DALTON

Co-ordination chemistry of the mixed phosphorus(III)–phosphorus(V) phosphazene ligand Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$: crystal structures of *cis*-[Pt(CH$_3$)X{Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P*,*P*′}] (X = CH$_3$ or I)†

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The ligand Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ **I** was smoothly oxidised at both terminal PPh$_2$ moieties with either elemental sulfur or grey selenium to give Ph$_2$P(E)NP(Ph)$_2$P(Ph)$_2$NP(E)Ph$_2$ (E = S **II** or Se **III**) in good yields. Oxidation of **I** with either aqueous H$_2$O$_2$ (30% w/w) or Bu^{t}OOH (in decane) gave the known dioxide compound [Ph$_2$P(O)]$_2$NH presumably *via* a sequence of oxidation, protonation and P–P bond-cleavage reactions. Complexation of **I** to several palladium(II), platinum(II) and gold(I) starting materials, at ambient temperature, afforded new metal complexes in which **I** adopts either *P*,*P*′-chelating or *P*,*P*′-bridging co-ordination modes. Reaction of **I** (1 equivalent) with the zerovalent compounds [M(PPh$_3$)$_4$] (M = Pt or Pd) in toluene proceeded cleanly, with P–P bond cleavage, and formation of the known four-membered metallacycles [M(Ph$_2$PNPPh$_2$-*P*,*P*′)$_2$]. All compounds were characterised by a combination of IR and NMR (^{1}H, ^{31}P-{^{1}H}, ^{195}Pt-{^{1}H}) spectroscopy and elemental analyses. Furthermore, the molecular structures of *cis*-[Pt(CH$_3$)X{Ph$_2$PNP(Ph)$_2$P(Ph)$_2$-NPPh$_2$-*P*,*P*′}] (X = CH$_3$ or I) have been determined by single-crystal X-ray diffraction and represent the first examples of MP$_4$N$_2$ metallacycles incorporating a late transition metal. The PtP$_4$N$_2$ rings in both compounds adopt ‘tub-like’ geometries.

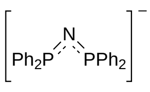
Bis(diphenylphosphino)amine, Ph$_2$PNHPPh$_2$ (hereafter abbreviated dppa), is an excellent ligand for complexation to a range of metals, reminiscent in many respects to the more familiar diphosphine ligand Ph$_2$PCH$_2$PPh$_2$ (dppm).[1–13] Moreover dppa is also a valuable phosphorus precursor to some attractive P–N containing compounds **A**–**C**. These may either be non-ligated or stabilised by co-ordination to a metal centre.[8–10,12–17] Recently there has been interest in the unusual P–P coupled diphosphazene Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ **I**, loosely related to the carbon backbone ligand Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb).[18–20] Indeed several synthetic routes (based on oxidative coupling reactions) to **I** utilising the lithiated anion [Ph$_2$PNPPh$_2$]$^-$ **A** have been developed, yet surprisingly the co-ordination chemistry of **I** has so far remained poorly understood.[21] In contrast, dppa and **A**–**C** can be complexed to a range of transition metals and, furthermore, several different ligating modes have been observed.[1–17,21–24]

The present work describes the preparation and characterisation of Ph$_2$P(E)NP(Ph)$_2$P(Ph)$_2$NP(E)Ph$_2$ (E = S or Se) in which the P–P bond remains intact and also new complexes of **I** in which both *P*,*P*′-chelating and *P*,*P*′-bridging bonding modes are observed. X-Ray crystallography has been used to determine unambiguously the structures of the platinum(II) complexes *cis*-[Pt(CH$_3$)X{Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P*,*P*′}] (X = CH$_3$ or I) which represent the first examples of seven-membered MP$_4$N$_2$ (M = late transition-metal ion) ring compounds. Part of this work has previously been communicated.[21]

