Co-ordination chemistry of the mixed phosphorus(III)–phosphorus(V) phosphazene ligand Ph₂PNP(Ph)₂P(Ph)₂NPPh₂: crystal structures of *cis*-[Pt(CH₃)X{Ph₂PNP(Ph)₂P(Ph)₂NPPh₂-*P*,*P*′}] (X = CH₃ or I) †

Alexandra M. Z. Slawin, Martin B. Smith and J. Derek Woollins*

Department of Chemistry, Loughborough University, Loughborough, Leics., UK LE11 3TU

The ligand Ph₂PNP(Ph)₂P(Ph)₂NPPh₂ **I** was smoothly oxidised at both terminal PPh₂ moieties with either elemental sulfur or grey selenium to give Ph₂P(E)NP(Ph)₂P(Ph)₂NP(E)Ph₂ (E = S **II** or Se **III**) in good yields. Oxidation of **I** with either aqueous H₂O₂ (30% w/w) or BuᵗOOH (in decane) gave the known dioxide compound [Ph₂P(O)]₂NH 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(PPh₃)₄] (M = Pt or Pd) in toluene proceeded cleanly, with P–P bond cleavage, and formation of the known four-membered metallacycles [M(Ph₂PNPPh₂-*P*,*P*′)₂]. All compounds were characterised by a combination of IR and NMR (¹H, ³¹P-{¹H}, ¹⁹⁵Pt-{¹H}) spectroscopy and elemental analyses. Furthermore, the molecular structures of *cis*-[Pt(CH₃)X{Ph₂PNP(Ph)₂P(Ph)₂NPPh₂-*P*,*P*′}] (X = CH₃ or I) have been determined by single-crystal X-ray diffraction and represent the first examples of MP₄N₂ metallacycles incorporating a late transition metal. The PtP₄N₂ rings in both compounds adopt 'tub-like' geometries.

Bis(diphenylphosphino)amine, Ph₂PNHPPh₂ (hereafter abbreviated dppa), is an excellent ligand for complexation to a range of metals, reminiscent in many respects to the more familiar diphosphine ligand Ph₂PCH₂PPh₂ (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 Ph₂PNP(Ph)₂P(Ph)₂NPPh₂ **I**, loosely related to the carbon backbone ligand Ph₂P(CH₂)₄PPh₂ (dppb).[18–20] Indeed several synthetic routes (based on oxidative coupling reactions) to **I** utilising the lithiated anion [Ph₂PNPPh₂]⁻ **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 Ph₂P(E)NP(Ph)₂P(Ph)₂NP(E)Ph₂ (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(CH₃)X{Ph₂PNP(Ph)₂P(Ph)₂NPPh₂-*P*,*P*′}] (X = CH₃ or I) which represent the first examples of seven-membered MP₄N₂ (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 Ph₂PNP(Ph)₂P(Ph)₂NPPh₂ **I** was prepared according to the procedure
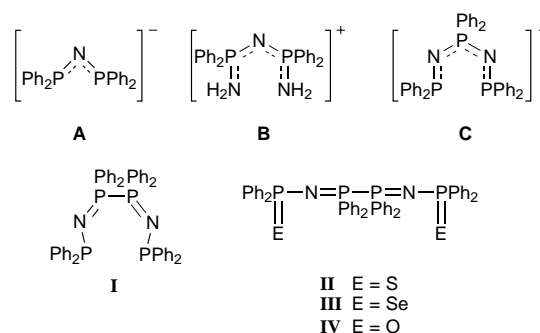
described by Braunstein *et al.*[19] The metal complexes [M(X)Y(cod)] (M = Pt or Pd; X, Y = Cl, Br, I or CH₃; cod = cycloocta-1,5-diene),[25–28] [PtCl₂(SEt₂)₂],[29] [{Pd(μ-Cl)(L–L)}₂] [HL–L = *N,N*-dimethylbenzylamine (C₉H₁₃N) or *N,N*-dimethyl-1-naphthylamine (C₁₂H₁₃N)],[30] [AuCl(tht)] (tht = tetrahydrothiophene)[31] and [M(PPh₃)₄][32] (M = Pt or Pd) were prepared according to literature methods. Aqueous H₂O₂ (30% w/w, Fluka), anhydrous BuᵗOOH in decane (Aldrich Chemical Co.) and MeI (Fisons) were used without further purification. Potassium tetrachloroplatinate(II), sodium tetrachloropalladate(II) and tetrachloroauric(III) acid were provided on loan by Johnson Matthey plc.

