Monoxidised Sulfur and Selenium Derivatives of Bis(diphenylphosphino)amine: Synthesis and Co-ordination Chemistry†

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The complexes *cis*/*trans*-[M{$Ph_2P(E)NHPPh_2$}$_2$]Cl_2 and [M{$Ph_2P(E)NPPh_2$}$_2$] (M = Pd or Pt) E = S or Se) have been prepared and characterised. The crystal structures of two representative examples, *trans*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 and *cis*-[Pt{$Ph_2P(Se)NPPh_2$}$_2$], have been determined. The $PtSeP_2N$ rings are puckered in both cases although there are some differences as a result of the formal charge upon the ligand and the *cis*/*trans* geometries. The *cis* neutral complex has shorter Pt–P and longer Pt–Se bonds than those of the *trans* protonated complex. Deprotonation of the ligand also results in a significant shortening of the P–N bond lengths.

The chemistry of $Ph_2PNHPPh_2$ and $Ph_2P(E)NH(E)PPh_2$ has developed rapidly in recent times[1–6] in part because of the relationship these molecules have to traditional phosphines such as $Ph_2PCH_2PPh_2$ and to acetylacetonates. An obvious extension to these investigations is the study of the chemistry of the monochalcogenides $Ph_2PNHP(E)Ph_2$ (E = S, Se or Te). By analogy with their methylene-bridged counterparts we anticipate that these molecules will exhibit a similar variety of co-ordination modes. Formation of heterobimetallics, reliant upon the different 'hard' and 'soft' characters of the donor atoms, and metallation of the nitrogen atom are potential routes to polynuclear species. To understand the chemistry of these molecules we have synthesised $Ph_2PNHP(E)Ph_2$ (E = S or Se) and investigated their reactivity with platinum(II) and palladium(II) centres. Here we report the preparation and spectroscopic study of *cis*/*trans*-[M{$Ph_2P(E)NHPPh_2$}$_2$]Cl_2 and [M{$Ph_2P(E)NPPh_2$}$_2$] (M = Pd or Pt, E = S or Se) together with X-ray studies upon *trans*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 and *cis*-[Pt{$Ph_2P(Se)NPPh_2$}$_2$].

Experimental

General experimental procedures and instrumentation were as described previously.[7] The complex [$PdCl_2$(cod)] was generated by the addition of cycloocta-1,5-diene (cod) to a methanolic suspension of $Na_2[PdCl_4]$.[8] Microanalyses were performed by the Imperial College or the Loughborough University services. In the ^{31}P NMR spectra we report *N* defined (conventionally) as *J*(A–X) + *J*(A–X′).

$Ph_2PNH(S)PPh_2$.—A suspension of $Ph_2PNHPPh_2$ (2.73 g, 7.1 mmol) and sulfur (217 mg, 6.8 mmol) in diethyl ether (150 cm^3) was stirred for 6 h. The solvent was removed *in vacuo* to give a viscous oil which was extracted into tetrahydrofuran (thf) (100 cm^3) and filtered through Celite. Concentration of the filtrate to 15–20 cm^3 followed by slow addition of hexane (50 cm^3) gave colourless crystals, collected by suction filtration. Yield: 2.39 g, 81% [Found (Calc. for $C_{24}H_{21}NP_2S$): C, 68.45 (69.05); H, 5.85 (5.05); N 2.95 (3.35)%]. ^{31}P-{^1H} NMR [$(CD_3)_2SO$]: δ(P_A) 27.6(d), δ(P_X) 60.9(d); $^2J(^{31}P_A-^{31}P_X)$ 86 Hz. Positive ion FAB mass spectrum: *m*/*z* 417, M^+.

$Ph_2PNH(Se)PPh_2$.—A suspension of $Ph_2PNHPPh_2$ (2.07 g, 5.4 mmol) and grey selenium (423 mg, 5.4 mmol) in diethyl ether (45 cm^3) was stirred for 3 h. The solvent was removed *in vacuo* to give a viscous oil which was extracted into thf (150 cm^3) and filtered through Celite. Concentration of the filtrate to 15–20 cm^3 followed by slow addition of hexane (25 cm^3) gave off-white crystals, collected by suction filtration. Yield: 2.42 g, 97% [Found (Calc. for $C_{24}H_{21}NP_2Se$): C, 61.65 (62.10); H, 5.05 (4.55); N, 2.65 (3.00)%]. ^{31}P-{^1H} NMR [$(CD_3)_2SO$]: δ(P_A) 29.3(d), δ(P_X) 58.2(d); $^2J(^{31}P_A-^{31}P_X)$ 93, $^1J(^{31}P_X-^{77}Se)$. 757 Hz. Positive ion FAB mass spectrum: *m*/*z* 465, $[M + H]^+$.

trans- and cis-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 **1**,**2**.—The compound $Ph_2PNHPPh_2$ (267 mg, 0.69 mmol) and grey selenium (54 mg, 0.68 mmol) were stirred together in CH_2Cl_2 (10 cm^3) for 2.5 h. The complex [$PtCl_2$(cod)] (129 mg, 0.34 mmol) was added, and the lime-green solution stirred for 3 h, during which time *trans*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 **1** separated as a green solid. Hexane (5 cm^3) was added to complete the precipitation of this isomer, which was separated from the supernatant solution by centrifugation and recrystallised from CH_2Cl_2–hexane at −20 °C. Evaporation of the supernatant solution gave *cis*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 **2**, recrystallised separately from CH_2Cl_2–hexane at −20 °C.

