Diphosphine derivatives of urea and thiourea

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The reaction of $(Me_3Si)HNC(O)NH(SiMe_3)$ or thiourea with PPh_2Cl gave $Ph_2PHNC(E)NHPPh_2$ (E = O **I** or S **II**) which may be oxidised at the phosphorus(III) centres to give $Ph_2P(E')HNC(E)NHP(E')Ph_2$ (E = O, E′ = O **III**, S **IV** or Se **V**; E = S, E′ = S **VI**). Compound **I** forms simple chelate *P,P′* complexes with platinum and palladium. The crystal structures of **II**·Me_2SO **IV** and *cis*-$[PdCl_2\{Ph_2PNHCONHPPh_2\text{-}P,P'\}]$ have been determined.

We have recently reported on a number of examples of complexes containing the $[R_2P(E)NP(E)R_2]^-$ anion which is readily synthesized by N–P bond-forming reactions.[1–4] However, several aspects of the chemistry of diazadiphosphapentan-ones and -thiones remain unexplored. While the co-ordination chemistry of a limited number of carbonyl compounds has been investigated,[5–7] their thiocarbonyl analogues have been overlooked. One important objective is to determine whether the C=S group has a greater tendency to co-ordinate to metal centres than does the carbonyl group. The effect which oxidation at the phosphorus centres has on the reactivity of the molecule concerned is another approach which is untested. In addition the nitrogen atoms represent further sites to be exploited, particularly so if deprotonation is an available option. Here, we describe the syntheses of $(Ph_2PNH)_2CO$ and its thiocarbonyl analogue $(Ph_2PNH)_2CS$ together with some examples of their co-ordination compounds and the formation of the phosphorus(v) species $(Ph_2PENH)_2CO$ and $(Ph_2PSNH)_2CS$. Three illustrative crystal structures are also reported.

Experimental

General experimental conditions were as described previously.[1,4] Thiourea was dried overnight at 100 °C before use, $(Me_3SiNH)_2CO$ and PPh_2Cl (Aldrich) were used as received.

Preparations

$(Ph_2PNH)_2CO$ I. A solution of chlorodiphenylphosphine (8.8 cm^3, 10.8 g, 48 mmol) in toluene (20 cm^3) was added dropwise over a period of 10 min to a stirred suspension of *N,N′*-bis(trimethylsilyl)urea (5.0 g, 24 mmol) in toluene (25 cm^3) at 70–80 °C. After 2 h the toluene was removed *in vacuo* and hexane (50 cm^3) added. The colourless solid was collected by suction filtration, and washed with further hexane and diethyl ether. Yield: 9.5 g, 92% [Found (Calc. for $C_{25}H_{22}N_2OP_2$): C, 69.15 (70.1); H, 5.10 (5.20); N, 6.55 (6.55%)]. IR (KBr): 3257s, 3071m, 3052m, 3012m, 3001w, 1957w, 1884w, 1815w, 1620vs, 1586 (sh), 1572 (sh), 1472vs, 1432s, 1402s, 1326w, 1309w, 1278w, 1185s, 1097m, 1069w, 1028m, 999m, 970w, 912w, 852w, 770s, 742vs, 695vs, 618w, 509s, 486m, 439m, 413w, 398w and 318w cm^{-1}.

$(Ph_2PNH)_2CS$ II. A solution of chlorodiphenylphosphine (13.2 cm^3, 16.2 g, 73 mmol) in tetrahydrofuran (thf) (30 cm^3) was added dropwise over a period of 40 min to a stirred suspension of thiourea (2.8 g, 37 mmol) and triethylamine (10.3 cm^3, 7.4 g, 73 mmol) in thf (110 cm^3). Stirring was continued for 45 min, during which time triethylammonium hydrochloride separated from the olive-green solution. This precipitate was removed by suction filtration, washed with thf (100 cm^3) and the combined filtrates concentrated *in vacuo* to a green oil. Trituration with ethanol (250 cm^3) gave **II** as a colourless solid. Yield: 7.48 g, 46% [Found (Calc. for $C_{25}H_{22}N_2P_2S$): C, 66.5 (67.55); H, 5.30 (4.90); N, 5.75 (5.60)%]. IR (KBr): 3220s, 3156s, 3061m, 2687w, 2347w, 1952w, 1890w, 1812w, 1457vs, 1432s, 1349w, 1307 (sh), 1281s, 1254vs, 1184m, 1167m, 1128m, 1099m, 1069m, 1026m, 1000m, 969w, 944w, 919w, 848w, 742vs, 734vs, 694vs, 618w, 577w, 513m, 504m, 498m, 467m, 443w, 436w and 391w cm^{-1}.

