Synthesis and Late Transition Metal Complexes of the Heterofunctional Phosphane *o*-$Ph_2PNHC_6H_4P(S)Ph_2$

Stephen M. Aucott,[a] Alexandra M. Z. Slawin,[a] and J. Derek Woollins*[a]

Keywords: Phosphorus−sulfur ligands / Monodentate complexes / Chelate complexes

The difunctional ligand *o*-$Ph_2PNHC_6H_4P(S)Ph_2$ (PS) has been prepared by treatment of the lithium amide salt of 2-(diphenylthiophosphanyl)aniline {2-$[Ph_2P(S)]C_6H_4NH_2$} with Ph_2PCl. The new ligand was oxidised to give the mixed chalcogen species $Ph_2P(E)NHC_6H_4P(S)Ph_2$, by treatment with H_2O_2 (where E = O) or aerial oxidation by recrystallisation from MeOH, and by reaction with Se_8 (where E = Se) in warm toluene. The complexes [M(Cl)(η^3-C_3H_5)(PS)] (M = Pt or Pd), *cis*-[$PtCl_2$(PS)(PMe_2Ph)], [(AuCl)(PS)], *cis*-[$MCl_2(PS)_2$] (M = Pt or Pd), *cis*-[$PtMe_2(PS)_2$] and *trans*-[PtMeCl$(PS)_2$] have been synthesised by reaction of either [Pt(μ-Cl)(μ-η^2:η^1-C_3H_5)]$_4$, [Pd(μ-Cl)(η^3-C_3H_5)]$_2$, [{PtCl(μ-Cl)(PMe_2Ph)}$_2$], [AuCl(tht)] (tht = tetrahydrothiophene), [$PdCl_2$(cod)] or [PtX_2(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 [M(Cl)(η^3-C_3H_5)(PS)] (M = Pt or Pd), *cis*-[$PtCl_2$(PS)(PMe_2Ph)], *cis*-[$PtCl_2(PS)_2$] and *trans*-[PtMeCl$(PS)_2$], using Ag[ClO_4], gave the monocationic [M(η^3-C_3H_5)(PS)][ClO_4] (M = Pt or Pd), *cis*-[PtCl(PS)(PMe_2Ph)][ClO_4], *trans*-[PtMe$(PS)_2$][ClO_4] or dicationic [$Pt(PS)_2$][ClO_4]$_2$ compounds in which the ligand (PS) is κ^2-*P*,*S*-bound. All compounds described here have been characterised by a combination of $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, microanalyses, FAB mass spectrometry and IR spectroscopy. The molecular structures of [AuCl($Ph_2PNHC_6H_4P$-$(S)Ph_2$-*P*)] in which there is an intramolecular hydrogen-bonding interaction between the amine proton and the sulfur atom of the thiophosphoryl group and *trans*-[$Pt(Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*)$_2$][ClO_4]$_2$·CH_2Cl_2·$2H_2O$ in which the perchlorate counterions are associated by hydrogen-bonding interactions to the amine protons of the κ^2-*P*,*S* ligands have been determined by single-crystal X-ray diffraction.

Introduction

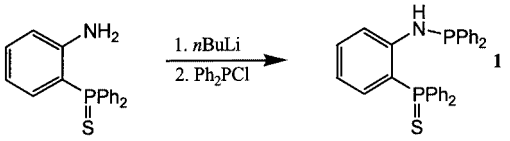
There are numerous examples in the literature of ligands containing both phosphorus and sulfur donor atoms. Meek and co-workers described the preparation of [*o*-(methylthio)phenyl]diphenylphosphane[1] − a ligand with an aromatic backbone which chelates to form five-membered C_2PSM rings.[1,2] Rigo and Bressan prepared a series of P−S donor ligands ($Ph_2PCH_2CH_2SR$) (R = Me, Et and Ph) by the addition of the appropriate chloro derivative $RS(CH_2)_2Cl$ to sodium diphenylphosphide in liquid ammonia.[3] The methylene-bridged ligand Ph_2PCH_2SMe 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−aminophosphane−sulfide ligands including $Ph_2PNHP(S)Ph_2$,[22] $Ph_2PNPhP(S)Ph_2$,[23] in addition to the methylene-, ethylene-, and −$[CH_2]_3$−backboned bis(phosphane−monosulfides) $Ph_2PCH_2P(S)Ph_2$,[24,25] $Ph_2PCH_2CH_2P(S)Ph_2$,[25] and $Ph_2PCH_2CH_2CH_2P(S)Ph_2$,[26] respectively. A logical extension to investigations into the reactivity of $Ph_2PNHC_6H_4PPh_2$ [27,28] is the chemistry of the monochalcogens $Ph_2P(E)NHC_6H_4PPh_2$ or $Ph_2PNHC_6H_4P(E)Ph_2$ (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 $Ph_2PNHC_6H_4P(S)Ph_2$ and investigated its reactivity towards Au^I, Pt^{II}, and Pd^{II}. In addition, we have prepared the mixed chalcogen compounds $Ph_2P(O)NHC_6H_4P(S)Ph_2$ and $Ph_2P(Se)NHC_6H_4P(S)Ph_2$.

[a] School of Chemistry, University of St Andrews, St Andrews, Fife, Scotland KY16 9ST, UK
Fax: (internat.) + 44-1334/4633784
E-mail: jdw3@st-and.ac.uk

Results and Discussion

Preparation and Characterisation of $Ph_2PNHC_6H_4P(S)Ph_2$

Treatment of 2-[diphenyl(thio)phosphanyl]aniline with *n*BuLi, at −78 °C in diethyl ether, followed by reaction with Ph_2PCl, gave **1** in good to excellent yields (71−85%) [Equation (1)].



(1)