Complex **1**: yield 122 mg (30% based upon Pt) [Found (Calc. for $C_{48}H_{42}Cl_2N_2P_4PtSe_2$): C, 48.35 (48.25); H, 3.75 (3.55); N, 2.20 (2.35)%]; ^{31}P-{^1H} NMR (CD_2Cl_2) δ(P_A) 73.5 (t), δ(P_X) 55.7 (t); $^1J(^{195}Pt-^{31}P_A)$ 2320, $^2J(^{195}Pt-^{31}P_X)$ 74, $^1J(^{31}P_X-^{77}Se)$ 480, *N* 110 Hz; ^{195}Pt-{^1H} NMR (CD_2Cl_2) δ −4975 (tt), $J(^{195}Pt-^{31}P)$ 2310 and 74 Hz; IR (KBr) ν(NH) 2727m (br), δ(NH) 1310m, γ(NH) 950s, ν(P_2N) 1136m and 810m, ν(PSe) 544s cm^{-1}; positive ion FAB mass spectrum *m*/*z* 1123, $[Pt(C_{24}H_{21}NP_2Se)_2]^+$.

Complex **2**: yield 83 mg (20% based upon Pt) [Found (Calc. for $C_{48}H_{42}Cl_2N_2P_4PtSe_2 \cdot CH_2Cl_2$): C, 46.50 (46.00); H, 3.30 (3.45); N, 2.10 (2.20)%]; ^{31}P-{^1H} NMR (CD_2Cl_2) δ(P_A) 63.8 (m), δ(P_X) 56.2 (m); $^1J(^{195}Pt-^{31}P_A)$ 3270, $^2J(^{195}Pt-^{31}P_X)$ unresolved, $^1J(^{31}P_X-^{77}Se)$ unresolved, *N* 31 Hz; ^{195}Pt-{^1H} NMR (CD_2Cl_2) δ −4784(tt), $^1J(^{195}Pt-^{31}P)$ 3357 Hz, ^2J unresolved; IR (KBr) ν(NH) 2738m (br), δ(NH) 1308m, γ(NH) 976s, ν(P_2N) 1168m and 800m, ν(PSe) 543s cm^{-1}; positive ion

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

FAB mass spectrum *m/z* 1123, $[Pt(C_{24}H_{21}NP_2Se)_2]^+$. Attempts to recrystallise **2** to give crystals suitable for X-ray studies were unsuccessful. Slow growth from a dilute CH_2Cl_2–hexane solution over the course of several weeks at −20 °C resulted in a change from green to brown, and pale brown crystals of *cis*-$[Pt\{Ph_2P(Se)NPPh_2\}_2]\cdot 2CH_2Cl_2$ **3** as determined by X-ray crystallography.

trans-$[Pd\{Ph_2P(Se)NHPPh_2\}_2]Cl_2$ **4**.—The compound $PH_2PNHPPh_2$ (63 mg, 0.16 mmol) and grey selenium (13 mg, 0.16 mmol) were stirred together in CH_2Cl_2 (5 cm^3) for 2 h. The complex $[PdCl_2(cod)]$ (23 mg, 0.08 mmol) was added and the orange solution stirred for 45 min. Upon filtration through glass wool–Celite, hexane (8 cm^3) was added and the mixture cooled to −20 °C to give orange crystals of **4**. Yield: 68 mg, 76% [Found (Calc. for $C_{48}H_{42}Cl_2N_2P_4PdSe_2$): C, 51.55 (52.10); H, 3.35 (3.85); N, 2.45 (2.55)%]. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ(P_A) 79.1 (t), δ(P_X) 59.7 (t); $^1J(^{31}P_X-^{77}Se)$ 523, *N* 104 Hz. IR (KBr): ν(NH) 2709m (br), δ(NH) 1310m, γ(NH) 957s, ν(P_2N) 1128m and 811m, ν(PSe) 542s cm^{-1}; positive ion FAB mass spectrum: *m/z* 1035, $[Pd(C_{24}H_{21}NP_2Se)_2]^+$.

trans- and cis-$[Pt\{Ph_2P(S)NPPh_2\}_2]$ **5,6**.—The compound $Ph_2PNH(S)PPh_2$ (150 mg, 0.36 mmol) and $[PtCl_2(cod)]$ (67 mg, 0.18 mmol) were stirred together in CH_2Cl_2 (15 cm^3) for 30 min. The solvent volume was reduced *in vacuo* until the solution became cloudy. A pale green solid, *trans*-$[Pt\{Ph_2P(S)NPPh_2\}_2]$ separated and was collected by centrifugation. Evaporation of the remaining solvent gave *cis*-$[Pt\{Ph_2P(S)NPPh_2\}_2]$, which was recrystallised from CH_2Cl_2–hexane.

Complex **5**: yield 52 mg, (28%) [Found (Calc. for $C_{48}H_{40}N_2P_4PtS_2$): C, 55.65 (56.10); H, 3.45 (3.90); N, 3.00 (2.70)%]; $^{31}P-\{^1H\}$ NMR (CD_2Cl_2) δ(P_A) 72.3 (t), δ(P_X) 74.7 (t); $^1J(^{195}Pt-^{31}P_A)$ 2370, $^2J(^{195}Pt-^{31}P_X)$ unresolved, *N* 94 Hz; $^{195}Pt-\{^1H\}$ NMR (CD_2Cl_2) δ −4750 (tt), $J(^{195}Pt-^{31}P)$ 2367 and 88 Hz; IR (KBr) ν(P_2N) 1150m and 805m, ν(PS) 570s cm^{-1}; positive-ion FAB mass spectrum *m/z* 1028, $[Pt(C_{24}H_{21}NP_2S)_2]^+$.

