

Bridge cleavage reactions of late transition-metal dimers with $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E}')\text{Ph}_2]^-$ ($\text{E} = \text{E}' = \text{S}$ or Se ; $\text{E} = \text{O}$ or S , $\text{E}' = \text{S}$ or Se)

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Reaction of the dinuclear complexes $[\{\text{Pd}(\mu\text{-Cl})(\text{L-L})\}_2]$ ($\text{L-L} = \text{C}_9\text{H}_{12}\text{N}$ or $\text{C}_{12}\text{H}_{12}\text{N}$), $[\{\text{Pt}(\mu\text{-OMe})(\text{C}_8\text{H}_{12}\text{OMe})\}_2]$, $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^t)\}_2]$ or $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ with $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) in thf gave the corresponding bridge cleaved, mononuclear compounds $[\text{Pd}(\text{L-L})\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}E, E'\}]$, $[\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}E, E'\}]$, $[\text{RuCl}\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}E, E'\}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^t)]$ or $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}E, E'\}]$ in high yields (64–97%). Transmetalation of $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) with $[\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)\}_2]$ in a 1 : 1 ratio gave $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}E, E'\}]$. In contrast, reaction of the potassium salt $\text{K}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) with $[\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)\}_2]$ under analogous conditions gave instead the dimeric species $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2\text{-}E\}\}_2]$. All new compounds have been characterised by a combination of multinuclear NMR [^1H , ^{31}P - $\{^1\text{H}\}$, ^{195}Pt - $\{^1\text{H}\}$] and IR spectroscopy, elemental analyses and in four cases by single crystal X-ray crystallography. The six-membered $\text{ME}_2\text{P}_2\text{N}$ metallacycles $[\text{Pd}(\text{C}_9\text{H}_{12}\text{N})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}Se, Se'\}]$, $[\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-}S, S'\}]$ and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-}S, S'\}]$ all adopt pseudo-boat conformations. In contrast $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2\text{-}Se\}\}_2]$ is binuclear with a central four-membered Pd_2Se_2 core and two pendant $\text{P}(\text{O})\text{Ph}_2$ moieties. The synthesis, characterisation and preliminary complexation studies of a new potassium salt, $\text{K}[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Ph}_2]$, prepared by deprotonation of $\text{Ph}_2\text{P}(\text{S})\text{NHP}(\text{Se})\text{Ph}_2$ with KOBu^t are also described.

The co-ordination chemistry of $\text{Ph}_2\text{PNHPPH}_2$ (dppa) and $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ ($\text{E} = \text{O}$, S or Se including some mixed chalcogenide donor atom combinations; $\text{R} = \text{Ph}$ typically) has attracted widespread attention by ourselves and others.^{1–37} The anion $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$, closely related to acetylacetonate (acac^-), forms many complexes with a diverse spectrum of metal ions, and moreover, selected complexes have found important applications in areas such as NMR shift reagents,¹¹ selective metal extractants³³ and in catalysis.¹⁰ Indeed, very recently the novel tetranuclear silver(I) cluster $[\{\text{Ag}\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}\}_4] \cdot 2\text{EtOH}$ reported by Rudler *et al.*¹⁰ was shown, in preliminary studies, to be a promising catalyst for alkene epoxidation.

Transition-metal complexes of acac and its derivatives have been well studied^{38,39} with a variety of ligating modes established, yet surprisingly only recently metal complexes containing novel ligand bonding modes for $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ have been described.^{7–10} Table 1 highlights a selection of ligating modes observed for $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$. Coincidentally four new co-ordination modes were reported in 1997 alone and confirmed unambiguously by X-ray crystallography.^{7–10} A common feature to both classes of ligand is the propensity to adopt a classical E, E' -chelation mode utilising both chalcogenide donor atoms.^{2–6,11–33}

We are particularly interested in this class of ligand for several reasons. (i) Most known metal complexes of $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ are homoleptic, *i.e.* $[\text{M}\{\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2\text{-}E, E'\}_n]$ where $n = 2$ or 3 .^{2–5,11–19,21–24,34} In contrast to the wealth of bis and tris chelate complexes documented only a handful of mixed complexes (with ancillary ligands such as chloride or tertiary phosphines) has been reported.^{18,20,26,27,29,31} (ii) There are remarkably very few examples of organometallic complexes bearing a chelating $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ and, of those reported, the majority are with Sn, *e.g.* $[\text{SnR}_2\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E}')\text{Ph}_2\text{-}E, E'\}_2]$ ($\text{R} = \text{Me}$,

Bu^n or Ph ; $\text{E} = \text{E}' = \text{O}$ or S ; $\text{E} = \text{O}$, $\text{E}' = \text{S}$].^{14,32} Examples incorporating transition metals are restricted to those of Mn, Os, Pt and Au.^{18,26,35,36} (iii) Metal complexes of $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ display a diverse array of $\text{ME}_2\text{P}_2\text{N}$ chelate ring conformations. Two noteworthy examples are $[\text{Mn}(\text{CO})_4\text{-}\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-}S, S'\}]$ in which the unit cell contains two independent molecules with the $\text{MnS}_2\text{P}_2\text{N}$ metallacycles adopting two different non-planar ring conformations²⁶ and secondly *cis*- $[\text{Pd}\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2\text{-}O, Se\}]$ in which two disparate PdOSEP_2N ring geometries were present *within* the same molecule.¹⁸ (iv) The potential of mixed anionic ligands $[\text{R}_2\text{P}(\text{O})\text{NP}(\text{E})\text{R}_2]^-$ ($\text{E} = \text{S}$ or Se) bearing both 'hard' and 'soft' donor centres to engage in new bonding modes (in addition to the orthodox O, E -chelate) has not been fully realised.^{9,14,18} A related mixed anionic ligand $[\text{Ph}_2\text{P}(\text{O})\text{NPPH}_2]^-$ can take on several ligating modes including P, O -chelating, P, O -bridging and P -monodentate^{40–42} but in contrast $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]^-$ ($\text{E} = \text{S}$ or Se) has so far been observed to form O, E -chelate metal complexes. It is for these reasons we have probed the co-ordination chemistry of this unique class of ligand with a range of late transition-metal fragments.

We report herein the first example of organo-ruthenium(II), -rhodium(III), -palladium(II) and -platinum(II) complexes of $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E}')\text{Ph}_2]^-$ ($\text{E} = \text{E}' = \text{S}$ or Se ; $\text{E} = \text{O}$ or S , $\text{E}' = \text{S}$ or Se) with σ -/ π -bonded carbon auxiliary ligands. These are readily accessible *via* facile bridge cleavage reactions of, in general, the corresponding dichloro-bridged precursors. All new compounds have been characterised by a combination of NMR spectroscopy [^1H , ^{31}P - $\{^1\text{H}\}$, ^{195}Pt - $\{^1\text{H}\}$], IR and elemental analysis. Three crystal structures have been determined: $[\text{Pd}(\text{C}_9\text{H}_{12}\text{N})\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}Se, Se'\}]$, $[\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-}S, S'\}]$ and $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-}S, S'\}]$. In each case the inorganic (carbon free) six-membered $\text{ME}_2\text{P}_2\text{N}$ metallacycle adopts a familiar pseudo-boat conformation. Our work has also revealed, by X-ray crystallography, a novel binding mode for $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]^-$ ($\text{E} = \text{S}$ or Se) as seen in the palladium(II) complex $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{O})\text{NP}$

