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The synthesis and co-ordination chemistry of new functionalised pyridylphosphines derived from Ph_2PCH_2OH †

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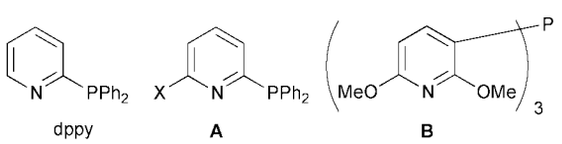
Condensation of Ph_2PCH_2OH with $H_2NC_5H_3(OH)N$ in methanol/toluene gave the new "hybrid" ligand $Ph_2PCH_2N(H)C_5H_3(OH)N$ **Ia**, which upon phosphorylation with either $ClP(O)R_2$ (R = Ph, OPh) or $ClPR_2$ afforded $Ph_2PCH_2N(H)C_5H_3(X)N$ [X = $OP(O)Ph_2$ **II**; $OP(O)(OPh)_2$ **III**; $OPPh_2$ **IV**]. Oxidation of **Ia** with aqueous H_2O_2 in thf gave $Ph_2P(O)CH_2N(H)C_5H_3(OH)N$ **V**. The dichloroplatinum(II) complexes **1**–**4** were prepared from $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) and **Ia**, **II** or **III** (2 equiv.) or **IV** (1 equiv.). Reaction of [AuCl(tht)] (tht = tetrahydrothiophene) with 1 equiv. of **Ia** gave [AuCl(**Ia**)] **5**. Bridge cleavage of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$ or $[\{MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh, Ir) with **Ia**–**IV** afforded either monometallic $[MCl_2(L)(PR_3)]$ **6**–**11** (M = Ru, Rh or Ir; L = η^6-*p*-cymene, η^5-C_5Me_5; PR_3 = **Ia**, **II** or **III**) or *P*,*P*′-bridged bimetallic $[\{MCl_2(L)\}_2$ **IV**] **12**–**15** (M = Ru, Rh or Ir; L = η^6-*p*-cymene, η^6-C_6Me_6, η^5-C_5Me_5) complexes. The neutral ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P\text{-}Ph_2PCH_2N(H)C_5H_3(X)\}]$ (X = OH **6a**; X = H **6b**) undergo isomerisation in $CDCl_3$ to give $[RuCl(\eta^6\text{-}p\text{-cymene})\{P,N(\text{pyridyl})\text{-}Ph_2PCH_2N(H)C_5H_3(X)N\}]Cl$ (X = OH **6c**; X = H **6d**). In contrast aged solutions (*ca.* 40 d) of **7**–**15** show no evidence (by $^{31}P\{^1H\}$ NMR) for *P*,*N*(pyridyl)-chelation. The X-ray structures of representative compounds have been determined, and confirm, in the case of **6c**/**6d**, a novel six-membered M–P–C–N–C–N metallacycle.

Introduction

Pyridylphosphines continue to induce much interest as excellent ligands for stabilising many transition-metal co-ordination and organometallic complexes.[1] Their extreme versatility stems primarily from the ease of synthesis and also by the facile nature which modification of the structure can influence ligand behaviour. One of the most common pyridylphosphines studied to date is $(2\text{-}C_5H_4N)PPh_2$ (dppy).[2] This ligand displays numerous ligating modes ranging from *P*-co-ordination, *P*,*N*-chelation and more commonly, *P*,*N*-bridging of two metal centres. Recently there has been considerable interest in the development of bidentate systems whereby the pyridyl group(s) adopt exocyclic positions[3] with respect to the P centre or constitute the linker[4,5] between two $-PR_2$ moieties. Examples of multifunctional P/N(pyridyl)/X (X = N,[6] O,[7] C[8]) or chiral pyridylphosphines in which the chirality can be located either at P[9] or in the backbone[10] have also been documented.



dppy **A** **B**

(X = Me, Br, OMe)