Complex **6** yield 85 mg (46%) [Found (Calc. for $C_{48}H_{40}N_2P_4PtS_2\cdot CH_2Cl_2$):C, 49.70 (48.75); H, 3.35 (3.50); N, 2.15 (2.30)%]; $^{31}P-\{^1H\}$ NMR (CD_2Cl_2)δ(P_A) 59.8(m), δ(P_X) 67.1(m); $^1J(^{195}Pt-^{31}P_A)$ 3240, $^2J(^{195}Pt-^{31}P_X)$ 77, *N* 24 Hz; $^{195}Pt-\{^1H\}$ NMR (CD_2Cl_2)δ −4673 (tt). $^1J(^{195}Pt-^{31}P)$ 3368 Hz; ^2J unresolved; IR (KBr) ν(P_2N) 1156m and 813m, ν(PS) 560s cm^{-1}; positive-ion FAB mass spectrum *m/z* 1028, $[Pt(C_{24}H_{21}NP_2S)_2]^+$.

trans- and cis-$[Pd\{Ph_2P(S)NHPPh_2\}_2]Cl_2$ **7,8**.—The compounds $[PdCl_2(cod)]$ (41 mg, 0.15 mmol) and $Ph_2PNH(S)PPh_2$ (120 mg, 0.29 mmol) were stirred together in CH_2Cl_2 (5 cm^3) for 1 h. Hexane (10 cm^3) was added and the mixture cooled to −2 °C to give **7,8** as a yellow solid. Yield: 129 mg, 85% [Found (Calc. for $C_{48}H_{42}Cl_2N_2P_4PdS_2$: C, 56.20 (56.95); H, 4.40 (4.20); N, 2.85 (2.75)%]. IR (KBr): ν(NH) 2700m (br), δ(NH) 1309m, γ(NH) 948s, ν(P_2N) 821m, ν(PS) 579s and 563s cm^{-1}. $^{31}P-\{^1H\}$ NMR ($CDCl_3$): **7** δ(P_A) 79.7 (t), δ(P_X) 76.1 (t); *N* 46 Hz; **8**, δ(P_A) 78.2 (m), δ(P_X) 68.8 (m); *N* 20 Hz. Positive-ion FAB mass spectrum: *m/z* 939, $[Pd(C_{24}H_{21}NP_2S)_2]^+$.

In-situ *use of* $Ph_2PNH(S)PPh_2$. The compound $Ph_2PNH(P)Ph_2$ (100 mg, 0.26 mmol) and sulfur (8 mg, 0.26 mmol) were stirred together in CH_2Cl_2 (5 cm^3) for 3.5 h. The complex $[PdCl_2(cod)]$ (36 mg, 0.126 mmol) was added and the yellow solution stirred for 15 min during which time a yellow solid, $[PdCl_2\{Ph_2PNH(S)Ph_2\}]$ deposited. This was recovered by centrifugation and slow diffusion of hexane into the CH_2Cl_2 solution gave *trans*- and *cis*-$[Pd\{Ph_2P(S)NHPPh_2\}_2]Cl_2$ **7,8** (55 mg, 43% based upon Pd). Concentration under reduced pressure gave $[Pd\{Ph_2P(S)NPPh_2\}\{N(SPPh_2)_2\}$ **9**, which was recrystallised as orange crystals from CH_2Cl_2–hexane at −20 °C. Yield: 20 mg, 16% based upon Pd [Found (Calc. for $C_{48}H_{40}N_2P_4PdS_3$): C, 59.00 (59.35); H, 4.25 (4.15); N, 2.55 (2.90)%]. IR (KBr): ν(P_2N) 1146m, 1122m and 827m, ν(PS) 588m and 571s cm^{-1}; positive-ion FAB mass spectrum: *m/z* 971, $[Pd(C_{24}H_{20}NP_2S)(C_{24}H_{20}NP_2S_2)]^+$.

X-Ray Crystallography.—Crystal data. **1**·$0.75CH_2Cl_2$, $C_{48.75}H_{43.5}Cl_{3.5}N_2P_4PtSe_2$, *M* = 1258.3, monoclinic, space group *C*2/*c*, *a* = 18.546(7), *b* = 17.964(9), *c* = 18.864(9) Å, β = 118.27(3)°, *U* = 5535 Å^3, *Z* = 4, D_c = 1.51 g cm^{-3}, green needles, crystal dimensions 0.13 × 0.16 × 0.36 mm, μ(Mo-Kα) = 4.19 mm^{-1}, *F*(000) = 2462.

3·$2CH_2Cl_2$, $C_{50}H_{44}Cl_4N_2P_4PtSe_2$, *M* = 1291.6, monoclinic, space group *C*2/*c*, *a* = 16.851(5), *b* = 9.675(4), *c* = 30.432(9) Å, β = 94.99(2)°, *U* = 4943 Å^3, *Z* = 4, D_c = 1.74 g cm^{-3}, pale brown hexagonal plates, crystal dimensions 0.12 × 0.36 × 0.38 mm, μ(Mo-Kα) = 4.69 mm^{-1}, *F*(000) = 2528.

Siemens P4/PC diffractometer, ω-scan method, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å, 2θ range 3.0–50°), 4833 and 4361 independent reflections for **1** and **3** respectively, 3590 and 3717 observed [$F_o > 4.0\sigma(F_o)$], corrected for Lorentz and polarisation factors, semiempirical absorption correction, maximum and minimum transmission factors 0.731, 1.00 and 0.400, 0.182 for **1** and **3** respectively.

The structures were solved by direct methods and the non-hydrogen atoms refined anisotropically. Hydrogen atoms were assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. In both structures the phenyl rings were refined as idealised rigid bodies. In **1** there was evidence for rotational disorder in one of the phenyl rings [C(7)–C(12)] though this could not be resolved into alternative partial-occupancy orientations. The included, partial occupancy (0.375) CH_2Cl_2 in **1** is disordered about a two-fold axis and the carbon and hydrogen atoms could not be located. In **1** the NH hydrogen atom was refined isotropically subject to a refined distance constraint. Refinement was by full-matrix least squares based on *F* (229 and 238 parameters for **1** and **3** respectively) to *R* = 0.0548, 0.0494 and *R'* = 0.0554, 0.0494 for **1**,**3** where $w^{-1} = \sigma^2(F) + 0.0005F^2$ in both cases. The maximum and minimum residual electron densities in the final Δ*F* maps were 2.23, 1.91 and −1.08, −1.47 e Å^{-3} and the mean and maximum shifts/errors in the final refinement 0.025, 0.022 and 1.478, 2.986 for **1**, **3** respectively. Computations were carried out using a Silicon Graphics IRIS computer with SHELXTL.[9]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Monoxidised diphosphinoamines $R_2PNXP(E)R_2$ (R, X = alkyl or aryl; E = S, Se or imine) are accessible by treatment of R_2PNXPR_2 with stoichiometric quantities of the appropriate oxidant (elemental chalcogen or azide) or through condensation of smaller fragments.[10,11] As $Ph_2PNHPPh_2$ is readily prepared in multigram quantities from PPh_2Cl and $NH(SiMe_3)_2$,[12] we chose to use the first of these methods.

