was prepared in the same way as **8** using [PtCl₂(cod)] (0.051 g, 0.136 mmol) in CH₂Cl₂ (2.5 mL) and **1** (0.138 g, 0.280 mmol). The resulting clear pale yellow solution was stirred for 2 h, and the product was precipitated by slow addition of diethyl ether (15 mL). The crude product was immediately redissolved in CH₂Cl₂ (5 mL) and reprecipitated by slow addition of diethyl ether (30 mL), washed with ice-cold CH₂Cl₂/diethyl ether (1:1) (4 mL) and diethyl ether (3 × 10 mL). The resulting white solid was collected by suction filtration and dried in vacuo. Yield: 0.150 g, 88%. ¹H NMR (CD₂Cl₂): δ = 7.90 [br. d, ²J(³¹P–¹H) = 7 Hz, 2 H, NH], 7.76–7.08 (m, 44 H, aromatics) and 6.71–6.58 (m, 4 H, aromatics) ppm. FAB⁺ MS: m/z = 1217/8 [M – Cl]⁺, 1182 [M – 2 Cl]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3125 [m, v(N–H)], 920 [s, v(P–N)], 634 [s, v(P=S)], 311 (w) + 290 (w) [v(Pt–Cl)] cm^{−1}. The product was consistently contaminated with an impurity (ca. 4–5%) observed as two singlets in the ³¹P{¹H} NMR at δ (P) = 40.2 and 40.8 ppm, thought to be *trans*-[PtCl₂{Ph₂PNHC₆H₄P(S)Ph₂-P}]₂.

trans-[PtClMe{Ph₂PNHC₆H₄P(S)Ph₂-P}]₂ (10): This was prepared in the same way as **8** using [PtClMe(cod)] (0.093 g, 0.263 mmol) in CH₂Cl₂ (4 mL) and **1** (0.270 g, 0.547 mmol). The white solid was collected by suction filtration, washed with CH₂Cl₂ (2 × 2 mL) and diethyl ether (3 × 10 mL) and dried in vacuo. Yield: 0.318 g, 98%. Selected IR data (KBr): $\tilde{\nu}$ = 3128 [br, v(N–H)], 911 [vs, v(P–N)], 633 [vs, v(P=S)], 288 [w, v(Pt–Cl)] cm^{−1}.

cis-[PtMe₂{Ph₂PNHC₆H₄P(S)Ph₂-P}]₂ (11): This was prepared in the same way as **8** using [PtMe₂(cod)] (0.070 g, 0.210 mmol) in toluene (4 mL) and **1** (0.210 g, 0.43 mmol). The resulting clear pale

yellow solution was stirred for 2 h resulting in the deposition of a light precipitate. Petroleum ether (60–80 °C) (30 mL) was added with stirring to further precipitate the product. The off-white solid was collected by suction filtration, washed with petroleum ether (60–80 °C) (3 × 10 mL), and dried in vacuo. Yield: 0.215 g, 84%. ^1H NMR (CDCl_3): δ = 8.10 (m, 2 H, NH), 7.86–6.59 (m, 48 H, aromatics) and 0.20 [dd, $^2J(^{195}\text{Pt}-^1\text{H})$ = 72 Hz, 6 H, PtMe] ppm. FAB⁺ MS: m/z = 1235 [$\text{M} + \text{Na}$]⁺, 1212 [M]⁺ and 1196 [$\text{M} - \text{Me}$]⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3168 [br, $\nu(\text{N}-\text{H})$], 902 [s, $\nu(\text{P}-\text{N})$], 634 [s, $\nu(\text{P}=\text{S})$] cm^{-1} .

[Pd($\eta^3\text{-C}_3\text{H}_5$){Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -P,S}][ClO₄] (12): To a stirred CH_2Cl_2 (15 mL) solution of **4** (0.171 g, 0.253 mmol) was added Ag[ClO₄] (0.055 g, 0.265 mmol) as a solid in one portion. The resulting mixture was stirred in the dark for 17 h and then filtered through Celite to remove the AgCl. The pale yellow filtrate was concentrated in vacuo to ca. 5–6 mL and upon addition of diethyl ether (25 mL) deposited a cream-coloured solid. The solid was collected by suction filtration, washed with diethyl ether (3 × 10 mL), and dried in vacuo. Yield: 0.172 g, 92%. ^1H NMR (CDCl_3): δ = 7.93–6.97 (m, 23 H, aromatics), 6.66 (m, 1 H, aromatics), 5.61 (m, 1 H, allyl), 5.21 [br. d, $^2J(^{31}\text{P}-^1\text{H})$ = 11 Hz, 1 H, NH], 4.76 (m, 1 H, allyl), 3.76 (m, 1 H, allyl), 3.56 (m, 1 H, allyl), 2.87 [br. d, $J(^1\text{H}-^1\text{H})$ = 13 Hz, 1 H, allyl] ppm. FAB⁺ MS: m/z = 641 [$\text{M} - \text{ClO}_4$]⁺, 600 [$\text{M} - \text{ClO}_4 - \text{C}_3\text{H}_5$]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3196 [br, $\nu(\text{N}-\text{H})$], 1099 [vs (br), $\nu(\text{ClO}_4)$], 907 [s, $\nu(\text{P}-\text{N})$], 622 [s, $\nu(\text{P}=\text{S})$] cm^{-1} .

