

# New complexes of functionalised ligands bearing P/N/Se or P<sub>2</sub>Se donor sets

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The new selenoether functionalised tertiary phosphines (2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>n</sub>SePh (*n* = 3 **1a**; 4 **1b**) were readily prepared by condensation of (2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=O and H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SePh (*n* = 3, 4) in absolute ethanol. Reaction of two equiv. of Ph<sub>2</sub>PCH<sub>2</sub>OH with H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SePh (*n* = 3, 4) affords the symmetrical ditertiary phosphines (Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SePh (*n* = 3 **2a**; 4 **2b**). Reaction of **1a–2b** with [MCl<sub>2</sub>(cod)] (M = Pt, Pd) gave the dichlorometal(II) chelate complexes **3a–4d** in which either six-membered *P,P'*- or *P,N*-ligation is observed. Chloro bridge cleavage of [{RuCl<sub>2</sub>(*p*-cymene)}<sub>2</sub>] or tht (tht = tetrahydrothiophene) substitution of [AuCl(tht)] with **2a** (or **2b**) gave the new complexes [{RuCl<sub>2</sub>(*p*-cymene)}<sub>2</sub>{μ-(*P,P'*-Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SePh}] (*n* = 3 **5a**; 4 **5b**) or [{AuCl}<sub>2</sub>{μ-(*P,P'*-Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SePh}] (*n* = 3 **6a**; 4 **6b**) in which the ligand *P,P'*-bridges two metal centres. Spectroscopic evidence suggests the pendant selenoether group in **3c** undergoes further reaction with [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] affording an unusual trinuclear palladium(II) complex **7**. Furthermore reaction of **3b** with 1 equiv. of Ag[BF<sub>4</sub>] in dichloromethane gave the cationic complex [PtCl(**1a**)] [BF<sub>4</sub>] **8** in which **1a** functions as a *P,N,Se*-tridentate ligand. All structures have been confirmed by a combination of spectroscopic, analytical and single crystal X-ray studies. The structure of **8** represents, to the best of our knowledge, an extremely rare example of a crystallographically characterised Group 10 metal complex with a *P/N/Se/Cl* coordination environment.

## Introduction

The chemistry of ligands bearing P/Se or P/N/Se donor sets has surprisingly been neglected with respect to ligands bearing P/X or P/N/X (X = O, S)<sup>1,2</sup> donor combinations. Studies of ligands bearing primarily P and Se donor atoms (*e.g.* **A–G** Chart 1) are sporadic yet some important features from these examples merit discussion. Ligands such as **A–C** incorporate both P and Se donors, separated by a carbon (alkyl, aryl) or nitrogen spacer.<sup>3–9</sup> Furthermore these ligands have been known for some time yet surprisingly their coordination chemistry has only been poorly studied.<sup>7–9</sup> By contrast, phosphine selenides such as **D–F** are known and form many complexes (especially with **D**) *via* ligation of the selenium donor atom or, in the case of **F**, as an anionic *N,Se*-bidentate ligand.<sup>10–12</sup>

As a consequence of the relatively weak P=Se bond, as in **D** [and also the diselenide {Ph<sub>2</sub>P(Se)}<sub>2</sub>NH], low valent metal centres undergo facile oxidative addition reactions with such compounds.<sup>13,14</sup> There are limited reports on phosphorus(III) ligands such as **G** in which a direct single P–Se bond exists as opposed to the P=Se double bond observed in **D–F**.<sup>15,16</sup>

As part of continuing studies in our group developing the use of Ph<sub>2</sub>PCH<sub>2</sub>OH<sup>17–20</sup> as a synthon to new phosphorus based ligands, we describe here the preparation of two classes of “hybrid” ligands with P/N/Se or P<sub>2</sub>Se donor sets. The procedure employed here should enable many future variants to be prepared using this facile method. Some initial studies on the coordination behaviour of the ligands has been evaluated with a range of ligating modes uncovered. In several cases X-ray crystal structures have been determined. The X-ray structure of **8** represents an extremely rare d<sup>8</sup> metal complex containing P/N/Se/Cl donor atoms. Ligands containing phosphorus–nitrogen donors have recently been shown to be efficient catalysts for the Heck reaction, coupling of organotannanes and aryl halides, oligomerisation of ethene and allylic alkylation.<sup>21</sup>

## Experimental

Standard Schlenk techniques were used for ligand syntheses whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. The amines H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>SePh (*n* = 3, 4),<sup>22</sup> Ph<sub>2</sub>PCH<sub>2</sub>OH<sup>23</sup> and the metal complexes [MCl<sub>2</sub>(cod)] (M = Pd, Pt),<sup>24</sup> [{RuCl(μ-Cl)(η<sup>6</sup>-*p*-cymene)}<sub>2</sub>]<sup>25</sup> and [AuCl(tht)]<sup>26</sup> were prepared according to previous known procedures. All other chemicals were obtained from commercial sources and used directly without further purification.

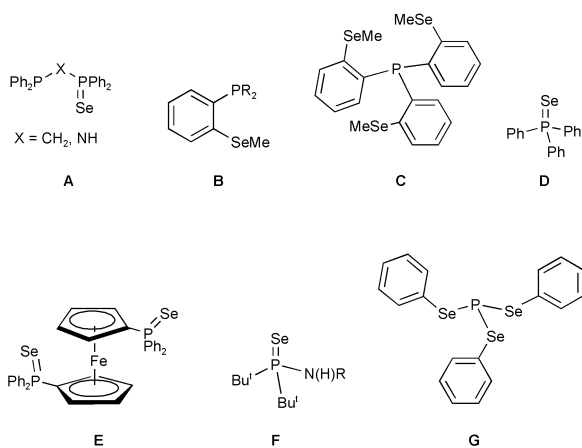


Chart 1

Infrared spectra were recorded as KBr pellets in the range 4000–200  $\text{cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier-transform spectrometer,  $^1\text{H}$  NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with chemical shifts ( $\delta$ ) in ppm to high frequency of  $\text{SiMe}_4$  and coupling constants ( $J$ ) in Hz,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a JEOL FX90Q (36.2 MHz) spectrometer with chemical shifts ( $\delta$ ) in ppm to high frequency of 85%  $\text{H}_3\text{PO}_4$  and coupling constants ( $J$ ) in Hz. All NMR spectra were measured in  $\text{CDCl}_3$  unless otherwise stated. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Precious metal salts were provided on loan by Johnson Matthey plc.

## Preparations

**(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh 1a.** A mixture of (2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)O (0.418 g, 0.410 mmol) and  $\text{H}_2\text{N}(\text{CH}_2)_3\text{SePh}$  (0.299 g, 0.410 mmol) in absolute ethanol (10  $\text{cm}^3$ ) was stirred under a nitrogen atmosphere at 50 °C for 3 h. The solvent was evaporated to dryness under reduced pressure to give a yellow oil. Yield: 0.59 g, 87%. Compound **1a** was of sufficient purity (as determined by  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopy) to be used directly in subsequent coordination studies. The same preparative method was used for **1b** (77%). Selected NMR data:  $^{31}\text{P}$ :  $\delta$  -13.0;  $^1\text{H}$ :  $\delta$  8.83 [ $^4J(\text{PH})$  4.4] ( $\text{CH}_{\text{imine}}$ ), 7.94–6.84 (arom. H), 3.56, 2.68, 1.88 ( $\text{CH}_2$ );  $m/z$  = 487 (M) for **1a**.  $^{31}\text{P}$ :  $\delta$  -13.3;  $^1\text{H}$ :  $\delta$  8.83 [ $^4J(\text{PH})$  4.4] ( $\text{CH}_{\text{imine}}$ ), 7.95–6.83 (arom. H), 3.47, 2.81, 1.57 ( $\text{CH}_2$ );  $m/z$  = 501 (M) for **1b**.

