Preparation and Characterisation of $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}(PR_3)_2]Cl$ (R = alkyl or aryl); Crystal Structure of $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)_2\text{-}Se,Se'\}]\cdot 0.5EtOH\cdot 0.3CH_2Cl_2$†

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Reaction of $NH(PPh_2)_2$ with selenium gives $Ph_2P(Se)NHP(Se)Ph_2$ which may be deprotonated with $KOBu^t$ to give $K[Ph_2P(Se)NP(Se)Ph_2]$. This can be treated with appropriate Group VIII metal complexes to give $[Rh\{N(SePPh_2)_2\}(cod)]$ (cod = cycloocta-1,5-diene), a series of complexes of formula $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}(PR_3)_2]Cl$ (PR_3 = PMe_3, PMe_2Ph, PEt_3, PPh_3, $\frac{1}{2}NH(PPh_2)_2$ or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) and $[MCl\{N(SePPh_2)_2\text{-}Se,Se'\}(PMe_2Ph)]$ (M = Pt or Pd). The new compounds have been characterised by ^{31}P and ^{195}Pt NMR and IR spectroscopy, FAB$^+$ mass spectrometry and microanalyses. Furthermore, a small quantity of a mixed-ligand complex $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)_2\text{-}Se,Se'\}]\cdot 0.5EtOH\cdot 0.3CH_2Cl_2$ has been characterised by X-ray crystallography and ^{31}P NMR spectroscopy. Its structure reveals an approximately planar five-membered $PdSeP_2N$ ring and a puckered six-membered $PdSe_2P_2N$ ring. In the crystal the molecules pack with channels which contain the disordered CH_2Cl_2 molecules running down the *a* direction.

There has been substantial interest[1–4] in the co-ordination chemistry of $Ph_2P(E)NHP(E)Ph_2$ (E = O **I** or S **II**) since it can be regarded as a non-carbon analogue of acetylacetone. Furthermore, the complexes formed adopt a range of ring conformations. Monosubstituted compounds $Ph_2P(E)NHPPh_2$ have also been described.[5,6] Although the chemistry of **I** and **II** is becoming relatively well developed there have been very few reports on the selenium analogue $Ph_2P(Se)NHP(Se)Ph_2$ **III**. Some rhenium(V) nitrido and amido complexes of the $[Ph_2P(Se)NP(Se)Ph_2]^-$ anion have been reported[7] and the unstable compound $[Re(O)Cl\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ has been described,[8] whilst we have recently reported[9] on some bis-homoleptic complexes $[M\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ (M = Pd or Pt). Furthermore, the related $Ph_2P(S)CHPPh_2$ ligand has been shown to be a good carbonylation catalyst when in a rhodium based system.[10]

Here, we report on the synthesis and characterisation of $[Rh\{N(SePPh_2)_2\text{-}Se,Se'\}(cod)]$ (cod = cycloocta-1,5-diene), a series of complexes of the formula $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}(PR_3)_2]Cl$ and $[MCl\{N(SePPh_2)_2\text{-}Se,Se'\}(PMe_2Ph)]$ (M = Pd or Pt). The new compounds have been characterised by ^{31}P and ^{195}Pt NMR and IR spectroscopy, FAB$^+$ mass spectrometry and microanalyses. Furthermore, we have isolated a small quantity of a mixed-ligand complex $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)\text{-}Se,Se'\}]\cdot 0.5EtOH\cdot 0.3CH_2Cl_2$ which has been characterised by X-ray crystallography and ^{31}P NMR spectroscopy.

Experimental

General chemicals, solvents, techniques and instrumentation were as described previously.[11] The complex $[PdCl_2(PMe_2Ph)_2]$ was made by the addition of stoichiometric quantities of PMe_2Ph to $[PdCl_2(cod)]$, $[\{MCl_2(PMe_2Ph)\}_2]$ (M = Pd or Pt) by heating $[MCl_2(PMe_2Ph)_2]$ with MCl_2,[12] and $[\{RhCl(cod)\}_2]$ was generated from $RhCl_3\cdot 3H_2O$ and cod in ethanol.[13] Potassium *tert*-butoxide was used as received (Aldrich).

Hexane and CH_2Cl_2 were dried and distilled under nitrogen before use, all other solvents and reagents were used as received. The reagents $NH(PPh_2)_2$, $NH(SPPh_2)_2$ and $Na[N(SPPh_2)_2]$ were prepared by literature methods.[5,6] The $^{31}P\text{-}\{^1H\}$ (109.4 MHz) and $^{195}Pt\text{-}\{^1H\}$ (57.9 MHz) NMR spectra were recorded in CD_2Cl_2 on a JEOL JNM EX270 spectrometer, infrared spectra (as KBr discs) on a Perkin-Elmer 1720X FTIR spectrometer. Microanalyses were performed by the Imperial College Microanalytical Service, FAB$^+$ mass spectra (3-nitrobenzyl alcohol matrix) were recorded on a Vacuum Generators Autospec Q instrument.

Syntheses.—$Ph_2P(Se)NHP(Se)Ph_2$ **III**. Bis(diphenylphosphino)amine (7.70 g, 20 mmol) and grey selenium (3.16 g, 40 mmol) were heated at reflux in toluene (150 cm^3) for 4 h. After cooling to room temperature the white precipitate of product **III** was filtered off, washed with toluene (3 × 15 cm^3) and diethyl ether (3 × 15 cm^3) and dried *in vacuo*. Yield: 9.1 g, 84% (Found: C, 52.75; H, 3.70; N, 2.50. $C_{24}H_{21}NP_2Se_2$ requires C, 53.05; H, 3.90; N, 2.60%). NMR ($CDCl_3$): ^{31}P, δ 53.2 [s, $^1J(^{31}P\text{-}^{77}Se)$ 786 Hz]; ^1H, δ(N*H*) 4.4(s). IR (KBr): δ(NH) 1324s, $\nu(P_2N)$ 1114s, ν(PSe) 546m cm^{-1}. FAB$^+$ MS: *m/z* 544 [*M*]$^+$.

