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Synthesis and characterisation of E,O-mixed donor (E = P, S or Se) ligand complexes of palladium(II) and platinum(II)

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Abstract

New palladium(II) and platinum(II) complexes with the hybrid ligands $Ph_2PNHP(O)Ph_2$, $[Ph_2PNP(O)Ph_2]^-$ or $[Ph_2P(E)NP(O)Ph_2]^-$ (E = S or Se) have been prepared and characterised. Hence reaction of the cyclometallated dimers $[\{Pd(\mu\text{-}Cl)(C\sim N)\}_2]$ [C ~ N = $C_{12}H_9N_2$ or $C_{13}H_8N$] with $Ph_2PNHP(O)Ph_2$ gave the mononuclear compounds $[PdCl(C\sim N)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$. Chloride abstraction, or amine deprotonation, afforded $[Pd(C\sim N)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$ or $[Pd(C\sim N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ bearing a neutral or anionic P,O-chelating ligand, respectively. Reaction of $[\{Pd(\mu\text{-}Cl)(C_9H_{12}N)\}_2]$ with $Ph_2PNHP(O)Ph_2$ in $CDCl_3$ solution gave the known, rather unstable compound, $[PdCl(C_9H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$. Spectroscopic and analytical evidence presented here suggest that $[PdCl(C_9H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ undergoes amine deprotonation/Pd–C bond rupture to give an isomeric compound, tentatively assigned as $[PdCl\{Ph_2PNP(O)Ph_2\text{-}P,O\}(NMe_2CH_2Ph)]$. Bridge cleavage of $[\{Pd(\mu\text{-}Cl)(C_{12}H_9N_2)\}_2]$ with the unsymmetrical anions $[Ph_2P(E)NP(O)Ph_2]^-$ (E = S or Se) gave the square–planar complexes $[Pd(C_{12}H_9N_2)\{Ph_2P(E)NP(O)Ph_2\text{-}E,O\}]$ exclusively as one isomer (E *trans* to N). In a similar manner the new metal(II) compounds $[PtCl\{Ph_2P(E)NP(O)Ph_2\text{-}E,O\}(PMe_2Ph)]$ (E *trans* to Cl) and $[Pd(C_9H_{15}O)\{Ph_2P(E)NP(O)Ph_2\text{-}E,O\}]$ (E *trans* to olefin double bond) were synthesised. All compounds were characterised by a combination of multinuclear NMR [^1H, $^{31}P\{^1H\}$, $^{195}Pt\{^1H\}$], IR spectroscopy and elemental analyses. Furthermore, the X-ray structures of $[Pd(C_{12}H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$ and $[Pd(C_{12}H_{12}N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ are reported and reveal, upon amine deprotonation, π-delocalisation within the P–N–P–O backbone of the anionic P,O-chelating ligand.

Keywords: Crystal structures; Palladium complexes; Cyclometallated complexes; P-ligand complexes

1. Introduction

Ligands with mixed donor sets have attracted much interest especially in recent years [1]. One particular class that has received widespread attention is hemilabile ligands in which both 'soft' (e.g. P) and 'hard' (e.g. N or O) donor centres are present [2,3]. The hard donor site coordinates only weakly to a late transition-metal centre and can readily be displaced by other ligands. This property has been extensively exploited in catalysis, e.g. the recent application of carbosilane dendrimers with hemilabile P,O ligands as olefin hydrovinylation catalysts [4]. We are primarily interested in heterofunctional ligands of the type $R_2PNHP(O)R_2$ [5,6] and $[R_2P(E)NP(O)R_2]^-$ (E = S or Se, R = Ph typically) [7–9] and their coordination chemistry to catalytically useful metals. A series of ligating modes have been unveiled for these extremely versatile ligands with the most common binding mode being P,O- or E,O-chelation. Furthermore the amine proton in the partially oxidised ligand $Ph_2PNHP(O)Ph_2$ is acidic and undergoes smooth deprotonation affording complexes with the unsymmetrical anion $[Ph_2PNP(O)Ph_2]^-$. In-

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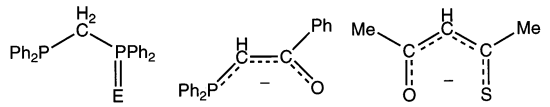
triguingly these hybrids are analogous to the carbon backbone systems $Ph_2PCH_2P(E)Ph_2$ (E = O or S) (**A**), $[Ph_2PCHC(O)Ph]^-$ (**B**) and $[MeC(S)CHC(O)Me]^-$ (**C**). Ligands such as **A** are efficient promoters for rhodium catalysed methanol carbonylations [10] while nickel(II) complexes of **B** and **C** are effective olefin oligomerisation catalysts [11,12]. Herein we report the synthesis, spectral and structural characterisation of some new palladium(II) and platinum(II) complexes with $Ph_2PNHP(O)Ph_2$, $[Ph_2PNP(O)Ph_2]^-$ and $[Ph_2P(E)NP(O)Ph_2]^-$ ligands.



