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New platinum(II) complexes of $Ph_2PNHP(O)Ph_2$ and $[Ph_2PNP(O)Ph_2]^-$

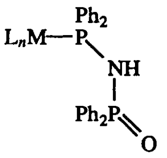
Alexandra M. Z. Slawin, Martin B. Smith and J. Derek Woollins *

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

Refluxing a suspension of *cis*-$[PtCl_2(HL)_2]$ [HL = $Ph_2PNHP(O)Ph_2$-*P*] in methanol for *ca.* 11 h led to Ph_2P–N bond cleavage of one of the HL ligands and formation of *cis*-$[PtCl_2(HL)(Ph_2POMe)]$ **1**. Prolonged refluxing of **1** in methanol (5 d) gave predominantly unchanged **1** in addition to some *cis*-$[PtCl_2(Ph_2POMe)_2]$ **2** and *cis*-$[PtCl(L)(Ph_2POMe)]$ **3** [L = $Ph_2PNP(O)Ph_2$-*P*,*O*]. Reaction of **1** with $KOBu^t$ afforded solely **3** in good yield. Bridge cleavage of $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ with 2 equivalents of HL gave *trans*-$[PtCl_2(HL)(PMe_2Ph)]$ **4a** which is smoothly isomerised to *cis*-$[PtCl_2(HL)(PMe_2Ph)]$ **4b** upon addition of trace amounts of HL. Complexes **4a** and **4b** reacted with $KOBu^t$ (*ca.* 1.4 equivalents) in methanol to yield *trans*- and *cis*-$[PtCl(L)(PMe_2Ph)]$ **5a** and **5b** respectively. Chloride abstraction of either **4a** or **4b** with $Ag[BF_4]$ in dichloromethane yielded the *P*,*O*-chelate cationic complexes *trans*- (**6a**) or *cis*-$[PtCl(HL)(PMe_2Ph)][BF_4]$ **6b** respectively. Further reaction of **5b** with $KOBu^t$ in methanol gave the hydroxide-bridged platinum(II) dimer $[\{Pt(\mu\text{-}OH)L(PMe_2Ph)\}_2]$ **7** in which the P-donor atom in L is co-ordinated to the platinum(II) centre and the O-donor atom is involved in an intramolecular hydrogen bond to the hydroxide ligand (X-ray evidence). All the compounds **1**–**7** have been characterised by a combination of $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ NMR, IR spectroscopy and microanalysis. Furthermore the solid-state structures of *cis*-$[PtCl_2(HL)(PMe_2Ph)]$, the geometric isomers *trans*- and *cis*-$[PtCl(L)(PMe_2Ph)]$ and $[\{Pt(\mu\text{-}OH)L(PMe_2Ph)\}_2]$ have been determined by single-crystal X-ray diffraction.

Previous work by ourselves[1–3] and others[4–6] has shown that a rich co-ordination chemistry exists for the versatile heterodifunctional compound $Ph_2PNHP(O)Ph_2$ (HL) closely related to the methylene-bridged monooxide $Ph_2PCH_2P(O)Ph_2$.[7–18] Transition-metal complexes of HL and $[Ph_2PNP(O)Ph_2]^-$ (L) exhibit several different bonding modes (types I–V) in which one or both of the P,O donor atoms are used in complexation as identified by solution and solid-state studies. Furthermore we recently described the synthesis and characterisation of the unusual palladium(II) complex $[PdCl\{Ph_2PNP(O)Ph_2\text{-}P,O\}(Ph_2POMe)]$ **A** prepared from the reaction of the cyclometallated dimer $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}o\text{-}C,N)\}_2]$ and 4 equivalents of HL in MeOH at ambient temperature.[1] In contrast, when the reaction was carried out in the same solvent using 2 equivalents of HL, $[\{Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}o\text{-}C,N)\}_2]$ and $KOBu^t$, we obtained $[Pd(C_6H_4CH_2NMe_2\text{-}o\text{-}C,N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ **B** in high yield.[1] The phosphinite ligand, Ph_2POMe, in compound **A** is presumably derived from methanolysis of a Ph_2P–N bond of an intermediate metal complex containing a HL ligand. Although we have not studied the mechanism of this reaction, a similar Ph_2P–N cleavage reaction has been observed[19] in the dication $[Pt(dppma)_2]^{2+}$ [dppma = bis(diphenylphosphino)methylamine, $Ph_2PN(Me)PPh_2$] but surprisingly $[Pt(dppa)_2]^{2+}$ [dppa = bis(diphenylphosphino)amine, $Ph_2PN(H)PPh_2$] shows no reaction under comparable experimental conditions. Krishnamurthy and co-workers[20] recently reported the facile Ph_2P–N bond cleavage in unsymmetrical diphosphazene complexes of palladium(II).

We report here our studies on the methanolysis reaction of *cis*-$[PtCl_2(HL)_2]$ which affords the mixed phosphorus-donor ligand platinum(II) complex *cis*-$[PtCl_2(HL)(Ph_2POMe)]$. Moreover the synthesis and characterisation of both isomers of $[PtCl_2(HL)(PMe_2Ph)]$ are described, the *trans* isomer being readily accessible from the facile bridge-cleavage reaction of $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ with HL. Both geometric isomers of the platinacycles $[PtCl(L)(PMe_2Ph)]$ and $[PtCl(HL)(PMe_2Ph)][BF_4]$ have been synthesized using similar procedures to those detailed previously for $[M\{Ph_2PNP(O)Ph_2\text{-}P,O\}_2]$ and $[M\{Ph_2PNHP(O)Ph_2\text{-}P,O\}_2][BF_4]_2$ (M = Pt or Pd).[3]



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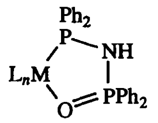

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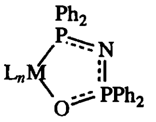

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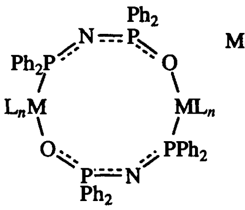

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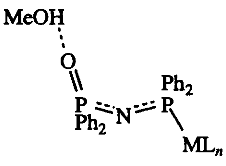

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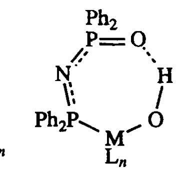

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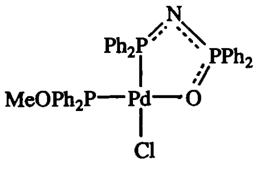

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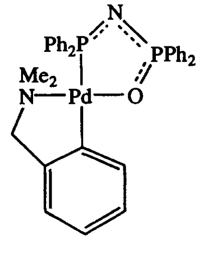

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The formation of a novel platinum(II) dimer $[\{Pt(\mu\text{-}OH)L(PMe_2Ph)\}_2]$ containing an unusual intramolecular hydrogen bond between the 'free' P=O group and the bridging hydroxide ligand (Type VI) is also described.