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Table 1 Classification of bonding motifs in metal complexes of $[R_2P(E)NP(E)R_2]^-$ (for clarity π delocalisation within the EPNPE backbone is not illustrated)

Ligand binding mode	Example(s)	Donor set	Ref.
	[Bi{Ph ₂ P(O)NP(O)Ph ₂ } ₃] [Ba{Ph ₂ P(S)NP(S)Ph ₂ } ₂] \cdot 2dme [M{Ph ₂ P(Se)NP(Se)Ph ₂ } ₂] (M = Sn, Pb, Zn, Cd or Hg)	<i>O,O</i> <i>S,S</i> <i>Se,Se</i>	12 2 4
	[{Au[Ph ₂ P(S)NP(S)Ph ₂ } ₂]	<i>S,S</i>	35
	K[Ph ₂ P(S)NP(S)Ph ₂]	<i>S,S</i>	30
	[Pd{(PhO) ₂ P(O)NP(S)(OPh) ₂ } ₂]	<i>N,S</i>	34
	[Hg(Ph){N[P(O)(OPh) ₂]} ₂]	<i>N</i>	37
	[Os ₃ H(CO) ₉ {Ph ₂ P(S)NP(S)Ph ₂ }]	<i>S,S</i>	8
	[Sm{ η^3 -N(SePPh ₂) ₂ { η^2 -N(SePPh ₂) ₂ }(thf) ₂]	<i>N,Se,Se</i>	7
	[{Na[Ph ₂ P(O)NP(S)Ph ₂] \cdot 2thf} ₂]	<i>O,S</i>	9
	[{Ag[Ph ₂ P(O)NP(O)Ph ₂ } ₄] \cdot 2EtOH	<i>N,O,O</i>	10
	[{Ag[Ph ₂ P(O)NP(O)Ph ₂ } ₄] \cdot 2EtOH	<i>N,O</i>	10
	[{Hg[(RO) ₂ P(O)NP(O)(OR)OC ₆ H ₄]} ₂] (R = Ph)	<i>C,N</i>	37
	[{Pd(η^3 -C ₃ H ₅)[Ph ₂ P(O)NP(E)Ph ₂ } ₂] (E = S or Se)	<i>E</i>	This work

(E)Ph₂-E}]₂. Full details of the synthesis and preliminary reactivity of a new mixed ligand [Ph₂P(S)NP(Se)Ph₂]⁻ are described.

Experimental

General

Unless otherwise stated, manipulations were carried out in air using previously distilled solvents. The potassium salts K[Ph₂-

P(E)NP(E)Ph₂]^{25,43} and K[Ph₂P(O)NP(E)Ph₂] (E = S or Se),¹⁸ the metal-(ii)/-(iii) complexes [{Pd(μ -Cl)(L-L)}₂] [HL-L = benzyl-dimethylamine (C₉H₁₃N) or dimethyl-1-naphthylamine (C₁₂H₁₃N)],⁴⁴ [{Pt(μ -OMe)(C₈H₁₂OMe)}₂] (C₈H₁₂OMe = 8-methoxycyclooct-4-ene-1-yl)⁴⁵ and [{RhCl(μ -Cl)(η^5 -C₅Me₅)}₂]⁴⁶ were prepared according to established literature methods. The compounds [{Pd(μ -Cl)(η^3 -C₃H₅)}₂], [{RuCl(μ -Cl)(η^6 -*p*-MeC₆H₄Pr^t)}₂] and KOBu^t were obtained commercially from Aldrich Chemical Co. and used without further purification.

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm⁻¹ on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ¹H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe₄ and coupling constants (J) in Hz (± 0.1), ³¹P-¹H} NMR spectra (36.2 MHz) on a JEOL FX90Q spectrometer with chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H₃PO₄ and coupling constants (J) in Hz (± 3) and ¹⁹⁵Pt-¹H} NMR spectra (53.7 MHz) on a Bruker AC250 FT spectrometer with δ referenced to external H₂PtCl₆ (in D₂O–HCl). All NMR spectra were measured in CDCl₃ 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

[Pd(C₉H₁₂N){Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] 1. To a solution of [$\{\text{Pd}(\mu\text{-Cl})(\text{C}_9\text{H}_{12}\text{N})\}_2$] (0.036 g, 0.0652 mmol) in thf (5 cm³) was added K[Ph₂P(Se)NP(Se)Ph₂] (0.078 g, 0.134 mmol) as a solid in one portion. After stirring for *ca.* 30 min the solution was evaporated to dryness under reduced pressure. The residue was extracted into CH₂Cl₂ (4 cm³) and the solution filtered through a small Celite pad. The volume was reduced to *ca.* 1 cm³ and addition of light petroleum (b.p. 60–80 °C, 25 cm³) followed by slow evaporation of the solvent to about half its original volume gave complex **1**. The solid was collected by suction filtration and dried *in vacuo*. Yield: 0.097 g, 95%.

In a similar manner the following complexes were prepared (yields given in Table 2): [Pd(C₉H₁₂N){Ph₂P(S)NP(S)Ph₂-S,S'}] **2**, [Pd(C₁₂H₁₂N){Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] **3**, [Pd(C₁₂H₁₂N){Ph₂P(S)NP(S)Ph₂-S,S'}] **4**, [Pt(C₈H₁₂OMe){Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] **5**, [Pt(C₈H₁₂OMe){Ph₂P(S)NP(S)Ph₂-S,S'}] **6**, [RuCl{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}(η^6 -*p*-MeC₆H₄Pr^t)] **7**, [RuCl{Ph₂P(S)NP(S)Ph₂-S,S'}(η^6 -*p*-MeC₆H₄Pr^t)] **8**, [RhCl(η^5 -C₅Me₅){Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] **9** and [RhCl(η^5 -C₅Me₅){Ph₂P(S)NP(S)Ph₂-S,S'}] **10**. Alternatively attempts to prepare the cationic compounds [RuCl{Ph₂P(S)NHP(S)Ph₂-S,S'}(η^6 -*p*-MeC₆H₄Pr^t)]Cl and [RhCl(η^5 -C₅Me₅){Ph₂P(S)NHP(S)Ph₂-S,S'}]Cl from [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^t)\}_2$] or [$\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2$] and 2 equivalents of Ph₂P(S)NHP(S)Ph₂ gave compounds **8** and **10** exclusively.

Slow diffusion of light petroleum (60–80 °C) into a CDCl₃ solution of compound **1** over *ca.* 14 d gave crystals suitable for X-ray crystallography. A CDCl₃–MeOH solution of **6** was allowed to stand for *ca.* 1 d affording crystals suitable for X-ray crystallography.

[Pd(η^3 -C₃H₅){Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] 11. To a solution of [$\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)\}_2$] (0.031 g, 0.0847 mmol) in thf (5 cm³) was added K[Ph₂P(Se)NP(Se)Ph₂] (0.100 g, 0.172 mmol) as a solid in one portion. After stirring for *ca.* 30 min the solution was evaporated to dryness under reduced pressure. The residue was extracted into CH₂Cl₂ (3 cm³) and the solution filtered through a small Celite pad. Reduction of the volume to *ca.* 1 cm³ followed by addition of light petroleum (b.p. 60–80 °C, 15 cm³) gave compound **11**. The product was collected by suction filtration. Yield: 0.099 g, 85%.