2. Experimental

2.1. Materials and physical measurements

Unless otherwise stated manipulations were carried out in air using predried solvents. The ligand $Ph_2PNHP(O)Ph_2$ [5] and the potassium salts $K[Ph_2P(E)NP(O)Ph_2]$ (E = S or Se) [9] and $K[Ph_2P(E)NP(E)Ph_2]$ (E = S or Se) [13] were prepared according to known procedures. The dimeric compounds $[\{Pd(\mu\text{-}Cl)(C\sim N)\}_2]$ ($HC\sim N = C_9H_{13}N$, $C_{12}H_{10}N_2$, $C_{13}H_9N$), $[\{Pd(\mu\text{-}Cl)(C_9H_{15}O)\}_2]$ ($C_9H_{15}O$ = 8-methoxycyclooct-4-en-1-yl) and $[\{PtCl(\mu\text{-}Cl)PMe_2Ph\}_2]$ were prepared according to previously published procedures [14–18]. $Ag[BF_4]$, $KOBu^t$ and NEt_3 were purchased from Aldrich Chemical 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) were recorded on a Bruker AC250 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $SiMe_4$ and coupling constants (J) in Hz. $^{31}P\{^1H\}$ NMR spectra (36.2 MHz) were recorded on a Jeol FX90Q spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz. $^{195}Pt\{^1H\}$ NMR spectra (53.7 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with δ referenced to external H_2PtCl_6 (in D_2O–HCl). All spectra were measured in $CDCl_3$ unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Precious metal salts were provided on loan by Johnson–Matthey.

2.2. Preparations

2.2.1. $[PdCl(C_{13}H_8N)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ (1)

The compounds $Ph_2PNHP(O)Ph_2$ (0.050 g, 0.125 mmol) and $[\{Pd(\mu\text{-}Cl)(C_{13}H_8N)\}_2]$ (0.040 g, 0.0623 mmol) were allowed to react in $CDCl_3$ (0.7 ml). After the pale yellow solution was stirred for 5 min, it was filtered to remove a small amount of black solid, and addition of petroleum ether (b.p. 60–80°C, 10 ml) afforded an off-white solid. Yield 0.066 g, 73%. FAB^+ MS: m/z 685 [M − Cl]. IR: 3121 (ν_{NH}), 1216 (ν_{PO}). ^1H NMR: 9.78–6.45 (arom. H).

2.2.2. $[PdCl(C_{12}H_9N_2)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ (2)

The compounds $Ph_2PNHP(O)Ph_2$ (0.295 g, 0.735 mmol) and $[\{Pd(\mu\text{-}Cl)(C_{12}H_9N_2)\}_2]$ (0.233 g, 0.361 mmol) were allowed to react in CH_2Cl_2 (25 ml) under a nitrogen atmosphere. After the orange solution was stirred for 45 min, it was concentrated in vacuo to approx. 1–2 ml, addition of petroleum ether (b.p. 60–80°C, 30 ml) and partial reduction of the solvent by evaporation afforded a yellow solid. The solid was collected by suction filtration and dried in vacuo. Yield 0.520 g, 99%. FAB^+ MS: m/z 688 [M − Cl]. IR: 3136 (ν_{NH}), 1218 (ν_{PO}).

2.2.3. $[Pd(C_{12}H_9N_2)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$ (3)

To a CH_2Cl_2 solution (20 ml) of $[PdCl(C_{12}H_9N_2)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ (0.107 g, 0.148 mmol) was added solid $Ag[BF_4]$ (0.037 g, 0.190 mmol). After stirring for 4 h, AgCl was removed by filtration through a small Celite pad, the volume concentrated by evaporation under reduced pressure to approx. 1–2 ml and then diethyl ether (5 ml) added. The solid product was collected by suction filtration and dried in vacuo. Yield 0.058 g, 50%. FAB^+ MS: m/z 688 [M − BF_4]. IR: 3177 (ν_{NH}), 1139 (ν_{PO}). ^1H NMR: 8.27–6.60 (arom. H).

Slow diffusion of diethyl ether into a $CDCl_3$ solution of $[Pd(C_{12}H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$ (**4**) [23] over several days gave crystals suitable for X-ray crystallography.

2.2.4. $[Pd(C_{12}H_9N_2)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ (5)

To a suspension of $[PdCl(C_{12}H_9N_2)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ (0.101 g, 0.139 mmol) in CH_3OH (1 ml) was added $KOBu^t$ (0.018 g, 0.160 mmol) yielding an immediate deep-orange solution followed by the formation of a solid. After stirring for approx. 10 min, the product was collected by suction filtration, washed with a small portion of CH_3OH (0.5 ml) and dried in vacuo. Yield 0.079 g, 82%. FAB^+ MS: m/z 688 [M]. IR: 1128 (ν_{PO}). ^1H NMR: 8.53–6.75 (arom. H).