Experimental

General

All reactions were carried out in air using distilled solvents. The compound $Ph_2PNHP(O)Ph_2$ (HL) and the platinum(II) complexes *cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}_2$] and [$\{PtCl(\mu$-$Cl)(PMe_2Ph)\}_2$] were prepared according to previous published procedures.[3,21] The reagents Ag[BF_4], $KOBu^t$ (95% purity), NEt_3 and $HBF_4 \cdot OEt_2$ (85% in diethyl ether) were obtained from the Aldrich Chemical Company 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, ^{31}P-$\{^1H\}$ NMR spectra (36.2 MHz) on a JEOL FX90Q spectrometer with chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4 and coupling constants (*J*) in Hz (± 3) and ^{195}Pt-$\{^1H\}$ NMR spectra (53.7 MHz) on a Bruker AC250 FT spectrometer with δ referenced to external H_2PtCl_6 (in D_2O–HCl). All NMR spectra were measured in $CDCl_3$. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Platinum salts were provided on loan by Johnson Matthey plc.

Preparation of the complexes

***cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(Ph_2POMe)$] 1.** A suspension of *cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}_2$] (0.207 g, 0.194 mmol) in MeOH (15 cm^3, HPLC grade) was refluxed for *ca.* 11 h. The solution was filtered to remove a small amount of solid material and the filtrate reduced to dryness *in vacuo*. Extraction with CH_2Cl_2 (3×1 cm^3) followed by filtration and addition of diethyl ether (15 cm^3) afforded a white solid. Yield 0.120 g, 70% [Found (Calc. for $C_{37}H_{34}Cl_2NO_2P_3Pt$): C, 49.95 (50.3); H, 3.75 (3.9); N, 1.5 (1.6)%]. Selected IR data (KBr): 3112 [ν(N–H)], 1223 [ν(P=O)] and 312, 283 cm^{-1} [ν(Pt–Cl)].

The filtrate was left to stand for *ca.* 1 d and the solution decanted from a small amount of solid that deposited. Evaporation of the solvent to dryness *in vacuo* and examination of the residue by ^{31}P-$\{^1H\}$ NMR spectroscopy showed the presence of two phosphorus-containing species identified as $Ph_2P(O)NH_2$ and $Ph_2P(O)OMe$ (*ca.* 5:1 ratio respectively, based on integration).

Methanolysis of complex 1. A MeOH (5 cm^3) solution of *cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(Ph_2POMe)$] (0.020 g, 0.023 mmol) was refluxed for 5 d and the colourless solution evaporated to dryness under reduced pressure. Examination of the residue by ^{31}P-$\{^1H\}$ NMR spectroscopy showed that only small amounts (< 10%) of *cis*-[$PtCl_2(Ph_2POMe)_2$] **2** were present in addition to several other species.

***cis*-[$PtCl\{Ph_2PNP(O)Ph_2$-*P*,*O*$\}(Ph_2POMe)$] 3.** To a suspension of *cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(Ph_2POMe)$] (0.101 g, 0.114 mmol) in MeOH (1 cm^3) was added solid $KOBu^t$ (0.015 g, 0.134 mmol). The mixture was stirred for 5 min, filtered and the white solid **3** washed with MeOH (2×0.5 cm^3). Yield 0.078 g, 81% [Found (Calc. for $C_{37}H_{33}ClNO_2P_3Pt$): C, 51.7 (52.45); H, 4.25 (3.95); N, 1.5 (1.65)%]. Selected IR data (KBr): 297 cm^{-1} [ν(Pt–Cl)].

***trans*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] 4a.** To a solution of [$\{PtCl(\mu$-$Cl)(PMe_2Ph)\}_2$] (0.100 g, 0.124 mmol) in dichloromethane (40 cm^3) was added dropwise over *ca.* 10 min a solution of $Ph_2PNHP(O)Ph_2$ (0.100 g, 0.249 mmol) in dichloromethane (20 cm^3). After stirring for 5 min the solution was concentrated under reduced pressure to *ca.* 2 cm^3 and addition of diethyl ether (50 cm^3) afforded the product **4a** as a pale yellow solid. Yield 0.177 g, 89% [Found (Calc. for $C_{32}H_{32}Cl_2NOP_3Pt$): C, 47.75 (47.7); H, 3.6 (4.0); N, 1.55 (1.75)%]. Selected IR data (KBr): 3173 [ν(N–H)], 1218 [ν(P=O)] and 320 cm^{-1} [ν(Pt–Cl)].

***cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] 4b.** To a dichloromethane solution (2 cm^3) of *trans*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] (0.165 g, 0.205 mmol) was added solid $Ph_2PNHP(O)Ph_2$ (< 0.005 g). After stirring for *ca.* 5 min, diethyl ether (15 cm^3) was added and the solid filtered off, washed with diethyl ether (5 cm^3) and dried *in vacuo*. Crude yield 0.157 g, 95% [Found (Calc. for $C_{32}H_{32}Cl_2NOP_3Pt$): C, 47.05 (47.7); H, 3.5 (4.0); N, 1.65 (1.75)%]. Selected IR data (KBr): 3119 [ν(N–H)], 1221 [ν(P=O)], 310 and 287 cm^{-1} [ν(Pt–Cl)]. The product was frequently contaminated with *cis*-[$PtCl_2(PMe_2Ph)_2$] (*ca.* 5%) which was readily identified by comparison of the ^{31}P NMR spectral parameters with those of an authentic sample. Crystals of **4b** suitable for X-ray crystallography were grown over *ca.* 1 d by slow diffusion of diethyl ether into a $CDCl_3$ solution.

