

Palladium(II) and Platinum(II) Complexes of the Heterodifunctional Ligand Ph₂PNHP(O)Ph₂

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

Department of Chemistry, Loughborough University, Loughborough, Leic. LE11 3TU, U.K.

Received September 26, 1995[®]

The noncomplexed ligand Ph₂PNHP(O)Ph₂ (**HL**) has been prepared, for the first time, from Ph₂PNHPPPh₂ (dppa) and H₂O₂ in moderate yield. On further treatment with H₂O₂ the phosphine oxide Ph₂P(O)NHP(O)Ph₂ (**1**) can be formed. Reaction of [MCl₂(COD)] (M = Pt or Pd; COD = cycloocta-1,5-diene) with 2 molar equiv of **HL** affords [MCl₂(**HL**)₂] (**4**, **5**) in which both ligands are monodentate *P*-bound. The analogous dibromo and diiodo derivatives [MX₂(**HL**)₂] (**6**–**9**) were prepared from either [MX₂(COD)] (M = Pt or Pd; X = Br or I) and **HL** or treatment of [MCl₂(**HL**)₂] with an excess of NaI. Facile base deprotonation of the amine proton in **4** or **5** affords a new class of metallacycles [M(L)₂] [L[−] = Ph₂PNP(O)Ph₂[−]] (**10**, **11**) incorporating two five-membered M–P–N–P–O rings. Compound **10** was independently made from [Pt(CH₃)₂(COD)] and 2 equiv of **HL** in toluene at ambient temperature whereas the reaction of [Pt(CH₃)Cl(COD)] with 2 equiv of **HL** affords solely *trans*-[Pt(CH₃)Cl(**HL**)₂] (**13**). Protonation of the neutral compound **10** with HCl in ethanol regenerates the ring-opened *cis* complex **4**. In contrast, addition of HBF₄·OEt₂ to **10** (or **11**) results in exclusive protonation at the nitrogen atom of the chelating ligands to give *cis*-[M{Ph₂PNHP(O)Ph₂-*P,O*}]₂[BF₄]₂ (**15**, **16**); both chelate rings remain intact. The dicationic compounds **15**, **16** can also be synthesized from **4**, **5** in dichloromethane using Ag[BF₄] as a chloride abstractor. All new compounds described have been characterized by a combination of multinuclear NMR spectroscopy, IR spectroscopy, and elemental analyses. The molecular structures of Ph₂PNHP(O)Ph₂, *cis*-[PtBr₂{Ph₂PNHP(O)Ph₂-*P*}]₂, *cis*-[Pt{Ph₂PNP(O)Ph₂-*P,O*}]₂, *trans*-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-*P*}]₂ and *cis*-[Pt{Ph₂PNHP(O)Ph₂-*P,O*}]₂[BF₄]₂ have been determined by single-crystal X-ray diffraction. Crystals of **HL** are triclinic, space group *P*1̄, with *a* = 10.410(2) Å, *b* = 12.083(2) Å, *c* = 9.036(4) Å, α = 103.05(2)°, β = 99.09(2)°, γ = 72.98(1)°, *V* = 1054 Å³, and *Z* = 2. The final *R* and *R*_w values were 0.061 and 0.047, respectively. Crystals of **6** are triclinic, space group *P*1̄, with *a* = 13.113(4) Å, *b* = 15.996(4) Å, *c* = 13.011(4) Å, α = 102.65(3)°, β = 117.39(2)°, γ = 101.03(2)°, *V* = 2225 Å³, and *Z* = 2. The final *R* and *R*_w values were 0.039 and 0.031, respectively. Crystals of **10** are monoclinic, space group *P*2₁/*a*, with *a* = 17.600(13) Å, *b* = 13.498(10) Å, *c* = 18.641(9) Å, β = 105.13(1)°, *V* = 4274 Å³, and *Z* = 4. The final *R* and *R*_w values were 0.041 and 0.036, respectively. Crystals of **13** are triclinic, space group *P*1̄, with *a* = 14.686(2) Å, *b* = 18.735(2) Å, *c* = 9.018(3) Å, α = 91.71(2)°, β = 102.27(2)°, γ = 68.54(1)°, *V* = 2253 Å³, and *Z* = 2. The final *R* and *R*_w values were 0.041 and 0.044, respectively. Crystals of **15** are orthorhombic, space group *P*2₁2₁2, with *a* = 14.100(2) Å, *b* = 19.002(1) Å, *c* = 9.145(2) Å, *V* = 2450 Å³, and *Z* = 2. The final *R* and *R*_w values were 0.052 and 0.057, respectively. The *P*-bound monodentate complexes contain ligands with similar bond lengths to the neutral compound, while deprotonation/chelation results in lengthening of the P–O and shortening of the P–N bond length as a result of electronic delocalization.

Introduction

The transition metal chemistry of bis(diphenylphosphino)-amine, NH(PPh₂)₂ (dppa), which is isoelectronic with bis(diphenylphosphino)methane, CH₂(PPh₂)₂ (dppm), has received widespread attention.¹ In contrast, there are limited examples of metal complexes^{2–4} of the neutral bis(chalcogenide) R₂P(E)NHP(E)R₂ (E = O, S; R = Me or Ph) whereas the metal

chemistry of tetraorganoimidodiphosphinate ligands, [R₂P(E)-NP(E)R₂][−] (E = O, S, Se; R = alkyl, aryl, aryloxy), is considerably better understood.^{4–22} Anionic ligands of this type have found important uses as metal extractants²³ but are also

[®] Abstract published in *Advance ACS Abstracts*, May 1, 1996.

- (1) Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *14*, 3367.
- (2) McQuillan, G. P.; Oxtan, I. A. *Inorg. Chim. Acta* **1978**, *29*, 69.
- (3) Cuadrado, I.; Moran, M. *Trans. Met. Chem.* **1984**, *9*, 96.
- (4) Day, R. O.; Holmes, R. R.; Schmidpeter, A.; Stoll, K.; Howe, L. *Chem. Ber.* **1991**, *124*, 2443.
- (5) Silvestru, C.; Rösler, R.; Haiduc, I.; Cea-Olivares, R.; Espinosa-Pérez, G. *Inorg. Chem.* **1995**, *34*, 3352.
- (6) Casas, J. S.; Castineiras, A.; Haiduc, I.; Sánchez, A.; Sordo, J.; Vázquez-López, E. M. *Polyhedron* **1995**, *14*, 805.
- (7) Haiduc, I.; Cea-Olivares, R.; Hernández-Ortega, S.; Silvestru, C. *Polyhedron* **1995**, *14*, 2041.
- (8) Zúñiga-Villarreal, N.; Silvestru, C.; Reyes Lezama, M.; Hernández-Ortega, S.; Alvarez Toledano, C. *J. Organomet. Chem.* **1995**, *496*, 169.
- (9) Casas, J. S.; Castineiras, A.; Haiduc, I.; Sánchez, A.; Sordo, J.; Vázquez-López, E. M. *Polyhedron* **1994**, *13*, 2873.

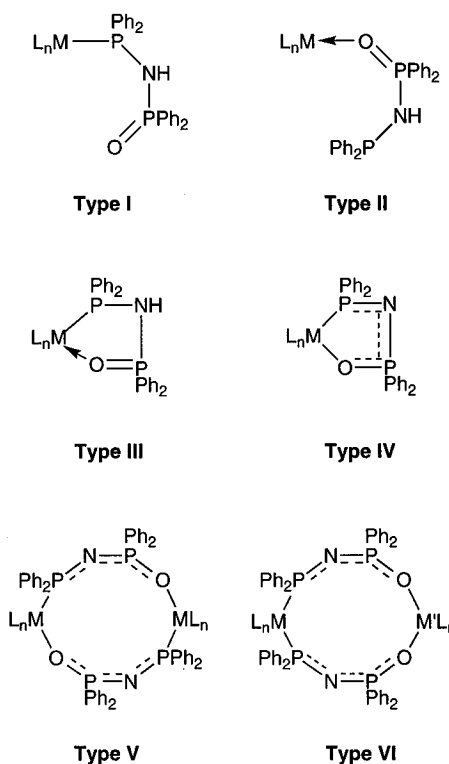
- (10) Silvestru, C.; Haiduc, I.; Cea-Olivares, R.; Zimbron, A. *Polyhedron* **1994**, *13*, 3159.
- (11) Haiduc, I.; Silvestru, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Polyhedron* **1993**, *12*, 69.
- (12) Bhattacharyya, P.; Novosad, J.; Phillips, J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 1607.
- (13) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2489.
- (14) Phillips, J. R.; Slawin, A. M. Z.; White, A. J. P.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2467.
- (15) Slawin, A. M. Z.; Ward, J.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1994**, 421.
- (16) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1993**, 723.
- (17) Rossi, R.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Casellato U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1992**, 435.
- (18) Bock, H.; Schödel, H.; Havlas, Z.; Herrmann, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1355.
- (19) Nouaman, M.; Zak, Z.; Herrmann, E.; Navrátil, O. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1147.
- (20) Cea-Olivares, R.; Nöth, H. *Z. Naturforsch.* **1987**, *42b*, 1507.

widely conceived as inorganic analogues of the more familiar β -diketonate ligands, most notably acetylacetonate (acac).