Several groups have recently reported various catalytic applications with pyridylphosphine complexes[11] and elegant work by Drent *et al.*[12] amply illustrates this point. These workers found efficient alkoxycarbonylation catalysts are generated from $Pd(OAc)_2$/dppy/CH_3SO_3H and noted high catalytic activity and selectivity. Moreover this mechanism[13] and aspects of co-ordination chemistry pertinent to this process[14] have been studied in detail by the groups of Matteoli and Edwards. One interesting observation from the work by Drent *et al.* was that substituted ligand systems **A**, *i.e.* in the 6-position, gave higher activity and selectivity relative to dppy.[12] The functionalisation of pyridylphosphines can lead to different reactivites[15] and furthermore, by introducing methoxy groups in 2,6-positions (*e.g.*, in **B**), affords active hydrogenation catalysts whilst the parent pyridylphosphine complexes were inactive.[16] This has been explained by the absence of *P*,*N*(pyridyl)-chelating modes when suitably modified with ether substituents.[16] Herein we report the synthesis and reactivity of a new class of pyridylphosphine and demonstrate, by incorporation of selected functional groups in the 3-position, whether the ligand adopts a *P*-, *P*,*N*(pyridyl)-chelate or *P*,*P*′-bridge co-ordination mode upon complexation. The X-ray structures of seven compounds have been determined and an array of H-bonding motifs observed.

Experimental

Standard Schlenk techniques were used for ligand syntheses whilst all other reactions were carried out in air using previously distilled solvents. The ligand Ph_2PCH_2OH was prepared from Ph_2PH and $(CH_2O)_n$ according to a literature method[17] as were the metal complexes $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene),[18] $[\{MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (M = Rh, Ir),[19] $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene}\}_2]$,[20] $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$[21] and [AuCl(tht)] (tht = tetrahydrothiophene).[22] All other chemicals were obtained from commercial sources and used directly without further purification.

IR spectra were recorded as KBr pellets in the range 4000–200 cm^{-1} on a Perkin-Elmer System 2000 Fourier-transform

† Electronic supplementary information (ESI) available: elemental analyses for **IA**, **Ib** and all other compounds. See http://www.rsc.org/suppdata/dt/b0/b003759l/

spectrometer, ^{1}H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $SiMe_4$ and coupling constants (J) in Hz, $^{31}P\{^1H\}$ NMR spectra were recorded on either a JEOL FX90Q (36.2 MHz) or a Bruker AC250 FT (101.3 MHz) spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz. All NMR spectra were measured in $CDCl_3$ unless otherwise stated. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Precious metal salts were provided on loan by Johnson Matthey plc.

Preparations

$Ph_2PCH_2N(H)C_5H_3(OH)N$ Ia. A mixture of Ph_2PCH_2OH (0.50 g, 2.31 mmol) and $H_2NC_5H_3(OH)N$ (0.254 g, 2.31 mmol) in methanol (8 cm^3) and toluene (13 cm^3) was refluxed under a nitrogen atmosphere for *ca.* 24 h. The solution was allowed to cool and the volume concentrated *in vacuo* to *ca.* 1–2 cm^3. Addition of diethyl ether (15 cm^3) gave a white solid **Ia** which was collected by suction filtration and dried *in vacuo*. Yield: 0.62 g, 87%. Selected data: IR: 3394, 2822 $\nu_{NH/OH}$ cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 9.70 (OH), 7.57–6.40 (arom. H), 5.61 [^3J(PH) 12.5 Hz, NH], 4.23 (CH_2). EI MS: *m/z* 308 (M^+). In a similar manner $Ph_2PCH_2N(H)C_5H_4N$ **Ib** was also prepared (79%). Selected data: IR: 3223 ν_{NH} cm^{-1}. ^{1}H NMR: δ 8.12–6.40 (arom. H), 4.50 (NH), 4.08 (CH_2).