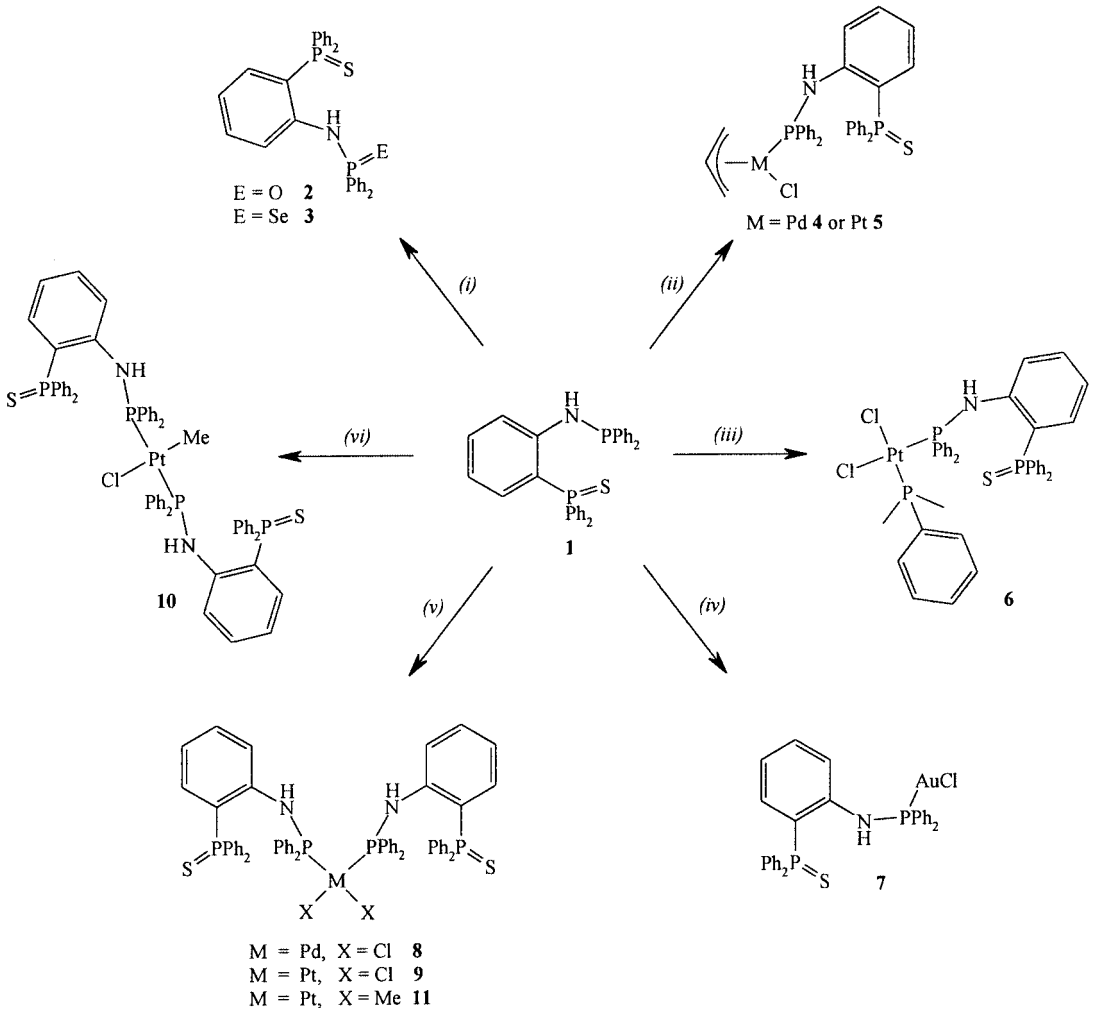
Attempted preparation of the oxo and seleno analogues $Ph_2PNHC_6H_4P(E)Ph_2$ (E = O, Se) under the same conditions resulted in re-isolation of the $Ph_2P(O)C_6H_4NH_2$ starting material and the formation of a complex mixture, respectively. Since the synthesis of the oxo and seleno ligands by the addition of Ph_2PCl to the lithium salt of the appropriate aniline proved unsuccessful, an alternative synthesis was sought. A second possible route to monochalcogen compounds of $Ph_2PNHC_6H_4PPh_2$ is by selective oxidation. This route has been applied to the synthesis of $Ph_2PNHP(E)Ph_2$ (E = O, S and Se).[22,29] A series of experiments involving the reaction of $Ph_2PNHC_6H_4PPh_2$ [27] with a slightly less than stoichiometric quantity of the appropriate chalcogen or aqueous H_2O_2 in various solvent systems at 0 °C gave poor results. These reactions usually resulted in the precipitation of the dichalcogen compounds $Ph_2P(E)NHC_6H_4P(E)Ph_2$,[28] while lesser amounts of starting material and both mixed P^{III},P^{V} species $Ph_2P(E)NHC_6H_4PPh_2$ and $Ph_2PNHC_6H_4P(E)Ph_2$ remain in solution. Separation of these mixtures was not attempted. $Ph_2PNHC_6H_4P(S)Ph_2$ (**1**) was isolated as a colourless solid and displays similar solubilities and the same sensitivity to air or light as $Ph_2PNHC_6H_4PPh_2$. The $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) of **1** displays two single resonances at $\delta(P_A) = 28.2$ ppm and $\delta(P_X) = 39.6$ ppm {the starting material 2-[diphenyl(thio)phosphanyl]aniline has $\delta(P) = 39.6$ ppm} for the $-NHPPh_2$ and $-P(S)Ph_2$ groups, respectively; the $^4J(^{31}P_A\text{-}^{31}P_X)$ coupling was not resolved. The ^1H NMR spectrum (in $CDCl_3$) showed the amine proton as a doublet at $\delta(H) = 5.68$ ppm [$^2J(^{31}P\text{-}^1H) = 9$ 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 $Ph_2P(E)NHC_6H_4P(S)Ph_2$

The syntheses of the mixed chalcogen species are straightforward (Scheme 1). The mixed sulfur,oxygen species $Ph_2P(O)NHC_6H_4P(S)Ph_2$ (**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 $Ph_2P(Se)NHC_6H_4P(S)Ph_2$ (**3**) in good yield (85%). Synthesis and characterisation of the disulfide has been reported elsewhere.[28] The mixed chalcogen species **2** and **3** are air- and moisture-tolerant colourless solids and in common with **1** display two sharp single resonances in their $^{31}P\{^1H\}$ NMR spectra (Table 1) with no observable $^4J(^{31}P_A\text{-}^{31}P_X)$ couplings in addition to amine proton resonances as broad doublets at $\delta(H) = 8.66$ ppm [$^2J(^{31}P\text{-}^1H) = 10$ Hz] (**2**) and $\delta(H) = 8.34$ ppm [$^2J(^{31}P\text{-}^1H) = 8$ 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 $Ph_2PNHC_6H_4P(S)Ph_2$