$[Ph_2P(O)NH]_2CO$ III. Aqueous hydrogen peroxide (30% w/w, 2 cm^3, 16 mmol) was added to a suspension of $(Ph_2PNH)_2CO$ (0.9 g, 2.1 mmol) in thf (30 cm^3) at 0 °C and the mixture stirred for 10 min. The solution was concentrated to 5 cm^3 and diethyl ether (50 cm^3) added. The colourless product **III** was collected by suction filtration and washed with further diethyl ether. Yield: 0.81 g, 83% [Found (Calc. for $C_{25}H_{22}N_2O_3P_2$): C, 63.2 (65.2); H, 4.70 (4.80); N, 5.95 (6.10)%]. IR (KBr): 3226m (br), 3150m, 3058m, 2898w, 1715s, 1471vs, 1439vs, 1253m, 1183s, 1127s, 1104s, 1072w, 1028w, 998w, 914w, 854w, 811m, 771m, 751s, 726s, 693s, 626w, 570m, 532s, 511m and 428w cm^{-1}.

$[Ph_2P(E)NH]_2CO$ (E = S IV or Se V) and $[Ph_2P(S)NH]_2CS$ VI. These compounds were prepared by the same general procedure. The compounds $(Ph_2PNH)_2CO$ or $(Ph_2PNH)_2CS$ (2 mmol) and the appropriate chalcogen (2–2.5 mmol) were heated to reflux in toluene (20 cm^3) for 10–20 min. The hot solution was filtered through Celite and the solvent removed from the filtrate *in vacuo*. The crude product was recrystallised from CH_2Cl_2–hexane at −20 °C. Yields were typically 60–80%. Compound **IV** [Found (Calc. for $C_{25}H_{22}N_2OP_2S_2$): C, 59.9 (60.95); H, 4.50 (4.15); N, 5.80 (5.70)%]. IR (KBr) 3096s, 3057m, 2915w, 2809w, 1985w, 1909w, 1810w, 1668vs, 1471s, 1436s, 1426s, 1338w, 1308w, 1257m, 1185w, 1158w, 1104s, 1066m, 1027w, 998w, 874m, 851w, 791w, 749m, 723s, 689s, 665m, 647m, 615w, 587w, 533s, 503m, 495s, 468w, 443w, 392m, 360w and 340w cm^{-1}. Compound **V** [Found (Calc. for $C_{25}H_{22}N_2OP_2Se_2$): C, 50.45 (51.2); H, 3.85 (3.80); N, 4.95 (4.80)%]: IR (KBr) 3328m, 3125s, 3052s, 2781w, 1965w, 1909w, 1817w, 1683vs, 1480s, 1436vs, 1410s, 1336w, 1310w, 1277w, 1255m, 1182w, 1159w, 1107s, 1100s, 1070w, 1049m, 1027m, 998m, 923w, 878m, 842w, 749s, 717s, 704s, 690s, 633m, 618w, 565s, 523s, 489m, 473m and 369m cm^{-1}. Compound **VI** [Found (Calc. for $C_{25}H_{22}N_2P_2S_3$): C, 58.15 (59.05); H, 4.20 (4.35); N, 5.45 (5.50)%]. IR (KBr): 3075s, 3056s, 2902w, 2873w, 1501s, 1481m, 1449m, 1437s, 1294m, 1270m, 1191s, 1181s, 1160m, 1111s, 1102s, 1070w, 1028w, 998m, 962m, 829s, 754m, 739s, 731s, 721s, 690s, 673m, 645m, 627m, 613m, 557s, 512s, 496m, 482m, 472m, 453w, 429w, 366w, 354w and 341w cm^{-1}.

***cis*-[PtCl$_2${Ph$_2$PNHCONHPPh$_2$-*P,P'*}] 1.** To a solution of [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) (0.052 g, 0.139 mmol) in dichloromethane (5 cm^3) was added solid Ph$_2$PNHCONHPPh$_2$ (0.060 g, 0.140 mmol). After stirring for *ca.* 17 h the white solid was collected by suction filtration. Yield: 0.078 g, 81%. Concentration of the filtrate by evaporation under reduced pressure to (*ca.* 1–2 cm^3) and addition of diethyl ether (10 cm^3) gave an additional crop of *cis*-[PtCl$_2${Ph$_2$PNHCONHPPh$_2$-*P,P'*}] [Found (Calc. for $C_{25}H_{22}Cl_2N_2OP_2Pt$): C, 42.85 (43.25); H, 3.25 (3.2); N, 4.1 (4.05)%]. Selected NMR (Me$_2$SO–C$_6$D$_6$) and IR data: ^{31}P-{^{1}H} NMR δ(P) 40.6, ^1J(PtP) 3779 Hz; ^{195}Pt-{^{1}H} NMR δ(Pt) −4545; IR (KBr disc) 3326, 3145 [ν(N–H)]; 1673 [ν(C=O)]; 324, 303 cm^{-1} [ν(Pt–Cl)].

