Co-ordination chemistry of a P,O-donor ligand: synthesis of new complexes of Ru, Rh and Ir containing Ph₂PNHP(O)Ph₂ or [Ph₂PNP(O)Ph₂]⁻

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Methylation of the monooxide $Ph_2PNHP(O)Ph_2$ (HL) with MeI in tetrahydrofuran afforded [{Ph₂P(Me)NP(O)Ph₂}₂H]I which contains a symmetrical hydrogen bond, whereas benzylation with $PhCH_2Br$ gave [Ph₂P(CH₂Ph)NP(OH)Ph₂]Br. The compound HL can be complexed, as a monodentate P-bound ligand, to various metal centres (Ru^{II}, Ru^{IV}, Rh^{III} and Ir^{III}). These compounds are excellent precursors for the construction of new five-membered metallacycles containing either M–P–N(H)–P–O or M–P–N–P–O rings. Treatment of [Ir{Ph₂PNHP(O)Ph₂-P,O}(cod)][BF₄] (cod = cycloocta-1,5-diene) with an excess of MeI gave the oxidative addition compound [IrI(Me){Ph₂PNHP(O)Ph₂-P,O}(cod)][BF₄] in which a cis configuration of the iodide and methyl ligands is tentatively assigned. Deprotonation of it with NEt₃ gave the known neutral iridium(III) complex [IrI(Me){Ph₂PNP(O)Ph₂-P,O}(cod)]. All compounds were characterised by a combination of $^{31}P-\{^1H\}$ and ^1H NMR spectroscopy, IR spectroscopy and microanalysis. The solid-state structures of [{Ph₂P(Me)NP(O)Ph₂}₂H]I, [Ph₂P(CH₂Ph)NP(OH)Ph₂]Br, [Rh{Ph₂PNHP(O)Ph₂-P,O}(cod)]-[BF₄]·0.33CHCl₃ and [RuCl{Ph₂PNP(O)Ph₂-P,O}(η⁶-p-MeC₆H₄Prⁱ)] have been elucidated by X-ray crystallography. The two complexes contain the P,O-chelating ligand $Ph_2PNHP(O)Ph_2$ and [Ph₂PNP(O)Ph₂]⁻ respectively. With the exception of the rhodium complex the P–N–P–O fragments all show π-electron delocalisation.

Tertiary phosphines and phosphine oxide ligands are ubiquitous in inorganic chemistry. Many studies have focused on the use of $(Ph_2P)_2NH$ and $[\{Ph_2P(O)\}_2N]^-$ as ligands for complexing a diverse range of metal ions[1–3] We have found that $Ph_2PNHP(O)Ph_2$ (HL) incorporating both 'soft' and 'hard' donor sites is an excellent compound for assembling new M–P–N–P–O metallacycles[4–7] and additionally undergoes other interesting transformations.[5,7,8] Associated mixed-donor systems such as $Ph_2P(CH_2)_nP(E)Ph_2$ ($n = 1$ or 2; E = O or S) have also found important applications in catalysis.[9–11]

Quaternisation of the monochalcogenides $Ph_2PCH_2P(E)Ph_2$ (E = O, S or Se) with MeX (X = Br or I) has hitherto been shown to afford the unsymmetrical compounds [Ph₂P(Me)-CH₂P(E)Ph₂]X containing both $Ph_2P(Me)$ and $P(E)Ph_2$ phosphorus(V) moieties.[12] Through this work we have found that methylation of HL with MeI yields the unusual alkylphosphonium salt [{Ph₂P(Me)NP(O)Ph₂}₂H]I in which two [Ph₂P(Me)-NP(O)Ph₂]⁻ molecules are linked by a symmetrical hydrogen bond (X-ray evidence). The corresponding reaction with $PhCH_2Br$ gave the tautomer [Ph₂P(CH₂Ph)NP(OH)Ph₂]Br (X-ray evidence), in which the original NH proton is located on the oxygen atom, and not [Ph₂P(CH₂Ph)NHP(O)Ph₂]Br. Previous work[4–7] has shown that a variety of co-ordination modes exist for HL and the deprotonated [Ph₂PNP(O)Ph₂]⁻ (L). Since very few platinum-group metal complexes of HL and L are documented we report here the synthesis and characterisation of some new complexes of Ru, Rh and Ir. Furthermore the oxidative addition of MeI to the iridium(I) compound [Ir{Ph₂PNHP(O)Ph₂-P,O}(cod)][BF₄] (cod = cycloocta-1,5-diene) has also been investigated.

Experimental

General

Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The compound $Ph_2PNHP(O)Ph_2$ (HL) and the metal complexes [MCl{Ph₂PNHP(O)Ph₂-

P}(cod)] (M = Rh or Ir), [{RhCl(μ-Cl)(η⁵-C₅Me₅)}₂] and [{RuCl(μ-Cl)(η³:η³-C₁₀H₁₆)}₂] were prepared according to literature methods.[4,5,13,14] The compounds [{RuCl(μ-Cl)(η⁶-p-MeC₆H₄Prⁱ)}₂], Ag[BF₄], $PhCH_2Br$, NEt₃ and KOBuᵗ were obtained from the Aldrich Chemical Company and MeI from Fisons and used without further purification. The iridium(III) dimer [{IrCl(μ-Cl)(η⁵-C₅Me₅)}₂] was a kind donation from Dr. J. Parr.

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm⁻¹ on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with δ in ppm (±0.01) referenced to external SiMe₄ and coupling constants (J) in Hz (±0.1) and $^{31}P-\{^1H\}$ NMR spectra (36.2 MHz) on a JEOL FX90Q spectrometer with δ in ppm (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±3). All NMR spectra were measured in CDCl₃. 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 plc.

