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Late transition-metal complexes with the heterofunctional phosphine $Ph_2PNHP(O)Ph_2$

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

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

The complexes [MCl(cod)(HL)] (M = Rh or Ir), [PdCl(η^3-C_3H_5)(HL)], [PdCl(L–L)(HL)], *trans*-[RhCl(CO)(HL)$_2$] and [AuCl(HL)] have been synthesised by reaction of either [{M(μ-Cl)(cod)}$_2$] (M = Rh or Ir; cod = cycloocta-1,5-diene), [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$], [{Pd(μ-Cl)(L–L)}$_2$] (L–L = $C_{12}H_{12}N$, $C_{10}H_8N$ or $C_9H_{12}N$), [{Rh(μ-Cl)(CO)$_2$}$_2$] or [AuCl(tht)] (tht = tetrahydrothiophene) with $Ph_2PNHP(O)Ph_2$ (HL). In all these complexes the ligand is monodentate *P*-bound. Chloride abstraction from [PdCl($C_{12}H_{12}N$)(HL)] or [PdCl(η^3-C_3H_5)(HL)], using Ag[BF$_4$], gave the cationic compounds [Pd($C_{12}H_{12}N$)(HL)][BF$_4$] or [Pd(η^3-C_3H_5)(HL)][BF$_4$] in which the ligand HL is *P*,*O*-chelated. Removal of the amine proton in metal complexes of HL (monodentate *P*-bound) with $KOBu^t$ afforded a new class of neutral metallacycles incorporating either an MP_2NO or $M_2P_4N_2O_2$ framework based on the $[Ph_2PNP(O)Ph_2]^-$ (L^-) ligand. Reaction of [{Pd(μ-Cl)($C_9H_{12}N$)}$_2$] with 4 equivalents of HL in methanol at ambient temperature yielded the neutral palladium(II) complex [PdCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(Ph_2POMe)] in which one HL ligand has undergone P–N bond scission. The reaction of the iridacycle [Ir(cod){$Ph_2PNP(O)Ph_2$-*P*,*O*}] with MeI was shown to proceed with *cis* addition affording the iridium(III) metallacycle [IrI(Me)(cod){$Ph_2PNP(O)Ph_2$-*P*,*O*}]. All compounds described have been characterised by a combination of ^{31}P-{^1H} NMR spectroscopy, microanalysis and in some cases by ^1H NMR and IR spectroscopy. The molecular structures of four complexes have been determined by single-crystal X-ray diffraction. The metallacycles show π-electron delocalisation in the P–N–P–O fragment.

The co-ordination chemistry of $Ph_2PNHPPh_2$ (dppa)[1] and $[R_2(E)PNP(E)R_2]^-$ (E = O, S or Se; R = Me, Ph or OPh)[2-15] has received widespread attention over the last few years, but in contrast only limited studies with $Ph_2(E)PNHP(E)Ph_2$[16-18] and the monochalcogenides $Ph_2PNHP(E)Ph_2$ (E = S or Se)[19] have been documented. Cavell and co-workers[20] have studied the metal chemistry of the related $Ph_2PNPhP(E)Ph_2$ (E = S or Se), whilst others[21,22] have described catalytic applications based on the methylene-bridged counterpart $Ph_2PCH_2P(S)Ph_2$. Several studies[23-33] have also focused on the monooxide $Ph_2PCH_2P(O)Ph_2$ incorporating both a 'soft' and 'hard' donor atom. In these systems, co-ordination to a metal centre is *via* a combination of either one or both of the donor atoms.

We recently reported the synthesis of $Ph_2PNHP(O)Ph_2$ (HL), incorporating an amine backbone, and have demonstrated using complexes of Pd^{II} and Pt^{II} that a variety of bonding modes exist for this partially oxidised compound.[34] In complexes HL can co-ordinate through the phosphorus(III) centre only or chelate using both phosphorus and oxygen centres. We also observed that the acidic amine proton is removed readily affording either *P*,*O*-chelate complexes based on an MP_2NO metallacycle or a *P*,*O*-bridging complex based on an $M_2P_4N_2O_2$ metallacycle.[35] In contrast heterofunctionalised *P*,*O*-chelating phosphines incorporating a carbon backbone have been extensively studied by Braunstein and co-workers[36-47] and others.[48-54] To our knowledge, Rossi *et al.*[55] reported the first examples of related inorganic (carbon-free) rhenium metallacycles containing either $Ph_2PNHP(O)Ph_2$ or deprotonated $[Ph_2PNP(O)Ph_2]^-$. These compounds were made from [AsPh$_4$][ReOCl$_4$] and the non-oxidised dppa under different experimental procedures. Recent work by Ellermann and co-workers[56] demonstrated the synthesis of the monodentate *P*-bound anion $[Ph_2PNP(O)Ph_2]^-$, from dppa, at a cobalt(I) centre.

In the present study we describe the reactivity of HL towards Pd^{II}, Rh^I, Ir^I and Au^I and include new examples of metallacycles derived from deprotonated HL. We also show the unexpected formation of a co-ordinated phosphinite derived from methanolysis of the P–N bond in HL.

Experimental

General

Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The compound $Ph_2PNHP(O)Ph_2$ was prepared as previously reported.[34] The complexes [{Pd(μ-Cl)(L–L)}$_2$] [HL-L = *N*,*N*-dimethylbenzylamine ($C_9H_{13}N$),[57] 8-methylquinoline ($C_{10}H_9N$)[58] or *N*,*N*-dimethyl-1-naphthylamine ($C_{12}H_{13}N$)[57]] and [AuCl(tht)][59] (tht = tetrahydrothiophene) were prepared according to literature methods. The compounds [{M(μ-Cl)(cod)}$_2$] (M = Rh or Ir; cod = cycloocta-1,5-diene), [{Rh(μ-Cl)(CO)$_2$}$_2$], [{Pd(μ-Cl)(η-C_3H_5)}$_2$] and Ag[BF$_4$] were obtained commercially (Aldrich or Fluorochem); $KOBu^t$ (Aldrich, 95% purity) and MeI (Fisons) were used without further purification.

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with δ referenced to external $SiMe_4$ and ^{31}P-{^1H} NMR spectra (36.2 or 101.3 MHz) either on a JEOL FX90Q or Bruker AC250 FT spectrometer with δ referenced to external H_3PO_4. Microanalyses were performed by the Loughborough University Service within this Department.

Sodium tetrachloropalladate and tetrachloroauric acid were provided on loan by Johnson Matthey plc.

Preparation of the complexes

[RhCl(cod){$Ph_2PNHP(O)Ph_2$-*P*}] 1. An orange solution of $Ph_2PNHP(O)Ph_2$ (0.295 g, 0.735 mmol) and [Rh_2(μ-Cl)$_2$(cod)$_2$] (0.173 g, 0.351 mmol) in CH_2Cl_2 (40 cm^3) was stirred for 40 min. The solvent was removed *in vacuo* to *ca.* 1–2 cm^3 and addition of diethyl ether (30 cm^3) afforded an orange solid which was collected by suction filtration and air dried. Yield 0.386 g, 85% [Found (Calc. for $C_{32}H_{33}ClNOP_2Rh$): C, 59.05 (59.30); H, 4.90 (5.15); N, 2.25 (2.15)%]. Selected IR data (KBr): 3193 [ν(N–H)] and 1223 cm^{-1} [ν(P=O)]. Slow diffusion of diethyl ether into a CH_2Cl_2 solution of complex **1** over the course of *ca.* 3 d gave crystals suitable for X-ray crystallography.

[IrCl(cod){Ph$_2$PNHP(O)Ph$_2$-*P*}] 2. An orange solution of Ph$_2$PNHP(O)Ph$_2$ (0.200 g, 0.498 mmol) and [Ir$_2$(μ-Cl)$_2$(cod)$_2$] (0.167 g, 0.249 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 45 min. The solvent was removed *in vacuo* to *ca.* 1–2 cm^3 and addition of diethyl ether (45 cm^3) afforded an orange solid which was collected by suction filtration. Yield 0.279 g, 76% [Found (Calc. for $C_{32}H_{33}ClIrNOP_2$): C, 51.85 (52.15); H, 4.40 (4.50); N, 2.05 (1.90)%]. Selected IR data (KBr): 3227 [ν(N–H)] and 1223 cm^{-1} [ν(P=O].

[PdCl(η^3-C$_3$H$_5$){Ph$_2$PNHP(O)Ph$_2$-*P*}] 3. A pale yellow solution of Ph$_2$PNHP(O)Ph$_2$ (0.362 g, 0.902 mmol) and [{Pd(μ-Cl)(η^3-C$_3$H$_5$)}$_2$] (0.161 g, 0.440 mmol) in CH_2Cl_2 (35 cm^3) was stirred for 1 h. The solvent was removed *in vacuo* to *ca.* 1–2 cm^3 and addition of diethyl ether (30 cm^3) afforded an off-white solid which was collected by suction filtration, washed with diethyl ether (5 cm^3) and air dried. Yield 0.481 g, 94% [Found (Calc. for $C_{27}H_{26}ClNOP_2Pd$): C, 55.40 (55.50); H, 4.15 (4.50); N, 2.55 (2.40)%]. Selected IR data (KBr): 3134 [ν(N–H)] and 1216 cm^{-1} [ν(P=O)].

[PdCl(C$_{12}$H$_{12}$N){Ph$_2$PNHP(O)Ph$_2$-*P*}] 4. The compound Ph$_2$PNHP(O)Ph$_2$ (0.113 g, 0.282 mmol) and [{Pd(μ-Cl)(C$_{12}$H$_{12}$N)}$_2$] (0.086 g, 0.138 mmol) were allowed to react in CH_2Cl_2 (10 cm^3). After the yellow solution was stirred for 50 min, it was concentrated *in vacuo* to *ca.* 1–2 cm^3 and addition of hexane (30 cm^3) afforded a pale yellow solid. Yield 0.170 g, 86% [Found (Calc. for $C_{36}H_{33}ClN_2OP_2Pd$): C, 60.60 (60.60); H, 4.35 (4.65); N, 3.95 (3.95)%]. Selected IR data (KBr): 3141 [ν(N–H)] and 1225 cm^{-1} [ν(P=O)].