***cis*-[PdCl$_2${Ph$_2$PNHCONHPPh$_2$-*P,P'*}] 2.** To a yellow solution of [PdCl$_2$(cod)] (0.075 g, 0.263 mmol) in dichloromethane (10 cm^3) was added solid Ph$_2$PNHCONHPPh$_2$ (0.113 g, 0.264 mmol). The solution turned pale yellow and after further stirring (*ca.* 90 min) the solid product deposited and was collected by suction filtration. Yield: 0.107 g, 67%. A second crop (0.050 g) was obtained upon reducing the volume of the filtrate under reduced pressure and addition of diethyl ether (20 cm^3) [Found (Calc. for $C_{25}H_{22}Cl_2N_2OP_2Pd$): C, 46.45 (49.55); H, 3.6 (3.65); N, 4.7 (4.65)%]. Selected NMR and IR data: ^{31}P-{^{1}H} NMR (Me$_2$SO–C$_6$D$_6$) δ(P) 62.9; IR(KBr disc) 3319, 3143 [ν(N–H)]; 1672 [ν(C=O)]; 313, 304 cm^{-1} [ν(Pd–Cl)]. Clear crystals suitable for X-ray crystallography were obtained from CHCl$_3$.

***cis*-[PtMe$_2${Ph$_2$PNHCONHPPh$_2$-*P,P'*}] 3.** To a solution of [PtMe$_2$(cod)] (0.040 g, 0.120 mmol) in dichloromethane (15 cm^3) was added solid Ph$_2$PNHCONHPPh$_2$ (0.051 g, 0.120 mmol) and the colourless solution stirred for *ca.* 30 min. The volume was reduced under reduced pressure to *ca.* 1–2 cm^3 and diethyl ether (20 cm^3) added. The white product was collected by suction filtration. Yield: 0.070 g, 90% [Found (Calc. for $C_{27}H_{28}N_2OP_2Pt$): C, 49.75 (49.6); H, 3.80 (4.35); N, 3.80 (4.3)%]. Selected NMR (CDCl$_3$) and IR data: ^{31}P-{^{1}H} NMR δ(P) 62.7, ^1J(PtP) 1931; ^{195}Pt-{^{1}H} NMR δ(Pt) −4699; ^{1}H NMR δ(H) 6.23, ^3J(PtH) 25.5 Hz (NH); IR (KBr disc) 3350, 3147 [ν(N–H)]; 1662 cm^{-1} [ν(C=O)].

***cis*-[PtMe(Cl){Ph$_2$PNHCONHPPh$_2$-*P,P'*}] 4.** To the solids [PtMe(Cl)(cod)] (0.013 g, 0.037 mmol) and Ph$_2$PNHCONHPPh$_2$ (0.016 g, 0.037 mmol) was added CDCl$_3$ (0.7 cm^3) and the reaction immediately monitored by ^{31}P-{^{1}H} NMR spectroscopy. The exclusive phosphorus-containing species observed after *ca.* 5 min was identified as *cis*-[PtMe(Cl){Ph$_2$PNHCONHPPh$_2$-*P,P'*}] and could be isolated by addition of diethyl ether (10 cm^3) to the CDCl$_3$ solution. The white product was collected by suction filtration. Yield: 0.022 g, 88% [Found (Calc. for $C_{26}H_{25}ClN_2OP_2Pt$): C, 45.65 (46.35); H, 3.5 (3.75); N, 4.3 (4.15)%]. Selected NMR (CDCl$_3$) and IR data: ^{31}P-{^{1}H} NMR δ(P$_A$ *trans* to CH$_3$) 60.7, ^1J(PtP$_A$) 1834, δ(P$_B$ *trans* to Cl) 52.4, ^1J(PtP$_B$) 4483, ^2J(P$_A$P$_B$) 24.2; ^{195}Pt-{^{1}H} NMR δ(Pt) −4618; ^{1}H NMR δ(H) 6.16 [^3J(PtH) 67.1] and 5.95 [^3J(PtH) 34.6 Hz] (both NH); IR (KBr disc) 3343, 3145 [ν(N–H)], 1667 [ν(C=O)]; 303 cm^{-1} [ν(Pt–Cl)].

Crystallography

Details of the data collections and refinement parameters are given in Table 1. All determinations were performed at room temperature using Cu-Kα radiation and ω scans. The structures were solved by direct methods (**II**·Me$_2$SO, **IV**) or the heavy-atom method (**2**) and all non-hydrogen atoms refined anisotropically. Absorption corrections were made with the program DIFABS unless stated otherwise.[8] The hydrogen atoms were refined in idealised positions. In **II**·Me$_2$SO the solvate molecule is disordered about the C_2 axis. Calculations were performed using SHELXTL[9] or teXsan.[10]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/187.