**(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>SePh 2a.** A mixture of Ph<sub>2</sub>PCH<sub>2</sub>OH (0.110 g, 0.509 mmol) and  $\text{H}_2\text{N}(\text{CH}_2)_3\text{SePh}$  (0.064 g, 0.299 mmol) in chloroform (10  $\text{cm}^3$ ) was stirred under a nitrogen atmosphere for ca. 15 min. The solvent was evaporated to dryness to give a yellow oil. Yield: 0.151 g, 83%. Selected NMR data:  $^{31}\text{P}$ :  $\delta$  -28.3;  $^1\text{H}$ :  $\delta$  7.38–7.20 (arom. H), 3.53 [ $^2J(\text{PH})$  3.2], 2.93, 2.64, 1.69 ( $\text{CH}_2$ );  $m/z$  = 611 (M) for **2a**.

**(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>SePh 2b.** A mixture of Ph<sub>2</sub>PCH<sub>2</sub>OH (0.390 g, 1.81 mmol) and  $\text{H}_2\text{N}(\text{CH}_2)_4\text{SePh}$  (0.205 g, 0.900 mmol) in methanol (10  $\text{cm}^3$ ) was stirred under a nitrogen atmosphere at 50 °C for 4 h. The solvent was evaporated to dryness under reduced pressure, triturated with two portions of cold methanol and dried *in vacuo* to give a yellow oil. Yield: 0.494 g, 88%. Selected NMR data:  $^{31}\text{P}$ : -28.2;  $^1\text{H}$ : 7.43–7.21 (arom. H), 3.54 [ $^2J(\text{PH})$  2.8], 2.78, 1.47 ( $\text{CH}_2$ );  $m/z$  = 625 (M) for **2b**.

***cis*-[PtCl<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>PPh<sub>2</sub>-P,P')}<sub>2</sub>]} 3a.** To a  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) solution of (Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>SePh (0.061 g, 0.100 mmol) was added [PtCl<sub>2</sub>(cod)] (0.037 g, 0.099 mmol). After stirring the solution for ca. 15 min, the volume was concentrated *in vacuo* to ca. 1–2  $\text{cm}^3$  and diethyl ether (20  $\text{cm}^3$ ) added. The white solid was collected by suction filtration and dried *in vacuo*. An additional crop could be obtained from the filtrate. Yield: 0.070 g, 81%. In a similar manner the following complexes were prepared: *cis*-[PtCl<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>4</sub>N(CH<sub>2</sub>PPh<sub>2</sub>-P,P')}<sub>2</sub>]} **3b** (95%), *cis*-[PdCl<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>PPh<sub>2</sub>-P,P')}<sub>2</sub>]} **3c** (92%) and *cis*-[PdCl<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>4</sub>N(CH<sub>2</sub>PPh<sub>2</sub>-P,P')}<sub>2</sub>]} **3d** (82%). Selected NMR and IR data:  $^{31}\text{P}$ :  $\delta$  -7.9 [ $^1J(\text{PtP})$  3400];  $^1\text{H}$ :  $\delta$  7.84–20 (arom. H), 3.39 [ $^3J(\text{PtH})$  38.1], 2.65, 2.41, 1.62 ( $\text{CH}_2$ );  $\nu_{\text{PtCl}}$  316, 293  $\text{cm}^{-1}$ ;  $m/z$  = 877 (M) for **3a**.  $^{31}\text{P}$ :  $\delta$  -8.3 [ $^1J(\text{PtP})$  3405];  $^1\text{H}$ :  $\delta$  7.82–7.22 (arom. H), 3.37 [ $^3J(\text{PtH})$  37.2], 2.70, 2.53, 1.71, 1.40 ( $\text{CH}_2$ );  $\nu_{\text{PtCl}}$  316, 293  $\text{cm}^{-1}$ ;  $m/z$  = 891 (M) for **3b**.  $^{31}\text{P}$ :  $\delta$  8.6;  $^1\text{H}$ :  $\delta$  7.87–7.23 (arom. H), 3.34, 2.71, 2.43, 1.63 ( $\text{CH}_2$ );  $\nu_{\text{PdCl}}$  291  $\text{cm}^{-1}$ ;  $m/z$  = 766 (M – Cl) for **3c**.  $^{31}\text{P}$ :  $\delta$  8.2;  $^1\text{H}$ :  $\delta$  7.87–7.26 (arom. H), 3.33, 2.74, 2.57, 1.74, 1.40 ( $\text{CH}_2$ );  $\nu_{\text{PdCl}}$  292  $\text{cm}^{-1}$  for **3d**.

***cis*-[PtCl<sub>2</sub>{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh-P,N}]} 4a.** To a  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) solution of (2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh (0.047 g, 0.097 mmol) was added [PtCl<sub>2</sub>(cod)] (0.036 g, 0.096 mmol). The solution was stirred for ca. 15 min, the volume concentrated *in vacuo* to ca. 1–2  $\text{cm}^3$  and diethyl ether (15  $\text{cm}^3$ ) added. The white solid was collected by suction filtration and dried *in vacuo*. Yield: 0.054 g, 75%. In a similar manner the complexes *cis*-[PtCl<sub>2</sub>{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>4</sub>SePh-P,N}]} **4b** (93%), *cis*-[PdCl<sub>2</sub>{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh-P,N}]} **4c** (93%) and *cis*-[PdCl<sub>2</sub>{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>4</sub>SePh-P,N}]} **4d** (94%) were also prepared. Selected NMR and IR data:  $^{31}\text{P}$ : 5.1 [ $^1J(\text{PtP})$  3735]; 8.25 [ $^3J(\text{PtH})$  102] ( $\text{CH}_{\text{imine}}$ ),  $^1\text{H}$ : 7.61–6.95 (arom. H), 4.72, 2.26, 1.64 ( $\text{CH}_2$ );  $\nu_{\text{PtCl}}$  341, 279  $\text{cm}^{-1}$ ;  $m/z$  = 716 (M – Cl) for **4a**.  $^{31}\text{P}$ :  $\delta$  5.3 [ $^1J(\text{PtP})$  3748]; 8.30 [ $^3J(\text{PtH})$  103] ( $\text{CH}_{\text{imine}}$ ),  $^1\text{H}$ :  $\delta$  7.75–6.94 (arom. H), 4.56, 2.66, 1.86, 1.28 ( $\text{CH}_2$ );  $\nu_{\text{PtCl}}$  338, 281  $\text{cm}^{-1}$ ;  $m/z$  = 730 (M – Cl) for **4b**.  $^{31}\text{P}$ :  $\delta$  31.0;  $^1\text{H}$ :  $\delta$  8.08 ( $\text{CH}_{\text{imine}}$ ), 7.73–6.89 (arom. H), 4.50, 2.27, 2.17 ( $\text{CH}_2$ );  $\nu_{\text{PdCl}}$  335, 267  $\text{cm}^{-1}$ ;  $m/z$  = 628 (M – Cl) for **4c**.  $^{31}\text{P}$ :  $\delta$  31.3;  $^1\text{H}$ :  $\delta$  8.14 ( $\text{CH}_{\text{imine}}$ ), 7.77–6.89 (arom. H), 4.36, 2.69, 1.79, 1.28 ( $\text{CH}_2$ );  $\nu_{\text{PdCl}}$  336, 269  $\text{cm}^{-1}$ ;  $m/z$  = 642 (M – Cl) for **4d**.