$K[N(SePPh_2)_2]$ **IV**. Potassium *tert*-butoxide (1.06 g, 9.4 mmol) was added to a suspension of $NH(SePPh_2)_2$ **III** (4.00 g, 7.4 mmol) in ethanol (50 cm^3) and stirred for 2 h. The colourless product was collected by suction filtration, washed with diethyl ether and air-dried. Yield: 4.08 g, 95% (Found: C, 48.95; H, 3.15; N, 2.40. $C_{24}H_{20}KNP_2Se_2$ requires C, 49.60; H, 3.45; N, 2.40%). $^{31}P\text{-}\{^1H\}$ NMR [$(CD_3)_2SO$]: δ 28.5 [s, $^1J(^{31}P\text{-}^{77}Se)$ 687 Hz]. FAB$^-$ MS: *m/z* 542 $[N(SePPh_2)_2]^-$.

$[Rh\{N(SePPh_2)_2\text{-}Se,Se'\}(cod)]$ **1**. The complex $[\{RhCl(cod)\}_2]$ (92 mg, 0.19 mmol) and $K[N(SePPh_2)_2]$ (220 mg, 0.38 mmol) were stirred in tetrahydrofuran (thf) (10 cm^3) for 1.5 h. The solvent was removed *in vacuo*, the crude product extracted into CH_2Cl_2 (10 cm^3) and the solution filtered through glass wool–Celite. Concentration of the filtrate to 2–3 cm^3 and

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

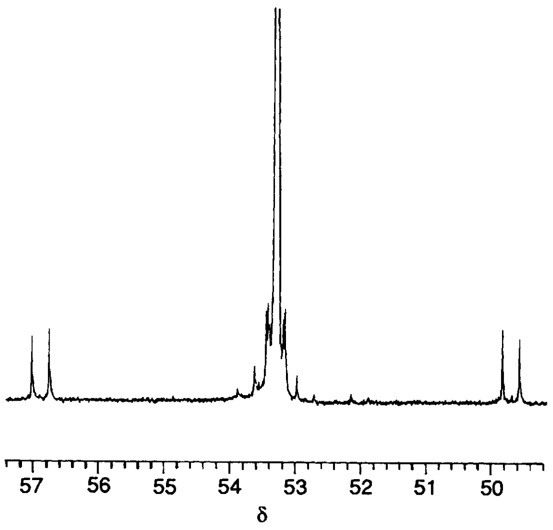

Fig. 1 ^{31}P-{^{1}H} NMR spectrum of **III**

addition of hexane (30 cm^3) gave complex **1** as an orange solid. Yield: 217 mg, 76% (Found: C, 50.65; H, 4.15; N, 1.75. $C_{32}H_{32}NP_2RhSe_2$ requires C, 51.00; H, 4.30; N, 1.85%). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 28.3 [d, $^{1}J(^{31}P-^{77}Se)$ 550, $^{2}J(^{31}P-^{103}Rh)$ 4 Hz].

[Pt{N(SePPh$_2$)$_2$-*Se,Se′*}(PR$_3$)$_2$]Cl (PR$_3$ = PMe$_3$ **2**, PMe$_2$-Ph **3**, PEt$_3$ **4**, PPh$_3$ **5**, ½NH(PPh$_2$)$_2$ **6** *or* ½Ph$_2$PCH$_2$CH$_2$PPh$_2$). The same general procedure was adopted for all compounds, illustrated here for PR$_3$ = PEt$_3$ **4**. The compounds *cis*-[PtCl$_2$(PEt$_3$)$_2$] (37 mg, 0.074 mmol) and K[N(SePPh$_2$)$_2$] (44 mg, 0.076 mmol) were stirred in thf (5 cm^3) for 5 min, giving a lime-green solution. The solvent was removed *in vacuo*, the residue extracted into CH$_2$Cl$_2$ (2 cm^3) and the solution filtered through glass wool–Celite. Addition of hexane (15 cm^3) and cooling to −20 °C gave yellow crystals of [Pt{N(SePPh$_2$)$_2$-*Se,Se′*}(PEt$_3$)$_2$]Cl. Yield: 44 mg, 60%.

A longer reaction time (24 h) was required for **6**. Complex **7** was recrystallised by slow evaporation at room temperature of a CH$_2$Cl$_2$–hexane solution. Isolated yields varied from 55 to 73%.

[MCl{N(SePPh$_2$)$_2$-*Se,Se′*}(PMe$_2$Ph)] (M = Pt **8** *or* Pd **9**). The complex [{MCl$_2$(PMe$_2$Ph)}$_2$] (M = Pd or Pt) (0.04 mmol) and K[N(SePPh$_2$)$_2$] (0.08 mmol) were stirred in thf (5 cm^3) for 10 min. The solvent was removed *in vacuo*, the residue extracted into CH$_2$Cl$_2$ (2 cm^3) and the solution filtered through glass wool–Celite. Addition of hexane (15 cm^3) and cooling to −20 °C gave yellow crystals of **8** (35 mg, 48%) or red crystals of **9** (27 mg, 42%). For **8** (Found: C, 39.80; H, 2.80; N, 1.70. $C_{32}H_{31}ClNP_3PtSe_2 \cdot CH_2Cl_2$ **8**·CH$_2$Cl$_2$ requires C, 39.80; H, 3.35; N, 1.40%). ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ(P$_A$) 17.6(d), δ(P$_B$) 27.7 (d), δ(P$_X$) −15.3 (dd); $^{2}J(^{195}Pt-^{31}P_A)$ 126, $^{2}J(^{195}Pt-^{31}P_B)$ 59, $^{1}J(^{195}Pt-^{31}P_X)$ 3318, $^{1}J(^{31}P_A-^{77}Se_A)$ 507, $^{1}J(^{31}P_B-^{77}Se_B)$ 535, $^{2}J(^{31}P_X-^{77}Se_B)$ 142, $^{3}J(^{31}P_A-^{31}P_X)$ 14.8 and $^{3}J(^{31}P_B-^{31}P_X)$ 9.4 Hz. For **9** (Found: C, 43.90; H, 3.20; N, 1.75. $C_{32}H_{31}ClNP_3PdSe_2 \cdot CH_2Cl_2$ **9**·CH$_2$Cl$_2$ requires C, 43.70; H, 3.65; N, 1.55%). ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ(P$_A$) 25.1 (d), δ(P$_B$) 31.3 (d), δ(P$_X$) −0.4 (dd); $^{1}J(^{31}P_A-^{77}Se_A)$ 514, $^{1}J(^{31}P_B-^{77}Se_B)$ 547, $^{2}J(^{31}P_X-^{77}Se_B)$ 156, $^{3}J(^{31}P_A-^{31}P_X)$ 16.1, $^{3}J(^{31}P_B-^{31}P_X)$ 12.1 Hz.