Only recently have the monochalcogenides $\text{Ph}_2\text{PNHP(E)Ph}_2$ ($\text{E} = \text{S}, \text{Se}$) been described²⁴ although Cavell has reported²⁵ the related ligands $\text{Ph}_2\text{PN(Ph)P(E)Ph}_2$ ($\text{E} = \text{S}, \text{Se}$). To further develop our understanding of these ligand systems, we sought to prepare the ligand $\text{Ph}_2\text{PNHP(O)Ph}_2$ (hereafter abbreviated **HL**) containing both a "soft" and a "hard" donor atom. Some studies with the isoelectronic ligands $\text{Ph}_2\text{PCH}_2\text{P(O)Ph}_2$ ^{26–36} and $\text{Ph}_2\text{PCH}_2\text{P(S)Ph}_2$ ^{37,38} have also been reported. We envisage five different possible modes of coordination of metal ions toward either neutral **HL** or anionic L^- as shown in Chart 1. Unidentate P -bonded coordination (type I) should be favored by low valent transition metals ("soft" metal atom) while O -bonded coordination (type II) should favor early transition metal ions ("hard" metal atom). The ligand may adopt a P,O -chelating mode in which the ligand is either neutral (type III) or anionic (type IV), in both cases resulting in five membered metallacycle formation. Alternatively bridging modes, types V and VI, are possible with formation of homobimetallic and heterobimetallic compounds. We have recently prepared a dimeric palladium(II) complex with two bridging anionic $[\text{Ph}_2\text{PNP(O)Ph}_2\text{-P,O}]^-$ ligands (type V).³⁹

Rossi and co-workers⁴⁰ have reported rhenium complexes of the neutral ligand **HL** and deprotonated L^- (types III and IV respectively). The bound ligands in both cases were prepared from the rhenium(V)-oxo complex $[\text{AsPh}_4][\text{ReOCl}_4]$ and $\text{NH}(\text{PPh}_2)_2$. More recently a Co(II) complex with both a chelating dppe and a monodentate P -bound $[\text{Ph}_2\text{PNP(O)Ph}_2]^-$ ligand has been reported from the nonoxidized ligand dppe with partial oxidation of the initially formed monodentate dppe ligand and then deprotonation.⁴¹ Here we describe a rational route to the

Chart 1



monochalcogenide $\text{Ph}_2\text{PNHP(O)Ph}_2$ and also the coordination chemistry of this ligand toward palladium(II) and platinum(II). The structures of the free ligand **HL** and of the complexes $\text{cis}[\text{PtBr}_2\{\text{Ph}_2\text{PNHP(O)Ph}_2\text{-P}\}_2]$, $\text{cis}[\text{Pt}\{\text{Ph}_2\text{PNP(O)Ph}_2\text{-P,O}\}_2]$, $\text{trans}[\text{Pt}(\text{CH}_3\text{Cl})\{\text{Ph}_2\text{PNHP(O)Ph}_2\text{-P}\}_2]$, and $\text{cis}[\text{Pt}\{\text{Ph}_2\text{PNHP(O)Ph}_2\text{-P,O}\}_2][\text{BF}_4]_2$ have been determined by single-crystal X-ray diffraction.

Experimental Section

Materials. The ligand $\text{Ph}_2\text{PNHPPh}_2$ (dppe) was prepared according to a literature method^{42a} as were the metal complexes $[\text{MX}_2(\text{COD})]$ ($\text{M} = \text{Pt}, \text{Pd}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CH}_3$).^{43–45} $[\text{PtCl}_2(\text{SEt}_2)_2]$,⁴⁶ $[\text{PtCl}_2(\text{PhCN})_2]$,⁴⁷ and $[\text{Pt}(\text{CH}_3\text{Cl})(\text{COD})]$.⁴⁸ BuOK (95% purity), NEt_3 , $\text{Ag}[\text{BF}_4]$, and $\text{HBF}_4 \cdot \text{OEt}_2$ (85%) were purchased from Aldrich Chemical Co. and used without further purification. Tetrahydrofuran, diethyl ether, toluene, and dichloromethane were dried and deaerated by standard methods prior to use. Potassium tetrachloroplatinate and sodium tetrachloropalladate were provided on loan by Johnson-Mathey Inc.

Instrumentation. Infrared spectra were recorded on KBr pellets in the range $4000\text{--}220\text{ cm}^{-1}$ on a Perkin-Elmer System 2000 FT-IR spectrometer. ^1H NMR spectra (250 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with δ referenced to external TMS. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (36.2 or 101.3 MHz) were recorded either on a Jeol FX90Q or a Bruker AC250 FT NMR spectrometer with δ referenced to external phosphoric acid. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra (53.7 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with

- (21) Laguna, A.; Laguna, M.; Rojo, A.; Nieves Fraile, M. *J. Organomet. Chem.* **1986**, 315, 269.
- (22) Czernuszewicz, R.; Maslowsky, Jr, E.; Nakamoto, K. *Inorg. Chim. Acta* **1980**, 40, 199.
- (23) Navrátil, O.; Herrmann, E.; Grossmann, G.; Teply, J. *Collect. Czech. Chem. Commun.* **1990**, 55, 364.
- (24) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3189.
- (25) Balakrishna, M. S.; Klein, R.; Uhlenbrock, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, 32, 5676.
- (26) Blagborough, T. C.; Davis, R.; Ivison, P. *J. Organomet. Chem.* **1994**, 467, 85.
- (27) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1993**, 204, 63.
- (28) Katti, K. V.; Barnes, C. L. *Inorg. Chem.* **1992**, 31, 4231.
- (29) Fontaine, X. L. R.; Fowles, E. H.; Layzell, T. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 1519.
- (30) Bondarenko, N. A.; Rudomino, M. V.; Tsvetkov, E. N. *Synthesis* **1991**, 125.
- (31) Carriedo, G. A.; Rodríguez, M. L.; García-Granda, S.; Aguirre, A. *Inorg. Chim. Acta* **1990**, 178, 101.
- (32) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, 26, 3727.
- (33) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1891.
- (34) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, 325, 285.
- (35) Bao, Q.-B.; Landon, S. J.; Rheingold, A. L.; Haller, T. M.; Brill, T. B. *Inorg. Chem.* **1985**, 24, 900.
- (36) Frew, A. A.; Hill, R. H.; Manojlovic-Muir, L.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 198.
- (37) Baker, M. J.; Giles, M. F.; Orpen, A. G.; Taylor, M. J.; Watt, R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 197.
- (38) Wong, T. Y. H.; Barnabas, A. F.; Sallin, D.; James, B. R. *Inorg. Chem.* **1995**, 34, 2278. $\text{Ph}_2\text{PCH}_2\text{P(S)Ph}_2$ is an end product obtained from the homogeneously catalyzed conversion of H_2S to H_2 .
- (39) Slawin, A. M. Z.; Smith, M. B.; Woollins, J. D. *Polyhedron* **1996**, 15, 1579.
- (40) Rossi, R.; Marvelli, L.; Marchi, A.; Magon, L.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **1994**, 339.
- (41) Pohl, D.; Ellermann, E.; Knoch, F. A.; Moll, M. *J. Organomet. Chem.* **1995**, 495, C6.

- (42) (a) Wang, F. T.; Najdzionek, J.; Leneker, K. L.; Wasserman, H.; Braitsch, D. M. *Synth. React. Inorg. Met. Org. Chem.* **1978**, 8, 119. For alternative synthetic routes to $\text{Ph}_2\text{P(O)NHP(O)Ph}_2$ see: (b) Fluck, E.; Goldmann, F. L. *Chem. Ber.* **1963**, 96, 3091. (c) Schmidpeter, A.; Groeger, H. *Chem. Ber.* **1967**, 100, 3979. (d) Williams, D. J. *Inorg. Nucl. Chem. Lett.* **1980**, 16, 189.
- (43) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, 98, 6521.
- (44) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, 13, 47.
- (45) Costa, E.; Pringle, P. G.; Ravetz, M. *Inorg. Synth.*, in press.
- (46) Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1960**, 6, 211.
- (47) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, 60, 882.
- (48) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, 59, 411.

δ referenced to external H₂PtCl₆ (in D₂O/HCl). Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Service within the Department of Chemistry.

Preparation of Ph₂PNHP(O)Ph₂ (HL). To a THF (50 cm³) solution of Ph₂PNHPPH₂ (2.58 g, 6.69 mmol) at 0 °C was added dropwise aqueous H₂O₂ (30% w/w, ca. 0.70 cm³) with vigorous stirring. Stirring was continued for 10 min and the resulting solution left at ca. -20 °C for 18 h. The white solid Ph₂P(O)NHP(O)Ph₂ was filtered off and the volume of the THF filtrate reduced to 5–10 cm³. Addition of diethyl ether (30 cm³) affords a white solid, **HL**, which was collected by suction filtration and dried in vacuo. Crude yield: 1.32 g, 49%. Anal. Calcd (found) for C₂₄H₂₁NOP₂: C, 71.80 (71.20); H, 5.30 (5.10); N, 3.50 (3.65). Selected IR data (KBr): 3049 ν (N—H), 1183 ν (P=O) cm⁻¹.