**[{RuCl<sub>2</sub>( $\eta^6$ -p-MeC<sub>6</sub>H<sub>4</sub><sup>*i*</sup>Pr)}<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>PPh<sub>2</sub>- $\mu$ -P,P')}<sub>2</sub>]} 5a.** To a  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) solution of (Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>SePh (0.088 g, 0.144 mmol) was added [{RuCl<sub>2</sub>( $\eta^6$ -p-MeC<sub>6</sub>H<sub>4</sub><sup>*i*</sup>Pr)}<sub>2</sub>] (0.088 g, 0.144 mmol). The solution was stirred for ca. 15 min and the volume concentrated *in vacuo* to ca. 1–2  $\text{cm}^3$ . Addition of diethyl ether (15  $\text{cm}^3$ ) gave an orange-brown solid which was collected by suction filtration and dried *in vacuo*. Yield: 0.153 g, 87%. [{RuCl<sub>2</sub>( $\eta^6$ -p-MeC<sub>6</sub>H<sub>4</sub><sup>*i*</sup>Pr)}<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>4</sub>N(CH<sub>2</sub>PPh<sub>2</sub>- $\mu$ -P,P')}<sub>2</sub>]} **5b** was prepared in an analogous manner (70%). Selected spectroscopic data:  $^{31}\text{P}$ :  $\delta$  19.1;  $^1\text{H}$ :  $\delta$  7.85–7.23 (arom. H), 3.70, 1.96, 1.55 ( $\text{CH}_2$ ) and additional resonances for  $\eta^6$ -p-MeC<sub>6</sub>H<sub>4</sub><sup>*i*</sup>Pr at 5.06–4.95, 2.35, 1.68 and 0.84 for **5a**.  $^{31}\text{P}$ :  $\delta$  19.1;  $^1\text{H}$ :  $\delta$  7.85–7.25 (arom. H), 3.67, 3.02, 1.67, 1.27 ( $\text{CH}_2$ ) and additional resonances for  $\eta^6$ -p-MeC<sub>6</sub>H<sub>4</sub><sup>*i*</sup>Pr at  $\delta$  5.05–4.93, 2.23, 1.65 and 0.83;  $m/z$  = 1202 (M – Cl) for **5b**.

**[{AuCl}<sub>2</sub>{PhSe(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>PPh<sub>2</sub>- $\mu$ -P,P')}<sub>2</sub>]} 6a.** A  $\text{CDCl}_3$  (0.5  $\text{cm}^3$ ) solution of [AuCl(tht)] (0.023 g, 0.0717 mmol) and (Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>SePh (0.022 g, 0.0360 mmol) was monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy and showed **6a** as the only phosphorus containing species. Solid **6a** was isolated upon addition of diethyl ether (10  $\text{cm}^3$ ) and collected by suction filtration. Yield: 0.021 g, 54%. Selected spectroscopic data:  $^{31}\text{P}$ :  $\delta$  16.3;  $^1\text{H}$ :  $\delta$  7.68–7.25 (arom. H), 4.19, 2.96, 2.53, 1.46 ( $\text{CH}_2$ );  $\nu_{\text{AuCl}}$  329  $\text{cm}^{-1}$ ;  $m/z$  = 1041 (M – Cl) for **6a**.  $^{31}\text{P}$ :  $\delta$  16.6;  $^1\text{H}$ :  $\delta$  7.70–7.26 (arom. H), 4.20, 2.80, 2.65, 1.30, 1.22 ( $\text{CH}_2$ );  $\nu_{\text{AuCl}}$  327  $\text{cm}^{-1}$ ;  $m/z$  = 1055 (M – Cl) for **6b**.

***cis*-[PdCl<sub>2</sub>]{PhSe(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>PPh<sub>2</sub>-P,P,Se)}<sub>2</sub> 7.** To a stirred solution of [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] (0.005 g, 0.019 mmol) in  $\text{CHCl}_3$  (1  $\text{cm}^3$ ) was added **3c** (0.030 g, 0.038 mmol) as a solid in one portion. After stirring the solution for ca. 15 min the volume was concentrated *in vacuo* to ca. 1–2  $\text{cm}^3$  and diethyl ether (10  $\text{cm}^3$ ) added. The solid was collected by suction filtration and dried *in vacuo*. Yield: 0.025 g, 75%. Selected spectroscopic data:  $^{31}\text{P}$ :  $\delta$  8.6.  $^1\text{H}$ :  $\delta$  7.88–7.38 (arom. H), 3.33, 2.71, 2.47, 1.61 ( $\text{CH}_2$ );  $\nu_{\text{PdCl}}$  357, 292  $\text{cm}^{-1}$ ;  $m/z$  = 1715 (M – Cl).

**[PtCl{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh-P,N,Se)}]BF<sub>4</sub> 8.** To a  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) suspension of Ag[BF<sub>4</sub>] (0.029 g, 0.149 mmol) was added [PtCl<sub>2</sub>{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh-P,N}]} (0.099 g, 0.132 mmol) and the mixture stirred in the dark for 2 h. The AgCl was removed by filtration through a Celite plug and the yellow solution evaporated to dryness. The residue was taken up in  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) and addition of diethyl ether (15  $\text{cm}^3$ ) gave a pale yellow solid **8** which was collected by suction filtration, washed with diethyl ether (5  $\text{cm}^3$ ) and

dried *in vacuo*. Yield: 0.088 g, 83%. Selected spectroscopic data:  $^{31}\text{P}$  [ $\text{CDCl}_3/(\text{CH}_3)_2\text{SO}$ ]:  $\delta$  7.6 [ $J(\text{PtP})$  3427 Hz];  $^1\text{H}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.43 [ $J(\text{PtH})$  112] ( $\text{CH}_{\text{imine}}$ ), 7.96–7.27 (arom. H), 4.13, 3.54, 1.91 ( $\text{CH}_2$ );  $\nu_{\text{CN}}$  1619,  $\nu_{\text{BF}}$  1060,  $\nu_{\text{PtCl}}$  334  $\text{cm}^{-1}$ ;  $m/z$  = 717 ( $\text{M} - \text{BF}_4$ ).