It has been reported that $Ph_2PNHPPh_2$ reacts with elemental sulfur and $AlCl_3$ in toluene at room temperature to give $Ph_2PNH(S)PPh_2$.[13] The $AlCl_3$ presumably forms a Lewis acid–base adduct with $Ph_2PNHPPh_2$, one of the phosphorus atoms of which coordinates to the aluminium centre, making it unavailable for further reaction. We anticipated that monoxidation of Ph_2PNHPh_2 by the correct quantity of chalcogen E could proceed without a Lewis acid [equation (1);

$$Ph_2PNHPPh_2 + E \longrightarrow Ph_2PNH(E)PPh_2 \qquad (1)$$

E = S, Se or Te]. For sulfur and selenium this is precisely what is observed. Diethyl ether suspensions of $Ph_2PNHPPh_2$ react with 1 equivalent (slightly less was used for sulfur) of elemental chalcogen at ambient temperature to give $Ph_2PNH(E)PPh_2$

(E = S or Se), as colourless solids which were purified by recrystallisation from thf–hexane. The conversion is quantitative for Se according to ^{31}P NMR spectroscopy (AX pair of doublets) with inevitably minor amounts ($\approx 5\%$) of the doubly oxidised product $Ph_2P(S)NH(S)PPh_2$ and $Ph_2PNHPPh_2$ in the sulfur reaction. When the precise amount of sulfur is employed greater quantities of $Ph_2P(S)NH(S)PPh_2$ are generated, inseparable from the monosulfide by conventional means. Interestingly, by ^{31}P NMR spectroscopy we have found that equimolar quantities of $NH(SePPh_2)_2$ and $Ph_2PNHPPh_2$ react rapidly (< 1 h) under ambient conditions in chloroform to give solely $Ph_2PNH(Se)PPh_2$, whereas $NH(SPPh_2)_2$ and $Ph_2PNHPPh_2$ undergo no sulfur transfer after several hours at room temperature indicating the greater lability of the P=Se bond in $NH(SePPh_2)_2$ compared with P=S in $NH(SPPh_2)_2$. In the ^{31}P NMR spectrum of $Ph_2PNH(Se)PPh_2$ the phosphorus(V) resonance lies to high frequency of that of the phosphorus(III) centre as judged by the ^{77}Se satellites; the spectral assignment of $Ph_2PNH(S)PPh_2$ can be made by analogy. The $^2J(^{31}P-^{31}P)$ couplings for these molecules (86 for the monosulfide **4**, 93 Hz for the monoselenide) fall within the range expected for $P(^{III})-N-P(^{V})$ compounds, typically 78–126 Hz.[14]

Infrared spectral data for $Ph_2PNH(E)PPh_2$ (E = S or Se) and $Ph_2PNHPPh_2$ are given in Table 1. Monoxidation of the amine produces minor changes in P_2N band energies with increases for NH modes, ν(NH) exceptionally moving to lower energy which may be an indication of intermolecular hydrogen bonding.

We have found that $Ph_2PNH(E)PPh_2$ (E = S or Se) decompose in $CDCl_3$ (Aldrich, 99%) to give mixtures of $Ph_2PNH(E)PPh_2$, the diphenylphosphine chalcogenide $PPh_2H(E)$ and the amide $Ph_2P(E)NH_2$ (Table 2). Notably the $^2J(^{31}P-^{31}P)$ coupling, for the residual $Ph_2PNH(E)PPh_2$ (E = S or Se) are slightly smaller in magnitude in $CDCl_3$ than the values measured in $(CD_3)_2SO$. Degradation, presumably catalysed by traces of acid from the solvent, is only partial even after several days at room temperature.

We have not been able to isolate a monotelluride $Ph_2PNH(Te)PPh_2$. This probably owes more to the air/moisture sensitivity of this species rather than to any inherent reluctance to form a P=Te bond, as trialkyl- and dialkylaryl-phosphine tellurides $R_3P=Te$ are available from PR_3 and tellurium in boiling toluene.[15] We have conducted the reaction of $Ph_2PNHPPh_2$ with stoichiometric amounts of metallic tellurium in CH_2Cl_2, diethyl ether or thf at room temperature. Even after several days a significant quantity of tellurium remains but ^{31}P NMR spectroscopy [$CDCl_3$ or $(CD_3)_2SO$] reveals that although there has been oxidation the compound formed is actually $Ph_2PNH(O)PPh_2$.[12]

In the reactions of the monoselenide described here, CH_2Cl_2 solutions of the compound generated *in situ* from $Ph_2PNHPPh_2$ and elemental selenium could be used rather than preformed $Ph_2PNH(Se)PPh_2$, although there is no special advantage in this. However, only preformed monosulfide $Ph_2PNH(S)PPh_2$ was used because of difficulties discussed below.

The reaction between $Ph_2PNH(Se)PPh_2$ and $[PtCl_2(cod)]$ gives two products according to ^{31}P NMR spectroscopy. The only clearly resolved features in the NMR spectra of crude mixtures are two different multiplets centred at δ 73.5 and 63.8 with ^1J(Pt–P) couplings of 2320 and 3270 Hz respectively. The compounds were separated by virtue of their different solubilities in CH_2Cl_2–hexane.