$Ph_2PCH_2N(H)C_5H_3\{OP(O)(OPh)_2\}N$ III. To a stirred suspension of **Ia** (0.328 g, 1.06 mmol) and triethylamine (0.108 g, 1.07 mmol) in toluene (10 cm^3) at 0 °C was added dropwise over 15 min a toluene (10 cm^3) solution of $ClP(O)(OPh)_2$ (0.289 g, 1.08 mmol). The resulting mixture was allowed to warm to room temperature and stirred for *ca.* 24 h. The mixture was allowed to settle, the toluene layer cannulated from the $[HNEt_3]Cl$ and the solution concentrated *in vacuo* to *ca.* 1–2 cm^3. Addition of diethyl ether (15 cm^3) gave a white solid **III** which was collected by suction filtration and dried *in vacuo*. Yield: 0.452 g, 79%. Selected data: IR: 3374 ν_{NH}, 1298 $\nu_{P=O}$ cm^{-1}. ^{1}H NMR: δ 8.00–6.51 (arom. H), 4.79 (NH), 4.19 (CH_2). In a similar manner the ligands $Ph_2PCH_2N(H)C_5H_3\{OP(O)Ph_2\}N$ **II** and $Ph_2PCH_2N(H)C_5H_3(OPPh_2)N$ **IV** were prepared although an analytically pure sample of **IV** could not be obtained. Selected data for **II**: IR: 3360 ν_{NH}, 1232 $\nu_{P=O}$ cm^{-1}. ^{1}H NMR: δ 7.87–6.37 (arom. H), 4.89 (NH), 4.24 (CH_2). Selected data for **IV**: IR: 3431 ν_{NH} cm^{-1}. ^{1}H NMR: δ 7.80–6.42 (arom. H), 4.91 (NH), 4.22 (CH_2).

$Ph_2P(O)CH_2N(H)C_5H_3(OH)N$ V. To a solution of **Ia** (0.100 g, 0.324 mmol) in thf (2 cm^3) was added aqueous H_2O_2 (30% w/w, 0.2 cm^3). The solution was stirred for *ca.* 34 h, decanted to remove some insoluble material and diethyl ether (15 cm^3) added. The off-white solid was collected by suction filtration and dried *in vacuo*. Yield: 0.051 g, 48%. Selected data: IR: 3418 ν_{NH}, 1150 ν_{PO} cm^{-1}. ^{1}H NMR: δ 7.84–6.45 (arom. H), 6.10 (NH), 4.51 (CH_2). Crystals of **V** suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a $CDCl_3$ solution over the course of several days.

$[Pt\{Ph_2PCH_2N(H)C_5H_3(OH)N\}_2]Cl_2$ 1. To a stirred solution of $[PtCl_2(cod)]$ (0.050 g, 0.13 mmol) in CH_2Cl_2 (10 cm^3) was added **Ia** (0.082 g, 0.267 mmol). After stirring the solution for *ca.* 15 min the volume was concentrated *in vacuo* to *ca.* 1–2 cm^3 and diethyl ether (15 cm^3) added. The white solid **1** was filtered and dried *in vacuo*. Yield: 0.18 g, 77%. Selected data: IR: 3402, 3231 $\nu_{NH/OH}$ cm^{-1}. The following dichloroplatinum(II) complexes were also prepared: *cis*-$[PtCl_2\{Ph_2PCH_2N(H)C_5H_3\{OP(O)Ph_2\}N\}_2]$ **2** (79%). Selected data: IR: 3398 ν_{NH}, 1244 $\nu_{P=O}$, 316, 290 ν_{PtCl} cm^{-1}. ^{1}H NMR: δ 8.16–6.33 (arom. H), 4.72 [^2J(PH) 6.9 Hz, CH_2]. FAB MS: *m/z* 1247 (M − Cl). *cis*-$[PtCl_2\{Ph_2PCH_2N(H)C_5H_3\{OP(O)(OPh)_2\}N\}_2]$ **3** (67%). Selected data: IR: 3396 ν_{NH}, 1299 $\nu_{P=O}$, 315, 283 ν_{PtCl} cm^{-1}. ^{1}H NMR: δ 7.53–6.40 (arom. H), 6.04 (NH), 4.77 [^2J(PH) 5.6 Hz, CH_2]. FAB MS: *m/z* 1311 (M − Cl). *cis*-$[PtCl_2\{Ph_2PCH_2N(H)C_5H_3(OPPh_2)N\}]$ **4** (94%) using 1 equiv. of **IV**. Selected data: IR: 3217 ν_{NH}, 321, 298 ν_{PtCl} cm^{-1}. Crystals of **2** suitable for X-ray crystallography were grown by slow diffusion of light petroleum (bp 60–80 °C) into a $CDCl_3$ solution over the course of several days.