$[Pd(C_{13}H_8N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ (**6**) was prepared in a similar manner (73%). FAB^+ MS: m/z 685 [M]. IR: 1136 (ν_{PO}). ^1H NMR: 9.30–7.05 (arom. H).

Slow diffusion of petroleum ether (b.p. 60–80°C) into a CH_2Cl_2 solution of [Pd($C_{12}H_{12}N$){Ph_2PNP-(O)Ph_2-*P*,*O*}] (**7**) [23] over several days gave crystals suitable for X-ray crystallography.

*2.2.5. [PdCl{$Ph_2PNP(O)Ph_2$-P,O}(NMe_2CH_2Ph)] (**8**)*

The compounds $Ph_2PNHP(O)Ph_2$ (0.070 g, 0.174 mmol) and [{Pd(μ-Cl)($C_9H_{12}N$)}$_2$] (0.045 g, 0.0815 mmol) were allowed to react in $CDCl_3$ (1 ml). After stirring the orange solution for 2 h, petroleum ether (b.p. 60–80°C, 25 ml) was added. A small amount of solid was removed by filtration (approx. 0.010 g) and slow evaporation of the solvent to approx. 5 ml gave an orange solid, which was collected by suction filtration and dried in vacuo. Yield 0.073 g, 66%. IR: 1132 (ν_{PO}). ^{1}H NMR: 8.00–7.14 (arom. H), 3.78 [^4J(PH) 3.4 Hz, CH_2], 2.56 [^4J(PH) 2 Hz, NMe_2].

*2.2.6. [Pd($C_{12}H_9N_2$){$Ph_2P(S)NP(O)Ph_2$-S,O}] (**9**)*

To a suspension of [{Pd(μ-Cl)($C_{12}H_9N_2$)}$_2$] (0.045 g, 0.070 mmol) in thf (5 ml) was added solid K[Ph_2-P(S)NP(O)Ph_2] (0.068 g, 0.141 mmol). After stirring for 30 min the orange solution was evaporated to dryness under reduced pressure. The residue was extracted into CH_2Cl_2 (4 ml) and filtered through a small Celite pad whereupon the volume was reduced in vacuo to approx. 1 ml and petroleum ether (b.p. 60–80°C, 15 ml) added. The solid was isolated by suction filtration and dried in vacuo. Yield 0.072 g, 72%. FAB$^+$ MS: *m*/*z* 719 [*M*]. IR: 577 (ν_{PS}). ^{1}H NMR: 7.97–7.12 (arom. H).

The following compounds were prepared in a similar manner: [Pd($C_{12}H_9N_2$){$Ph_2P(Se)NP(O)Ph_2$-*Se*,*O*}] (**10**) (92%). FAB$^+$ MS: *m*/*z* 767 [*M*]. IR: 560 (ν_{PSe}). ^{1}H NMR: 7.96–7.07 (arom. H). [Pd($C_{12}H_9N_2$){Ph_2P-(S)NP(S)Ph_2-*S*,*S*′}] (**11**) (95%). IR: 584, 577, 570 (ν_{PS}). ^{1}H NMR: 8.03–7.22 (arom. H). [Pd($C_{12}H_9N_2$)-{$Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se*′}] (**12**) (90%). IR: 544 (ν_{PSe}). ^{1}H NMR: 8.08–7.22 (arom. H). [PtCl{$Ph_2P(S)$-NP(O)Ph_2-*S*,*O*}(PMe_2Ph)] (**13**) (92%). IR: 576 (ν_{PS}), 314 (ν_{PtCl}). ^{1}H NMR: 7.94–7.31 (arom. H), 1.61 (PMe_2Ph). [PtCl{$Ph_2P(Se)NP(O)Ph_2$-*Se*,*O*}(PMe_2Ph)] (**14**) (88%). IR: 557 (ν_{PSe}), 313 (ν_{PtCl}). ^{1}H NMR: 7.96–7.31 (arom. H), 1.66 (PMe_2Ph).

Table 1
Microanalysis data for complexes **1**–**3**, **5**, **6**, **8**–**16** [a]

	Analysis (%)		
	C	H	N
1	61.35 (61.60)	4.15 (4.05)	3.70 (3.90)
2	59.10 (59.70)	4.30 (4.20)	5.35 (5.80)
3	55.15 (55.75)	3.80 (3.90)	5.30 (5.40)
5 [b]	61.35 (61.25)	4.05 (4.45)	5.85 (5.95)
6	64.45 (64.85)	4.05 (4.15)	3.95 (4.10)
8	58.10 (58.50)	4.65 (4.90)	3.60 (4.15)
9	59.80 (60.05)	3.70 (4.05)	5.60 (5.85)
10	56.00 (56.40)	3.60 (3.80)	5.20 (5.50)
11	58.20 (58.75)	3.85 (4.00)	5.85 (5.70)
12	51.90 (52.10)	3.40 (3.55)	4.85 (5.05)
13	47.80 (47.95)	3.75 (3.90)	1.15 (1.75)
14	45.05 (45.30)	3.45 (3.70)	1.55 (1.65)
15	57.20 (58.45)	4.95 (5.20)	1.60 (2.05)
16	54.20 (54.65)	4.65 (4.90)	1.55 (1.95)

[a] Calculated values in parentheses.
[b] As H_2O solvate.