Experimental

General

Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The ligand Ph$_2$PNP(Ph)$_2$-P(Ph)$_2$NPPh$_2$ **I** was prepared according to the procedure described by Braunstein *et al.*[19] The metal complexes [M(X)-Y(cod)] (M = Pt or Pd; X, Y = Cl, Br, I or CH$_3$; cod = cycloocta-1,5-diene),[25–28] [PtCl$_2$(SEt$_2$)$_2$],[29] [{Pd(μ-Cl)(L–L)}$_2$] [HL–L = *N*,*N*-dimethylbenzylamine (C$_9$H$_{13}$N) or *N*,*N*-dimethyl-1-naphthylamine (C$_{12}$H$_{13}$N)],[30] [AuCl(tht)] (tht = tetrahydrothiophene)[31] and [M(PPh$_3$)$_4$][32] (M = Pt or Pd) were prepared according to literature methods. Aqueous H$_2$O$_2$ (30% w/w, Fluka), anhydrous Bu^{t}OOH in decane (Aldrich Chemical Co.) and MeI (Fisons) were used without further purification. Potassium tetrachloroplatinate(II), sodium tetrachloropalladadate(II) and tetrachloroauric(III) acid were provided on loan by Johnson Matthey plc.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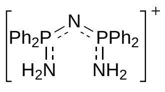
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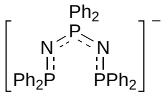
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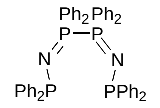
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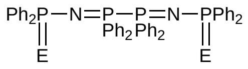
II E = S
III E = Se
IV E = O

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^{1}H NMR spectra (250 MHz) on a Bruker AC250 Fourier-transform spectrometer with chemical shifts (δ) in ppm (±0.01) to high frequency of Si(CH$_3$)$_4$ and coupling constants (*J*) in Hz (±0.1 Hz), ^{31}P-{^{1}H} NMR spectra (36.2 or 101.3 MHz) either on a JEOL FX90Q or Bruker AC250 Fourier-transform spectrometer with chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H$_3$PO$_4$ and coupling constants (*J*) in Hz (±3) and ^{195}Pt-{^{1}H} NMR spectra (53.7 MHz) on a Bruker AC250 Fourier-transform spectrometer with chemical shifts (δ) referenced to external H$_2$PtCl$_6$ (in D$_2$O–HCl). All NMR spectra were measured in CDCl$_3$ unless otherwise stated. Elemental analyses (Perkin-Elmer 2400 CHN

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† This paper is dedicated to Professor Sir Geoffrey Wilkinson FRS who provided inspiration and friendship through many years. He is sadly missed.

elemental analyser) were performed by the Loughborough University Service within the Department of Chemistry.

Preparation of the compounds

$Ph_2P(S)NP(Ph)_2P(Ph)_2NP(S)Ph_2$ II. To a solution of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.352 g, 0.458 mmol) in thf (30 cm^3) was added elemental sulfur (0.029 g, 0.905 mmol) as a solid in one portion. After stirring for *ca.* 5 min a white solid **II** deposited and the resulting mixture was stirred for 2.5 h. The solid was collected by suction filtration. Yield: 0.303 g, 80%. Selected spectroscopic data: δ (^{1}H) 7.83–7.49 and 7.35–7.18 (aromatic H); IR (KBr) 1207, 1174 (ν_{PN}), 603 cm^{-1} (ν_{PS}).

$Ph_2P(Se)NP(Ph)_2P(Ph)_2NP(Se)Ph_2$ III. To the solids $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.440 g, 0.572 mmol) and grey Se (0.096 g, 1.216 mmol) was added tetrahydrofuran (thf) (45 cm^3). The mixture was heated under reflux for 2 h, cooled and evaporated to dryness under reduced pressure. Extraction into CH_2Cl_2 (*ca.* 50 cm^3), filtration through a small Celite pad and evaporation to dryness gave a pale yellow solid. Recrystallisation from CH_2Cl_2–Et_2O gave the product **III** as a white solid. Yield: 0.402 g, 76%. Selected spectroscopic data: δ (^{1}H) 7.83–7.51 and 7.35–7.18 (aromatic H); IR (KBr) 1206, 1174, 1160 (ν_{PN}), 550 cm^{-1} (ν_{PSe}).

Reaction of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ with aqueous H_2O_2 (30% w/w). Under aerobic conditions, a thf (1 cm^3) solution of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.050 g, 0.065 mmol) was treated with aqueous H_2O_2 (30% w/w, 1 drop, *ca.* 0.038 g). The solution was stirred for *ca.* 21 h during which time $[Ph_2P(O)]_2NH$ was deposited, collected by suction filtration and dried *in vacuo*. Yield: 0.042 g, 77%. Alternatively the same product was obtained using anhydrous Bu^{t}OOH in decane. An authentic sample of $[Ph_2P(O)]_2NH$ was prepared by oxidation of dppa with aqueous H_2O_2 according to ref. 13.