In a similar manner [Pd(η^3 -C₃H₅){Ph₂P(S)NP(S)Ph₂-S,S'}] **12** and the binuclear compounds [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}_2\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2\text{-Se}\}_2$] **13** and [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}_2\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{S})\text{Ph}_2\text{-S}\}_2$] **14** were synthesized (yields given in Table 2). Slow diffusion of MeOH into a CH₂Cl₂ solution of compound **12** over *ca.* 10 d gave crystals suitable for X-ray crystallography. A CDCl₃–light petroleum (b.p. 60–80 °C) solution of compound **13** was allowed to stand for *ca.* 3 d affording crystals suitable for X-ray crystallography.

Ph₂P(S)NHP(Se)Ph₂ V. A mixture of Ph₂P(S)NHPPh₂ (1.151 g, 2.757 mmol) and grey Se (0.305 g, 3.863 mmol) in thf (5 cm³) was stirred under a nitrogen atmosphere for *ca.* 3 h. Unchanged Se was removed by filtration through a Celite pad and the volume concentrated *in vacuo* to *ca.* 5–10 cm³. Addition of light petroleum (b.p. 60–80 °C, 30 cm³) afforded a white solid which was collected by suction filtration. Yield: 1.100 g, 80%.

K[Ph₂P(S)NP(Se)Ph₂] X. Under aerobic conditions, to a suspension of Ph₂P(S)NHP(Se)Ph₂ (0.495 g, 0.997 mmol) in MeOH (25 cm³) was added KOBu^t (0.117 g, 1.043 mmol) as a solid in one portion. The solution was stirred for *ca.* 45 min and the solvent removed to dryness *in vacuo*. Yield: 0.517 g, 97%.

[Pd(C₉H₁₂N){Ph₂P(S)NP(Se)Ph₂-S,Se}] 15. To a solution of [$\{\text{Pd}(\mu\text{-Cl})(\text{C}_9\text{H}_{12}\text{N})\}_2$] (0.049 g, 0.089 mmol) in thf (5 cm³) was added K[Ph₂P(S)NP(Se)Ph₂] (0.096 g, 0.180 mmol) as a solid in one portion. After stirring for *ca.* 1 h the yellow solution was evaporated to dryness under reduced pressure. The solid was extracted into CH₂Cl₂ (3 cm³), filtered through a small Celite pad and the volume concentrated to *ca.* 1–2 cm³. Addition of light petroleum (b.p. 60–80 °C, 20 cm³) afforded the product **15** [as a mixture of two isomers **15a** and **15b** established by ³¹P-¹H} NMR spectroscopy (see Table 3 for data)] which was collected by suction filtration and dried *in vacuo*. Yield: 0.127 g, 97%.

In a similar manner the following compounds were prepared (yields given in Table 2): [Pd(C₁₂H₁₂N){Ph₂P(S)NP(Se)Ph₂-S,Se}] **16** (mixture of two isomers **16a** and **16b**), [Pd(η^3 -C₃H₅){Ph₂P(S)NP(Se)Ph₂-S,Se}] **17**, [RuCl{Ph₂P(S)NP(Se)Ph₂-S,Se'}(η^6 -*p*-MeC₆H₄Pr^t)] **18** and [RhCl(η^5 -C₅Me₅){Ph₂P(S)NP(Se)Ph₂-S,Se}] **19**.

X-Ray crystallography

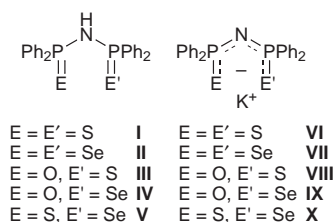
The crystal structures of compounds **1**, **6**, **12** and **13** were obtained using either a Rigaku AFC7S serial diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.54178$ Å) and ω scans or a Siemens SMART diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71037$ Å). Details of the crystal data collections and refinements are given in Table 4. For the SMART data, intensities were collected using 0.3 or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data were integrated using the SAINT⁴⁸ program) and for the Rigaku AFC7S data collections by ω scans over a single quadrant of reciprocal space. All data were corrected for Lorentz-polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections (for **6** and **12**) or by DIFABS⁴⁹ (for **1** and **13**).

Structures were solved by direct methods and refined by full-matrix least squares against F (TEXSAN⁵⁰) for data with $I > 2\sigma(I)$ or F^2 (SHELXTL⁴⁷) for all data. A standard SHELXTL weighting scheme was used for compounds **6** and **12** whilst in the case of **1** and **13** the weighting scheme for the Rigaku/TEXSAN was as previously reported.¹⁸ The CHCl₃ solvent molecule in **13** was disordered in two orientations of 60 and 40% for the three chlorine atoms. The C–H proton was idealised with respect to the major occupancy. Hydrogen atoms were placed in calculated positions ignoring any influence of the metal atoms. All other hydrogen atoms were assigned isotropic displacement parameters and constrained to idealised geometries. Refinements converged to residuals given in Table 4. In both **12** and **13** refinement of the allyl group was ill behaved. All calculations were made with programs of SHELXTL or TEXSAN systems.

CCDC reference number 186/1034.

Results and Discussion

The neutral phosphorus(v) compounds **I–IV** are readily accessible in either one (or two) simple steps starting from commercially available or readily synthesized $\text{Ph}_2\text{PNHPPh}_2$.^{18,25,43} Mixed phosphorus-(iii)/-(v) compounds bearing a single oxidised phosphorus centre, $\text{Ph}_2\text{P(E)NHPPh}_2$, have previously been isolated and moreover, in the case where $\text{E} = \text{O}$, a rich and diverse co-ordination chemistry of this ligand has been reported.^{40–42,51} We have now prepared a new asymmetrical ligand, $\text{Ph}_2\text{P(S)NHP(Se)Ph}_2$, closely related to its methylene counterpart $\text{Ph}_2\text{P(S)CH}_2\text{P(Se)Ph}_2$ previously described by Grim and Walton.⁵² Reaction of $\text{Ph}_2\text{P(S)NHPPh}_2$ ⁵³ with grey selenium in thf gave, after separation of unchanged excess of Se and subsequent work-up, $\text{Ph}_2\text{P(S)NHP(Se)Ph}_2$ **V** in 80% yield. The spectroscopic and analytical data for **V** are given in Tables 2 and 3. The ³¹P resonances were confidently assigned by comparison of the spectral data with those of **I** and **II** { $\delta(\text{P})$ 55.8 **I**; 52.7 [¹*J*(PSe) 793 Hz] **II**; 57.1, 52.7 [¹*J*(PSe) 783 Hz] **V**} and in the ¹H NMR spectrum the NH proton was found at $\delta(\text{H})$ 4.49. Deprotonation of the acidic NH proton under similar conditions^{18,25} to those described for **VI–IX** gave $\text{K}[\text{Ph}_2\text{P(S)NP(Se)Ph}_2]$ **X** in addition to small amounts of **VI**. The spectroscopic and analytical data for **X** are given in Tables 2 and 3. The ³¹P resonances match well with data reported for **VI–IX** { $\delta(\text{P})$ 37.7 **VI**; 28.5 [¹*J*(PSe) 687 Hz] **VII**; 35.3, 13.9, ²*J*(P_sP_o) 3.3 Hz **VIII**; 23.6 [¹*J*(PSe) 664 Hz], 12.9, ²*J*(P_sP_o) 2.2 Hz **IX**; 37.6, 26.7 [¹*J*(PSe) 682 Hz], ²*J*(P_sP_{se}) 6.8 Hz **X**}.^{18,25}