The purity of the product was routinely shown, by ³¹P{¹H} NMR spectroscopy, to be 90–95%, and this crude material was used without further purification. The minor contaminant identified was Ph₂P(O)-NHP(O)Ph₂. Slow diffusion of diethyl ether into a THF/H₂O solution of **HL** gave crystals suitable for X-ray crystallography.

Oxidation of Ph₂PNHP(O)Ph₂ to Ph₂P(O)NHP(O)Ph₂ (1). A THF (ca. 0.3 cm³) solution of Ph₂PNHP(O)Ph₂ (0.020 g, 0.050 mmol) was treated with aqueous H₂O₂ (30% w/w, 2 drops, ca. 0.020 g) and the solution examined by ³¹P{¹H} NMR spectroscopy. Quantitative conversion to Ph₂P(O)NHP(O)Ph₂ (**1**) was observed as shown by a single ³¹P resonance at 20.7 ppm. Compound **1** was collected by suction filtration. Yield: 0.021 g, quantitative.

Preparation of cis-[PtCl₂{Ph₂PNHP(O)Ph₂-P}₂] (4). Method A. [PtCl₂(COD)] (0.096 g, 0.257 mmol) and Ph₂PNHP(O)Ph₂ (0.205 g, 0.548 mmol) were dissolved in CH₂Cl₂ (10 cm³) and stirred for 75 min. The volume of the solution was concentrated under reduced pressure to ca. 1–2 cm³ whereupon a white solid **4** deposited. Further precipitation was induced by addition of diethyl ether (30 cm³) and the solid collected by filtration. Yield: 0.257 g, 94%. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄PtCl₂: C, 53.95 (53.25); H, 3.95 (3.85); N, 2.60 (2.85). Selected IR data (KBr): 3293, 3172 ν (N—H), 1217 ν (P=O), 315, 283 ν (Pt—Cl) cm⁻¹.

Alternatively complex **4** can be prepared in excellent yield (>95%) from either [PtCl₂(SEt₂)₂] or [PtCl₂(PhCN)₂] under similar conditions.

Method B. A white suspension of cis-[Pt{Ph₂PNP(O)Ph₂-P,*O*}]₂ (0.032 g, 0.032 mmol) in EtOH (2 cm³) was treated with concentrated HCl (2 drops, ca. 0.092 g) and the mixture stirred for 10 min. The solid was filtered and dried. Yield: 0.033 g, 97%. ³¹P{¹H} NMR spectroscopy showed the exclusive formation of cis-[PtCl₂{Ph₂PNHP(O)Ph₂-P}]₂ (**4**).

Preparation of cis- and trans-[PdCl₂{Ph₂PNHP(O)Ph₂-P}]₂ (5a, 5b). To a CH₂Cl₂ (20 cm³) solution of [PdCl₂(COD)] (0.149 g, 0.522 mmol) was added Ph₂PNHP(O)Ph₂ (0.430 g, 1.07 mmol) as a solid in one portion to give a yellow solution. After ca. 10–15 min, a yellow precipitate formed and the mixture was stirred for a further 90 min. The solid was collected by suction filtration and dried. Yield: 0.441 g, 86%. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄PdCl₂: C, 58.80 (57.50); H, 4.35 (4.10); N, 2.85 (2.85). Selected IR data (KBr): 3176 ν (N—H), 1219 ν (P=O), 332, 293 ν (Pd—Cl) cm⁻¹.

Preparation of cis-[PtBr₂{Ph₂PNHP(O)Ph₂-P}]₂ (6). To a CH₂Cl₂ (10 cm³) solution of [PtBr₂(COD)] (0.079 g, 0.171 mmol) was added Ph₂PNHP(O)Ph₂ (0.144 g, 0.359 mmol) as a solid in one portion. The pale yellow solution was stirred for ca. 1 h and filtered and the volume concentrated in vacuo to ca. 1–2 cm³. Addition of diethyl ether (10 cm³) gave the solid product. Yield: 0.170 g, 86%. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄PtBr₂: C, 49.80 (50.10); H, 3.65 (3.70); N, 2.40 (2.80). Selected IR data (KBr): 3293, 3166 ν (N—H), 1217 ν (P=O) cm⁻¹. Slow diffusion of diethyl ether into a CH₂Cl₂ solution of [PtBr₂(COD)] and 2 equiv of **HL** gave crystals of **6** suitable for X-ray crystallography.

The corresponding palladium(II) compound [PdBr₂{Ph₂PNHP(O)Ph₂-P}]₂, **7**, was prepared as the *trans*-isomer. Yield: 0.067 g, 91%. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄PdBr₂: C, 53.95 (53.30); H, 3.95 (3.90); N, 2.60 (2.70). Selected IR data (KBr): 3177 ν (N—H), 1220 ν (P=O) cm⁻¹.

Preparation of trans-[PdI₂{Ph₂PNHP(O)Ph₂-P}]₂ (9). [PdCl₂{Ph₂PNHP(O)Ph₂-P}]₂ (0.100 g, 0.102 mmol) and NaI (0.160 g, 1.067 mmol) in acetone (15 cm³) were stirred for ca. 3 h. The solvent was evaporated to dryness in vacuo and distilled water (25 cm³) added.

The solid was filtered, washed with MeOH, and dried. Yield: 0.109 g, 92%. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄PdI₂: C, 49.55 (49.35); H, 3.65 (3.20); N, 2.40 (3.25). Selected IR data (KBr): 3149 ν (N—H), 1221 ν (P=O) cm⁻¹.

The corresponding platinum(II) compound [PtI₂{Ph₂PNHP(O)Ph₂-P}]₂ **8** was synthesized as an isomeric mixture of *cis*- and *trans*-isomers from [PtI₂(COD)] and 2 equiv of **HL** or alternatively from compound **4** and an excess of NaI. Yield: 0.101 g, 90%. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄PtI₂: C, 46.05 (46.60); H, 3.40 (2.95); N, 2.25 (2.25). Selected IR data (KBr): 3288, 3205, 3152 ν (N—H), 1220 ν (P=O) cm⁻¹.

Preparation of cis-[Pt{Ph₂PNP(O)Ph₂-P,*O*}]₂ (10). Method A. To a suspension of cis-[PtCl₂{Ph₂PNHP(O)Ph₂-P}]₂ (0.073 g, 0.068 mmol) in MeOH (1 cm³) was added ^tBuOK (0.016 g, 0.143 mmol) as a solid in one portion. The resulting suspension was stirred for ca. 5 min and the solid collected by suction filtration, washed with distilled water (1 cm³) and MeOH (1 cm³), and dried in vacuo. Yield: 0.056 g, 82%. Anal. Calcd (found) for C₄₈H₄₀N₂O₂P₄Pt: C, 57.90 (57.35); H, 4.05 (3.85); N, 2.80 (2.85).

Method B. To [Pt(CH₃)₂(COD)] (0.046 g, 0.138 mmol) and Ph₂PNHP(O)Ph₂ (0.110 g, 0.274 mmol) was added toluene (3 cm³). After 28 h of stirring, the pale yellow solution was filtered and diethyl ether (5 cm³) added to yield a white solid. The solid was collected by suction filtration and dried in vacuo. Yield: 0.071 g, 52%.

Preparation of cis-[Pd{Ph₂PNP(O)Ph₂-P,*O*}]₂ (11). To a yellow suspension of [PdCl₂{Ph₂PNHP(O)Ph₂-P}]₂ (0.088 g, 0.090 mmol) in MeOH (1 cm³) was added ^tBuOK (0.021 g, 0.187 mmol) as a solid in one portion. The resulting deep yellow suspension was stirred for ca. 5 min and the solid collected by suction filtration, washed with distilled water (1 cm³) and MeOH (1 cm³), and dried in vacuo. Yield: 0.059 g, 73%. The compound **11** could be recrystallized from CH₂Cl₂/Et₂O. Anal. Calcd (found) for C₄₈H₄₀N₂O₂P₄Pd: C, 63.55 (63.25); H, 4.45 (4.25); N, 3.10 (3.05).

Preparation of trans-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-P}]₂ (13). To [Pt(CH₃)Cl(COD)] (0.050 g, 0.141 mmol) and Ph₂PNHP(O)Ph₂ (0.120 g, 0.299 mmol) was added CH₂Cl₂ (3 cm³) and the solution stirred for 20 min. After filtering, addition of diethyl ether (30 cm³) afforded a white solid which was collected by suction filtration and dried in vacuo. Yield: 0.120 g, 81%. Anal. Calcd (found) for C₄₉H₄₅N₂O₂P₄PtCl: C, 56.15 (55.55); H, 4.35 (4.05); N, 2.65 (3.00). Selected IR data (KBr): 3198, 3135 ν (N—H), 1232, 1222 ν (P=O), 298 ν (Pt—Cl) cm⁻¹. Slow diffusion of diethyl ether into a CH₂Cl₂ solution gave crystals of **13** suitable for X-ray crystallography.