***cis*-$[PtCl_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ 1.** Under aerobic conditions, to a solution of $[PtCl_2(cod)]$ (0.074 g, 0.198 mmol) in CH_2Cl_2 (20 cm^3) was added $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.156 g, 0.203 mmol). The solution was stirred for 10 min, filtered and the volume concentrated by evaporation under reduced pressure to *ca.* 1–2 cm^3. Addition of Et_2O (25 cm^3) gave the product **1** which was collected by suction filtration and dried *in vacuo*. Yield: 0.185 g, 90%. Alternatively **1** was synthesized from $[PtCl_2(SEt_2)_2]$ in 84% yield. Selected spectroscopic data: δ (^{1}H) 7.62–7.04 (aromatic H); IR (KBr) 1206, 1181, 1161 (ν_{PN}), 306, 279 cm^{-1} (ν_{PtCl}).

The following compounds were prepared in a similar manner (yields in parentheses): *cis*-$[PtBr_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **2** (92%), *cis*-$[PtI_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **3** (93%), *cis*-$[PdCl_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **4** (76%), *cis*-$[PdBr_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **5** (90%), *cis*-$[Pt(CH_3)_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **6** (91%) and *cis*-$[Pt(CH_3)Cl\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **7** (63%). Selected spectroscopic data: **2**, δ (^{1}H) 7.62–7.04 (aromatic H); IR (KBr) 1197, 1180, 1161 cm^{-1} (ν_{PN}); **3**, δ (^{1}H) 7.61–7.03 (aromatic H); IR (KBr) 1181, 1161 cm^{-1} (ν_{PN}); **4**, IR (KBr) 1182, 1161 (ν_{PN}); 304, 276 cm^{-1} (ν_{PdCl}); **5**, IR (KBr) 1182, 1162 cm^{-1} (ν_{PN}); **6**, δ (^{1}H) 7.43–6.97 (aromatic H) and 0.09 [Pt–CH_3, *J*(PtH) 65.7, *J*(PH) 12.7 Hz]; **7**, δ (^{1}H) 7.61–7.08 (aromatic H) and 0.27 (Pt–CH_3); IR (KBr) 279 cm^{-1} (ν_{PtCl}).

Slow evaporation of a CH_2Cl_2–light petroleum (b.p. 60–80 °C) filtrate gave crystals of complex **6** suitable for X-ray crystallography.

***cis*-$[Pt(CH_3)I\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ 8.** A solution of *cis*-$[Pt(CH_3)_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ (0.029 g, 0.0292 mmol) in CH_2Cl_2 (*ca.* 0.6 cm^3) was treated with iodomethane (*ca.* 0.18 g, 43-fold molar excess). After stirring for *ca.* 30 min, light petroleum (b.p. 60–80 °C) (3 cm^3) was added and the solid product **8** collected by suction filtration. Yield: 0.028 g, 88%. Selected spectroscopic data: δ (^{1}H) 7.58–7.05 (aromatic H) and 0.63 (Pt–CH_3). Slow diffusion of light petroleum into a $CDCl_3$ solution of complex **8** over the course of *ca.* 8 d gave crystals suitable for X-ray crystallography.

$[\{PdCl(C_9H_{12}N)\}_2\{\mu\text{-}Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\}]$ 9. To a yellow solution of $[\{Pd(\mu\text{-}Cl)(C_9H_{12}N)\}_2]$ (0.040 g, 0.0724 mmol) in CH_2Cl_2 (10 cm^3) was added solid $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.056 g, 0.0728 mmol). The solution was stirred for 30 min, filtered and the volume concentrated under reduced pressure to *ca.* 1–2 cm^3. Addition of light petroleum (15 cm^3) gave the solid product **9** which was collected by suction filtration and dried *in vacuo*. Yield: 0.080 g, 84%. Selected spectroscopic data: δ (^{1}H) 7.97–6.25 (aromatic H), 3.79 (N–CH_2) and 2.50 [^4J(PH) 2.3 Hz, $N(CH_3)_2$].

In a similar manner the complex $[\{PdCl(C_{12}H_{12}N)\}_2\{\mu\text{-}Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\}]$ **10** was prepared in 90% yield. Selected spectroscopic data: δ (^{1}H) 7.84–5.30 (aromatic H) and 3.09 [^4J(PH) 2.3 Hz, $N(CH_3)_2$].