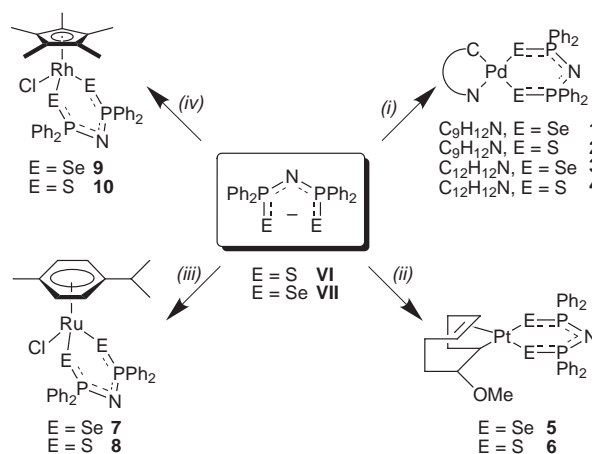


Chelate and bridging complexes of $[\text{Ph}_2\text{P(E)NP(E')Ph}_2]^-$

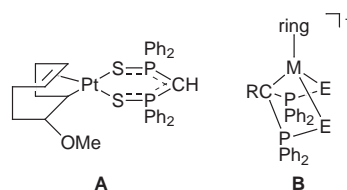
Transmetalation of the potassium salts **VI** and **VII** with the organometallic metal-(ii) or -(iii) precursors [$\{\text{Pd}(\mu\text{-Cl})(\text{L-L})\}_2$] ($\text{L-L} = \text{C}_9\text{H}_{12}\text{N}$ or $\text{C}_{12}\text{H}_{12}\text{N}$), [$\{\text{Pt}(\mu\text{-OMe})(\text{C}_8\text{H}_{12}\text{OMe})\}_2$], [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^{\text{d}})\}_2$] or [$\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2$] in either tetrahydrofuran or methanol gave the following series of mononuclear complexes: $[\text{Pd}(\text{L-L})\{\text{Ph}_2\text{P(E)NP(E)Ph}_2\text{-E,E}'\}]$ [$\text{C}_9\text{H}_{12}\text{N}$, $\text{E} = \text{Se}$ **1** or S **2**; $\text{C}_{12}\text{H}_{12}\text{N}$, $\text{E} = \text{Se}$ **3** or S **4**], $[\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})\{\text{Ph}_2\text{P(E)NP(E)Ph}_2\text{-E,E}'\}]$ ($\text{E} = \text{Se}$ **5** or S **6**), $[\text{RuCl}\{\text{Ph}_2\text{P(E)NP(E)Ph}_2\text{-E,E}'\}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^{\text{d}})]$ ($\text{E} = \text{Se}$ **7** or S **8**) and $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{P(E)NP(E)Ph}_2\text{-E,E}'\}]$ ($\text{E} = \text{Se}$ **9** or S **10**) (Scheme 1). Reactions were complete within *ca.* 30 min and all complexes were isolated from CH_2Cl_2 –light petroleum (b.p. 60–80 °C). The compounds **1–10** were air stable both in the solid state and in solution. Complex **6** containing the anionic nitrogen backbone ligand $[\text{Ph}_2\text{P(S)NP(S)Ph}_2]^-$ is akin to the known neutral complex $[\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})\{\text{Ph}_2\text{P(S)CHP(S)Ph}_2\text{-S,S}'\}]$ **A** prepared from $\text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2$ and [$\{\text{Pt}(\mu\text{-Cl})(\text{C}_8\text{H}_{12}\text{OMe})\}_2$] in acetone with $\text{Na}[\text{BF}_4]$.⁵³ Recently Valderrama *et al.*⁵⁵ reported some interesting methylene deprotonation reactions in complexes of the type $[\text{MCl}(\eta^2\text{-L})(\text{ring})]^+$ [ring = C_5Me_5 , C_6Me_6 or $\text{C}_{10}\text{H}_{14}$; $\text{M} = \text{Ru}^{\text{II}}$, Rh^{III} or Ir^{III} ; $\text{L} = \text{Ph}_2\text{P(E)CH(R)P(E)Ph}_2$ ($\text{R} = \text{H}$ or Me ; $\text{E} = \text{S}$ or Se)] giving novel complexes **B** containing an anionic $\text{C,E,E}'$ -tridentate ligand. In attempts to synthesize the cations $[\text{RuCl}\{\text{Ph}_2\text{P(S)NHP(S)Ph}_2\text{-S,S}'\}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^{\text{d}})]\text{Cl}$ and $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\{\text{Ph}_2\text{P(S)NHP(S)Ph}_2\text{-S,S}'\}]\text{Cl}$ from [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^{\text{d}})\}_2$] or [$\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2$] and 2 equivalents of **I** we were able only to isolate the deprotonated compounds **8** and **10** respectively in moderate to good yields. The reaction of [$\{\text{Pd}(\mu\text{-Cl})(\text{C}_9\text{H}_{12}\text{N})\}_2$] with **I** in CDCl_3 gave a single com-

Table 2 Microanalytical data (calculated values are given in parentheses) and yields for compounds **V**, **X** and **1–19**

Compound	Yield (%)	Analysis (%)		
		C	H	N
V	80	58.15 (58.05)	4.25 (4.25)	2.85 (2.80)
X	97	53.35 (53.90)	3.55 (3.80)	2.75 (2.60)
1	95	49.95 (50.60)	3.95 (4.15)	3.70 (3.60)
2	90	56.95 (57.50)	4.50 (4.70)	3.75 (4.05)
3	97	51.45 (52.80)	3.70 (3.95)	2.95 (3.40)
4	90	59.30 (59.60)	3.85 (4.45)	3.10 (3.85)
5	92	44.85 (45.20)	3.95 (4.05)	1.60 (1.60)
6	95	50.45 (50.65)	4.40 (4.50)	1.80 (1.80)
7	89	49.90 (50.20)	3.90 (4.20)	1.10 (1.70)
8	64	56.45 (56.75)	4.55 (4.75)	1.15 (1.95)
9	80	49.90 (50.05)	4.10 (4.35)	1.00 (1.70)
10	77	56.00 (56.55)	4.70 (4.90)	2.05 (1.95)
11	85	46.80 (47.10)	3.55 (3.50)	2.20 (2.05)
12	94	53.75 (54.50)	4.05 (4.05)	2.20 (2.35)
13	78	51.10 (51.80)	3.80 (3.85)	2.60 (2.25)
14	85	55.65 (56.00)	4.05 (4.20)	1.95 (2.40)
15	97	53.80 (53.85)	4.45 (4.40)	3.60 (3.80)
16	93	55.70 (56.00)	4.00 (4.20)	3.90 (3.65)
17	84	49.95 (50.45)	3.80 (3.95)	2.05 (2.20)
18	91	50.30 (53.30)	4.15 (4.50)	1.40 (1.85)
19	79	52.55 (53.10)	4.30 (4.60)	1.70 (1.80)



Scheme 1 Reactions carried out in thf: (i) [$\{\text{Pd}(\mu\text{-Cl})(\text{L-L})\}_2$] ($\text{L-L} = \text{C}_9\text{H}_{12}\text{N}$ or $\text{C}_{12}\text{H}_{12}\text{N}$), (ii) [$\{\text{Pt}(\mu\text{-OMe})(\text{C}_8\text{H}_{12}\text{OMe})\}_2$], (iii) [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^{\text{d}})\}_2$], (iv) [$\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2$]



ound, identified by ³¹P-¹H NMR as the homoleptic bis species $[\text{Pd}\{\text{Ph}_2\text{P(S)NP(S)Ph}_2\text{-S,S}'\}_2]$.²³