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 Fourier-transform spectrometer with chemical shifts (δ) in ppm (±0.01) to high frequency of Si(CH₃)₄ and coupling constants (*J*) in Hz (±0.1 Hz), ³¹P-{¹H} 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% H₃PO₄ and coupling constants (*J*) in Hz (±3) and ¹⁹⁵Pt-{¹H} NMR spectra (53.7 MHz) on a Bruker AC250 Fourier-transform spectrometer with chemical shifts (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 analyser) were performed by the Loughborough University Service within the Department of Chemistry.

Preparation of the compounds

Ph$_2$P(S)NP(Ph)$_2$P(Ph)$_2$NP(S)Ph$_2$ II. To a solution of Ph$_2$-PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ (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$_2$P(Se)NP(Ph)$_2$P(Ph)$_2$NP(Se)Ph$_2$ III. To the solids Ph$_2$-PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ (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$_2$Cl$_2$ (*ca.* 50 cm^3), filtration through a small Celite pad and evaporation to dryness gave a pale yellow solid. Recrystallisation from CH$_2$Cl$_2$–Et$_2$O 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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ with aqueous H$_2$O$_2$ (30% w/w). Under aerobic conditions, a thf (1 cm^3) solution of Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ (0.050 g, 0.065 mmol) was treated with aqueous H$_2$O$_2$ (30% w/w, 1 drop, *ca.* 0.038 g). The solution was stirred for *ca.* 21 h during which time [Ph$_2$P(O)]$_2$NH 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$_2$P(O)]$_2$NH was prepared by oxidation of dppa with aqueous H$_2$O$_2$ according to ref. 13.

***cis*-[PtCl$_2${Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] 1.** Under aerobic conditions, to a solution of [PtCl$_2$(cod)] (0.074 g, 0.198 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added Ph$_2$PNP(Ph)$_2$P(Ph)$_2$-NPPh$_2$ (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$_2$O (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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] **2** (92%), *cis*-[PtI$_2${Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] **3** (93%), *cis*-[PdCl$_2${Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] **4** (76%), *cis*-[PdBr$_2${Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] **5** (90%), *cis*-[Pt-(CH$_3$)$_2${Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] **6** (91%) and *cis*-[Pt-(CH$_3$)Cl{Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*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$_2$Cl$_2$–light petroleum (b.p. 60–80 °C) filtrate gave crystals of complex **6** suitable for X-ray crystallography.

***cis*-[Pt(CH$_3$)I{Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] 8.** A solution of *cis*-[Pt(CH$_3$)$_2${Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P′*}] (0.029 g, 0.0292 mmol) in CH$_2$Cl$_2$ (*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$_9$H$_{12}$N)}$_2${μ-Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$}] 9. To a yellow solution of [{Pd(μ-Cl)(C$_9$H$_{12}$N)}$_2$] (0.040 g, 0.0724 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added solid Ph$_2$PNP(Ph)$_2$-P(Ph)$_2$NPPh$_2$ (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)}$_2${μ-Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$}] **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)$_2${μ-Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$}] 11. To a solution of [AuCl(tht)] (0.104 g, 0.324 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added solid Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ (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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ with [Pt(PPh$_3$)$_4$]. To the solids Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$ (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$_2$PNPPh$_2$-*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$_2$PNP(Ph)$_2$-P(Ph)$_2$NPPh$_2$ (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$_2$PNPPh$_2$-*P,P′*)$_2$] **13**. Yield: 0.061 g, 78%.