$[(AuCl)_2\{\mu\text{-}Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\}]$ 11. To a solution of [AuCl(tht)] (0.104 g, 0.324 mmol) in CH_2Cl_2 (5 cm^3) was added solid $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.126 g, 0.164 mmol). After *ca.* 5 min solid **11** deposited and the mixture was stirred for *ca.* 70 min. The product was collected by suction filtration and dried *in vacuo*. Yield: 0.153 g, 77%. Selected spectroscopic data: δ (^{1}H) 7.66–7.29 (aromatic H); IR (KBr) 1191, 1176, 1152 (ν_{PN}), 324 cm^{-1} (ν_{AuCl}).

Reaction of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ with $[Pt(PPh_3)_4]$. To the solids $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.129 g, 0.168 mmol) and $[Pt(PPh_3)_4]$ (0.208 g, 0.167 mmol) was added toluene (20 cm^3). After stirring for *ca.* 24 h the white product $[Pt(Ph_2PNPPh_2\text{-}P,P')_2]$ **12** was collected by suction filtration and dried *in vacuo*. Yield: 0.145 g, 90%. Examination of the filtrate residue by ^{31}P-{^{1}H} NMR spectroscopy revealed only PPh_3 [δ(P) −4.6] was present. In a similar manner the reaction of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$ (0.070 g, 0.091 mmol) with $[Pd(PPh_3)_4]$ (0.103 g, 0.089 mmol) was studied and found to give $[Pd(Ph_2PNPPh_2\text{-}P,P')_2]$ **13**. Yield: 0.061 g, 78%.

No reaction between $[M(PPh_3)_4]$ (M = Pt or Pd) and $Ph_2P(E)NP(Ph)_2P(Ph)_2NP(E)Ph_2$ (E = S or Se) in toluene was observed even after prolonged (>10 d) stirring at ambient temperature.

X-Ray crystallography

The crystal structures of compounds **6** and **8** were obtained using a Rigaku AFC7S diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.541 78 Å) and ω scans at room temperature. Details of the data collections and refinements are given in Table 3. Empirical absorption corrections (DIFABS)[33] were applied. The structures were solved by the heavy-atom method.[34] In **8** the CH_3 and I groups are disordered. The molecule was refined with both C and I atoms in 50% occupancy at each site. The disordered I atom positions were refined anisotropically and the disordered C atom positions isotropically, with no H atoms on the 50% occupancy methyl carbons being included in the refinement. All of the other non-hydrogen atoms were refined anisotropically. The C–H atoms were idealised and fixed (C–H 0.95 Å). No additional constraints or restraints were applied. Refinement was by full-matrix least-squares methods based on *F*. Calculations were performed using TEXSAN.[35]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/570.

Table 1 Microanalytical data for the new compounds (calculated values in parentheses)

Compound	Analysis (%)		
	C	H	N
II	69.2 (69.2)	4.55 (4.85)	3.25 (3.35)
III	62.2 (62.2)	4.15 (4.35)	2.95 (3.0)
1	55.1 (55.7)	4.0 (3.9)	2.7 (2.7)
2	51.2 (51.3)	3.6 (3.6)	2.6 (2.5)
3	47.4 (47.35)	3.2 (3.3)	1.5 (2.3)
4	60.25 (60.95)	4.4 (4.25)	3.0 (2.95)
5	55.05 (55.7)	3.9 (3.9)	2.45 (2.7)
6	60.0 (60.4)	4.25 (4.65)	2.6 (2.8)
7	56.6 (58.0)	4.15 (4.3)	2.8 (2.75)
8	53.25 (53.20)	4.15 (3.95)	2.7 (2.55)
9	61.6 (62.05)	4.95 (4.65)	3.9 (4.0)
10	59.55 (60.0)	4.9 (4.9)	4.3 (4.25)
11	46.45 (46.75)	2.9 (3.25)	2.4 (2.25)