Results and Discussion

The reaction between PPh$_2$Cl and commercially available *N,N'*-bis(trimethylsilyl)urea proceeds in toluene at 70–80 °C to give Ph$_2$PNHC(O)NHPPh$_2$ **I** [equation (1)]. Addition of

$$2PPh_2Cl + (Me_3SiNH)_2CO \longrightarrow Ph_2PNHC(O)NHPPh_2 + 2SiMe_3Cl \quad (1)$$

the chlorophosphine to the urea suspension leads to rapid dissolution of the urea followed within minutes by precipitation of colourless **I**, often leading to a viscous mixture which resists stirring. Removal of the solvent *in vacuo* followed by washing of the precipitate with hexane leads to near-quantitative recovery of this product. Air- and moisture-tolerant, **I** is readily soluble only in Me$_2$SO, due perhaps to strong intermolecular hydrogen bonding between the carbonyl group and amine protons of adjacent molecules in the solid state. The infrared spectrum contains a sharp band at 3257 cm^{-1} which corresponds to ν(NH), suggesting that intermolecular hydrogen bonding is relatively weak. The ν(CO) absorption is at 1620 cm^{-1}; ν(CN) is assigned to the intense band at 1472 cm^{-1}.

Whilst Schmutzler and co-workers[11] reported that the monosulfide Ph$_2$P–P(S)Ph$_2$ is the only phosphorus-containing product from the reaction between PPh$_2$Cl and thiourea, we find that in thf at room temperature the thiocarbonyl analogue of diphosphine **I**, Ph$_2$PNHC(S)NHPPh$_2$ **II**, can be prepared [equation (2)]. Accompanying consumption of the insoluble

$$2PPh_2Cl + NH_2C(S)NH_2 + 2NEt_3 \longrightarrow Ph_2PNHC(S)NHPPh_2 + 2[NEt_3H]Cl \quad (2)$$

thiourea is precipitation of [NEt$_3$H]Cl, the supernatant solution turning green as this mildly exothermic reaction proceeds. Removal of the ammonium salt by filtration, evaporation of the thf *in vacuo* and trituration of the resultant green oil with ethanol gives **II** in typically 46% yield. Following collection by suction filtration, concentration of the ethanol filtrate leads to isolation of the more soluble by-products, of which Ph$_2$P–P(S)Ph$_2$ [δ(P) 47.8 and −11.6, ^1J(P–P) 254 Hz] is the most abundant. While the position of the trimethylsilyl groups in (Me$_3$SiNH)$_2$CO dictates the regioselectivity in its reaction with PPh$_2$Cl, there is no such control for thiourea. Thus it is conceivable that other molecules such as Ph$_2$PNHC(S)NH$_2$ or (Ph$_2$P)$_2$NC(S)NH$_2$ are among the products. There are two minor differences between our synthetic procedure and that of Schmutzler and co-workers. First, we have employed a shorter reaction time (45 min *vs.* 5 h) and secondly addition of the chlorophosphine is performed at room temperature over a period of 10 min, as opposed to at −20 °C. The effects of these changes are hard to quantify, but they are sufficient to allow us to generate **II** in moderate yield. Unlike the carbonyl compound **I**, **II** is moderately soluble in a range of solvents such as Me$_2$SO, thf, acetone or CHCl$_3$. It decomposes more rapidly in solution than **I**, giving rise to as yet

Table 1 Details of the X-ray data collections and refinements

	$II{\cdot}Me_2SO$[a]	IV[b]	$2{\cdot}H_2O$[b]
Empirical formula	$C_{25}H_{22}N_2P_2S{\cdot}C_2H_6OS$	$C_{25}H_{22}N_2OP_2S_2$	$C_{25}H_{22}Cl_2N_2OP_2Pd{\cdot}H_2O$
M	522.6	492.5	623.73
Colour, habit	Colourless, square plate	Clear, block	Clear, prism
Crystal size/mm	0.30 × 0.30 × 0.06	0.32 × 0.48 × 0.63	0.18 × 0.21 × 0.29
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbcn*	$P2_1/n$	$P2_1/n$
a/Å	9.742(2)	11.755(1)	12.322(4)
b/Å	11.339(2)	9.163(2)	15.726(3)
c/Å	28.059(3)	22.697(2)	13.926(3)
β/°		95.578(8)	90.69(2)
U/Å^3	2768	2433	2698
Z	4	4	4
D_c/Mg m^{-3}	1.25	1.34	1.53
μ/mm^{-1}	3.00	3.34	8.69
2θ range/°	3–128	6–120	6–120
$F(000)$	1096	1024	1256
Independent reflections (R_{int})	2299	3902 (0.039)	4199 (0.040)
Observed reflections	1742	3375	2752
No. parameters refined	161	312	308
Data/parameter ratio	10.8/1	10.8/1	8.9/1
Absorption correction	Face indexed	DIFABS	DIFABS
Minimum, maximum transmission	0.45, 0.82	0.82, 1.00	0.52, 1.00
p in weighting scheme	0.0005	0.0050	0.0030
Final R, R'	0.0465, 0.0524	0.035, 0.041	0.060, 0.053
Largest Δ/σ	0.012	0.06	0.10
Largest difference peak, hole/e Å^{-3}	0.34, −0.25	0.26, −0.25	0.68, −0.90