*2.2.7. [Pd($C_9H_{15}O$){$Ph_2P(Se)NP(O)Ph_2$-Se,O}] (**16**)*

To a suspension of [{Pd(μ-Cl)($C_9H_{15}O$)}$_2$] (0.039 g, 0.0694 mmol) in CH_3OH (1 ml) was added solid K[$Ph_2P(Se)NP(O)Ph_2$] (0.075 g, 0.145 mmol). The mixture was stirred for 10 min and the solid isolated by suction filtration. Yield 0.071 g, 71%. IR: 560 (ν_{PSe}). ^{1}H NMR: 7.95–7.37 (arom. H), 5.92, 5.49, 3.42–3.16, 2.33–1.83 ($C_9H_{15}O$).

[Pd($C_9H_{15}O$){$Ph_2P(S)NP(O)Ph_2$-*S*,*O*}] (**15**) was prepared in a similar manner (67%). IR: 577 (ν_{PS}). ^{1}H NMR: 7.98–7.36 (arom. H), 5.92, 5.51, 3.38–3.24, 2.40–1.83 ($C_9H_{15}O$). The solids **15** and **16** were recrystallised from CH_2Cl_2–petroleum ether (b.p. 60–80°C). Microanalytical and spectroscopic data are given in Tables 1 and 2.

2.3. X-ray crystallography

The crystal structures of **4** and **7** were determined using either a Rigaku AFC7S serial diffractometer with graphite-monochromated (Cu Kα) radiation ($\lambda = 1.541$ 78 Å) and ω-scans or a Bruker SMART diffractometer with graphite-monochromated (Mo Kα) radiation ($\lambda =$ 0.710 37 Å). Details of the crystal data collections and refinements are given in Table 3. For the SMART data, intensity data 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 intergrated using the SAINT [19] 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 or by empirical methods [20].

Structures were solved by direct methods and refined by full-matrix least-squares against *F* (TEXSAN [21]) or F^2 (SHELXTL [22]) for all data with $I > 2\sigma(I)$. A standard SHELXTL weighting scheme was used for **7** whilst in the case of **4** the weighting scheme for the Rigaku/TEXSAN was as previously reported [9]. The N–H proton in **4** was located from a ΔF map. All other hydrogen atoms were assigned isotropic displacement parameters and were constrained to idealised geometries. Refinements converged to residuals given in Table 3. All calculations were made with programs of the TEXSAN or SHELXTL systems.

Table 2
Selected NMR data for complexes **1**–**16**

	$\delta(P_E)$ [a]	$\delta(P_O)$	$J(P_EP_O)$	J(PSe)	$\delta(PMe_2Ph)$	δ(Pt)
1	72.3	21.1	33			
2	69.4	21.9	31			
3	73.3	53.9	22			
4	67.8 [b]	59.0	35			
5	70.3	54.5	22			
6	68.8	52.2	20			
7	68.7 [b]	50.2	20			
8	65.8	58.8	9			
9	32.8	27.3				
10	17.3	27.6		506		
11	39.1, 37.2					
12	29.0, 26.0			572, 519		
13	25.9 (123) [c]	31.0			−23.4 (3968) [d]	−3817 [e]
14	9.6 (127) [c]	31.1		475	−25.1 (3964) [d]	−3915 [e]
15	32.8	25.2	4			
16	18.1	25.4	2	510		

[a] E = nothing, S or Se.
[b] Taken from Ref. [23].
[c] $^2J(PtP_E)$.
[d] ^1J(PtP).
[e] Doublet-of-doublets.