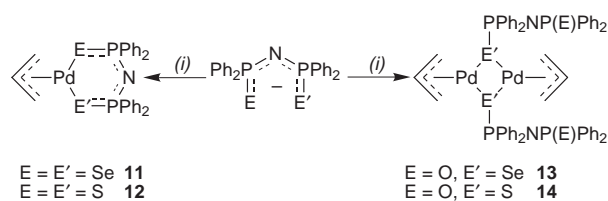
The spectroscopic and analytical data for the organometallic complexes **1–10** are in good accord with the proposed structures (see Tables 2 and 3 for characterising data). Upon chelation to Ru^{II} , Rh^{III} , Pd^{II} or Pt^{II} there is a small (*ca.* ± 4 ppm) change in $\delta(\text{P})$ for the ligated $[\text{Ph}_2\text{P(E)NP(E)Ph}_2]^-$ ($\text{E} = \text{S}$ or Se) ligand and reduction in ¹*J*(PSe) of *ca.* 100–150 Hz in comparison with $\text{K}[\text{Ph}_2\text{P(E)NP(E)Ph}_2]$. The $\delta(\text{P})$ for compounds **8** and **10** obtained *via* the two independent routes described above were identical.

Reaction of the potassium salts **VI–IX** with [$\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)\}_2$] (1:1 ratio) in thf gave new compounds with the apparent stoichiometry $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P(E)NP(E')Ph}_2\}]$ [$\text{E} = \text{E}' = \text{Se}$ **11** or S **12**; $\text{E} = \text{O}$, $\text{E}' = \text{Se}$ **13** or S **14**] (Scheme 2).

Table 3 Selected NMR (δ , J/Hz) and IR data (cm^{-1}) for compounds **V**, **X** and **1–19**

Compound	NMR				IR	
	^{31}P	$^1J(\text{PSe})$	$^2J(\text{PP})$	^{195}Pt	$\nu(\text{PS})$	$\nu(\text{PSe})$
V ^a	57.1 52.7	783	28		645	548
X ^b	37.6 26.7	682	7		596	547
1 ^c	28.2 ^d 27.5	559 532	n.r.			545
2 ^e	39.4 ^d 38.5		4		575	
3 ^f	28.6 ^d 28.1	557 532	n.r.			544
4 ^g	39.9 ^d 38.8		4		574	
5	25.5 (124) ^h 25.3 (49)	536 528	n.r.	-3965		545
6	36.7 (44) 35.6 (114) ⁱ		4	-3894	587	
7 ^j	29.0	563				541
8 ^k	39.9				573	
9 ^l	24.6	580				541
10 ^m	36.2				579	
11 ⁿ	26.2	550				542
12 ^o	37.9				574	
13 ^p	26.7 19.1	528	4			545
14 ^q	35.3 27.1		4		581	
15 ^r	40.9, 26.8 40.5, 24.3 ^s	558 524	n.r. 2		589	538
16 ^t	41.2, 27.4 41.0, 24.7 ^s	555 524	n.r. 2		582	536
17 ^u	40.2, 23.3	541	4		580	542
18 ^v	38.9, 21.8	568	3		574	540
19 ^w	42.4, 26.1	559	7		570	538

n.r. = Not resolved. ^a ^1H NMR: δ 7.98–7.82, 7.46–7.30 (aromatic H); 4.49 (NH). $\nu(\text{P}_2\text{NH})$ 922 cm^{-1} . ^b ^1H NMR: δ 8.00–7.91, 7.24–7.22 (aromatic H) [recorded in $(\text{CD}_3)_2\text{SO}$]. ^c ^1H NMR: δ 8.03–7.95, 7.48–6.94 (aromatic H); 3.85 (CH_2); 2.56 (NMe_2). ^d No attempts to assign $\delta(\text{P})$ were made. ^e ^1H NMR: δ 8.00–7.95, 7.53–6.93 (aromatic H); 3.83 (CH_2); 2.54 (NMe_2). ^f ^1H NMR: δ 8.06–7.20 (aromatic H); 3.15 (NMe_2). ^g ^1H NMR: δ 8.05–7.24 (aromatic H); 3.13 (NMe_2). ^h Value in parentheses denotes $^2J(\text{PtP})$; Se *trans* to olefinic double bond. ⁱ ^1H NMR: δ 7.98–7.88, 7.45–7.37 (aromatic H) and the expected $\text{C}_8\text{H}_{12}\text{OMe}$ resonances. ^j Value in parentheses denotes $^2J(\text{PtP})$; S *trans* to olefinic double bond. ^k ^1H NMR: δ 7.99–7.88, 7.45–7.37 (aromatic H) and the expected $\text{C}_8\text{H}_{12}\text{OMe}$ resonances. ^l ^1H NMR: δ 8.28–8.19, 7.60–7.01 (aromatic H) and the expected $\text{C}_{10}\text{H}_{14}$ resonances. ^m ^1H NMR: δ 8.26–8.18, 7.61–7.02 (aromatic H) and the expected $\text{C}_{10}\text{H}_{14}$ resonances. ⁿ ^1H NMR: δ 8.14–6.80 (aromatic H); 1.34 (C_5Me_5). ^o ^1H NMR: δ 8.25–6.91 (aromatic H); 1.39 (C_5Me_5). ^p ^1H NMR: δ 7.99–7.95, 7.40–7.38 (aromatic H) and η^3 -allyl resonances. ^q ^1H NMR: δ 8.03–7.87, 7.40–7.24 (aromatic H) and η^3 -allyl resonances. ^r ^1H NMR: δ 7.95–7.77, 7.37–7.31 (aromatic H) and η^3 -allyl resonances. ^s ^1H NMR: δ 7.95–7.77, 7.36–7.29 (aromatic H) and η^3 -allyl resonances. ^t ^1H NMR: δ 7.95–7.84, 7.36–6.65 (aromatic H); 3.76, 3.74 (CH_2) and 2.51, 2.41 (NMe_2 , values given first correspond to the minor isomer). ^u Major isomer observed. ^v ^1H NMR: δ 8.05–7.19 (aromatic H); 3.16, 3.09 (NMe_2 , value given first corresponds to the minor isomer). ^w ^1H NMR: δ 8.03–7.89, 7.39–7.37 (aromatic H) and η^3 -allyl resonances. ^x ^1H NMR: δ 8.27–8.18, 7.63–6.05 (aromatic H) and $\text{C}_{10}\text{H}_{14}$ resonances. ^y ^1H NMR: δ 8.12–7.01 (aromatic H); 1.41 (C_5Me_5).


