New Inorganic Metallacycles and the First Six-Membered Covalent "True" Heterocycle − Oxidation of $RC(E)NHPPh_2$ (E = O or S; R = H_2N, Ph, or Py) with O, S, or Se to Give $RC(E)NHP(E')Ph_2$ (E′ = O, S, Se) and Their Coordination Chemistry

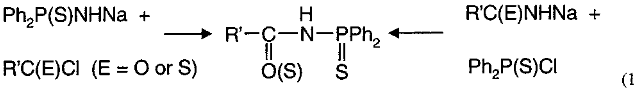
David J. Birdsall,[a] Jason Green,[a] Tuan Q. Ly,[a] Josef Novosad,[b] Marek Necas,[b] Alexandra M. Z. Slawin,[a] J. Derek Woollins,*[a] and Zdirak Zak[b]

Keywords: Metallacycles / Solid-state structures / Heterocycles / Oxidations

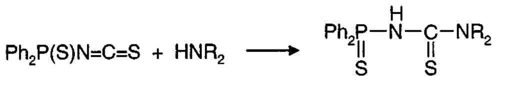
Direct oxidation of $PhC(O)NHPPh_2$, $H_2NC(S)NHPPh_2$, $(C_5H_4N)C(S)NHPPh_2$ with O_2, S_8, or Se gives $[PhC(O)NHP(O)Ph_2]$ (**1**), $[H_2NC(S)NHP(S)Ph_2]$ (**2**), $[H_2NC(O)NHP(S)Ph_2]$ (**3**), $[PhC(O)NHP(S)Ph_2]$ (**4**), $[(C_5H_4N)C(S)NHP(S)Ph_2]$ (**5**), and $[H_2NC(S)NHP(Se)Ph_2]$ (**6**). Deprotonation of **1**, **2**, **4**–**6** with potassium *tert*-butoxide gives $K[PhC(O)NP(O)Ph_2]$ (**7**), $K[H_2NC(S)NP(S)Ph_2]$ (**8**), $K[PhC(O)NP(S)Ph_2]$ (**9**), $K[(C_5H_4N)C(S)NP(S)Ph_2]$ (**10**), and $K[H_2NC(S)NP(Se)Ph_2]$ (**11**). Reaction of **4** with KOBu and $[Cu(Ph_3P)_2][NO_3]$ gives $[Cu(Ph_3P)(PhC(O)NP(S)Ph_2)]$ (**12**) which is the first crystallographically characterised example of a non-ionic six-membered "true" heterocycle (i.e. a ring in which every heterocatom is different). **9** and **10** were treated with $[PdCl_2(COD)]$ to give $[Pd\{PhC(O)NP(S)Ph_2\}_2]$ (**13**) and $[Pd\{(C_5H_4N)C(O)NP(S)Ph_2\}_2]$ (**14**), respectively The anion of **8** coordinates to zinc forming $[Zn\{H_2NC(S)NP(S)Ph_2\}_2]$ (**15**). Treatment of **2** or **8** with $[PtCl_2(COD)]$ gives $[Pt\{H_2NC(S)NP(S)Ph_2\}\{H_2NC(S)NHP(S)Ph_2\}]^+Cl^-$ (**16**) and $[Pt\{H_2NC(S)NP(S)Ph_2\}_2]$ (**17**), respectively. The X-ray structures of **12**, **15–17** are reported.

Introduction

We have reported extensively[1] on the coordination chemistry of imidophosphinates in part as a consequence of their relationship to *acac*. Furthermore, monochalcogenides and molecules of the type $[Ph_2PNHP(E)Ph_2]$ (E = O, S, or Se)[2−11] have been developed and shown to chelate to range of late transition metals through both phosphorus and chalcogen donor atoms. The chemistry of phosphane derivatives of urea and thiourea were first studied during the 1960s. Three known methods of preparing such derivatives are shown below (Equation 1 and 2).[12−20]



$$Ph_2P(S)NHNa + R'C(E)Cl\ (E = O\ or\ S) \longrightarrow R'{-}\underset{\|\atop O(S)}{C}{-}\overset{H}{N}{-}\underset{\|\atop S}{P}Ph_2 \longleftarrow R'C(E)NHNa + Ph_2P(S)Cl \quad (1)$$



$$Ph_2P(S)N{=}C{=}S + HNR_2 \longrightarrow Ph_2\underset{\|\atop S}{P}{-}\overset{H}{N}{-}\underset{\|\atop S}{C}{-}NR_2 \quad (2)$$

Schmutzler et al. reported that the reaction of thiourea and chlorodiphenylphosphane at −20 °C did not give the expected *N*,*N*′-bis(diphenylphosphanyl)thiourea, $Ph_2PHNC(S)NHPPh_2$, but only gave $Ph_2P{-}P(S)Ph_2$.[21] Later, Bhattacharyya et al. carried out the reaction at room temperature and obtained *N*,*N*′-bis(diphenylphosphanyl)-thiourea in up to 46 % yield.[22] We have recently described[23] the formation of some phosphanylurea and related systems Here, we report on the oxidation of the phosphanylurea and phosphanyl-thiourea derivatives. Demonstrative examples of coordination complexes are also described, including the first example of a non-ionic six-membered "true" heterocycle.

Results and Discussion

The ligands were synthesised by direct oxidation of the phosphanylureas or phosphanylthioureas with the appropriate oxidising reagents generalised in Equation 1. $PhC(O)NHPPh_2$ oxidises readily with oxygen by dissolving it in tetrahydrofuran and stirring overnight exposed to air. However, $H_2NC(S)NHPPh_2$ is more stable and does not oxidise in air, when treated with aqueous hydrogen peroxide as well as the oxidation of P^{III} to P=O, most of the C=S is converted into C=O in the course of the reaction, the by-product, $H_2NC(O)NHP(O)Ph_2$,was identified by ^{31}P-NMR, infrared, and mass spectroscopy.

Oxidation of the phosphanylurea/thiourea derivatives by elemental sulfur is readily achieved in tetrahydrofuran at room temperature. $H_2NC(O/S)NHPPh_2$ react with S_8 to form (Equation 3) $[H_2NC(S)NHP(S)Ph_2]$ (**2**) and $[H_2NC(O)NHP(S)Ph_2]$ (**3**), respectively. Treatment of $RC(O)NHPPh_2$ (R = Ph and Py, 3-C_5H_4N, Py = pyridyl) with S_8 gave $[PhC(O)NHP(S)Ph_2]$ (**4**) and $[PyC(O)NHP(S)Ph_2]$ (**5**), respectively.

$[H_2NC(S)NHP(Se)Ph_2]$ (**6**) was prepared by allowing $H_2NC(S)NHPPh_2$ to react with grey selenium in tetrahydrofuran with warming for one hour. The solution was then filtered and its solvent removed to give a white powder.