Treatment of suspensions of the di- and tetranuclear species $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ and $[Pt(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}C_3H_5)]_4$ (in toluene and THF, respectively) with **1**, results in bridge cleavage to give the mononuclear complexes $[MCl(\eta^3\text{-}C_3H_5)(Ph_2PNHC_6H_4P(S)Ph_2\text{-}P)]$ [where M = Pd (**4**) (83%) or Pt (**5**) (88%)] (Scheme 1). The $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectra of **4** and **5** show the $-NHPPh_2$ resonances at $\delta(P) = 55.3$ (**4**) and 51.0 ppm [$^1J(^{195}Pt\text{-}^{31}P)$ 4946 Hz] (**5**) and the pendent $-P(S)Ph_2$ group resonances at $\delta(P) = 39.8$ (**4**) and 39.9 ppm (**5**) which are similar to that of the "free" ligand. The unsymmetrical mixed-ligand complex *cis*-$[PtCl_2\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}(PMe_2Ph)]$ (**6**) was prepared by chloride bridge cleavage of the platinum(II) dimer $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ with **1** in CH_2Cl_2 (Scheme 1). The $^{31}P\{^1H\}$ NMR ($CDCl_3$) 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 $\delta(P) = -16.3$ ppm [$^1J(^{195}Pt\text{-}^{31}P) = 3436$ Hz] assigned to the PMe_2Ph group and $\delta(P) = 32.6$ ppm [$^1J(^{195}Pt\text{-}^{31}P) = 4100$ Hz] to the $-NHPPh_2$ group of **1**. Furthermore, the chemical shift of the pendent $-P(S)Ph_2$ group [$\delta(P) = 39.4$ ppm] is similar to that observed for **1** and displays no platinum satellites indicating no interaction of the $-P(S)Ph_2$ 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*-$PtCl_2$ geometry. The reaction between $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ 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 $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) of the isolated product showed the resonances of **6** and additional lines which display a large $^2J(^{31}P\text{-}^{31}P)$ 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 $^1J(^{195}Pt\text{-}^{31}P)$ couplings that are characteristically smaller than those previously observed for the *cis* isomer **6**. The doublet centred at $\delta(P) = -6.9$ ppm [$^1J(^{195}Pt\text{-}^{31}P) = 2531$ Hz] is assigned to the coordinated PMe_2Ph group and the doublet at $\delta(P) = 46.1$ ppm [$^1J(^{195}Pt\text{-}^{31}P) = 2715$ Hz]



Scheme 1. *(i)* H_2O_2(aq), THF or Se_8, C_6H_5Me, 60 °C; *(ii)* $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$, C_6H_5Me or $[Pt(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}C_3H_5)]_4$, THF; *(iii)* $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$, 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 $[AuCl(Ph_2PNHC_6H_4P(S)Ph_2\text{-}P)]$ (**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 δ(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 $[AuCl\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P\}]$ (**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 δ(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 ν(N−H) band at $\tilde{\nu}$ = 3109 cm^{-1} has undergone a large shift to lower frequency compared to that of **1** [ν(N−H) at $\tilde{\nu}$ = 3223 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 CH_2Cl_2 solution of **7** with diethyl ether. The crystal structure of [AuCl{$Ph_2PNHC_6H_4P(S)Ph_2$-*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 CH_2Cl_2 solution of [$PdCl_2$(cod)] gave a pale-yellow precipitate after only 5 min of stirring. The product, characterised as *cis*-[$PdCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (**8**), was recovered in near quantitative yield (97%). The extreme insolubility of this material in all common organic solvents prevented measurement of its $^{31}P\{^1H\}$, ^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 ν(Pd−Cl), consistent with *cis*-$PdCl_2$ geometry. The ν(NH) stretch at $\tilde{\nu}$ = 3106 cm^{-1} like that of [AuCl{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (**7**) occurs at a much lower frequency than in the "free" ligand [ν(NH) at $\tilde{\nu}$ = 3223 cm^{-1}]. This suggests that the amine protons of *cis*-[$PdCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (**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*-[$PtCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (**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 CH_2Cl_2/diethyl ether as a colourless solid in 88% yield (Scheme 1). Once dry, **9** displayed limited solubility in $CHCl_3$ but was readily soluble in CH_2Cl_2. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) of *cis*-[$PtCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] showed two distinct phosphorus environments at δ(P) = 37.6 ppm [$^1J(^{195}Pt\text{-}^{31}P)$ = 4103] and δ(P) = 40.6 ppm, corresponding to the coordinated phosphorus(III) centres and the "dangling" phosphorus(V) moieties, respectively. The large $^1J(^{195}Pt\text{-}^{31}P_A)$ 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 $-P(S)Ph_2$ group is similar to that found in **1** [δ(P) = 39.6 ppm] implying no interaction with the metal centre. The $^{31}P\{^1H\}$ 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 δ(P) = 40.2 and 40.8 ppm thought to be *trans*-[$PtCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*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 ν(Pt−Cl) stretches at $\tilde{\nu}$ = 311 and 290 cm^{-1}, consistent with a *cis*-$PtCl_2$ geometry. The 2:1 molar ratio reaction of **1** with a CH_2Cl_2 solution of [PtClMe(cod)] results in the deposition of a colourless solid and near-quantitative recovery (98%) of the surprisingly insoluble complex *trans*-[PtClMe{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (**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{$Ph_2PNHC_6H_4P(S)Ph_2$}$_2$]. 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 [$PtMe_2$(cod)] in CH_2Cl_2 produces an off-white powder, characterised as the dimethyl derivative *cis*-[$PtMe_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (**11**), as is evident from the $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) where the much smaller $^1J(^{195}Pt\text{-}^{31}P)$ coupling constant of 2059 Hz is concordant with *cis* (P *trans* to CH_3) geometry. The coordinated $-NHPPh_2$ and "dangling" $-P(S)Ph_2$ group resonances occur at δ(P) = 55.3 and 39.6 ppm, respectively. The ^1H NMR ($CDCl_3$) spectrum displays the amine protons as a broad multiplet at δ(H) = 8.1 ppm and the $PtMe_2$ moiety at δ(H) = 0.20 ppm as a double doublet, flanked by ^{195}Pt satellites [$^2J(^{195}Pt\text{-}^1H)$ = 72 Hz]. In all of the above complexes (**4**−**11**) the IR spectra (KBr) provide additional evidence of coordination through P only showing strong ν(P=S) absorption at $\tilde{\nu} \approx$ 632−634 cm^{-1} ["free" ligand ν(P=S) at $\tilde{\nu}$ = 634 cm^{-1}] which is characteristic of no interaction between the $-P(S)Ph_2$ group and the metal centre.