Preparations

[{Ph₂P(Me)NP(O)Ph₂}₂H]I. To a 5 mm NMR tube containing a tetrahydrofuran (thf) (ca. 0.5 cm³) solution of Ph₂PNH-P(O)Ph₂ (0.030 g, 0.075 mmol) was added MeI (0.072 g, 0.507 mmol, 6.8 equivalents) and the reaction monitored by $^{31}P-\{^1H\}$ NMR spectroscopy over a period of ca. 30 min. The major product identified was [{Ph₂P(Me)NP(O)Ph₂}₂H]I which could be isolated by layering the solution with diethyl ether and leaving to stand for ca. 1 d. A white crystalline solid deposited and was collected by suction filtration and dried in vacuo. Yield 0.029 g, 80%. ^1H NMR data: δ 7.72–7.28 (aromatic H) and 2.15 [²J(PH) 12.5 Hz, PCH₃]. Suitable crystals for X-ray crystallography were grown from CDCl₃–diethyl ether.

[Ph₂P(CH₂Ph)NP(OH)Ph₂]Br. A 5 mm NMR tube was charged with Ph₂PNHP(O)Ph₂ (0.030 g, 0.0747 mmol) and

PhCH$_2$Br (ca. 0.1 g, 0.585 mmol) in thf (0.5 cm^3). The solution was warmed to 50 °C for ca. 6 h and the product isolated by addition of diethyl ether (5 cm^3). Yield 0.016 g, 37%. ^{1}H NMR data: δ 7.68–7.02 (aromatic H) and 4.38 [^2J(PH) 12.5 Hz, PCH$_2$]. Slow diffusion of diethyl ether into a CDCl$_3$ solution of the salt gave crystals suitable for X-ray crystallography.

[RuCl$_2$\{Ph$_2$PNHP(O)Ph$_2$-P\}(η^6-p-MeC$_6$H$_4$Pr^i)] 1. To a suspension of [\{RuCl(μ-Cl)(η^6-p-MeC$_6$H$_4$Pr^i)\}$_2$] (0.113 g, 0.185 mmol) in thf (20 cm^3) was added Ph$_2$PNHP(O)Ph$_2$ (0.150 g, 0.374 mmol) as a solid. The suspension dissolved and the product 1 precipitated. After stirring for ca. 90 min, the volume was concentrated to ca. 5–10 cm^3 and petroleum (b.p. 60–80 °C, 20 cm^3) added. The solid was isolated by suction filtration and dried in vacuo. Yield 0.253 g, 97%. This procedure was extended to include the preparation of the following dichlorometal compounds: [RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)\{Ph$_2$PNHP(O)Ph$_2$-P\}] 2 (97%), [RhCl$_2$(η^5-C$_5$Me$_5$)\{Ph$_2$PNHP(O)Ph$_2$-P\}] 3 (88%) and [IrCl$_2$(η^5-C$_5$Me$_5$)\{Ph$_2$PNHP(O)Ph$_2$-P\}] 4 (98%).

[Rh\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(cod)][BF$_4$] 5. To a CH$_2$Cl$_2$ (20 cm^3) solution of [RhCl\{Ph$_2$PNHP(O)Ph$_2$-P\}(cod)] (0.097 g, 0.150 mmol) was added solid Ag[BF$_4$] (0.045 g, 0.231 mmol). After stirring for 20 min, AgCl was removed by filtration through a Celite pad and the volume reduced in vacuo to ca. 1–2 cm^3. Addition of diethyl ether (10 cm^3) gave a yellow precipitate which was collected by suction filtration. Yield 0.087 g, 78%. Crystals of complex 5 suitable for X-ray crystallography were grown from CDCl$_3$–diethyl ether over a period of ca. 2 d. The above procedure was extended to include the preparation of the following compounds: [Ir\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(cod)][BF$_4$] 6 (92%), [RuCl\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(η^6-p-MeC$_6$H$_4$Pr^i)][BF$_4$] 7 (84%), [RuCl(η^3:η^3-C$_{10}$H$_{16}$)\{Ph$_2$PNHP(O)Ph$_2$-P,O\}][BF$_4$] 8 (84%), [RhCl(η^5-C$_5$Me$_5$)\{Ph$_2$PNHP(O)Ph$_2$-P,O\}][BF$_4$] 9 (77%) and [IrCl(η^5-C$_5$Me$_5$)\{Ph$_2$PNHP(O)Ph$_2$-P,O\}][BF$_4$] 10 (62%).

[RuCl\{Ph$_2$PNP(O)Ph$_2$-P,O\}(η^6-p-MeC$_6$H$_4$Pr^i)] 11. To a suspension of [RuCl$_2$\{Ph$_2$PNHP(O)Ph$_2$-P\}(η^6-p-MeC$_6$H$_4$Pr^i)] (0.104 g, 0.147 mmol) in MeOH (1 cm^3) was added solid KOBu^t (0.019 g, 0.169 mmol). The mixture was stirred for 5 min and the product 11 filtered off, washed with MeOH (1 cm^3) and dried in vacuo. Yield 0.092 g, 93%. Slow diffusion of petroleum (b.p. 40–60 °C) into a CH$_2$Cl$_2$ solution of 11 over ca. 7 d gave crystals suitable for X-ray crystallography. The above procedure was extended to include the preparation of the following compounds: [RuCl(η^3:η^3-C$_{10}$H$_{16}$)\{Ph$_2$PNP(O)Ph$_2$-P,O\}] 12 (84%) and [RhCl(η^5-C$_5$Me$_5$)\{Ph$_2$PNP(O)Ph$_2$-P,O\}] 13 (77%). The iridium(III) compound [IrCl(η^5-C$_5$Me$_5$)\{Ph$_2$PNP(O)Ph$_2$-P,O\}] 14 was prepared from [IrCl$_2$(η^5-C$_5$Me$_5$)\{Ph$_2$PNHP(O)Ph$_2$-P\}] and NEt$_3$ (56%).

[IrI(Me)\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(cod)][BF$_4$] 15. A solution of [Ir\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(cod)][BF$_4$] (0.027 g, 0.033 mmol) in CH$_2$Cl$_2$ (1 cm^3) was treated with an excess of MeI (0.160 g, 1.130 mmol) and the solution monitored by ^{31}P-\{^{1}H\} NMR spectroscopy. After 48 h only [IrI(Me)\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(cod)][BF$_4$] 15 was observed and was isolated by addition of diethyl ether (10 cm^3). Yield 0.017 g, 55%. ^{1}H NMR data: δ 8.06–7.38 (aromatic H); 6.26, 5.83, 4.41, 3.87 (=CH, cod), 2.75–1.25 (CH$_2$, cod) and 2.32 [^3J(PH) 5.0 Hz, IrCH$_3$].