[a] Siemens P4/PC diffractometer, SHELXTL, $F > 4.0\sigma(F)$, refinement on F with $w^{-1} = \sigma^2(F) + pF^2$. [b] Rigaku AFC7S diffractometer, teXsan, $I > 3.0\sigma(I)$, refinement on F with $w^{-1} = \sigma^2(F) + pF^2$.

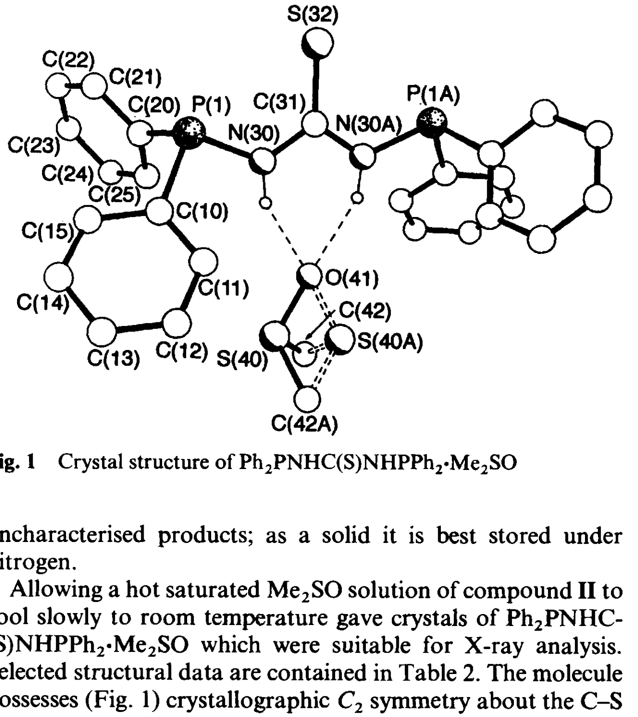

Fig. 1 Crystal structure of $Ph_2PNHC(S)NHPPh_2{\cdot}Me_2SO$

uncharacterised products; as a solid it is best stored under nitrogen.

Allowing a hot saturated Me_2SO solution of compound **II** to cool slowly to room temperature gave crystals of $Ph_2PNHC(S)NHPPh_2{\cdot}Me_2SO$ which were suitable for X-ray analysis. Selected structural data are contained in Table 2. The molecule possesses (Fig. 1) crystallographic C_2 symmetry about the C–S bond, with one molecule of disordered Me_2SO solvate present. The PN(CS)NP backbone of the structure is planar (maximum deviation from the mean plane 0.003 Å), consistent with an sp^2 hybridisation of the nitrogen atoms and C(31). The pyramidal geometry at phosphorus is somewhat distorted with all of the angles substantially less than 109°. There is strong hydrogen bonding between the amine protons and the oxygen atom of the Me_2SO molecule [H(30)···O(41) 1.99, O···N 2.82 Å, N–H···O 154°] which, in conjunction with the bulkiness of the phosphine substituents, is responsible for the *syn,syn* orientation of the nitrogen–phosphorus bonds relative to C(31)–S(32); this, notably, is opposite to the conformation generally adopted by diphosphines of this type.[5,12–16] Consequently the non-bonded P···P distance of 5.44 Å greatly exceeds the range of typical values (2.80–3.00 Å), whilst the C–S, P–N and N–C bond lengths are comparable to those found in related structures.[5,12–16] For **II**·Me_2SO the non-bonded P···S distance is 3.23 Å and the N···N separation is 2.27 Å.

Table 2 Selected bond lengths (Å) and angles (°) for $Ph_2PNHC(S)NHPPh_2{\cdot}Me_2SO$

P(1)–N(30)	1.719(2)	N(30)–C(31)	1.357(3)
C(31)–S(32)	1.660(4)	Mean P–C (aryl)	1.83
N(30)–C(31)–S(32)	123.5(2)	N(30)–C(31)–N(30A)	113.1(3)
C(20)–P(1)–N(30)	101.9(1)	C(10)–P(1)–N(30)	98.4(1)
P(1)–N(30)–C(31)	124.0(2)	C(10)–P(1)–C(20)	100.0(1)

For the thiocarbonyl **II** the ν(NH) bands appear at 3220 and 3156 cm^{-1} with ν(CN) at 1457 cm^{-1}. The infrared spectrum of **II**·Me_2SO contains considerably more bands than the spectra obtained from batches free of solvate, as a consequence of the hydrogen bonding observed in the solid state and absorptions of the Me_2SO molecule.