### X-Ray crystallography

Suitable crystals of **3b**, **3c-CHCl<sub>3</sub>**, **4d-2.5CHCl<sub>3</sub>** and **6a** were grown by vapour diffusion of diethyl ether into chloroform solutions over several days. For **4b**, suitable crystals were obtained by slow diffusion of diethyl ether into dichloromethane solutions over several days. For **8**, good quality crystals were obtained by vapour diffusion of diethyl ether into acetonitrile solutions over several days. All measurement were made on a Bruker AXS SMART 1000 CCD area-detector diffractometer, at 150 K, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and narrow frame exposures (0.3°) in  $\omega$ . Cell parameters were refined from the observed ( $\omega$ ) angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for **4d** and **6a**) and refined on  $F^2$  values for all unique data by full-matrix least-squares. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in a riding model with  $U_{\text{iso}}$  set to be 1.2 times  $U_{\text{eq}}$  of the carrier atom. For **3b** there were clear indications that the data were twinned, but no satisfactory twin law(s) could be established. Four of the five largest residual peaks are close to the N atoms, two in each molecule. However, these were not in chemically reasonable positions attributable to a minor compound of a different composition, nor could they be successfully refined as partially occupied atoms. We therefore conclude that these peaks are artifacts of the unmodelled twinning. There are two molecules in the asymmetric unit, in one atom Se(1) is disordered over two sites with relative occupancies 82.0:18.0(4)%.

For **4d-2.5CHCl<sub>3</sub>** the end of the Se-containing chain, including C(23), Se(1) and the terminal phenyl group, was disordered over two sets of positions, modelled as equally occupied. Additionally, one  $\text{CHCl}_3$  solvent molecule is disordered over two sets of equally occupied positions with one Cl atom common to both. When one of these sets of positions is occupied,

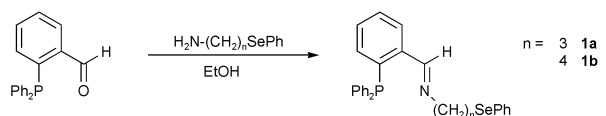
another half-occupied  $\text{CHCl}_3$  molecule is also present. The disorder in the Se-containing chain correlates with the disorder in the solvent molecules such that the structure comprises a solid solution of **4d-2CHCl<sub>3</sub>** with **4d-3CHCl<sub>3</sub>**, giving **4d-2.5CHCl<sub>3</sub>** as the overall composition.

Programs used were Bruker AXS SMART and SAINT for diffractometer control and frame integration,<sup>27</sup> Bruker SHELXTL for structure solution, refinement and molecular graphics<sup>28</sup> and local programs.

CCDC reference numbers 190642–190647. See <http://www.rsc.org/suppdata/nj/b2/b204005k/> for crystallographic files in CIF or other electronic format.

### Results and discussion

Schiff base condensation reactions of  $(2\text{-Ph}_2\text{P})\text{C}_6\text{H}_4\text{C(H)=O}$  with various amines has previously been reported and shown to represent a useful entry to functionalised tertiary phosphine ligands.<sup>1,29</sup> We find that  $(2\text{-Ph}_2\text{P})\text{C}_6\text{H}_4\text{C(H)=O}$  reacts smoothly with the primary amines  $\text{H}_2\text{N}(\text{CH}_2)_n\text{SePh}$  ( $n$  = 3, 4)<sup>22</sup> in ethanol at 50 °C to give, in high yields (as oils), the new selenoether functionalised ligands **1a** and **1b** (eqn. (1)). The purity of these compounds was ascertained from spectroscopic and MS studies (see Experimental section) and were found to be sufficiently pure for their coordination chemistry to be studied (see below). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show single resonances at *ca.*  $\delta(\text{P})$  –13 ( $\text{CDCl}_3$ ) shifted marginally with respect to that found for  $(2\text{-Ph}_2\text{P})\text{C}_6\text{H}_4\text{C(H)=O}$  [ $\delta(\text{P})$  –11.6 (in  $\text{CDCl}_3$ )]. Further confirmation came from  $^1\text{H}$  NMR spectroscopy which clearly showed, for  $(2\text{-Ph}_2\text{P})\text{C}_6\text{H}_4\text{C(H)=O}$ , the absence of a doublet signal at  $\delta(\text{H})$  10.5<sup>30</sup> [ $\text{C(H)=O}$  proton]. By contrast an imine proton resonance at  $\delta$  8.83 was observed as a doublet as a result of  $^4J(\text{PH})$  coupling (4.4 Hz). The *E*-conformer was assigned by simple analogy with other iminophosphine based ligands bearing different functional motifs.<sup>1,29</sup>

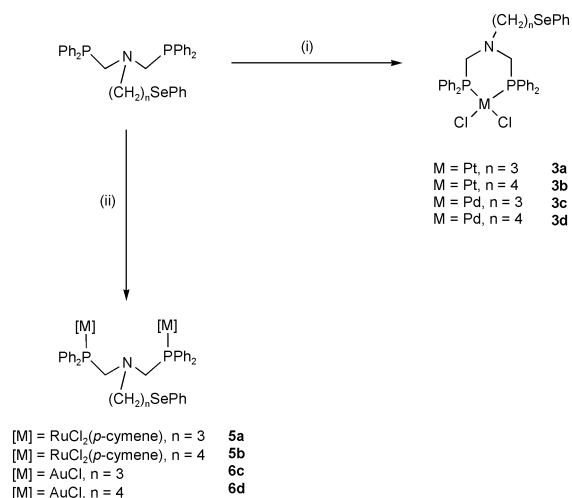


We,<sup>17–20</sup> and others,<sup>31</sup> have shown that  $\text{Ph}_2\text{PCH}_2\text{OH}$  is a versatile precursor for synthesising new tertiary phosphines

**Table 1** Details of the X-ray data collections and refinements for compounds **3b**, **3c-CHCl<sub>3</sub>**, **4b**, **4d-2.5CHCl<sub>3</sub>**, **6a** and **8**

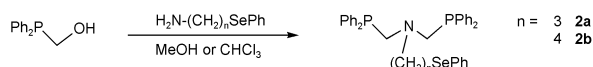
Compound	<b>3b</b>	<b>3c-CHCl<sub>3</sub></b>	<b>4b</b>	<b>4d-2.5CHCl<sub>3</sub></b>	<b>6a</b>	<b>8</b>
Empirical formula	$\text{C}_{36}\text{H}_{37}\text{Cl}_2\text{N}$ $\text{P}_2\text{PtSe}$	$\text{C}_{35}\text{H}_{35}\text{Cl}_2\text{NP}_2\text{PdSe}$ $\text{CHCl}_3$	$\text{C}_{29}\text{H}_{28}\text{Cl}_2$ $\text{NPtSe}$	$\text{C}_{29}\text{H}_{28}\text{Cl}_2\text{NPPdSe}$ $2.5\text{CHCl}_3$	$\text{C}_{35}\text{H}_{35}\text{Au}_2$ $\text{Cl}_2\text{NP}_2\text{Se}$	$\text{C}_{28}\text{H}_{26}\text{BClF}_4$ $\text{NPtSe}$
<i>M</i>	890.56	907.21	766.44	976.17	1075.37	803.78
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Trigonal	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P3_2$	$P2_1/c$
<i>a</i> /Å	11.2388(7)	14.6694(10)	19.9268(7)	10.2746(8)	9.5384(4)	9.8693(7)
<i>b</i> /Å	14.3914(8)	11.6913(8)	10.3898(4)	14.3334(11)	9.5384(4)	23.8471(17)
<i>c</i> /Å	21.7918(13)	22.9159(16)	26.4969(10)	14.3424(11)	33.0881(16)	11.7404(8)
$\alpha$ /°	100.185(2)	90	90	98.698(2)	90	90
$\beta$ /°	90.251(2)	102.898(2)	92.509(2)	108.957(2)	90	99.652(2)
$\gamma$ /°	99.638(2)	90	90	100.683(2)	120	90
<i>U</i> /Å <sup>3</sup>	3418.0(4)	3831.0(5)	5480.5(4)	1911.5(3)	2607.1(2)	2724.0(3)
<i>Z</i>	4	4	8	2	3	4
$\mu/\text{mm}^{-1}$	5.45	1.89	6.72	2.17	9.75	6.69
Measured reflections	24506	29211	47536	15524	22423	23695
Independent reflections ( $R_{\text{int}}$ )	11930 (0.0234)	7530 (0.0535)	13305 (0.0325)	8565 (0.0331)	8193 (0.0217)	6526 (0.0447)
Reflections with $F^2 > 2\sigma(F^2)$	10135	5274	10564	6163	7867	4923
Final $R$ , $^a R_w$ <sup>b</sup>	0.033, 0.079	0.053, 0.155	0.025, 0.057	0.044, 0.121	0.018, 0.035	0.034, 0.082