Results and Discussion

Oxidation reactions of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$

Previous work by ourselves[36,37] has shown that dppa can be selectively monooxidised to afford the unsymmetrical ligands $Ph_2PNHP(E)Ph_2$ (E = O, S or Se). Further oxidation leads to the formation of the doubly oxidised compounds $[Ph_2P(E)]_2NH$.[13,37–39] We have found that compound **I** can also be smoothly oxidised, under conditions similar to those employed for dppa, with elemental sulfur or grey selenium in thf to yield $Ph_2P(E)NP(Ph)_2P(Ph)_2NP(E)Ph_2$ (E = S **II**, E = Se **III**), both isolated as white air-stable solids in 80 and 76% yields respectively. Moreover the P–P bond in these ligands is not cleaved (X-ray evidence).[21] This contrasts with the analogous reaction of **I** in thf, with either aqueous H_2O_2 (30% w/w) or anhydrous Bu^tOOH (in decane) which did not lead to the expected formation of $Ph_2P(O)NP(Ph)_2P(Ph)_2NP(O)Ph_2$ **IV** but instead gave the known compound $[Ph_2P(O)]_2NH$ in 77% yield. However, careful monitoring (by $^{31}P-\{^1H\}$ NMR spectroscopy) of the reaction of **I** (in thf) with H_2O_2 revealed the formation of both $[Ph_2P(O)]_2NH$ [δ(P) 18.8] and a second species tentatively assigned to **IV** [δ P^{III}, P^V 14.1, 9.6, *J*(PP) not resolved]. After leaving samples to stand for several hours only $[Ph_2P(O)]_2NH$ precipitated from solution. No attempts to prepare **IV** using alternative oxidants or varying the experimental conditions have been tried. We, and others,[18] have observed that solutions of **I** in various solvents are unstable and decompose. Hence, in thf we have identified a range of phosphorus-containing compounds including dppa, $Ph_2PNHP(O)Ph_2$ and $[Ph_2P(O)]_2NH$ in addition to several other uncharacterised species.

The mixed phosphorus(V) compounds **II** and **III** have the expected analytical (Table 1) and spectroscopic properties (Table 2 and Experimental section). Hence in the IR spectra of **II** and **III** $\nu_{(PS)}$ and $\nu_{(PSe)}$ are found at 603 and 550 cm^{-1} respectively, *cf.* $Ph_2PNHP(S)Ph_2$ [$\nu_{(PS)}$ 634 cm^{-1}], $[Ph_2P(S)]_2NH$ [$\nu_{(PS)}$ 645 cm^{-1}], $Ph_2PNHP(Se)Ph_2$ [$\nu_{(PSe)}$ 551 cm^{-1}] and $[Ph_2P(Se)]_2NH$ [$\nu_{(PSe)}$ 546 cm^{-1}].[37,38] In the $^{31}P-\{^1H\}$ NMR spectrum of **III** the ^1J(PSe) coupling constant of 714 Hz is smaller in magnitude than that reported for $Ph_2PNHP(Se)Ph_2$ (757 Hz) and $[Ph_2P(Se)]_2NH$ (793 Hz).[37,38] The crystal structure of **III** has previously been reported by us and is in accord with the formulation shown.[21]

Chelate complexes of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$

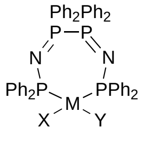
Treatment of [M(X)Y(cod)] (M = Pt or Pd; X, Y = Cl, Br, I or CH_3; cod = cycloocta-1,5-diene) with compound **I** (1:1 molar ratio) in CH_2Cl_2 at room temperature gave the complexes *cis*-$[M(X)Y\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ **1–7** in reasonable to good yields (63–93%). Alternatively complex **1** can be readily prepared from $[PtCl_2(SEt_2)_2]$. The *cis* geometries of **1–7** were established in solution by multinuclear NMR spectroscopy (Table 2). The chemical shifts (δ P^{III}) for **1–3** are typically observed at *ca.* 23.0 ppm (*cf.* **I** δ P^{III} 43), whilst on going from Cl > Br > I in the platinum(II) series **1–3** there is a small reduction in the magnitude of the ^1J(PtX) coupling constant [*J*(PtP) 4049 for **1**, 4001 for **2**, 3845 Hz for **3**]. For all the dihalogeno complexes *J*(PP) was not resolved (at 36.2 MHz) whereas for the dimethylplatinum(II) complex **6** *J*(PP) is *ca.* 13 Hz. In the $^{195}Pt-\{^1H\}$ NMR spectra of **1–3** and **6** the expected 1:2:1 triplet was observed whilst the resonances for **7** and **8** were doublet of doublets (Table 2). When the complexes **1** and **2** are left to stand in $CDCl_3$ for prolonged periods (*ca.* 5 d) only trace amounts of a decomposition product (δP 21.0) are observed and tentatively assigned as $[Ph_2P(O)]_2NH$. In contrast $^{31}P-\{^1H\}$ NMR spectra of freshly prepared $CDCl_3$ solutions of *cis*-$[PdX_2\{Ph_2PNP(Ph)_2P(Ph)_2NPPh_2\text{-}P,P'\}]$ (X = Cl **4** or Br **5**) indicate only single phosphorus-containing species. However after *ca.* 2 h conversion into new species (δ P^{III}, P^V 52.9, 20.3 in the case of **4**; 51.7, 19.2 in the case of **5**) is then observed whereas after several hours insoluble products are formed and identified by IR (KBr pellets) as *cis*-$[PdX_2(Ph_2PNHPPh_2\text{-}P,P')]$ (X = Cl or Br).‡ Clearly the P–P bond is susceptible to cleavage under these conditions.