---

[a] Department of Chemistry, University of St Andrews,
St Andrews, Scotland KY16
E-mail: J.D.Woollins@st-and.ac.uk
[b] Department of Chemistry, Masaryk University, Czech Republic

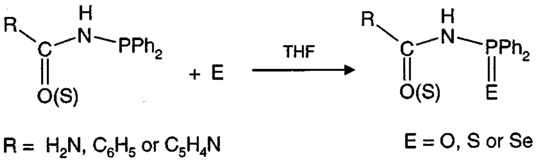
1434−1948/99/0909−1445 $ 17.50+.50/0

Table 1. $^{31}P-\{^1H\}$ NMR [ppm, relative to 85% H_3PO_4] for compounds **1−11**

	δ =		δ =
1 [PhC(O)NHP(O)Ph_2]	24	**7** K[PhC(O)NP(O)Ph_2]	17
2 [H_2NC(S)NHP(S)Ph_2]	52	**8** K[H_2NC(S)NP(S)Ph_2]	37
3 [H_2NC(O)NHP(S)Ph_2]	53		
4 [PhC(O)NHP(S)Ph_2]	56	**9** K[PhC(O)NP(S)Ph_2]	44
5 [PyC(O)NHP(S)Ph_2]	56	**10** K[PyC(O)NP(S)Ph_2]	41
6 [H_2NC(S)NHP(Se)Ph_2]	45	**11** K[H_2NC(S)NP(Se)Ph_2]	29
Note: Py = 3-C_5H_4N	[^1J(PSe) 783]		[^1J(PSe) 530]

Table 2. Selected infrared data [cm^{-1}] in compounds **1−11**

	ν(NH)	ν(CO, S)	ν(CN)	ν(PN)	ν(PO, S, Se)
1 [PhC(O)NHP(O)Ph_2]	3107m-sh, 3066 s	1669 vs	1456 vs	838 s, 807 w	1199 vs
2 [H_2NC(S)NHP(S)Ph_2]	3381 w, 3294 s, 3074 s	1054 s	1484 vs	835 s, 810 s	642 s, 632 s
3 [H_2NC(O)NHP(S)Ph_2]	3492m, 3333m, 3187m	1704 vs, 1682 vs, 1650 vs	1477 vs	912m, 872 w	636m
4 [PhC(O)NHP(S)Ph_2]	3159m, 3070m	1651 vs	1454 vs	880 w, 832m	636 vs
5 [PyC(O)NHP(S)Ph_2]	3368 vw, 3182 s	1656 vs	1482m	842m, 815m	639 vs
6 [H_2NC(S)NHP(Se)Ph_2]	3364 w, 3284m, 3072m	1052m	1482 vs	832 s, 807 s	555 vs
7 K[PhC(O)NP(O)Ph_2]		1523 vs	1591 s	896 s, 842 s	1141 s
8 K[H_2NC(S)NP(S)Ph_2]	3364m, 3280m, 3164 w			856 vw, 836 vw	624m, 607 s
9 K[PhC(O)NP(S)Ph_2]		1519 vs	1588m	895 w, 838 s	627 s, 612 s
10 K[PyC(O)NP(S)Ph_2]	3322 vw, 3237 vw	1526 vs	1590 vs	906 s, 830 vs	626 vs, 613 vs
11 K[H_2NC(S)NP(Se)Ph_2]	3353m, 3162m			885 w, 851 w	544 vs



(3)

After trituration with diethyl ether the product was obtained in 67 % yield.

All of the compounds are air stable colourless solids except **6** which turns red when exposed to air over a week; it can be stored under nitrogen almost indefinitely. The ^{31}P-NMR showed the shifts of P^{III} to P^V shown in Table 1. All the P=O, S, and Se derivatives display singlets in their phosphorus NMR spectra.

Compounds **1−6** can exist in three tautomeric forms (**A** − **C**, Figure 1). Their infrared spectra (Table 2) suggest form (**B**) is predominant in the solid state. The spectra of the compounds show peaks at around 3200 cm^{-1} indicating ν(NH) character. The vibrations at around 1665 cm^{-1} and 1100 cm^{-1} are indicative of ν(C=O) and ν(C=S) double bonds. The bands at around 1470 cm^{-1} are characteristic of ν(C−N) single bond [lower than ca. 1650 cm^{-1} for ν(C=N)]. All these compounds also have bands around 850 cm^{-1} reflecting the single bond character of ν(PN) compared to the double bond vibration at higher frequency around 1300 cm^{-1}. Furthermore vibrations at around 630 cm^{-1} and 1180 cm^{-1} for ν(P=S) and ν(P=O) support structure (**B**) in solid state.

Compounds **1**, **2**, **4−6** were easily deprotonated upon treatment with KO*t*Bu in THF at room temperature to give K[PhC(O)NP(O)Ph_2] (**7**), K[H_2NC(S)NP(S)Ph_2] (**8**), K[PhC(O)NP(S)Ph_2] (**9**), K[PyC(O)NP(S)Ph_2] (**10**), and K[H_2NC(S)NP(Se)Ph_2] (**11**) (Equation 4). The solutions were filtered through celite and the solvent removed to give the products analytically pure. All the compounds are colourless in appearance.

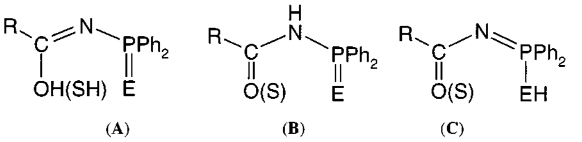
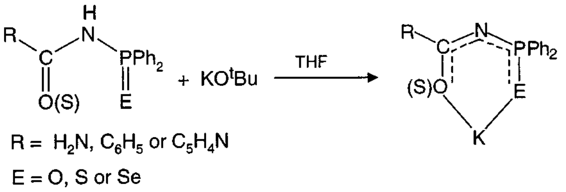


Figure 1. Tautomeric forms of RC(E)NHP(E′)Ph_2 (E = O or S; E′ = O, S, or Se)



(4)

It can be seen by ^{31}P NMR that the displacement of an amino proton by an electropositive element (potassium) in general shields the nucleus under scrutiny and it is observed at lower frequency (Table 1). Upon deprotonation the ν(C=O) vibration shifts around 130 cm^{-1} to lower frequency, whilst the ν(C=S) cannot be easily identified. Concurrently the bond order of the P−N bond has increased and the & uψ;(CN) is observed at higher frequency in the deprotonated compounds.

The X-ray structure of **4** shows[24] the compound is in the keto form with the proton bonded to the nitrogen and not to the terminal chalcogen atoms. The geometry of this compound can be compared with [*i*Pr_2P(S)NHP(S)*i*Pr_2]

which also exists in a *syn* conformation.[27] The molecular structure of $K[PhC(O)NP(S)Ph_2]$ **9** shows the ligand is coordinated to potassium via oxygen and sulfur donor atoms in a six-membered chelate ring arrangement in which the ring can be viewed as a true heterocycle containing six different atoms from Groups 1, 14, 15, and 16 of the periodic table. There are few previous crystallographic determinations to make comparisons. The most appropriate is $K[N\{P(S)Ph_2\}_2]$.[28]

Reaction of $K[PhC(O)NP(S)Ph_2]$ **9** with $Cu(PPh_3)_2(NO_3)$ gives $Cu(PhC(O)NP(S)Ph_2)(PPh_3)$ **12** which is the first example of a non-ionic six-membered true heterocycle. In **12** the X-ray structure (Table 3, Figure 2) reveals that copper is trigonal [Cu lies 0.03 Å out of the Cu−O−S−P(2) mean plane) and that the Cu−S−P−N−C−O ring is non-planar in what can best be described as a pseudo boat conformation. The P(1)−S−Cu−O mean plane [max. deviation 0.16 Å for Cu] is inclined by 142° to the O−C(37)−N−P(1) mean plane [max. deviation 0.01 Å for C(37)].