$[AuCl\{Ph_2PCH_2N(H)C_5H_3(OH)N\}]$ 5. To a stirred solution of [AuCl(tht)] (0.050 g, 0.153 mmol) in CH_2Cl_2 (10 cm^3) was added **Ia** (0.049 g, 0.153 mmol). After stirring the solution for 15 min the volume was concentrated *in vacuo* to *ca.* 1–2 cm^3. Addition of diethyl ether gave a white solid **5** which was collected by suction filtration and dried *in vacuo*. Yield: 0.045 g, 52%. Selected data: IR: 3606, 3411 $\nu_{NH/OH}$, 325 ν_{AuCl} cm^{-1}.

$[RhCl_2(\eta^5\text{-}C_5Me_5)\{Ph_2PCH_2N(H)C_5H_3\{OP(O)(OPh)_2\}N\}]$ 11. To the solids $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (0.030 g, 0.0485 mmol) and **III** (0.050 g, 0.0926 mmol, *ca.* 2 equiv.) was added CH_2Cl_2 (10 cm^3). The solution was stirred for *ca.* 30 min and the volume reduced to *ca.* 1–2 cm^3 by evaporation under reduced pressure. Addition of light petroleum (bp 60–80 °C, 10 cm^3) gave **11** which was collected by suction filtration and dried *in vacuo*. Yield: 0.074 g, 90%. Selected data: IR: 3443, 3432 ν_{NH}, 1303 $\nu_{P=O}$ cm^{-1}. ^{1}H NMR: δ 7.94–6.22 (arom. H), 5.91 (NH), 5.00 (CH_2), 1.38 [J(PH) 4.2 Hz, C_5Me_5]. FAB MS: *m/z* 813 (M − Cl). Using a similar procedure the following complexes were prepared: $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2PCH_2N(H)C_5H_3(OH)N\}]$ **6a** (90%). Selected data: IR: 3474, 3416, 3235 $\nu_{NH/OH}$ cm^{-1}. FAB MS: *m/z* 615 (M). $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2PCH_2N(H)C_5H_4N\}]$ **6b** (81%). Selected data: IR: 3298 ν_{NH} cm^{-1}. ^{1}H NMR: δ 7.90–5.98 (arom. H), 5.37 (NH), 5.30–5.19 [$CH_3C_6H_4CH(CH_3)_2$], 4.75 (CH_2), 2.56 [$CH_3C_6H_4CH(CH_3)_2$], 1.89 [$CH_3C_6H_4CH(CH_3)_2$], 0.92 [$CH_3C_6H_4CH(CH_3)_2$]. FAB MS: *m/z* 599 (M). $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2PCH_2N(H)C_5H_3[OP(O)Ph_2]N\}]$ **7** (77%). Selected data: IR: 3365 ν_{NH}, 1235 $\nu_{P=O}$ cm^{-1}. ^{1}H NMR: δ 7.93–6.09 (arom. H), 5.63 (NH), 5.29–5.21 [$CH_3C_6H_4CH(CH_3)_2$], 4.90 (CH_2), 2.55 [$CH_3C_6H_4CH(CH_3)_2$], 1.84, [$CH_3C_6H_4CH(CH_3)_2$], 0.91 [$CH_3C_6H_4CH(CH_3)_2$]. FAB MS: *m/z* 815 (M). $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2PCH_2N(H)C_5H_3[OP(O)(OPh)_2]N\}]$ **8** (77%). Selected data: IR: 3311 ν_{NH}, 1295 $\nu_{P=O}$ cm^{-1}. ^{1}H NMR: δ 7.90–6.21 (arom. H), 5.45 (NH), 5.29–5.18 [$CH_3C_6H_4CH(CH_3)_2$], 4.88 (CH_2), 2.56 [$CH_3C_6H_4CH(CH_3)_2$], 1.88, [$CH_3C_6H_4CH(CH_3)_2$], 0.90 [$CH_3C_6H_4CH(CH_3)_2$]. FAB MS: *m/z* 847 (M). $[RhCl_2(\eta^5\text{-}C_5Me_5)\{Ph_2PCH_2N(H)C_5H_3(OH)N\}]$ **9**. Selected data: IR: 3407, 3251 $\nu_{NH/OH}$ cm^{-1}. FAB MS: *m/z* 581 (M − Cl). $[RhCl_2(\eta^5\text{-}C_5Me_5)\{Ph_2PCH_2N(H)C_5H_3[OP(O)Ph_2]N\}]$ **10** (85%). Selected data: IR: 3298 ν_{NH}, 1240 $\nu_{P=O}$ cm^{-1}. ^{1}H NMR: δ 7.98–6.13 (arom. H), 6.08 (NH), 5.03 [J(PH) 5.1 Hz, CH_2], 1.41 [J(PH) 3.2 Hz, C_5Me_5]. ESMS: *m/z* 782 (M − Cl).