[IrI(Me)\{Ph$_2$PNP(O)Ph$_2$-P,O\}(cod)] 16. To a CDCl$_3$ (0.5 cm^3) solution of [IrI(Me)\{Ph$_2$PNHP(O)Ph$_2$-P,O\}(cod)][BF$_4$] (0.006 g, 0.0064 mmol) was added NEt$_3$ (0.009 g, 0.089 mmol) and the solution examined by ^{31}P-\{^{1}H\} NMR spectroscopy. An immediate reaction occurred and the exclusive product observed was the neutral complex [IrI(Me)\{Ph$_2$PNP(O)Ph$_2$-P,O\}(cod)] 16 the ^{31}P NMR data of which matched well with those reported in ref. 5.

Spectroscopic and microanalysis data for all new complexes are compiled in Tables 1 and 2.

X-Ray crystallography

The crystal structures of [\{Ph$_2$P(Me)NP(O)Ph$_2$\}$_2$H]I, [Ph$_2$P(CH$_2$Ph)NP(OH)Ph$_2$]Br, 5 and 11 were determined using a Rigaku AFC7S diffractometer with graphite-monochromated (Cu-Kα) radiation and ω scans. Details of the data collections and refinements are given in Table 7. Empirical absorption corrections (DIFABS) were applied.[15] The structures were solved by the heavy atom method[16] and all of the non-hydrogen atoms refined anisotropically. The carbon atom of the partial occupancy CHCl$_3$ solvate in complex 5 was refined isotropically. In all four structures all CH protons were refined in idealised geometries. In [\{Ph$_2$P(Me)NP(O)Ph$_2$\}$_2$H]I the O–H–O H atom was located from a ΔF map on a crystallographic centre of symmetry. In [Ph$_2$P(CH$_2$Ph)NP(OH)Ph$_2$]Br the OH H atom was located from a ΔF map; furthermore partial disorder was observed, P(2) being refined in two locations (each of 50% occupancy) with a benzylic CH$_2$ group [50% occupancy] associated with each partial-occupancy phosphorus. Each CH$_2$ group is associated with a 50% occupancy benzylic Ph group which overlays the Ph group (50% occupancy) associated with the other partial occupancy P(2) atom. With both partial-occupancy phosphorus atoms one Ph[C(19)–C(24)] was not disordered or associated with any benzylic group. The half-occupancy protons associated with C(25a) and C(25b) were not included in the refinement. Refinement was by full-matrix least-squares methods on F. Calculations were performed using TEXSAN.[17]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/294.

Results and Discussion

Alkylation studies of the monooxide Ph$_2$PNHP(O)Ph$_2$

Previous work by Marjoral and co-workers[18] has shown that (Ph$_2$P)$_2$NH (dppa) undergoes prototropism upon reaction with CF$_3$SO$_3$Me or [CPh$_3$][BF$_4$] to give [Ph$_2$P(H)=NP(R)Ph$_2$]X (R = Me or CPh$_3$, X = CF$_3$SO$_3$ or PF$_6$) (Scheme 1). Further-

R = Me, X = CF$_3$SO$_3$
R = CPh$_3$, X = PF$_6$
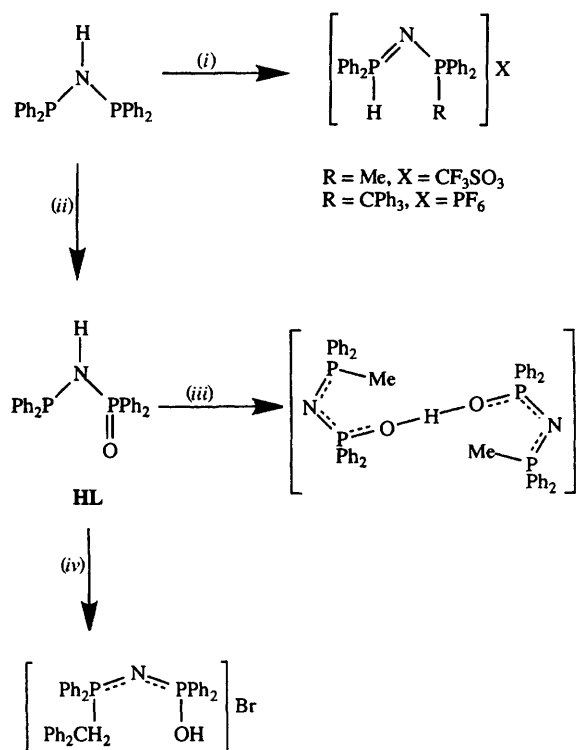
Scheme 1 (i) CF$_3$SO$_3$Me or [CPh$_3$][PF$_6$], CH$_2$Cl$_2$; (ii) H$_2$O$_2$, thf; (iii) MeI, thf; (iv) PhCH$_2$Br, thf thf; (iii)

Table 1 Selected $^{31}P\text{-}\{^1H\}$ NMR and IR data

| Compound	δ(P)		J(PP)/Hz	ν(N–H)/cm^{-1}	ν(P=O)/cm^{-1}
	PPh$_2$	P(O)Ph$_2$			
[{Ph$_2$P(Me)NP(O)Ph$_2$}$_2$H]I	18.5^a	22.3	n.o.^{b}		
[Ph$_2$P(CH$_2$Ph)NP(OH)Ph$_2$]Br	25.9^a	22.4	n.o.^{b}		
1	62.1	20.4	39.6	3244	1212
2	58.5	19.6	44.0	3132	1217
3	66.2 (147.4)^c	21.1 (4.4)^d	41.1	3212	1215
4	35.7	21.1	37.4	3223	1215
5	75.6 (154)^c	61.5	35	3173	
6	69.6	65.5	30.5	3163	
7	82.1	65.0	28.6	3209	
8	66.5	65.8	34.4	3192	
9	76.5 (146.6)^c	58.0	24.9	3213	
10	65.9	58.4	22.0	3208	
11	75.7	69.6	30.8		
12	67.0	55.0	41.8		
13	72.5 (128.5)^c	63.3	24.9		
14	74.7	50.7	26.4		
15	61.7	28.2	22	3180	

^{a} Assignment tentative only. ^{b} Not observed. ^{c} ^1J(RhP) coupling constant. ^{d} ^3J(RhP) coupling constant (measured at 101.3 MHz).