The more insoluble of the complexes was shown by spectroscopic and single-crystal X-ray diffraction to be *trans*-$[Pt\{Ph_2P(Se)NHPPh_2\}_2]Cl_2$ **1** (Fig. 1, Tables 3 and 4). The X-ray analysis shows the platinum to have a square-planar geometry and to be co-ordinated by two neutral $Ph_2PNH(Se)PPh_2$ ligands. The complex has C_i symmetry, the platinum atom being positioned on a crystallographic symmetry centre. The angles at platinum are in the range 89.7(1)–90.3(1)°. Each $PtSeP_2N$ ring has a slightly folded geometry with N and P(1) deviating (in the same direction) 0.55 and 1.01 Å from the co-ordination plane (Fig. 2). The Pt–P and Pt–Se bond lengths are 2.300(3) and 2.431(2) Å respectively. The nitrogen–phosphorus(III) bond length N–P(2) [1.684(10) Å] is *ca.* 0.05 Å shorter than the nitrogen–phosphorus(V) bond N–P(1) [1.625(9) Å]. The P–N distances are comparable to those in the related complexes $[ReCl_3(OH_2)\{Ph_2P(O)NHPPh_2\}]$ and $[ReCl_4\{Ph_2P(O)NHPPh_2\}]$.[16] The P(1)–N–P(2) angle [122.1(5)°] is consistent with sp^2 hybridisation of the nitrogen atoms. The geometry at the phosphorus atoms does not deviate markedly from tetrahedral. All of the P–N distances imply substantial delocalisation over the P–N–P part of the ring; the P–Se bond [2.186(3) Å] is significantly longer than a formal P=Se bond, consistent with the above bonding pattern. Similar observations were made[6] in the case of $[Pt\{N(PPh_2Se)_2\}_2]$. The protonated nitrogen is involved in a strong N–H ··· Cl hydrogen bond to the chloride counter ion (N ··· Cl 2.97, H ··· Cl 2.01 Å, N–H ··· Cl 164°). Within the crystal there are no significant intermolecular contacts involving the core ring atoms of the cation. There is however, a fairly short intermolecular C–H ··· Cl contact from one of the *m*-phenyl protons attached to C(2) [C ··· Cl 3.59, H ··· Cl 2.70 Å, C–H ··· Cl 155°].

Table 1 Infrared assignments (cm^{-1}) for $Ph_2PNHPPh_2$ and $Ph_2PNH(E)PPh_2$, (E = S or Se)

		$Ph_2PNH(E)PPh_2$	
	$Ph_2PNHPPh_2$	E = S	Se
ν(NH)	3230s	3165m	3143m
δ(NH)	1250m	1310m	1311m
γ(NH)	898s	914s	913s
$\nu_{asym}(P_2N)$	795w	791m	790m
$\nu_{sym}(P_2N)$	689s	696s	696s
ν(PE)		634s	551s
$\delta(P_2N)$	353m	383m	375m

Table 2 $^{31}P-\{^1H\}$ NMR data for $PPh_2H(E)$ and $Ph_2P(E)NH_2$ (E = S or Se)

	δ(P)		^1J(P-H)/Hz		^1J(P-Se)/Hz
	S	Se	S	Se	
$PPh_2H(E)$	3.3	6.9	478	483	758
$Ph_2P(E)NH_2$	48.9	41.9	—	—	686

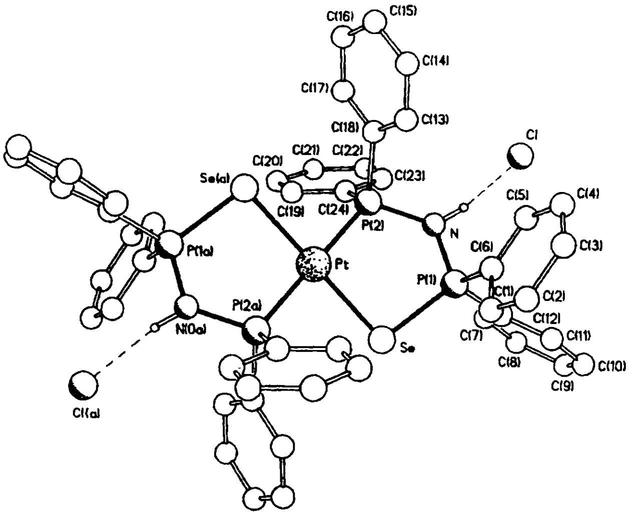

Fig. 1 Crystal structure of *trans*-$[Pt\{Ph_2P(Se)NHPPh_2\}_2]Cl_2 \cdot 0.75CH_2Cl_2$ **1**

Table 3 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Pt	0	5000	0
Se	1105(1)	5731(1)	4(1)
P(1)	507(2)	6814(2)	−169(2)
C(1)	1384(5)	7080(5)	1471(5)
C(2)	1512	7435	2178
C(3)	941	7950	2164
C(4)	243	8109	1441
C(5)	115	7754	733
C(6)	686	7240	748
C(7)	744(9)	7292(6)	−1435(7)
C(8)	1047	7769	−1815
C(9)	1493	8400	−1414
C(10)	1636	8553	−633
C(11)	1333	8076	−254
C(12)	887	7445	−655
N	−471(5)	6699(5)	−740(6)
P(2)	−936(2)	5875(2)	−803(2)
C(13)	−1504(5)	6417(6)	209(5)
C(14)	−2090	6525	465
C(15)	−2886	6264	−2
C(16)	−3097	5894	−724
C(17)	−2511	5785	−980
C(18)	−1715	6047	−513
C(19)	−1658(9)	4895(4)	2096(6)
C(20)	−2116	4715	−2910
C(21)	−2417	5280	−3486
C(22)	−2261	6023	−3249
C(23)	−1804	6203	−2435
C(24)	−1502	5639	−1859
Cl	−1419(2)	8081(2)	−1445(2)
Cl(1)*	0	4737(10)	2500
Cl(2)*	5000	1323(10)	2500

* Occupancy 0.375.