3. Results and discussion

3.1. Palladium(II) complexes of $Ph_2PNHP(O)Ph_2$ and $[Ph_2PNP(O)Ph_2]^-$

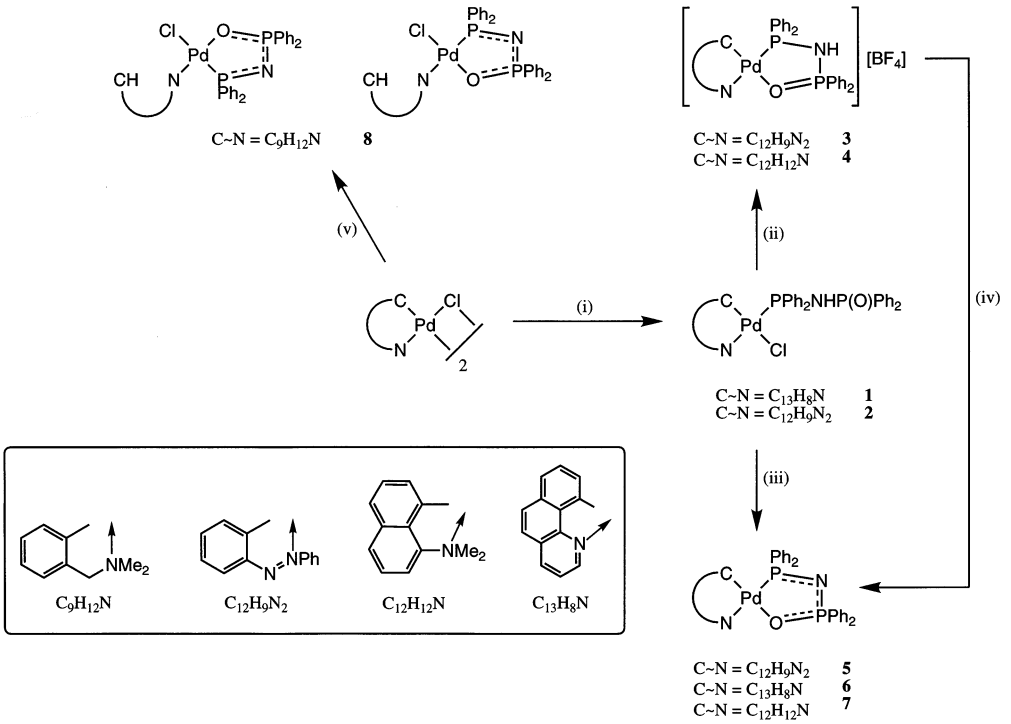
Reaction of the cyclometallated dimers [{Pd(μ-Cl)(C ∼ N)}$_2$] [C ∼ N = $C_{13}H_8N$, $C_{12}H_9N_2$] with Ph_2-PNHP(O)Ph_2 in either $CDCl_3$ or CH_2Cl_2 afforded in good yield, the chloro-bridge cleaved products [Pd-Cl(C ∼ N){Ph_2PNHP(O)Ph_2-*P*}] [C ∼ N = $C_{13}H_8N$ (**1**); C ∼ N = $C_{12}H_9N_2$ (**2**)]. The spectroscopic and analytical data (Tables 1 and 2, Section 2) are in full agreement with the proposed structures (Scheme 1). Hence the $^{31}P\{^1H\}$ NMR spectra of both **1** and **2** show an AX spin system in accordance with two inequivalent P nuclei. The downfield resonance [δ(P) 72.3 ppm for **1**; δ(P) 69.4 ppm for **2**] corresponds to the metal bound P^{III} centre, whereas the doublet centred at approx. 20 ppm is typical for a non-coordinated phosphoryl group. Furthermore **1** and **2** display similar $\delta(P_O)$ to the free ligand $Ph_2PNHP(O)Ph_2$ and the palladium(II) complexes [$PdCl_2${Ph_2PNHP(O)Ph_2-*P*}$_2$] and [PdCl(C ∼ N)-{Ph_2PNHP(O)Ph_2-*P*}] [C ∼ N = $C_9H_{12}N$, $C_{10}H_8N$, $C_{12}H_{12}N$), in which the phosphine oxide moiety is 'dangling' [5,23].

Compound **2** undergoes chloride abstraction with $Ag[BF_4]$ in CH_2Cl_2 to give the monocation [Pd($C_{12}H_9$-N_2){Ph_2PNHP(O)Ph_2-*P*,*O*}][BF_4] (**3**) in reasonable yield. We have previously used this procedure [23] to induce P,O-chelation as exemplified by the synthesis of [Pd($C_{12}H_{12}N$){Ph_2PNHP(O)Ph_2-*P*,*O*}][BF_4] (**4**). The $^{31}P\{^1H\}$ NMR spectrum of **3** was particularly informative showing a significant downfield shift for P_O [$\delta(P_O)$ 53.9 ppm] and a small change in δ(P) for the coordinated P^{III} centre (Table 2). This is fully consistent with P,O-chelation and hence formation of a five-membered Pd–P–N–P–O metallacycle. To our knowledge no X-ray structures of cyclometallated metal complexes

Table 3
Details of the X-ray data collections and refinements for complexes **4** and **7**

	4	**7**
Empirical formula	$C_{36}H_{33}BN_2OF_4P_2Pd$	$C_{36.25}H_{32.50}Cl_{0.50}N_2OP_2Pd$
Formula weight	764.82	698.21
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	12.247(3)	9.3228(1)
b (Å)	17.501(2)	18.1784(2)
c (Å)	16.1626(9)	21.7966(2)
α (°)		110.95(1)
β (°)	97.40(1)	98.705(1)
γ (°)		90.734(1)
U (Å^3)	3435(1)	3400.99(6)
T (K)	293	298(2)
Z	4	4 [a]
μ (mm^{-1})	5.81	0.709
Measured reflections	5579	14436
Independent reflections (R_{int})	5302 (0.082)	9459 (0.0324)
Observed reflections ($I > 2.0\sigma(I)$)	3055	9409
Final R, R'	0.043, 0.045	0.042, 0.104

[a] Two independent molecules.