A similar procedure to that described for **11** was used (1 equiv. of **IV** per dimer) to prepare the following bimetallic complexes: $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2\{Ph_2PCH_2N(H)C_5H_3(OPPh_2)N\}]$ **12** (74%). Selected data: IR: 3407 ν_{NH} cm^{-1}. ^{1}H NMR: δ 8.00–6.10 (arom. H), 6.05 (NH), 5.37–5.10 [$CH_3C_6H_4CH(CH_3)_2$, CH_2], 2.69, 2.40 [$CH_3C_6H_4CH(CH_3)_2$], 1.87, 1.56 [$CH_3C_6H_4CH(CH_3)_2$], 1.06, 0.69 [$CH_3C_6H_4CH(CH_3)_2$]. FAB MS: *m/z* 1107 (M). $[\{RuCl_2(\eta^6\text{-}C_6Me_6)\}_2\{Ph_2PCH_2N(H)C_5H_3(OPPh_2)N\}]$ **13** (81%). Selected data: IR: 3385 ν_{NH} cm^{-1}. ^{1}H NMR: δ 8.15–6.00 (arom. H), 5.00 (CH_2), 1.83, 1.66 (C_6Me_6). ES MS: *m/z* 1127 (M − Cl). $[\{RhCl_2(\eta^5\text{-}C_5Me_5)\}_2\{Ph_2PCH_2N(H)C_5H_3(OPPh_2)N\}]$ **14** (88%). Selected data: IR: 3422 ν_{NH} cm^{-1}. ^{1}H NMR: δ 8.18–7.30 (arom. H), 6.14, 5.24 (CH_2, NH), 1.46 [J(PH) 3.5 Hz, C_5Me_5], 1.24 [J(PH) 4 Hz, C_5Me_5]. FAB MS: *m/z* 1073 (M − Cl). $[\{IrCl_2(\eta^5\text{-}C_5Me_5)\}_2\{Ph_2PCH_2N(H)$-

$C_5H_3(OPPh_2)N\}$] **15** (81%). Selected data: IR: 3426 ν_{NH} cm^{-1}. ^1H NMR: δ 8.21–6.12 (arom. H), 5.40 (NH), 1.47 [*J*(PH) 2.2 Hz, C_5Me_5], 1.25 [*J*(PH) 2.4 Hz, C_5Me_5]. ES MS: *m*/*z* 1254 (M − Cl). Crystals suitable for X-ray crystallography were grown by slow diffusion of either light petroleum (bp 60–80 °C) (for **6d**) or diethyl ether (for **8**, **12**, **14**) into a $CDCl_3$ solution over the course of several days. A $CDCl_3$ solution of **6c** was allowed to stand for several days to afford X-ray quality crystals.

X-Ray crystallography

Data for compounds **V**, **2**, **8**, **12** and **14** were collected on a Nonius Kappa CCD diffractometer at 100(2) K using an Oxford Cryostream low temperature attachment. Structures were solved using SHELXS-97[23] and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-97[23]) with the aid of the program XSeed.[24] In general all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride, except for NH protons which were located on the final difference Fourier map and refined freely.