***trans*-[$PtCl\{Ph_2PNP(O)Ph_2$-*P*,*O*$\}(PMe_2Ph)$] 5a.** A suspension of *trans*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] (0.101 g, 0.125 mmol) in MeOH (1 cm^3) was treated with $KOBu^t$ (0.020 g, 0.178 mmol). The suspension dissolved rapidly and the resultant yellow solution was stirred for *ca.* 5 min whereupon the solid product deposited. The solid was collected by suction filtration, washed with MeOH (2×0.5 cm^3 portions) and dried *in vacuo*. Yield 0.060 g. An additional crop of **5a** was collected from the filtrate. Yield 0.026 g, overall yield 89% [Found (Calc. for $C_{32}H_{31}ClNOP_3Pt$): C, 49.35 (49.95); H, 3.3 (4.05); N, 1.9 (1.8)%]. Selected IR data (KBr): 316 cm^{-1} [ν(Pt–Cl)]. Crystals of **5a** suitable for X-ray crystallography were grown over *ca.* 5 d by slow diffusion of diethyl ether into a $CDCl_3$ solution.

***cis*-[$PtCl\{Ph_2PNP(O)Ph_2$-*P*,*O*$\}(PMe_2Ph)$] 5b.** To a suspension of *cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] (0.100 g, 0.124 mmol) in MeOH (2 cm^3) was added $KOBu^t$ (0.020 g, 0.178 mmol) and the white mixture stirred for 5 min. The product was filtered off by suction filtration and dried *in vacuo*. Yield 0.084 g, 88% [Found (Calc. for $C_{32}H_{31}ClNOP_3Pt$): C, 49.4 (49.95); H, 3.65 (4.05); N, 1.8 (1.8)%]. Selected IR data (KBr): 292 cm^{-1} [ν(Pt–Cl)]. Slow diffusion of MeOH into a $CDCl_3$ solution of **5b** over the course of *ca.* 7 d gave crystals suitable for X-ray crystallography.

***trans*-[$PtCl\{Ph_2PNHP(O)Ph_2$-*P*,*O*$\}(PMe_2Ph)$][BF_4] 6a.** To a solution of *trans*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] (0.080 g, 0.099 mmol) in CH_2Cl_2 (20 cm^3) was added solid Ag[BF_4] (0.019 g, 0.098 mmol, *ca.* 1 equivalent). After stirring for 3 h the AgCl was filtered off through a small Celite plug, the solution concentrated by evaporation under reduced pressure to *ca.* 1–2 cm^3 and diethyl ether (50 cm^3) added. The yellow product was collected by suction filtration, washed with diethyl ether (10 cm^3) and dried *in vacuo*. Yield 0.065 g, 76% [Found (Calc. for $C_{32}H_{32}BClF_4NOP_3Pt$): C, 44.7 (44.85); H, 3.15 (3.75); N, 1.3 (1.65)%]. Selected IR data (KBr): 3145 [ν(N–H)] and 321 cm^{-1} [ν(Pt–Cl)].

***cis*-[$PtCl\{Ph_2PNHP(O)Ph_2$-*P*,*O*$\}(PMe_2Ph)$][BF_4] 6b.** A solution of *cis*-[$PtCl_2\{Ph_2PNHP(O)Ph_2$-*P*$\}(PMe_2Ph)$] (0.079 g, 0.098 mmol) in CH_2Cl_2 (20 cm^3) was treated with solid Ag[BF_4] (0.019 g, 0.098 mmol, 1 equivalent). After stirring for 2 h the AgCl was removed by filtration through a small Celite pad, the solution concentrated by evaporation under reduced pressure to *ca.* 1–2 cm^3 and diethyl ether (30 cm^3) added. The white product was collected by suction filtration and dried *in vacuo*. Yield 0.055 g, 65% [Found (Calc. for $C_{32}H_{32}BClF_4NOP_3Pt$): C, 44.65 (44.85); H, 3.15 (3.75); N, 1.5 (1.65)%].

Selected IR data (KBr): 3129 [ν(N–H)] and 316 cm^{-1} [ν(Pt–Cl)].

Alternatively, compound **6a** was obtained (^{31}P NMR evidence) by addition of $HBF_4{\cdot}OEt_2$ (two drops) to a $CDCl_3$ (0.5 cm^3) solution of *trans*-[PtCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(PMe_2Ph)] (0.020 g, 0.026 mmol). Compound **6b** was likewise prepared.

[{Pt(μ-OH){$Ph_2PNP(O)Ph_2$-*P*}(PMe_2Ph)}$_2$] 7. A suspension of *cis*-[PtCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(PMe_2Ph)] (0.054 g, 0.0702 mmol) in wet MeOH (1 cm^3) was treated with solid $KOBu^t$ (0.012 g, 0.107 mmol). After stirring for *ca.* 16 h the product was filtered off, washed with MeOH and dried *in vacuo*. Yield 0.039 g, 74% [Found (Calc. for $C_{64}H_{64}N_2O_4P_6Pt_2$): C, 49.55 (51.2); H, 4.05 (4.3); N, 1.7 (1.85)%]. Slow diffusion of diethyl ether into a $CDCl_3$ solution of **7** over *ca.* 2 d gave crystals suitable for X-ray crystallography.

The NMR spectroscopic data for all the new complexes are compiled in Table 1.

X-Ray crystallography

The crystal structures of complexes **4b**, **5a**, **5b** and **7** were determined using a Rigaku AFC7S diffractometer with graphite-monochromated (Cu-Kα) radiation (λ = 1.541 78 Å) and ω scans. Details of the data collections and refinements are given in Table 2. Empirical absorption corrections (DIFABS)[22] were applied. The structures were solved by the heavy-atom method[23] and all of the non-hydrogen atoms refined anisotropically. The H on O(1) in compound **7** was located from a Δ*F* map and allowed to refine isotropically with no distance restraint. All other H atoms were idealised and fixed (C, N–H 0.95 Å). No additional constraints or restraints were applied. Refinement was by full-matrix least-squares methods. Calculations were performed using TEXSAN.[24]

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.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/251.