Monitoring the reaction of complex **6** in toluene with an

Table 2 Selected spectroscopic data for compounds **II**, **III** and **1–13**

Compound	δ			Additional data
	P^{III} [a]	P^V	Pt	
II	47.2	13.5		*J*(PP) 7.2
III	38.4	14.5		*J*(PSe) 714 *J*(PP) 7.2
1	22.9 (4049)	1.1	−4157	
2	23.0 (4001)	0.3	−4408	
3	22.7 (3845)	−0.9	−4902	
4	48.8 [b]	−1.4		
5	47.8 [b]	−2.1		
6	51.7 (2111)	−0.1 [c]	−4354	*J*(PP) 13.3
7	54.4 (2006) [d] 29.1 (4694) [f]	4.1, 0.8 [e]	−4281	
8	48.5 (2072) [d] 31.3 (4556) [f,g]	2.3, −1.7 [e]	−4602	
9	60.6	15.8		
10	62.4	15.3		
11	50.8	16.6		*J*(PP) 8.3
12	−15.9 (1667) [h] −17.4 (1660) [i]			
13	−6.5 [j]			

[a] Values in parentheses denote ^1J(PtP)/Hz. [b] Decomposes in solution. [c] ^3J(PtP)/Hz not observed. [d] P *trans* to CH_3. [e] Several *J*(PP) values between 5 and 35 Hz. [f] P *trans* to X (Cl or I). [g] Measured *in situ*. [h] Measured *in situ* in CH_2Cl_2–CD_2Cl_2 ($\omega_{\frac{1}{2}}$ 35 Hz). [i] Taken from ref. 8. [j] Measured *in situ* in CH_2Cl_2–CD_2Cl_2.



1 M = Pt, X = Y = Cl
2 M = Pt, X = Y = Br
3 M = Pt, X = Y = I
4 M = Pd, X = Y = Cl
5 M = Pd, X = Y = Br
6 M = Pt, X = Y = CH_3
7 M = Pt, X = CH_3, Y = Cl
8 M = Pt, X = CH_3, Y = I

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‡ Authentic samples of *cis*-$[PdX_2(Ph_2PNHPPh_2\text{-}P,P')]$ were prepared from $[PdX_2(cod)]$ (X = Cl or Br) and 1 equivalent of $Ph_2PNHPPh_2$ in CH_2Cl_2.

Table 3 Details of the X-ray data collections and refinements for compounds **6** and **8**

	6	**8**
Empirical formula	$C_{50}H_{46}N_2P_4Pt$	$C_{49}H_{43}IN_2P_4Pt$
M	993.91	1105.78
Crystal colour, habit	Clear, plate	Yellow, prism
Crystal dimensions/mm	0.20 × 0.03 × 0.29	0.12 × 0.21 × 0.21
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pccn*	*Pbca*
a/Å	12.255(6)	20.807(8)
b/Å	34.724(9)	34.700(4)
c/Å	20.847(8)	12.453(5)
U/Å^3	8871	8990
Z	8	8
D_c/g cm^{-3}	1.49	1.63
μ/mm^{-1}	7.64	12.63
$2\theta_{max}$/°	120.0	119.9
F(000)	3984	4336
Measured reflections	7294	7366
Observed reflections [$I > 2.0\sigma(I)$]	2968	2748
Reflection: parameter ratio	5.8:1	5.3:1
Minimum, maximum transmission	0.73, 1.00	0.59, 1.00
Weighting scheme *p*	0.004	0.002
No. variables	515	523
Final *R*, *R′*	0.037, 0.032	0.045, 0.041
Maximum Δ/σ	0.64	0.64
Largest difference peak, hole/e Å^{-3}	0.62, −0.74	0.66, −0.95

$R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; weighting scheme defined in ref. 35.