Bidentate Coordination Chemistry of $Ph_2PNHC_6H_4P(S)Ph_2$

We have previously reported that chelation of the potentially bidentate mixed P^{III},P^V P,O ligand $Ph_2PNHP(O)Ph_2$[34] the P,N ligand Ph_2PNHpy,[35] and the unsymmetric P,P′ ligand $Ph_2PNHC_6H_4PPh_2$[27] can be induced by the use of halide abstractors such as $Ag[BF_4]$ and $Ag[ClO_4]$ in CH_2Cl_2. This preparative technique has been extended with good results to bring about the chelation of monodentate $Ph_2PNHC_6H_4P(S)Ph_2$ (**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(η^3-C_3H_5){$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}][ClO_4] (**12**) and [Pt(η^3-C_3H_5)-

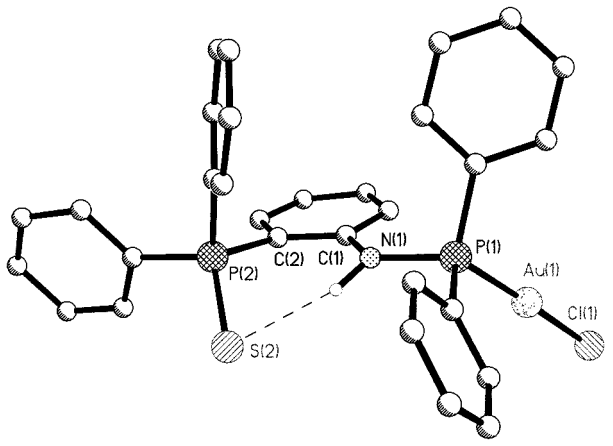
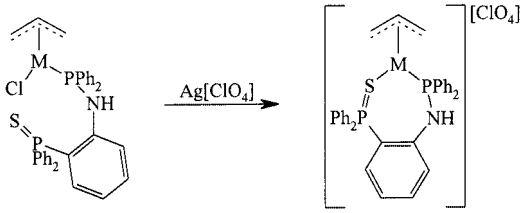


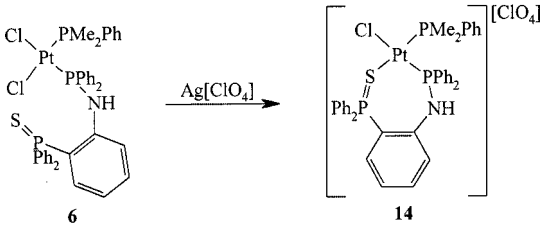
Figure 1. Crystal structure of [AuCl($Ph_2PNHC_6H_4P(S)Ph_2$-*P*)] (**7**)

{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}][ClO_4] (**13**) [Equation (2)] was achieved by the addition of a small excess of Ag[ClO_4] to CH_2Cl_2 solutions of **3** and **4**.

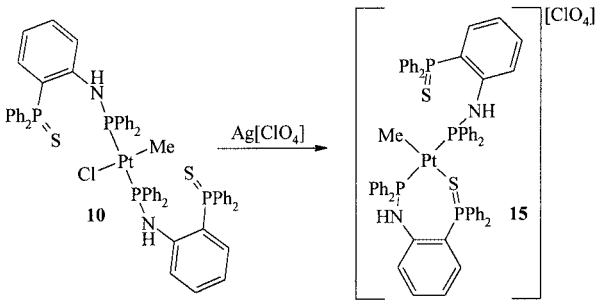


(2)

The products **12** and **13** were isolated in excellent yields (92 and 95%, respectively) as cream-coloured solids. The $^{31}P\{^1H\}$ NMR spectra for complexes **12** and **13** are of the AX type and show two sharp doublets at δ(P^{III}) = 69.5 ppm and δ(P^V) = 46.4 ppm for **12** and δ(P^{III}) = 58.3 ppm and δ(P^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 $^2J(P^{III}\text{-}P^V)$ couplings of 16 (**12**) and 13 Hz (**13**), the corresponding platinum satellites for compound **13** are particularly diagnostic and show a large $^1J(^{195}Pt\text{-}P^{III})$ coupling of 4720 Hz and a much smaller $^2J(^{195}Pt\text{-}P^V)$ coupling of 123 Hz. The complexes *cis*-[PtCl{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}(PMe_2Ph)][ClO_4] (**14**) and *trans*-[PtMe{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}][ClO_4] (**15**) were prepared from *cis*-[$PtCl_2$\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*\}(PMe_2Ph)] (**6**) and *trans*-[PtMeCl{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (**10**) in an identical manner to complexes **12** and **13** [Equations (3) and (4), respectively).



(3)



(4)