Table 4 Selected bond lengths (Å) and angles (°) for *trans*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2·0.75CH_2Cl_2 **1**

Pt–Se	2.431(2)	Se–P(1)	2.186(3)
N–P(2)	1.684(10)	Pt–P(2)	2.300(3)
P(1)–N	1.625(9)	Mean P–C(aryl)	1.80
Se–Pt–P(2)	90.3(1)	P(2)–Pt–Se(a)	89.7(1)
P(2)–Pt–P(2a)	180.0	Pt–Se–P(1)	96.5(1)
Se–P(1)–N	108.3(3)	Pt–P(2)–N	110.6(3)
Se–Pt–Se(a)	180.0	P(1)–N–P(2)	122.1(5)
N···Cl	2.97	N–H···Cl	164.0
H···Cl	2.01		

By analogy with rhenium complexes containing similar ligands[16,17] and [PtCl(PR_3)($Ph_2PNHPPh_2$)Cl, broad bands in the infrared spectrum of **1** at 2727 and 2507 cm^{-1} are assigned to the ν(NH) and 2δ(NH) modes respectively, a further indication of the strong N–H···Cl hydrogen bonding observed in the solid state. The in-plane and out-of-plane NH deformations are observed at 1310 and 950 cm^{-1}. The vibrations of the P_2N system are shifted to higher energy upon co-ordination; $\nu_{asym}(P_2N)$ moves to 1136 cm^{-1} into the same region as comparable vibrations of [N($EPPh_2$)$_2$]$^-$ complexes are seen,[18–20] with $\nu_{sym}(P_2N)$ at 810 cm^{-1}.

The ^{31}P NMR spectrum of complexes contain broad lines at room temperature with consequent loss of resolution, which may indicate that dissociation of metal–ligand bonds is fast on the NMR time-scale. This effect is more pronounced at 109.4 and 202.5 MHz than at lower magnetic fields. Thus the spectrum in Fig. 3 was recorded at 36.2 MHz. This complex exhibits an AA'XX' type pattern; owing to the *trans* disposition of the A nuclei *J*(A–A') is an order of magnitude greater than the remaining ^{31}P–^{31}P couplings, reducing the spectrum to deceptively simple triplets for P_A and P_X from which N [= J(A–X) + J(A–X')], the separation of the outermost lines of either triplet, is the only parameter which can be computed.

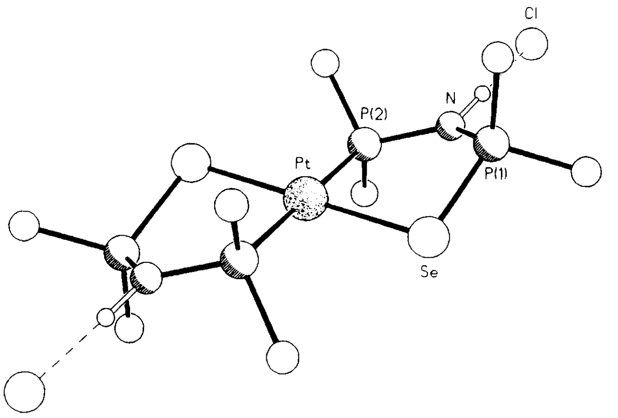

Fig. 2 Core geometry and NH···Cl bonding in the structure of complex **1**

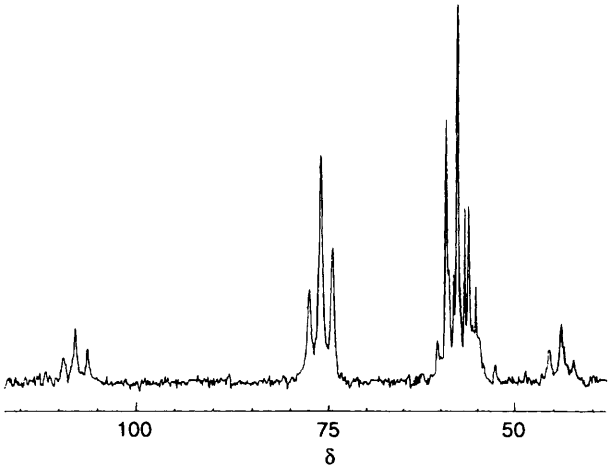

Fig. 3 The ^{31}P-{^1H} NMR spectrum of *trans*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2

The infrared spectrum of the more soluble component from the reaction of $Ph_2PNH(Se)PPh_2$ with [$PtCl_2$(cod)] is similar to that of complex **1** [ν(NH) 2738, δ(NH) 1308, γ(NH) 976, ν(P_2N) 1168 and 800 cm^{-1}] and the most intense peak in the mass spectrum appears at *m*/*z* 1123, the same mass-to-charge ratio as that of **1**. Thus we conclude that the product is the geometric isomer *cis*-[Pt{$Ph_2P(Se)NHPPh_2$}$_2$]Cl_2 **2**; the ^{31}P NMR spectrum is in accord with this formulation. Attempts to grow crystals of **2** from concentrated CH_2Cl_2 solutions using hexane as a precipitant gave only a colourless amorphous solid. Slow growth from a dilute CH_2Cl_2-hexane solution over the course of several weeks at −20 °C resulted in a change from green to brown, and gave pale brown crystals of *cis*-[Pt{$Ph_2P(Se)NPPh_2$}$_2$]·2CH_2Cl_2 **3** as determined by X-ray crystallography (Fig. 4, Tables 5 and 6).

The X-ray analysis of complex **3** shows the molecule to have crystallographic C_2 symmetry. The geometry at platinum is distorted square planar; there is a contraction in the Se–Pt–Se' angle [80.6(1)°] which is accompanied by a widening of the P(2)–Pt–P(2') angle [99.1(1)°], the *trans* P(2)–Pt–Se' angle being 169.7(1)°. There is an additional small tetrahedral distortion. The Pt–P bond length [2.287(2) Å] is significantly shorter than that in **1** as a consequence of the difference in the *trans* substituents. There is a concomitant lengthening of the Pt–Se bond length in **3** relative to **1** [2.480(1) *cf.* 2.431(2) Å].