Table 2 Microanalytical data (calculated values in parentheses)

Compound	C	H	N
[{Ph$_2$P(Me)NP(O)Ph$_2$}$_2$H]I	62.30 (62.65)	4.80 (4.95)	2.90 (2.90)
[Ph$_2$P(CH$_2$Ph)NP(OH)Ph$_2$]Br	64.75 (65.05)	4.55 (4.95)	2.35 (2.45)
1	57.45 (57.70)	4.95 (5.00)	2.05 (2.00)
2	57.50 (57.55)	5.15 (5.25)	2.05 (1.95)
3	57.30 (57.45)	5.20 (5.10)	1.65 (1.90)
4	52.30 (51.05)	4.50 (4.55)	1.60 (1.75)
5	52.00 (52.55)	4.55 (4.50)	1.95 (1.90)
6	46.10 (48.75)	3.80 (4.25)	1.65 (1.80)
7	53.35 (53.80)	4.55 (4.65)	2.00 (1.85)
8	53.45 (53.65)	4.75 (4.90)	1.60 (1.85)
9	52.75 (53.60)	4.55 (4.75)	1.85 (1.85)
10	47.45 (48.00)	3.70 (4.25)	1.65 (1.65)
11	60.55 (60.80)	5.15 (5.10)	2.20 (2.10)
12	60.50 (60.65)	5.15 (5.40)	2.20 (2.10)
13	59.85 (60.60)	5.20 (5.25)	2.25 (2.10)
14	52.95 (53.50)	4.40 (4.65)	2.40 (1.85)
15	43.05 (42.60)	3.80 (3.90)	1.35 (1.50)

more the anion [Ph$_2$PNPPh$_2$]$^-$, derived from deprotonation of dppa with LiBu^n, reacts with MeI to give instead [Ph$_2$(Me)-P=N=P(Me)Ph$_2$]I with phosphorus quaternisation, whilst methylation at sulfur in Me$_2$P(S)NHP(S)Me$_2$ affords [(MeS)-PMe$_2$NPMe$_2$(SMe)]I.[19,20] The presence of the two tautomers [Re(Ph$_2$PNHPPh$_2$-P)(CO)$_5$]$^+$ and [Re{Ph$_2$P=NP(H)Ph$_2$-P}(CO)$_5$]$^+$ in solution was shown by NMR spectroscopy.[21] We recently reported[4] the synthesis of the heterodifunctional compound Ph$_2$PNHP(O)Ph$_2$ (HL) and were intrigued as to its reactivity towards alkylating agents. The alkylation of HL with an excess of iodomethane in thf gave the compound [{Ph$_2$P-(Me)NP(O)Ph$_2$}$_2$H]I in high yield (80%). The $^{31}P\text{-}\{^1H\}$ NMR spectrum show singlet resonances at δ 18.5 and 22.3 [^2J(PP) coupling not resolved] consistent with two inequivalent phosphorus nuclei and, in the ^1H NMR spectrum (Experimental section), the expected doublet for the methyl protons (PCH$_3$) was observed.

The crystal structure (Fig. 1, Table 3) reveals that quaternisation of P(2) is accompanied by proton migration from the nitrogen centre to oxygen. For HL the crystal structure clearly established protonation at N with strong N–H···O hydrogen bonds to give dimers.[4] In the dioxygen compound Ph$_2$P(O)-NP(OH)Ph$_2$ one of the oxygen atoms is protonated[22] whilst in the analogous Ph$_2$P(E)NHP(E)Ph$_2$ (E = S or Se) the proton lies on the nitrogen.[22–24] In [{Ph$_2$P(Me)NP(O)Ph$_2$}$_2$H]I the O···H···O hydrogen atom occupies a crystallographic centre of symmetry. Linear hydrogen bonds are well established
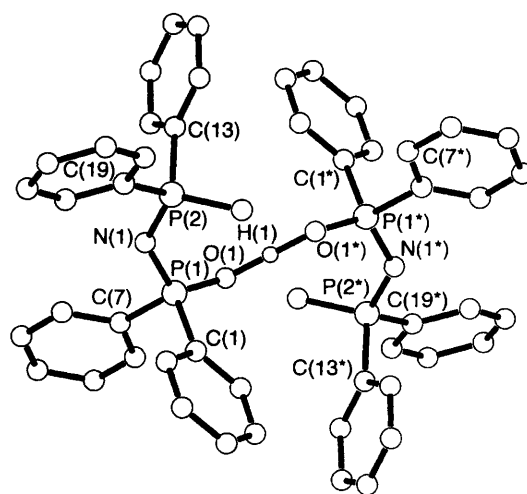
Fig. 1 Crystal structure of [{Ph$_2$P(Me)NP(O)Ph$_2$}$_2$H]I (I$^-$ counter ion omitted for clarity)
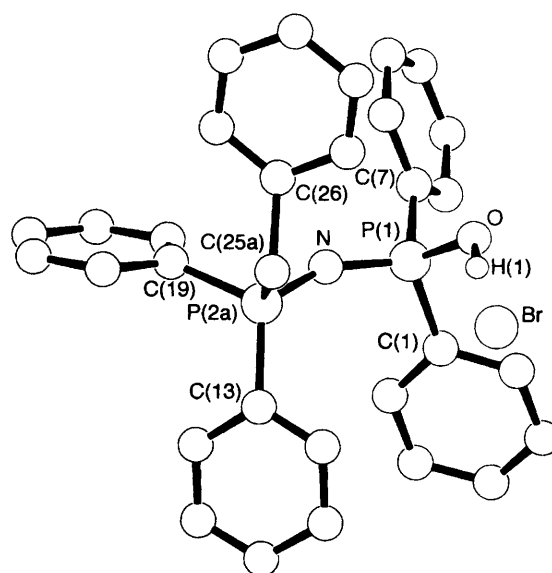
Fig. 2 Crystal structure of [Ph$_2$P(CH$_2$Ph)NP(OH)Ph$_2$]Br [P(2) and C(25) are disordered and P(2a) and C(25a) are 50% occupancy sites]