[PdCl(C$_{10}$H$_8$N){Ph$_2$PNHP(O)Ph$_2$-*P*}] 5. The compound Ph$_2$PNHP(O)Ph$_2$ (0.036 g, 0.090 mmol) and [{Pd(μ-Cl)(C$_{10}$H$_8$N)}$_2$] (0.024 g, 0.042 mmol) were allowed to react in $CDCl_3$ (0.7 cm^3). After the deep yellow solution was stirred for 5 min, it was filtered to remove a small amount of black solid, and addition of hexane (10 cm^3) afforded an off-white solid. Yield 0.035 g, 60% [Found (Calc. for $C_{34}H_{29}ClN_2OP_2Pd$): C, 59.20 (59.55); H, 4.05 (4.25); N, 3.95 (4.10)%].

***In situ* observation of [PdCl(C$_9$H$_{12}$N){Ph$_2$PNHP(O)Ph$_2$-*P*}] 6.** To the solids [{Pd(μ-Cl)(C$_9$H$_{12}$N)}$_2$] (0.011 g, 0.020 mmol) and Ph$_2$PNHP(O)Ph$_2$ (0.017 g, 0.042 mmol) was added $CDCl_3$ (0.5 cm^3) and the reaction monitored immediately by ^{31}P-{^{1}H} NMR spectroscopy. The initial spectrum was in excellent agreement with the formation of [PdCl(C$_9$H$_{12}$N){Ph$_2$PNHP(O)Ph$_2$-*P*}] **6**, however, after *ca.* 20 min its conversion into two new species was observed. ^{31}P-{^{1}H} NMR data for the major species observed: δ(P$_A$) 66.3, δ(P$_X$) 58.8, ^2J(P$_A$P$_X$) 8.8 Hz. A minor product observed was identified as *cis*-[Pd{Ph$_2$PNP(O)Ph$_2$-*P*,*O*}$_2$], ^{31}P-{^{1}H} NMR data in good agreement with those in ref. 34.

***trans*-[RhCl(CO){Ph$_2$PNHP(O)Ph$_2$-*P*}$_2$] 7.** To the solids [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.029 g, 0.075 mmol) and Ph$_2$PNHP(O)Ph$_2$ (0.124 g, 0.309 mmol) was added CH_2Cl_2 (4 cm^3) accompanied by the evolution of CO gas. After stirring the solution for *ca.* 20 min the volume was concentrated by reduction of the solvent *in vacuo* and diethyl ether (20 cm^3) added. The pale yellow solid was collected by suction filtration. The product can be recrystallised from CH_2Cl_2–diethyl ether. Yield 0.130 g, 90% [Found (Calc. for $C_{49}H_{42}ClN_2O_3P_4Rh$); C, 62.45 (60.70); H, 4.45 (4.40); N, 3.55 (2.90)%]. Selected IR data (KBr): 3244, 3216 [ν(N–H)], 1977 [ν(C=O)], 1221 cm^{-1} [ν(P=O)].

Reaction of [{Rh(μ-Cl)(CO)$_2$}$_2$] with 2 equivalents of HL. To the solids [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.036 g, 0.093 mmol) and Ph$_2$PNHP(O)Ph$_2$ (0.076 g, 0.189 mmol) was added CH_2Cl_2 (4 cm^3) and the resulting yellow solution left to stand. Within *ca.* 10 min a yellow solid deposited and this mixture was stored at *ca.* −20 °C for 2 h. The solid product **8** was collected by suction filtration. Yield 0.085 g, 81% [Found (Calc. for $C_{25}H_{21}ClNO_2P_2Rh$): C, 52.55 (52.90); H, 3.35 (3.75); N, 3.15 (2.45)%]. Selected IR data (KBr): 3055 [ν(N–H)], 1981 [ν(C=O)], 1135 cm^{-1} [ν(P=O, tentative assignment)].

[AuCl{Ph$_2$PNHP(O)Ph$_2$-*P*}] 9. To a solution of [AuCl(tht)] (0.259 g, 0.808 mmol) in CH_2Cl_2 (10 cm^3) was added, as a solid in one portion, Ph$_2$PNHP(O)Ph$_2$ (0.340 g, 0847 mmol). After dissolution a white solid formed and the resulting mixture was stirred for *ca.* 20 min. The product was collected by suction filtration and washed with diethyl ether (5 cm^3). Yield 0.453 g, 88% [Found (Calc. for $C_{24}H_{21}AuClNOP_2$): C, 45.35 (45.50); H, 3.05 (3.35); N, 2.35 (2.20)%]. Selected IR data (KBr): 3009 [ν(N–H)], 1184 cm^{-1} [ν(P=O)].

[Pd(C$_{12}$H$_{12}$N){Ph$_2$PNHP(O)Ph$_2$-*P*,*O*}][BF$_4$] 10. To a CH_2Cl_2 solution (20 cm^3) of [PdCl(C$_{12}$H$_{12}$N){Ph$_2$PNHP(O)Ph$_2$-*P*}] (0.086 g, 0.121 mmol) was added solid Ag[BF$_4$] (0.023 g, 0.118 mmol). After stirring for 4.5 h, the AgCl was removed by filtration through a small Celite pad, the volume concentrated by evaporation under reduced pressure to *ca.* 2–3 cm^3 and diethyl ether (50 cm^3) added. The solid product was collected by suction filtration and dried *in vacuo*. Yield 0.064 g, 70% [Found (Calc. for $C_{36}H_{33}BF_4N_2OP_2Pd$): C, 56.15 (56.55); H, 4.25 (4.35); N, 3.75 (3.65)%]. Selected IR data: 3175 cm^{-1} [ν(N–H)].

[Pd(η^3-C$_3$H$_5$){Ph$_2$PNHP(O)Ph$_2$-*P*,*O*}][BF$_4$] 11. To [PdCl(η^3-C$_3$H$_5$){Ph$_2$PNHP(O)Ph$_2$-*P*}] (0.100 g, 0.171 mmol) in CH_2Cl_2 (20 cm^3) was added solid Ag[BF$_4$] (0.045 g, 0.231 mmol). After stirring for 20 min, the AgCl was filtered off through a small Celite plug, the volume of the filtrate reduced to *ca.* 2 cm^3 by evaporation under reduced pressure, and diethyl ether (10 cm^3) added. The white solid was collected and dried. Yield 0.100 g, 87% [Found (Calc. for $C_{27}H_{26}BF_4NO_2P_2Pd$): C, 50.80 (51.00); H, 3.80 (4.15); N, 2.25 (2.20)%]. Selected IR data (KBr): 3180 cm^{-1} [ν(N–H)].

[Rh(cod){Ph$_2$PNP(O)Ph$_2$-*P*,*O*}] 12. A suspension of [RhCl(cod){Ph$_2$PNHP(O)Ph$_2$-*P*}] (0.165 g, 0.255 mmol) in MeOH (7 cm^3) was treated with KOBu^t (0.030 g, 0.267 mmol). The suspension dissolved rapidly and the resultant yellow solution was stirred for *ca.* 5 min. Slow evaporation of the solvent *in vacuo* afforded some yellow solid **12** with further precipitation induced by the addition of distilled water (2 cm^3). The product was filtered off, washed with a small portion of MeOH (1 cm^3) and diethyl ether (1 cm^3). Yield 0.114 g, 73% [Found (Calc. for $C_{32}H_{32}NOP_2Rh$): C, 62.35 (62.85); H, 4.95 (5.30); N, 2.40 (2.30)%].

[Ir(cod){Ph$_2$PNP(O)Ph$_2$-*P*,*O*}] 13. A suspension of [IrCl(cod){Ph$_2$PNHP(O)Ph$_2$-*P*}] (0.153 g, 0.208 mmol) in MeOH (7 cm^3) was treated with KOBu^t (0.028 g, 0.250 mmol). The suspension rapidly dissolved and an orange solid **13** separated within a few minutes. After stirring the suspension for 10 min the product was collected by suction filtration, washed with a small portion of distilled water (1 cm^3) and MeOH (1 cm^3). Yield 0.119 g, 82% [Found (Calc. for $C_{32}H_{32}IrNOP_2$): C, 54.70 (54.85); H, 4.60 (4.60); N, 2.20 (2.00)%].

[{Pd(η^3-C_3H_5)[$Ph_2PNP(O)Ph_2$-*P*,*O*]}$_2$] 14. Under aerobic conditions, a suspension of [PdCl(η^3-C_3H_5){$Ph_2PNHP(O)Ph_2$-*P*}] (0.114 g, 0.195 mmol) in MeOH (1 cm^3) was treated with KOBu^t (0.025 g, 0.223 mmol). The suspension dissolved and the solid product **14** separated within a few minutes. After stirring the suspension for *ca.* 5 min the product was collected by suction filtration, washed with a small portion of distilled water (1 cm^3) and MeOH (1 cm^3). Yield: 0.076 g, 71%. An additional crop (0.016 g) of **14** was obtained upon leaving the filtrate to stand [Found (Calc. for $C_{54}H_{50}N_2O_2P_4Pd_2$): C, 57.70 (59.20); H, 4.35 (4.60); N, 2.65 (2.55)%].

[Pd($C_{12}H_{12}N$){$Ph_2PNP(O)Ph_2$-*P*,*O*}] 15. Under aerobic conditions, to a suspension of [PdCl($C_{12}H_{12}N$){$Ph_2PNHP(O)Ph_2$-*P*}] (0.109 g, 0.153 mmol) in MeOH (1 cm^3) was added KOBu^t (0.020 g, 0.178 mmol). The mixture was stirred for *ca.* 5 min and the solid product collected by suction filtration, washed with a small portion of distilled water (1 cm^3) and MeOH (1 cm^3). Yield: 0.086 g, 83% [Found (Calc. for $C_{36}H_{32}N_2OP_2Pd$): C, 63.45 (63.85); H, 4.45 (4.75); N, 4.55 (4.15)%].

[Pd($C_{10}H_8N$){$Ph_2PNP(O)Ph_2$-*P*,*O*}] 16. Under aerobic conditions, to a suspension of [PdCl($C_{10}H_8N$){$Ph_2PNHP(O)Ph_2$-*P*}] (0.049 g, 0.071 mmol) in MeOH (0.5 cm^3) was added KOBu^t (0.009 g, 0.080 mmol) yielding a deep yellow solution. After stirring for *ca.* 5 min, a white solid deposited from solution and was collected by suction filtration and washed with a small portion of distilled water (1 cm^3). Yield: 0.023 g, 50%. A second crop was obtained from the filtrate (0.010 g) [Found (Calc. for $C_{34}H_{28}N_2OP_2Pd$): C, 62.10 (62.90); H, 4.15 (4.35); N, 4.40 (4.30)%].