Table 4 Selected bond distances (Å) and angles (°) for complexes **6** and **8**

	6	**8**
P(1)–N(1)	1.648(8)	1.628(10)
N(1)–P(2)	1.575(8)	1.589(9)
P(2)–P(3)	2.290(4)	2.242(5)
P(3)–N(2)	1.561(8)	1.552(10)
N(2)–P(4)	1.647(8)	1.652(10)
Pt–P(1)	2.283(3)	2.284(4)
Pt–P(4)	2.285(3)	2.279(4)
Pt–C(49)	2.21(1)	
Pt–C(50)	2.209(9)	
Pt–P(1)–N(1)	120.3(3)	118.9(4)
P(1)–N(1)–P(2)	126.9(5)	130.4(6)
N(1)–P(2)–P(3)	105.6(4)	104.0(4)
P(2)–P(3)–N(2)	110.1(4)	108.5(4)
P(3)–N(2)–P(4)	138.5(6)	139.6(7)
N(2)–P(4)–Pt	121.2(3)	120.4(4)
P(4)–Pt–P(1)	94.0(1)	94.0(1)
P(1)–Pt–C(49)	93.6(3)	
P(1)–Pt–C(50)	173.3(2)	
P(4)–Pt–C(49)	172.4(3)	
P(4)–Pt–C(50)	92.2(2)	
C(49)–Pt–C(50)	80.2(3)	

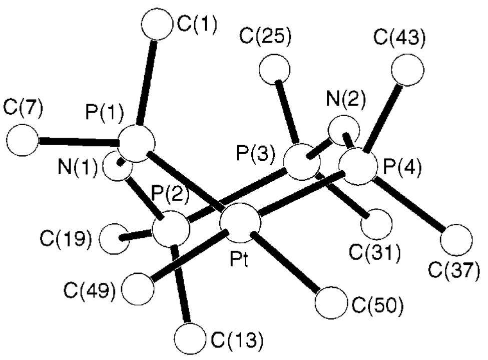


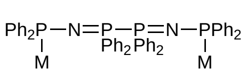
Fig. 1 Crystal structure of *cis*-[Pt(CH_3)$_2${$Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$-*P*,*P′*}] **6**. Phenyl groups and CH protons omitted for clarity. The structure of complex **8** is very similar and is not illustrated. The numbering scheme is the same for the PtP_4N_2 rings in **6** and **8**

excess of CH_3I by ^{31}P-{^1H} NMR spectroscopy indicated the exclusive formation of *cis*-[Pt(CH_3)I{$Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$-*P*,*P′*}] **8** (Tables 1 and 2 for characterising data). We did not observe the formation of any intermediate platinum(IV), species *e.g.* [PtMe$_3$I{$Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$-*P*,*P′*}].

The crystal structure of compound **6** (Table 4, Fig. 1) reveals square-planar co-ordination of the platinum(II) centre with the PtP_4N_2 ring adopting a 'tub-like' geometry. This can be envisaged as being made up of a Pt–P(1)–N(1)–P(2) plane of atoms [maximum deviation from mean plane 0.08 Å for N(1)] which is folded with respect to the Pt–P(2)–P(3)–P(4) mean plane (fold angle 109°). The N(2) atom lies out (0.37 Å) of the Pt–P(2)–P(3)–P(4) plane and is on the same side of the molecule as the Pt–P(1)–N(1)–P(2) plane. The bond lengths and angles in **6** are broadly as anticipated. The P(2)–P(3) distance is 2.290(4) Å whilst the P–N bond lengths divide into two groups: P(1)–N(1) and P(4)–N(2) are 1.648(8) and 1.647(8) Å respectively whilst P(2)–N(1) and P(3)–N(2) are 1.575(8) and 1.561(8) Å respectively reflecting some degree of bond alternation as one would expect from simple bonding descriptions. Interestingly the P–P distance in **6** is elongated with respect to the same bond in free **I** [2.232(2) Å],[19] **III** [2.218(4) Å][21] and the gold(I) compound [(AuCl)$_2${μ-$Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$}] [2.215(7) Å][21] whilst the P–N bond lengths are not so dramatically influenced. The lengthening of the P–P bond does not appear to be a consequence of ring formation since in the cyclic arsenic salt [$AsPPh_2NP(Ph)_2P(Ph)_2NPPh_2$]I·4$C_4H_8O$ the P–P distance is 2.241(3) Å.[18] The crystal structure of **8** (Table 4 for selected bond lengths and angles) is very similar to that of **6**.