[Pt($\eta^3\text{-C}_3\text{H}_5$){Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -P,S}][ClO₄] (13): This was prepared in the same way as **12** using **5** (0.183 g, 0.239 mmol) and Ag[ClO₄] (0.052 g, 0.251 mmol). The mixture was filtered through Celite and concentrated in vacuo to ca. 3 mL whereupon an off-white solid **13** was deposited. Further precipitation was induced by the addition of diethyl ether (35 mL). The resulting cream-coloured powder was collected by suction filtration, washed with diethyl ether (3 × 10 mL), and dried in vacuo. Yield: 0.188 g, 95%. ^1H NMR (CD_2Cl_2): δ = 7.88–6.95 (m, 23 H, aromatics), 6.63 (m, 1

H, aromatics), 5.81 [br. d, $^2J(^{31}\text{P}-^1\text{H})$ = 8, $^3J(^{195}\text{P}-^1\text{H})$ = 82 Hz, 1 H, NH], 4.97 [m, $^3J(^{195}\text{P}-^1\text{H})$ = 64 Hz, 1 H, allyl], 4.39 (br. m, 1 H, allyl), 3.37 (m, 1 H, allyl), 2.94 (m, 1 H, allyl) and 2.27 [m, $^3J(^{195}\text{P}-^1\text{H})$ = 71 Hz, 1 H, allyl] ppm. FAB⁺ MS: m/z = 730 [$\text{M} - \text{ClO}_4$]⁺, 689 [$\text{M} - \text{ClO}_4 - \text{C}_3\text{H}_5$]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3185 [br, $\nu(\text{N}-\text{H})$], 1098 [vs (br), $\nu(\text{ClO}_4)$], 907 [m, $\nu(\text{P}-\text{N})$], 623 [m, $\nu(\text{P}=\text{S})$] cm^{-1} .

cis-[PtCl{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -P,S}(PMe₂Ph)][ClO₄] (14): This was prepared in the same way as **12** using **6** (0.142 g, 0.158 mmol) and Ag[ClO₄] (0.032 g, 0.154 mmol). The resulting cream-coloured powder was collected by suction filtration, washed with diethyl ether (3 × 10 mL), and dried in vacuo. Yield: 0.144 g, 95%. ^1H NMR (CDCl_3): δ = 7.93–7.77 (m, 2 H, aromatics), 7.64–7.00 (m, 21 H, aromatics and NH), 6.87 (m, 2 H, aromatics) and 1.38 [d, $^2J(^{31}\text{P}-^1\text{H})$ = 11, $^3J(^{195}\text{Pt}-^1\text{H})$ = 34 Hz, 6 H, PMe] ppm. FAB⁺ MS: m/z = 862 [$\text{M} - \text{ClO}_4$]⁺, 827 [$\text{M} - \text{ClO}_4 - \text{Cl}$]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3216 [br, $\nu(\text{N}-\text{H})$], 1100 [vs (br), $\nu(\text{ClO}_4)$], 910 [s, $\nu(\text{P}-\text{N})$], 622 [m, $\nu(\text{P}=\text{S})$], 302 [w, $\nu(\text{Pt}-\text{Cl})$] cm^{-1} .

trans-[PtMe{Ph₂PNHC₆H₄P(S)Ph₂-P}{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -P,S}][ClO₄] (15): This was prepared in the same way as **12** using **10** (0.150 g, 0.122 mmol) and Ag[ClO₄] (0.026 g, 0.125 mmol). The white solid was collected by suction filtration, washed with diethyl ether (3 × 10 mL), and dried in vacuo. Yield: 0.129 g, 82%. ^1H NMR (CD_2Cl_2): δ = 8.62 [m, $^3J(^{195}\text{Pt}-^1\text{H})$ = 34 Hz, 1 H, NH], 7.77–6.61 (m, 48 H, aromatics), 5.78 [m, $^3J(^{195}\text{Pt}-^1\text{H})$ = 54 Hz, 1 H, NH], –0.20 [br. t, $^2J(^{195}\text{Pt}-^1\text{H})$ = 76, $^3J(^{31}\text{P}-^1\text{H})$ = 15 Hz, 3 H, PtMe] ppm. FAB⁺ MS: m/z = 1197/1198 [$\text{M} - \text{ClO}_4$]⁺, 1182 [$\text{M} - \text{ClO}_4 - \text{Me}$]⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3190 [w, $\nu(\text{N}-\text{H})$], 1100 [vs (br), $\nu(\text{ClO}_4)$], 916 [m, $\nu(\text{P}-\text{N})$], 622 [s, $\nu(\text{P}=\text{S})$] cm^{-1} .