Consistent with their structure, the ^{31}P NMR spectra of compounds **I** and **II** are singlets, while in the ^{13}C NMR the carbonyl resonances [$\delta(^{13}C)$ in Table 3] appear as triplets as a result of ^2J coupling to two equivalent phosphorus nuclei. Positive-ion FAB mass spectrometry further verifies their identity as diphosphines.

Oxidation of compound **I** by hydrogen peroxide, sulfur or selenium leads to phosphorus(V) derivatives $Ph_2P(E)NHC(O)NHP(E)Ph_2$ (E = O **III**, S **IV** or Se **V**) [equations (3) and (4)]. The dioxide **III** has previously been prepared from

$$(Ph_2PNH)_2CO + H_2O_2 \longrightarrow \underset{\textbf{III}}{[Ph_2P(O)NH]_2CO} \quad (3)$$

$$(Ph_2PNH)_2CO + 2\,E \longrightarrow [Ph_2P(E)NH]_2CO \quad (4)$$
$$E = S\ \textbf{IV}\ \text{or}\ Se\ \textbf{V}$$

$Ph_2PNCNPPh_2$ or $Ph_2P(O)NCNP(O)Ph_2$[17] and by condensation of smaller fragments.[18] There is little agreement between the published infrared spectral data[17] and our own, however no chemical shift data have been reported which can confirm

Table 3 The $^{31}P-\{^1H\}$, $^{13}C-\{^1H\}$ NMR and positive-ion FAB mass spectrometric data for the diphosphines

Compound	Solvent	$\delta(^{31}P)$	$\delta(^{13}C)$	^2J(P–C)/Hz	*m/z*
I	$(CD_3)_2SO$	25.1	159.3	17.0	428
II	$(CD_3)_2SO$	30.8	189.2	24.0	443
III	$(CD_3)_2SO$	19.5	152.2[a]	—	461
IV	$CDCl_3$	52.2	154.7	—	493
V	$CDCl_3$	47.0[b]	153.6	—	589
VI	$CDCl_3$	53.0	183.2	—	508

[a] Spectrum recorded in CH_3OD. [b] $^1J(^{31}P-^{77}Se)$ 784 Hz.

identification. The disulfide **IV** and diselenide **V** have not been previously reported. The compounds are air-stable colourless solids, **IV** and **V** being soluble in chlorinated solvents, **III** only partially soluble in methanol or Me_2SO.

While the oxidation of compound **II** by sulfur proceeds in refluxing toluene to give the disulfide $Ph_2P(S)NHC(S)NHP(S)Ph_2$ **VI** we have been unable to isolate samples of the thiocarbonyl analogues of **IV** and **V**. Treatment of **II** with aqueous H_2O_2 at 0 °C converts the C=S group into C=O in addition to oxidation of the phosphorus centres, giving $[Ph_2P(O)NH]_2CO$, confirmed by ^{31}P NMR and infrared spectroscopy; the reaction between **II** and selenium in refluxing toluene or in thf at room temperature leads to a mixture of unidentified compounds according to ^{31}P NMR spectroscopy. A singlet at δ 48.0 with selenium satellites $[^1J(^{31}P-^{77}Se)$ 801 Hz$]$ may correspond to the desired product, but we have no further evidence to support this as all attempts at separation have failed.

The dioxidised derivatives display singlets in their phosphorus-31 NMR spectra (Table 3), with ^{77}Se satellites for **V**. No $^2J(^{31}P-^{13}C)$ couplings between the phosphorus nuclei and the carbon atom of the carbonyl or thiocarbonyl group were resolved. In the infrared spectra, oxidation of **I** lowers δ(NH) by over 100 cm^{-1} and increases ν(CO) by 50–100 cm^{-1} for **III** and **IV**. The former may arise from greater intermolecular hydrogen bonding compared with **I**. There is a shift to low frequency of the carbonyl resonance in the ^{13}C NMR spectrum upon oxidation; a correlation exists with ν(CO) in the vibrational spectra for **I** and **III**, **IV**. The increase in ν(CO) and hence of C–O bond order upon oxidation of **I** indicates a reduction in the contributions of N=C–OH tautomers, as a result of the electron-withdrawing influences of the adjacent phosphorus(V) centres; the ν(CN) frequencies seem oblivious to the effects of oxidation (1471, 1471 and 1480 cm^{-1} for **III**, **IV** and **V** respectively, *cf.* 1472 cm^{-1} for **I**). We assign strong bands at 647 and 565 cm^{-1} in the infrared spectra of **IV** and **V** to the ν(PS) and ν(PSe) stretches respectively; for **III** ν(PO) appears as an intense absorption at 1183 cm^{-1}. For **VI** the ν(NH) bands overlap with the ν(C–H) vibrations of the phenyl rings. By analogy with **IV** we assign an absorption of medium intensity at 645 cm^{-1} to ν(PS).