Scheme 1. (i) $Ph_2PNHP(O)Ph_2$; (ii) $Ag[BF_4]$; (iii) $KOBu^t$; (iv) NEt_3; (v) $Ph_2PNHP(O)Ph_2$, 2 h.

bearing a neutral P,O-chelating $Ph_2PNHP(O)Ph_2$ have been described (vide infra) although the η^3-allyl complex $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$ has been structurally characterised [6].

The amine proton in either **1** (or **2**) can readily be removed upon treatment with $KOBu^t$ in CH_3OH affording the mixed chelate complexes $[Pd(C\sim N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ [$C\sim N = C_{12}H_9N_2$ (**5**); $C\sim N = C_{13}H_8N$ (**6**)]. A similar procedure was previously described for the related complex $[Pd(C_{12}H_{12}N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ (**7**) [23]. Alternatively we find that treatment of $CDCl_3$ solutions of **2** (or **3**) with excess NEt_3 gave **5** ($^{31}P\{^1H\}$ NMR evidence). Compound **5** was characterised by the usual spectroscopic and analytical methods (Tables 1 and 2). Amine deprotonation of the coordinated $Ph_2PNHP(O)Ph_2$ ligand in **5** and **6** was confirmed by the loss of the ν_{NH} band in the IR spectrum. Furthermore a fall of approx. 80–90 cm^{-1} in ν_{PO} supported a P,O-chelation mode.

Reaction of $[\{Pd(\mu\text{-}Cl)(C_9H_{12}N)\}_2]$ with $Ph_2PNHP(O)Ph_2$ was previously shown to give $[PdCl(C_9H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ [23]. Upon standing in $CDCl_3$ solution for approx. 20 min ^{31}P resonances attributed to $[PdCl(C_9H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ diminish and a new set of resonances appears, one of these at significantly higher frequency. Here we suggest a structure for the species **8** based on spectroscopic and microanalytical data (Tables 1 and 2). The $^{31}P\{^1H\}$ NMR spectrum of **8**, isolated from $CDCl_3$ solution upon addition of petroleum ether (b.p. 60–80°C), showed two ^{31}P signals at δ(P) 65.8 and 58.8 ppm [$J(PP_O)$ 9 Hz]. This clearly implies that the phosphoryl group is involved in P,O-chelation and moreover, the ^{31}P NMR data compare well with related palladium(II) compounds displaying this mode of ligation [5,23]. The IR spectrum shows no ν_{NH} absorption, also mirrored in the ^1H NMR spectrum, suggesting a deprotonated $[Ph_2PNP(O)Ph_2]^-$ ligand is present within the metal coordination sphere. The ^1H NMR spectrum confirms the presence of $PhCH_2NMe_2$, as opposed to a cyclometallated ligand, with the remaining coordination site presumably occupied by a chloride. In contrast there is some literature precedence for compounds with a carbon σ-bonded C∼N ligand [24] formed by similar bridge cleavage reactions of *ortho*-metallated dimers with tertiary phosphines (four equiv.) [24]. We apparently do not observe this reactivity here and believe that traces of acid may be responsible for protonation of the Pd–C bond. Monitoring the reaction of **8** with one equiv. of $Ph_2PNHP(O)Ph_2$ in the presence of NEt_3 by $^{31}P\{^1H\}$ NMR showed the predominant species to be the known bis chelate $[Pd\{Ph_2PNP(O)Ph_2\text{-}P,O\}_2]$ [5]. The exact isomer of **8** formed is uncertain and could not clearly be established from NMR data. Attempts to grow suitable crystals of **8** for an X-ray analysis have so far been unsuccessful.

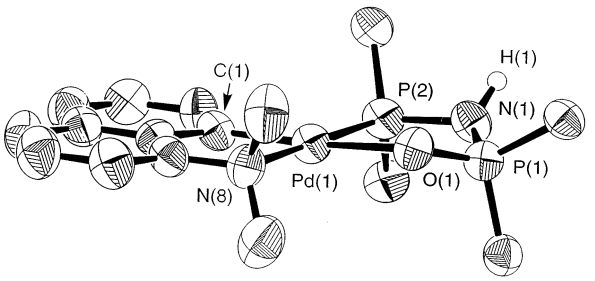


Fig. 1. Crystal structure of $[Pd(C_{12}H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$. Thermal ellipsoids are drawn at 50% probability. All CH protons and the BF_4^- anion are omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) for complexes **4** and **7**