Table 3. Selected bond lengths [Å] and angles [°] in $[Cu(PPh_3)($ $PhC(O)NP(S)Ph_2)]$ **12**

Cu−O 2.013(2)	P(1)−N 1.621(3)
Cu−P(2) 2.1897(10)	N−C(37) 1.326(4)
Cu−S 2.223(1)	C(37)−O 1.270(3)
S−P(1) 2.011(1)	
O−Cu−P(2) 112.4(1)	N−P(1)−S 119.0(1)
O−Cu−S 106.2(1)	C(37)−N−P(1) 121.1(2)
P(2)−Cu−S 141.3(4)	O−C(37)−N 126.4(3)
P(1)−S−Cu 92.3(1)	C(37)−O−Cu 125.7(2)

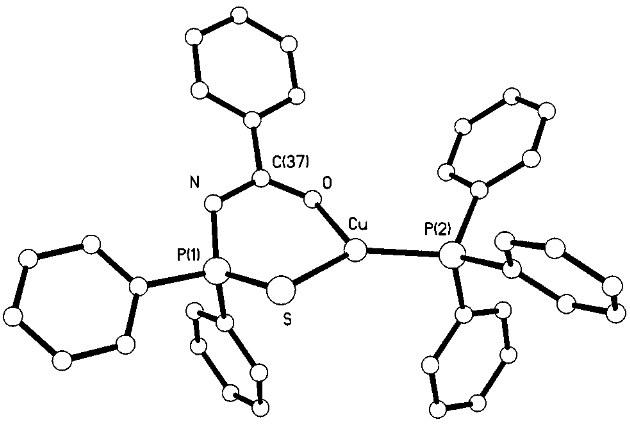


Figure 2. Molecular structure of $[Cu(PPh_3)($ $PhC(O)NP(S)Ph_2)]$ **12** in the crystal

Two equivalents of the ligand salt $K[PhC(O)NP(S)Ph_2]$ (**9**) was treated with $[PdCl_2(COD)]$ in dichloromethane to give an orange solution immediately (Equation 5). The product $[Pd\{PhC(O)NP(S)Ph_2\}_2]$ (**13**) was triturated with petroleum ether and a yield of 57% was collected. $[Pd\{PyC(O)NP(S)Ph_2\}_2]$ (**14**) was prepared in the same way with $K[PyC(O)NP(S)Ph_2]$ (**10**) and $[PdCl_2(COD)]$ and was isolated as red powder (93%). The compounds **13** and **14** show the correct parent ion mass numbers [779 and 780 *m/z*] and isotope distributions in their FAB mass spectra and have satisfactory elemental analysis. The $^{31}P\{^1H\}$ NMR spectra display a singlet for both compounds at δ = 30 for **13** and 31 for **14** whilst their infrared spectra show similar features with the vibrational patterns simplified compared to the ligand salts and free ligands. The P=S vibrational frequencies have shifted around 50 cm^{-1} lower compared to the free ligands. In compound **13** the ν(CO) band is reduced significantly by 166 cm^{-1} which is in the range of a C−O single bond. The ν(CO) band for **14** appears to be a lot more complicated and are assigned at 1609, 1585, 1551, and 1508 cm^{-1}. The ν(PN) band in the palladium complexes have shifted [926 and 804 cm^{-1} for **13**; 920 and 818 cm^{-1} for **14**] to a higher frequency indicating an increase in the P−N bond order. The ligands seem to have coordinated to a palladium atom through their PS and CO donor groups to form metal complexes as six-membered chelate compounds. There are two possible isomers, *cis* or *trans*, that these compounds can form.

$$[PdCl_2(COD)] + 2K[RC(O)NP(S)Ph_2] \longrightarrow$$

$$R = C_6H_5 \text{ or } C_5H_4N$$

$$[Pd\{RC(O)NP(S)Ph_2\}_2] + 2KCl \qquad (5)$$

Ojima et al.[14][15] proposed that some diphenylphosphanylthioylthioureato metal(II) complexes have a chelate structure consisting of five different atoms − C, N, P, 2 S, and M^{II}. One of those complexes, where M = Ni, was later confirmed by Iwamoto et al.[29] with a molecular structure from X-ray crystallography studies however there has been little further work done in this area.

The zinc complex $[Zn\{H_2NC(S)NP(S)Ph_2\}_2]$ (**15**) was obtained by the addition of $ZnCl_2$ to a tetrahydrofuran solution of $K[H_2NC(S)NP(S)Ph_2]$ (Equation 6) in 75% yield.

$$ZnCl_2 + 2K[H_2NC(S)NP(S)Ph_2] \longrightarrow$$

$$[Zn\{H_2NC(S)NP(S)Ph_2\}_2] + 2KCl \qquad (6)$$

The X-ray structure of **15** (Table 4, Figure 3) reveals the expected tetrahedral coordination at zinc with the ZnS_2PCN ring adopting an approximately boat conformation Zn(1)−S(1)−S(2)−C(1) [max. deviation 0.08 Å for S(2)] is inclined by 137° to P(1)−N(1)−C(1)−S(1) [max. deviation 0.29 Å for N(1)].

Table 4. Selected bond lengths [Å] and angles [°] in $[Zn\{H_2NC(S)NP(S)Ph_2\}_2]$ **15**

Zn(1)−S(1) 2.351(2)	Zn(1)−S(2) 2.338(2)
P(1)−S(1) 2.014(2)	P(1)−N(1) 1.637(5)
N(1)−C(1) 1.334(8)	N(2)−C(1) 1.343(8)
C(1)−S(2) 1.748(6)	
S(1)−Zn(1)−S(2) 107.1(1)	Zn(1)−S(1)−P(1) 95.5(1)
S(1)−Zn(1)−S(1A) 116.1(1)	S(1)−Zn(1)−S(2A) 106.5(1)
S(1)−P(1)−N(1) 116.9(2)	P(1)−N(1)−C(1) 125.3(9)
N(1)−C(1)−N(2) 116.2(5)	N(2)−C(1)−S(2) 114.7(5)
N(1)−C(1)−S(2) 129.0(5)	C(1)−S(2)−Zn(1) 109.3(2)

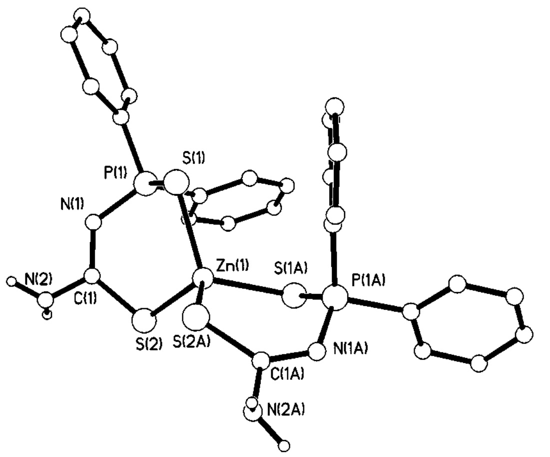


Figure 3. Molecular structure of $[Zn\{H_2NC(S)NP(S)Ph_2\}_2]$ **15** in the crystal

Reaction of equimolar amounts of $[H_2NC(S)NHP(S)Ph_2]$ (**2**) and $[PtCl_2(COD)]$ in dichloromethane was expected to give a six-membered chelate complex $PtCl_2\{H_2NC(S)NHP(S)Ph_2\}$. However, two singlets with unresolved ^2J platinum satellites were observed in the ^{31}P-NMR spectrum. Mass spectrometry reveals that two ligands have coordinated to the metal centre. The two NMR signals may be assigned to a neutral and a deprotonated ligand in $Pt\{H_2NC(S)NHP(S)Ph_2\}\{H_2NC(S)NP(S)Ph_2\}]Cl$ (**16**) (vide infra). The reaction was repeated using 2 molar equivalents of $K[H_2NC(S)NP(S)Ph_2]$, in dichloromethane to give the yellow crystalline $[Pt\{H_2NC(S)NP(S)Ph_2\}_2]$ (**17**) (Equation. 7).

$$[PtCl_2(COD)] + 2K[H_2NC(S)NP(S)Ph_2] \longrightarrow [Pt\{H_2NC(S)NP(S)Ph_2\}_2] + 2KCl \qquad (7)$$

Compound **17** displays a singlet [$\delta = 33$] with characteristic ^2J platinum coupling [$^2J(P-Pt) = 114$ Hz]. Compound **16** and **17** both displayed the correct mass values with the appropriate isotope distributions for $[Pt\{H_2NC(S)NP(S)Ph_2\}_2]$ obtained from FAB mass spectroscopy. Confirmation of the stoichiometry in the complexes was obtained from satisfactory elemental analysis data.