[Pd($C_9H_{12}N$){$Ph_2PNP(O)Ph_2$-*P*,*O*}] 17. The compound $Ph_2PNHP(O)Ph_2$ (0.123 g, 0.306 mmol) and [{Pd(μ-Cl)($C_9H_{12}N$)}$_2$] (0.082 g, 0.149 mmol) were allowed to react in MeOH (1.5 cm^3) under aerobic conditions. To the pale yellow solution was immediately added KOBu^t (0.036 g, 0.321 mmol) and the product separated from solution as an off-white solid. After the mixture was stirred for 5 min, the solid was filtered off, washed with distilled water (2 cm^3) and MeOH (2 cm^3). Yield 0.182 g, 96% [Found (Calc. for $C_{33}H_{32}N_2OP_2Pd{\cdot}CH_3OH$): C, 60.35 (60.65); H, 5.25 (5.40); N, 4.20 (4.15)%]. Slow diffusion of MeOH into a CH_2Cl_2 solution of complex **17** over the course of *ca.* 1 d gave crystals suitable for X-ray crystallography.

[PdCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(Ph_2POMe)] 18. The compound $Ph_2PNHP(O)Ph_2$ (0.193 g, 0.481 mmol) and [{Pd(μ-Cl)($C_9H_{12}N$)}$_2$] (0.067 g, 0.121 mmol) were allowed to react in MeOH (4 cm^3) under aerobic conditions. The pale yellow solution was stirred for *ca.* 5 min, filtered and left to stand for *ca.* 12 d. The deposited solids were collected by suction filtration, suspended in toluene (10 cm^3) and stirred for 1 h. After filtration, the product was washed with diethyl ether (5 cm^3) and dried *in vacuo.* Yield 0.104 g, 57% [Found (Calc. for $C_{37}H_{33}ClNO_2P_3Pd{\cdot}0.5CH_2Cl_2$): C, 54.85 (56.25); H, 4.15 (4.30); N, 1.75 (1.75)%]. Slow diffusion of diethyl ether into a CH_2Cl_2 solution of complex **18** over the course of *ca.* 1 d gave crystals suitable for X-ray crystallography.

Alternatively, compound **18** was prepared by refluxing a methanolic solution of [{Pd(μ-Cl)($C_9H_{12}N$)}$_2$] and $Ph_2PNHP(O)Ph_2$ for 2 h. The solid was collected by suction filtration, washed with small portions of MeOH (3 × 1 cm^3) and dried in air. Yield: 46%.

[PdI{$Ph_2PNP(O)Ph_2$-*P*,*O*}(Ph_2POMe)] 19. The compound [PdCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(Ph_2POMe)] (0.055 g, 0.069 mmol) in acetone (10 cm^3) was treated with NaI (0.110 g, 0.734 mmol). The orange solution was stirred for 1 h and the solvent reduced to dryness *in vacuo.* Addition of distilled water (10 cm^3) yielded a solid which was collected by suction filtration. Crude yield: 0.055 g. The solid was recrystallised from CH_2Cl_2 (1 cm^3)–diethyl ether (12 cm^3) [Found (Calc. for $C_{37}H_{34}INO_2P_3Pd$): C, 51.70 (52.20); H, 3.70 (4.05); N, 1.65 (1.65)%].

***cis*-[$PdCl_2${$Ph_2PNHP(O)Ph_2$-*P*}(Ph_2POMe)] 20.** A $CDCl_3$ (0.5 cm^3) solution of [PdCl{$Ph_2PNP(O)Ph_2$-*P*,*O*}(Ph_2POMe)] (0.030 g, 0.038 mmol) was treated with concentrated HCl (11 mol dm^{-3}, *ca.* 1 drop). The immediate formation of complex **20** was confirmed by ^{31}P-{^1H} NMR spectroscopy. The solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2 (0.5 cm^3)–diethyl ether (10 cm^3). Yield 0.026 g, 87% [Found (Calc. for $C_{37}H_{34}Cl_2NO_2P_3Pd$): C, 55.95 (55.90); H, 4.25 (4.30); N, 1.90 (1.75)%]. Selected IR data (KBr): 1222 cm^{-1} [ν(P=O)].

Reaction of iodomethane with [Ir(cod){$Ph_2PNP(O)Ph_2$-*P*,*O*}] 13. A deep orange $CDCl_3$ (*ca.* 0.5 cm^3) solution of [Ir(cod){$Ph_2PNP(O)Ph_2$-*P*,*O*}] (0.025 g, 0.036 mmol) was treated with iodomethane (16-fold molar excess) and the reaction monitored by ^{31}P-{^1H} NMR spectroscopy. Two new species [IrI(Me)(cod){$Ph_2PNP(O)Ph_2$-*P*,*O*}] **21a** and **21b** were observed. After monitoring the reaction for *ca.* 30 min only **21a** remained and was isolated upon addition of hexane (15 cm^3). Yield 0.020 g, 67% [Found (Calc. for $C_{33}H_{35}IIrNOP_2$): C, 46.45 (47.05); H, 3.90 (4.20); N, 1.80 (1.65)%]. A $CDCl_3$–hexane solution of **21a** was left over the course of *ca.* 6 d to give crystals suitable for X-ray crystallography.

Spectroscopic data for all the new complexes are compiled in Table 1.

X-Ray crystallography

The crystal structures of complexes **1**, **17**, **18** and **21a** 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 2. Empirical absorption corrections (DIFABS)[60] were applied. The structures were solved by the heavy-atom method[61] and all of the non-hydrogen atoms refined anisotropically. The C–H atoms were idealised and fixed (C–H 0.95 Å). No additional constraints or restraints were applied. Refinement was by full-matrix least-squares methods based on *F*. Calculations were performed using TEXSAN.[62]

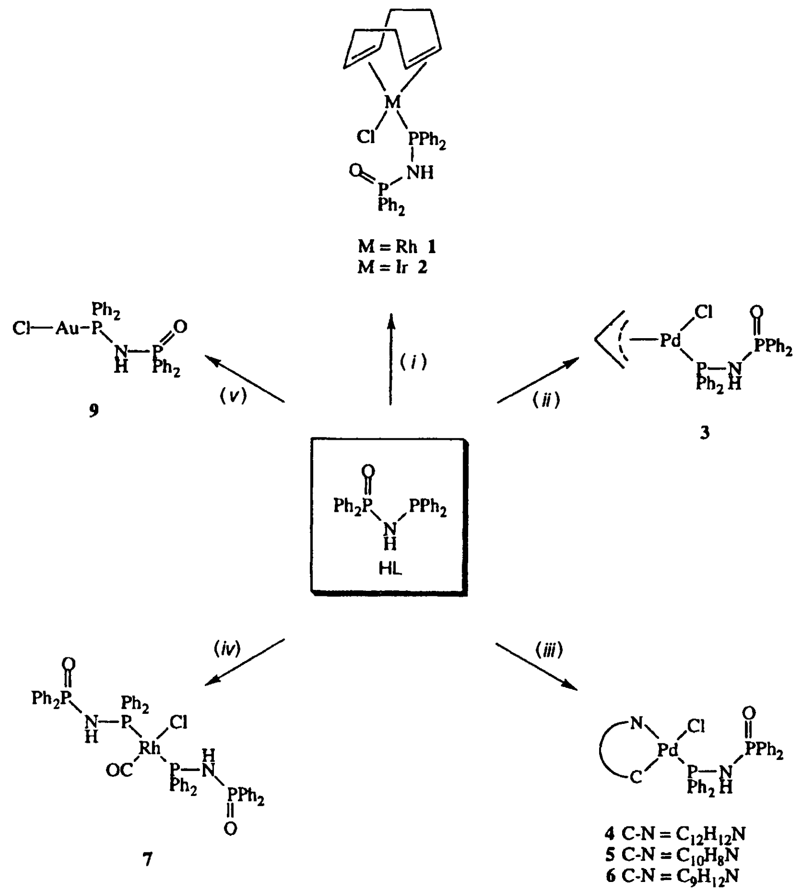
Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

P-Monodentate and *P*,*O*-chelate complexes of $Ph_2PNHP(O)Ph_2$

The compound HL may co-ordinate as a unidentate ligand through P or by chelation (through P,O). We have studied its ligating behaviour towards a range of late transition metals. Thus when [{M(μ-Cl)(cod)}$_2$] (M = Rh or Ir) was treated with HL in CH_2Cl_2 at ambient temperature the yellow (or orange) mononuclear complexes [MCl(cod){$Ph_2PNHP(O)Ph_2$-*P*}] (M = Rh **1** or Ir **2**) were isolated in 85 and 76% yield respectively (Scheme 1). Both complexes are air- and moisture-stable in the solid state and moderately stable in solution.