Data for **6c** and **6d** were collected either on a Bruker SMART diffractometer with graphite-monochromated (Mo-Kα) radiation (λ = 0.710 37 Å) or a Rigaku AFC7S serial diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.541 78 Å) and ω scans. Structures were solved by direct methods and refined by full-matrix least squares against *F* (TEXSAN[25]) for data with $I > 3\sigma(I)$ or F^2 (SHELXTL[26]) for all data. A standard SHELXTL weighting scheme was used for **6c** whilst in the case of **6d** the weighting scheme for the Rigaku/TEXSAN was as previously reported.[27] The C–H proton of the half weight $CHCl_3$ solvate in **6c** and the N–H/O–H protons were all idealised. Table 1 shows crystallographic data for compounds **V**, **2**, **6c**, **6d**, **8**, **12** and **14**.

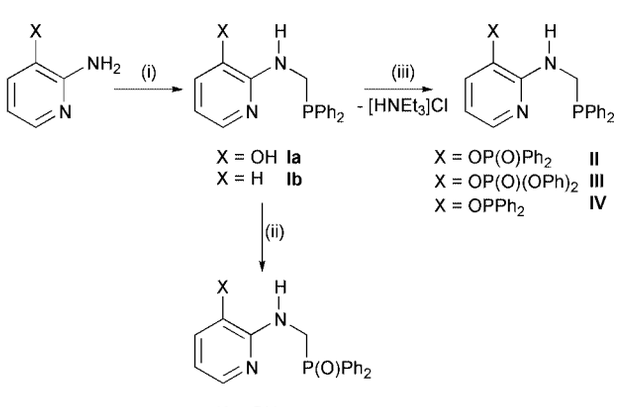
CCDC reference number 186/2065.

See http://www.rsc.org/suppdata/dt/b0/b003759l/ for crystallographic files in .cif format.

Results and discussion

Ligand syntheses

The synthesis of the new pyridylphosphinoalcohol **Ia** was readily accomplished by the condensation reaction of Ph_2PCH_2OH **C** and commercially available $H_2NC_5H_3(OH)N$ in methanol/toluene (Scheme 1). An attempt to prepare the substituted ditertiary phosphine $(Ph_2PCH_2)_2NC_5H_3(OH)N$ using 2 equiv. of **C** gave only **Ia** and unreacted **C** [$^{31}P\{^1H\}$ NMR evidence]. A similar procedure was recently employed for the construction of dendrimers terminally coated with $-N(CH_2PPh_2)_2$



Scheme 1 *Reagents and conditions*: (i) Ph_2PCH_2OH; (ii) aq. H_2O_2; (iii) $ClP(O)Ph_2$, $ClP(O)(OPh)_2$ or $ClPPh_2$, NEt_3.

Table 1 Details of the X-ray data collections and refinements for compounds **V**, **2**, **6c**, **6d**, **8**, **12** and **14**

Compound	V	2	6c	6d	8	12	14
Empirical formula	$C_{18}H_{17}N_2O_2P$	$C_{60}H_{54}Cl_2N_2O_5P_4Pt$	$C_{28.50}H_{31.50}Cl_{3.50}N_2OPRu$	$C_{29}H_{57}Cl_5N_2PRu$	$C_{40}H_{40}Cl_2N_2O_4P_2Ru$	$C_{54.50}H_{66.50}Cl_{11.50}N_2O_2P_2Ru_2$	$C_{51}H_{57}Cl_7N_2OP_2Rh_2$
M	324.31	1272.92	674.17	717.89	846.65	1453.35	1229.90
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.7043(6)	10.9899(5)	11.0689(7)	10.980(2)	7.3753(3)	11.2902(3)	9.6851(3)
b/Å	10.8681(8)	15.8626(8)	12.2999(8)	12.228(3)	12.8896(3)	13.6623(4)	16.4272(7)
c/Å	17.2011(11)	16.8562(11)	23.989(2)	24.193(3)	20.6503(5)	21.4044(7)	16.6831(8)
a/°	90.024(4)	81.161(3)			106.031(2)	93.695(2)	99.178(3)
β/°	91.491(4)	76.380(3)	102.825(1)	101.96(2)	99.091(2)	104.682(2)	91.764(3)
γ/°	100.7774	77.645(3)			93.886(2)	101.304(2)	92.281(3)
U/Å^3	1597.95(19)	2773.2(3)	3184.6(4)	3178(1)	1850.2(1)	3109.1(1)	2616.4(9)
T/K	100(2)	100(2)	293(2)	293	100(2)	100(2)	100(2)
Z	4	2	4	4	2	2	2
μ/mm^{-1}	0.18	2.79	0.86	0.99	0.70	1.07	1.09
Measured reflections	9398	20959	18840	6198	15074	18624	19114
Independent reflections (R_{int})	5614 (0.0850)	12428 (0.0538)	7483 (0.171)	5873 (0.043)	8461 (0.0416)	10808 (0.1074)	11885 (0.0388)
Final *R*, R_w	0.056, 0.111	0.066, 0.129	0.071, 0.139	0.040, 0.038	0.033, 0.066	0.059, 0.142	0.040, 0.080