No reaction between [M(PPh$_3$)$_4$] (M = Pt or Pd) and Ph$_2$P(E)NP(Ph)$_2$P(Ph)$_2$NP(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 Ph₂PNP(Ph)₂P(Ph)₂NPPh₂

Previous work by ourselves[36,37] has shown that dppa can be selectively monooxidised to afford the unsymmetrical ligands Ph₂PNHP(E)Ph₂ (E = O, S or Se). Further oxidation leads to the formation of the doubly oxidised compounds [Ph₂P(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 Ph₂P(E)NP(Ph)₂P(Ph)₂NP(E)Ph₂ (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 H₂O₂ (30% w/w) or anhydrous Bu^{t}OOH (in decane) which did not lead to the expected formation of Ph₂P(O)NP(Ph)₂P(Ph)₂NP(O)Ph₂ **IV** but instead gave the known compound [Ph₂P(O)]₂NH in 77% yield. However, careful monitoring (by ³¹P-{¹H} NMR spectroscopy) of the reaction of **I** (in thf) with H₂O₂ revealed the formation of both [Ph₂P(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 [Ph₂P(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, Ph₂PNHP(O)Ph₂ and [Ph₂P(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** ν$_{(PS)}$ and ν$_{(PSe)}$ are found at 603 and 550 cm⁻¹ respectively, *cf.* Ph₂PNHP(S)Ph₂ [ν$_{(PS)}$ 634 cm⁻¹], [Ph₂P(S)]₂NH [ν$_{(PS)}$ 645 cm⁻¹], Ph₂PNHP(Se)Ph₂ [ν$_{(PSe)}$ 551 cm⁻¹] and [Ph₂P(Se)]₂NH [ν$_{(PSe)}$ 546 cm⁻¹].[37,38] In the ³¹P-{¹H} NMR spectrum of **III** the ¹J(PSe) coupling constant of 714 Hz is smaller in magnitude than that reported for Ph₂PNHP(Se)Ph₂ (757 Hz) and [Ph₂-P(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]
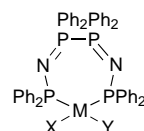
Chelate complexes of Ph₂PNP(Ph)₂P(Ph)₂NPPh₂

Treatment of [M(X)Y(cod)] (M = Pt or Pd; X, Y = Cl, Br, I or CH₃; cod = cycloocta-1,5-diene) with compound **I** (1:1 molar ratio) in CH₂Cl₂ at room temperature gave the complexes *cis*-[M(X)Y{Ph₂PNP(Ph)₂P(Ph)₂NPPh₂-*P*,*P'*}] **1–7** in reasonable to good yields (63–93%). Alternatively complex **1** can be readily

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	4.1, 0.8^e	−4281	
	29.1 (4694)^f			
8	48.5 (2072)^d	2.3, −1.7^e	−4602	
	31.3 (4556)^{f,g}			
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 CH₃. ^{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 CH₂Cl₂–CD₂Cl₂ (ω½ 35 Hz). ^{i} Taken from ref. 8. ^{j} Measured *in situ* in CH₂Cl₂–CD₂Cl₂.

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 = CH₃
7 M = Pt, X = CH₃, Y = Cl
8 M = Pt, X = CH₃, Y = I

prepared from [PtCl₂(SEt₂)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 ¹⁹⁵Pt-{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 CDCl₃ for prolonged periods (*ca.* 5 d) only trace amounts of a decomposition product (δP 21.0) are observed and tentatively assigned as [Ph₂P(O)]₂NH. In contrast ³¹P-{¹H} NMR spectra of freshly prepared CDCl₃ solutions of *cis*-[PdX₂{Ph₂PNP(Ph)₂P(Ph)₂NPPh₂-*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*-[PdX₂(Ph₂PNHPPh₂-*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

---

‡ Authentic samples of *cis*-[PdX₂(Ph₂PNHPPh₂-*P*,*P'*)] were prepared from [PdX₂(cod)] (X = Cl or Br) and 1 equivalent of Ph₂PNHPPh₂ in CH₂Cl₂.