Table 4 Selected bond lengths (Å) and angles (°) for $Ph_2P(S)NHC(O)NHP(S)Ph_2$

S(1)–P(1)	1.931(1)	P(2)–N(2)	1.686(2)
P(1)–N(1)	1.702(2)	N(1)–C(13)	1.367(3)
O(1)–C(13)	1.219(3)	N(2)–C(13)	1.379(3)
S(2)–P(2)	1.942(1)	N(1)–H(1)	1.028(2)
N(2)–H(2)	0.952(2)	Mean P–C(aryl)	1.80
N(1)–P(1)–S(1)	116.07(9)	N(2)–P(2)–S(2)	114.6(1)
P(2)–N(2)–C(13)	134.6(2)	C(13)–N(1)–P(1)	121.8(2)
O(1)–C(13)–N(1)	121.9(2)	O(1)–C(13)–N(2)	120.4(2)
N(2)–C(13)–N(1)	117.7(2)		

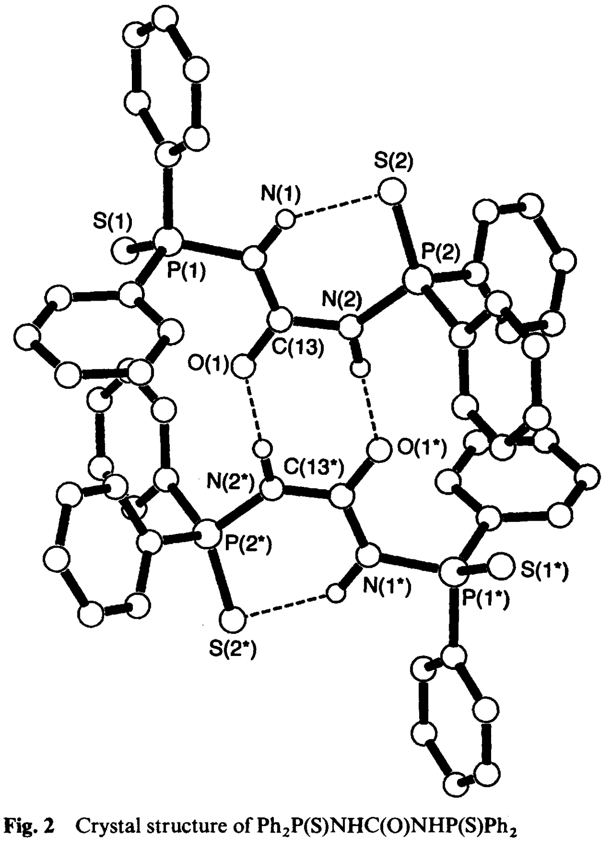

Fig. 2 Crystal structure of $Ph_2P(S)NHC(O)NHP(S)Ph_2$

In the solid state compound **IV** exists (Table 4, Fig. 2) with P(1)–S(1) in an approximately *syn* orientation to C(13)–O(1), S(2)–P(2) being *anti* with respect to C(13)–O(1). This is intermediate between the *syn,syn* orientation of the diphenylphosphino substituents in **II** and the *anti,anti* conformation adopted by other linear diazadiphosphapentan-ones and -thiones.[5,12,14,15] There is an intramolecular hydrogen bond [H(1n) ··· S(2) 2.20, N(1) ··· S(2) 3.10 Å, N–H ··· S(2) 146°] as well as intermolecular hydrogen-bonding interactions between the O(1) and H(2) atoms of adjacent molecules [H(2) ··· O(1*) 1.86, N(2) ··· O(1*) 2.81 Å, N(2)–H(2) ··· O(1*) 175.3°] which, combined with the steric bulk of the diphenylphosphinothioyl moieties, dictates the molecular conformation. Overall P(1)–N(1)–C(13)–O(1)–N(2)–P(2)–S(2) are close to planar [maximum deviation from the mean plane 0.11 Å for O(1)] with S(1) lying 1.42 Å from this plane. The phosphorus–nitrogen and -sulfur bond lengths are inequivalent with P(2)–N(2) and P(1)–S(1) being the shorter within each pair. The N(1)–C(13) and N(2)–C(13) distances are the same within statistical significance. The P(2)–N(2)–C(13) angle is substantially more open than C(13)–N(1)–P(1) [134.5(2) and 121.8(2)° respectively]; despite this enlargement the nitrogen atoms and C(13) are essentially sp^2 hybridised. Overall, the P–N, N–C and C–O bond lengths for **IV** are comparable with the corresponding parameters in related structures.[5,12,14,15]