Results and Discussion

Methanolysis of *cis*-[PtCl$_2${$Ph_2PNHP(O)Ph_2$-*P*}$_2$]

When a suspension of *cis*-[PtCl$_2${$Ph_2PNHP(O)Ph_2$-*P*}$_2$] is refluxed in methanol for *ca.* 11 h the white solid slowly dissolves affording a colourless solution from which the platinum(II) complex *cis*-[PtCl$_2${$Ph_2PNHP(O)Ph_2$-*P*}(Ph_2POMe)] **1** was isolated in 70% yield. Mixed-ligand phosphine complexes of platinum(II) and palladium(II) have previously been documented.[25–27] The ^{31}P-{^{1}H} NMR spectrum of **1** is particularly informative and shows a high-frequency resonance at δ(P) 80.4 [^1J(PtP) 4333 Hz], assigned to the co-ordinated Ph_2POMe, which is similar to δ(P) 85.6 [^1J(PtP) 4175 Hz] recorded for *cis*-[PtCl$_2$(Ph_2POMe)$_2$] **2**.[3] Likewise δ(P) 36.4 for the co-ordinated $Ph_2PNHP(O)Ph_2$ in **1** is comparable to that observed for *cis*-[PtCl$_2${$Ph_2PNHP(O)Ph_2$-*P*}$_2$] (δ 35.7).[3] In addition the ^{31}P NMR spectrum of **1** is in good agreement with a mutual *cis* configuration of ligands, especially diagnostic is the small *J*(PP) value of 13.2 Hz, and is further supported by the IR spectrum (KBr) which clearly shows two ν(Pt–Cl) stretches at 312 and 283 cm^{-1}. Upon work-up of the filtrate we have isolated two phosphorus(V)-containing compounds which have been identified as $Ph_2P(O)NH_2$ **I** [δ(P) 22.3] and $Ph_2P(O)OMe$ **II** [δ(P) 33.2]. Compound **II** was independently synthesized by H_2O_2 oxidation of Ph_2POMe. The amine product **I** is as anticipated from methanolysis of the metal-co-ordinated Ph_2P–N bond whereas **II** is presumably derived from cleavage of the $Ph_2P(O)$–N bond. We have not been able to identify any other platinum(II) species such as those containing a Ph_2PNH_2 ligand but related complexes [Pt{$Ph_2PN(Me)PPh_2$}(Ph_2PNHMe)(Ph_2POMe)]$^{2+}$ and [PdCl$_2${PhP($NHPr^i$)($OC_6H_3Me_2$-3,5}(Ph_2POMe)] are known.[19,20] We have shown that **II** is not derived from dissociation of Ph_2POMe in **1** followed by oxidation. Under identical experimental conditions using **2** instead we were unable to detect any **II** (^{31}P NMR evidence).

In contrast when an oxygen-free methanol solution of free HL was refluxed for 10 h, then evaporated to dryness *in vacuo*, the ^{31}P-{^{1}H} NMR spectrum of the residue showed only trace amounts of **I** and **II** in addition to unreacted HL.

Further refluxing (5 d) a methanol solution of complex **1** affords insignificant amounts of **2** (< 10%), as a consequence of Ph_2P–N bond cleavage of the second HL ligand, in addition to another platinum(II) species identified as *cis*-[PtCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(Ph_2POMe)] **3**. Surprisingly the cleavage of this second Ph_2P–N bond to give **2** is remarkably slow. More conveniently, **3** can be prepared in good yield (81%) by deprotonation of the amine proton in **1** with $KOBu^t$ (spectroscopic data in Table 1 and Experimental section).

Preliminary studies have shown that the corresponding palladium(II) compound [PdCl$_2${$Ph_2PNHP(O)Ph_2$-*P*}$_2$] undergoes similar chemistry in refluxing methanol although reduced reflux times (*ca.* 6 h) are required. Moreover we also observe the formation of palladium metal in addition to *cis*-[PdCl$_2$(Ph_2POMe)$_2$], $Ph_2P(O)NH_2$, $Ph_2P(O)OMe$ and other uncharacterised products.

Preparation of [PtCl$_2${$Ph_2PNHP(O)Ph_2$-*P*}(PMe_2Ph)] complexes

Whilst the synthesis of the mixed-ligand complex **1** discussed above represents a rather unusual reaction we sought a more general route to complexes of the type [PtCl$_2$(HL)(PR_3)]. We found that bridge cleavage of the platinum dimer [{PtCl(μ-Cl)(PMe_2Ph)}$_2$] with HL in dichloromethane affords the yellow unsymmetrical complex *trans*-[PtCl$_2$(HL)(PMe_2Ph)] **4a**. Isomerisation upon addition of a small amount of HL to a CH_2Cl_2 solution of **4a** gives *cis*-[PtCl$_2$(HL)(PMe_2Ph)] **4b** (Scheme 1), whereas in the absence of added HL no isomerisation was observed even after allowing a $CDCl_3$ solution to stand for over 1 month at ambient temperature. The ^{31}P-{^{1}H} NMR spectrum of **4a** is particularly informative and reveals a large phosphorus–phosphorus coupling constant indicative of a structure with a mutual *trans* arrangement of monodentate phosphine ligands. Furthermore the chemical shifts of the pendant P=O groups in **4a** [δ(P) 21.6] and **4b** [δ(P) 22.2] are similar to those observed in free HL [δ(P) 21.4][3] indicating no interaction of the phosphoryl moiety with the platinum centre. This is also reflected from both ambient (298 K) and low-temperature (213 K) ^{31}P NMR spectra (CD_2Cl_2) of **4a** and **4b** which showed sharp resonances with no significant change in line shape. Suitable crystals of complex **4b** were grown by slow diffusion of diethyl ether into a $CDCl_3$ solution and the molecular structure is shown in Fig. 1 (Table 3). The crystal structure reveals square-planar co-ordination of the platinum [maximum deviation from the Pt–Cl(1)–Cl(2)–P(2)–P(3) mean plane 0.10 Å for Cl(1)] with the P–N–P backbone of $Ph_2PNHP(O)Ph_2$ being inclined by 28° to the co-ordination plane. The P–N–P angle in the ligand is 134.2(3)° and the P(1)–N and P(2)–N distances are 1.661(4) and 1.684(5) Å respectively. There is an intramolecular hydrogen bond between Cl(2) and H(1) (Cl ··· H 2.14 Å). This type of hydrogen bond was also observed in the rhodium(I) complex [RhCl(cod){$Ph_2PNHP(O)Ph_2$-*P*}] (cod = cycloocta-1,5-diene) and the platinum(II) complex *cis*-[PtBr$_2${$Ph_2PNHP(O)Ph_2$-*P*}$_2$].[1,3] In common with previous structures the NH proton is *anti* with

Table 1 The ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} NMR data (δ, *J*/Hz) for compounds **1**–**7**[a]