<sup>a</sup>  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$  based on observed data. <sup>b</sup>  $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$  based on all data.

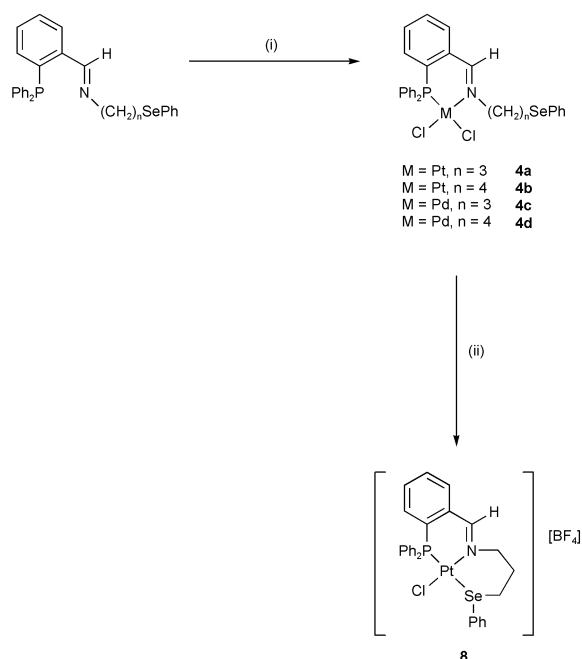


**Scheme 1** (i)  $[\text{MCl}_2(\text{cod})]$ , 1 equiv. **2**,  $\text{CH}_2\text{Cl}_2$  (ii)  $[\{\text{RuCl}_2(\mu\text{-Cl})(\eta^6\text{-p-cymene})\}_2]$ , 1 equiv. **2**,  $\text{CH}_2\text{Cl}_2$  or  $[\text{AuCl}(\text{tht})]$ , 0.5 equiv. **2**,  $\text{CH}_2\text{Cl}_2$

by virtue of the reactive primary hydroxo group. Condensation of  $\text{Ph}_2\text{PCH}_2\text{OH}$  (2 equiv.) with  $\text{H}_2\text{N}(\text{CH}_2)_n\text{SePh}$  ( $n = 3, 4$ ) gave (as oils) the new ditertiary phosphines  $(\text{Ph}_2\text{PCH}_2)_2\text{N}(\text{CH}_2)_n\text{SePh}$  **2a** ( $n = 3$ ) and **2b** ( $n = 4$ ) containing a selenoether group in the ligand backbone (eqn. (2)). So far we have been unable to isolate intermediates of the type  $(\text{Ph}_2\text{PCH}_2)\text{NH}(\text{CH}_2)_n\text{SePh}$  bearing a single “ $\text{Ph}_2\text{PCH}_2$ ” group although we have observed, by  $^{31}\text{P}\{^1\text{H}\}$  NMR, their transient formation in solution [ $\delta(\text{P})$  ca.  $-20$ ]. The  $^{31}\text{P}$  chemical shifts are comparable to  $(\text{Ph}_2\text{PCH}_2)_2\text{NPh}$  [ $\delta(\text{P}) -21.3$ ] and related systems and in accord with bis substitution.<sup>31</sup>



Reaction of either 1 equiv. of **1** or **2** with  $[\text{MCl}_2(\text{cod})]$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) gave the new complexes  $[\text{MCl}_2(\mathbf{1})]$  **3a–3d** or  $[\text{MCl}_2(\mathbf{2})]$  **4a, 4b** respectively in high yields (Schemes 1 and 2). The new complexes were characterised by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, IR (Experimental section) and microanalysis (Table 2). Downfield  $\delta(\text{P})$  shifts were observed and



**Scheme 2** (i)  $[\text{MCl}_2(\text{cod})]$ , 1 equiv. **1**,  $\text{CH}_2\text{Cl}_2$  (ii)  $\text{Ag}[\text{BF}_4]$ ,  $\text{CH}_2\text{Cl}_2$

**Table 2** Microanalytical data for compounds **3–8**<sup>a</sup>

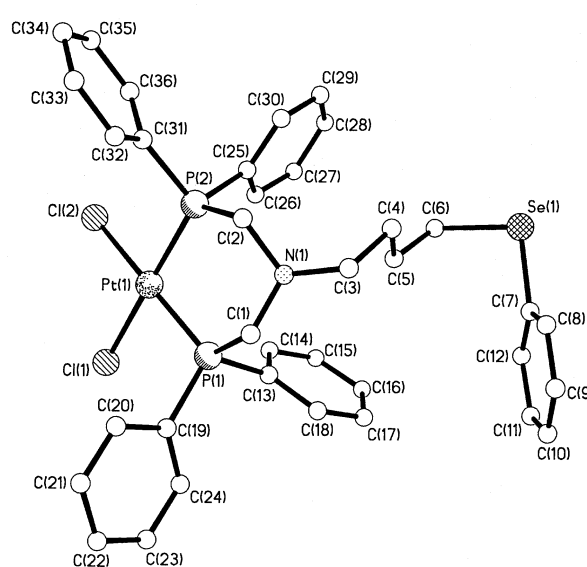
Compound	Analysis (%)		
	C	H	N
<b>3a</b> <sup>b</sup>	64.85 (64.40)	4.00 (3.95)	1.65 (1.50)
<b>3b</b> <sup>b</sup>	47.35 (47.00)	3.90 (4.10)	1.55 (1.50)
<b>3c</b> <sup>b</sup>	50.90 (51.35)	4.35 (4.40)	1.90 (1.70)
<b>3d</b> <sup>c</sup>	50.90 (50.90)	4.45 (4.40)	1.70 (1.65)
<b>4a</b>	44.75 (44.70)	3.80 (3.50)	1.85 (1.85)
<b>4b</b>	45.80 (45.45)	3.65 (3.70)	1.65 (1.85)
<b>4c</b>	50.30 (50.65)	4.20 (3.95)	2.10 (2.10)
<b>4d</b> <sup>b</sup>	49.40 (49.20)	3.95 (4.05)	1.80 (1.95)
<b>5a</b> <sup>b</sup>	52.90 (52.70)	4.90 (5.10)	1.15 (1.10)
<b>5b</b> <sup>d</sup>	50.05 (50.50)	5.15 (4.90)	0.95 (1.05)
<b>6a</b>	39.00 (39.10)	3.20 (3.30)	1.25 (1.30)
<b>6b</b>	39.05 (39.75)	3.35 (3.45)	1.25 (1.30)
<b>7</b>	47.60 (47.95)	4.05 (4.00)	1.55 (1.60)
<b>8</b>	42.00 (41.85)	3.30 (3.25)	1.60 (1.75)

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Contains 0.5 mol  $\text{CH}_2\text{Cl}_2$ .