Table 2 Selected ^{31}P NMR data for compounds **Ia**–**IV** and **1**–**15**

Compound	δ(P)	$\delta(P_O)$	J(PtP)/Hz	J(RhP)/Hz	J(PP)[k]
Ia	−16.8[a]				
Ib	−17.4				
II	−15.2	34.6			
III	−15.2[b,c]	−15.0			
IV	−15.2				
	114.3[d]				
V	35.3				
1	3.5[a]		3550		
2	8.8	33.4	3700		
3	7.5	−16.3	3669		
4	18.6[e,f]		3559		20
	105.9		4188		
5	27.9[g]				
6a	20.7[h]				
6b	19.7[i]				
7	21.9	34.4			
8	21.4	−16.6			
9	22.4[j]			136	
10	25.9	33.2		141	
11	26.7	−16.5		145	
12	26.0[f]				
	121.6				
13	24.6[f]				
	120.2				
14	29.2[f]			141	
	119.3			172	
15	−5.2[f]				
	76.0				

[a] Recorded in $(CD_3)_2SO$. [b] Tentative assignment. [c] One phosphorus resonance at δ(P) −16.6 (36.2 MHz). [d] $OPPh_2$ group, recorded in C_7H_8–C_6D_6 insert. [e] Recorded *in situ*. [f] $CPPh_2$ group. [g] Recorded in $CDCl_3$–CH_3OH. [h] δ(P) 31.6 for *P*,*N*(pyridyl)-chelate species **6c**. [i] δ(P) 33.0 for *P*,*N*(pyridyl)-chelate species **6d**. [j] Minor species at δ(P) 26.2, J(RhP) 14.1 Hz. [k] No J(PP) couplings resolved for either **II**–**IV**, **2**, **3**, **7**, **8** or **10**–**15**.

moieties.[28] The condensed ligand **Ia** was isolated in good yield as a white solid and could routinely be prepared in gram quantities. Ligand **Ia** is freely soluble in polar solvents [MeOH, Me_2CO and Me_2SO], displays moderate solubility in CH_2Cl_2 and toluene and poor solubility in Et_2O. The $^{31}P\{^1H\}$ NMR spectrum of **Ia** [$(CD_3)_2SO$] shows a single P resonance at δ(P) −16.8 (Table 2), shifted upfield by *ca*. 7 ppm with respect to that observed for **C** [δ(P) −9.9 ($CDCl_3$)]. Furthermore there is negligible change in δ(P) in comparison with $Ph_2PCH_2N(H)C_5H_4N$ **Ib** [δ(P) −17.4] bearing no additional functional group. Other characterising data for **Ia** (and **Ib**) are given in the Experimental section. Elemental analyses for **Ia**, **Ib** and all other compounds reported here have been deposited as electronic supplementary information (ESI).†