Compound	δ(P_A)	δ(P_B)	δ(P_C)	*J*(P_AP_B)	*J*(P_AP_C)	*J*(P_BP_C)	δ(Pt)
1	36.4 (3963)	22.8 (110)	80.4 (4333)	26.4	13.2	33.7	−4324
3	48.6 (3400)	69.3 (138.6)	77.7 (5010)	13.2	13.2		−4229
4a	42.7 (2657)	21.6 (79.2)	−9.1 (2481)	33.9	522	11	−4016
4b	36.1 (3915)	22.2 (101.2)	−16.8 (3550)	26.4	17.6		−4402
5a	53.1 (2480)	83.7 (44)	−5.1 (2422)	35.8	475	41.1	−3554
5b	46.5 (3383)	68.6 (132)	−24.7 (4025)	8.8	13.2		−4280
6a	55.8 (2516)	74.9 n.r.[b]	−5.0 (2600)	30.9	480	22.1	−3538
6b	51.9 (3656)	62.6 n.r.	−23.1 (3770)	17.6	17.6		−4310
7	7.1 (3466)	21.0 (52.8)	−15.4 (3831)	13.2	17.6		−3770

[a] P_A = Pt–PPh_2, P_B = P(O)Ph_2, P_C = Ph_2POMe or PMe_2Ph. Values in parentheses denote *J*(PtP)/Hz. [b] n.r. = Not resolved.

Table 2 Details of the X-ray data collections and refinements for compounds **4b**, **5a**, **5b** and **7**

	4b	**5a**	**5b**	**7**
Empirical formula	$C_{32}H_{32}Cl_2NOP_3Pt$	$C_{32}H_{31}ClNOP_3Pt$	$C_{32}H_{31}ClNOP_3Pt{\cdot}CHCl_3$	$C_{64}H_{64}N_2O_4P_6Pt_2$
M	805.53	769.07	888.45	1501.24
Crystal colour, habit	Clear, needle	Yellow, prism	Clear, hexagon	Clear, block
Crystal dimensions/mm	0.08 × 0.10 × 0.33	0.20 × 0.23 × 0.43	0.13 × 0.24 × 0.36	0.20 × 0.20 × 0.20
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	11.302(2)	12.017(4)	14.893(3)	12.061(5)
b/Å	14.268(2)	14.934(3)	16.679(2)	18.695(3)
c/Å	10.689(1)	8.930(3)	15.916(3)	14.044(3)
α/°	90.48(1)	92.90(2)		
β/°	108.90(1)	104.87(3)	116.51(9)	107.12(2)
γ/°	98.11(1)	84.52(2)		
U/Å^3	1612	1541	3538	3026
Z	2	2	4	2
D_c/g cm^{-3}	1.66	1.66	1.67	1.65
μ/mm^{-1}	11.44	10.66	11.42	10.08
$2\theta_{max}$/°	120.2	120.0	120.2	120.2
F(000)	792	756	1744	1480
Measured reflections	5056	4819	5710	4911
Independent reflections (R_{int})	4775 (0.070)	4565 (0.118)	5477 (0.086)	4677 (0.263)
Observed reflections [$I > 2.00\sigma(I)$]	4357	4283	4658	3535
Reflection parameter ratio	12.0:1	12.13:1	11.97:1	9.90:1
Minimum, maximum transmission	0.72, 1.00	0.68, 1.00	0.63, 1.00	0.59, 1.00
p in weighting scheme	0.000	0.003	0.004	0.002
No. variables	362	353	389	357
Final *R*,*R'*	0.029, 0.029	0.033, 0.034	0.044, 0.042	0.049, 0.047
Maximum Δ/σ	0.02	0.11	0.38	0.29
Largest difference peak, hole/e Å^{-3}	0.85, −1.00	1.38, −1.63	1.70, −1.65	2.01, −1.75

Table 3 Selected bond lengths (Å) and angles (°) for complex **4b**

Pt–Cl(1)	2.353(2)	Pt–Cl(2)	2.360(2)
Pt–P(2)	2.243(1)	Pt–P(3)	2.251(2)
P(1)–O	1.473(4)	P(1)–N	1.661(4)
P(2)–N	1.684(5)		
Cl(1)–Pt–Cl(2)	86.90(6)	Cl(1)–Pt–P(2)	174.54(6)
Cl(1)–Pt–P(3)	85.57(6)	Cl(2)–Pt–P(2)	90.01(5)
Cl(2)–Pt–P(3)	172.30(6)	P(2)–Pt–P(3)	97.62(6)
O–P(1)–N	114.2(3)	Pt–P(2)–N	108.9(2)
P(1)–N–P(2)	134.2(3)		

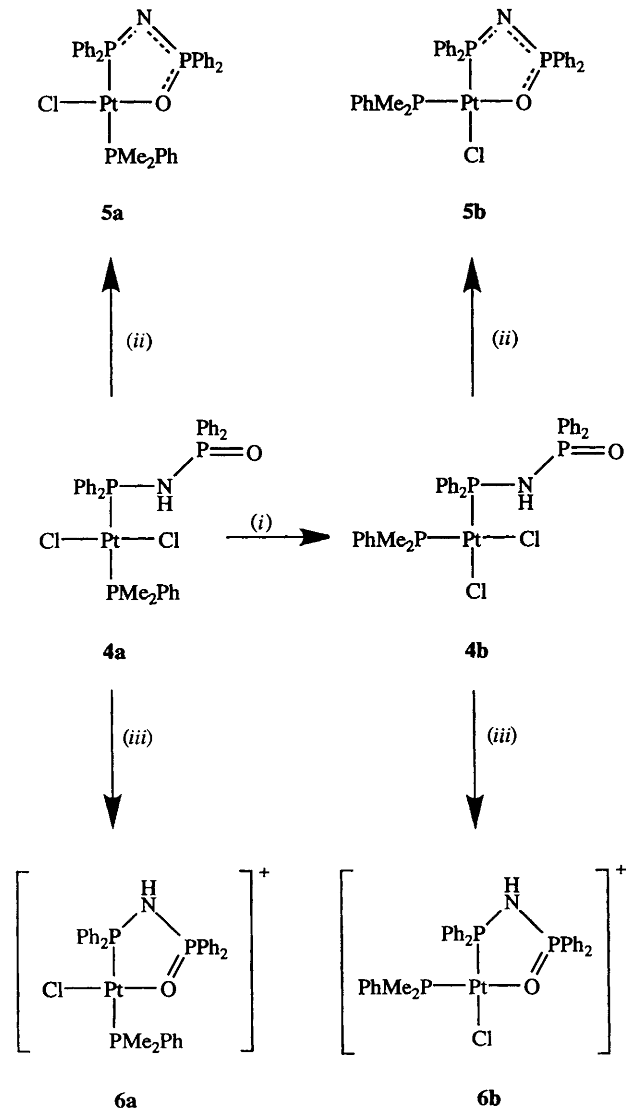
Table 4 Selected bond lengths (Å) and angles (°) for complexes **5a** and **5b**