Reaction between [PdCl$_2$(PMe$_2$Ph)$_2$] *and* K[N(SePPh$_2$)$_2$].—The compounds [PdCl$_2$(PMe$_2$Ph)$_2$] (37 mg, 0.08 mmol) and K[N(SePPh$_2$)$_2$] **IV** (47 mg, 0.08 mmol) were stirred in thf (5 cm^3) for 20 min. The solvent was removed *in vacuo*, extracted into CH$_2$Cl$_2$ (5 cm^3) and filtered through glass wool–Celite. Concentration to *ca.* 2 cm^3, followed by addition of hexane (10 cm^3) and cooling to −20 °C gave 5 mg of orange crystals, found by single-crystal X-ray diffraction to be [Pd{Ph$_2$PNP(Se)Ph$_2$-*P,Se*}{N(SePPh$_2$)$_2$-*Se,Se′*}]·0.5EtOH·0.3CH$_2$Cl$_2$ **10**.

Crystallography.—$C_{48}H_{40}N_2P_4PdSe_3 \cdot 0.5C_2H_5OH \cdot 0.3CH_2Cl_2$, $M = 1160.5$, triclinic, space group $P\bar{1}$, $a = 9.273(5)$, $b = 20.855(11)$, $c = 14.291(8)$ Å, $\alpha = 89.67(2)$, $\beta = 108.83(2)$, $\gamma = 90.35(2)°$, $U = 2616$ Å^3, $Z = 2$, $D_c = 1.47$ g cm^{-3}, crystal dimensions 0.23 × 0.27 × 0.32 mm, μ(Mo-Kα) = 2.63 mm^{-1}, $F(000) = 1151$. Siemens P4/PC diffractometer ω-scan method, graphite-monochromated Mo-Kα radiation (2θ range 3.0–45°), 5361 independent reflections, 3919 observed [$F_o > 4.0\sigma(F_o)$], corrected for Lorentz and polarisation factors, empirical absorption correction (SHELXA), maximum and minimum transmission factors 0.822 and 0.260 respectively. The crystal decomposed during the data collection, limiting the 2θ range. Because of this decomposition and since no other adequate crystal was available for recollection of the data no azimuthal data were measured and thus an empirical absorption correction was applied.

The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The phenyl rings were refined as rigid bodies. A Δ*F* map revealed the presence of a partial occupancy (50%) disordered ethanol molecule as well as severely disordered partial occupancy (30%) CH$_2$Cl$_2$. The CH$_2$Cl$_2$ molecules are oriented such that there is partial overlap of the chlorine and carbon sites; only the partial-weight chlorine sites have been refined. Both the carbon and hydrogen of the CH$_2$Cl$_2$ and the hydroxyl proton of the ethanol were not included in the refinement. All partial-occupancy atoms were refined isotropically. Hydrogen atoms on the phenyl rings were assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to $R = 0.057$ and $R' = 0.059$ where $w^{-1} = \sigma^2(F) + 0.0007F^2$. The maximum and minimum residual electron densities in the final Δ*F* map were 0.83 and −0.68 e Å^{-3} and the mean and maximum shifts/errors in the final refinement were 0.002 and 0.032 respectively. Computations were carried out using a Silicon Graphics IRIS with SHELXTL.[14]

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

Results and Discussion

The generation of NH(EPPh$_2$)$_2$ (E = O **I** or S **II**) from NH(PPh$_2$)$_2$ is straightforward.[15] The only published route to the diselenium compound NH(SePPh$_2$)$_2$ **III** requires use of highly toxic potassium selenocyanate, followed by acidic work-up.[15] We have established[9] that the reaction of NH(PPh$_2$)$_2$ with grey selenium leads directly to analytically pure **III**. Treatment of **III** with KOBu^t in ethanol gives the potassium salt K[Ph$_2$P(Se)NP(Se)Ph$_2$] **IV**, which can be recrystallised from acetone–CH$_2$Cl$_2$. It is this compound which has been used in the majority of the reactions described here.

The ^{31}P-{^{1}H} NMR spectrum of **III** and **IV** consist of a singlet of 92% intensity from molecules containing two selenium atoms with no nuclear spin and 8% of an AA′X spin system arising from the Ph$_2$P(Se)NHP(^{77}Se)Ph$_2$ isotopomer (A,A′ = ^{31}P; X = ^{77}Se), in which the phosphorus atoms are magnetically inequivalent (Fig. 1). Owing to the AA′X component of their spectra, the A–A′ [$^{2}J(^{31}P-^{31}P)$] coupling for **III** and **IV** can be measured directly; it is the separation between the outermost pair of ^{77}Se satellites on either side of the main resonance. The $^{1}J(^{31}P-^{77}Se)$ (786 and 687 Hz for **III** and **IV** respectively) and $^{2}J(^{31}P-^{31}P)$ (29 and 6 Hz respectively) couplings are reduced in magnitude upon deprotonation, whilst in the IR spectrum of **IV** the $\nu_{asym}(P_2N)$ band moves from 1112 cm^{-1} to 1206 cm^{-1} (Table 1). These data are indicative of a decrease in the P–Se bond order upon removal of the amine proton and greater electron delocalisation within the SePNPSe chain. The situation is comparable to NH(SPPh$_2$)$_2$ **II** and its potassium salt K[N(SPPh$_2$)$_2$] **V**, for which crystallographic analysis[16,17] indicates shortening of the P–N bonds and increases in the P–S lengths and N–P–S angles upon deprotonation, accompanied by an increase in $\nu_{asym}(P_2N)$ from 922 cm^{-1} to 1199 cm^{-1} in the IR spectrum.