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	$0.20 \times 0.03 \times 0.29$	$0.12 \times 0.21 \times 0.21$
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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*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$_4$N$_2$ rings in **6** and **8**

excess of CH$_3$I by ^{31}P-{^{1}H} NMR spectroscopy indicated the exclusive formation of *cis*-[Pt(CH$_3$)I{Ph$_2$PNP(Ph)$_2$P(Ph)$_2$-NPPh$_2$-*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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$-*P,P'*}].
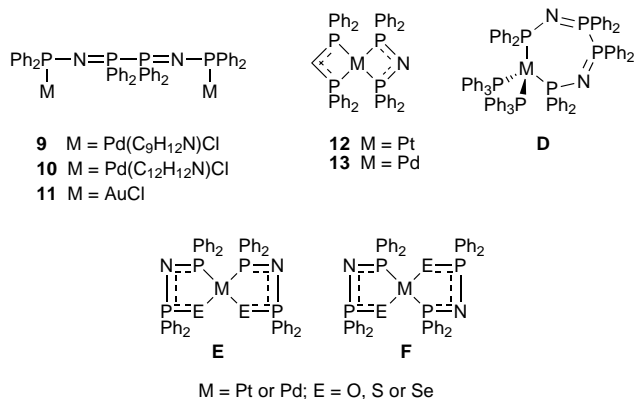
The crystal structure of compound **6** (Table 4, Fig. 1) reveals square-planar co-ordination of the platinum(II) centre with the PtP$_4$N$_2$ ring adopting a 'tub-like' geometry. This can be envisaged as being made up of a Pt–P(1)–N(1)–P(2) plane of atoms [maximum deviation from mean plane 0.08 Å for 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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$}] [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$_2$NP(Ph)$_2$P(Ph)$_2$NPPh$_2$]I·4C$_4$H$_8$O 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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$

The bridge-cleavage reaction of [{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)] with 1 equivalent of compound **I** in CH$_2$Cl$_2$ yields the dimeric complexes [{Pd(L–L)Cl}$_2$-{μ-Ph$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$}] (L–L = C$_9$H$_{12}$N **9** or C$_{12}$H$_{12}$N **10**). Related cyclopalladated dimers with bridging Ph$_2$X-(CH$_2$)$_2$XPh$_2$ (X = P or As) ligands are known.[40] In the ^{31}P-{^{1}H} 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$_2$PNP(Ph)$_2$P(Ph)$_2$NPPh$_2$}] **11** as a white solid in 77% yield.

Ph₂P—N=P—P=N—PPh₂
 | Ph₂Ph₂ |
 M   M

9 M = Pd(C₉H₁₂N)Cl
10 M = Pd(C₁₂H₁₂N)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(PPh₃)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(PPh₃)₄] (1 : 1 ratio) in toluene yields the homoleptic metal(II) complexes [M(Ph₂PNPPh₂-*P,P′*)₂] (M = Pt **12** or Pd **13**). ³¹P-{¹H} NMR spectroscopy revealed the predominant species upon evaporation of the toluene filtrate to be PPh₃. The ³¹P spectral data (Table 2) for **12** are in good agreement with those previously reported by Browning and Farrar.[8] Monitoring these reactions by ³¹P-{¹H} NMR spectroscopy showed that oxidative addition was both clean and facile with only [M(Ph₂PNPPh₂-*P,P′*)₂] and displaced PPh₃ identified as the sole products. We did not detect the formation of any intermediates (*e.g.* the d¹⁰ species **D**) in these reactions. Mixed metal(0) complexes of the type [M(PR₃)₂(P–P)] (P–P = chelating diphosphine) have previously been documented.[41]

Neutral compounds of the type [M{Ph₂PNP(E)Ph₂-*P,E*}₂] **E** (*cis*) and **F** (*trans*) are known[36,37] and can be readily synthesized from the monoxidised ligand Ph₂PNHP(E)Ph₂ and [MCl₂(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(PPh₃)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 [R₂P(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{(Prⁱ₂PS)₂-NH}{(Prⁱ₂PS)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(PPh₃)₄], but under similar conditions no reaction was observed with **II** (or **III**).