The ^{31}P-{^1H} NMR data for both complexes (Table 1) and the ^{31}P NMR spectrum of **1** (AMX spin system) are shown in Fig. 1. The high-frequency resonance shows a $^1J(RhP)$ coupling constant of 159.0 Hz (^{103}Rh, $I = \frac{1}{2}$, 100% abundance), $^2J(P_AP_X)$ of 39.5 Hz; the upfield signals are at a similar chemical shift to that observed for free HL but show, in addition, a small $^3J(RhP)$ coupling of 4.6 Hz. In the IR spectra vibrations at 3193



Scheme 1 (*i*) $[\{M(\mu\text{-Cl})(cod)\}_2]$ (M = Rh or Ir), 2 HL; (*ii*) $[\{Pd(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)\}_2]$, 2 HL; (*iii*) $[\{Pd(\mu\text{-Cl})(L\text{–}L)\}_2]$, 2 HL; (*iv*) $[\{Rh(\mu\text{-Cl})(CO)_2\}_2]$, 4 HL; (*v*) [AuCl(tht)], HL

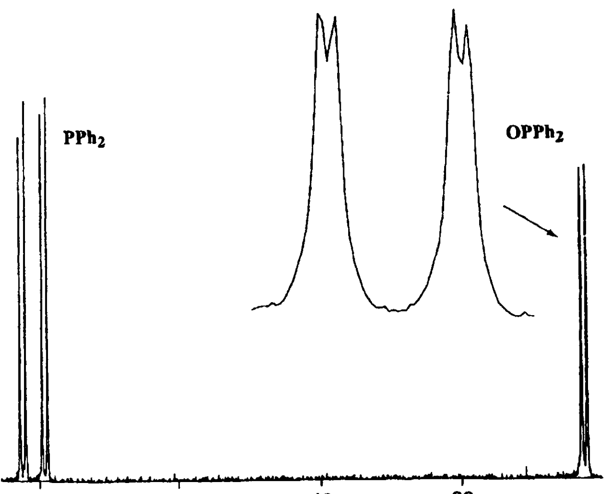


Fig. 1 The $^{31}P\text{-}\{^1H\}$ NMR spectrum (101.3 MHz) of $[RhCl(cod)\{Ph_2PNHP(O)Ph_2\text{-}P\}]$ **1**

[ν(N–H)], 1223 [ν(P=O)] (for **1**) and 3227 [ν(N–H)], 1223 cm^{-1} [ν(P=O)] (for **2**) are observed whereas for HL these are found at 3049 [ν(N–H)] and 1183 cm^{-1} [ν(P=O)].[34] The lower ν(P=O) for HL is a consequence of the different hydrogen-bonding arrangements observed in it[34] and in **1** (X-ray evidence, see below).

We have also studied further bridge-cleavage reactions using HL. Hence treatment of $[\{Pd(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)\}_2]$ with 2 equivalents of HL affords complex **3** (Scheme 1) which we have previously reported.[35] In a similar fashion the reactivity of the cyclometallated dimers $[\{Pd(\mu\text{-Cl})(L\text{–}L)\}_2]$ (L–L = $C_{12}H_{12}N$, $C_{10}H_8N$ or $C_9H_{12}N$) with HL yields [PdCl(L–L)(HL)] **4**–**6** (Scheme 1). With the exception of compound **6**, which was characterised in solution only (it decomposes to give one major uncharacterised species, the identity of which is currently under investigation), **3**–**5** were isolated as air-stable solids. Although we have not been able to isolate **6** the ^{31}P NMR spectral data are consistent with the structure shown. The $^{31}P\text{-}\{^1H\}$ NMR spectra (Table 1) of **4**–**6** in $CDCl_3$ show two sharp doublets (AX spectrum) in agreement with the inequivalent phosphorus (P^{III} and P^V) moieties. To confirm that the high-frequency doublet is due to the phosphorus(III) centre we have measured ($CDCl_3$ solution) the $^{31}P\text{-}\{^1H\}$ NMR spectra of $[\{PdCl(L\text{–}L)\}_2(\mu\text{-}Ph_2PNHPPh_2)]$ (L–L = $C_{12}H_{12}N$ or $C_9H_{12}N$), prepared from $[\{Pd(\mu\text{-Cl})(L\text{–}L)\}_2]$ and 1 equivalent of dppa: δ 70.8 and 71.2. Related dimeric complexes with bridging diphosphine or diarsine ligands have previously been reported.[63] The phosphorus(V) chemical shifts for **4**–**6** are close to the value observed for free HL indicating no interaction of the free phosphoryl group with the metal centre. Significant changes are observed when the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4** is recorded in MeOH (C_6D_6 insert). The resonance of P^V is shifted by *ca.* 30 ppm (*cf.* δ 21.1 when recorded in $CDCl_3$) and there is negligible shift of that of P^{III}, accompanied by a reduction in the magnitude of $^2J(PP)$. When the solution is evaporated to dryness and the residue redissolved in $CDCl_3$ the original ^{31}P NMR spectrum was restored. We believe that in methanolic solutions there is evidence for a P=O interaction with the metal centre presumably *via* chloride loss (see below). A similar behaviour was noted when methanolic solutions of **1** were examined by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

The *trans* N–Pd–P geometry was inferred from the magnitude of the *J*(PH) couplings observed in the ^1H NMR spectra for complexes **4**–**6** which corresponded well to those of related compounds.[41–44,46,49,52]

The reaction of the rhodium dimer $[\{Rh(\mu\text{-Cl})(CO)_2\}_2]$ with 4 equivalents of HL proceeds rapidly, with the evolution of CO

Table 1 The $^{31}P-\{^1H\}$[a] and ^1H NMR data[b] for the new complexes **1**–**21b**

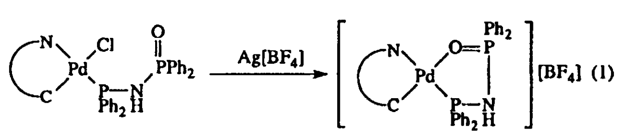
Compound	$\delta(P_A)$[c]	$\delta(P_X)$[c]	$J(P_AP_X)$	Others
1[d,e]	60.4	21.3	39.5	$^1J(RhP_A)$ 159.0, $^3J(RhP_X)$ 4.6
2[f]	49.2	22.6	35.2	
3[g]	60.8	22.6	37.4	
4[h]	73.3	21.1	33.0	
5[i]	66.4	21.7	35.0	
6[j]	71.7	21.0	33.0	
7[d]	62.4	20.8	26.4	$^1J(RhP_A)$ 126.6, $^3J(RhP_X)$ 2.5
8[k]	86.6	54.7	32.3	$^1J(RhP_A)$ 160.6
9	53.9	26.4	n.r.[l]	
10[g]	67.8	59.0	35.0	
11[m]	73.4	51.5	22.0	
12[d,n]	69.8	63.0	39.8	$^1J(RhP_A)$ 146.3, $^nJ(RhP_X)$ 3.0[o]
13[p]	76.4	63.1	39.6	
14[g]	66.8	62.5	35.0	
15[q]	68.7	50.2	19.8	
16[r]	61.5	50.4	24.2	
17[s]	67.2	49.8	22.0	
18[d,t]	70.2	60.6	12.8	$\delta(PPh_2OMe)$ 113.2, $^2J(Ph_2POMeP_A)$ 33.0, $^3J(Ph_2POMeP_X)$ 6.3
19[d,u]	70.5	67.4	16.5	$\delta(Ph_2POMe)$ 115.5, $^2J(Ph_2POMeP_A)$ 45.3, $^3J(Ph_2POMeP_X)$ 6.3
20[d,v]	57.3	22.0	33.0	$\delta(Ph_2POMe)$ 106.8, $^2J(Ph_2POMeP_A)$ 26.0
21a[w]	68.2	19.9	26.4	
21b[x]	75.3	23.0	26.4	

[a] Spectra (36.2 MHz) measured in $CDCl_3$ unless otherwise stated. Chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. Coupling constants (J) in Hz (±3). [b] Spectra (250 MHz) measured in $CDCl_3$ unless otherwise stated. Chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz (±0.1). [c] P_A = phosphorus(III) centre, P_X = phosphorus(V) centre. [d] Spectrum (101.3 MHz) measured in $CDCl_3$. [e] ^{31}P NMR (MeOH–C_6D_6 insert): $\delta(P_A)$ 71.4, $^1J(RhP)$ 158.4 Hz; $\delta(P_X)$ 50.1. ^1H NMR: δ 7.96–6.72 (aromatic H); 5.60, 2.92 (=CH, cod); 2.38–1.87 (CH_2, cod). [f] ^1H NMR: δ 7.90–6.84 (aromatic H); 5.25, 2.55 (=CH, cod); 2.27–1.44 (CH_2, cod). [g] ^1H NMR spectrum shows the expected resonances for both phenyl and η^3-allyl groups. [h] ^{31}P NMR (MeOH–C_6D_6 insert): $\delta(P_A)$ 72.2, $\delta(P_X)$ 50.5 (P–P coupling not fully resolved), $^2J(P_AP_X)$ 22.0 Hz. ^1H NMR: δ 8.20–6.26 (aromatic H); 3.54 [$^4J(PH)$ 2.8 Hz, NMe_2]. [i] ^1H NMR: δ 9.61–9.58, 8.31–7.26 (aromatic H); 2.95 [$^3J(PH)$ 5.0 Hz, CH_2Pd]. [j] After *ca.* 20 min one major species: $\delta(P_A)$ 65.9, $\delta(P_X)$ 58.8, $^2J(P_AP_X)$ 8.8 Hz. ^1H NMR: δ 7.90–7.05 (aromatic H); 3.69 [$^4J(PH)$ 2.5, NCH_2]; 2.47 (NMe_2). [k] Measured in Me_2SO–C_6D_6 insert. [l] n.r. = Not resolved. [m] ^1H NMR: δ 7.99–6.62 (aromatic H); 3.49 [$^4J(PH)$ 2.5, Hz, NMe_2]. [n] ^1H NMR: δ 7.73–7.27 (aromatic H); 5.48, 3.26 (=CH, cod); 2.34, 1.98 (CH_2, cod). [o] Contribution from $^2J(RhP_X)$ and $^3J(RhP_X)$. [p] ^1H NMR: δ 7.64–7.22 (aromatic H); 5.04, 2.98 (=CH, cod); 2.10–1.57 (CH_2, cod). [q] ^1H NMR: δ 7.93–6.83 (aromatic H); 3.43 [$^4J(PH)$ 2.3 Hz, NMe_2]. [r] ^1H NMR: δ 9.24, 8.29–7.36 (aromatic H); 3.10 (CH_2Pd). [s] ^1H NMR: δ 7.83–6.61 (aromatic H); 3.86 [$^4J(PH)$ 1.8 (NCH_2)]; 2.86 [$^4J(PH)$ 2.5 Hz, NMe_2]. [t] ^1H NMR: δ 7.81–7.27 (aromatic H); 2.81 [$^3J(PH)$ 12.5 Hz, OMe]. [u] ^1H NMR: δ 7.81–7.27 (aromatic H); 2.76 [$^3J(PH)$ 11.9 Hz, OMe]. [v] ^1H NMR: δ 8.10–7.27 (aromatic H); 2.64 [$^3J(PH)$ 10.0 Hz, OMe]. [w] ^1H NMR: δ 8.11–7.26 (aromatic H); 6.18, 5.60, 4.07, 3.71 (=CH, cod); 3.00–1.00 (CH_2, cod); 2.31 [$^3J(PH)$ 5.0 Hz, IrMe]. [x] Characterised by $^{31}P-\{^1H\}$ NMR spectroscopy only.