The chemistry of **III** is poorly developed by comparison with its dioxo- and dithio-analogues. With 'soft' selenium atoms, we anticipated that the $[N(SePPh_2)_2]^-$ anion would favour co-ordination to metals in low oxidation states although the existence of stable rhenium(v)–nitrido and –imido complexes containing this ligand[7] rather refutes this, although the instability[8] of $[Re(O)Cl\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ must be noted. We have already reported[9] on homoleptic platinum and palladium complexes $[M\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ (M = Pd **11** or Pt **12**). We have now found that cleavage of dimeric $[\{RhCl(cod)\}_2]$ by the potassium salt gives $[Rh\{N(SePPh_2)_2\text{-}Se,Se'\}(cod)]$ **1**, the ^{31}P NMR spectrum of which contains a doublet from a ^2J coupling of the phosphorus atoms to the ^{103}Rh nucleus (^{103}Rh, $I = \frac{1}{2}$, 100% abundance) with selenium satellites [^1J(P–Se) 550, ^2J(Rh–P) 4 Hz]. Infrared and FAB$^+$ mass spectral data for **1** (Tables 1 and 2) agree well with the above formulation, with absorptions at 2939, 2910, 2875 and 2828 cm^{-1} due to the ν(C–H) vibrations of the co-ordinated cod ligand as well as the expected $\nu_{asym}(P_2N)$ and ν(PSe). Dichloromethane solutions of **1** darken from orange to brown over several days in air, reminiscent of the behaviour of the platinum complex **12**. Elution through a short silica column with CH_2Cl_2 frees **1** from the more polar contaminant and restores its original colour. In principle, displacement of the diene from **1** by stronger donors such as phosphines should lead to further mixed-ligand systems. Whilst this is the case upon carbonylation of $[M\{CH_2(SPPh_2)_2\text{-}S,S'\}(cod)]ClO_4$ (M = Rh or Ir),[18] the analogous selenium complex $[Rh\{CH_2(SePPh_2)_2\text{-}Se,Se'\}(cod)]ClO_4$ is resistant to displacement of cod by either CO or an excess of $CH_2(SePPh_2)_2$.[19]

Salt elimination between **IV** and *cis*-$[PtCl_2(PR_3)_2]$ leads to cationic complexes **2**–**7** with displacement of both chloride ligands [equation (1)].

$$[PtCl_2(PR_3)_2] + K[N(SePPh_2)_2] \xrightarrow{thf} [Pt\{N(SePPh_2)_2\text{-}Se,Se'\}(PR_3)_2]Cl + KCl \quad (1)$$

Extraction into CH_2Cl_2, filtration through Celite and addition of hexane gives the products as air-stable yellow solids which decompose slowly in chlorinated solvents. Microanalytical data for these complexes are given in Table 2. FAB$^+$ mass spectrometry (Table 1) confirms the mononuclear nature of the complexes, with the peak of greatest relative abundance being due to $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}(PR_3)_2]^+$. The calculated isotopomeric distributions agree well with the experimentally observed manifolds. In the $^{31}P\text{-}\{^1H\}$ NMR spectra of **2**–**7** multiplets of AA′XX′ type (A,A′ = PR_3; X,X′ = PSe) with ^1J and ^2J (^{195}Pt–^{31}P) couplings and ^1J(^{31}P–^{77}Se) satellites are observed (Table 3, Figs. 2 and 3).

A number of trends are apparent from the data in Table 3. ^2J(Pt–P_X) is largest for complexes **6** and **7** which contain chelating diphosphines, and δ(P_X) lies at lowest frequency for these complexes. The ^1J(Pt–P_A) coupling for **6** is the smallest observed owing to the four-membered platinacycle,[20] whilst the ^1J(^{31}P–^{77}Se) couplings are independent of the phosphine. The ^2J(^{31}P–^{31}P) coupling within the $NH(PPh_2)_2$ chelate of **6** is significantly smaller in magnitude than that observed[11] for $[PtX(PR_3)\{NH(PPh_2)_2\text{-}P,P'\}]X$, typically 50 Hz, which reflects the influence of the co-ligands on the metal-mediated ^2J(P–Pt–P) component of this coupling and differences in the PNP bond angles of the diphosphine. The *J*(Pt–P) couplings are comparable to those in the complexes $[Pt\{N(SPPh_2)_2\text{-}S,S'\}(PR_3)_2]Cl$ (PR_3 = PEt_3 or PPh_3)[21] with the chemical shifts of the selenophosphoryl units *ca.* 10 ppm to low frequency of the thiophosphoryl centres.

Algebraic analysis to determine the ^2J and ^3J (^{31}P–^{31}P) couplings in **2**–**7** is not possible in all cases. For complexes **2** and **3** there is insufficient enhancement in resolution of the multiplet structure upon zero-filling of the spectrum to enable us to compute these values, but there is no such problem for **4**–**7**. For complexes **4** and **5**, six lines are visible within each half-spectrum, from which we conclude that one of the couplings, most likely to be *J*(X–X′) [$J(P^V\text{–}P^V)$], is zero. Resolution enhancement for the bis-chelate complexes **6** and **7** reveals eight lines in each half-spectrum, which indicates that *J*(X–X′) is non-zero. The ^{31}P–^{31}P coupling constants for **4**–**7** obtained by algebraic analysis or iterative fitting of the data[22] are collected in Table 4. It is notable that the (A–A′) and (X–X′) couplings are equivalent for **7** while the value of (X–X′) [$J(P^V\text{–}P^V)$] for the $N(SePPh_2)_2$ complex **11** exceeds that of $K[N(SePPh_2)_2]$ **IV**.

Table 1 $^{195}Pt\text{-}\{^1H\}$ NMR, IR and FAB$^+$ mass spectral data for $[N(SePPh_2)_2]^-$ compounds

Compound	δ(^{195}Pt)[a]	ν(P_2N)/cm^{-1}	ν(PSe)/cm^{-1}	*m*/*z* (M^+)
III		1114, 781	546	544
IV		1206, 790	545	542
1		1167, 815	543	752
2	−4728	1151, 808	543	890
3	−4770	1141, 802	543	1014
4	−4787	1151, 814	545	974
5	−4849	1139, 823	537	1263
6	−4399	1170, 807	544	1122
7	−4975	1173, 813	545	1136
8	−4280	1171, 808	543	911
9	—	1170, 807	542	788[b]
12	−4248	1157, 805	536	1283

[a] $^{195}Pt\text{-}\{^1H\}$ NMR recorded as CD_2Cl_2 solutions. [b] Corresponds to $[M - Cl]^+$