The infrared spectrum of compound **16** shows a close similarity to[23] $[Pt\{H_2NC(S)NHPPh_2\}_2]^{2+} \cdot 2\,Cl^-$ but with additional peaks at 598 and 576 cm^{-1} due to the two different phosphorus-sulfur vibrations Two broad ν(PN) vibrations are observed at 922 and 883 cm^{-1}. Close inspection of the peaks due to the NH_2 groups reveals two overlapping peaks resulting in very broad bands. Compound **17** displays an infrared spectrum which is very similar to that of **15**; with the ν(PS) vibration in **17** seen at 577 cm^{-1} and the ν(PN) vibration as a broad band at 883 cm^{-1}.

The X-ray structure of **16** (Table 5, Figure 4) shows that the two chelates are bound to a platinum atom by four sulfur donor atoms forming two six-membered rings in the *trans* configuration. Interestingly only one ligand is deprotonated which is supported by the notable differences in the P−N bond lengths for the two rings [P(1)−N(1) 1.56(3) P(21)−N(21) 1.65(2) Å] with deprotonation giving the shorter P−N length which is comparable to those in **15**. Furthermore the presence of the N−H proton in chelate **A** is supported by the close proximity of the chloride counter ion which H-bonds to the NH and NH_2 groups [N(22)···Cl(1) 3.38 Å, N−H···Cl 154°; N(21)···Cl(1) 3.10 Å, N−H···Cl 125°] to give a six-membered H−N−C−N−H−Cl ring. The chloride ion also H-bonds to the adjacent cation [N(2′)···Cl(1) 3.40 Å, N−H···Cl 160°] thus linking the cations and anions into chains. The square planar complex contains two six-membered rings though there are significant differences in ring conformation which may be due to one chelate ring being deprotonated. In chelate **A** (neutral ligand) the two Pt−S bond lengths are 2.317(7) and 2.322(8) Å with no significant differences between the sulfur donors bound by carbon and phosphorus atoms; the P=S bond length [1.97(1) Å] is similar to those in $[PhC(O)NHP(S)Ph_2]$ [1.94(6) Å] and $[\{(PhO)_2P(S)NC(S)N(n\text{Pr})_2\}_2Ni]$[30] which haa a P−S bond with substantial delocalisation and a bond length of 1.978(1) Å. The P−N and N−C bonds distances are appropriate for a limited degree of delocalisation and compare well with those in $[Pt\{H_2NC(S)NHPPh_2\}_2]^{2+} \cdot 2\,Cl^-$ [1.676(1) and 1.38(2) Å]. The most dramatic change observed is the lengthening of the C=S bond by about 0.1 Å compared to that in $[Pt\{H_2NC(S)NHPPh_2\}_2]^{2+} \cdot 2\,Cl^-$ to an observed single bond value [1.75(3) Å] similar to that in $[\{Ph_2(S)PNC(S)NH(CH_3)\}_2Ni]$ [1.760(9) Å].[29] There are significant differences in bond lengths in chelate **B** (deprotonated anionic ligand). The two Pt−S and P=S bond lengths are similar to those in chelate **A**. The P−N appears to be partially double [1.56(3) Å] and the C−N and C=S are similar to those in the neutral ligand The ring conformations are different; **A** is a "twist chair" conformation whilst **B** contains a relatively planar fragment −S(2)−P(1)−N(1)−C(1)−S(1) [max deviation 0.25 Å for N(1)] which is inclined by 63° to the Pt(1)−S(1)−S(2) plane.

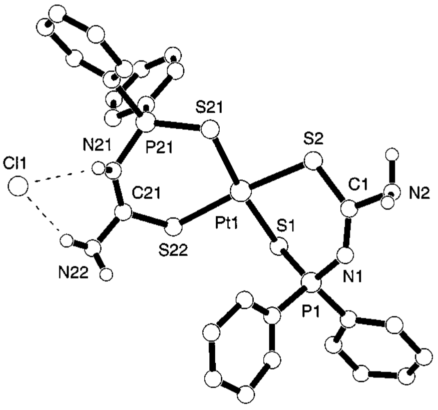


Figure 4. Molecular structure of *trans*-$[Pt\{H_2NC(S)NP(S)Ph_2\}\{H_2NC(S)NHP(S)Ph_2\}]^+Cl^-$ **16** in the crystal

Table 5. Selected bond lengths [Å] and angles [°] in *trans*-[Pt{$H_2NC(S)NP(S)Ph_2$}{$H_2NC(S)NHP(S)Ph_2$}]$^+Cl^-$ **16**

Chelate **A**		Chelate **B** (deprotonated)	
Pt−S(21)	2.316(7)	Pt−S(1)	2.324(7)
Pt−S(22)	2.322(8))	Pt−S(2)	2.313(8)
S(21)−P(21)	1.97(1)	S(1)−P(1)	1.98(1)
P(21)−N(21)	1.65(2)	P(1)−N(1)	1.56(3)
N(21)−C(21)	1.30(3)	N(1)−C(1)	1.30(3)
C(21)−S(22)	1.75(3)	C(1)−S(2)	1.73(3)
C(21)−N(22)	1.34(3)	C(1)−N(2)	1.40(3)
S(21)−Pt−S(22)	101.9(3)	S(1)−Pt−S(2)	90.6(3)
S(2)−Pt−S(21)	83.7(3)	S(1)−Pt−S(22)	83.9(3)
Pt−S(22)−C(21)	112(1)	Pt−S(2)−C(1)	108(1)
Pt−S(21)−P(21)	102.0(4)	Pt−S(1)−P(1)	97.4(4)
S(22)−C(21)−N(21)	127(2)	S(2)−C(1)−N(1)	134(2)
C(21)−N(21)−P(21)	125(2)	C(1)−N(1)−P(1)	126(2)
N(1)−C(1)−N(2)	115(3)	N(21)−C(21)−N(22)	121(2)
N(21)−P(21)−S(21)	113.4(9)	N(1)−P(1)−S(1)	118(1)
S(22)−C(21)−N(22)	112(2)	S(2)−C(1)−N(2)	110(2)

The X-ray structure of **17** (Table 6, Figure 5) reveals that the two deprotonated ligands are bound to the square planar platinum atom in a *cis* configuration. The PtS_4 coordination sphere resembles that in bis(dithiobiureto)palladium(II)[31] and imidodiphosphinatoplatinum(II).[32] The bond lengths within the rings of **17** are similar to those of ring **B** in **16** and the ring conformations mostly closely resembles that of the deprotonated ring **B** in **16**. In **17** both rings consist of fairly planar S−P−N−C−S backbones [max. deviations for the two rings being 0.25 Å for C(1) and 0.31 Å for C(21)] which are inclined to the coordination plane by 60° in each case.