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 $^{31}P\{^1H\}$ NMR spectrum of **14** reveals a small $^2J(^{31}P\text{-}^{31}P)$ coupling of 15 Hz, confirming that *cis* geometry was retained upon chelation. The low-frequency double doublet at δ(P) = −4.4 ppm [$^1J(^{195}Pt\text{-}^{31}P)$ = 3390 Hz] is assigned to the PMe_2Ph ligand and displays two P-P couplings, the previously mentioned $^2J(^{31}P\text{-}^{31}P)$ *cis* coupling and a $^3J(^{31}P\text{-}^{31}P)$ *trans* coupling of 9 Hz. The −$NHPPh_2$ group P resonance appears as a doublet at δ(P) = 40.5 ppm [$^1J(^{195}Pt\text{-}^{31}P)$ = 3821 Hz] and displays only the *cis* $^2J(^{31}P\text{-}^{31}P)$ coupling. The high-frequency resonance at δ(P) = 43.6 ppm appears as a doublet and is assigned to the coordinated −$P(S)Ph_2$ group by virtue of the small $^2J(^{195}Pt\text{-}^{31}P)$ coupling of 47 Hz. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) of **15** shows four unique phosphorus environments. The first resonance at δ(P) = 43.1 ppm, assigned to the pendant −$P(S)Ph_2$ group, appears as a singlet with no platinum satellites which is consistent with noncoordinating behaviour. The double doublet resonance at δ(P) = 44.7 ppm, assigned to the coordinated −$P(S)Ph_2$ group of the chelating ligand, shows two distinct $^3J(^{31}P\text{-}^{31}P)$ couplings of 3 and 11 Hz in addition to platinum satellites with a small $^2J(^{195}Pt\text{-}^{31}P)$ coupling of 70 Hz. The doublet at δ(P) = 59.2 ppm, assigned to the −$NHPPh_2$ group of the nonchelating ligand, is coupled to the coordinated P^V centre [$^3J(^{31}P\text{-}^{31}P)$ = 11 Hz] and displays a small $^1J(^{195}Pt\text{-}^{31}P)$ coupling of 3192 Hz which is characteristic of mutual *trans* phosphane geometry. The high-frequency resonance at δ(P) = 64.4 ppm is assigned to the −$NHPPh_2$ 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 [$MCl(\eta^3\text{-}C_3H_5)$\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*\}] [where M = Pd (**4**) or Pt (**5**)] to [$M(\eta^3\text{-}C_3H_5)$\{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*\}][ClO_4] [where M = Pd (**12**) or Pt (**13**)]. The phosphorus atom of this group is *cis*-coupled to the coordinated −$P(S)Ph_2$ group as suggested by the small $^3J(^{31}P\text{-}^{31}P)$ *cis* coupling of 3 Hz. The $^1J(^{195}Pt\text{-}^{31}P)$ 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* $^2J(^{31}P\text{-}^{31}P)$ coupling, which we would expect to be of the order of ca. 500 Hz in magnitude. ($^{31}P\text{-}^{31}P$) 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 $^2J(^{31}P\text{-}^{31}P)$ *trans* coupling between the two coordinated chemically inequivalent $-NHPPh_2$ groups. The ^1H NMR spectrum of **15** (in CD_2Cl_2) is consistent with the proposed structure and shows two multiplets at δ(H) = 8.62 ppm [$^3J(^{195}Pt\text{-}^1H)$ = 34 Hz] and δ(H) = 5.78 ppm [$^3J(^{195}Pt\text{-}^1H)$ = 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 δ(H) = −0.20 ppm with typical $^2J(^{195}Pt\text{-}^1H)$ and $^3J(^{31}P\text{-}^1H)$ couplings of 76 and 15 Hz, respectively. The IR spectrum is diagnostic and shows two ν(N−H) bands at $\tilde{\nu}$ = 3190 and 3144 cm^{-1} and two ν(P=S) bands at $\tilde{\nu}$ = 632 and 622 cm^{-1}, corresponding to pendant and coordinated $-P(S)Ph_2$ groups, respectively. In addition, the ν(P−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*-[$PtCl_2$\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*\}$_2$] (**9**) with 2 equiv. of $Ag[ClO_4]$ in CH_2Cl_2 resulted in abstraction of both chloride ligands and the formation of the dicationic bis(chelate) species *cis*-[Pt\{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*\}$_2$][ClO_4]$_2$ (**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 $^{31}P\{^1H\}$ NMR spectrum at δ(P) = 42.9 and 55.3 ppm [$^1J(^{195}Pt\text{-}^{31}P)$ = 2596 Hz], which was thought to be the *trans* isomer of **16**, formed from the suspected *trans*-[$PtCl_2$\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*\}$_2$] impurity in **9**. The complex is readily soluble in CH_2Cl_2 and MeOH but sparingly so in $CHCl_3$. The ^{31}P NMR spectrum (in CD_2Cl_2) of the platinum complex **16** shows two sets of resonances at δ(P) = 48.8 ppm [$^1J(^{195}Pt\text{-}^{31}P_X)$ = 3649 Hz] and δ(P) = 45.3 ppm [$^2J(^{195}Pt\text{-}^{31}P_A)$ = 38 Hz], corresponding to the coordinated phosphorus(III) and phosphorus(V) groups, respectively. Once again, chelation results in a shift of signals in both phosphorus environments to higher frequency relative to those of the neutral species *cis*-[$PtCl_2$\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*\}$_2$] (**9**) [$\delta(P^{III})$ = 37.6 ppm and $\delta(P^V)$ = 40.6ppm]. The $^1J(^{195}Pt\text{-}^{31}P^{III})$ 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 $J(^{31}P_A\text{-}^{31}P_X)$ coupling constant of 5 Hz. It is unclear whether the observed $J(^{31}P_A\text{-}^{31}P_X)$ coupling of 5 Hz is *cis* or *trans* in origin or a combination of both as the $^{31}P\{^1H\}$ NMR spectra of *cis*-[PtCl\{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*\}(PMe_2Ph)][ClO_4] (**14**) (see above), which has a single PtP_2C_2SN ring, and, as such, no *trans*-P−Pt−S−P grouping, contain no such coupling. However, the $^{31}P\{^1H\}$ NMR spectra of *trans*-[PtMe\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*\}\{$Ph_2PNHC_6H_4P(S)Ph_2$-*k*^{2}-*P*,*S*\}][ClO_4] (**15**) shows two distinct *cis* $^3J(^{31}P_A\text{-}^{31}P_X)$ couplings (see above). The IR spectrum supports the bis(chelate) structure, most notably by the observed shift to lower wavenumber of the ν(P=S) band [623 cm^{-1} vs. 634 cm^{-1} found in **9**] which is a trend also observed in all of the previously described k^2-*P*,*S* chelate complexes (**12**−**15**). An attempt to grow crystals of *cis*-[Pt\{$Ph_2PNHC_6H_4P(S)Ph_2$-*k*^{2}-*P*,*S*\}$_2$][ClO_4]$_2$ (**16**), suitable for X-ray crystallographic analysis by layering a CH_2Cl_2 solution with diethyl ether, resulted in crystallisation of the *trans* isomer. A $^{31}P\{^1H\}$ NMR study of CD_2Cl_2 and CD_2Cl_2/Et_2O 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\{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-

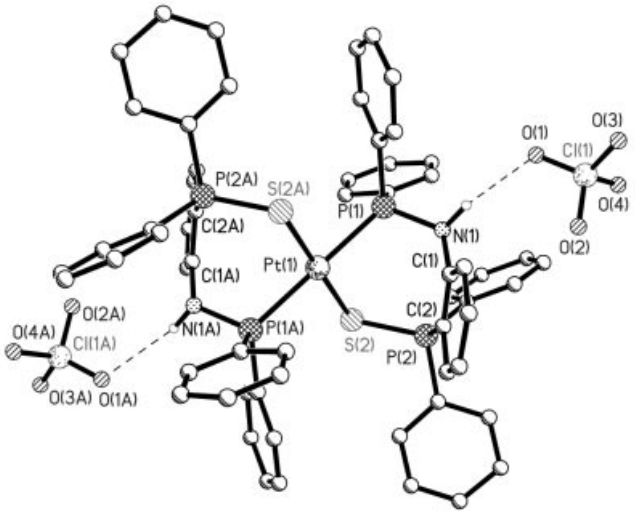


Figure 2. Crystal structure of *trans*-[Pt\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*,*S*\}$_2$][ClO_4]$_2$·CH_2Cl_2·$2H_2O$; the CH_2Cl_2 and water molecules are omitted for clarity

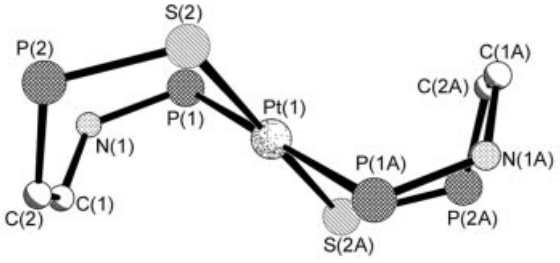


Figure 3. Core geometry of *trans*-[Pt\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*,*S*\}$_2$][ClO_4]$_2$

Table 2. Selected bond lengths [Å] and angles [°] for *trans*-[Pt\{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*,*S*\}$_2$][ClO_4]$_2$·CH_2Cl_2·$2H_2O$