Scheme 2 (i) [$\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)_2\}$], thf

The ^{31}P - $\{^1\text{H}\}$ NMR spectra of **11** and **12** each reveal a single resonance at $\delta(\text{P})$ 26.2 [$^1J(\text{PSe})$ 550 Hz] and 37.9 respectively. For **13** and **14** the ^{31}P - $\{^1\text{H}\}$ NMR spectra each show two doublets consistent with two inequivalent phosphorus nuclei P_E and P_O . Conformation of an η^3 -allyl group in **11–14** was obtained by ^1H NMR spectroscopy and furthermore, in the case of **12** and **13**, by X-ray crystallography (see below). In compounds **11** and **12** the ligand $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$ behaves as a typical *E,E'*-chelate whereas in **13** and **14** the ligand $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]^-$ bridges two palladium(II) metal centres yielding a binuclear complex with a four-membered Pd_2E_2 core. We recently described the unexpected formation of a ten-membered palladacycle [$\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)[\text{Ph}_2\text{P}(\text{O})\text{NPPh}_2\text{-O,P}]\}_2$]

containing a head to tail bridging arrangement of two anionic asymmetrical $[\text{Ph}_2\text{P}(\text{O})\text{NPPh}_2]^-$ ligands.⁴¹

Preliminary co-ordination studies with $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Ph}_2]^-$

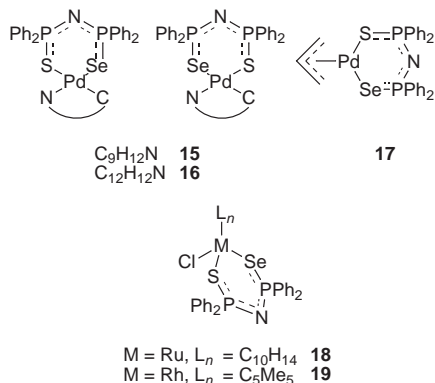
Whilst the symmetrical ligands $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ containing two identical 'soft' donor atoms have received widespread attention, the asymmetrical ligands $[\text{R}_2\text{P}(\text{O})\text{NP}(\text{E})\text{R}_2]^-$ bearing a 'soft' and 'hard' donor centre have only attracted interest in the last few years.^{14,18,32} Furthermore we are unaware of any reports of co-ordination complexes with the mixed ligand $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Ph}_2]^-$ **X** bearing two dissimilar 'soft' donor atoms. Reaction of **X** with the cyclopalladated compounds [$\{\text{Pd}(\mu\text{-Cl})(\text{L-L})\}_2$] ($\text{L-L} = \text{C}_9\text{H}_{12}\text{N}$ or $\text{C}_{12}\text{H}_{12}\text{N}$) gave $[\text{Pd}(\text{L-L})\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Ph}_2\text{-S,Se}\}]$ as a mixture of two isomers in an approximate ratio of 4.6:1 (for **15**) and 4.9:1 (for **16**) (from integration of the ^{31}P signals). The distribution of isomers was unaltered even after allowing CDCl_3 solutions to stand for periods up to 15 d. In contrast reactions performed under similar conditions with $\text{K}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) gave $[\text{Pd}(\text{L-L})\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2\text{-O,E}\}]$ as one isomer (*O trans* to *C*) only.⁵⁶ The complexes $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Ph}_2\text{-S,Se}\}]$ **17**, $[\text{RuCl}\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{Se})\text{Ph}_2\text{-S,Se}\}(\eta^6\text{-p-MeC}_6\text{H}_4\text{Pr}^j)]$

Table 4 Details of the X-ray data collections and refinements for compounds **1**, **6**, **12** and **13**

	1	6	12	13
Empirical formula	C ₃₃ H ₃₂ N ₂ P ₂ PdSe ₂	C ₃₃ H ₃₅ NOP ₂ PtS ₂	C ₂₇ H ₂₅ NP ₂ PdS ₂	C ₅₆ H ₅₂ Cl ₆ N ₂ O ₂ P ₄ Pd ₂ Se ₂
<i>M</i>	782.90	782.77	595.94	1492.37
Crystal system	Triclinic ^a	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> 2/ <i>a</i>
<i>a</i> /Å	11.808(1)	10.647(1)	11.005(1)	19.927(4)
<i>b</i> /Å	12.077(1)	12.491(1)	15.583(1)	10.861(3)
<i>c</i> /Å	11.717(2)	12.647(1)	17.478(1)	28.788(2)
α /°	94.23(1)	98.36(1)	114.31(1)	
β /°	106.36(1)	95.61(1)	93.77(1)	92.99(1)
γ /°	86.44(1)	102.93(1)	98.57(1)	
<i>U</i> /Å ³	1597(3)	1607(7)	2674(9)	6222(2)
<i>T</i> /K	293	293	293	293
<i>Z</i>	2	2	4	4
μ /mm ⁻¹	8.64	4.62	0.99	9.66
Measured reflections	5014	7004	11 590	5079
Independent reflections (<i>R</i> _{int})	4748 (0.112)	4600 (0.268) ^b	7538 (0.017)	4918 (0.361) ^b
Observed reflections [<i>I</i> > 2.0 σ (<i>I</i>)]	4125	3194	5789	2706
Final <i>R</i> , <i>R</i> ' ^c	0.047, 0.057	0.059, 0.138	0.030, 0.090	0.071, 0.062

^a Standard setting 11.717, 11.808, 12.077 Å; 86.43, 85.77, 73.64°. ^b Poor crystal quality/disorder. ^c Weighting scheme as described in refs. 18 (for compounds **1** and **13**) and 47 (for **6** and **12**); *R* values are for observed data.

18 and [RhCl(η^5 -C₅Me₅){Ph₂P(S)NP(Se)Ph₂-S,Se}] **19** were synthesized under similar conditions to those described above for **7–14**. Despite several attempts we were unable to obtain analytically pure samples of **18** and **19** although spectroscopic evidence was in good agreement with the proposed formulations. In particular the ³¹P chemical shifts for P_S and P_{Se} in compounds **15–19** were similar to those for **1–10**.



Crystal structures of compounds **1**, **6**, **12** and **13**

The crystal structure of compound **1** (Fig. 1 and Table 5) reveals an approximately square planar co-ordination of the Pd^{II} with two bidentate anionic ligands. The ligands are arranged in a slightly distorted square planar geometry [Se(1)–Pd–Se(2) 101.27(3), Se(1)–Pd–C(27) 86.9(2), Se(2)–Pd–N(2) 91.1(2)°]. The Pd–Se bond lengths reflect the nature of the *trans* ligand [2.4069(9) for Se(1) *trans* to N(2) and 2.560(1) Å for Se(2) *trans* to C(27)]. Upon complexation the PdSe₂P₂N ring adopts a pseudo-boat conformation with P(1) and Se(2) at the stern and prow of the boat. The two planar fragments Pd–Se(1)–P(1)–Se(2) [maximum deviation from this mean plane is 0.11 Å for P(1)] and P(1)–N(1)–P(2)–Se(2) [maximum deviation from this mean plane is 0.35 Å for N(1)] are inclined by 58° to each other. Within the six-membered ring there is evidence for π delocalisation as reflected in the P–Se bond lengths [2.184(2) for Se(1), 2.155(2) Å for Se(2)] which are comparable to those distances reported for [Pd{Ph₂PNP(Se)Ph₂-P,Se}{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}]·0.5EtOH·0.3CH₂Cl₂ [2.172(4) and 2.174(5) Å for the Se,Se'-chelate ring], [Pd{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}₂]·CHCl₃ [2.189(3) and 2.178(3) Å] and [Pd{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] [2.194(2) and 2.181(2) Å]^{5,23,25} but longer than those observed in **II** [2.085(1) and 2.101(1) Å].²³ The P(1)–N(1)–P(2) angle in **1** [124.9(4)°] is