Table 3 Selected bond lengths (Å) and angles (°) for [{Ph₂P(Me)NP-(O)Ph₂}₂H]I

P(1)–O(1)	1.530(3)	P(1)–N(1)	1.580(4)
P(2)–N(1)	1.579(4)	P(2)–C(25)	1.772(5)
P–C range	1.790(5)–1.794(5)		
O(1)–P(1)–N(1)	118.4(2)	N(1)–P(2)–C(25)	115.5(2)
P(1)–N(1)–P(2)	131.5(3)		

Table 4 Selected bond lengths (Å) and angles (°) for [Ph₂P(CH₂Ph)-NP(OH)Ph₂]Br

P(1)–O	1.561(3)	P(1)–N	1.552(4)
P(2a)–N	1.589(4)	P(2b)–N	1.565(4)
P–C range	1.470(10)–1.932(7)		
O–P(1)–N	117.3(2)	P(1)–N–P(2b)	152.6(3)
P(1)–N–P(2a)	152.5(3)		

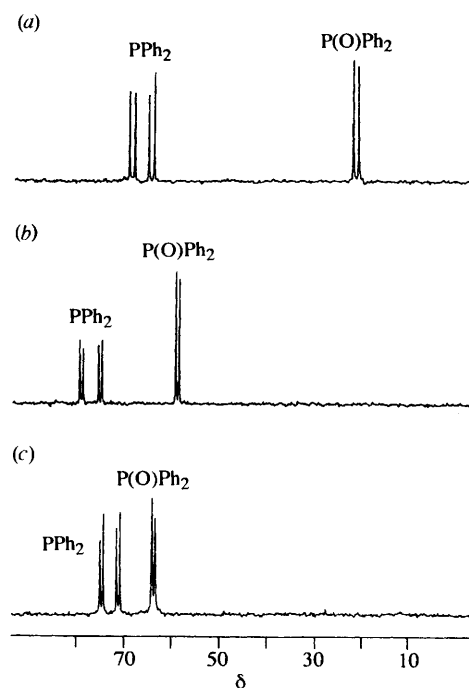**Table 5** Selected bond lengths (Å) and angles (°) for complex 5

Rh–P(2)	2.272(2)	Rh–O	2.092(4)
Rh–C(25)	2.243(7)	Rh–C(26)	2.242(7)
Rh–C(29)	2.123(7)	Rh–C(30)	2.101(7)
P(1)–O	1.507(4)	P(1)–N	1.651(5)
P(2)–N	1.697(5)		
P(2)–Rh–O	85.9(1)	P(2)–Rh–C(25)	162.3(2)
P(2)–Rh–C(26)	161.0(2)	P(2)–Rh–C(29)	98.9(2)
P(2)–Rh–C(30)	94.7(2)	O–Rh–C(25)	91.8(2)
O–Rh–C(26)	87.6(2)	O–Rh–C(29)	159.9(2)
O–Rh–C(30)	161.3(2)	O–P(1)–N	108.4(2)
Rh–P(2)–N	103.6(2)	Rh–O–P(1)	120.0(2)
P(1)–N–P(2)	119.0(3)		

Fig. 3 The ³¹P-{¹H} NMR spectra (36.2 MHz) of (a) [RhCl₂(η⁵-C₅Me₅){Ph₂PNHP(O)Ph₂-P}], (b) [RhCl(η⁵-C₅Me₅){Ph₂PNHP(O)Ph₂-P,O}][BF₄] and (c) [RhCl(η⁵-C₅Me₅){Ph₂PNP(O)Ph₂-P,O}]

1 M = Ruᴵᴵ, L = η⁶-p-MeC₆H₄Prⁱ
2 M = Ruᴵⱽ, L = η³:η³-C₁₀H₁₆
3 M = Rhᴵᴵᴵ, L = C₅Me₅
4 M = Irᴵᴵᴵ, L = C₅Me₅

and the O · · · O separation observed here [2.40(1) Å] is identical to that seen in Ph₂P(O)NP(OH)Ph₂. In a recent classification this O · · · O distance is regarded as being associated with a very strong hydrogen bond and it was noted that these very short bonds are often linear/symmetrical.[25] The P(1)–O(1) · · · H angle is 129.9°. The P(1)–O(1) bond length is longer than in HL [P–O 1.530(3) vs. 1.508(2) Å respectively] whilst the P(1)–N(1) and P(2)–N(1) bond lengths are much shorter than in HL [P(1)–N(1) 1.580(4), P(2)–N(1) 1.579(4) vs. 1.651(3), 1.707(3) Å respectively]. The P(1)–N(1)–P(2) angle [131.5(3)°] is increased with respect to HL [125.6(2)°]. There are no other significant intermolecular interactions.
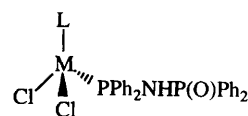
The corresponding reaction of HL with PhCH₂Br gave a crystalline solid having an apparent stoichiometry of [Ph₂P-(CH₂Ph)NHP(O)Ph₂]Br from microanalysis (Table 2). Two singlet resonances were observed (Table 1) in the ³¹P-{¹H} NMR spectrum although again we did not observe a ²J(PP) coupling. Firmly to establish the structure a single-crystal X-ray study was undertaken (Fig. 2, Table 4). The structure is disordered at P(2) and a detailed discussion of the geometry is thus not worthwhile. However, it is evident that proton transfer has also occurred. The P(1)–O bond length together with the O–H(1) · · · Br hydrogen bond [O · · · Br 3.04, H(1) · · · Br 1.92 Å] are in accord with this analysis. Furthermore, the P–N bond lengths are ca. 1.57 Å.