Preparation of trans-[Pt(CH₃)I{Ph₂PNHP(O)Ph₂-P}]₂ (14). To a solution of trans-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-P}]₂ (0.057 g, 0.054 mmol) in MeOH (10 cm³) was added NaI (0.079 g, 0.527 mmol) in MeOH (1 cm³). The colorless solution was stirred for ca. 1 h and evaporated to dryness under reduced pressure. To the residue was added distilled water (5 cm³). The solid product was collected by suction filtration and dried. Yield: 0.053 g, 85%. Anal. Calcd (found) for C₄₉H₄₅N₂O₂P₄PtI: C, 51.65 (51.25); H, 4.00 (3.95); N, 2.45 (2.45). Selected IR data (KBr): 3166 ν (N—H), 1220 ν (P=O) cm⁻¹.

Preparation of cis-[Pt{Ph₂PNHP(O)Ph₂-P,*O*}]₂[BF₄]₂ (15). Method A. To a CDCl₃ (0.6 cm³) solution of cis-[Pt{Ph₂PNP(O)Ph₂-P,*O*}]₂ (0.054 g, 0.054 mmol) was added HBF₄·OEt₂ (6 drops). The colorless solution was stirred for 10 min. Addition of diethyl ether (2 cm³) afforded a white solid, which was collected by suction filtration and dried, in quantitative yield. Anal. Calcd (found) for C₄₈H₄₂N₂O₂P₄-PtB₂F₈: C, 49.20 (48.85); H, 3.60 (3.10); N, 2.40 (2.40). Selected IR data (KBr): 3168 ν (N—H) cm⁻¹.

Method B. To a solution of [PtCl₂{Ph₂PNHP(O)Ph₂-P}]₂ (0.103 g, 0.096 mmol) in dichloromethane (50 cm³) was added solid Ag[BF₄] (0.040 g, 0.206 mmol). After stirring for ca. 4 h, the AgCl was filtered through a small pad of Celite and the filtrate reduced in volume under reduced pressure to ca. 1–2 cm³. Addition of diethyl ether (15 cm³) gave a white solid, **15**. Yield: 0.085 g, 75%. Slow diffusion of diethyl ether into a MeOH solution gave crystals of **15** suitable for X-ray crystallography.

The complex cis-[Pd{Ph₂PNHP(O)Ph₂-P,*O*}]₂[BF₄]₂ **16** was synthesized either from cis-[Pd{Ph₂PNP(O)Ph₂-P,*O*}]₂ and HBF₄·Et₂O (Yield: 0.063 g, 98%) or chloride abstraction from complex **5** using Ag[BF₄] in dichloromethane (Yield: 0.047 g, 42%). Anal. Calcd

Table 1. Crystallographic Data for Ph₂PNHP(O)Ph₂ (**HL**), *cis*-[PtBr₂{Ph₂PNHP(O)Ph₂-P}₂] (**6**), *cis*-[Pt{Ph₂PNP(O)Ph₂-P,O}₂] (**10**), *trans*-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-P}₂] (**13**) and *cis*-[Pt{Ph₂PNHP(O)Ph₂-P,O}₂][BF₄]₂ (**15**)

	HL	6	10	13	15
chem formula	C ₂₄ H ₂₁ NOP ₂	C ₄₈ H ₄₂ N ₂ O ₂ P ₄ PtBr ₂	C ₄₈ H ₄₀ N ₂ O ₂ P ₄ Pt	C ₄₉ H ₄₅ N ₂ O ₂ P ₄ PtCl	C ₄₈ H ₄₂ N ₂ O ₂ P ₄ PtB ₂ F ₈
fw	401.38	1157.67	995.84	1048.34	1171.46
cryst syst	triclinic	triclinic	monoclinic	triclinic	orthorhombic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ 2 ₁ 2 (No. 18)
<i>a</i> (Å)	10.410(2)	13.113(4)	17.600(13)	14.686(2)	14.100(2)
<i>b</i> (Å)	12.083(2)	15.996(4)	13.498(10)	18.735(2)	19.002(1)
<i>c</i> (Å)	9.036(4)	13.011(4)	18.641(9)	9.018(3)	9.145(2)
α (deg)	103.05(2)	102.65(3)		91.71(2)	
β (deg)	99.09(2)	117.39(2)	105.13(1)	102.27(2)	
γ (deg)	72.98(1)	101.03(2)		68.54(1)	
<i>V</i> (Å ³)	1054	2225	4274	2253	2450
<i>Z</i>	2	2	4	2	2
ρ_{calcd} (g cm ⁻³)	1.27	1.73	1.55	1.55	1.59
μ (cm ⁻¹)	19.8	98.0	76.5	78.2	70.0
<i>R</i> ^a	0.061	0.039	0.041	0.041	0.052
<i>R</i> _w ^b	0.047	0.031	0.036	0.044	0.057

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

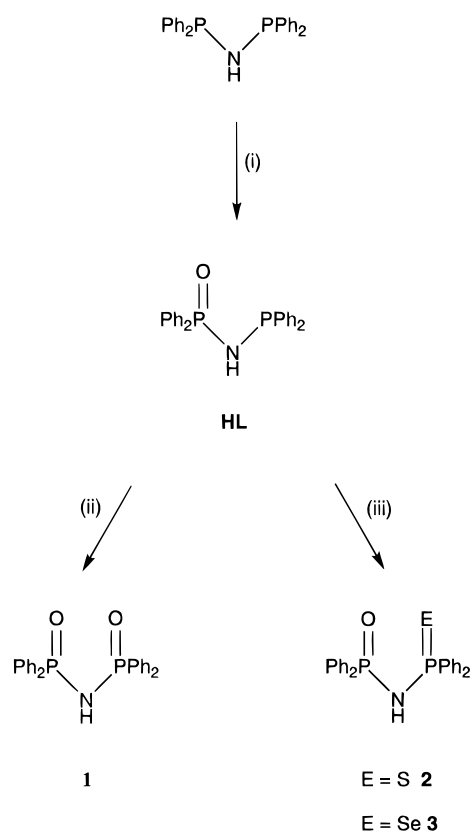
(found) for C₄₈H₄₂N₂O₂P₄PdBr₂F₈: C, 53.25 (53.10); H, 3.90 (3.65); N, 2.60 (2.60). Selected IR data (KBr): 3165 ν (N—H) cm⁻¹.

X-ray Crystallographic Analyses of Ph₂PNHP(O)Ph₂ (HL**), *cis*-[PtBr₂{Ph₂PNHP(O)Ph₂-P}₂] (**6**), *cis*-[Pt{Ph₂PNP(O)Ph₂-P,O}₂] (**10**), *trans*-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-P}₂] (**13**), and *cis*-[Pt{Ph₂PNHP(O)Ph₂-P,O}₂][BF₄]₂ (**15**).** Details of crystal data collection and refinements are given in Table 1. Data were collected on a Rigaku AFC7S diffractometer [Cu K α radiation (λ = 1.541 78 Å), ω -scans] at 20.0 °C. Unit cell parameters were determined by centering 20 reflections and in every case three standard reflections were monitored every 150 reflections. The data sets were corrected for absorption (DIFABS).^{49a} Structure solution^{49b} (heavy atom method) and refinement employed the TEXSAN software package.^{49c} The non-hydrogen atoms were refined anisotropically except for **6** where the phenyl carbon atoms were refined isotropically. In **15** the phenyl rings and the [BF₄]⁻ counterion were refined as rigid bodies. All N—H protons were located from ΔF maps. In **6** the N—H protons were idealized, in all other cases the N—H protons were allowed to refine isotropically. All remaining hydrogen atoms were idealized (C—H = 0.95 Å). The polarity of **15** was tested by a Flack parameter refinement which refined to 0.08(3) indicating the correct absolute stereochemistry.

Results and Discussion

Reaction of dppa with 2 equiv of aqueous H₂O₂ has been shown to proceed with formation of Ph₂P(O)NHP(O)Ph₂ (**1**).^{42a} We have found that controlled oxidation of Ph₂PNHPPH₂ with aqueous H₂O₂ (30% w/w) in THF at 0 °C affords the heterodifunctional ligand Ph₂PNHP(O)Ph₂ **HL** (Scheme 1). Although we were unable to prevent the formation of **1**, the low solubility of this species in THF at 0 °C enabled removal by simple filtration from the **HL** which remained in solution. In addition, we also noted the presence of residual dppa which was also readily separated from **HL**. The mixed P, O ligand was isolated as a white air stable solid in moderate yield (49%) and had a purity by ³¹P{¹H} NMR spectroscopy which routinely exceeded 90%. The ligand **HL** is soluble in toluene, chlorinated solvents, acetone, THF, low molecular weight alcohols (e.g. MeOH), and dmsO. In THF/C₆D₆ solution, the ³¹P{¹H} NMR spectrum of **HL** showed two sharp doublets at 28.0 ppm and 21.4 ppm, assigned to the phosphorus(III) and phosphorus(V) centers respectively, with a ²J(P_AP_X) coupling of 61.6 Hz (Table 2).