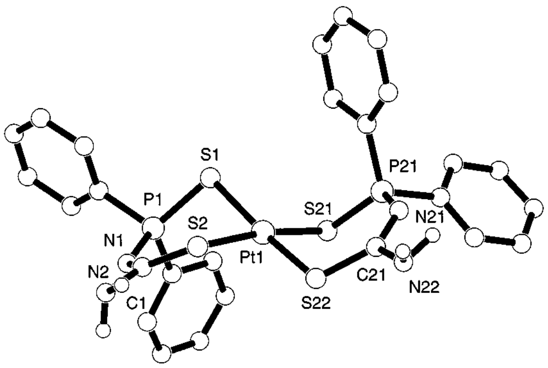


Figure 5. Molecular structure of *cis*-[Pt{$H_2NC(S)NP(S)Ph_2$}$_2$]·(Et_2O) **17** in the crystal

When we attempted to react [$H_2NC(S)NHP(Se)Ph_2$] **6** with [$PtCl_2(COD)$], red selenium deposited out of solution. The reaction was monitored by ^{31}P NMR which revealed a signal at 70 ppm with platinum-satellites which identified the product as [Pt{$H_2NC(S)NHPPh_2$}$_2$]$^{2+}$ · 2 Cl^-.

This work has demonstrated the ease of formation of hybrid organic/inorganic ligands which have elements of *acac* and imidophosphinate ligand systems. The usefulness of these ligands in metal specific coordination and catalysis awaits investigation.

Table 6. Selected bond lengths [Å] and angles [°] in *cis*-[Pt{$H_2NC(S)NP(S)Ph_2$}$_2$] · (Et_2O) **17**

Pt−S(1)	2.322(4)	Pt−S(21)	2.330(4)
Pt−S(2)	2.312(4)	Pt−S(22)	2.307(4)
S(1)−P(1)	1.987(7)	S(21)−P(21)	2.004(7)
P(1)−N(1)	1.62(1)	P(21)−N(21)	1.61(1)
N(1)−C(1)	1.34(2)	N(21)−C(21)	1.32(2)
C(1)−S(2)	1.70(2)	C(21)−S(22)	1.72(2)
C(1)−N(2)	1.37(2)	C(21)−N(22)	1.37(2)
S(1)−Pt−S(2)	93.0(1)	S(21)−Pt−S(22)	93.0(1)
S(1)−Pt−S(21)	90.6(2)	S(2)−Pt−S(22)	84.2(1)
Pt−S(2)−C(1)	108.6(6)	Pt−S(22)−C(21)	109.7(6)
Pt−S(1)−P(1)	99.0(2)	Pt−S(21)−P(21)	98.2(2)
S(1)−P(1)−N(1)	120.5(5)	S(21)−P(21)−N(21)	119.8(6)
P(1)−N(1)−C(1)	127(1)	P(21)−N(21)−C(21)	129(1)
N(1)−C(1)−N(2)	112(2)	N(21)−C(21)−N(22)	116(1)
N(1)−C(1)−S(2)	133(1)	N(21)−C(21)−S(22)	132(1)
S(2)−C(1)−N(2)	114(1)	S(22)−C(21)−N(22)	112(1)

Experimental Section

General: Diethyl ether, petroleum ether (60−80 °C) and tetrahydrofuran were purified by reflux over sodium and distillation under nitrogen. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. − Infrared spectra were recorded from KBr discs on a Perkin−Elmer system spectrometer. − ^{31}P NMR spectra on a Jeol FX90Q operating at 36.21MHz; ^1H-, ^{13}C-, and ^{31}P-NMR spectra on a Bruker AC250 operating at 250, 62.9, and 101.3MHz respectively. − Fast atom bombardment mass spectra were measured by the Swansea mass spectrometry service.

[PhC(O)NHP(O)Ph$_2$] (1): A solution of $PhC(O)NHPPh_2$ (760 mg, 2.49 mmol) in THF (50 mL) was stirred overnight in air. The solution was filtered and the filtrate was reduced to dryness to give a white powder. It was recrystallised from CH_2Cl_2/Et_2O to give a yield of 795 mg (99 %). M.p. 197−199°C. − ^{31}P NMR ($CDCl_3$): δ = 24. − IR (KBr disc, cm^{-1}): 3159 m, 3066 s, 2842 mw, 1669 vs, 1591 m, 1500 s, 1456 vs, 1439 vs, 1267 s, 1199 vs, 1128 vs, 1108 s, 1072 m, 1027 m, 998 w, 875 m, 838 s, 807 w, 754 s, 728 vs, 711 vs, 692 vs, 525 vs, 476 w, 296 w. − FAB (*m*/*z*): 344 [M + Na]$^+$ and 322 [M + H]$^+$. − $C_{19}H_{16}NO_2P$ (321.32): found C 70.66, H 4.72, N 3.87; (calcd. C 71.02, H 5.02, N 4.36 %).

[$H_2NC(S)NHP(S)Ph_2$] (2): To a suspension of $H_2NC(S)NH_2$ (8.5 g, 112 mmol) in THF (300 mL) was added Et_3N (15.5 mL, 111 mmol) and DMAP (100 mg, 10 mmol). A THF (200 mL) solution of Ph_2PCl (15 mL, 83 mmol) was then added dropwise over 3 h. The solution was filtered into another flask containing S (2.7 g, 83 mmol) and the residue washed with THF (100 mL). After 30 min of stirring the solution was evaporated to dryness and extracted with CH_2Cl_2 (200 mL). The extract was concentrated and triturated with Et_2O to give a microcrystalline product 9.4 g (39 %). Mp: 144−145 °C. − ^{31}P NMR ($CDCl_3$): δ = 52. − IR (KBr disc, cm^{-1}): 3381 w, 3294 s, 3141 m−sh, 3074 s, 2943 w, 2877 w, 1619 vs, 1586 w, 1484 vs, 1425 vs, 1309 w, 1278 m, 1111 s, 1102 s, 1054 s, 1029 m, 997 m, 835 s, 810 s, 749 s, 719 vs, 690 s, 642 s, 632 s, 614 m, 572 m, 521 vs, 495 s, 482 s, 464 m, 418 w, 404 m, 347 w, 301 m. − FAB (*m*/*z*): 315 [M + Na]$^+$ and 293 [M]$^+$. − $C_{13}H_{13}N_2PS_2$ (292.35): found C 53.18, H 4.46, N 9.91; (calcd. C 53.41, H 4.48, N 9.58 %).

[$H_2NC(O)NHP(S)Ph_2$] 3: To a solution of $H_2NC(O)NHPPh_2$ (3.5 g, 14.3 mmol) in THF (100 mL) was added S (451 mg, 14.1 mmol). The reaction was stirred for 4 h. The solution was filtered and the solvent removed to give a yield of 2.5 g (62 %). Mp: 162−166 °C. − ^{31}P NMR ($CDCl_3$): δ = 53. − IR

(KBr disc, cm^{-1}): 3492 m, 3333 m, 3187 m, 3056 w, 2956 vw, 1704 vs, 1682 vs, 1650 vs, 1615 vs, 1461 vs, 1436 vs, 1343 m, 1246 w, 1178 w, 1106 vs, 998 w, 912 m, 872 w, 747 s, 716 vs, 692 vs, 656 m, 634 m, 613 m, 590 m, 513 m, 496 s, 460 w. − FAB (*m/z*): 299 [M + Na]$^+$ and 277 [M]$^+$. $C_{13}H_{13}N_2OPS$ (276.29): found C 55.88, H 4.74, N 10.14; (calcd. C 56.51, H 4.74, N 10.64 %)

[PhC(O)NHP(S)Ph$_2$] 4: To a solution of PhC(O)NH$_2$ (3.2 g, 7.7 mmol) in THF (150 mL) was added Et$_3$N (3.9 mL, 30 mmol), DMAP (200 mg, 20 mmol) and neat Ph$_2$PCl (5 mL, 27.9 mmol) − the solution was heated at reflux overnight. S (1.78 g, 55.7 mmol) was added and stirred overnight at room temperature. The solution was filtered and the filtrate was reduced to dryness to a white powder. It was then triturated with Et$_2$O (200 mL) to give a yield of 6.43 g (34 %). Mp: 186−190 °C. − ^{31}P NMR (CDCl$_3$): δ = 56. − IR (KBr disc, cm^{-1}): 3159 m, 3060 w, 2857 vw, 1651 vs, 1600 m, 1581 w, 1496 m, 1480 w, 1454 vs, 1436 vs, 1266 s, 1180 vw, 1102 s, 1071 w, 1024 w, 999 w, 952 vw, 880 w, 832 m, 796 w, 745 s, 726 vs, 715 vs, 690 vs, 669 m, 636 vs, 615 m, 516 s, 497 s, 398 w. FAB (*m/z*): 361 [MH + Na]$^+$ and 337 [MH + H]$^+$. − $C_{19}H_{16}NOPS$ (337.38): found C 67.25, H 4.54, N 4.02; (calcd. C 67.64, H 4.78, N 4.15 %).