Table 2 Microanalytical data (%) for $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}(PR_3)_2]Cl$ (calculated values in parentheses)

Complex	PR_3	C	H	N
2	PMe_3	37.30 (38.95)	4.10 (4.15)	1.15 (1.50)
3	PMe_2Ph	44.15 (45.80)	4.25 (4.05)	1.45 (1.35)
4	PEt_3	42.45 (42.85)	4.85 (5.00)	1.55 (1.40)
5	PPh_3	52.50 (55.55)	4.20 (3.90)	0.95 (1.10)
6	$\frac{1}{2}NH(PPh_2)_2$	47.85 (49.80)	2.20 (3.55)	1.75 (2.40)
7	$\frac{1}{2}Ph_2PCH_2CH_2PPh_2$	48.80 (51.25)	3.85 (3.80)	1.25 (1.20)

Table 3 ^{31}P-{^{1}H} NMR data for [Pt{N(SePPh$_2$)$_2$-*Se,Se'*}(PR$_3$)$_2$]Cl

Complex	δ(P$_A$)	δ(P$_X$)	^1J(Pt–P$_A$)	^2J(Pt–P$_X$)	^1J(P–Se)	N*
			Hz			
2	−23.3	27.4	3057	70	510	3.4
3	−13.1	26.9	3103	71	501	6.0
4	9.0	26.6	3081	70	512	4.1
5	16.2	27.0	3227	69	512	10.7
6	−0.5	22.1	2696	97	516	8.7
7	49.6	23.6	3066	84	514	13.2

* N is the separation between the strongest pair of lines within each multiplet. A,A′ = P^{III}, X,X′ = P^V.

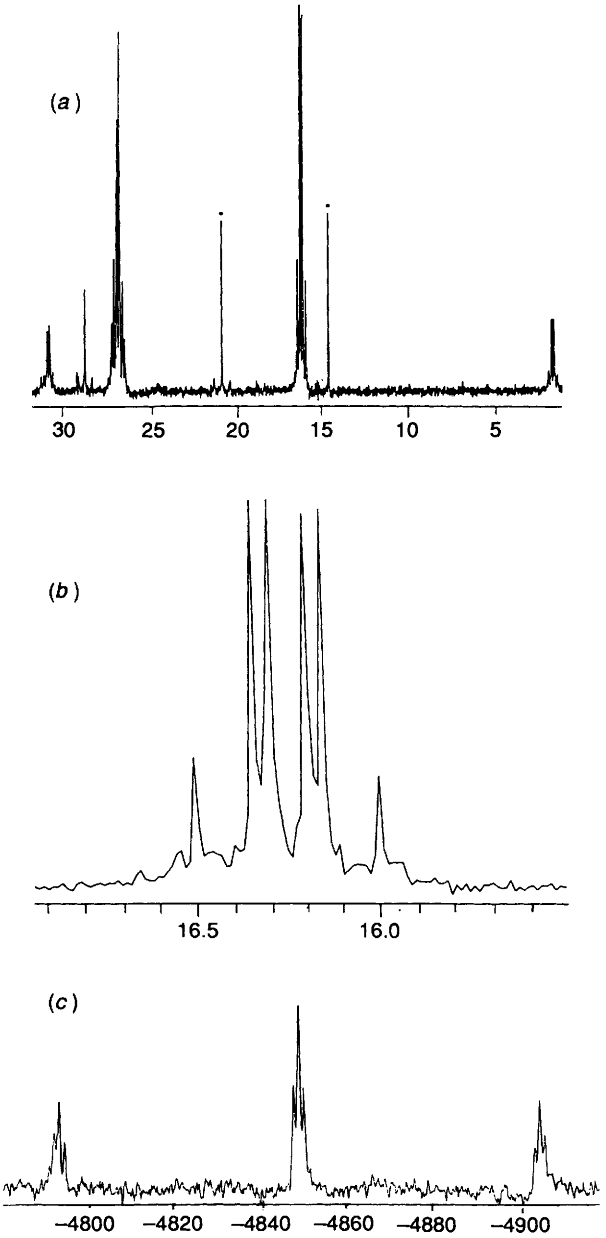

Fig. 2 (*a*) ^{31}P-{^{1}H} NMR spectrum with (*b*) expansion of the PR$_3$ region for [Pt{N(SePPh$_2$)$_2$-*Se,Se'*}(PPh$_3$)$_2$]Cl; (*c*) ^{195}Pt-{^{1}H} NMR spectrum of [Pt{N(SePPh$_2$)$_2$-*Se,Se'*}(PPh$_3$)$_2$]Cl (* denotes impurities)

Table 4 ^{31}P–^{31}P Coupling constants for [Pt{N(SePPh$_2$)$_2$-*Se,Se'*}-(PR$_3$)$_2$]Cl (Hz)*

Complex	J(A–A′)	J(A–X)	J(A–X′)	J(X–X′)
4	16.2	14.3	−10.3	0.0
5	17.5	22.7	−12.0	0.0
6	5.6	8.7	−3.1	10.2
7	1.0	12.2	−4.9	1.0

* A,A′ = PR$_3$, X,X′ = PSe.