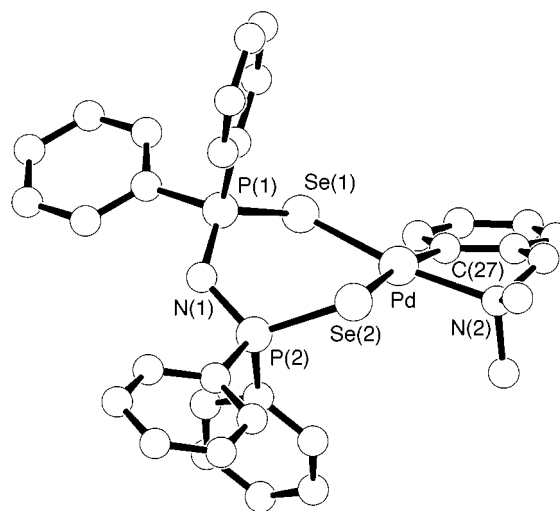


Fig. 1 Crystal structure of [Pd(C₉H₁₂N){Ph₂P(Se)NP(Se)Ph₂-Se,Se'}] **1** (hydrogen atoms omitted for clarity)

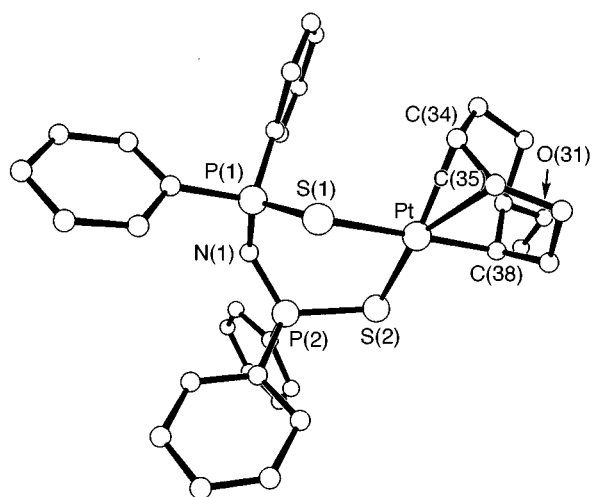
similar to that in [Pd{Ph₂PNP(Se)Ph₂-P,Se}{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}]·0.5EtOH·0.3CH₂Cl₂ [123.2(6)°], [Pd{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}₂]·CHCl₃ [122.9(5)°] and [Pd{Ph₂P(Se)NP(Se)Ph₂-Se,Se'}₂] [127.0(3)°] but somewhat contracted with respect to **II** [P–N–P 132.3(2)°]. Bond lengths and angles for the cyclometallated ring in **1** are similar to those reported for [Pd(C₉H₁₂N){Ph₂PNP(O)Ph₂-P,O}] and [Pd(C₉H₁₂N)(L–L)] [where L–L = Ph₂PCH₂CO₂-P,O, Ph₂PCH=C(OEt)O-P,O or (C₆H₁₁)₂PCMe₂CH₂COMe-P,O].^{40,57}

The crystal structure of compound **6** (Fig. 2 and Table 5) shows that the complex is roughly square planar with Pt–S distances of 2.442(2) [S *trans* to σ -bonded C(38)] and 2.309(4) Å, comparable to those observed in [Pt(C₈H₁₂OMe){Ph₂P(O)NP(S)Ph₂-O,S}] [Pt–S 2.310(3) Å], [Pt{Ph₂P(S)NP(S)Ph₂-S,S'}(PEt₃)₂]PF₆ [Pt–S 2.393(3) Å] and [PtCl{Ph₂P(S)NP(S)Ph₂-S,S'}(PPh₃)] [Pt–S 2.301(2) (S *trans* to Cl) and 2.372(2) Å].^{18,20,27} Furthermore the [Ph₂P(S)NP(S)Ph₂][–] ligand clearly adopts a chelating mode of bonding with the formation of a PtS₂P₂N ring with a pseudo-boat conformation. The two planar fragments Pt–S(1)–P(2)–S(2) [maximum deviation from this mean plane is 0.13 Å for S(2)] and S(1)–P(1)–N(1)–P(2) [maximum deviation from this mean plane is 0.01 Å for N(1)] are inclined to each other by 56°. The P–N bonds are shorter in **6** [1.598(11) and 1.585(11) Å] than in free **I** [1.671(2) and 1.684(2) Å] whilst the P–S bonds are longer [2.026(5) and

Table 5 Selected bond distances (Å) and angles (°) for complexes **1**, **6** and **12**

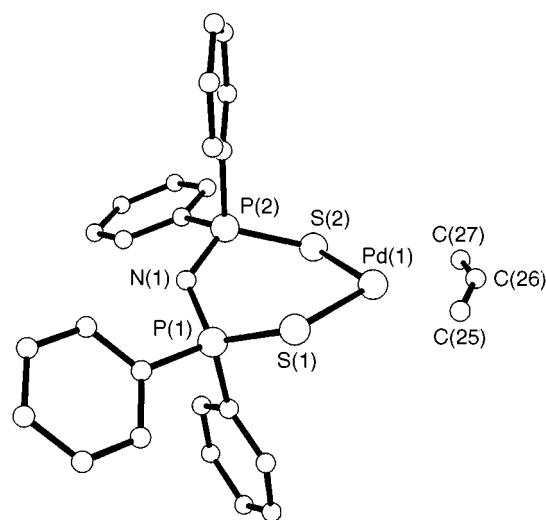
	1 (M = Pd, E = Se)	6 (M = Pt, E = S)	12 (M = Pd, E = S) *
M(1)–E(1)	2.4069(9)	2.442(4)	2.3769(9) [2.3654(9)]
E(1)–P(1)	2.184(2)	2.026(5)	2.0201(12) [2.0216(12)]
P(1)–N(1)	1.598(5)	1.598(11)	1.589(3) [1.595(3)]
N(1)–P(2)	1.589(6)	1.585(11)	1.584(3) [1.595(3)]
P(2)–E(2)	2.155(2)	2.025(6)	2.0185(12) [2.0166(12)]
E(2)–M(1)	2.560(1)	2.309(4)	2.3749(10) [2.3739(11)]
Pd–N(2)	2.120(6)		
Pd–C(27)	2.013(8)		
Pt–C(34)		2.16(2)	
Pt–C(35)		2.163(14)	
Pt–C(38)		2.05(2)	
Pd(1)–C(25)			2.134(4) [2.128(5)]
Pd(1)–C(26)			2.078(5) [2.080(6)]
Pd(1)–C(27)			2.136(4) [2.132(5)]
M(1)–E(1)–P(1)	109.33(6)	101.7(2)	103.66(4) [105.65(4)]
E(1)–P(1)–N(1)	118.5(2)	115.6(4)	117.79(11) [117.78(11)]
P(1)–N(1)–P(2)	124.9(4)	126.7(6)	129.7(2) [128.8(2)]
N(1)–P(2)–E(2)	116.9(2)	117.4(5)	118.76(12) [119.35(11)]
P(2)–E(2)–M(1)	99.84(6)	109.3(2)	105.76(4) [106.17(4)]
E(2)–M(1)–E(1)	101.27(3)	99.66(14)	107.83(3) [106.75(3)]
Se(1)–Pd–C(27)	86.9(2)		
Se(1)–Pd–N(2)	167.2(2)		
Se(2)–Pd–N(2)	91.1(2)		
Se(2)–Pd–C(27)	171.2(2)		
S(1)–Pt–C(34)		89.9(4)	
S(1)–Pt–C(35)		95.3(5)	
S(1)–Pt–C(38)		172.8(5)	
S(2)–Pt–C(38)		84.4(5)	
S(2)–Pt–C(35)		157.8(5)	
S(2)–Pt–C(34)		157.8(5)	
S(1)–Pd(1)–C(25)			92.7(2) [93.2(2)]
S(1)–Pd(1)–C(26)			126.8(2) [126.9(2)]
S(1)–Pd(1)–C(27)			161.0(2) [161.2(2)]
S(2)–Pd(1)–C(25)			159.4(2) [159.9(2)]
S(2)–Pd(1)–C(26)			125.3(2) [126.3(2)]
S(2)–Pd(1)–C(27)			91.1(2) [91.9(2)]

* Value in square brackets are the equivalent parameter in the second molecule.