[PyC(O)NHP(S)Ph$_2$] 5: To a solution of PyC(O)NH$_2$ (3.4 g, 27.8 mmol) in THF (150 mL) was added Et$_3$N (3.9 mL, 30 mmol), DMAP (200 mg, 20 mmol) and neat Ph$_2$PCl (5 mL, 27.9 mmol) − the solution was heated at reflux overnight. S (890 mg, 27.8 mmol) was added and the raction was stirred for 1 h. at room temperature. The solution was filtered and the filtrate reduced to dryness to a white powder. The product was recrystallised from CH$_2$Cl$_2$/Et$_2$O to give 4.4 g (47 %). Mp: 195−198 °C. − ^{31}P NMR (CDCl$_3$): δ = 56. − IR (KBr disc, cm^{-1}): 3368 vw, 3182 s, 3077 w, 1656 vs, 1588 s, 1573 m, 1482 m, 1457 vs, 1437 s, 1413 s, 1269 s, 1104 s, 1020 m, 998 w, 878 m, 842 m, 815 m, 742 vs, 724 s, 715 vs, 7703 s, 691 vs, 662 m, 639 vs, 615 m, 516 m, 499 s, 477 w, 457 w, 412 w, 402 w, 297 w. − FAB (*m/z*): 361 [M + Na]$^+$ and 339 [M + H]$^+$. − $C_{18}H_{15}N_2OPS$ (338.36): found C 64.15, H 4.41, N 8.19; (calcd. C 63.89, H 4.47, N 8.28 %).

[H$_2$NC(S)NHP(Se)Ph$_2$] 6: To a solution of H$_2$NC(S)NHPPh$_2$ (2.20 g, 8.45 mmol) in THF (50 mL) was added Se (0.67 g, 8.45 mmol) and the mixture stirred for 1 h. The solution was filtered through celite and reduced to dryness to give 1.63 g (67 %) of white powder. Mp: 141−144 °C. − ^{31}P NMR (THF/C$_6$D$_6$): δ = 45 [^1J(PSe) 783 Hz]. − IR (KBr disc, cm^{-1}): 3364 w, 3284 m, 3072 m, 2940 w, 2875 w, 1619 vs, 1482 vs, 1424 vs, 1308 w, 1278 m, 1107 m, 1052 m, 996 w, 832 s, 807 s, 748 vs, 715 s, 701 vs, 688 vs, 640 m, 555 vs, 515 vs, 490 s, 473 m, 409 m, 396 m, 304 w m 284 m. − FAB (*m/z*): 339 [M]$^+$. − $C_{13}H_{13}N_2PSSe$ (339.25): found C 45.98, H 3.76, N 8.30; (calcd. C 46.02, H 3.86, N 8.26 %).

K[PhC(O)NP(O)Ph$_2$] 7: To a solution of [PhC(O)NHP(O)Ph$_2$] (500 mg, 1.56 mmol) in THF (50 mL) was added KO*t*Bu (0.57 g, 5.12 mmol). After stirring overnight the solution was filtered through celite, and then reduced to dryness to give 557 mg (100 %) of white powder. Mp: 286−290 °C. − ^{31}P NMR (THF/C$_6$D$_6$): δ = 17. − IR (KBr disc, cm^{-1}): 3397 w, 3056 m, 2974 w, 2866 w, 1649 m, 1624 m, 1591 s, 1523 vs, 1481 m, 1436 s, 1376 vs, 1298 m, 1171 s, 1153 s, 1141 s, 1120 s, 1101 s, 1066 s, 1026 s, 896 vs, 842 vs, 755 s, 719 vs, 701 vs, 547 vs, 527 vs, 459 m, 435 m, 324 m, 303 m. − FAB (*m/z*): 360 [M + H]$^+$. − $C_{19}H_{15}KNO_2P$ (338.38): found C 63.23, H 4.35, N 3.74; (calcd. C 63.50, H 4.21, N 3.90 %).

K[H$_2$NC(S)NP(S)Ph$_2$] 8: Was prepared in a similar fashion to **7**, yield 1.3 g 79 %. Mp: 155−157 °C. − ^{1}H NMR ([D$_6$]DMSO): 7.85 (aromatic), 7.34 (aromatic) and 3.30 (2 H, s, NH). − ^{13}C NMR: 189 (CS), 142 (C$_6$H$_5$) 141 (C$_6$H$_5$), 131 (C$_6$H$_5$), 130 (C$_6$H$_5$) and 128 (C$_6$H$_5$). − ^{31}P NMR: 37 ppm. − IR (KBr disc, cm^{-1}): 3364 s, 3280 m, 3164 w, 3054 w, 1604 s, 1479 s, 1431 vs, 1402 s, 1307 s, 1291 s, 1104 s, 1055 vw, 1026 vw, 999 vw, 884 vw, 856 vw, 836 vw, 809 vw, 746 s, 712 vs, 693 s, 624 m, 607 s, 521 s, 416 vw. − FAB (*m/z*): 331 M + H]$^+$. − $C_{13}H_{12}KN_2PS_2$ (330.44): found C 47.18, H 3.75, N 7.99; (calcd. C 47.25, H 3.66, N 8.48 %).

K[PhC(O)NP(S)Ph$_2$] 9: Was prepared in a similar fashion to **7**, yield 1.1 g, 100 %. Mp: 286−290 °C. − ^{31}P NMR ([D$_6$]DMSO): δ = 44. − IR (KBr disc, cm^{-1}): 3434 w, 3053 w, 2968 w, 2852 w, 1588 m, 1519 vs, 1479 w, 1436 m, 1360 vs, 1297 w, 1102 m, 1068 m, 1024 m, 895 m, 884 w, 838 s, 816 w, 748 w, 723 vs, 710 s, 695 s, 672 w, 627 s, 612 s, 516 m, 503 s, 306 w. − FAB (*m/z*): 399 [MH + Na]$^+$, 377 [MH + H]$^+$. − $C_{19}H_{15}KNOPS$ (375.4): found C 60.34, H 4.12, N 3.45; (calcd. C 60.78, H 4.03, N 3.73 %).

K[PyC(O)NP(S)Ph$_2$] 10: Was prepared in a similar fashion to **7**, yield 2.30 g, 94 %. Mp: 308−312 °C. − ^{31}P NMR (THF/C$_6$D$_6$): δ = 41. − IR (KBr disc; cm^{-1}): 3322 vw, 3237 vw, 3072 w, 3053 w, 1676 w, 1590 vs, 1526 vs, 1476 m, 1436 s, 1417 m, 1371 vs, 1314 m, 1305 m, 1193 m, 1164 s, 1102 s, 1028 s, 906 s, 893 m, 830 vs, 748 vs, 717 s, 707 vs, 694 vs, 626 vs, 613 vs, 503 vs, 413 w, 305 m. − FAB (*m/z*): 377 [M + H]$^+$. − $C_{18}H_{14}KN_2OPS$ (376.45): found C 57.25, H 3.37, N 7.01**;** (calcd. C 57.43, H 3.75, N 7.44 %).