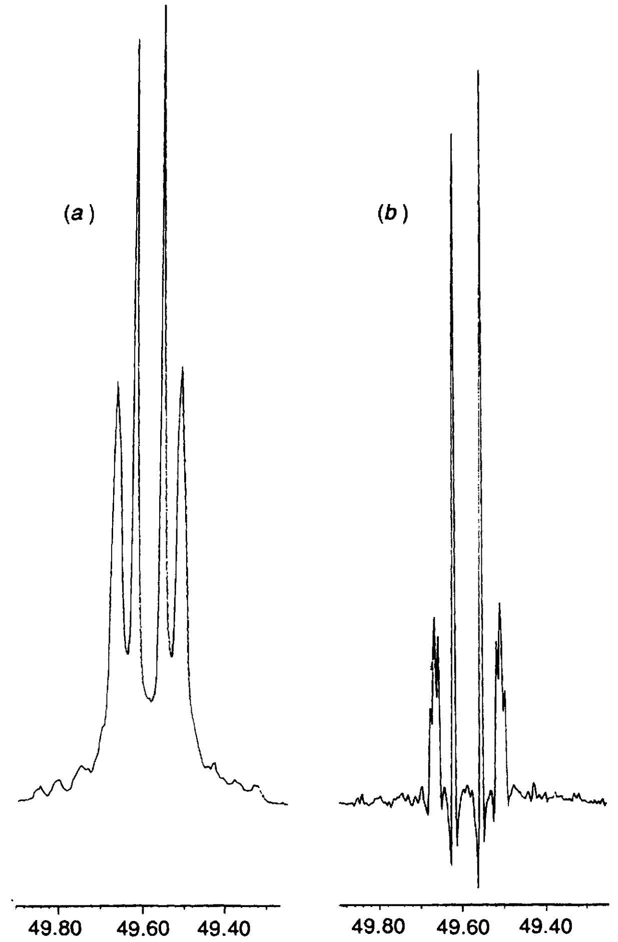

Fig. 3 (*a*) AA′ (dppe) region with (*b*) resolution enhancement of the ^{31}P-{^{1}H} NMR spectrum of [Pt{N(SePPh$_2$)$_2$-*Se,Se'*}(Ph$_2$PCH$_2$-CH$_2$PPh$_2$)]Cl at 202.5 MHz

It is also apparent that the *trans* J(A–X′) coupling is smaller in magnitude than *cis* J(A–X).

Treatment of [{MCl$_2$(PMe$_2$Ph)}$_2$] (M = Pt or Pd) with 2 equivalents of **IV** proceeds with cleavage of the chloro-bridged dimer [equation (2)]. In addition, small quantities of [M{N(SePPh$_2$)$_2$-*Se,Se'*}$_2$] are evident by ^{31}P NMR in the case

Table 5 Atomic coordinates (× 10^4) for complex **10** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	2 356(1)	7 329(1)	8 878(1)	C(25)	3 465(12)	4 919(5)	11 142(9)
Se(1)	3 156(2)	7 122(1)	7 389(1)	C(26)	2 833	4 338	11 307
P(1)	1 685(5)	7 749(2)	6 270(2)	C(27)	1 401	4 326	11 429
C(1)	−748(18)	6 974(5)	6 404(8)	C(28)	599	4 895	11 386
C(2)	−2 300	6 858	6 212	C(29)	1 231	5 476	11 221
C(3)	−3 368	7 303	5 671	C(30)	2 664	5 489	11 099
C(4)	−2 884	7 863	5 322	C(31)	5 722(19)	6 422(6)	12 575(12)
C(5)	−1 332	7 979	5 515	C(32)	7 246	6 440	13 170
C(6)	−264	7 534	6 056	C(33)	8 386	6 260	12 784
C(7)	1 996(12)	6 982(4)	4 764(7)	C(34)	8 001	6 061	11 803
C(8)	2 322	6 867	3 893	C(35)	6 477	6 043	11 208
C(9)	2 766	7 372	3 401	C(36)	5 337	6 224	11 594
C(10)	2 884	7 992	3 780	N(3)	2 552(11)	6 803(4)	11 119(6)
C(11)	2 558	8 107	4 651	P(4)	1 927(4)	7 398(1)	10 346(2)
C(12)	2 114	7 602	5 143	C(37)	−530(14)	7 607(4)	11 032(5)
N(1)	1 897(12)	8 504(5)	6 451(7)	C(38)	−2 072	7 638	10 941
P(2)	2 215(5)	8 823(2)	7 500(2)	C(39)	−3 176	7 550	10 020
C(13)	1 365(14)	9 909(5)	6 364(6)	C(40)	−2 740	7 431	9 190
C(14)	903	10 545	6 177	C(41)	−1 198	7 400	9 282
C(15)	596	10 906	6 908	C(42)	−93	7 488	10 203
C(16)	750	10 631	7 827	C(43)	4 388(12)	8 070(4)	11 565(7)
C(17)	1 213	9 995	8 015	C(44)	5 174	8 609	12 048
C(18)	1 520	9 634	7 284	C(45)	4 408	9 187	12 004
C(19)	5 210(19)	8 820(4)	7 615(6)	C(46)	2 855	9 227	11 479
C(20)	6 766	8 916	8 081	C(47)	2 069	8 687	10 997
C(21)	7 305	9 094	9 074	C(48)	2 835	8 109	11 040
C(22)	6 288	9 176	9 600	O(81)	3 217(31)	66(12)	4 236(17)
C(23)	4 731	9 079	9 133	C(82)	4 132(51)	476(19)	4 914(30)
C(24)	4 192	8 901	8 141	C(83)	5 623(57)	186(24)	5 440(33)
Se(2)	1 103(2)	8 380(1)	8 468(1)	Cl(1)	8 623(48)	4 644(19)	3 981(30)
Se(3)	3 260(2)	6 240(1)	9 265(1)	Cl(2)	5 188(74)	4 742(29)	4 300(44)
P(3)	3 436(5)	6 228(2)	10 837(2)	Cl(3)	6 233(64)	4 613(24)	3 965(39)

Table 6 Selected bond lengths (Å) and angles (°) for $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)_2\text{-}Se,Se'\}]\cdot 0.5EtOH\cdot 0.3CH_2Cl_2$

Pd–Se(1)	2.510(2)	Pd–Se(2)	2.463(2)
Pd–Se(3)	2.425(2)	Pd–P(4)	2.264(4)
N(1)–P(1)	1.598(10)	N(1)–P(2)	1.581(10)
N(3)–P(3)	1.581(11)	N(3)–P(4)	1.636(9)
P(1)–Se(1)	2.172(4)	P(2)–Se(2)	2.174(5)
P(3)–Se(3)	2.200(4)	Mean P–C(aryl)	1.79
Pd–Se(1)–P(1)	103.2(1)	Pd–Se(2)–P(2)	103.9(1)
Pd–Se(3)–P(3)	98.3(1)	Pd–P(4)–N(3)	116.3(4)
Se(1)–P(1)–N(1)	117.3(4)	Se(2)–P(2)–N(1)	116.3(5)
Se(3)–P(3)–N(3)	112.4(4)	P(1)–N(1)–P(2)	123.2(6)
P(3)–N(3)–P(4)	120.4(7)	Se(1)–Pd–Se(2)	101.8(1)
Se(3)–Pd–P(4)	90.3(1)	P(4)–Pd–Se(1)	170.6(1)
Se(3)–Pd–Se(2)	172.5(1)	Se(2)–Pd–P(4)	87.0(1)
Se(1)–Pd–Se(3)	81.4(1)		