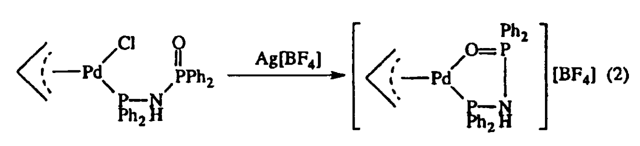
gas, to give the pale yellow complex *trans*-[RhCl(CO){$Ph_2PNHP(O)Ph_2$-*P*}$_2$] **7**; characterising data given in Table 1 and the Experimental section. A single ν(CO) (KBr disc) was observed in the IR spectrum at 1977 cm^{-1}; the $^{31}P-\{^1H\}$ NMR spectrum shows a doublet of triplets [$\delta(P_A)$ 62.4, $^1J(RhP)$ 126.6 Hz] and a triplet [$\delta(P_X)$ 20.8, $^3J(RhP)$ 2.5, $J(P_AP_X)$ 26.4 Hz]. In contrast when [{Rh(μ-Cl)(CO)$_2$}$_2$] is allowed to react with 2 equivalents of HL in CH_2Cl_2 a deep yellow solid **8** having the apparent stoichiometry [RhCl(CO){$Ph_2PNHP(O)Ph_2$}] was isolated. The most striking differences are seen in the $^{31}P-\{^1H\}$ NMR and IR spectra. The high-frequency shift of the P=O group [$\delta(P_X)$ 54.7 *vs.* 20.8 for **7**] in the ^{31}P spectrum suggests chelation of the O donor atom. This is also supported by the IR spectrum (KBr disc) which showed a significant shift for the P=O group (1135 *vs.* 1221 cm^{-1} for **7**). We tentatively suggest that **8** has an analogous structure to that of the isoelectronic complex *cis*-[RhCl(CO){$Ph_2PCH_2P(O)Ph_2$-*P*,*O*}] (P *trans* to Cl) reported by Wegman *et al.*[30] Upon further reaction of a dimethyl sulfoxide (dmso) solution of **8** with 1 equivalent of HL complex **7** was formed instantly (^{31}P NMR evidence).

We have also studied the reaction of HL and [AuCl(tht)] in CH_2Cl_2 which afforded the two-co-ordinate complex [AuCl{$Ph_2PNHP(O)Ph_2$-*P*}] **9** in good yield. The $^{31}P-\{^1H\}$ NMR spectrum showed two singlets; the P–P coupling was not resolved.

Since the pendant P=O group is suitably disposed for chelation we treated complexes **3** and **4** with the chloride abstractor Ag[BF_4] in a non-co-ordinating solvent and isolated in good yields the cationic species **10** and **11** [equations (1) and (2)]. Chelation was deduced by the significant high-frequency shift of the P=O group (^{31}P NMR), absence of ν(P=O) in the IR spectra and, in the case of **11**, a single-crystal structure.[35]



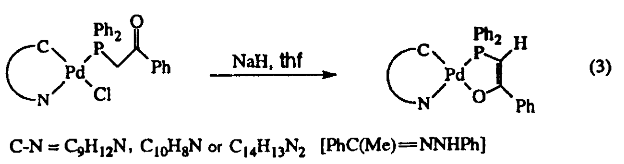
10 C-N = $C_{12}H_{12}N$



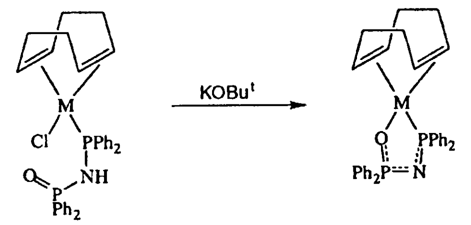
11

P,*O*-Chelate and -bridging complexes of [$Ph_2PNP(O)Ph_2$]$^-$

Braunstein and co-workers[43] found that efficient deprotonation of the methylene proton in related ketophosphine complexes was achieved using NaH in tetrahydrofuran (thf) [equation (3)]. We find that deprotonation of the NH proton using KOBu^t in methanol is an alternative efficient method for synthesising complexes of [$Ph_2PNP(O)Ph_2$]$^-$. This differs with



C-N = $C_9H_{12}N$, $C_{10}H_8N$ or $C_{14}H_{13}N_2$ [PhC(Me)=NNHPh] the propensity of $Ph_2PNRP(X)Ph_2$ (X = S or Se, R = H or Ph) to co-ordinate either as a neutral ligand (through P, X)[19,20] or to undergo slow deprotonation in the absence of *any* base as observed from previous studies within our group.[19] Deprotonation of the amine proton in either **1** or **2** with $KOBu^t$ affords a transient $[MCl(cod)\{Ph_2PNP(O)Ph_2\text{-}P\}]^-$ anion (M = Rh or Ir), which we have not observed, followed by intramolecular ring closure affording the metallacyclic complexes $[M(cod)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ (M = Rh **12** or Ir **13**) [equation (4)].



(4)

12 M = Rh
13 M = Ir

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **12** is shown in Fig. 2. Confirmation that ring closure has resulted was inferred by the high-frequency shift (*ca.* 40 ppm) of the phosphorus(V) resonance, with a small $J(RhP_X)$ coupling constant of 3.0 Hz. The $^1J(RhP)$ coupling constant of 146.3 Hz is comparable to that observed for **1** indicating a negligible change upon five-membered ring formation (see Table 1 for spectroscopic data). Furthermore **12** and **13** are analogous to the metallacyclic compounds $[M(cod)(Ph_2PCH_2PPh_2{=}N)]$ (M = Rh or Ir) **A** containing the isoelectronic mixed-donor-atom ligand $[Ph_2PCH_2PPh_2{=}N]^-$.[64]

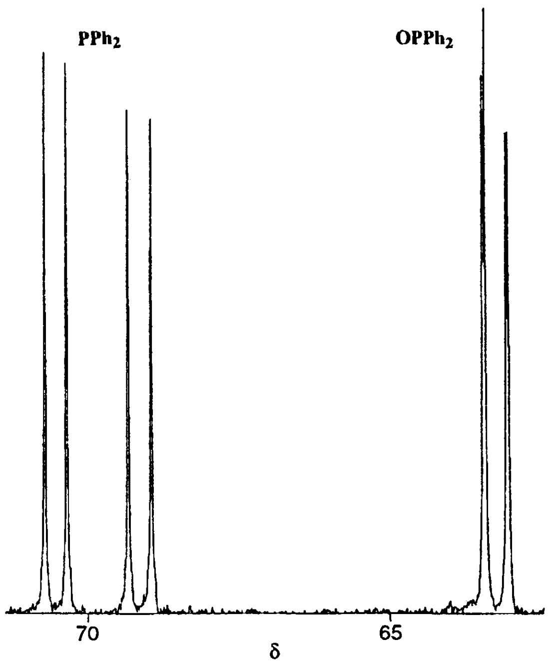


Fig. 2 The $^{31}P\text{-}\{^1H\}$ NMR spectrum (101.3 MHz) of $[Rh(cod)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ **12**

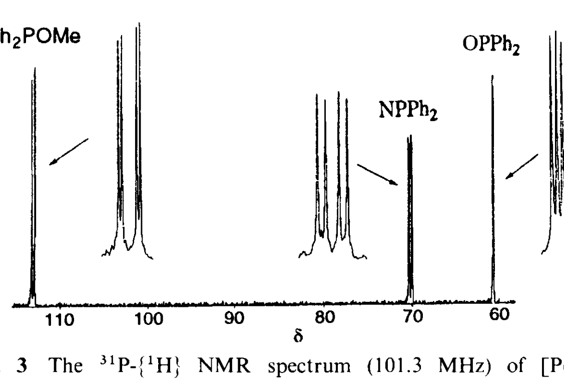
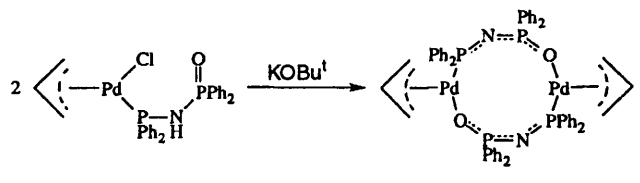


Fig. 3 The $^{31}P\text{-}\{^1H\}$ NMR spectrum (101.3 MHz) of $[PdCl\{Ph_2PNP(O)Ph_2\text{-}P,O\}(Ph_2POMe)]$ **18**

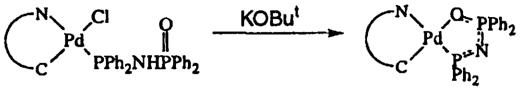
The chelating behaviour of compounds **12** and **13** should be contrasted with the reaction of **3** and $KOBu^t$ in MeOH. Surprisingly, once deprotonated, the anionic ligand forms a novel P,O bridge between two metal centres yielding the palladium(II) dimer $[\{Pd(\eta^3\text{-}C_3H_5)[Ph_2PNP(O)Ph_2\text{-}P,O]\}_2]$ **14** [equation (5)].[35]



(5)

14

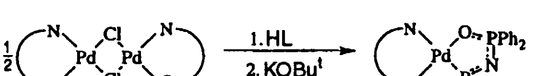
We have also studied the reaction of complexes **4** and **5** with base and found the efficient formation of the five-membered palladacycles **15** and **16** incorporating two five-membered bicyclic rings, one an organic ring and the other an inorganic (carbon-free) ring [equation (6)]. The versatility of this



(6)

15 C-N = $C_{12}H_{12}N$
16 C-N = $C_{10}H_8N$

reaction was demonstrated by the high-yield (96%) one-pot synthesis of the closely related metallacyclic compound $[Pd(C_9H_{12}N)\{Ph_2PNP(O)Ph_2\text{-}P,O\}]$ **17** starting from the cyclometallated dimer $[\{Pd(\mu\text{-}Cl)(C_9H_{12}N)\}_2]$ [equation (7)].



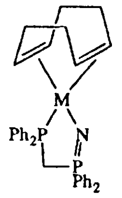
(7)

17 C-N = $C_9H_{12}N$

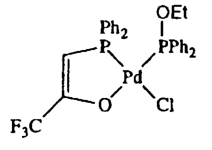
Spectroscopic (^{31}P) data for these complexes are given in Table 1; most significant is the absence of a doublet centred around δ 21 which is replaced by a new doublet to high frequency typical of *P,O*-chelation. The crystal structure of one of these compounds (**17**, see below) was determined to establish the configuration of the bidentate ligands around the palladium.