Scheme 1^a



^a Key: (i) H₂O₂, 0 °C, THF; (ii) CDCl₃, H₂O₂; (iii) E, THF (E = S or Se).

In the X-ray structure of **HL** the molecule (Figure 1) has typical bond lengths and angles with the most notable feature being the almost perfect *syn* arrangement of the N—H proton and the P=O oxygen atom. This arrangement is a consequence of a hydrogen-bonded dimer pair formation [N $\cdots$ O 2.83 Å, H $\cdots$ O 1.72 Å, N—H $\cdots$ O 167(1)°]. In **HL** the P(2) $\cdots$ O(1) distance is 4.21 Å which suggested to us that all of the coordination modes in Chart 1 could be possible.

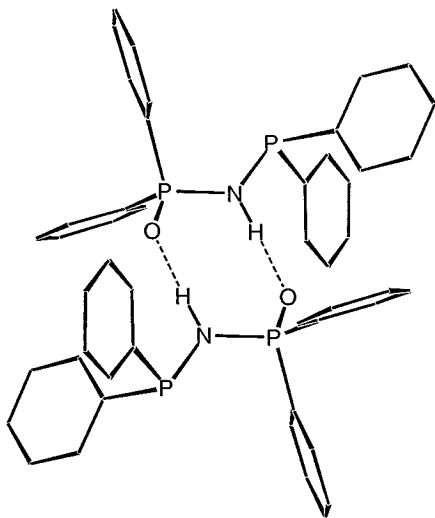
Solutions of **HL** are relatively stable toward aerial oxidation. However, treatment with aqueous H₂O₂ in THF results in rapid oxidation and formation [shown by ³¹P{¹H}] of bis(diphenylphosphinoyl)amine, **1**, which has previously been reported.⁴² Reaction with other chalcogenides affords the mixed phosphorus(V) ligands Ph₂P(E)NHP(O)Ph₂ [E = S (**2**), Se (**3**)].⁵⁰

(49) (a) DIFABS: Walker, N. G.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, 39, 158. (b) DIRDIF 92-PATY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992. (c) TEXSAN: *Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

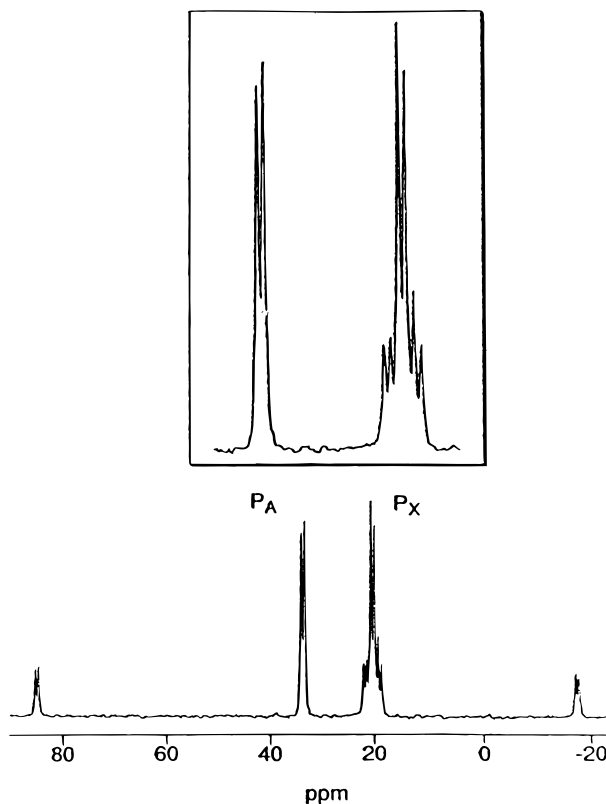
Table 2. Selected ³¹P{¹H}, ¹⁹⁵Pt{¹H}, and ¹H NMR data^a

compound	δ(P _A) ^b	¹ J(PtP _A)	δ(P _X) ^b	¹ J(PtP _X) ^c	N ^d	δ(Pt) ^e
dppa	43.1					
HL ^f	28.0 ^g		21.4		61.6 ^h	
1			20.7			
4	35.7 ⁱ	3955	21.6	114	22	-4351
5a	58.3 ^j		21.1		36.0	
5b	46.7		20.9		24.8	
6	37.6 ⁱ	3933	22.1	104	24	-4592
7	48.5 ^k		22.7		22	
8a	36.8 ^l	3821	21.2	108	29	
8b	35.4	2544	22.8	83	21	
9	45.4 ^k		24.1		23	
10	31.9	3880	62.3	167	4.3 ^m	-4184
11	54.1		63.4		6.3 ^m	
12	58.7 ^{n,o}	2050	22.7		23	
13	56.0 ^p	3202	22.6	84	17.6	-4638
14	55.6 ^q	3154	23.9	88	10.1	-4906
15	37.4 ^r	3924	62.8	88	2.9 ^m	-4239 ^s
16	56.3 ^r		68.1		6.3 ^m	

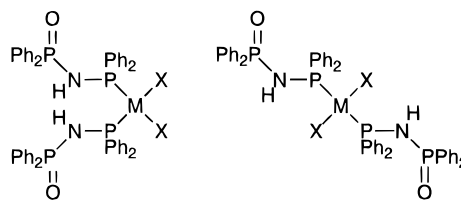
^a ³¹P{¹H} NMR spectra (36.2 MHz) measured in CDCl₃ unless otherwise stated. Chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H₃PO₄. Coupling constants (*J*) in Hz (±3). ¹⁹⁵Pt{¹H} NMR spectra (53.7 MHz) measured in CDCl₃ unless otherwise stated. ¹H NMR spectra (250 MHz) measured in CDCl₃. Chemical shifts (δ) in ppm (±0.01) to high frequency of SiMe₄ and coupling constants (*J*) in Hz (±0.1). ^b P_A = phosphorus(III) center, P_X = phosphorus(V) center. ^c In the monodentate complexes this is ³J(PtP_X), while in the chelate complexes there are contributions from ²J(PtP_X) and ³J(PtP_X). ^d *N* = |²J(P_AP_X) + ⁴J(P_AP_X)|. ^e Triplet of triplets. ^f In CDCl₃ δ(P_A) 27.8 ppm, δ(P_X) 25.2 ppm, ²J(P_AP_X) 59.0 Hz. Additional uncharacterized species at δ(P) +18.8 ppm and δ(P) -0.3 ppm observed. ^g Spectrum measured in THF/C₆D₆. ^h ²J(P_AP_X) value. ⁱ The *cis*-isomer exclusively. ^j Mixture of *cis* and *trans*-isomers observed in a 1:3.7 ratio respectively. ^k The *trans*-isomer exclusively. ^l Mixture of *cis* and *trans*-isomers observed in a 1:1.2 ratio respectively. ^m Value taken from spectrum measured at 101.3 MHz. ⁿ In addition to other uncharacterized species. ^o Comparative data for the complex *cis*-[Pt(CH₃)₂{Ph₂PNHPPH₂-P}₂]: δ(P_A) 63.1 ppm, ¹J(PtP) 2058 Hz, δ(P_X) 30.6 ppm, *N* 11 Hz (measured in CDCl₃). ^p Selected ¹H NMR data: δ(H) -0.13 ppm, ²J(PtH) 81.2 Hz, ³J(PH) 7.4 Hz (PtCH₃ resonance). ^q Selected ¹H NMR data: δ(H) -0.11 ppm, ²J(PtH) 77.0 Hz, ³J(PH) 7.7 Hz (PtCH₃ resonance). ^r Spectrum measured in MeOH/C₆D₆. ^s Spectrum measured in CDCl₃/MeOH.

**Figure 1.** Line drawing of the crystal structure of Ph₂PNHP(O)Ph₂ (HL) showing a hydrogen-bonded dimer pair. Selected bond lengths (Å) and angles (deg): P(1)–O(1) 1.508(2), P(1)–N(1) 1.651(3), P(2)–N(1) 1.707(3); O(1)–P(1)–N(1) 111.0(1), P(1)–N(1)–P(2) 125.6(2).

The 2:1 molar ratio reaction of HL with [MCl₂(COD)] [M = Pt, Pd] in dichloromethane at room temperature affords exclusively *cis*-[PtCl₂{Ph₂PNHP(O)Ph₂-P}₂] (**4**) and a mixture

**Figure 2.** ³¹P{¹H} NMR spectrum (36.2 MHz) of *cis*-[PtCl₂{Ph₂PNHP(O)Ph₂-P}₂] (**4**).

of *cis*- (**5a**) and *trans*-[PdCl₂{Ph₂PNHP(O)Ph₂-P}₂] (**5b**).