Metal complexes of the monooxide Ph₂PNHP(O)Ph₂

We have previously shown that the direct reaction between HL and bimetallic systems such as [{Pd(μ-Cl)(η³-C₃H₅)}₂] is an excellent preparative method for the synthesis of neutral mononuclear compounds bearing a pendant –P(O)Ph₂ group.[5–7] The reaction of the dinuclear chloride complexes [{RuCl-(μ-Cl)(η⁶-p-MeC₆H₄Prⁱ)}₂], [{RuCl(μ-Cl)(η³:η³-C₁₀H₁₆)}₂] or [{MCl(μ-Cl)(η⁵-C₅Me₅)}₂] (M = Rh or Ir) with 2 equivalents of HL proceeds rapidly, at room temperature, to give the mononu-

clear complexes [RuCl₂{Ph₂PNHP(O)Ph₂-P}(η⁶-p-MeC₆H₄Prⁱ)] 1, [RuCl₂(η³:η³-C₁₀H₁₆){Ph₂PNHP(O)Ph₂-P}] 2, [RhCl₂(η⁵-C₅Me₅){Ph₂PNHP(O)Ph₂-P}] 3 and [IrCl₂(η⁵-C₅Me₅){Ph₂-PNHP(O)Ph₂-P}] 4 in excellent yields (88–98%).

The compounds 1–4 display the expected spectroscopic and analytical properties (Tables 1 and 2). Particularly diagnostic is δ(P) for the 'dangling' P(O)Ph₂ group which, for these complexes, is found at δ ca. 20 and is similar to that observed for HL [δ(P) 21.4].[4] As a representative example, the ³¹P-{¹H} NMR spectrum of the half-sandwich rhodium(ɪɪɪ) complex 3 is shown in Fig. 3(a). The ¹J(RhP) and ³J(RhP) coupling constants of 3 are 147.4 and 4.4 Hz respectively (cf. 158 and 4.1 Hz for the rhodium(ɪ) complex [RhCl{Ph₂PNHP(O)Ph₂-P}(cod)]). Furthermore the IR spectra (KBr) of 1–4 reveal in all cases a strong ν(P=O) absorption at ca. 1215 cm⁻¹ in accord with co-ordination through P only and no interaction of the phosphoryl group with the metal centre (see below).

Previous studies from our group have found that [MCl{Ph₂PNHP(O)Ph₂-P}(cod)] (M = Rh or Ir) can be efficiently deprotonated with KOBuᵗ in MeOH to give the neutral metallacycles [M{Ph₂PNP(O)Ph₂-P,O}(cod)].[5] We also find that chloride abstraction from [MCl{Ph₂PNHP(O)Ph₂-P}(cod)] (M = Rh or Ir) with Ag[BF₄] in dichloromethane affords the cationic species [M{Ph₂PNHP(O)Ph₂-P,O}-(cod)][BF₄] (M = Rh 5 or M = Ir 6) (Scheme 2). Moreover the generality of this reaction has been extended to the preparation of the new complexes [RuCl{Ph₂PNHP(O)Ph₂-P,O}(η⁶-p-MeC₆H₄Prⁱ)][BF₄] 7, [RuCl(η³:η³-C₁₀H₁₆){Ph₂PNHP(O)Ph₂-P,O}][BF₄] 8, [RhCl(η⁵-C₅Me₅){Ph₂PNHP(O)Ph₂-P,O}][BF₄]
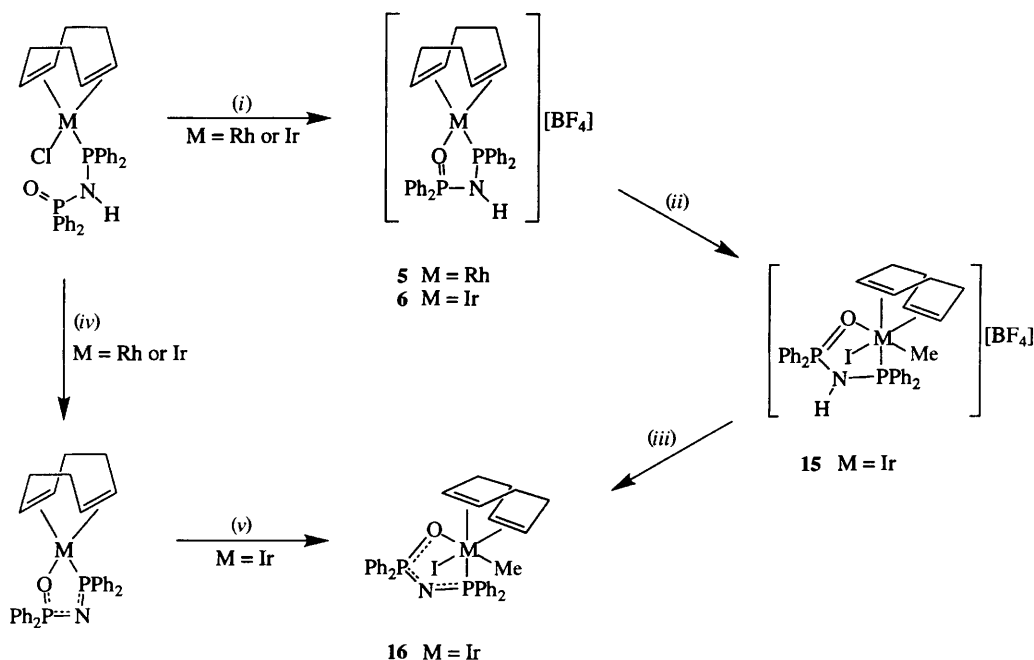
Scheme 2 (i) Ag[BF₄], CH₂Cl₂; (ii) MeI, CH₂Cl₂; (iii) NEt₃, CH₂Cl₂; (iv) KOBuᵗ, MeOH; (v) MeI, CDCl₃