	4	**7** [a]
Bond lengths		
Pd(1)–P(2)	2.226(2)	2.2608(12) [2.2600(13)]
P(2)–N(1)	1.690(6)	1.630(4) [1.633(4)]
N(1)–P(1)	1.658(6)	1.586(4) [1.602(4)]
P(1)–O(1)	1.512(4)	1.528(4) [1.525(4)]
O(1)–Pd(1)	2.151(5)	2.130(3) [2.158(3)]
Pd(1)–C(1)	1.970(7)	1.996(5) [1.986(5)]
Pd(1)–N(8)	2.112(5)	2.145(4) [2.160(4)]
Bond angles		
Pd(1)–P(2)–N(1)	103.1(2)	105.74(14) [106.14(14)]
P(2)–N(1)–P(1)	117.9(3)	118.1(2) [116.7(2)]
N(1)–P(1)–O(1)	108.4(3)	115.1(2) [116.4(2)]
P(1)–O(1)–Pd(1)	113.8(2)	114.4(2) [112.1(2)]
O(1)–Pd(1)–P(2)	87.7(1)	86.38(9) [86.11(9)]
O(1)–Pd(1)–N(8)	91.5(2)	88.57(14) [89.44(13)]
O(1)–Pd(1)–C(1)	172.9(2)	171.9(2) [173.1(2)]
C(1)–Pd(1)–N(8)	84.4(3)	83.8(2) [84.1(2)]
C(1)–Pd(1)–P(2)	96.3(2)	101.54(14) [100.3(2)]
N(8)–Pd(1)–P(2)	178.8(2)	171.48(11) [175.55(11)]

[a] Equivalent parameters for the second molecule are given in square brackets.

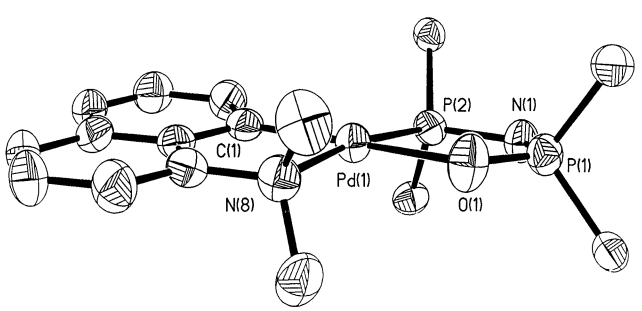


Fig. 2. Crystal structure of $[Pd(C_{12}H_{12}N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]\cdot 0.5CH_2Cl_2$ showing one of the independent molecules only. Thermal ellipsoids are drawn at 50% probability. All CH protons and the solvent molecules are omitted for clarity.

3.2. Crystal structures of $[Pd(C_{12}H_{12}N)\{Ph_2PNHP(O)Ph_2\text{-}P,O\}][BF_4]$ and $[Pd(C_{12}H_{12}N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]\cdot 0.5CH_2Cl_2$

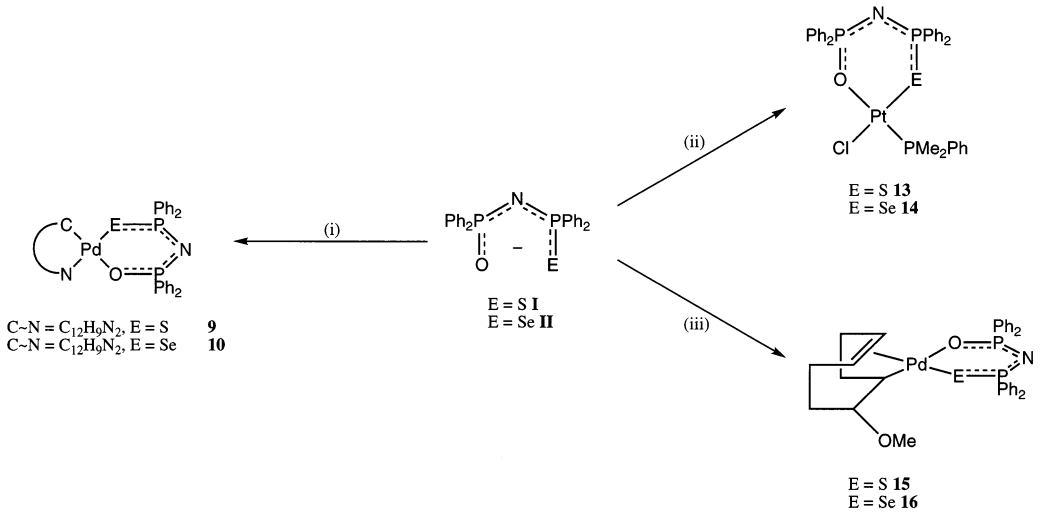
The X-ray structure of **4** (Fig. 1, Table 4) shows the palladium centre is bound by a chelating $Ph_2PNHP(O)Ph_2$ and an anionic cyclometallated ligand in a slightly distorted square–planar geometry. The coordination angles are in the range 84.4(3)–96.3(2)° and the Pd is 0.05 Å out of the plane of its four donor substituents. The Pd–P–N–P–O five-membered ring is slightly puckered [O(1) lies 0.32 Å below the PdP_2NO ring]. The molecular structure confirms an arrangement in which the P^{III} centre is *trans* to the nitrogen of the cyclometallated ring. There is also an intermolecular N(1)–H(1)···F(1) hydrogen bond [N(1)···F(1) 2.84 Å, H(1)···F(1) 2.11 Å, N(1)–H(1)···F(1) 130°] to the BF_4^- counterion.