K[H$_2$NC(S)NP(Se)Ph$_2$] 11: Was prepared in a similar fashion to **7**, yield 317 mg, 59 %. Mp: 120−125 °C. − ^{31}P NMR (THF/C$_6$D$_6$): δ = 29 [^1J(PSe) 530 Hz]. − IR (KBr disc, cm^{-1}): 3353 m, 3162 w, 3051 w, 1605 vs, 1476 s, 1431 vs, 1306 vs, 1103 vs, 1025 m, 999 m, 885 w, 851 w, 743 vs, 712 s, 699 vs, 544 vs, 516 vs, 408 m. − FAB (*m/z*): 346 [M − S]$^+$. − ($C_{13}H_{12}KN_2PSSe$ (377.34): found C 41.29, H 3.43, N 6.97; calcd. C 41.38, H 3.21, N 7.42 %).

[Cu(PPh$_3$)(PhC(O)NP(S)Ph$_2$)] 12: To a suspension of PhC(O)NP(S)Ph$_2$ (0.21 g, 0.62 mmol) in methanol (20 mL) was added KO*t*Bu (0.07 g, 0.62 mmol), after stirring for 10 minutes a solution of Cu(PPh$_3$)$_2$(NO$_3$) (0.40 g, 0.62 mmol) in CHCl$_3$ (25 mL) was added dropwise. The mixture was refuxed for two hours, cooled and the white precipitate was filtered off, washed with diethyl ether and dried in vacuo. Yield 0.24 g, 59%, M.p. 246 °C. ^{31}P δ = 28.4. − $C_{37}H_{30}CuNOP_2S$ (662.20): Found C 67.10, H 4.65, N 2.02, S 4.80 (calcd. C 67.11, H4.57, N 2.12, S 4.84%). − IR (KBr disc, cm^{-1}): 3058 w, 1500 m, 1435 m, 1376 vs, 1304 w, 1180 w, 1111 m, 1109 w, 822 m, 718 s, 695 s, 593 s, 528 m 508 m. − Mass Spec. Parent ion not observed.

[Pd{PhC(O)NP(S)Ph$_2$}$_2$] 13: To a solution of [PdCl$_2$(COD)] (30 mg, 105 μmol) in CH$_2$Cl$_2$ (10 mL) was added K[PhC(O)NP(S)Ph$_2$] (80 mg, 213 μmol). After 1 h of stirring the solution was filtered through celite and reduced to dryness. After trituration with petroleum ether, 47 mg (57 %) of product was collected. Mp: 136−139 °C. − ^{31}P NMR (DCM/C$_6$D$_6$): δ = 30. − IR (KBr disc, cm^{-1}): 3052 w, 3055 m, 1588 m, 1485 vs, 1436 vs, 1372 vs, 1304 m, 1181 m, 1113 s, 1103 s, 1068 w, 1026 m, 998 w, 926 m, 795 m, 804 m, 745 m, 720 s, 701 vs, 689 vs, 618 w, 590 vs, 552 m 511 vs, 489 m, 418 w, 337 w. − FAB (*m/z*): 802 [M + Na]$^+$ and 779 [M]$^+$. − $C_{38}H_{30}N_2O_2P_2PdS_2$ (779.16): found C 58.66, H 3.88, N 3.24; (calcd. C 58.58, H 3.88, N 3.60 %).

[Pd{PyC(O)NP(S)Ph$_2$}$_2$] 14: To a solution of [PdCl$_2$(COD)] (38 mg, 133 μmol) in CH$_2$Cl$_2$ (10 mL) was added K[PyC(O)NP(S)Ph$_2$] (100 mg, 266 μmol), which gave a red solution immediately. After overnight stirring the solution was filtered through celite and reduced to dryness. The compound was then triturated with petroleum ether (60−80°C) gave a yield of 97 mg (93 %). Mp: 155−158 °C. − ^{31}P NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ = 31. − IR (KBr disc, cm^{-1}): 3053 w, 2923 w, 1609 s, 1585 s, 1551 s, 1508 s, 1479 w, 1436 s,

Table 7. Details of the crystal data and refinements

Compound	**12**	**15**	**16**	**17**
Empirical formula	$C_{37}H_{30}CuNP_2S$	$C_{28}H_{27.5}Cl_5N_4P_2S_4Zn$	$C_{26}H_{26}N_4P_2S_4PtClO_{0.5}$	$C_{30}H_{34}N_4P_2S_4PtO$
Formula weight	662.2	852.8	823.2	851.9
Colour	Colourless	Colourless	Yellow	Yellow
Size [mm]	0.25 × 0.25 × 0.15	0.25 × 0.15 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.03 × 0.1
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space Group	*P*-1	*C*2/*c*	*C*2/*c*	*P*-1
a	10.828(2)	19.074(1)	23.176(5)	12.645(5)
b	12.704(3)	12.801(1)	14.04(1)	13.988(3)
c	13.161(3)	19.411(1)	26.237(5)	10.838(2)
α	100.50(3)	90	90	99.25(2)
β	105.86(3)	114.53(1)	122.92(1)	100.98(2)
γ	106.95(3)	90	90	65.49(2)
Volume [Å^3]	1597	4311	7166	1705
Z	2	4	8	2
Density (calc.) [g/cm^3]	1.38	1.31	1.53	1.66
μ [mm^{-1}]	0.88	1.17	10.9	10.8
F(000)	684	1730	3224	844
Ind.Refl./Observed Refl	4617/4219	3073/3019	5743/1864	5077/3659
Final*R*1/*wR*2	0.030/0.080	0.076/0.207	0.059/0.067	0.080/0.083
Largest Difference Peak/Hole [eÅ^{-3}]	0.25, −0.265	1.00, −0.551	1.03, −0.63	1.44, −2.05

1375 s, 1341 vs, 1307 s, 1174 m, 1103 s, 1058 w, 1026 w, 998 w, 920 w, 818 m, 746 s, 720 m, 690 vs, 619 w, 572 vs, 505 s, 415 w. − FAB (*m*/*z*): 780 [M]$^+$. − $C_{36}H_{28}N_4O_2P_2PdS_2$ (781.13): found C 55.33, H 3.91, N 6.79; (calcd. C 55.35, H 3.61, N 7.17 %).

[Zn{H$_2$NC(S)NP(S)Ph$_2$}$_2$] 15: To a solution of K[H_2NC(S)NP(S)Ph$_2$] (61 mg, 184 μmol) in THF (20 mL) was added $ZnCl_2$ (50 mg, 367 μmol). After stirring overnight, the solution was filtered through celite, and the filtrate reduced to dryness to give a white powder (178 mg, 75 %). Mp: 132−136 °C. − ^{31}P NMR (THF/C_6D_6 insert): δ = 41. − IR (KBr disc, cm^{-1}): 3464 w, 3306 m, 3160 w, 3053 w, 2970 vw, 1588 vs, 1478 vs, 1436 vs, 1311 s, 1161 m, 1104 s, 1027 w, 998 w, 873 s, 748 m, 719 s, 707 vs, 691 s, 638 m, 577 vs, 556 s, 499 m. − FAB (*m*/*z*): 671 [MH$_2$ + Na]$^+$ and 649 [MH$_2$ + H]$^+$. − $C_{26}H_{24}N_4P_2S_4Zn$ (648.07): found C 48.04, H 3.76, N 8.32; (calcd. C 48.18, H 3.73, N 8.64 %).