When a methanolic solution of $[\{Pd(\mu\text{-}Cl)(C_9H_{12}N)\}_2]$ and 4 equivalents of HL, in the absence of base, is left to stand for *ca.* 12 d the major product isolated (57%) in addition to small amounts of **17** and the bis(chelate) complex *cis*-$[Pd\{Ph_2PNP(O)Ph_2\text{-}P,O\}_2]$[34] is the neutral complex $[PdCl\{Ph_2PNP(O)Ph_2\text{-}P,O\}(Ph_2POMe)]$ **18**. Alternatively when such a methanol solution is refluxed for *ca.* 2 h compound **18** can be isolated albeit in a lower yield. The $^{31}P\text{-}\{^1H\}$ NMR spectrum is shown in Fig. 3 and clearly reveals three unique phosphorus environments; the lack of any large phosphorus–phosphorus couplings eliminates a mutual *trans* arrangement of Ph_2POMe and the phosphorus(III) centre of the $[Ph_2PNP(O)Ph_2]^-$ ligand. Metathesis of **18** with NaI in acetone gave the iodo complex **19** which exhibited a similar ^{31}P NMR spectrum.

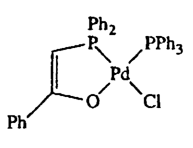
A single-crystal X-ray diffraction study unambiguously verified the structure of complex **18** (see below). To our knowledge the only related palladium(II) complexes containing



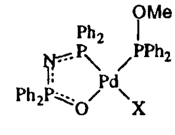
A M = Rh or Ir



B



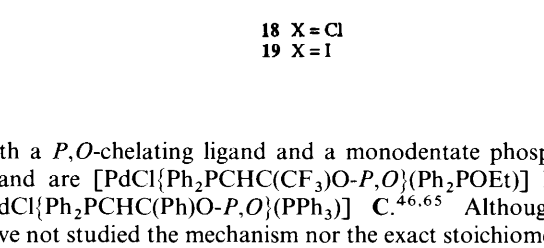
C



18 X = Cl
19 X = I

both a *P*,*O*-chelating ligand and a monodentate phosphorus ligand are [PdCl{Ph$_2$PCHC(CF$_3$)O-*P*,*O*}(Ph$_2$POEt)] **B** and [PdCl{Ph$_2$PCHC(Ph)O-*P*,*O*}(PPh$_3$)] **C**.[46,65] Although we have not studied the mechanism nor the exact stoichiometry of the reaction we believe that a co-ordinated M–Ph$_2$PNHP(O)Ph$_2$ ligand undergoes P–N bond cleavage in methanol. Furthermore, this reaction is similar to the penultimate step in the synthesis of **B**, *i.e.* nucleophilic displacement of CF$_3$CC$^-$ from phosphorus by ethoxide to generate the ethoxydiphenylphosphine ligand, Ph$_2$POEt. We have not identified the fate of the remaining phosphorus fragment formed upon rupture of the P–N bond nor any other intermediates. We are unaware of any other examples in which dppa or its derivatives undergoes P–N bond cleavage under extremely mild conditions.

The Pd–O bond in complex **18** is readily cleaved upon treatment with concentrated HCl affording the mixed-ligand palladium complex **20** [equation (8)] in which the stereochemistry of the two monodentate ligands is *cis* (from ^{31}P-{^{1}H} NMR, Table 1). There was no evidence for the *trans*-isomer of [PdCl$_2${Ph$_2$PNHP(O)Ph$_2$-*P*}(Ph$_2$POMe)] in CDCl$_3$ solution. After *ca.* 1 d the ^{31}P-{^{1}H} NMR spectrum shows, in addition to **20**, small amounts of the known complexes *cis*-[PdCl$_2$(Ph$_2$POMe)$_2$] and *trans*-[PdCl$_2${Ph$_2$PNHP(O)Ph$_2$-*P*}$_2$][34] presumably formed by ligand scrambling. Palladium(II) complexes of the type [PdCl$_2$L′(L″)] (L′ and L″ = monodentate ligands) have previously been reported.[66] Addition of KOBu^t to solutions of **20** regenerates **18** (^{31}P NMR evidence).



(8)

18 **20**

Oxidative-addition reactions of iridium(I) complexes have been extensively studied. We were interested to see whether the iridium complex **13** reacts with electrophiles either at the metal centre (oxidative addition) or at the nitrogen atom of the IrP$_2$NO ring. In previous work[34] we showed that protonation of *cis*-[Pt{Ph$_2$PNP(O)Ph$_2$-*P*,*O*}$_2$] with an excess of HBF$_4$·OEt$_2$ occurs at both nitrogen atoms. We treated the iridacycle [Ir(cod){Ph$_2$PNP(O)Ph$_2$}] **13** with MeI (16-fold molar excess) and initial monitoring of the reaction by ^{31}P-{^{1}H} NMR spectroscopy showed an immediate reaction affording two new species **21a** and **21b** (1 : 1 ratio). After *ca.* 30 min complete isomerisation to **21a** had occurred and this complex was isolated by addition of hexane. Proton NMR spectroscopy showed the presence of a co-ordinated methyl group [δ(H) 2.31, ^3J(PH) 5.0 Hz], cycloocta-1,5-diene and phenyl resonances of the ligand (Table 1). We infer that oxidative addition has occurred with the formation of [IrI(Me)(cod){Ph$_2$PNP(O)Ph$_2$}] although we were puzzled by the ^{31}P NMR data which suggested the presence of a 'dangling' P=O group. Since the data led to no conclusion about the exact nature of the ligand nor the stereochemistry of the iridium(III) species, an X-ray diffraction study was undertaken (see below). We have not established the structure of **21b** but believe it is a second isomer of [IrI(Me)(cod){Ph$_2$PNP(O)Ph$_2$}]. Further work is underway to identify this species.

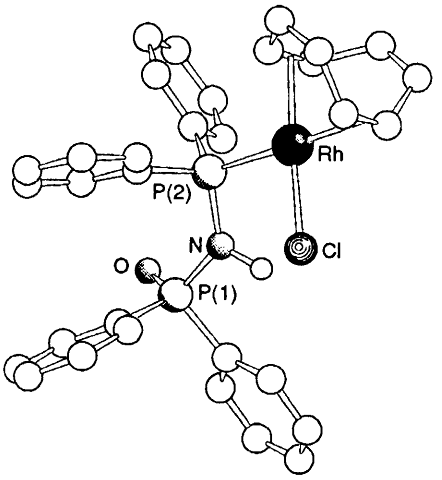


Fig. 4 Crystal structure of [RhCl(cod){Ph$_2$PNHP(O)Ph$_2$-*P*}] **1** (CH protons omitted for clarity)

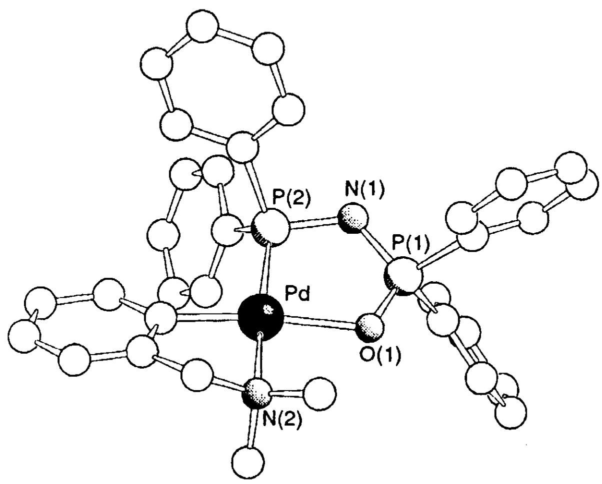


Fig. 5 Crystal structure of [Pd(*o*-C$_6$H$_4$CH$_2$NMe$_2$){Ph$_2$PNP(O)Ph$_2$-*P*,*O*}]·MeOH **17** (CH protons and solvent molecules omitted for clarity)

Crystal structures of complexes 1, 17, 18 and 21a

Crystals of complex **1** were grown by slow diffusion of diethyl ether into a CH$_2$Cl$_2$ solution and the molecular structure is shown in Fig. 4 (Table 3). The structure reveals a square-planar rhodium centre co-ordinated by a π-bound cod ligand, a

Table 2 Details of the X-ray data collections and refinements for compounds **1**, **17**, **18** and **21a***

	1	**17**	**18**	**21a**
Empirical formula	$C_{32}H_{33}ClNOP_2Rh$	$C_{34}H_{36}N_2O_2P_2Pd$	$C_{37.50}H_{34}Cl_2NO_2P_3Pd$	$C_{33}H_{35}IIrNOP_2$
M	647.92	673.02	800.91	842.72
Crystal colour, habit	Orange, prism	Clear, block	Clear, plate	Yellow, block
Crystal dimensions/mm	0.20 × 0.20 × 0.43	0.24 × 0.26 × 0.35	0.20 × 0.01 × 0.40	0.21 × 0.23 × 0.31
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	14.332(1)	9.064(8)	13.66(1)	15.478(5)
b/Å	10.877(2)	24.934(8)	18.311(5)	10.946(6)
c/Å	18.888(1)	14.064(7)	16.608(6)	19.144(4)
β/°	97.074(7)	98.88(5)	113.85(4)	111.46(2)
U/Å^3	2922	3140	3799	3018
D_c/g cm^{-3}	1.47	1.42	1.40	1.85
μ/mm^{-1}	6.80	5.98	6.68	17.61
$2\theta_{max}$/°	120.2	120.2	120.1	120.6
F(000)	1328	1384	1628	1632
Measured reflections	4836	5141	6138	5044
Independent reflections (R_{int})	4628 (0.013)	4805 (0.116)	5865 (0.046)	4512 (0.175)
Observed reflections [$I > 3.0\sigma(I)$]	3986	3561	3959	3543
Reflection/parameter ratio	11.6:1	9.6:1	9.1:1	10.0:1
Minimum, maximum transmission	0.45, 1.00	0.72, 1.00	0.76, 1.00	0.63, 1.00
Weighting scheme, p	0.002	0.006	0.007	0.008
No. variables	344	371	434	353
Final R,R'	0.037, 0.045	0.034, 0.034	0.056, 0.071	0.033, 0.036
Maximum Δ/σ	0.40	0.02	5.64	0.01
Largest difference peak hole/e Å^{-3}	0.33, −0.63	0.38, −0.55	1.13, −0.63	0.91, −1.05

* Details in common: monoclinic; $Z = 4$; $w^{-1} = \sigma^2(F_o)$.