7	M = Ruᴵᴵ, L = η⁶-p-MeC₆H₄Prⁱ	11
8	M = Ruᴵⱽ, L = η³:η³-C₁₀H₁₆	12
9	M = Rhᴵᴵᴵ, L = C₅Me₅	13
10	M = Irᴵᴵᴵ, L = C₅Me₅	14

9 and [IrCl(η⁵-C₅Me₅){Ph₂PNHP(O)Ph₂-P,O}][BF₄] **10**. The ruthenium(ıv) compound **8** was independently observed as the sole product when CDCl₃ solutions of **2** are left to stand for ca. 10 d (³¹P NMR evidence). A similar behaviour however was not seen when CDCl₃ solutions of either **1, 3** or **5** were left for ca. 2 d. The P,O-chelation in complexes **5–10** was deduced from (i) ³¹P-{¹H} NMR spectroscopy [Fig. 3(b), illustrated for the rhodium(ıı) complex **9**] which shows a new doublet for the P(O)Ph₂ group to high frequency consistent with ring closure, (ii) IR spectroscopy which confirms that the NH proton is retained in these complexes but the v(P=O) absorption at ca. 1215 cm⁻¹ is shifted to lower frequency as a result of chelation and, in the case of **5**, the structure was established unequivocally by X-ray crystallography.

Crystals of complex **5** suitable for X-ray crystallography were grown from CDCl₃–Et₂O and found to crystallise as [Rh{Ph₂PNHP(O)Ph₂-P,O}(cod)][BF₄]·0.33CHCl₃ (Fig. 4, Table 5). The geometry of the RhNOP₂ ring is very similar to that observed in the PdNOP₂ ring of [Pd(η³-C₃H₅){Ph₂PNHP-(O)Ph₂-P,O}][BF₄].⁶ The ring is slightly distorted from planar with a maximum deviation of 0.23 Å for O from the Rh–O–P(1)–N–P(2) mean plane. The P(2)–Rh–O angle is 85.9(1)° whilst the P(1)–N and P(2)–N distances are 1.651(5) and 1.697(5) Å respectively and the P(1)–O distance is 1.507(4) Å. These distances are as expected for a protonated ligand and, furthermore the NH proton is involved in a bifurcated hydrogen bond to the [BF₄]⁻ counter ion [H · · · F(2) 2.49, H · · · F(1) 2.62, N · · · F(1) 3.29, N · · · F(2) 3.30 Å] with both F(1) and F(2) lying ca. 0.6 Å above the RhNOP₂ mean plane. There is a slight

Fig. 4 Crystal structure of [Rh{Ph₂PNHP(O)Ph₂-P,O}(cod)][BF₄]·0.33CHCl₃ **5** (solvent molecule omitted for clarity)

pyramidalisation of the nitrogen atom which lies 0.11 Å out of the plane of the three substituents.

Deprotonation of complexes **1–4** with either KOBuᵗ or NEt₃ gave [RuCl{Ph₂PNP(O)Ph₂-P,O}(η⁶-p-MeC₆H₄Prⁱ)] **11**, [RuCl(η³:η³-C₁₀H₁₆){Ph₂PNP(O)Ph₂-P,O}] **12**, [RhCl(η⁵-C₅Me₅)-{Ph₂PNP(O)Ph₂-P,O}] **13** and [IrCl(η⁵-C₅Me₅){Ph₂PNP(O)-Ph₂-P,O}] **14**. Alternatively the cationic complex **8** can be efficiently deprotonated upon addition of NEt₃ (³¹P NMR evidence). The ³¹P-{¹H} NMR data for complexes **11–14** [Table 1, Fig. 3(c) for the half-sandwich rhodium(ıı) complex **13**] confirm that both deprotonation and chelation have resulted. The molecular structure of **11** is shown in Fig. 5 with selected bond lengths and angles in Table 6. The molecule has a three-legged 'piano stool' structure and the Ru atom is co-ordinated to an arene group, a Cl atom and both P and O atoms of [Ph₂PNP(O)Ph₂]⁻ thereby forming a five-membered chelate ring. Moreover the RuNOP₂ ring planarity is not influenced by protonation/deprotonation of the nitrogen atom. The maximum

deviation of the Ru–O–P(1)–N–P(2) mean plane is 0.24 Å for N. As anticipated the P–N bonds are shorter than those in the protonated version of the MNOP$_2$ ring (*e.g.* in **5**), however the P–O bond length is not especially sensitive to protonation.

We have previously observed that the two chelate rings in the dicationic complex *cis*-[Pt{Ph$_2$PNHP(O)Ph$_2$-*P,O*}$_2$][BF$_4$]$_2$ can be opened upon addition of LiCl to give *cis*-[PtCl$_2${Ph$_2$PNHP(O)Ph$_2$-*P*}$_2$].[4] Reaction of either **5** or **7** in MeOH with an excess of LiCl regenerates either [RhCl-{Ph$_2$PNHP(O)Ph$_2$-*P*}(cod)] or [RuCl$_2${Ph$_2$PNHP(O)Ph$_2$-*P*}(η^6-*p*-MeC$_6$H$_4$Pr^i)] illustrating the ease in which the Rh–OPPh$_2$ bond can be cleaved.
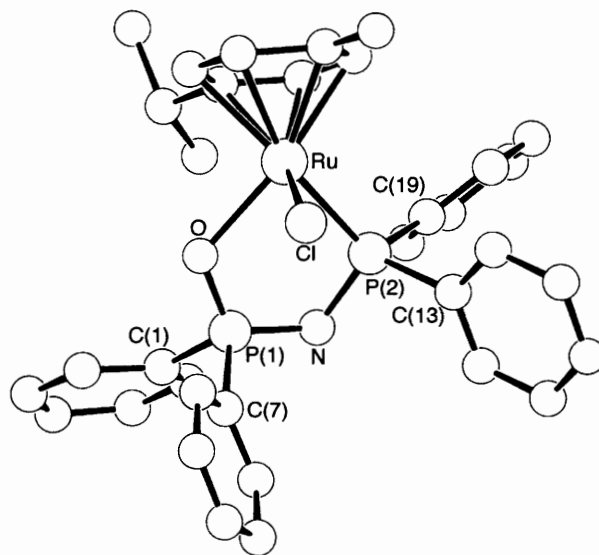
Reaction of [Ir{Ph$_2$PNHP(O)Ph$_2$-*P,O*}(cod)][BF$_4$] with MeI