M = Pt	X = Cl	4	M = Pd	X = Cl	5b
M = Pd	X = Cl	5a	M = Pd	X = Br	7
M = Pt	X = Br	6	M = Pt	X = I	8b
M = Pt	X = I	8a	M = Pd	X = I	9

The ³¹P{¹H} NMR spectrum of **4** (Figure 2) shows two sets of resonances corresponding to the coordinated phosphorus(III) center and the "dangling" phosphorus(V) moiety. A large ¹J(PtP_A) coupling constant of 3955 Hz is in good agreement with a *cis* disposition of ligands (i.e. phosphorus *trans* to chloride). In addition ¹⁹⁵Pt satellites are also observed for the uncoordinated phosphorus(V) group [³J(PtP_X) 114 Hz]. Since the chemical shift for the pendant P=O group is comparable to that in HL we infer that in compound **4** (and **5**) there is no chelating interaction with the metal center, and hence a dicationic species such as [Pt{Ph₂PNHP(O)Ph₂-P,₂O}₂]Cl₂ is not formed under these experimental conditions (see below for further discussion). Further support comes from the IR spectrum (KBr pellet) which shows two distinct ν(Pt–Cl) stretches at 315 and 283 cm⁻¹ consistent with a *cis*-PtCl₂ geometry. In contrast, we observe that the neutral palladium complex **5** is present as a mixture of *cis*-**5a** and *trans*-**5b** isomers; the *trans* isomer is the predominant species observed in CDCl₃ solutions (1:3.7 ratio as determined by ³¹P{¹H} NMR).

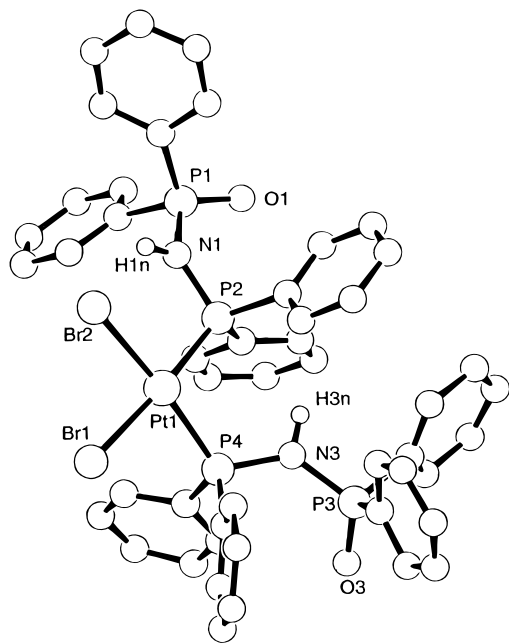
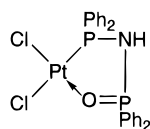


Figure 3. Crystal structure of *cis*-[PtBr₂{Ph₂PNHP(O)Ph₂-P}₂] (**6**). Selected bond lengths (Å) and angles (deg): Pt(1)–Br(1) 2.472(2), Pt(1)–Br(2) 2.480(2), Pt(1)–P(2) 2.241(5), Pt(1)–P(4) 2.248(4), P(1)–O(1) 1.47(1), P(1)–N(1) 1.67(1), P(2)–N(1) 1.68(1), P(3)–O(3) 1.492(9), P(3)–N(3) 1.71(1), P(4)–N(3) 1.68(1); Br(1)–Pt(1)–Br(2) 86.34(7), Br(1)–Pt(1)–P(2) 173.6(1), Br(1)–Pt(1)–P(4) 85.8(1), Br(2)–Pt(1)–P(2) 91.2(1), Br(2)–Pt(1)–P(4) 171.6(1), P(2)–Pt(1)–P(4) 97.0(2), O(1)–P(1)–N(1) 113.3(6), Pt(1)–P(2)–N(1) 111.3(4), O(3)–P(3)–N(3) 115.5(6), Pt(1)–P(4)–N(3) 115.3(4), P(1)–N(1)–P(2) 132.6(7), P(3)–N(3)–P(4) 130.3(7).

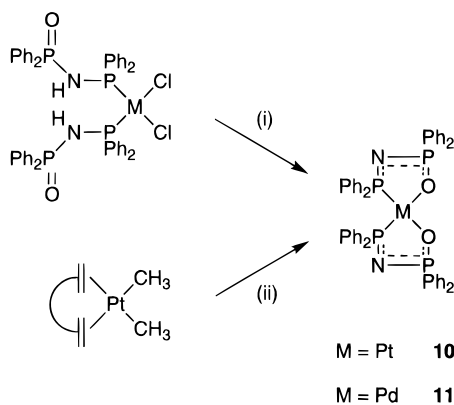
The reaction of [PtCl₂(COD)] with 1 equiv of **HL** did not lead to the formation of the neutral chelate complex [PtCl₂{Ph₂PNHP(O)Ph₂-P,O}] (**A**) but instead gave a mixture of **4**, unreacted starting material, and free COD as revealed by a combination of ¹H and ³¹P{¹H} NMR spectroscopy. In contrast, Cavell and co-workers²⁵ were able to prepare analogous compounds to **A** using the related ligands Ph₂PN(Ph)P(E)Ph₂ (E = S or Se).



Compound A

Treatment of [MX₂(COD)] (M = Pt, Pd; X = Br, I) with 2 equiv of **HL** (or metathesis of **4** or **5** with NaI) gave the following compounds: *cis*-[PtBr₂{Ph₂PNHP(O)Ph₂-P}₂] (**6**), *trans*-[PdBr₂{Ph₂PNHP(O)Ph₂-P}₂] (**7**), *cis*- and *trans*-[PtI₂{Ph₂PNHP(O)Ph₂-P}₂] (**8a**, **8b**), and *trans*-[PdI₂{Ph₂PNHP(O)Ph₂-P}₂] (**9**). Characterizing data for **4–9** are given in Table 2 and the Experimental Section. Suitable crystals of **6** were grown by layering a dichloromethane solution of [PtBr₂(COD)] / **HL** with diethyl ether. From X-ray studies, the molecule (Figure 3) adopts a square planar geometry at platinum with *cis* bromides and phosphorus coordination of the neutral ligands. There is a slight twist about the coordination plane with P(2) and P(4) lying –0.16 and +0.10 Å with respect to the PtBr₂P₂ mean plane. Within the ligand, the P–N bond lengths are similar to those in the free ligand while the P=O bond length (which is no longer involved in a strong hydrogen bond) is slightly shorter in **6** than in **HL** [1.47(1) and 1.492(9) Å; cf. 1.508(2) Å]. Interestingly the N–H protons in the ligand (which were located by ΔF maps) are no longer *syn* with respect to the P=O

Scheme 2^a



^a Key: (i) ^tBuOK, MeOH; (ii) 2 **HL**, toluene.

oxygen atoms. H(1n) is involved in an intramolecular H-bond to Br(2) (2.34 Å) which results in H(1n) being almost perfectly *anti* with respect to O(1). H(3n) is also very close to *anti*. From the IR spectrum, the observation of two ν(N–H) absorptions at 3293 and 3166 cm^{–1} is consistent with only one of the NH groups being involved in an intramolecular hydrogen bond to Br.

Previous work has demonstrated that β-ketophosphine metal complexes can be deprotonated to afford coordinated phosphino enolate ligands.^{51–56} Using a suitable base (e.g. the metal alkoxide ^tBuOK) we find that the acidic proton of the bound **HL** ligand in the complexes **4** and **5** are readily removed, affording the bischolate complexes [M{Ph₂PNP(O)Ph₂-P,O}₂] [M = Pt (**10**); M = Pd (**11**)] (Scheme 2). An alternative route to **10**, albeit in lower yield (52% vs 82%), is the reaction of [Pt(CH₃)₂(COD)] with 2 equiv of **HL** in toluene at ambient temperature.

The ³¹P{¹H} NMR spectrum of the platinum complex **10** shows a large ¹J(PtP_A) coupling constant of 3880 Hz (of similar magnitude to **4**) and a small ¹J(PtP_X) coupling constant [contributions from ²J(PtP_X) and ³J(PtP_X)] of 167 Hz. The large shift of the δ(³¹P) for the P=O group upon chelation is probably due to the chelate ring effect, a feature that has been well studied with other phosphorus-based ligands forming five-membered rings.⁵⁷

In the X-ray structure of **10** (Figure 4) the square planar platinum is *cis* coordinated by the two deprotonated [Ph₂PNP(O)Ph₂][–] ligands [maximum deviation from the PtP₂O₂ mean plane 0.12 Å for O(1)]. The two PtP₂NO five-membered rings are slightly puckered [Pt(1)–O(1)–P(1)–N(1)–P(2) mean plane, with maximum deviation of N(1) 0.23 Å below the plane, and Pt(1)–O(3)–P(3)–N(3)–P(4) with maximum deviation of N(3) 0.28 Å above the plane]. Within the rings the phosphorus centers are slightly distorted from tetrahedral while the Pt–O–P and P–N–P angles are all ca. 115°. The P=O bonds are lengthened and the P–N bonds are shortened with respect to the free ligand as a consequence of the delocalization associated with deprotonation. The P–Pt–P angle [103.2(1)°]

- (51) Braunstein, P.; Chauvin, Y.; Nähring, J.; Dusaouy, Y.; Bayeul, D.; Tiripicchio, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1995**, 851.
- (52) Braunstein, P.; Chauvin, Y.; Nähring, J.; DeCain, A.; Fischer, J. *J. Chem. Soc. Dalton Trans.* **1995**, 863.
- (53) Braunstein, P.; Kelly, D. G.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1993**, 32, 4845.
- (54) Matt, D.; Huhn, M.; Fischer, J.; De Cian, A.; Kläui, W.; Tkatchenko, I.; Bonnet, M. C. *J. Chem. Soc., Dalton Trans.* **1993**, 1173.
- (55) Braunstein, P.; Matt, D.; Nobel, D.; Balegroune, F.; Bouaoud, S.-E.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1988**, 353.
- (56) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, 25, 3765.
- (57) Garrou, P. E. *Chem. Rev.* **1981**, 81, 229.