Table 5 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
Pt	0	1216(1)	2500
Se	384(1)	−740(1)	3001(1)
P(1)	446(1)	418(2)	3625(1)
C(1)	−359(4)	496(7)	4375(2)
C(2)	−994	237	4628
C(3)	−1639	−556	4454
C(4)	−1647	−1089	4028
C(5)	−1012	−829	3775
C(6)	−367	−36	3948
C(7)	1399(3)	−1538(5)	4080(2)
C(8)	2060	−1964	4354
C(9)	2621	−995	4521
C(10)	2520	400	4414
C(11)	1859	825	4140
C(12)	1299	−144	3972
N	478(4)	2035(6)	3547(2)
P(2)	306(1)	2750(2)	3061(1)
C(13)	1341(3)	4986(6)	3256(2)
C(14)	2054	5700	3228
C(15)	2615	5213	2954
C(16)	2462	4011	2708
C(17)	1748	3298	2735
C(18)	1188	3785	3009
C(19)	−519(3)	5302(5)	2978(2)
C(20)	−1180	6135	3029
C(21)	−1817	5619	3243
C(22)	−1791	4271	3407
C(23)	−1130	3439	3356
C(24)	−493	3954	3142
C(30)	91(7)	4293(14)	4387(4)
Cl(1)	−231(3)	5976(4)	4275(2)
Cl(2)	1083(3)	4267(6)	4576(2)

Table 6 Selected bond lengths (Å) and angles (°) for *cis*-[Pt{$Ph_2P(Se)NPPh_2$}$_2$]·$2CH_2Cl_2$ **3**

Pt–Se	2.480(1)	Pt–P(2)	2.287(2)
Se–P(1)	2.200(2)	P(1)–N	1.584(7)
N–P(2)	1.635(6)	P–C (aryl) (mean)	1.81
Se–Pt–P(2)	90.4(1)	P(2)–Pt–Se′	169.7(1)
P(2)–Pt–P(2′)	99.1(1)	Pt–Se–P(1)	97.6(1)
Se–P(1)–N	111.9(2)	Pt–P(2)–N	114.3(2)
Se–Pt–Se′	80.6(1)	P(1)–N–P(2)	123.3(4)

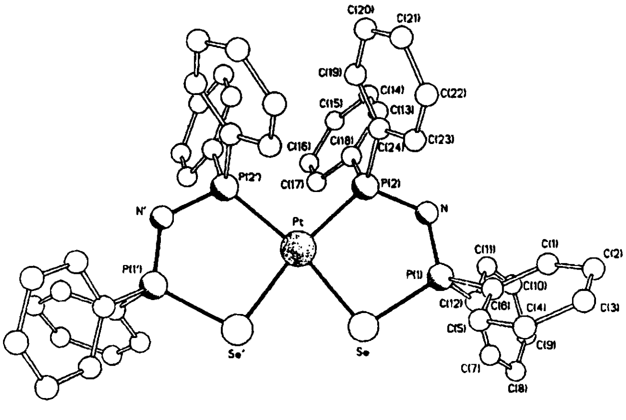

Fig. 4 Crystal structure of *cis*-[Pt{$Ph_2P(Se)NPPh_2$}$_2$]·$2CH_2Cl_2$ **3**

Deprotonation of the nitrogen gives rise to a significant shortening of both P–N bond lengths [P(1)–N 1.584(7), P(2)–N 1.635(6) Å, *cf.* 1.625(9) and 1.684(10) for **1**] although there is no dramatic enlargement of the P–N–P angle [123.3(4) *cf.* 122.1(5)°]. Associated with the shortening of the P–N bonds is a noticeable increase in the P–Se bond length [2.200(2) in **3** *cf.* 2.186(3) Å in **1**]. There are small distortions in the tetrahedral geometries at the phosphorus centres with angles ranging between 102.3(3) and 111.9(2) at P(1) and 103.0(3) and 115.3(2)° at P(2). The rings are less puckered than in **1**; the Pt–P(1)–P(2)–N atoms are coplanar to within 0.04 Å with the selenium atom displaced from this plane by 0.42 Å. The shortening of the P–N bond lengths in this complex compared with **1** (each by *ca.* 0.05 Å) resembles the differences in the corresponding distances of the rhenium complexes containing $Ph_2PNH(O)PPh_2$ and $[Ph_2PN(O)PPh_2]^-$ ligands described by Rossi and co-workers.[16] The bonding parameters within the metallacycles [P–N and P–Se distances, P(1)–N–P(2) angle] are similar to those in *trans*-[ReO(OEt){$Ph_2P(Se)NPPh_2$}$_2$],[21] and within the five-membered ring of [Pd{$Ph_2P(Se)NPPh_2$}{N-$(SePPh_2)_2$}][22] although the M–P and M–Se distances are not strictly comparable due to the different covalent radii of the metal atoms. The only significant non-bonding interactions are intramolecular π–π stacking interactions between the phenyl rings attached to P(2) and their C_2-related counterparts. The ring centroid–ring centroid distance is 3.69 Å.

In accord with the absence of amine protons according to X-ray analysis, the infrared spectrum of the neutral complex contains no vibrations assignable to NH protons, although the P_2N band energies (1153 and 795 cm^{-1}) are very similar to those of **2**, which is difficult to reconcile with the shortening of the P–N bonds relative to the protonated complex **1**.

The ^{31}P NMR spectrum of the *cis* complex **2** consists of AA′XX′ type multiplets with platinum satellites, for which algebraic analysis is straightforward. Complex **3** [$\delta(P_A)$ 64.1, $\delta(P_X)$ 50.3, ^1J(Pt–P) 3280, J(A–X) 39.4, J(A–X′) −8.5, J(A–A′) 6.7, J(X–X′) 0 Hz] has similar coupling constants to those of **2** although the $\delta(P_X)$ value (for P=Se) has shifted to lower frequency upon deprotonation.