Oxidative-addition reactions represent a fundamental key step in many catalytic processes, *e.g.* methanol carbonylation using either the Monsanto catalyst [RhI$_2$(CO)$_2$]$^-$ or *cis*-[RhI(CO){Ph$_2$PCH$_2$P(S)Ph$_2$-*P,S*}]. Much emphasis has been directed towards establishing reaction mechanisms and also using models to study intermediates in such cases. Consequently oxidative-addition reactions of square-planar complexes of Rh^I and Ir^I have been the subject of considerable interest particularly with iodomethane. Furthermore the *trans* stereochemistry of Me and I is favoured as confirmed (by X-ray crystallography) in the isostructural compounds

[IrI(Me){MeC(O)CHC(E)Me-*O,E*}(cod)] (E = O or S).[26,27] Recently, we reported the preparation and full characterisation of the IrNOP$_2$ metallacycle [IrI(Me){Ph$_2$PNP(O)Ph$_2$-*P,O*}-(cod)] containing a *cis* arrangement of Me and I ligands.[5] We now find that reaction of **6** with iodomethane in CDCl$_3$ (Scheme 2) affords a new compound characterised, in solution by NMR spectroscopy, as [IrI(Me){Ph$_2$PNHP(O)Ph$_2$-*P,O*}-(cod)][BF$_4$] **15**. In the ^{1}H NMR spectrum the IrCH$_3$ group appears as the expected doublet due to coupling to phosphorus, whilst in the ^{31}P-{^{1}H} NMR spectrum the two inequivalent phosphorus nuclei appear as two doublets with a *J*(PP) coupling of 22 Hz. The cationic compound **15**, in which the iodo and methyl compounds are tentatively assigned a *cis* configuration, is smoothly deprotonated to give [IrI(Me){Ph$_2$PNP(O)Ph$_2$-*P,O*}(cod)] **16**. Complex **16**, which was independently made from the oxidative addition of MeI to [Ir{Ph$_2$PNP(O)Ph$_2$-

Fig. 5 Crystal structure of [RuCl{Ph$_2$PNP(O)Ph$_2$-*P,O*}(η^6-*p*-MeC$_6$H$_4$Pr^i)] **11**

Table 6 Selected bond lengths (Å) and angles (°) for complex **11**

Ru–Cl	2.412(3)	Ru–P(2)	2.336(4)
Ru–O	2.156(8)	P(1)–O	1.496(9)
P(1)–N	1.607(10)	P(2)–N	1.64(1)
Ru–C range	2.14(1)–2.24(1)		
Cl–Ru–P(2)	90.2(1)	Cl–Ru–O	85.2(2)
P(2)–Ru–O	81.3(2)	O–P(1)–N	115.5(6)
Ru–P(2)–N	109.1(4)	Ru–O–P(1)	118.0(4)
P(1)–N–P(2)	112.2(7)	Cl–Ru–C range	90.9(4)–157.0(5)
P(2)–Ru–C range	92.2(4)–162.3(4)	O–Ru–C range	91.1(4)–155.5(5)

Table 7 Details of the X-ray data collections and refinements

	[{Ph$_2$P(Me)NP(O)Ph$_2$}$_2$H]I	[Ph$_2$P(CH$_2$Ph)NP(OH)Ph$_2$]Br	**5**	**11**
Empirical formula	C$_{50}$H$_{47}$IN$_2$O$_2$P$_4$	C$_{31}$H$_{28}$BrNOP$_2$	C$_{32}$H$_{33}$BF$_4$NOP$_2$Rh· 0.33CHCl$_3$	C$_{34}$H$_{34}$ClNOP$_2$Ru
M	958.73	572.42	739.02	671.12
D$_c$/g cm^{-3}	1.34	1.38	1.47	1.44
Crystal colour, habit	Clear, block	Clear, block	Yellow, hexagon	Orange, plate
Crystal dimensions/mm	0.10 × 0.10 × 0.20	0.20 × 0.20 × 0.30	0.20 × 0.50 × 0.50	0.20 × 0.03 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/c	P2$_1$/c	P2$_1$/c	Pbca
a/Å	22.683(6)	14.594(5)	10.503(4)	19.694(2)
b/Å	9.134(6)	9.988(7)	16.896(5)	25.879(6)
c/Å	23.148(5)	19.976(5)	19.147(3)	12.132(3)
β/°	96.53(2)	108.86(2)	100.49(2)	
U/Å^3	4764	2755	3341	6183
Z	4	4	4	8
μ/mm^{-1}	68.6	3.32	6.20	6.09
2θ$_{max}$/°	120.3	120.3	120.5	120.0
F(000)	1960	1176	1501	2752
Measured reflections	3915	4582	5483	5128
Independent reflections (R$_{int}$)	3802 (0.074)	4390 (0.095)	5411 (0.113)	
Observed reflections [I > 3.00σ(I)]	2534	3504	3936	2680
Reflection/parameter ratio	9.5 : 1	10.2 : 1	9.6 : 1	7.4 : 1
Minimum, maximum transmission	0.75, 1.00	0.74, 1.00	0.53, 1.00	0.95, 1.00
p in weighting scheme	0.002	0.002	0.007	0.003
No. variables	268	344	411	362
Final R, R'	0.037, 0.036	0.058, 0.049	0.053, 0.053	0.070, 0.069
Maximum Δ/σ	0.09	0.42	1.70	0.02
Largest difference peak, hole/e Å^{-3}	0.40, −0.62	0.48, −0.40	0.69, −0.66	0.58, −0.66

$P,O\}(\text{cod})]$, was recognised by comparison of its ^{31}P NMR data with those reported in the literature.[5]

The reactivity of HL towards alkylating agents and late transition metals has been studied. Our work has shown that a variety of metallacycles containing a P–N–P–O unit are accessible. Further studies are currently in progress.

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