cis-[Pt{Ph₂PNHC₆H₄P(S)Ph₂- κ^2 -P,S}][ClO₄]₂ (16): This was prepared in the same way as **12** using **9** (0.200 g, 0.160 mmol) in CH_2Cl_2 (25 mL) and Ag[ClO₄] (0.068 g, 0.328 mmol). The filtered reaction mixture was concentrated to ca. 2–4 mL, and diethyl ether (20 mL) was added causing an off-white crystalline solid to precip-

Table 3. $^{31}\text{P}\{^1\text{H}\}$ NMR data for complexes of Ph₂PNHC₆H₄P(S)Ph₂. (where P_A = aminophosphane –NHPPH₂ and P_X = thiophosphoryl –P(S)Ph₂ moieties)

Compound	Chemical shifts/ppm		Coupling constants/Hz		
	$\delta(\text{P}_A)$	$\delta(\text{P}_X)$	$^1J(\text{Pt}-\text{P}_A)$	$^2J(\text{Pt}-\text{P}_X)$	$^3J(\text{P}_A-\text{P}_X)$
1 ^[a]	28.2	39.6	—	—	—
2 ^[a]	18.4	39.7	—	—	—
3 ^[a]	47.0 (783) ^[b]	40.0	—	—	—
4 ^[c]	55.3	39.8	—	—	—
5 ^[c]	50.1	39.9	4946	—	—
6 ^{[a][d]}	32.6	39.4	4100	—	—
7 ^[a]	58.2	40.1	—	—	—
8	—	—	—	—	—
9 ^[a]	37.6	40.6	4103	—	—
10	—	—	—	—	—
11 ^[e]	55.3	39.6	2059	—	—
12 ^[c]	69.5	46.4	—	—	16
13 ^[f]	58.3	45.6	4720	123	13
14 ^{[a][g]}	40.5	43.6	3821	47	n.o. ^[h]
15 ^[c]	56.2, [69.4] ^[i]	43.1, [44.7] ^[i]	3192, [3225] ^[i]	70	11, [3] ^[i]
16 ^[e]	48.8	45.3	3649	38	5

^[a] Spectra (36.2 MHz) measured in CDCl_3 . ^[b] Values in parentheses denote $^1J(^{77}\text{Se}-^{31}\text{P})/\text{Hz}$. ^[c] Spectra (109.4 MHz) measured in CDCl_3 . ^[d] Other $^{31}\text{P}\{^1\text{H}\}$ spectral parameters for **6** $\delta(\text{PMe}_2\text{Ph})$ –16.3 [$^1J(^{195}\text{Pt}-\text{PMe}_2\text{Ph})$ 3436 Hz], $^2J(\text{PMe}_2\text{Ph}-\text{P}_A)$ 18 Hz. ^[e] Spectra (101.3 MHz) measured in CD_2Cl_2 . ^[f] Spectra (109.4 MHz) measured in CDCl_3/dms . ^[g] Other $^{31}\text{P}\{^1\text{H}\}$ spectral parameters for **14** $\delta(\text{PMe}_2\text{Ph})$ –4.4(dd) [$^1J(^{195}\text{Pt}-\text{PMe}_2\text{Ph})$ 3390 Hz], $^2J(\text{PMe}_2\text{Ph}-\text{P}_A)$ 15, $^3J(\text{PMe}_2\text{Ph}-\text{P}_X)$ 9 Hz. ^[h] n.o. = Not observed. ^[i] Values in square brackets denote $^{31}\text{P}-\{^1\text{H}\}$ parameters for the chelating (PS) ligand of **15**.