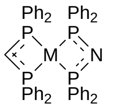
Bridging complexes of $Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$

The bridge-cleavage reaction of [{Pd(μ-Cl)(L–L)}$_2$] [HL–L = *N*,*N*-dimethylbenzylamine ($C_9H_{13}N$) or *N*,*N*-dimethyl-1-naphthylamine ($C_{12}H_{13}N$)] with 1 equivalent of compound **I** in CH_2Cl_2 yields the dimeric complexes [{Pd(L–L)Cl}$_2$-{μ-$Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$}] (L–L = $C_9H_{12}N$ **9** or $C_{12}H_{12}N$ **10**). Related cyclopalladated dimers with bridging Ph_2X-(CH_2)$_2$$XPh_2$ (X = P or As) ligands are known.[40] In the ^{31}P-{^1H} NMR spectra of **9** and **10** the phosphorus(V) resonance is found at higher frequency (typically by *ca.* 15 ppm) than that observed for the chelate complexes **1**–**8** (typically *ca.* 0 ppm, Table 2). We have also prepared the dimeric gold(I) compound [(AuCl)$_2${μ-$Ph_2PNP(Ph)_2P(Ph)_2NPPh_2$}] **11** as a white solid in 77% yield.

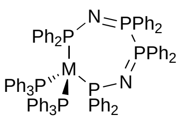


$\underset{M}{Ph_2P}-N=\underset{Ph_2}{P}-\underset{Ph_2}{P}=N-\underset{M}{PPh_2}$

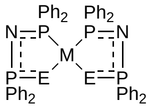
9 M = Pd($C_9H_{12}N$)Cl
10 M = Pd($C_{12}H_{12}N$)Cl
11 M = AuCl



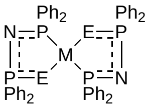
12 M = Pt
13 M = Pd



D



E



F

M = Pt or Pd; E = O, S or Se

Oxidative-addition reactions with ligands I–III

A preliminary study on the reactivity of **I**–**III** with the zerovalent compounds [$M(PPh_3)_4$] (M = Pt or Pd) was undertaken in order to probe the susceptibility of the P–P bond to cleavage. We find that reaction of **I** with [$M(PPh_3)_4$] (1 : 1 ratio) in toluene yields the homoleptic metal(II) complexes [$M(Ph_2PNPPh_2$-*P*,*P*′$)_2$] (M = Pt **12** or Pd **13**). $^{31}P-\{^1H\}$ NMR spectroscopy revealed the predominant species upon evaporation of the toluene filtrate to be PPh_3. The ^{31}P spectral data (Table 2) for **12** are in good agreement with those previously reported by Browning and Farrar.[8] Monitoring these reactions by $^{31}P-\{^1H\}$ NMR spectroscopy showed that oxidative addition was both clean and facile with only [$M(Ph_2PNPPh_2$-*P*,*P*′$)_2$] and displaced PPh_3 identified as the sole products. We did not detect the formation of any intermediates (*e.g.* the d^{10} species **D**) in these reactions. Mixed metal(0) complexes of the type [$M(PR_3)_2$(P–P)] (P–P = chelating diphosphine) have previously been documented.[41]

Neutral compounds of the type [$M\{Ph_2PNP(E)Ph_2$-*P*,*E*$\}_2$] **E** (*cis*) and **F** (*trans*) are known[36,37] and can be readily synthesized from the monoxidised ligand $Ph_2PNHP(E)Ph_2$ and [MCl_2(cod)] (M = Pt or Pd) in the presence or absence of base. We were interested to see whether compounds **II** and **III** would be suitable precursors and undergo P–P cleavage to yield analogous complexes. Treatment of [$M(PPh_3)_4$] (M = Pt or Pd) with **II** (or **III**) in toluene for several days at ambient temperature gave no reaction (**II** and **III** recovered unchanged) which may in part reflect either the low solubility of **II** (or **III**) in toluene or the poor donor ability of these ligands. Related metal complexes containing the neutral chelating ligand $[R_2P(E)]_2NH$ (R = alkyl or aryl, E = S or Se) are, to the best of our knowledge, restricted only to the cationic palladium(II) compound [$Pd\{(Pr^i{}_2PS)_2NH\}\{(Pr^i{}_2PS)_2N\}$]Cl in which one of the ligands is protonated.[42]

Conclusion

The results of our study clearly illustrate that compound **I** has the propensity to form several late transition-metal complexes in which the ligand adopts either a *P*,*P*′-chelating or *P*,*P*′-bridging mode. We also observe that the P–P bond in **I** is readily cleaved by [$M(PPh_3)_4$], but under similar conditions no reaction was observed with **II** (or **III**).

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