$$[\{MCl_2(PMe_2Ph)\}_2] + 2K[N(SePPh_2)_2] \longrightarrow [MCl\{N(SePPh_2)_2\text{-}Se,Se'\}(PMe_2Ph)] + 2KCl \quad (2)$$
$$M = Pt\ \mathbf{8}\ \text{or}\ Pd\ \mathbf{9}$$

of the platinum reaction. For complexes **8** and **9** the PMe_2Ph resonance is a double doublet flanked by selenium satellites, with doublets for the chelate phosphorus nuclei, which are chemically inequivalent. This provides further indications that P^V–P^V couplings can be too small to be resolved for this ligand. For **9** assignment of the selenophosphoryl groups follows from the ^2J(Pt–P) couplings, the larger value being associated with the P=Se unit *trans* to the chloride ligand, in accord with its weaker *trans* influence compared to PMe_2Ph. By this analysis P_B lies to high frequency of P_A, with $|J(P_A–P_X)| > |J(P_B–P_X)|$, *cf.* the relationship between $|J(A–X)|$ and $|J(A–X')|$ for **8**. The palladium complex **9** for which of course there is no phosphorus coupling to the metal is assigned on this basis. However the additional information provided by the $^1J(^{31}P–^{77}Se)$ couplings casts doubts upon these assignments, as the above analysis requires $J(P_B–Se)$ for **9** (547 Hz) to be substantially larger than those observed for **8** (535 Hz), with $J(P_A–Se)$ closer to the values expected for a selenophosphoryl unit *trans* to PR_3.

As noted by other workers using this ligand,[7] there is a reduction in the magnitude of $^1J(^{31}P–^{77}Se)$ upon co-ordination of the $[N(SePPh_2)_2]^-$ anion in complexes **1**–**9**, which mirrors that observed when $CH_2(SePPh_2)_2$ ligates to a metal centre.[23,24] The presence of selenium satellites for the PMe_2Ph resonance in **8** and **9** is unexpected considering that *trans* ^2J(P–Se) couplings are not apparent for **8**, as is the large magnitude of this coupling *cf.* P_4Se_3 for which $|^2J(P–Se)|$ is 57 Hz.[25]

The platinum-195 NMR spectra of **8** comprise 1:2:1 triplets of 1:2:1 triplets, with $\delta(^{195}Pt)$ for the bis(monophosphine) complexes **2**–**5** moving to lower frequency as the cone angle of PR_3 increases. For **8** an eight-line pattern from coupling of the platinum nucleus to three inequivalent phosphorus atoms is observed, while the comparatively high chemical shift of **6** is consistent with the presence of a four-membered platinacycle.[20]

In the infrared spectra of **2**–**9** the P_2N and PSe vibrations of the $[N(SePPh_2)_2]^-$ ligand are well separated from absorptions of PR_3. The $\nu_{asym}(P_2N)$ vibration appears as a strong band between 1140 and 1175 cm^{-1}, reduced in energy relative to the potassium salt **IV** while $\nu_{sym}(P_2N)$, a band of medium intensity between 800 and 815 cm^{-1}, moves to higher energy; ν(PSe) is not greatly affected by co-ordination.

We have isolated small quantities of an unexpected product from the reaction of **IV** with $[PdCl_2(PMe_2Ph)_2]$, conducted by a method identical to that used for the preparation of **8**. Following extraction into CH_2Cl_2 and addition of hexane as before, a small crop of orange crystals was isolated upon cooling to −20 °C, which was presumed to be $[Pd\{N(SePPh_2)_2\text{-}Se,Se'\}(PMe_2Ph)_2]Cl$. However X-ray crystallographic analysis has revealed the structure to be the novel mixed-chelate $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)_2\text{-}Se,Se'\}]\cdot 0.5EtOH\cdot 0.3CH_2Cl_2$ **10**.

The crystal structure of **10** (Tables 5 and 6, Fig. 4) shows the palladium to be co-ordinated by one $[N(SePPh_2)_2]^-$ and one $[Ph_2PNP(Se)Ph_2]^-$ anion in a slightly distorted square-planar geometry. The Se(1)–Pd–Se(2) angle [101.8(1)°] is enlarged whilst the Se(2)–Pd–P(4) and Se(1)–Pd–Se(3) angles are contracted [87.0(1) and 81.4(1)° respectively]. The bond lengths and angles within the Pd–Se(3)–P(3)–N(3)–P(4) ring are comparable with the corresponding parameters in *trans*-$[Re(O)(OEt)\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}_2]$.[8] Within the five-membered ring the Pd, N(3), P(3) and P(4) atoms are essentially coplanar with Se(3) lying 0.35 Å out of this plane. Extending to include the other two co-ordinated selenium atoms the Se(1)Se(2)P(3)P(4)N(3)Pd atoms are coplanar to within 0.05 Å, with Se(3) displaced out of this plane by 0.41 Å. There is significant puckering of the six-membered chelate ring, as observed[9] in the structure of $[Pt\{N(SePPh_2)_2\text{-}Se,Se'\}_2]\cdot CHCl_3$ **12**$\cdot CHCl_3$. Atom P(1) is displaced above the co-ordination plane in the same sense as Se(3) whilst N(1) and P(2) are displaced in the opposite direction. The six-membered $PdSe_2P_2N$ ring has, in common with that in **12** a pseudo-boat conformation with variations in the equivalent torsion angles of up to 24° (Table 7). The differences between **10** and **12** further reinforce the view that there is substantial stereochemical freedom for this ring although there is clearly some delocalisation (see below); d_π–p_π overlap does not require special geometries at the heavy atoms[26] and so this may play a part here. Whereas the Pd–Se(2) and Pd–Se(3) distances differ only slightly [2.463(2) *cf.* 2.425(2) Å] the Pd–Se(1) bond [2.510(2) Å] is significantly longer reflecting the greater *trans* influence of phosphorus [P(4)] *versus* selenium. The P–Se distance within the five-membered ring is significantly longer [2.200(4) Å] than those in the six-membered ring [2.172(4) and 2.174(5) Å]. Furthermore the N(3)–P(4) bond in the five-membered ring [1.636(9) Å] is significantly longer than the remaining P–N bonds (Table 6). Interestingly the P–Se distances in the six-membered ring of **10** are equivalent although they differ in the homoleptic complex **12**.