**Fig. 2** Crystal structure of $[\text{Pt}(\text{C}_8\text{H}_{12}\text{OMe})\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-S,S}'\}]$ **6** (hydrogen atoms omitted for clarity)

2.025(6) Å] than in the parent disulfide [1.950(1) and 1.936(1) Å] indicating some delocalisation within the metallacycle.⁵⁸ The P(1)–N(1)–P(2) angle in **6** [126.7(6)°] is contracted with respect to the angle observed in **1** [132.62(11)°].

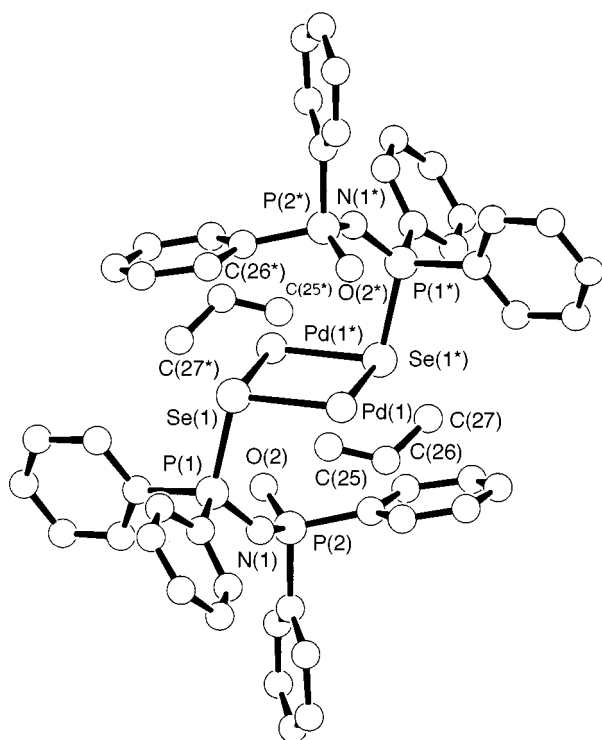
The crystal structure of compound **12** (Fig. 3 and Table 5) reveals two independent molecules and established unequivocally that both are monomeric six-membered $\text{PdS}_2\text{P}_2\text{N}$ chelate ring complexes. The $\text{PdS}_2\text{P}_2\text{N}$ ring adopts a pseudo-boat con-

**Fig. 3** Crystal structure of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-S,S}'\}]$ **12** showing one of the two independent molecules (hydrogen atoms omitted for clarity)

formation in both molecules with shorter P–N [1.589(3) and 1.584(3) (molecule 1); both 1.595(3) Å (molecule 2)] and longer P–S bonds [2.0201(12) and 2.0185(12) (molecule 1); 2.0216(12) and 2.0166(12) Å (molecule 2)] than in free **1** consistent with some delocalisation within the ring. The two planar fragments Pd(1)–S(1)–P(2)–S(2) [maximum deviation from this mean plane is 0.21 Å for S(2) (molecule 1) and 0.25 Å for S(4)

Table 6 Selected bond distances (Å) and angles (°) for complex **13**

Pd(1)–Se(1)	2.477(2)	P(2)–O(2)	1.448(9)
Pd(1)–Se(1*)	2.475(2)	Pd(1)–C(25)	2.01(2)
Se(1)–P(1)	2.225(3)	Pd(1)–C(26)	2.14(1)
P(1)–N(1)	1.539(9)	Pd(1)–C(27)	2.06(2)
N(1)–P(2)	1.613(9)		
Se(1)–Pd(1)–Se(1*)	88.80(5)	Se(1)–Pd(1)–C(25)	99.7(4)
Pd(1)–Se(1)–Pd(1*)	91.20(5)	Se(1)–Pd(1)–C(26)	133.1(6)
Pd(1)–Se(1)–P(1)	101.32(9)	Se(1)–Pd(1)–C(27)	168.6(4)
Pd(1*)–Se(1)–P(1)	102.16(9)	Se(1*)–Pd(1)–C(25)	171.1(4)
Se(1)–P(1)–N(1)	120.1(3)	Se(1*)–Pd(1)–C(26)	136.9(6)
P(1)–N(1)–P(2)	136.8(6)	Se(1*)–Pd(1)–C(27)	100.9(4)
N(1)–P(2)–O(1)	120.3(5)		

**Fig. 4** Crystal structure of $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2\text{-Se}]\}_2] \cdot 2\text{CHCl}_3$, **13** (hydrogen atoms and solvent molecules omitted for clarity). The molecule contains an inversion centre and the starred atoms are generated from the inversion centre

(molecule 2)] and S(1)–P(1)–N(1)–P(2) [maximum deviation from this mean plane is 0.22 Å for N(1) (molecule 1) and 0.24 Å for N(3) (molecule 2)] are inclined to each other by 42 (molecule 1) and 37° (molecule 2) respectively.

In contrast the crystal structure of compound **13** (Fig. 4 and Table 6) reveals that a binuclear complex is formed in which two $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)$ metal fragments are bridged by two $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2\text{-Se}]^-$ ligands forming a four-membered Pd_2Se_2 core. To the best of our knowledge this represents the first example of a crystallographically characterised Pd_2Se_2 ring system. The binuclear compound is disposed about a crystallographic centre of symmetry at the midpoint of the planar Pd_2Se_2 ring. The Pd_2Se_2 ring is strictly planar [Se(1)⋯Se(1*) 3.46, Pd(1)⋯Pd(1*) 3.54 Å]. A comparison of bond lengths and angles within the Se(1)–P(1)–N(1)–P(2)–O(2) backbone is especially noteworthy. The Se(1)–P(1), P(1)–N(1) and N(1)–P(2) bond lengths indicate some degree of delocalisation within the $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2]^-$ ligand and are similar to those reported for *cis*- $[\text{Pd}\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{Se})\text{Ph}_2\text{-O,Se}\}_2]$.¹⁸ The P(2)–O(2) bond length [1.448(9) Å] in **13** is shorter than that observed for $\text{Ph}_2\text{P}(\text{O})\text{NHPPH}_2$ [1.508(2) Å] which exists in the solid state as a hydrogen-bonded dimer pair.⁵¹ There is a disordered CHCl_3

solvate which displays a close contact with the PO functionality (C⋯O 3.11, H⋯O 2.16 Å; C–H⋯O 163°). Bond lengths for the allyl group in **12** and **13** are similar to those reported for $[\{\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)\}_2]$.⁵⁹

It is apparent from this work that $[\text{R}_2\text{P}(\text{E})\text{NP}(\text{E})\text{R}_2]^-$ is a versatile chelating ligand ideally suited for ligation to a variety of late transition-metal organometallic fragments. Unexpectedly we have also demonstrated an unprecedented bonding mode for the unsymmetrical ligands $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]^-$ (E = S or Se). Further studies extending the scope of these reactions may be beneficial.

Acknowledgements

We should like to thank the EPSRC for support and Johnson Matthey plc for loan of precious metals.

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Received 8th April 1998; Paper 8/02676I