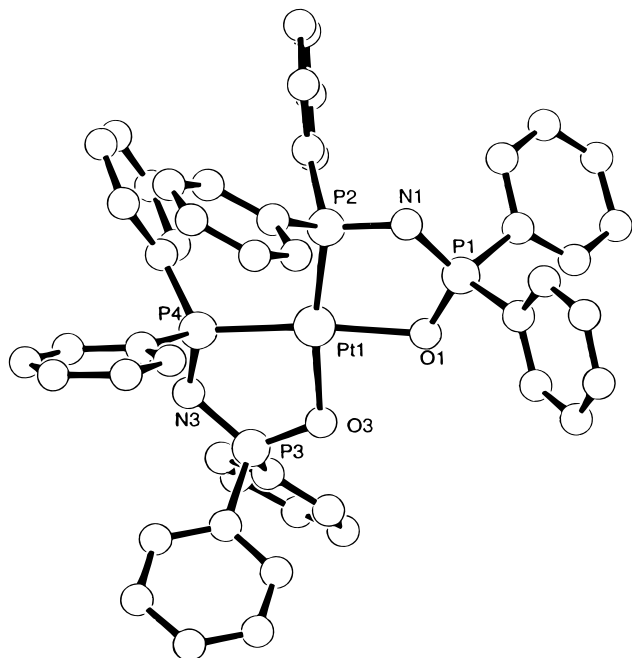


Figure 4. Crystal structure of $\text{cis}[\text{Pt}\{\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2\text{-P,O}\}_2]$ (**10**). Selected bond lengths (Å) and angles (deg): Pt(1)–P(2) 2.235(3), Pt(1)–P(4) 2.235(3), Pt(1)–O(1) 2.110(6), Pt(1)–O(3) 2.103(6), P(1)–O(1) 1.535(7), P(1)–N(1) 1.604(8), P(2)–N(1) 1.618(9), P(3)–O(3) 1.527(7), P(3)–N(3) 1.577(8), P(4)–N(3) 1.641(8); P(2)–Pt(1)–P(4) 103.2(1), P(2)–Pt(1)–O(1) 86.1(2), P(2)–Pt(1)–O(3) 170.7(2), P(4)–Pt(1)–O(1) 169.9(2), P(4)–Pt(1)–O(3) 86.0(2), O(1)–Pt(1)–O(3) 84.9(3), O(1)–P(1)–N(1) 114.7(4), Pt(1)–P(2)–N(1) 106.9(3), O(3)–P(3)–N(3) 114.4(4), Pt(1)–P(4)–N(3) 105.4(3), Pt(1)–O(1)–P(1) 114.3(4), Pt(1)–O(3)–P(3) 114.7(4), P(1)–N(1)–P(2) 115.3(5), P(3)–N(3)–P(4) 115.4(5).

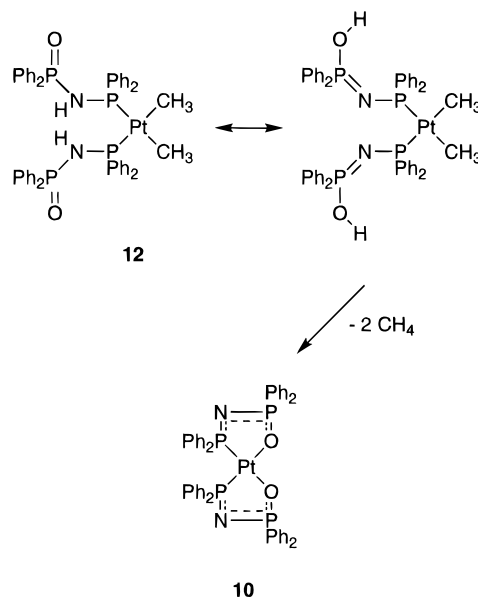
is enlarged, presumably as a consequence of the steric bulk of the ligand; there are weak face-face phenyl–phenyl interactions between the phenyl rings on the coordinated phosphorus atoms.

We have recently reported that the monochalcogenide ligands $\text{Ph}_2\text{PNHP}(\text{E})\text{Ph}_2$ (E = S, Se) can either coordinate as a neutral chelating ligand or undergo deprotonation in the absence of base.²⁴ This contrasts with our findings presented here.

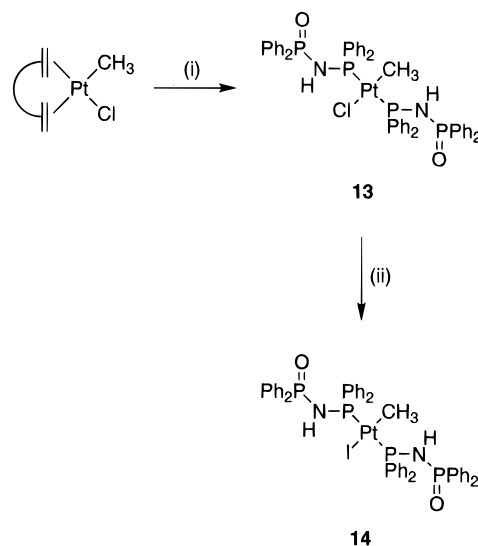
A possible mechanism to account for the formation of the platinum bischelat complex **10** from $[\text{Pt}(\text{CH}_3)_2(\text{COD})]$ is shown in Scheme 3. We tentatively suggest that the complex $\text{cis}[\text{Pt}(\text{CH}_3)_2\{\text{PPh}_2\text{NHP}(\text{O})\text{Ph}_2\text{-P}\}_2]$ (**12**) is initially formed which can exist in a resonance stabilized form (tautomeric) suitably disposed for intramolecular protonolysis with concomitant evolution of CH_4 . Although no attempts to test for CH_4 formation or isolate any intermediates in this reaction were pursued, we have observed the formation of **12** in solution ($^{31}\text{P}\{^1\text{H}\}$ NMR evidence).

In view of the above observations we were intrigued as to the reactivity of the organoplatinum compound $[\text{Pt}(\text{CH}_3)\text{Cl}(\text{COD})]$ with **HL**. Instead of the anticipated $[\text{Pt}\{\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2\text{-P,O}\}\{\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2\text{-P}\}]$ complex we obtained $\text{trans}[\text{Pt}(\text{CH}_3)\text{Cl}\{\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2\text{-P}\}_2]$ (**13**) which could be metathesized to the (methyl)iodo compound $\text{trans}[\text{Pt}(\text{CH}_3)\text{I}\{\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2\text{-P}\}_2]$ (**14**) (Scheme 4). The characterizing data are given in Table 2. In the X-ray structure of **13** (Figure 5) the molecule adopts a *trans* square planar conformation with the P–N–P backbone of the ligands lying approximately in the coordination plane [maximum deviation from the PtP_2CCl mean plane of C(49) 0.20 Å below the plane]. Interestingly, the potential for N–H···Cl hydrogen bonding appears to favor the P–NH–P(O) ligands pointing in the same direction as each other [i.e. the molecule has an approximate mirror plane running through the C(49)–Pt–Cl vector]. The H···Cl distances are

Scheme 3. Proposed Mechanism for Formation of **10**.



Scheme 4^a



^a Key: (i) 2 **HL**, CH_2Cl_2 ; (ii) NaI, MeOH.

2.3 and 2.4 Å. The Pt–(P–N–P)₂ unit thus lies close to coplanar with the coordination plane [maximum deviations from the $\text{PtClCP}_4\text{N}_2$ plane are 0.3 Å above the plane for both nitrogen atoms with both oxygen atoms being 0.7 Å from this plane; the noncoordinated phosphorus atoms are 0.04 Å from this plane]. In common with **6** the N–H protons are *anti* with respect to the respective oxygen atoms. Two N–H stretches at 3198 and 3135 cm^{-1} are also observed in the IR spectrum of **13**.