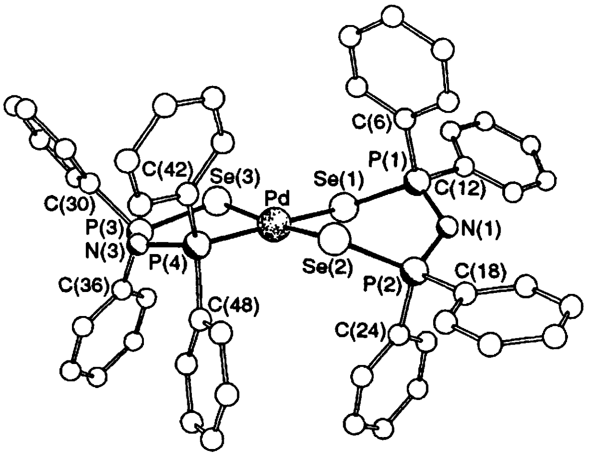

Fig. 4 The molecular structure of $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)_2\text{-}Se,Se'\}]$

Within the crystal of **10** the molecules pack to form channels that extend along the crystallographic *a* direction (Fig. 5). The included, disordered, CH_2Cl_2 solvent molecules lie in a plane within these channels. The channels are bounded by the phenyl rings of the ligands, these in turn enter into face-to-face π–π stacking interactions.

There are no bands arising from nitrogen-bound hydrogen atoms in the infrared spectrum of **10**. The $\nu(P_2N)$ bands are observed at 1144 and 816 cm^{-1}, with $\nu(PSe)$ at 542 cm^{-1}. The peak of greatest relative abundance in the FAB^+ mass spectrum of this complex is the parent ion at *m*/*z* 1113, the experimentally observed and calculated manifolds being in good agreement.

From a subsequent repetition of the reaction, the ^{31}P NMR

Table 7 Comparative torsion angles for $[M\{N(SePPh_2)\text{-}Se,Se'\}_2]$ (M = Pd **11** or Pt **12**)[9] and the six-membered ring in **10** (mean e.s.d. less than 1°)

	10	**11**	**12**
Se(2)–M–Se(1)–P(1)	−20	4	4
M–Se(1)–P(1)–N(1)	65	50	50
Se(1)–P(1)–N(1)–P(2)	−39	−44	−44
P(1)–N(1)–P(2)–Se(2)	−35	−24	−23
Se(1)–M–Se(2)–P(2)	−27	−48	−48
N(1)–P(2)–Se(2)–M	68	72	72

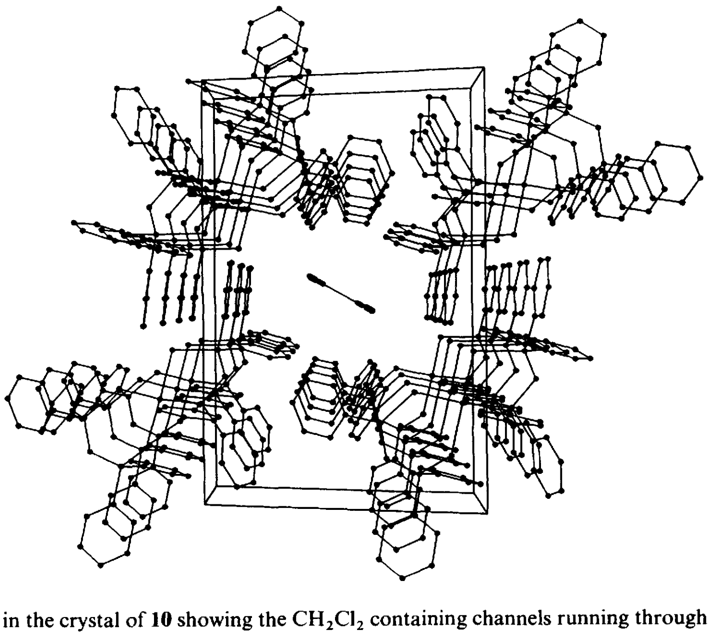

Fig. 5 View down the *a* direction in the crystal of **10** showing the CH_2Cl_2 containing channels running through the centre of the unit cell and the aromatic π–π stacking

Table 8 Phosphorus-31 NMR parameters for $[Pd\{Ph_2PNP(Se)Ph_2\text{-}P,Se\}\{N(SePPh_2)_2\text{-}Se,Se'\}]\cdot 0.5EtOH\cdot 0.3CH_2Cl_2$

		J(PP)/Hz			
	δ_P	P(1)	P(2)	P(3)	P(4)
P(1)	30.3	—			
P(2)	27.3	*	—		
P(3)	52.6	*	*	—	
P(4)	82.4	10.8	17.2	47.0	—

* Coupling not resolved.

spectrum of the crude mixture was found to contain two broad humps, suggesting an exchange process. Gel permeation chromatography removes the species responsible for the line broadening without separating any metal complexes from each other, the products eluting together as a single red fraction. Analysis by ^{31}P NMR spectroscopy shows the major component of the mixture is $[PdCl\{N(SePPh_2)_2\text{-}Se,Se'\}(PMe_2Ph)]$ **9**, with small quantities of **10**, as well as $[Pd\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ and $PMe_2Ph{=}Se$ [δ_P 16.7, ^1J(P–Se) 706 Hz]. It is possible that **10** is generated by selenium abstraction from either $[Pd\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ or $[N(SePPh_2)_2]^-$ by the displaced PMe_2Ph. Phosphorus-31 NMR spectral data for **10** are collected in Table 8. The phosphorus atoms P(1), P(2) and P(3) appear as doublets from coupling solely to P(4), the latter resonance comprising a multiplet, P^V–P^V couplings being unresolved. Atom P(1) is judged to lie to high frequency of P(2) on the basis of the greater *trans* influence of P(4) compared with Se(3). The high frequency shifts of P(3) and P(4), the phosphorus atoms of the $[Ph_2PNP(Se)Ph_2]^-$ chelate, are consistent with the known shielding effects of five-membered rings.[20]

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