	5a	**5b**
Pt–Cl	2.289(2)	2.361(2)
Pt–P(2)	2.297(2)	2.240(2)
Pt–P(3)	2.317(2)	2.214(2)
Pt–O	2.038(4)	2.098(5)
P(1)–O	1.540(5)	1.539(5)
P(1)–N	1.599(5)	1.591(6)
P(2)–N	1.637(5)	1.620(6)
Cl–Pt–P(2)	95.01(6)	170.25(8)
Cl–Pt–P(3)	90.57(7)	88.89(8)
Cl–Pt–O	176.4(1)	85.7(1)
P(2)–Pt–P(3)	173.74(6)	100.43(8)
P(2)–Pt–O	84.6(1)	85.0(1)
P(3)–Pt–O	90.0(1)	174.5(1)
O–P(1)–N	115.2(3)	113.1(3)
Pt–P(2)–N	107.7(2)	107.2(2)
Pt–O–P(1)	116.3(2)	115.4(3)
P(1)–N–P(2)	113.0(3)	114.3(4)

respect to the P=O oxygen atom in the co-ordination complex.[1,3,4]

Preparation of [PtCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(PMe_2Ph)] and [PtCl{$Ph_2PNHP(O)Ph_2$-*P*,*O*}(PMe_2Ph)][BF_4] complexes

Since the amine proton in complex **4a** or **4b** is acidic, treatment with $KOBu^t$ in methanol affords the five-membered chelate complexes [PtCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(PMe_2Ph)] **5a** (P *trans* to P) and **5b** (P *cis* to P) respectively (Scheme 1). Alternatively dechlorination of **4a** or **4b** with Ag[BF_4] (1 equivalent) in CH_2Cl_2 gave the cationic complexes [PtCl{$Ph_2PNHP(O)Ph_2$-*P*,*O*}(PMe_2Ph)][BF_4] **6a** (*trans*) and **6b** (*cis*) (Scheme 1). Deprotonation of the amine proton in either **6a** or **6b** with NEt_3 (in $CDCl_3$) gave exclusively **5a** or **5b** respectively, whilst in separate experiments protonation of **5a** or **5b** with $HBF_4{\cdot}OEt_2$ afforded **6a** or **6b**. In the complexes **5a**–**6b** retention of configuration was retained as indicated by ^{31}P-{^{1}H} NMR spectroscopy (Table 1). The high-frequency shift of the P=O



Scheme 1 (*i*) HL, CH_2Cl_2; (*ii*) $\mathrm{KOBu^t}$, MeOH; (*iii*) $\mathrm{Ag[BF_4]}$, CH_2Cl_2

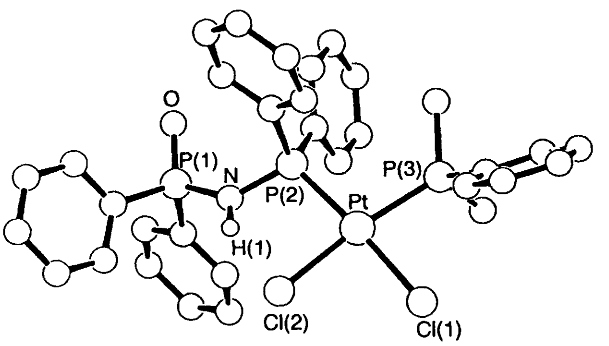


Fig. 1 Crystal structure of *cis*-$[\mathrm{PtCl_2\{Ph_2PNHP(O)Ph_2\text{-}\mathit{P}\}(PMe_2Ph)}]$ **4b**

group upon chelation is probably due to the chelate-ring effect. The crystal structures of **5a** and **5b** allow the stereochemistry to be determined unequivocally. Thus **5a** contains *trans* P atoms (Fig. 2 and Table 4) whilst **5c** is *cis* (Fig. 3 and Table 4). Both **5a** and **5b** are square planar at platinum [maximum deviations from Pt–Cl–P(2)–O–P(3) mean plane 0.12 (O) and 0.06 Å (Cl) for **5a** and **5b** respectively]. The five-membered rings in both structures are slightly puckered with O lying 0.23 Å below the Pt–P(2)–N–P(1)–O mean plane in **5a** and N lying 0.28 Å above the mean plane in **5b**. The P–N bond lengths are significantly different, P(1)–N [1.599(5) and 1.591(6) Å for **5a** and **5b**] being shorter than P(2)–N [1.637(5) and 1.620(6) Å for **5a** and **5b**] in both structures though both bonds are shorter than in free HL [1.651(3) and 1.707(3) Å respectively] and in **4b** [1.661(4) and 1.684(5) Å respectively]. As would be expected the differences in *trans* ligand affect all of the metal donor-atom bond lengths. In **5a** both Pt–P bonds are significantly longer than those in **5b** since the P atoms are *trans* to each other in **5a**. Furthermore the Pt–Cl and Pt–O bonds in **5b** are longer than in **5a** [Pt–Cl 2.289(2) and 2.361(2) and Pt–O 2.038(4) and 2.098(5) Å respectively].