The X-ray structure of **7** (Fig. 2, Table 4) reveals that the palladium centre is bound by two bidentate anionic $[Ph_2PNP(O)Ph_2]^-$ and $C_{12}H_{12}N$ ligands in a slightly distorted square–planar geometry with coordination angles in the range 83.8(2)–101.54(14)° (molecule 1) and 84.1(2)–100.3(2)° (molecule 2). The Pd–P–N–P–O ring conformation in **7** is nearly planar [N(1) lies 0.03 Å out of the plane (molecule 1); 0(41) lies 0.12 Å out of the plane (molecule 2)]. Furthermore the P^{III} centre of $[Ph_2PNP(O)Ph_2]^-$ is again *trans* to the nitrogen of the cyclometallated ring.

A brief comparison of the PdP_2NO metallacycles is especially noteworthy. In **4** the P–N, N–P and P–O distances are 1.690(6), 1.658(6) and 1.512(4) Å, respectively and similar to those in the free ligand $Ph_2PNHP(O)Ph_2$ which exists in the solid state as a hydrogen-bonded dimer pair [5]. Within the anionic ligand $[Ph_2PNP(O)Ph_2]^-$ in **7** there is a significant shortening of the P–N bonds and a small lengthening of the P–O bond as a consequence of deprotonation.

3.3. Palladium(II) and platinum(II) complexes of $[Ph_2P(E)NP(O)Ph_2]^-$

Reaction of the cyclopalladated azobenzene dimer $[\{Pd(\mu\text{-}Cl)(C_{12}H_9N_2)\}_2]$ with $K[Ph_2P(E)NP(O)Ph_2]$ [E = S (**I**); E = Se (**II**)] in thf, gave after work-up, the mononuclear complexes $[Pd(C_{12}H_9N_2)\{Ph_2P(E)NP(O)Ph_2\text{-}E,O\}]$ [E = S (**9**); E = Se (**10**)] (Scheme 2) in good yields as yellow and orange solids, respectively. $^{31}P\{^1H\}$ NMR clearly establishes that a single isomer is present in $CDCl_3$ solution since two resonances were observed consistent with two inequivalent phosphorus nuclei. No isomerism was observed even after allowing $CDCl_3$ solutions to stand for 4 days. The ^{31}P chemical shift for P_E moves upfield on going from E = S [$\delta(P_S)$ 32.8 ppm for **9**] to E = Se [$\delta(P_{Se})$ 17.3 ppm for **10**] whereas $\delta(P_O)$ in both compounds is very similar (approx. 27 ppm).



Scheme 2. (i) [{Pd(μ-Cl)(C ~ N)}$_2$]; (ii) [{PtCl(μ-Cl)(PMe$_2$Ph)}$_2$]; (iii) [{Pd(μ-Cl)(C$_9$H$_{15}$O)}$_2$].

By analogy with related compounds [23] this isomer has an arrangement in which E is *trans* to N. We have also prepared, for comparison, the organometallic complexes [Pd(C$_{12}$H$_9$N$_2$){Ph$_2$P(E)NP(E)Ph$_2$-*E*,*E*′}] [E = S (**11**); E = Se (**12**)] (see Tables 1 and 2 and Section 2 for characterising data).

This general procedure was extended to the synthesis of [PtCl{Ph$_2$P(E)NP(O)Ph$_2$-*E*,*O*}(PMe$_2$Ph)] [E = S (**13**); E = Se (**14**)] and [Pd(C$_9$H$_{15}$O){Ph$_2$P(E)NP(O)Ph$_2$-*E*,*O*}] [E = S (**15**); E = Se (**16**)] in yields ranging from 67–92% (Scheme 2). Spectroscopic and analytical data are given in Tables 1 and 2 and Section 2. The NMR data reveal, in all cases, the presence of one isomer in solution [25]. In the platinum(II) complexes **13** and **14** *J*(PtP) are very similar (3968 Hz for **13**; 3984 Hz for **14**) suggesting that the PMe$_2$Ph ligand is *trans* to the same donor atom (i.e. oxygen). The ^{195}Pt{^{1}H} NMR spectra show a doublet-of-doublets at δ(Pt) −3817 ppm (**13**) and −3915 (**14**) ppm.

In conclusion, mixed palladium(II) and platinum(II) complexes with Ph$_2$PNHP(O)Ph$_2$, [Ph$_2$PNP(O)Ph$_2$]$^-$ or [Ph$_2$P(E)NP(O)Ph$_2$]$^-$ and various ancillary ligands can be conveniently made.

4. Supplementary material

The crystallographic data of the structures described in this publication have been deposited with the Cambridge Crystallographic Data Centre as CCDC numbers 128062 (**4**) and 128063 (**7**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@cam.ac.uk or www:http://www.ccdc.cam.ac.uk). The information comprises atomic coordinates, anisotropic displacement parameters, listings of bond lengths and angles and hydrogen atom coordinates.

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