In order to ascertain the stability of the chelate rings we tested the reactivity of **10** and **11** toward protonation (Scheme 5). The M–P–N–P–O chelate rings are readily cleaved to regenerate **4** by addition of concentrated HCl to an ethanolic suspension of **10** at ambient temperature; the retention of the *cis* geometry was confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR. When compound **10** was treated with the noncoordinating acid $\text{HBF}_4\cdot\text{OEt}_2$, the cationic complex $\text{cis}[\text{Pt}\{\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2\}_2][\text{BF}_4]_2$ (**15**) could be isolated in excellent yield. Compound **15** can also be made by chloride abstraction from compound **4** in dichloromethane. The analogous palladium(II) complex (**16**) could be prepared in a similar way. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **15** reveals that upon protonation the $^1J(\text{PtP}_A)$ coupling constant is marginally

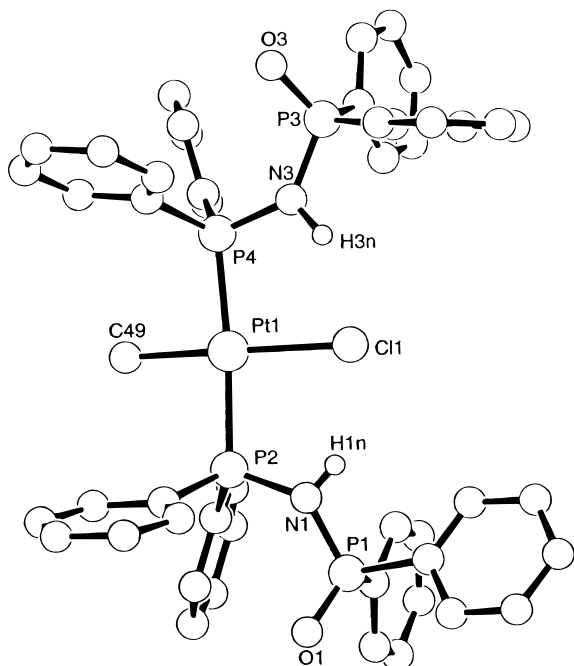
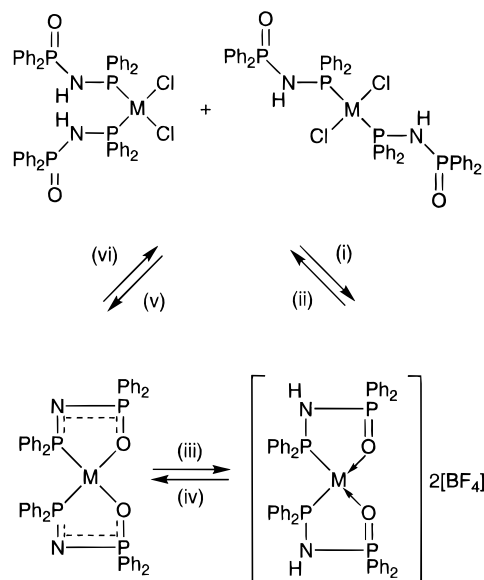


Figure 5. Crystal structure of *trans*-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-P}₂] (**13**). Selected bond lengths (Å) and angles (deg): Pt(1)–Cl(1) 2.423(2), Pt(1)–P(2) 2.298(2), Pt(1)–P(4) 2.292(2), Pt(1)–C(49) 2.070(6), P(1)–O(1) 1.465(5), P(1)–N(1) 1.667(5), P(2)–N(1) 1.679(4), P(3)–O(3) 1.478(4), P(3)–N(3) 1.669(5), P(4)–N(3) 1.695(5); Cl(1)–Pt(1)–P(2) 91.71(5), Cl(1)–Pt(1)–P(4) 91.95(5), Cl(1)–Pt(1)–C(49) 174.8(2), P(2)–Pt(1)–P(4) 173.39(5), P(2)–Pt(1)–C(49) 88.4(2), P(4)–Pt(1)–C(49) 88.5(2), O(1)–P(1)–N(1) 113.9(3), Pt(1)–P(2)–N(1) 110.7(2), O(3)–P(3)–N(3) 114.3(2), Pt(1)–P(4)–N(3) 108.4(2), P(1)–N(1)–P(2) 131.6(3), P(3)–N(3)–P(4) 131.3(3).

Scheme 5^a



^a Key: (i) Ag[BF₄], CH₂Cl₂; (ii) LiCl; (iii) HBF₄·OEt₂; (iv) NEt₃; (v) ^tBuOK, MeOH; (vi) HCl, EtOH. M = Pt, Pd.

increased to 3924 Hz and the *J*(PtP_X) coupling constant is reduced to 88 Hz. Interestingly, Shaw and co-workers³⁴ suggest that, in the related dications [Pt{PPh₂CH₂P(O)Ph₂-P,O}₂]²⁺2X[−] (X = NO₃ or PF₆), the coupling between Pt and P(O) (typically 70 Hz) is mainly a three-bond coupling. A single-crystal X-ray diffraction study of one of these complexes, **15**, confirms that protonation has occurred at the nitrogen atom of both chelate rings. The structure of the complex is shown in Figure 6. The structure of **15** has crystallographic C₂ symmetry. The neutral ligands are *cis* coordinated to the square planar center. A

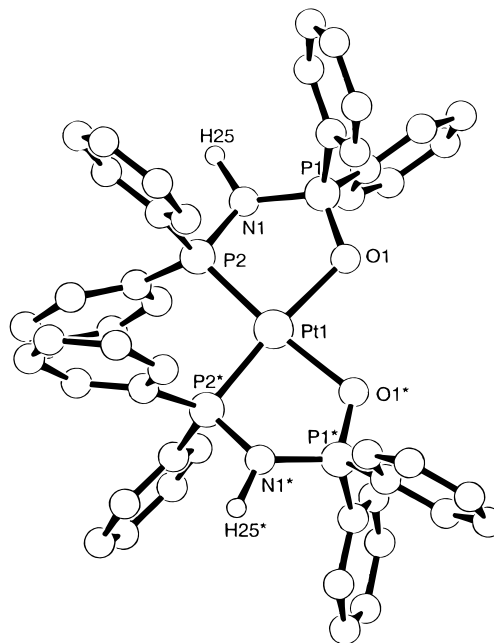


Figure 6. Crystal structure of the dication in *cis*-[Pt{Ph₂PNHP(O)Ph₂-P,O}₂][BF₄]₂ (**15**). Selected bond lengths (Å) and angles (deg): Pt(1)–P(2) 2.213(4), Pt(1)–P(2*) 2.213(4), Pt(1)–O(1) 2.108(10), Pt(1)–O(1*) 2.108(10), P(1)–O(1) 1.502(9), P(1)–N(1) 1.640(12), P(2)–N(1) 1.700(11); P(2)–Pt(1)–P(2*) 98.5(2), P(2)–Pt(1)–O(1) 87.3(3), P(2)–Pt(1)–O(1*) 174.2(3), O(1)–Pt(1)–O(1*) 86.9(5), O(1)–P(1)–N(1) 107.2(6), Pt(1)–P(2)–N(1) 101.4(4), Pt(1)–O(1)–P(1) 118.6(6), P(1)–N(1)–P(2) 118.1(7).

comparison with the deprotonated complex **10**, reveals that the P–N bond lengths [1.640(12) Å, P(1)–N(1), and 1.700(11) Å, P(2)–N(1)] are longer and the P=O bond distance (1.502 Å) is shorter in **15**, i.e. there is less delocalization in the complex containing the neutral ligand. The PtP₂NO ring in **15** is slightly puckered in a manner similar to those in **10** [N(1) lies 0.37 Å below the PtP₂NO plane]. The BF₄[−] counterions are involved in bifurcated H-bonds to the N–H proton [H(25)–F(1) 2.21 Å, H(25)–F(2) 1.94 Å, N⋯B 3.73 Å]. Deprotonation of the amine proton in **15** with NEt₃ regenerates the *bis* chelate **10** while treatment of **15** with an excess of LiCl in MeOH regenerates compound **4**.

Concluding Remarks

We have shown that the mixed P(III)–N–P(V) ligand Ph₂PNHP(O)Ph₂ can be prepared by oxidation of Ph₂PNHPPH₂ and that this ligand has the potential to ligate in a variety of bonding modes. Apart from behaving as a classical unidentate *P*-bonded ligand, participation of the functional P=O group can be induced by facile deprotonation of the amine proton on the ligand to generate bis(chelate)metal complexes. Acid treatment either regenerates the starting dichloro complex (with HCl) or protonates the nitrogen of the M–P–N–P–O ring (with HBF₄·OEt₂). The compounds described represent to our knowledge relatively rare examples of Pd and Pt coordinated by neutral phosphine oxides or by anionic oxygen donor centers. Further studies are currently in progress into the synthesis of heterobimetallic complexes incorporating both early and late transition metal moieties.

Acknowledgment. We should like to thank the EPSRC for support and Johnson-Matthey Inc. for loans of precious metals.

Supporting Information Available: Tables giving experimental crystallographic details, bond lengths, bond angles, and anisotropic displacement parameters for non-hydrogen atoms and atomic coordinates for hydrogen atoms of **HL**, **6**, **10**, **13**, and **15** (33 pages). Ordering information is given on any current masthead page.