<sup>c</sup> Contains 0.5 mol  $\text{CHCl}_3$ . <sup>d</sup> Contains 1.0 mol  $\text{CHCl}_3$ .

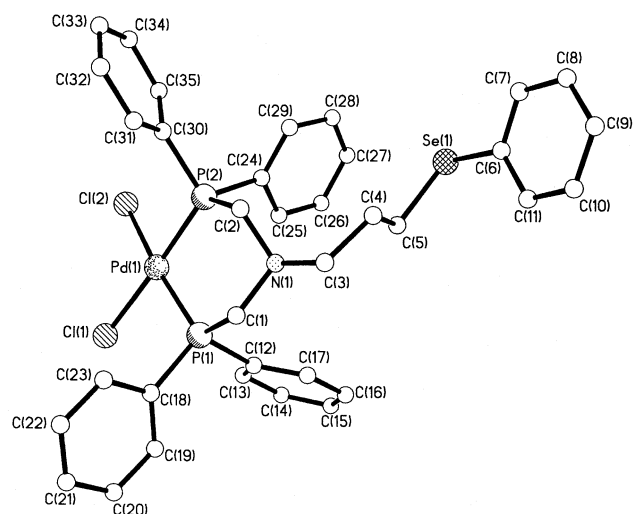
moreover, in the case of the platinum(II) complexes,  $^1J(\text{PtP})$  was typically around 3400 Hz (for **3a, 3b**) compared with ca. 3700 Hz (for **4a–4c**). This former  $^1J(\text{PtP})$  coupling compares well with that found for  $[\text{PtCl}_2(\text{dppp})]$  [ $\delta(\text{P}) -5.5$ ,  $^1J(\text{PtP})$  3409 Hz ( $\text{CDCl}_3$ )] indicating a negligible difference between N(R) and  $\text{CH}_2$  groups in the backbone of the ditertiary phosphine.

The X-ray structures of **3b** (Fig. 1) and **3c**· $\text{CHCl}_3$  (Fig. 2) have been determined with selected bond lengths and angles given in Table 3. Both complexes display a *cis* configuration with respect to the two phosphorus donors, the metal(II) centre in a near square planar geometry [Cl(1)–Pt(1)–P(1) 86.03(5), Cl(2)–Pt(1)–P(2) 89.19(5), Cl(1)–Pt(1)–Cl(2) 89.50(5), P(1)–Pt(1)–P(2) 94.79(5)° and Cl(3)–Pt(2)–P(3) 86.96(5), Cl(4)–Pt(2)–P(4) 88.91(5), Cl(3)–Pt(2)–Cl(4) 89.50(5) and P(3)–Pt(2)–P(4) 94.70(5)° for the two independent molecules **I** and **II** in **3b**; Cl(2)–Pd(1)–P(2) 88.87(6), Cl(1)–Pd(1)–P(1) 89.09(6), Cl(1)–Pd(1)–Cl(2) 90.13(6) and P(1)–Pd(1)–P(2) 92.24(6)° for **3c**· $\text{CHCl}_3$ ]. The M–Cl and M–P bond distances



**Fig. 1** X-Ray crystal structure of **3b** showing one of the two independent molecules. The second independent molecule has a different orientation of the selenoether group. Both molecules have similar bond lengths and angles. Hydrogen atoms omitted for clarity.





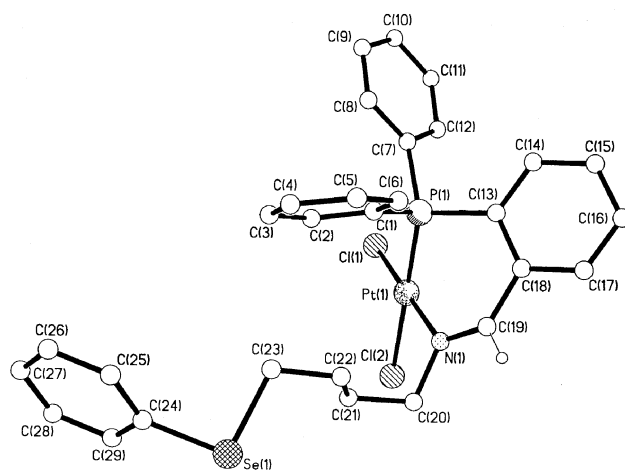
**Fig. 2** X-Ray crystal structure of **3c**·CHCl<sub>3</sub>. Solvent molecule and H-atoms omitted for clarity.

are unexceptional and compare well, in the case of **3c**·CHCl<sub>3</sub>, with those of [PdCl<sub>2</sub>{(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>NPh}].<sup>32</sup> Furthermore the long M...N separation (av. 3.671 Å for **3b**; 3.775 Å for **3c**·CHCl<sub>3</sub>) indicates no significant bonding between these two atoms. The conformation of the M–P–C–N–C–P six-membered ring in **3c**·CHCl<sub>3</sub> is best described as an envelope with N(1) out of the plane [mean plane Pd(1), P(1), P(2), C(1), C(2) ± 0.152 Å]. It is noteworthy that the pendant selenoether group is clearly amenable to further coordination chemistry.

The X-ray crystal structures of **4b** (Fig. 3) and **4d**·2.5CHCl<sub>3</sub> (Fig. 4) have been determined with selected bond lengths and angles given in Table 4. Both structures show the presence of a chelating iminophosphine ligand and two chloride ligands with the metal(II) centre being in a near square planar geometry [N(1)–Pt(1)–P(1) 87.07(7), Cl(1)–Pt(1)–Cl(2) 87.77(3), N(1)–Pt(1)–Cl(2) 91.03(7), P(1)–Pt(1)–Cl(1) 94.19(3)° and Cl(3)–Pt(2)–Cl(4) 88.70(3), P(2)–Pt(2)–Cl(4) 90.07(3),

**Table 3** Selected bond distances (Å) and angles (°) for compounds **3b**, **3c**·CHCl<sub>3</sub> and **6a** (equivalent parameters for independent molecules are given in parentheses)