Co-ordination of $Ph_2PNH(Se)PPh_2$ to Pt^{II} in complexes **1** and **2** results in deshielding of the phosphorus(III) atoms while the resonances of the phosphorus(V) nuclei move only slightly to lower frequency. The $^1J(^{195}Pt-^{31}P)$ couplings of **1** and **2** define which are the phosphorus(III) and (V) centres; while ^2J(Pt–P) for **1** can be measured from the ^{31}P or ^{195}Pt NMR spectrum, this coupling is not clearly observed in either spectrum for **2**.

The reaction between [$PdCl_2$(cod)] and the monoselenide $Ph_2PNH(Se)PPh_2$ leads to a *trans* complex according to ^{31}P NMR spectroscopy, the only instance in which a single isomer is obtained. The infrared spectrum of this complex is identical in appearance to that of **1**, confirming that both possess the same *trans* geometry and furthermore that the amine protons remain bound to the nitrogen atoms upon chelation of the ligands. Hence the product can be formulated as the palladium analogue of **1**, *trans*-[Pd{$Ph_2P(Se)NHP(Se)Ph_2$}$_2$]Cl_2 **4**.

The ^{31}P NMR spectra of crude mixtures obtained from the reaction of the monosulfide $Ph_2PNH(S)PPh_2$ with [$PtCl_2$(cod)] reveal a 2 : 1 mixture of *cis* and *trans* isomeric complexes. The insolubility of the *trans* compound is such that NMR spectra of the pure complex cannot be obtained after precipitation. This does however mean that separation of the isomers can be achieved by slow concentration of CH_2Cl_2 solutions. Algebraic analysis for the *cis* isomer reveals J(A–A′) = 8.7, J(X–X′) = 0, J(A–X) = 30.0, J(A–X′) = −6.5 Hz [where A,A′ = P^{III}, X,X′ = P^V]. In this instance the infrared spectrum of each isomer indicates, by the absence of bands between 2800 and 2400 and *ca.* 950 cm^{-1} that the ligands have undergone deprotonation upon co-ordination, enabling formulation of the complexes as *trans*- and *cis*-[Pt{$Ph_2P(S)NPPh_2$}$_2$] **5**,**6**. The compound $Ph_2PNH(S)PPh_2$ reacts with [$PdCl_2$(cod)] to generate a mixture of *cis* and *trans* isomers (in the ratio ≈ 1 : 5). However, their solubilities are so similar that cocrystallisation occurs from CH_2Cl_2–hexane. The presence of bands at 2700, 1309 and 948 cm^{-1} in the infrared spectrum suggests that the nitrogen atoms are protonated; consequently we believe the complexes are *trans*- and *cis*-[Pd{$Ph_2P(S)NHPPh_2$}$_2$]Cl_2 **7**,**8**. Uniquely we cannot identify which are the phosphorus(III) and

(V) centres as there are no ^{195}Pt or ^{77}Se satellites to facilitate analysis. Furthermore the multiplets for **8** cannot be resolved clearly enough to allow calculation of the P–P couplings. For **7**,**8**, and indeed for **5**,**6** as well, it is notable that both the phosphorus nuclei of the ligands experience deshielding upon co-ordination.

When [$PdCl_2$(cod)] is added to an *in situ* mixture generated from $Ph_2PNHPPh_2$ and sulfur in CH_2Cl_2 after 2–4 h at room temperature a yellow solid rapidly separates, which was collected by centrifugation. Although insoluble in organic solvents, its identity can be deduced by infrared spectroscopy; intense absorptions at 3171, 1171 and 821 cm^{-1} reveal this compound to be [$PdCl_2(Ph_2PNHPPh_2)$], authentic samples of which are readily prepared for comparative purposes from [$PdCl_2$(cod)] and $Ph_2PNHPPh_2$. Strong bands at 472, 492 and 507 cm^{-1} further suggest the presence of a four-membered chelate ring, *cf.* [$PtCl_2(Ph_2PNHPPh_2)$]. Slow diffusion of hexane into the CH_2Cl_2 solution recovered from the centrifugation gives crystals of *trans*- and *cis*-[$Pd\{Ph_2P(S)NHPPh_2\}_2]Cl_2$ **7**,**8** verified by ^{31}P NMR and infrared spectroscopy. The ^{31}P NMR spectrum of the remaining CH_2Cl_2–hexane solution contains three doublets with a multiplet to high frequency. Evaporation of the solvent gave an orange solid, for which the peak of highest relative abundance in its positive-ion FAB mass spectrum appears at *m*/*z* 971, indicating this compound is the unsymmetrical chelate [$Pd\{Ph_2P(S)NPPh_2\}\{N(SPPh_2)_2\}$] **9**. The ^{31}P NMR spectral parameters δ 37.5[d,P(2) of $N(SPPh_2)_2$], 40.2 [d,P(1) of $N(SPPh_2)_2$], 73.5 [d, P(3) of monosulfide and 84.0 [m, P(4) of monosulfide]; *J*(P–P) 8.1 (P^1–P^4), 12.1 (P^2–P^4) and 39.0 Hz (P^3–P^4). The thiophosphoryl group containing P(1) is *trans* to the phosphorus(III) P(4).

The phosphorus-31 NMR spectrum of complex **9** is qualitatively similar to that of its selenium analogue[22] and our assignments are made on the same basis. In its vibrational spectrum, the absence of absorptions between 2800 and 2400 cm^{-1} or *ca.* 950 cm^{-1}, the regions where characteristic vibrations of the NH group of co-ordinated $Ph_2PNH(S)PPh_2$ ligands are seen, is the basis for our formulation as a neutral complex. Absorptions of the P_2N systems appear as medium-strong bands at 1146, 1122 and 827 cm^{-1}.

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