Table 4. Microanalytical data for compounds **1–16** (calculated values in parentheses) where PS = *P*-bound and PS* = *PS*-bound Ph₂PNHC₆H₄P(S)Ph₂

Compound		C	H	N
1	(PS)	73.41 (73.01)	5.46 (5.11) /P'	3.04 (2.84)
2	[P(O)S]	71.69 (70.72)	5.25 (4.95)	2.47 (2.75)
3	[P(Se)S]	62.04 (62.94),	4.43 (4.40)	2.56 (2.45)
4	[PdCl(C ₃ H ₅){PS}]	58.14 (58.59)	3.98 (4.47)	2.01 (2.07)
5	[PtCl(C ₃ H ₅){PS}]	52.08 (51.80)	3.74 (3.95)	1.77 (1.83)
6	[PtCl ₂ (PMe ₂ Ph){PS}]	50.95 (50.84)	3.86 (4.04)	2.27 (1.56)
7	[AuCl{PS}]	49.22 (49.63)	3.57 (3.47)	1.70 (1.93)
8	[PdCl ₂ {PS}] ₂	61.69 (61.89)	4.54 (4.33)	2.37 (2.41)
9	[PtCl ₂ {PS}] ₂	57.20 (57.51)	4.35 (4.02)	2.15 (2.24)
10	[PtClMe{PS}] ₂	60.02 (59.44)	4.34 (4.33)	2.42 (2.27)
11	[PtMe ₂ {PS}] ₂	61.03 (61.43)	4.71 (4.66)	2.14 (2.31)
12	[Pd(C ₃ H ₅){PS*}][ClO ₄]	53.25 (53.53)	3.69 (4.08)	1.87 (1.89)
13	[Pt(C ₃ H ₅){PS*}][ClO ₄]	47.71 (47.80)	3.26 (3.65)	1.61 (1.69)
14	[PtCl(PMe ₂ Ph){PS*}][ClO ₄]	46.73 (47.46)	3.70 (3.77)	1.37 (1.46)
15	[PtMe{PS}{PS*}][ClO ₄]	55.87 (56.50)	4.16 (4.12)	2.24 (2.16)
16	[Pt{PS*}] ₂ [ClO ₄] ₂	51.70 (52.18)	3.53 (3.65)	1.78 (2.03)

itate. The cream-coloured microcrystalline product was collected by suction filtration, washed with diethyl ether (2 × 10 mL) and dried in vacuo. Yield: 0.194 g, 88%. ¹H NMR (CD₂Cl₂): δ = 7.96–7.85 (m, 8 H, aromatics), 7.69–6.88 (m, 36 H, aromatics) and 6.72–6.59 (m, 6 H, aromatics and NH) ppm. FAB⁺ MS: *m/z* = 1281/1282 [M – ClO₄]⁺ and 1182 [M – 2 ClO₄]²⁺. Selected IR data (KBr): $\tilde{\nu}$ = 3164 [br, ν (N–H)], 1099 [vs (br), ν (ClO₄)], 927 [m, ν (P–N)], 623 [s, ν (P=S)] cm^{–1}. The product was consistently contaminated with an impurity (ca. 5%) observed as two triplets in the ³¹P{¹H} NMR spectrum at δ(P) = 42.9 and 55.3 ppm [¹J(¹⁹⁵Pt–³¹P) = 2596 Hz] thought to be *trans*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂-*P*,*S*}₂][ClO₄]₂.

The ³¹P{¹H} spectroscopic and microanalytical data for all new compounds are compiled in Tables 3 and 4, respectively.

X-ray Crystallography: X-ray diffraction measurements were made with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) using a Siemens SMART diffractometer, intensity data 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 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 (SADABS) or by semi-empirical methods.^[44] Structures were solved by direct methods and refined by full-matrix least squares against *F*² (SHELXTL).^[44] All hydrogen atoms (except those on the water molecules of complex **16**, which we have not included in the refinement) were assigned isotropic displacement parameters and were constrained to idealised geometries. All calculations were made with SHELXTL.^[44] C₃₀H₂₅AuClNP₂S (**7**), *M* = 725.9, monoclinic, space group *C2/c*, *a* = 18.2461(2), *b* = 9.3531(2), *c* = 33.2678(3) Å, β = 92.23(1)°, *V* = 5673.1(1) Å³, *T* = 293 K, *Z* = 8, μ(Mo-*K*_α) = 5.487 mm^{–1}, 16863 reflections measured, 6645 unique (*R*_{int} = 0.0475), observed independent reflections 4353, final *R*1[*I* > 2σ(*I*)] = 0.0459. C₆₀H₅₀N₂P₄PtS₂[ClO₄]₂[CH₂Cl₂][H₂O]₂ (**16**), *M* = 1502.0, monoclinic, space group *P2₁/n*, *a* = 12.4175(4), *b* = 20.5319(7), *c* = 13.8955(5) Å, β = 99.38(1)°, *V* = 5673.1(1) Å³, *T* = 293 K, *Z* = 2, μ(Mo-*K*_α) = 2.364 mm^{–1}, 21230 reflections measured, 8178 unique (*R*_{int} = 0.0430), observed independent

reflections 5041, final *R*1[*I* > 2σ(*I*)] = 0.0487. CCDC-164211 and -164212 contain the supplementary crystallographic data for the structures **7** and **16** reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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