[Pt{H$_2$NC(S)NHP(S)Ph$_2$}{H$_2$NC(S)NP(S)Ph$_2$}]$^+$Cl$^-$ 16: To a solution of [H_2NC(S)NHP(S)Ph$_2$] (78 mg, 267 μmol) in CH_2Cl_2 (20 mL) was added [PtCl$_2$(COD)] (100 mg, 267 μmol) giving yellow precipitates immediately. After overnight stirring the residue was filtered to give a yield of 96 mg (85 %). Decomp. temp: >160 °C. − ^{31}P NMR (CH$_3$OH/C_6D_6 insert): δ = 29.25, 29.54 [^2J(P−Pt) broad unresolved]. − IR (KBr disc, cm^{-1}): 3261 m, 3055 m, 2697 vw, 1603 s, 1500 s, 1437 vs, 1390 m, 1312 s, 1184 w, 1163 vw, 1106 vs, 998 w, 922 vw, 883 w, 748 m, 708 s, 688 s, 618 w, 598 m, 576 s, 551 m, 495 m, 365 vw. − FAB (*m*/*z*): 777 [M − H]$^+$. − $C_{26}H_{26}ClN_4P_2PtS_4$ (815.24): found C 38.66, H 3.10, N 7.05; (calcd. C 38.41, H 2.97, N 6.88 %).

[Pt{H$_2$NC(S)NP(S)Ph$_2$}$_2$] 17: To a suspension of K[H_2NC(S)NP(S)Ph$_2$] (61 mg, 184 μmol) in CH_2Cl_2 (10 mL) was added [PtCl$_2$(COD)] (32 mg, 85 μmol) gave a yellow solution. After 1 h stirring the solution was filtered through celite and the filtrate kept in a refrigerator overnight; a yellow crystalline product was collected (35 mg, 53 %). Mp: 144−148 °C. − ^{31}P NMR (CH$_2$Cl$_2$/C_6D_6 insert): δ = 33 [^2J(P−Pt) 114 Hz]. − IR (KBr disc, cm^{-1}): 3460 w, 3328 w, 3157 vw, 3053 vw, 1588 vs, 1484 vs, 1436 vs, 1308 s, 1161 m, 1112 s, 1105 s, 1027 vw, 999 w, 883 s, 748 m, 720 s, 707 vs, 691 s, 577 vs, 558 s, 502 m, 356 vw. − FAB (*m*/*z*): 778 [M + H]$^+$ and 777 [M]$^+$. − $C_{26}H_{24}N_4P_2PtS_4$ (777.77): found C 39.75, H 2.81, N 6.81; (calcd. C 40.15, H 3.11, N 7.20 %).

Crystallography: Details of the data collections and refinements are summarised in Table 7 Experimental details for **1** and **9** have been previously reported.[24] Data were collected at room temperature using a KUMA KM-4 and Mo radiation for **12** or with a SMART system for **15** and using Cu radiation with ω scans with a Rigaku AFC7S diffractometer for **16** and **17**. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on *F* using teXsan[25] (**16**, **17**) or using F^2 and SHELXTL[26] (**12**, **15**). Crystallographic Data for the structural analyses has been deposited with the Cambridge Crystallographic data centre, CCDC Nos: 115899, 115900, 115901, and 115902 Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. (Fax +44 1223/ 336-033 or Email deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

We are grateful to the JREI for an equipment grant. JN is grateful to the Royal Society of Chemistry for a journal grant for international authors. JN, MN and ZZ wish to express their gratitude to the Grant Agency of the Czech Republic for Grant Nos. 203/97/0955, 203/98/0676 abd 203/99/0067.

---

[1] J. D.Woollins, *J. Chem. Soc., Dalton Trans.* **1996**, 2893.
[2] R. Rossi, L. Marvelli, A. Marchi, L. Magon, V. Bertolasi, V. Ferretti, *J. Chem. Soc., Dalton Trans.* **1994**, 339.
[3] D. Pohl, E. Ellermann, F. A. Knoch, M. J. Moll, *J. Organomet. Chem.* **1995**, *495*, C6.
[4] A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *J. C.hem. Soc., Dalton Trans.* **1996**, 1283.
[5] P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *Inorg. Chem.* **1996**, *35*, 3675.
[6] A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *Polyhedron* **1996**, *15*, 1579.

[7] M. S. Balakrishna, R. Klein, S. Uhlenbrock, A. A. Pinkerton, R. G. Cavell, *Inorg. Chem.* **1993**, *32*, 5676.
[8] P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1995**, 3189
[9] A. M. Z. Slawin, M. B. Smith, J. D.Woollins, *J. Chem. Soc., Dalton Trans.* **1996**, 4575.
[10] A. M. Z. Slawin, M. B. Smith, J. D.Woollins, *J. Chem. Soc., Dalton Trans.* **1996**, 1283.
[11] T. Q. Ly, F. E. Mabbs, A. M. Z. Slawin, J. D. Woollins. *Inorganic Chemistry Communications*, **1998**, *1*, 143
[12] D. T. Elmore, J. R. Ogle, *J. Chem. Soc.* **1959**, 2286.
[13] A. Schmidpeter, H. Groeger, *Chem. Ber.* **1967**, *100*, 3052; H. Groeger, A. Schmidpeter, *Chem. Ber.* **1967**, *100*, 3216.
[14] I. Ojima, T. Iwamoto, T. Onishi, N. Inamoto, K. Tamaru, *Chem. Commun.* **1969**, 1501.
[15] I. Ojima, T. Iwamoto, T. Onishi, N. Inamoto, K. Tamaru, *Bull. Chem. Soc. Japan* **1971**, *44*, 2150.
[16] I. Ojima, K.-Y. Akiba, N. Inamoto, *Bull. Chem. Soc. Japan* **1973**, *46*, 2559.
[17] A. Spencer, J. M. Swan, H. B. Wright, *Aust. J. Chem.* **1969**, *22*, 2359.
[18] A. Ziegler, V . P. Botha, I. Haiduc, *Inorg. Chim. Acta* **1975**, *15*, 123.
[19] J. Bödeker, H. Zärtner, *J. Prakt. Chem.* **1976**, *318*, 149.
[20] N. G. Zabirov, V. N. Solov′ev, F. M. Shamsevaleev, R. A. Cherkasov, A. N. Chekhlov, A. G. Tsifarkin, I. V. Martynov, *J. Gen. Chem. USSR* **1991**, *61*, 597.
[21] M. Gruber, P. G. Jones, R. Schmutzler, *Chem. Ber.* **1990**, *123*, 1313.
[22] P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1996**, 3647.
[23] T. Q.Ly, A. M. Z.Slawin, J. D.Woollins, *Polyhedron*, in press.
[24] T. Q.Ly, A. M. Z.Slawin, J. D.Woollins, *Angew.Chem.Int.Ed.-Engl.* **1998**, *37*, 2501.
[25] *TeXsan*, Molecular Structure Corporation, The Woodlands, Texas (**1992**, **1996**)
[26] *SHELXTL*. Siemens X-Ray Madison (**1998**).
[27] D. Cupertino, R. Keyte, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Inorg. Chem.* **1996**, *35*, 2695.
[28] A. M. Z. Slawin, J. Ward, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Chem. Commun.* **1994**, 421.
[29] T. Iwamoto, F. Ebina, H. Nakazawa, C. Nakatsuka, *Bull. Chem. Soc. Japan.* **1979**, *52*, 1857.
[30] Z. Zák, T. Glowiak, N. T. T. Chau, E. Herrmann, *Z. Anorg. Allg. Chem.* **1990**, *586*, 136.
[31] R. L. Girling, E. L. Amma, *Chem. Commun.* **1968**, 1487.
[32] J. Phillips, A. M. Z. Slawin, A. J. P. White, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1995**, 2467.

Received March 12, 1999
[I99097]