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)···O(2) 2.27(7) Å, O(1)···N(1) 3.03(1) Å, N(1)−H(1n)···O(1) 134(7)°]. 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 *t*BuOK, to afford neutral chelate ring metallacycles.[29,30] Upon reaction of complexes **8** and **9** with *t*BuOK 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 $[M\{Ph_2PNC_6H_4P(S)Ph_2$-κ^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 *t*BuOK 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 currently 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 $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$,[36] $[Pt(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}C_3H_5)]_4$,[37] $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$,[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 × 10 mL) and dried overnight in vacuo. Yield: 4.07 g, 85%. ^1H NMR ($CDCl_3$): δ = 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, $^2J(^{31}P\text{-}^1H)$ = 9 Hz, 1 H, NH] ppm. FAB^+ MS: m/z = 494 $[M]^+$. Selected IR data (KBr): $\tilde{\nu}$ = 3223 [br, ν(N−H)], 896 [vs, ν(P−N)], 634 [vs, ν(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 × 5 mL) and dried in vacuo. Yield: 0.445 g, 90%. ^1H NMR ($CDCl_3$): δ = 8.66 [br. d, $^2J(^{31}P\text{-}^1H)$ = 10 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,ν(N−H)], 1212 [s, ν(P=O)], 924 [s, ν(P−N)], 632 [vs, ν(P=S)] cm^{-1}. **Method B:** $Ph_2PNHC_6H_4P(S)Ph_4$ (**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%. $^{31}P\{^1H\}$ NMR ($CDCl_3$) and microanalytical data are similar to those of the material generated by Method A.

$Ph_2P(Se)NHC_6H_4P(S)Ph_2$ (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 ($CDCl_3$): δ = 8.34 [br. d, $^2J(^{31}P\text{-}^1H)$ = 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, ν(N−H)], 925 [vs, ν(P−N)], 631 [s, ν(P=S)], 548 [vs, ν(P=Se)] cm^{-1}.

[PdCl(η³-C_3H_5){$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (4): To a stirred toluene (15 mL) suspension of [Pd(μ-Cl)(η³-C_3H_5)]$_2$ (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 ($CDCl_3$): 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 $[M - Cl - C_3H_5]^{2+}$. Selected IR data (KBr): $\tilde{\nu}$ = 3144 [br, ν(N−H)], 912 [m, ν(P−N)], 632 [m, ν(P=S)] cm^{-1}.

[PtCl(η³-C_3H_5){$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (5): To a stirred THF (20 mL) suspension of [Pt(μ-Cl)(μ-η²:η¹-C_3H_5)]$_4$ (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 ($CDCl_3$): δ = 8.07 [s, $^3J(^{195}Pt\text{-}^1H)$ = 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, $^3J(^{195}Pt\text{-}^1H)$ = 78 Hz, 1 H, allyl] ppm. FAB^+ MS: *m*/*z* = 765 $[M]^+$, 730 $[M - Cl]^+$, 689 $[M - Cl - C_3H_5]^{2+}$. Selected IR data (KBr): $\tilde{\nu}$ = 3142 [br, ν(N−H)], 912 [s, ν(P−N)], 634 [s, ν(P=S)], 298 [w, ν(Pt−Cl)] cm^{-1}.

***cis*-[$PtCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}(PMe_2Ph)] (6):** To a stirred CH_2Cl_2 (25 mL) solution of [{PtCl(μ-Cl)(PMe_2Ph)}$_2$] (0.126 g, 0.156 mmol) was added dropwise over 10 min a CH_2Cl_2 (20 mL) solution of **1** (0.154 g, 0.312 mmol). The resulting pale yellow solution 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 ($CDCl_3$): 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, $^2J(^{31}P\text{-}^1H)$ = 11, $^3J(^{195}Pt\text{-}^1H)$ = 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, ν(N−H)], 912 [s, ν(P−N)], 634 [m, ν(P=S)], 317 (w) + 291 (w) [ν(PtCl)] cm^{-1}.

[AuCl{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}] (7): To a stirred solution of [AuCl(tht)] (0.045 g, 0.140 mmol) in CH_2Cl_2 (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 ($CDCl_3$): δ = 8.00 [br. d, $^2J(^{31}P\text{-}^1H)$ = 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, ν(N−H)], 927 [m, ν(P−N)], 632 [s, ν(P=S)], 339 [w, ν(Au−Cl)] cm^{-1}.

***cis*-[$PdCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (8):** To a stirred solution of [$PdCl_2$(cod)] (0.078 g, 0.273 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (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, ν(N−H)], 919 [vs, ν(P−N)], 632 [vs, ν(P=S)], 318 (w) + 298 (w) [ν(Pd−Cl)] cm^{-1}.

***cis*-[$PtCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (9):** This compound was prepared in the same way as **8** using [$PtCl_2$(cod)] (0.051 g, 0.136 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (5 mL) and reprecipitated by slow addition of diethyl ether (30 mL), washed with ice-cold CH_2Cl_2/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 (CD_2Cl_2): δ = 7.90 [br. d, $^2J(^{31}P\text{-}^1H)$ = 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, ν(N−H)], 920 [s, ν(P−N)], 634 [s, ν(P=S)], 311 (w) + 290 (w) [ν(Pt−Cl)] cm^{-1}. The product was consistently contaminated with an impurity (ca. 4−5%) observed as two singlets in the $^{31}P\{^1H\}$ NMR at δ(P) = 40.2 and 40.8 ppm, thought to be *trans*-[$PtCl_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$].

***trans*-[PtClMe{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (10):** This was prepared in the same way as **8** using [PtClMe(cod)] (0.093 g, 0.263 mmol) in CH_2Cl_2 (4 mL) and **1** (0.270 g, 0.547 mmol). The white solid was collected by suction filtration, washed with CH_2Cl_2 (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, ν(N−H)], 911 [vs, ν(P−N)], 633 [vs, ν(P=S)], 288 [w, ν(Pt−Cl)] cm^{-1}.

***cis*-[$PtMe_2${$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}$_2$] (11):** This was prepared in the same way as **8** using [$PtMe_2$(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%. ^{1}H NMR ($CDCl_3$): δ = 8.10 (m, 2 H, NH), 7.86−6.59 (m, 48 H, aromatics) and 0.20 [dd, $^2J(^{195}Pt\text{-}^1H)$ = 72 Hz, 6 H, PtMe] ppm. FAB$^+$ MS: *m*/*z* = 1235 [M + Na]$^+$, 1212 [M]$^+$ and 1196 [M − Me]$^+$. Selected IR data (KBr): $\tilde{\nu}$ = 3168 [br, ν(N−H)], 902 [s, ν(P−N)], 634 [s, ν(P=S)] cm^{-1}.