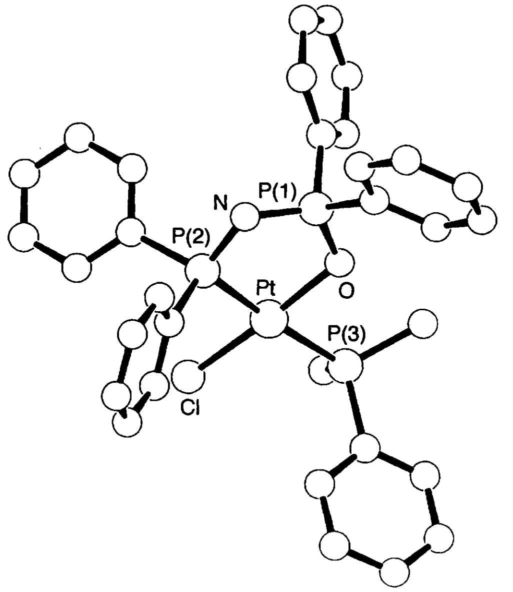


Fig. 2 Crystal structure of *trans*-$[\mathrm{PtCl\{Ph_2PNP(O)Ph_2\text{-}\mathit{P,O}\}(PMe_2Ph)}]$ **5a**

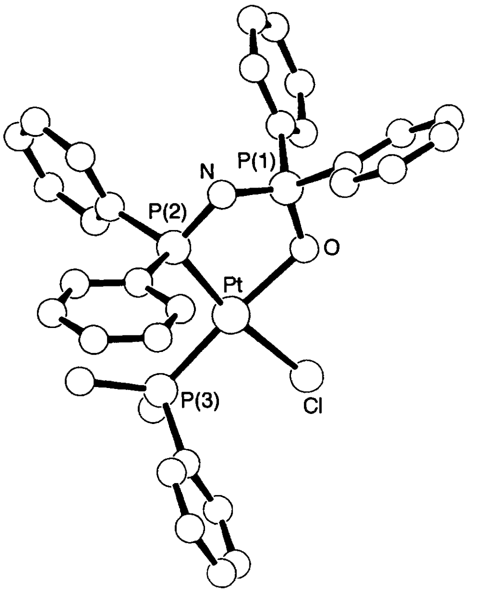


Fig. 3 Crystal structure of *cis*-$[\mathrm{PtCl\{Ph_2PNP(O)Ph_2\text{-}\mathit{P,O}\}(PMe_2Ph)}]$ **5b** (solvent molecule omitted for clarity)

Reaction of *cis*-$[\mathrm{PtCl\{Ph_2PNP(O)Ph_2\text{-}\mathit{P,O}\}(PMe_2Ph)}]$ with $\mathrm{KOBu^t}$

When a suspension of complex **5b** in wet (*i.e.* undried) methanol was treated with $\mathrm{KOBu^t}$ (*ca.* 1.5 equivalents) and stirred for 16 h at ambient temperature a new white solid **7** was isolated. In the

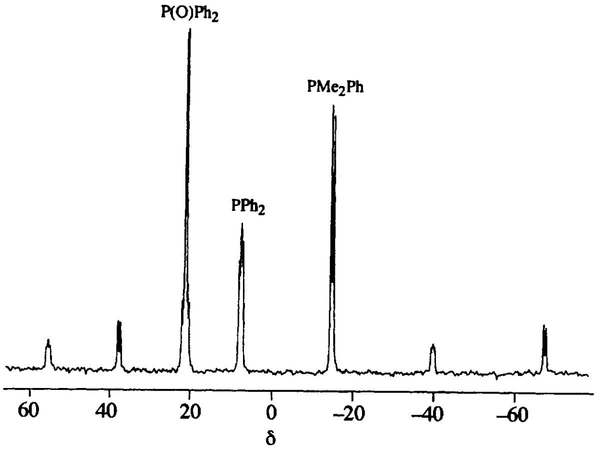


Fig. 4 The ^{31}P-{^{1}H} NMR spectrum (36.2 MHz) of $[\{Pt(\mu\text{-}OH)\{Ph_2PNP(O)Ph_2\text{-}P\}(PMe_2Ph)\}_2]$ **7**

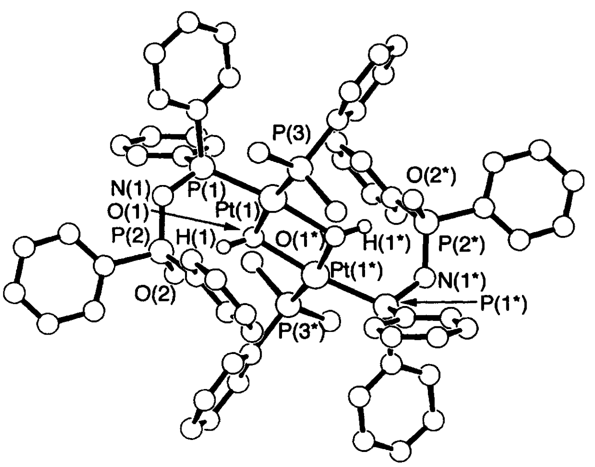


Fig. 5 Crystal structure of $[\{Pt(\mu\text{-}OH)\{Ph_2PNP(O)Ph_2\text{-}P\}(PMe_2Ph)\}_2]$ **7**

Table 5 Selected bond lengths (Å) and angles (°) for complex **7**

Pt(1)–P(1)	2.220(2)	Pt(1)–P(3)	2.224(3)
Pt(1)–O(1)	2.096(7)	Pt(1)–O(1*)	2.102(6)
P(1)–N(1)	1.585(10)	P(2)–O(2)	1.481(7)
P(2)–N(1)	1.619(8)	O(1)–H(1)	0.97(10)
P(1)–Pt(1)–P(3)	97.86(10)	P(1)–Pt(1)–O(1)	89.9(2)
P(1)–Pt(1)–O(1*)	169.9(2)	P(3)–Pt(1)–O(1)	169.7(2)
P(3)–Pt(1)–O(1*)	91.7(2)	O(1)–Pt(1)–O(1*)	80.2(3)
Pt(1)–P(1)–N(1)	116.8(3)	O(2)–P(2)–N(1)	119.3(5)
Pt(1)–O(1)–Pt(1*)	99.8(3)	P(1)–N(1)–P(2)	121.2(5)

The two halves of the molecule are related by the symmetry operation $-x, -y, 1 - z$.