As would be expected, reaction of compound **I** with $[ML_2(cod)]$ (L = Cl or Me, M = Pd or Pt) proceeds smoothly with displacement of cod and formation of *P,P'*-chelate complexes **1**–**4**. The new complexes gave satisfactory

Table 5 Selected bond lengths (Å) and angles (°) for *cis*-[PdCl$_2${Ph$_2$PNHCONHPPh$_2$-*P*,*P*′}]

Pd–Cl(1)	2.359(3)	Pd–Cl(2)	2.340(2)
Pd–P(1)	2.200(3)	Pd–P(2)	2.216(2)
P(1)–N(1)	1.680(7)	P(2)–N(2)	1.687(8)
N(1)–C(1)	1.362(11)	N(2)–C(1)	1.389(12)
C(1)–O(1)	1.226(11)		
Cl(1)–Pd–Cl(2)	93.2(1)	P(1)–Pd–P(2)	91.4(1)
Cl(1)–Pd–P(2)	88.1(1)	Cl(2)–Pd–P(1)	87.7(1)
Pd–P(1)–N(1)	114.7(3)	Pd–P(2)–N(2)	115.9(3)
P(1)–N(1)–C(1)	126.7(7)	P(2)–N(2)–C(1)	130.5(7)
N(1)–C(1)–O(1)	121.7(10)	N(2)–C(1)–O(1)	119.5(9)

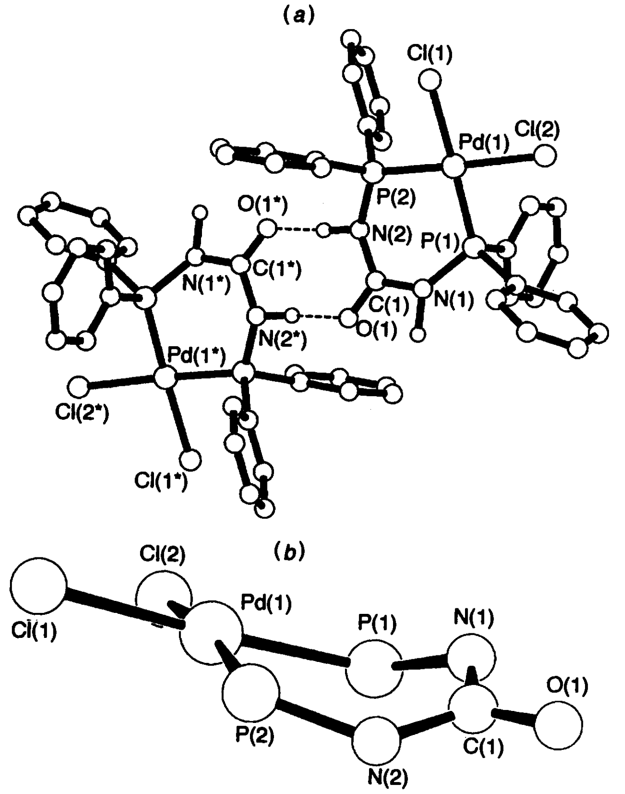

Fig. 3 Crystal structure of *cis*-[PdCl$_2${Ph$_2$PNHCONHPPh$_2$-*P*,*P*′}] (*a*) showing the dimer pair formation and (*b*) the core illustrating the pseudo-boat conformation of the ring

microanalyses and NMR and IR spectra which allowed identification as simple chelate metal(II) complexes. The crystal structure of **2**·H$_2$O reveals (Table 5, Fig. 3) that the square-planar palladium centre [maximum deviation from the Pd–Cl(1*)–Cl(2)–P(1)–P(2) mean plane 0.18 Å for Cl(2)] is part of a puckered pseudo-boat-like six-membered PdP$_2$N$_2$C ring with the co-ordination plane and the P(1)–N(1)–N(2)–C(1) mean planes being inclined by 36°. Within the metallacycle there appears to have been some slight contractions in the P–N bond lengths compared to **II**·Me$_2$SO, though whether this is a consequence of co-ordination or the change from a C=O to a C=S group is difficult to judge. The backbone of the ligand in **2**·H$_2$O is involved in a pair of hydrogen bonds (about a crystallographic centre of symmetry) to adjacent molecules [H(2n)···O(1*) 1.95, N(2)···O(1*) 2.80 Å, N(2)–H(2n)···O(1*) 151°] to form dimer pairs of molecules. The H$_2$O solvate is hydrogen bonded to the other N–H group of the ligand backbone [H(1n)···O(2) 1.74, N(1)···O(2) 2.75 Å, N(1)–H(1n)···O(2) 144°].

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Received 28*th May* 1996; *Paper* 6/03700C