[Pd(η^3-C_3H_5){$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}][ClO_4] (12): To a stirred CH_2Cl_2 (15 mL) solution of **4** (0.171 g, 0.253 mmol) was added Ag[ClO_4] (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%. ^{1}H 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, $^2J(^{31}P\text{-}^1H)$ = 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, $J(^1H\text{-}^1H)$ = 13 Hz, 1 H, allyl] ppm. FAB$^+$ MS: *m*/*z* = 641 [M − ClO_4]$^+$, 600 [M − ClO_4 − C_3H_5]$^{2+}$. Selected IR data (KBr): $\tilde{\nu}$ = 3196 [br, ν(N−H)], 1099 [vs (br), ν(ClO_4)], 907 [s, ν(P−N)], 622 [s, ν(P=S)] cm^{-1}.

[Pt(η^3-C_3H_5){$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}][ClO_4] (13): This was prepared in the same way as **12** using **5** (0.183 g, 0.239 mmol) and Ag[ClO_4] (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%. ^{1}H NMR (CD_2Cl_2): δ = 7.88−6.95 (m, 23 H, aromatics), 6.63 (m, 1 H, aromatics), 5.81 [br. d, $^2J(^{31}P\text{-}^1H)$ = 8, $^3J(^{195}P\text{-}^1H)$ = 82 Hz, 1 H, NH], 4.97 [m, $^3J(^{195}P\text{-}^1H)$ = 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, $^3J(^{195}P\text{-}^1H)$ = 71 Hz, 1 H, allyl] ppm. FAB$^+$ MS: *m*/*z* = 730 [M − ClO_4]$^+$, 689 [M − ClO_4 − C_3H_5]$^{2+}$. Selected IR data (KBr): $\tilde{\nu}$ = 3185 [br, ν(N−H)], 1098 [vs (br), ν(ClO_4)], 907 [m, ν(P−N)], 623 [m, ν(P=S)] cm^{-1}.

***cis*-[PtCl{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}(PMe_2Ph)][ClO_4] (14):** This was prepared in the same way as **12** using **6** (0.142 g, 0.158 mmol) and Ag[ClO_4] (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%. ^{1}H 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, $^2J(^{31}P\text{-}^1H)$ = 11, $^3J(^{195}Pt\text{-}^1H)$ = 34 Hz, 6 H, PMe] ppm. FAB$^+$ MS: *m*/*z* = 862 [M − ClO_4]$^+$, 827 [M − ClO_4 − Cl]$^{2+}$. Selected IR data (KBr): $\tilde{\nu}$ = 3216 [br, ν(N−H)], 1100 [vs (br), ν(ClO_4)], 910 [s, ν(P−N)], 622 [m, *ν*(P=S)], 302 [w, *ν*(Pt-Cl)] cm^{-1}.

***trans*-[PtMe{$Ph_2PNHC_6H_4P(S)Ph_2$-*P*}{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}][ClO_4] (15):** This was prepared in the same way as **12** using **10** (0.150 g, 0.122 mmol) and Ag[ClO_4] (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%. ^{1}H NMR (CD_2Cl_2): δ = 8.62 [m, $^3J(^{195}Pt\text{-}^1H)$ = 34 Hz, 1 H, NH], 7.77−6.61 (m, 48 H, aromatics), 5.78 [m, $^3J(^{195}Pt\text{-}^1H)$ = 54 Hz, 1 H, NH], −0.20 [br. t, $^2J(^{195}Pt\text{-}^1H)$ = 76, $^3J(^{31}P\text{-}^1H)$ = 15 Hz, 3 H, PtMe] ppm. FAB$^+$ MS: *m*/*z* = 1197/1198 [M − ClO_4]$^+$, 1182 [M − ClO_4 − Me]$^+$. Selected IR data (KBr): $\tilde{\nu}$ = 3190 [w, ν(N−H)], 1100 [vs (br), ν(ClO_4)], 916 [m, *ν*(P−N)], 622 [s, ν(P=S)] cm^{-1}.

***cis*-[Pt{$Ph_2PNHC_6H_4P(S)Ph_2$-κ^2-*P*,*S*}$_2$][ClO_4]$_2$ (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[ClO_4] (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. $^{31}P\{^1H\}$ NMR data for complexes of $Ph_2PNHC_6H_4P(S)Ph_2$. (where P_A = aminophosphane −NHPPh$_2$ and P_X = thiophosphoryl −P(S)Ph$_2$ moieties)

Compound	Chemical shifts/ppm		Coupling constants/Hz		
	δ(P_A)	δ(P_X)	^1J(Pt-P_A)	^2J(Pt-P_X)	^3J(P_A-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[e]	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 $^1J(^{77}Se\text{-}^{31}P)$/Hz. [c] Spectra (109.4 MHz) measured in $CDCl_3$. [d] Other $^{31}P\{^1H\}$ spectral parameters for **6** δ (PMe_2Ph) −16.3 [$^1J(^{195}Pt-PMe_2Ph)$ 3436 Hz], $^2J(PMe_2Ph\text{-}P_A)$ 18 Hz. [e] Spectra (101.3 MHz) measured in CD_2Cl_2. [f] Spectra (109.4 MHz) measured in $CDCl_3$/dmso. [g] Other $^{31}P\{^1H\}$ spectral parameters for **14** δ (PMe_2Ph) −4.4(dd) [$^1J(^{195}Pt-PMe_2Ph)$ 3390 Hz], $^2J(PMe_2Ph\text{-}P_A)$ 15, $^3J(PMe_2Ph\text{-}P_x)$ 9 Hz. [h] n.o. = Not observed. [i] Values in square brackets denote $^{31}P\text{-}\{^1M\}$ 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 $Ph_2PNHC_6H_4P(S)Ph_2$

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	$[PdCl(C_3H_5)\{PS\}]$	58.14 (58.59)	3.98 (4.47)	2.01 (2.07)
5	$[PtCl(C_3H_5)\{PS\}]$	52.08 (51.80)	3.74 (3.95)	1.77 (1.83)
6	$[PtCl_2(PMe_2Ph)\{PS\}]$	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	$[Pd(C_3H_5)\{PS^*\}][ClO_4]$	53.25 (53.53)	3.69 (4.08)	1.87 (1.89)
13	$[Pt(C_3H_5)\{PS^*\}][ClO_4]$	47.71 (47.80)	3.26 (3.65)	1.61 (1.69)
14	$[PtCl(PMe_2Ph)\{PS^*\}][ClO_4]$	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 (CD_2Cl_2): 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 $[M - ClO_4]^+$ and 1182 $[M - 2\ ClO_4]^{2+}$. Selected IR data (KBr): $\tilde{\nu}$ = 3164 [br, ν(N−H)], 1099 [vs (br), ν(ClO_4)], 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 $^{31}P\{^1H\}$ NMR spectrum at δ(P) = 42.9 and 55.3 ppm [$^1J(^{195}Pt-^{31}P)$ = 2596 Hz] thought to be *trans*-$[Pt\{Ph_2PNHC_6H_4P(S)Ph_2\text{-}P,S\}_2][ClO_4]_2$.