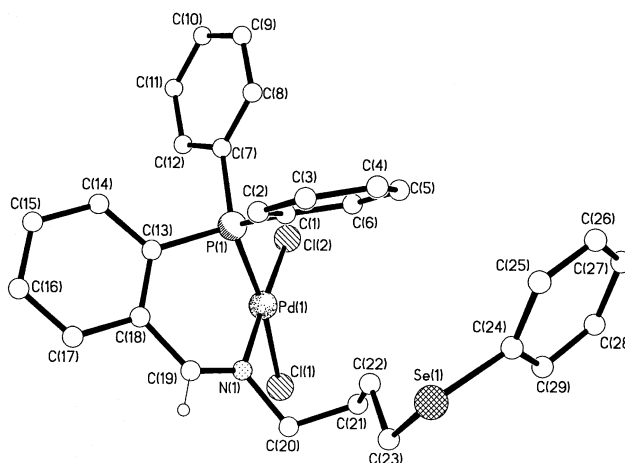
	<b>3b</b> (M = Pt)	<b>3c</b> ·CHCl <sub>3</sub> (M = Pd)	<b>6a</b> (M = Au)
M(1)–P(1)	2.2269(14) [2.2269(14)]	2.2459(17)	2.2335(9)
M(1)–P(2)	2.2334(14) [2.2305(14)]	2.2409(17)	2.2347(9)
M(1)–Cl(1)	2.3482(14) [2.3604(13)]	2.3580(17)	2.2903(9)
M(1)–Cl(2)	2.3684(14) [2.3708(13)]	2.3697(16)	
M(2)–Cl(2)			2.2979(9)
P(1)–C(1)	1.837(6) [1.829(5)]	1.827(6)	1.842(4)
C(1)–N(1)	1.437(7) [1.453(7)]	1.478(8)	1.480(4)
N(1)–C(2)	1.473(7) [1.465(7)]	1.452(8)	1.459(4)
C(2)–P(2)	1.829(6) [1.836(5)]	1.840(6)	1.845(3)
P(1)–M(1)–P(2)	94.79(5) [94.70(5)]	92.24(6)	
P(1)–M(1)–Cl(1)	86.03(5) [86.96(5)]	89.09(6)	171.09(4)
P(1)–M(1)–Cl(2)	172.75(5) [172.08(5)]	169.99(6)	
Cl(1)–M(1)–P(2)	177.88(5) [178.29(5)]	177.83(7)	
Cl(2)–M(1)–P(2)	89.19(5) [88.91(5)]	88.87(6)	
Cl(2)–M(2)–P(2)			178.13(3)
Cl(1)–M(1)–Cl(2)	89.80(5) [89.50(5)]	90.13(6)	
M(1)–P(1)–C(1)	116.2(2) [117.32(18)]	118.2(2)	115.45(11)
P(1)–C(1)–N(1)	109.5(4) [111.6(4)]	112.6(4)	110.5(2)
C(1)–N(1)–C(2)	111.0(4) [109.9(4)]	109.4(5)	110.5(3)
N(1)–C(2)–P(2)	110.4(4) [112.0(4)]	112.0(4)	113.5(2)
C(2)–P(2)–M(1)	117.18(18) [117.71(18)]	118.8(2)	111.25(11)



**Fig. 3** X-Ray crystal structure of **4b** showing one of the two independent molecules. The second independent molecule has a different orientation of the selenoether group. Both molecules have similar bond lengths and angles. Most of the H-atoms omitted for clarity.

N(2)–Pt(2)–Cl(3) 91.31(8) and N(2)–Pt(2)–Cl(3) 91.31(8)° for the two independent molecules **I** and **II** in **4b**; [Cl(1)–Pd(1)–Cl(2) 89.76(4), N(1)–Pd(1)–P(1) 86.94(9), N(1)–Pd(1)–Cl(1) 91.66(9) and P(1)–Pd(1)–Cl(2) 91.93(4)° for **4d**·2.5CHCl<sub>3</sub>]. The M–Cl distances are different as a consequence of the relative *trans* influences of N and P. Hence for **4d**·2.5CHCl<sub>3</sub> the Pd–Cl bond distances are 2.2816(10) (Cl *trans* to N) and 2.3911(11) Å (Cl *trans* to P) whereas this difference is less pronounced for **4b** [2.2918(8) and 2.3021(9) (Cl *trans* to N); 2.3698(8) and 2.3633(9) Å (Cl *trans* to P)]. In **4b** the coordination environment around each platinum centre is different *i.e.* in **I** the five atoms (inclusive of Pt) are essentially planar (±0.043 Å) whilst in **II**, the five atoms are much more distorted (±0.152 Å). By contrast, the coordination surrounding Pd in **4d**·2.5CHCl<sub>3</sub> is intermediate (±0.109 Å) between that observed for the two independent molecules in **4b**. Within the M–P–C–C–N six-membered rings the plane defined by C(13)–C(18)–C(19) [or C(42)–C(47)–C(48)] is folded out of this plane with respect to the N–M–P plane. This general conformation is presumably enforced by the presence of a more rigid phenylene group in the backbone of the *P,N*-chelating ligand.

Ligands such as **1** can also adopt bridging coordination modes by appropriate reaction with either [{RuCl(μ-Cl)(η<sup>6</sup>-*p*-cymene)}<sub>2</sub>] or [AuCl(tht)]. The complexes **5** and **6** could be



**Fig. 4** X-Ray crystal structure of **4d**·2.5CHCl<sub>3</sub>. Disorder in the Se-containing chain, solvent molecules and most of the H-atoms omitted for clarity.

**Table 4** Selected bond distances (Å) and angles (°) for compounds **4b**, **4d**·2.5CHCl<sub>3</sub> and **8** (equivalent parameters for independent molecules are given in parentheses)

	<b>4b</b> (M = Pt)	<b>4d</b> ·2.5CHCl <sub>3</sub> (M = Pd)	<b>8</b> (M = Pt)
M(1)–P(1)	2.2100(8) [2.1992(9)]	2.2175(10)	2.2407(14)
M(1)–N(1)	2.047(3) [2.037(3)]	2.054(3)	2.028(4)
M(1)–Cl(1)	2.2918(8) [2.3633(9)]	2.3911(11)	2.3085(13)
M(1)–Cl(2)	2.3698(8) [2.3021(9)]	2.2816(10)	
N(1)–C(19)	1.286(4) [1.278(4)]	1.279(5)	1.283(7)
M(1)–Se(1)			2.4889(6)
P(1)–M(1)–N(1)	87.07(7) [90.95(8)]	86.94(9)	87.50(13)
P(1)–M(1)–Cl(1)	94.19(3) [171.37(4)]	172.64(4)	93.06(5)
P(1)–M(1)–Cl(2)	177.63(3) [90.07(3)]	91.93(4)	
N(1)–M(1)–Cl(1)	177.12(8) [91.31(8)]	91.66(9)	178.80(13)
N(1)–M(1)–Cl(2)	91.03(7) [173.02(8)]	177.32(9)	
Cl(1)–M(1)–Cl(2)	87.77(3) [88.70(3)]	89.76(4)	
M(1)–N(1)–C(19)	125.8(2) [128.3(3)]	126.9(3)	127.1(4)
N(1)–M(1)–Se(1)			95.74(12)
P(1)–M(1)–Se(1)			176.74(4)
Cl(1)–M(1)–Se(1)			83.69(4)

isolated in good yield, and in the case of **6a**, an X-ray structure determination undertaken (Fig. 5, Table 3). The structure confirms that **1a** bridges two (AuCl) metal fragments and are *anti* with respect to each other. The geometry about each gold(i) centre is essentially linear [Cl(1)–Au(1)–P(1) 171.09(4); Cl(2)–Au(2)–P(2) 178.13(3)°]. A weak auriphilic interaction [Au(1)···Au(2) 3.408 Å] is evident between adjacent gold centres, the closest intermolecular Au···Au contact being 8.01 Å.