analogous reaction using **5a** only unchanged starting material was recovered even after stirring for 62 h. The ^{31}P-{^{1}H} NMR spectrum of **7** (Fig. 4) revealed a single species in which there are clearly three phosphorus environments. The phosphoryl group at δ(P) 21.0 suggests that the $[Ph_2PNP(O)Ph_2]^-$ ligand is bound exclusively through the P donor atom. Although the exact structure could not be ascertained from the NMR spectrum alone the crystal structure of **7** reveals a binuclear compound with hydroxide bridges (Fig. 5 and Table 5). Complex **7** represents a rare example of a crystallographically characterised hydroxoplatinum dimer containing phosphine ligands.[28–32] The Pt(1)–O(1) bond length is 2.096(7) Å and the Pt(1)–O(1)–Pt(1*) angle is 99.8(3)°, whilst the Pt(1) ··· Pt(1*) and O(1) ··· O(1*) distances are 3.21 and 2.70 Å respectively. Interestingly the $Ph_2PNP(O)Ph_2$ ligand adopts a significantly different conformation in **7** with the P(1)–N(1)–P(2)–O(2) atoms forming a planar fragment which is hydrogen bonded [H(1) ··· O(2) 1.76, O(1) ··· O(2) 2.73 Å, O(1)–H(1) ··· O(2) 170°, Fig. 6] to form a pseudo-seven-membered ring contained in a bispirocyclic system. Ellermann and co-workers[5] found that the cobalt(I)-co-ordinated $[Ph_2PNP(O)Ph_2]^-$ anion is stabilised by the formation of an intermolecular hydrogen bond to a methanol solvate molecule. The P–N bond lengths show a similar alternation to those in **5a** and **5b** and are appropriate for a monodeprotonated ligand.

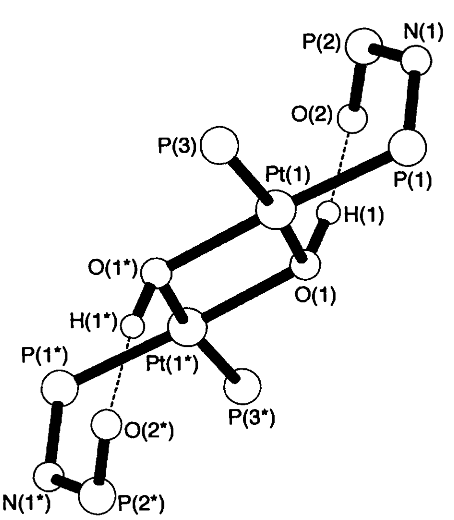


Fig. 6 Core geometry in $[\{Pt(\mu\text{-}OH)\{Ph_2PNP(O)Ph_2\text{-}P\}(PMe_2Ph)\}_2]$ **7**

We have shown that refluxing a methanol solution of *cis*-$[PtCl_2(HL)_2]$ results in Ph_2P–N bond cleavage of one co-ordinated HL ligand to give *cis*-$[PtCl_2(HL)(Ph_2POMe)]$. Furthermore a well established procedure has been used here to prepare *trans*-$[PtCl_2(HL)(PMe_2Ph)]$ suggesting that other *trans*-$[PtCl_2(HL)(PR_3)]$ complexes should be attainable by this route. New examples of five-membered Pt–P–N–P–O platinacycles incorporating neutral or anionic *P,O* chelating ligands have also been synthesized. The $[Ph_2PNP(O)Ph_2\text{-}P]^-$ anion can be stabilised on a platinum(II) centre by intramolecular hydrogen bonding.

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References

1 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 1283.

2 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Polyhedron*, 1996, **15**, 1579.

3 P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 3765.

4 M. Paul and H. Schmidbaur, *Chem. Ber.*, 1996, **129**, 77.

5 D. Pohl, J. Ellermann, F. A. Knoch and M. Moll, *J. Organomet. Chem.*, 1995, **495**, C6.

6 R. Rossi, L. Marvelli, A. Marchi, L. Magon, V. Bertolasi and V. Ferretti, *J. Chem. Soc., Dalton Trans.*, 1994, 339.

7 T. C. Blagborough, R. Davis and P. Ivison, *J. Organomet. Chem.*, 1994, **467**, 85.

8 R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, 1993, **204**, 63.

9 K. V. Katti and C. L. Barnes, *Inorg. Chem.*, 1992, **31**, 4231.

10 X. L. R. Fontaine, E. H. Fowles, T. P. Layzell, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 1519.

11 N. A. Bondarenko, M. V. Rudomino and E. N. Tsevkov, *Synthesis*, 1991, 125.

12 G. A. Carriedo, M. L. Rodríguez, S. García-Granda and A. Aguirre, *Inorg. Chim. Acta*, 1990, **178**, 101.
13 D. J. Darensbourg, D. J. Zalewski, C. Plepys and C. Campana, *Inorg. Chem.*, 1987, **26**, 3727.
14 R. W. Wegman, A. G. Abatjoglou and A. M. Harrison, *J. Chem. Soc., Chem. Commun.*, 1987, 1891.
15 S. J. Higgins, R. Taylor and B. L. Shaw, *J. Organomet. Chem.*, 1987, **325**, 285.
16 D. E. Berry, J. Browning, K. R. Dixon and R. W. Hilts, *Can. J. Chem.*, 1988, **66**, 1272.
17 Q.-B. Bao, S. J. Landon, A. L. Rheingold, T. M. Haller and T. B. Brill, *Inorg. Chem.*, 1985, **24**, 900.
18 A. A. Frew, R. H. Hill, L. Manojlovic-Muir and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1982, 198.
19 C. S. Browning and D. H. Farrar, *J. Chem. Soc., Dalton Trans.*, 1995, 2005 and refs. therein.
20 R. P. Kamalesh Babu, S. S. Krishnamurthy and M. Nethaji, *Polyhedron*, 1996, **15**, 2689.
21 W. Baratta and P. S. Pregosin, *Inorg. Chim. Acta*, 1993, **209**, 85.
22 DIFABS, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
23 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.
24 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.
25 J. A. Rahn, M. S. Holt and J. H. Nelson, *Polyhedron*, 1989, **8**, 897.
26 A. W. Verstuyft, D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1976, **15**, 1128.
27 A. W. Verstuyft and J. H. Nelson, *Synth. React. Inorg. Metal-Org. Chem.*, 1975, **5**, 69.
28 B. Longato, G. Pilloni, G. Valle and B. Corain, *Inorg. Chem.*, 1988, **27**, 956.
29 J. J. Li and P. R. Sharp, *Inorg. Chem.*, 1994, **33**, 183.
30 G. Trovó, G. Bandoli, U. Casellato, B. Corain, M. Nicolini and B. Longato, *Inorg. Chem.*, 1990, **29**, 4616.
31 T. Yoshida, S. Tanaka, T. Adachi, T. Yoshida, K. Onitsuka and K. Sonogashira, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 319.
32 G. W. Bushnell, *Can. J. Chem.*, 1978, **56**, 1773.

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