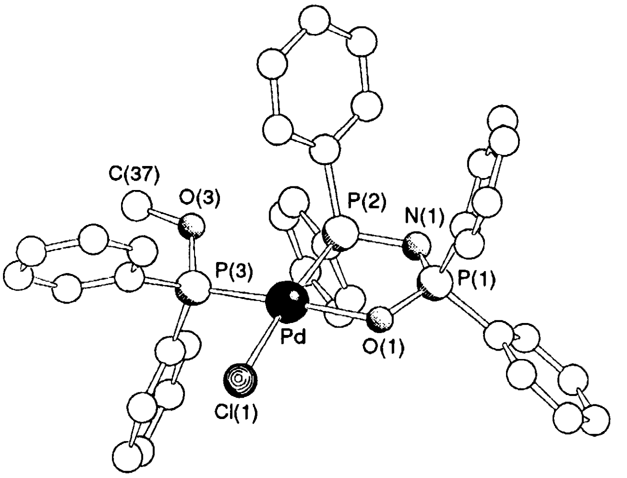


Fig. 6 Crystal structure of $[PdCl\{Ph_2PNP(O)Ph_2\text{-}P,O\}(Ph_2POMe)]\cdot 0.5CH_2Cl_2$ **18** (CH protons and solvent molecules omitted for clarity)

Table 3 Selected bond distances (Å) and angles (°) for complex **1**

Rh–Cl	2.377(2)	P(2)–N	1.701(4)
Rh–P(2)	2.289(1)	P(2)–C(21)	1.812(6)
Rh–C(1)	2.129(6)	P(2)–C(27)	1.802(5)
Rh–C(2)	2.127(6)	C(1)–C(2)	1.371(9)
Rh–C(5)	2.247(6)	C(1)–C(8)	1.510(9)
Rh–C(6)	2.231(6)	C(2)–C(3)	1.514(10)
P(1)–O	1.478(4)	C(3)–C(4)	1.421(12)
P(1)–N	1.672(4)	C(5)–C(6)	1.370(9)
P(1)–C(9)	1.788(6)	C(6)–C(7)	1.511(9)
P(1)–C(15)	1.797(6)	C(7)–C(8)	1.446(10)
Cl–Rh–P(2)	90.07(5)	Rh–P(2)–C(21)	118.61(17)
Cl–Rh–C(1)	161.81(21)	Rh–P(2)–C(27)	112.81(18)
Cl–Rh–C(2)	160.01(20)	N–P(2)–C(21)	106.03(24)
Cl–Rh–C(5)	89.36(21)	N–P(2)–C(27)	108.20(23)
Cl–Rh–C(6)	89.32(17)	C(21)–P(2)–C(27)	102.88(26)
P(2)–Rh–C(1)	91.45(17)	P(1)–N–P(2)	132.64(27)
P(2)–Rh–C(2)	94.96(18)	Rh–C(1)–C(2)	71.10(39)
P(2)–Rh–C(5)	166.22(21)	Rh–C(1)–C(8)	109.97(47)
P(2)–Rh–C(6)	158.12(21)	C(2)–C(1)–C(8)	126.53(67)
C(1)–Rh–C(2)	37.59(24)	Rh–C(2)–C(1)	71.31(39)
C(1)–Rh–C(5)	93.38(26)	Rh–C(2)–C(3)	110.74(54)
C(1)–Rh–C(6)	82.58(23)	C(1)–C(2)–C(3)	124.31(64)
C(2)–Rh–C(5)	81.19(27)	C(2)–C(3)–C(4)	118.77(74)
C(2)–Rh–C(6)	93.04(24)	C(3)–C(4)–C(5)	118.10(76)
C(5)–Rh–C(6)	35.64(24)	Rh–C(5)–C(4)	108.55(55)
O–P(1)–N	114.95(22)	Rh–C(5)–C(6)	71.54(38)
O–P(1)–C(9)	112.17(25)	C(4)–C(5)–C(6)	125.24(80)
O–P(1)–C(15)	113.10(24)	Rh–C(6)–C(5)	72.82(39)
N–P(1)–C(9)	108.22(24)	Rh–C(6)–C(7)	106.59(44)
N–P(1)–C(15)	102.37(22)	C(5)–C(6)–C(7)	125.48(75)
C(9)–P(1)–C(15)	105.15(25)	C(6)–C(7)–C(8)	119.07(60)
Rh–P(2)–N	107.74(15)	C(1)–C(8)–C(7)	117.50(63)

chloride and a neutral HL. The Rh–P(2) [2.289(1) Å] and Rh–Cl [2.377(2) Å] bond lengths are in good agreement with those reported for the related complex $[RhCl(cod)\{P(C_6H_4\text{-}F\text{-}p)_3\}]$.[67] The $Ph_2PNHP(O)Ph_2$ ligand has a shortened P=O bond compared to that observed for the non-co-ordinated but strongly P=O ··· H–N hydrogen-bonded starting material. The P–N distances are little affected by co-ordination. The most notable effect is the change in the stereochemistry of the HN–P=O unit. In the structure of HL the NH proton and the P=O oxygen are *syn* whereas here they are *anti*. The difference is attributable to different hydrogen-bonding patterns. In 'free' HL the molecules form dimer pairs *via* N–H ··· O′=P′ hydrogen-bonds. In **1** there is a strong intramolecular N–H ··· Cl hydrogen bond (Cl ··· H 2.32 Å).

Crystals of complex **17** suitable for a structure determination were grown from CH_2Cl_2–MeOH (Fig. 5, Table 4). The palladium has a near square-planar geometry with two co-ordinated anionic bidentate ligands each forming a five-membered ring (phosphorus *trans* to nitrogen). The bond distances for the C–N cyclometallated ring are similar to those observed for the complexes $[Pd(L\text{–}L)(Ph_2PCH_2CO_2\text{-}P,O)]$, $[Pd(L\text{–}L)\{Ph_2PCH{=}C(OEt)O\text{-}P,O\}]$ and $[PdCl(L\text{–}L)\{(C_6H_{11})_2PCMe_2CH_2COMe\text{-}P,O\}]$ (L–L = $C_9H_{12}N$).[44]

Crystals of complex **18** were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution and the molecular structure is shown in Fig. 6 (Table 5). It confirms a square-planar environment around the palladium with the Ph_2POMe ligand *trans* to the oxygen atom of the bidentate ligand.

The molecular structure of complex **21a** is shown in Fig. 7 (Table 6). The Ir–C (olefinic) distances range from 2.191(8) to 2.325(9) Å with an average of 2.195 Å for Ir–C(31)/Ir–C(32) and

Table 4 Selected bond distances (Å) and angles (°) for complex **17**

Pd–P(2)	2.242(1)	P(1)–C(7)	1.805(5)
Pd–O(1)	2.132(3)	P(2)–N(1)	1.634(4)
Pd–N(2)	2.137(3)	P(2)–C(13)	1.821(5)
Pd–C(29)	1.975(5)	P(2)–C(19)	1.820(4)
P(1)–O(1)	1.516(3)	N(2)–C(25)	1.468(6)
P(1)–N(1)	1.602(4)	N(2)–C(26)	1.484(6)
P(1)–C(1)	1.809(5)	N(2)–C(27)	1.478(6)
P(2)–Pd–O(1)	86.29(9)	P(1)–N(1)–P(2)	117.05(23)
P(2)–Pd–N(2)	172.05(11)	Pd–N(2)–C(25)	111.27(32)
P(2)–Pd–C(29)	100.02(15)	Pd–N(2)–C(26)	112.91(31)
O(1)–Pd–N(2)	91.71(14)	Pd–N(2)–C(27)	104.63(29)
O(1)–Pd–C(29)	173.48(16)	C(25)–N(2)–C(26)	107.78(41)
N(2)–Pd–C(29)	82.26(18)	C(25)–N(2)–C(27)	110.20(40)
O(1)–P(1)–N(1)	114.90(19)	C(26)–N(2)–C(27)	110.04(41)
O(1)–P(1)–C(1)	108.27(22)	N(2)–C(27)–C(28)	108.88(40)
O(1)–P(1)–C(7)	110.01(21)	C(27)–C(28)–C(29)	117.83(44)
N(1)–P(1)–C(1)	108.26(21)	C(27)–C(28)–C(33)	121.19(47)
N(1)–P(1)–C(7)	109.38(21)	C(29)–C(28)–C(33)	120.95(48)
C(1)–P(1)–C(7)	105.60(23)	Pd–C(29)–C(28)	112.36(35)
Pd–P(2)–N(1)	106.39(14)	Pd–C(29)–C(30)	130.26(38)
Pd–P(2)–C(13)	119.55(17)	C(28)–C(29)–C(30)	117.27(44)
Pd–P(2)–C(19)	114.05(15)	C(29)–C(30)–C(31)	121.57(49)
N(1)–P(2)–C(13)	107.03(21)	C(30)–C(31)–C(32)	119.51(52)
N(1)–P(2)–C(19)	105.69(20)	C(31)–C(32)–C(33)	119.98(50)
C(13)–P(2)–C(19)	103.21(22)	C(28)–C(33)–C(32)	120.71(49)
Pd–O(1)–P(1)	114.77(18)		