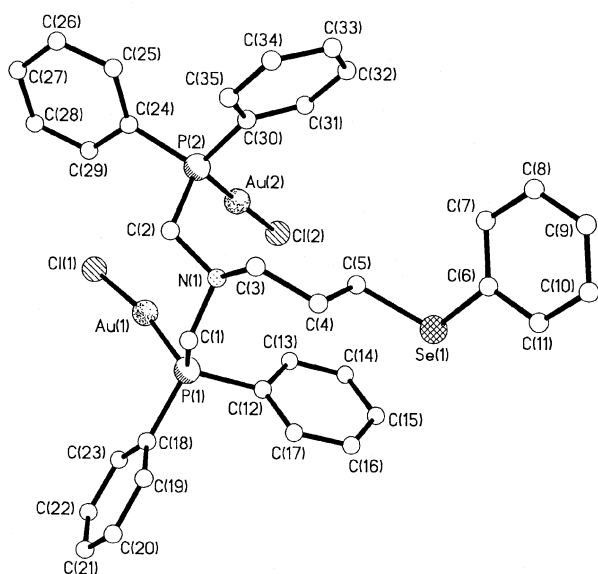
A preliminary study of the reaction of **3c** with [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] in CHCl<sub>3</sub> was undertaken to ascertain whether the pendant Se group can be used in further complexation. A solid was isolated in 75% yield and whose NMR data are similar to those of **3c**. The mass spectrum and microanalytical data suggest a compound of composition “(PdCl<sub>2</sub>)<sub>3</sub>(**2a**)<sub>2</sub>” and IR spectroscopy indicates a *cis* configuration at each palladium centre. Further studies are currently in progress.

In order to probe whether intramolecular selenoether coordination can be induced, reaction of **4a** with approximately one equiv. of Ag[BF<sub>4</sub>] in dichloromethane gave the cationic complex [PtCl{(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>C(H)=N(CH<sub>2</sub>)<sub>3</sub>SePh-P,N,Se}]BF<sub>4</sub> **8** in 83%. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed

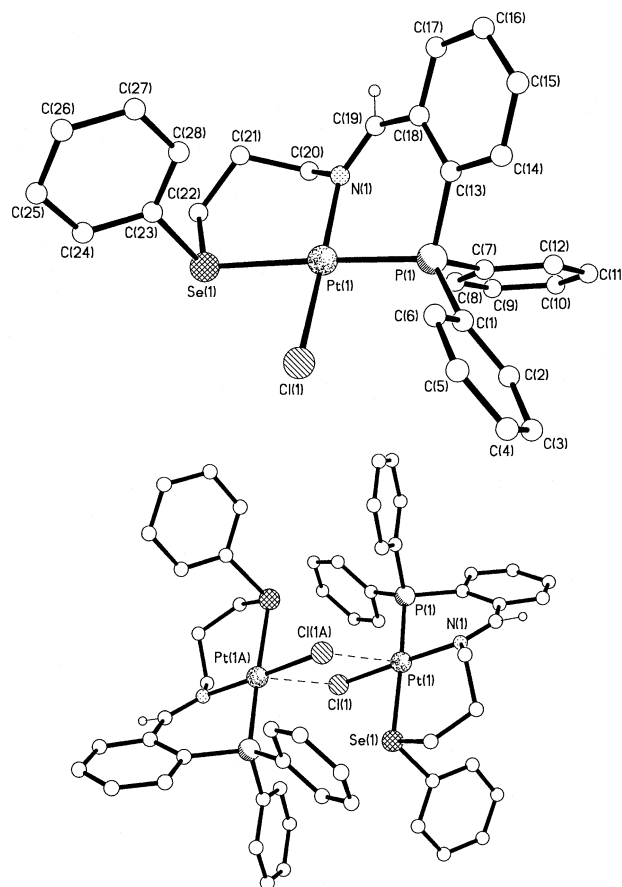
a negligible shift in δ(P) (7.6 *cf.* 5.1 for **4a**) and a reduction in <sup>1</sup>J(PtP) of *ca.* 300 Hz, consistent with the change in the *trans* ligand [PhSe(CH<sub>2</sub>)<sub>3</sub>N *vs.* Cl]. In addition, we observe a <sup>2</sup>J(PSe) of 163 Hz and in keeping with a *trans* disposition of P and Se donor atoms. The <sup>1</sup>H NMR spectrum shows an imine resonance at δ 8.43 flanked by <sup>195</sup>Pt satellites [<sup>3</sup>J(PtH) 112 Hz]. Other supporting data are given in the Experimental section.

The X-ray structure of **8** (Table 4, Fig. 6(a)) clearly shows the platinum(ii) to be in a near square planar geometry [Cl(1)–Pt(1)–Se(1) 83.69(4), N(1)–Pt(1)–P(1) 87.50(13), P(1)–Pt(1)–Cl(1) 93.06(5), N(1)–Pt(1)–Se(1) 95.74(12)°] and coordinated by P, N, Se and Cl donor centres (five atoms are essentially planar *i.e.* ±0.011 Å). Surprisingly only one other coordination environment<sup>33</sup> of this type has been observed previously.<sup>34</sup> The Pt(1)–P(1) bond length [2.2407(14) Å] is slightly longer than that found in the related complex **4b** [2.2100(8) and 2.1992(9) Å] and broadly as expected for the different *trans* influences of the Se and Cl donor atoms. The N(1)–C(19) bond distance [1.283(7) Å] is similar to that observed in **4b** [1.286(4) and 1.278(4) Å], **4d**·2.5CHCl<sub>3</sub> [1.2789(5) Å] and previously reported uncomplexed iminophosphine ligands.<sup>1a,30</sup> The tridentate ligand forms two stable six-membered chelate rings. The two six-membered rings adopt slight different ring geometries, the Pt(1)–P(1)–C(13)–C(18)–C(19)–N(1) ring is ostensibly similar to that seen in **4b** and **4d**·2.5CHCl<sub>3</sub>, whilst the Pt(1)–N(1)–C(20)–C(21)–C(22)–Se(1) ring adopts a boat conformation. Cations pair up (Fig. 6(b)) into weakly bound dimers *via* Pt···Cl interactions [Pt(1)···Cl(1) 3.624 Å, Pt(1)–Cl(1)···Pt(1A) 93.3°].

The synthesis of new “hybrid” ligands bearing P/N/Se or P<sub>2</sub>/Se donor sets has been demonstrated and represent an extremely uncommon family of ligands bearing this donor set combination. Our approach here is both simple,



**Fig. 5** X-Ray crystal structure of **6a**. Hydrogen atoms omitted for clarity.



**Fig. 6** (a) X-Ray crystal structure of **8** (b) weak dimer pair association. The [BF<sub>4</sub>]<sup>−</sup> counter ion and most H-atoms omitted for clarity.

reproducible and permits a facile route to reasonable quantities of these ligands. In preliminary studies their ligating ability has been demonstrated to give complexes broadly as expected. Halide abstraction was found to induce complexation of the selenoether group affording a *P,N,Se*-terdentate bound ligand. We are presently investigating the use of complexes such as **3–6** as “metalloligands” for preparing new homo and hetero-nuclear metal complexes. Further studies are in progress and will be reported in due course.

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