The $^{31}P\{^1H\}$ 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). 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] $C_{30}H_{25}AuClNP_2S$ (**7**), *M* = 725.9, monoclinic, space group *C*2/*c*, *a* = 18.2461(2), *b* = 9.3531(2), *c* = 33.2678(3) Å, β = 92.23(1)°, *V* = 5673.1(1) Å^3, *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[$I > 2\sigma(I)$] = 0.0459. $C_{60}H_{50}N_2P_4PtS_2[ClO_4]_2[CH_2Cl_2][H_2O]_2$ (**16**), *M* = 1502.0, monoclinic, space group $P2_1/n$, *a* = 12.4175(4), *b* = 20.5319(7), *c* = 13.8955(5) Å, β = 99.38(1)°, *V* = 5673.1(1) Å^3, *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[$I > 2\sigma(I)$] = 0.0487. CCDC-164211 and -164212 contain the supplementary crystallographic data for 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].

Acknowledgments

We should like to thank the EPSRC for financial support and Johnson Matthey for the loan of precious metals. We would also like to thank the Joint Research Equipment Initiative for equipment grants.

[1] M. E. Workmann, G. Dyer, D. W. Meek, *Inorg. Chem.* **1967**, *6*, 1543−1548.
[2] A. Benefiel, D. M. Roundhill, W. C. Fultz, A. L. Rheingold, *Inorg. Chem.* **1984**, *23*, 3316−3324.
[3] P. Rigo, M. Bressan, *Inorg. Chem.* **1975**, *14*, 1491−1494.
[4] G. K. Anderson, R. Kumar, *Inorg. Chim. Acta* **1985**, 97, L21−L23.
[5] G. K. Anderson, R. Kumar, *J. Organomet. Chem.* **1988**, *342*, 263−268.
[6] E. W. Abel, J. C. Dormer, D. Ellis, K. G. Orrell, V. Sik, M. B. Hursthouse, M. A. Mazid, *J. Chem. Soc., Dalton Trans.* **1992**, 1073−1080.
[7] A. D. Zotto, P. Rigo, *Inorg. Chim. Acta* **1988**, *147*, 55−59.
[8] M. Bressan, C. Bonuzzi, F. Morandini, A. Morvillo, *Inorg. Chim. Acta* **1991**, *182*, 153−156.
[9] P. Di Bernardo, M. Tolazzi, P. Zanonato, *J. Chem. Soc., Dalton Trans.* **1995**, 1349−1355.
[10] K. Issleib, W. Gans, *Z. Anorg. Allg. Chem.* **1981**, *475*, 116−130.
[11] K. Issleib, W. Gans, *Z. Anorg. Allg. Chem.* **1982**, *491*, 163−174.
[12] P. H. Leung, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1992**, *31*, 1406−1410.
[13] S. T. Liu, D. R. Hou, T. C. Lin, M. C. Cheng, S. M. Peng, *Organometallics* **1995**, *14*, 1529−1532.
[14] U. Kunze, H. Jawad, E. Boziaris, *J. Organomet. Chem.* **1986**, *312*, 67−80.
[15] M. Alvarez, N. Lugan, B. Donnadieu, R. Mathieu, *Organometallics* **1995**, *14*, 365−370.
[16] M. Alvarez, N. Lugan, B. Donnadieu, R. Mathieu, *Inorg. Chem.* **1993**, *32*, 5652−5657.

[17] O. Clot, M. O. Wolf, G. P. A. Yap, B. O. Patrick, *J. Chem. Soc., Dalton Trans.* **1995**, 2729−2737.
[18] S. Y. Siah, P. H. Leung, K. F. Mok, *Polyhedron* **1994**, *13*, 3253−3255.
[19] S. O. Grim, P. H. Smith, I. J. Colquhoun, W. McFarlane, *Inorg. Chem.* **1980**, *19*, 3195−3198.
[20] I. J. Colquhoun, S. O. Grim, W. McFarlane, J. D. Mitchell, P. H. Smith, *Inorg. Chem.* **1981**, *20*, 2516−2521.
[21] T. C. Blagborough, R. Davis, P. Ivison, *J. Organomet. Chem.* **1994**, *467*, 85−94.
[22] P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1995**, 3189−3194.
[23] M. S. Balakrishna, R. Klien, S. Uhlenbrock, A. A. Pinkerton, R. G. Cavell, *Inorg. Chem.* **1993**, *32*, 5676−5681.
[24] M. J. Baker, M. F. Giles, A. G. Orpen, M. J. Taylor, R. J. Watt, *J. Chem. Soc., Chem. Commun.* **1995**, 197−198.
[25] G. P. Suranna, P. Mastrorilli, C. F. Nobile, W. Keim, *Inorg. Chim. Acta* **2000**, *305*, 151−156.
[26] I. M. Aladzheva, O. V. Bykhovskaya, D. I. Lobanov, P. V. Petrovskii, M. Y. Antipin, K. A. Lysenko, T. A. Mastryukova, M. I. Kabachnik, *Phosphorus, Sulfur, Silicon* **1996**, *111*, 116.
[27] S. M. Aucott, A. M. Z. Slawin, J. D. Woollins, *J. Organomet. Chem.* **1999**, *582*, 83−89.
[28] S. M. Aucott, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2001**, 2279−2287.
[29] P. Haake, R. M. Pfeiffer, *J. Chem. Soc., Chem. Commun.* **1969**, 1330.
[30] P. Haake, R. M. Pfeiffer, *J. Am. Chem. Soc.* **1970**, *92*, 4996−4997.
[31] P. Haake, R. M. Pfeiffer, *J. Am. Chem. Soc.* **1970**, *92*, 5243.
[32] D. G. Cooper, J. Powell, *J. Am. Chem. Soc.* **1973**, *95*, 1102−1108.
[33] A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1996**, 4567−4573.
[34] P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *Inorg. Chem.* **1996**, *35*, 3675−3682.
[35] S. M. Aucott, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2000**, 2559−2575.
[36] A. L. Balch, L. S. Benner, *Inorg. Synth.* **1990**, *28*, 340−342.
[37] J. Lukas, *Inorg. Synth.* **1974**, *15*, 75−81.
[38] W. Baratta, P. S. Pregosin, *Inorg. Chim. Acta* **1993**, *209*, 85−87.
[39] H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411−428.
[40] E. Costa, P. G. Pringle, M. Ravetz, *Inorg. Synth.* **1997**, *31*, 284−292.
[41] D. Drew, J. R. Doyle, *Inorg. Synth.* **1972**, *13*, 47−55.
[42] J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521−6528.
[43] R. Uson, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *26*, 85−91.
[44] *SHELXTL, Structure Solution and Determination Package*, Bruker AXS, Madison, WI, USA, **1999**.

Received February 4, 2002
[I02057]