Table 5 Selected bond distances (Å) and angles (°) for complex **18**

Pd–Cl(1)	2.361(3)	P(1)–C(7)	1.832(12)
Pd–P(2)	2.255(3)	P(2)–N(1)	1.614(9)
Pd–P(3)	2.199(3)	P(2)–C(13)	1.800(12)
Pd–O(1)	2.128(7)	P(2)–C(19)	1.813(11)
Cl(2)–C(40)	1.644(37)	P(3)–O(3)	1.598(6)
Cl(3)–C(40)	1.541(35)	P(3)–C(25)	1.813(11)
P(1)–O(1)	1.533(7)	P(3)–C(31)	1.798(11)
P(1)–N(1)	1.610(9)	O(3)–C(37)	1.421(13)
P(1)–C(1)	1.797(11)		
Cl(1)–Pd–P(2)	174.49(11)	Pd–P(2)–C(19)	114.80(38)
Cl(1)–Pd–P(3)	87.45(10)	N(1)–P(2)–C(13)	108.67(55)
Cl(1)–Pd–O(1)	90.60(19)	N(1)–P(2)–C(19)	104.67(52)
P(2)–Pd–P(3)	96.02(11)	C(13)–P(2)–C(19)	105.80(53)
P(2)–Pd–O(1)	85.80(19)	Pd–P(3)–O(3)	111.85(31)
P(3)–Pd–O(1)	177.37(20)	Pd–P(3)–C(25)	112.12(35)
O(1)–P(1)–N(1)	114.56(44)	Pd–P(3)–C(31)	114.73(40)
O(1)–P(1)–C(1)	108.61(46)	O(3)–P(3)–C(25)	104.74(46)
O(1)–P(1)–C(7)	108.27(49)	O(3)–P(3)–C(31)	105.12(45)
N(1)–P(1)–C(1)	107.86(51)	C(25)–P(3)–C(31)	107.56(52)
N(1)–P(1)–C(7)	110.38(55)	Pd–O(1)–P(1)	114.09(36)
C(1)–P(1)–C(7)	106.88(52)	P(3)–O(3)–C(37)	124.10(73)
Pd–P(2)–N(1)	106.49(33)	P(1)–N(1)–P(2)	115.32(53)
Pd–P(2)–C(13)	115.77(41)		

Table 6 Selected bond distances (Å) and angles (°) for complex **21a**

Ir–I	2.703(1)	P(2)–N	1.621(7)
Ir–P(2)	2.329(2)	P(2)–C(13)	1.832(8)
Ir–O	2.218(5)	P(2)–C(19)	1.828(8)
Ir–C(25)	2.147(8)	C(31)–C(32)	1.355(12)
Ir–C(31)	2.198(9)	C(31)–C(38)	1.455(12)
Ir–C(32)	2.191(8)	C(32)–C(33)	1.544(13)
Ir–C(35)	2.325(9)	C(33)–C(34)	1.519(13)
Ir–C(36)	2.279(9)	C(34)–C(35)	1.501(12)
P(1)–O	1.517(6)	C(35)–C(36)	1.363(13)
P(1)–N	1.595(7)	C(36)–C(37)	1.512(12)
P(1)–C(1)	1.819(8)	C(37)–C(38)	1.535(13)
P(1)–C(7)	1.809(8)		
I–Ir–P(2)	93.48(5)	O–P(1)–C(1)	109.25(34)
I–Ir–O	83.01(13)	O–P(1)–C(7)	108.89(37)
I–Ir–C(25)	82.93(21)	N–P(1)–C(1)	109.10(36)
I–Ir–C(31)	161.11(23)	N–P(1)–C(7)	111.09(38)
I–Ir–C(32)	159.71(27)	C(1)–P(1)–C(7)	103.25(38)
I–Ir–C(35)	87.13(21)	Ir–P(2)–N	107.85(24)
I–Ir–C(36)	90.89(22)	Ir–P(2)–C(13)	117.78(27)
P(2)–Ir–O	82.34(15)	Ir–P(2)–C(19)	117.93(28)
P(2)–Ir–C(25)	89.06(23)	N–P(2)–C(13)	105.59(38)
P(2)–Ir–C(31)	90.52(23)	N–P(2)–C(19)	105.74(37)
P(2)–Ir–C(32)	97.89(26)	C(13)–P(2)–C(19)	100.75(36)
P(2)–Ir–C(35)	168.68(24)	Ir–O–P(1)	116.59(27)
P(2)–Ir–C(36)	156.68(25)	P(1)–N–P(2)	118.21(41)
O–Ir–C(25)	163.02(26)	Ir–C(31)–C(32)	71.73(54)
O–Ir–C(31)	79.24(26)	Ir–C(31)–C(38)	111.72(61)
O–Ir–C(32)	115.06(29)	C(32)–C(31)–C(38)	126.31(89)
O–Ir–C(35)	108.93(26)	Ir–C(32)–C(31)	72.31(55)
O–Ir–C(36)	75.47(28)	Ir–C(32)–C(33)	114.55(63)
C(25)–Ir–C(31)	115.62(31)	C(31)–C(32)–C(33)	123.47(81)
C(25)–Ir–C(32)	80.52(33)	C(32)–C(33)–C(34)	114.57(76)
C(25)–Ir–C(35)	79.80(33)	C(33)–C(34)–C(35)	114.32(84)
C(25)–Ir–C(36)	114.22(34)	Ir–C(35)–C(34)	109.07(58)
C(31)–Ir–C(32)	35.96(32)	Ir–C(35)–C(36)	70.92(55)
C(31)–Ir–C(35)	92.53(31)	C(34)–C(35)–C(36)	124.52(87)
C(31)–Ir–C(36)	78.50(32)	Ir–C(36)–C(35)	74.65(52)
C(32)–Ir–C(35)	78.47(33)	Ir–C(36)–C(37)	110.88(59)
C(32)–Ir–C(36)	85.29(32)	C(35)–C(36)–C(37)	123.28(84)
C(35)–Ir–C(36)	34.43(31)	C(36)–C(37)–C(38)	114.16(78)
O–P(1)–N	114.64(33)	C(31)–C(38)–C(37)	113.78(81)

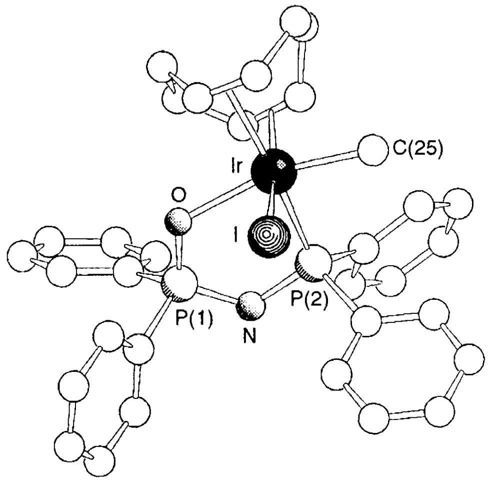


Fig. 7 Crystal structure of [IrI(Me)(cod){$Ph_2PNP(O)Ph_2$-*P,O*}] **21a** (CH protons omitted for clarity)

2.302(9) Å for Ir–C(35)/Ir–C(36) and can be compared with those in *trans*-[$IrCl_2$(acac)(cod)] and [IrI(Me)(acac)(cod)] (acac = acetylacetonate).[68,69] The Ir–C (methyl) and Ir–I distances of 2.147(8) and 2.703(1) Å respectively differ slightly from those reported for the complex [IrI(Me)(acac)(cod)].[69] The solid-state structure shows a *cis* oxidative addition of MeI and contrasts the *trans* addition seen with [Ir(acac)(cod)].[69]

A comparison of the MP_2NO metallacycles in complexes **17**, **18** and **21a** reveals a shortening of the P–N bonds and lengthening of the P–O bonds as a result of deprotonation/complexation (Table 7). Furthermore the P–N–P angle is significantly contracted relative to that in free HL and **1**. Interestingly there are differences in the planarity of the MP_2NO rings. Thus, the MP_2NO mean plane for **21a** has a maximum deviation from the mean plane of 0.08 Å for O(1), whilst in **17** the maximum deviation is 0.10 Å for N(1) and in **18** this rises to 0.26 Å [at N(1)]. Clearly, the energy differences associated with slight differences in planarity are not large. The ability of P–N rings such as phosphazene to form delocalised systems with no requirement for planarity is well documented.

In complex **18** the non-bonded Pd $\cdots$ O(3) distance is 3.16 Å. There are no significant intermolecular contacts in **1**, **18** or **21a** although in **17** there is a strong hydrogen bond between the methanol O–H and $[Ph_2PNP(O)Ph_2]^-$ ligand nitrogen (O $\cdots$ N 2.87, H $\cdots$ N 1.79 Å, O–H $\cdots$ N 175°).

Table 7 Comparison of selected bond distances (Å) and angles (°) for compounds **1**, **17**, **18** and **21a** together with HL[a] and $[AsPh_4][ReCl_4L]$[b]

	1	**17**	**18**	**21a**	HL	$[AsPh_4][ReCl_4L]$
M–O(1)		2.132(3)	2.128(7)	2.218(5)		2.054(3)
O(1)–P(1)	1.478(4)	1.516(3)	1.533(7)	1.517(6)	1.508(2)	1.543(3)
P(1)–N(1)	1.672(4)	1.602(4)	1.610(9)	1.595(7)	1.651(3)	1.594(4)
N(1)–P(2)	1.701(4)	1.634(4)	1.614(9)	1.621(7)	1.707(3)	1.621(4)
P(2)–M	2.289(1)	2.242(1)	2.255(3)	2.329(2)		2.490(1)
M–O(1)–P(1)		114.8(2)	114.1(4)	116.6(3)		121.1(2)
O(1)–P(1)–N(1)	115.0(2)	114.9(2)	114.6(4)	114.6(3)	111.0(1)	113.8(2)
P(1)–N(1)–P(2)	132.6(3)	117.1(2)	115.3(5)	118.2(4)	125.6(2)	116.4(2)
N(1)–P(2)–M	107.7(2)	106.4(1)	106.5(3)	107.8(2)		104.7(1)
P(2)–M–O(1)		86.29(9)	85.8(2)	82.3(1)		81.2(1)

[a] From ref. 34. [b] From ref. 55.

We have shown that a range of transition-metal complexes with HL are accessible and deprotonation affords a chelating or bridging ligand. Furthermore we have demonstrated that the $[Ph_2PNP(O)Ph_2]^-$ anion can be stabilised by incorporation into a metallacycle. The instability of the P–N bond in HL was illustrated by its facile cleavage affording a palladium-bound Ph_2POMe ligand. Further studies will concentrate on elucidating the mechanism involved in the formation of **18**. We are also investigating the synthesis of new heterobimetallics using HL as a bridging ligand.

Acknowledgements

We are grateful to the EPSRC for support and to Johnson Matthey for loans of precious metals.

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Received 28th September 1995; *Paper* 5/06405H