Acknowledgements

References

1 D. I. Arnold, F. A. Cotton and F. E. Kühn, *Inorg. Chem.*, 1996, **35**, 4733, 5764.
2 F. A. Cotton and F. E. Kühn, *Inorg. Chim. Acta*, 1996, **252**, 257.
3 R. Graziani and U. Casellato, *Acta Crystallogr., Sect. C*, 1996, **52**, 850.
4 M. Paul and H. Schmidbaur, *Chem. Ber.*, 1996, **129**, 77.
5 D. Pohl, J. Ellermann, M. Moll, F. A. Knoch and W. Bauer, *Z. Anorg. Allg. Chem.*, 1996, **622**, 283.
6 P. Bhattacharyya and J. D. Woollins, *Polyhedron*, 1995, **14**, 3367 and refs. therein.
7 D. Pohl, J. Ellermann, F. A. Knoch and M. Moll, *J. Organomet. Chem.*, 1995, **495**, C6.
8 C. S. Browning and D. H. Farrar, *J. Chem. Soc., Dalton Trans.*, 1995, 521.
9 D. Pohl, J. Ellermann, F. A. Knoch, M. Moll and W. Bauer, *Chem. Ber.*, 1994, **127**, 2167.
10 D. Pohl, J. Ellermann, F. A. Knoch, M. Moll and W. Bauer, *J. Organomet. Chem.*, 1994, **481**, 259.
11 G. Liehr, G. Szucsányi and J. Ellermann, *J. Organomet. Chem.*, 1984, **265**, 95.
12 H. Schmidbaur, S. Lauteschläger and B. Milewski-Mahrla, *J. Organomet. Chem.*, 1983, **254**, 59.
13 F. T. Wang, J. Najdzionek, K. L. Leneker, H. Wasserman and D. M. Braitsch, *Synth. React. Inorg. Metal-Org. Chem.*, 1978, **8**, 119.
14 M. Gómez, G. Muller, J. Sales and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1993, 221.
15 J. Ellermann and M. Lietz, *Z. Naturforsch., Teil B*, 1980, **35**, 64.
16 J. Ellermann, J. Sutter, C. Schelle, F. A. Knoch and M. Moll, *Z. Anorg. Allg. Chem.*, 1993, **619**, 2006.
17 J. Ellermann, J. Sutter, F. A. Knoch and M. Moll, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 700.
18 M. Dotzler, A. Schmidt, J. Ellermann, F. A. Knoch, M. Moll and W. Bauer, *Polyhedron*, 1996, **15**, 4425.
19 P. Braunstein, R. Hasselbring, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Chem. Commun.*, 1995, 37.
20 J. Ellermann, P. Gabold, F. A. Knoch, M. Moll, A. Schmidt and M. Schütz, *Z. Naturforsch., Teil B*, 1996, **51**, 201.
21 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Chem. Commun.*, 1996, 2095.
22 K. V. Katti, H. W. Roesky and M. Rietzel, *Inorg. Chem.*, 1987, **26**, 4032.
23 H. W. Roesky, K. V. Katti, U. Seseke, M. Witt, E. Egert, R. Herbst and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 477.
24 H. W. Roesky, K. V. Katti, U. Seseke, H.-G. Schmidt, E. Egert, R. Herbst and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1987, 847.
25 J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
26 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 47.
27 E. Costa, P. G. Pringle and M. Ravetz, *Inorg. Synth.*, 1997, **31**, 284.
28 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.
29 G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1960, **6**, 211.
30 A. C. Hope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.
31 R. Uson, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
32 R. Ugo, F. Cariati and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105; D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.
33 DIFABS, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
34 DIRDIF 92, PATTY, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
35 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Woodlands, TX, 1985, 1992.
36 P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 3675.
37 P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 3189.
38 P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607.
39 I. Haiduc, in *Inorganic Experiments*, ed. J. D. Woollins, VCH, Weinheim, 1994.
40 J. Dehand, M. Pfeffer and M. Zinsius, *Inorg. Chim. Acta*, 1975, **13**, 229.
41 B. R. James and M. B. Smith, unpublished work; P. A. Chaloner and G. T. L. Broadwood-Strong, *J. Chem. Soc., Dalton Trans.*, 1996, 1039.
42 D. Cupertino, R. Keyte, A. M. Z. Slawin, J. D. Woollins and D. J. Williams, *Polyhedron*, 1996, **15**, 4441.