The ligands $Ph_2PCH_2N(H)C_5H_3(X)N$ [X = $OP(O)Ph_2$ **II**; $OP(O)(OPh)_2$ **III**; $OPPh_2$ **IV**] were conveniently prepared from **Ia** upon stoichiometric reaction with $ClP(O)Ph_2$, $ClP(O)(OPh)_2$ or $ClPPh_2$ and NEt_3 in toluene (Scheme 1). Although **IV** could not be crystallised it was sufficiently pure (by NMR) to be used directly in the complexation studies described below. All spectroscopic evidence for **II**–**IV** concurs with the proposed structures. Hence the $^{31}P\{^1H\}$ NMR spectrum of **IV** showed two equally intense P resonances at δ(P) −15.2 (P^{III}–C) and 114.3 (P^{III}–O) respectively. Additionally no J(PP) coupling was observed between the two chemically inequivalent phosphorus(III) nuclei with similar observations seen in most co-ordination complexes of **IV**. The absence of any J(PP) coupling was also the case for **II** and **III**. The infrared spectra of **II** and **III** show strong absorptions at 1232 and 1298 cm^{-1}, respectively, and assigned to $\nu_{P=O}$. Pringle and co-workers[29] recently described an isomeric series of phosphonated triarylphosphines, $Ph_2PC_6H_4P(O)(OEt)_2$, and demonstrated the hydroformylation activity of their platinum(II) complexes in the presence of $SnCl_2$.

Table 3 Selected bond distances (Å) and angles (°) for compound **V** (equivalent values for second molecule are given in square brackets)

P(1)–O(1)	1.501(2) [1.505(1)]	O(1)–P(1)–C(1)	112.19(14) [112.26(14)]
P(1)–C(1)	1.807(3) [1.804(3)]	O(1)–P(1)–C(1)	111.90(13) [110.90(12)]
P(1)–C(7)	1.792(3) [1.801(3)]	O(1)–P(1)–C(1)	111.62(12) [111.19(12)]
P(1)–C(13)	1.794(3) [1.804(3)]	P(1)–C(1)–N(1)	111.3(2) [110.9(2)]
C(1)–N(1)	1.453(4) [1.448(4)]		
N(1)–C(2)	1.378(4) [1.380(4)]		

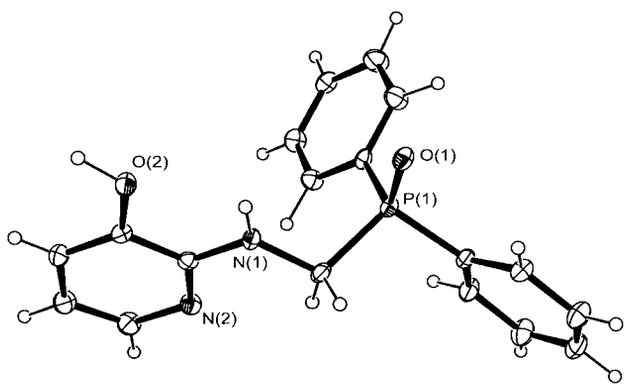
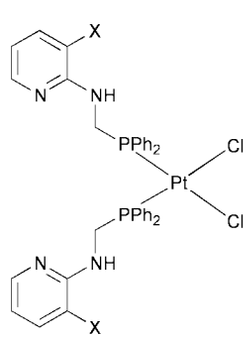


Fig. 1 Crystal structure of one of the independent molecules of **V**. Displacement ellipsoids are shown at the 30% probability level.

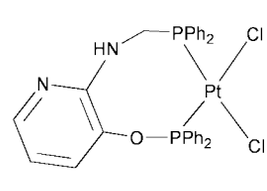
Whilst there was little evidence for aerial oxidation of **Ia** in the solid state or in solution, the addition of aqueous H_2O_2 affords the corresponding oxide $Ph_2P(O)CH_2N(H)C_5H_3(OH)N$ **V** in modest yield (48%). Pyridylphosphine oxides have recently been described by Minghetti *et al.*[30] and shown to behave either as *N*(pyridyl)-donor or *N*(pyridyl),*O*-chelating ligands upon complexation to palladium(II) and platinum(II) centres. The X-ray structure (Fig. 1, Table 3) of **V** shows two independent molecules with distorted tetrahedral geometries. The P–O distances [1.501(2), 1.505(1) Å] in **V** are slightly longer than those in other triarylphosphine oxides[30–32] and may be a consequence of strong intermolecular O–H···OP H-bonding linking molecules into dimer pairs [O(2)···O(3) 2.61, H(2O)···O(3) 1.78 Å; O(2)–H(2O)···O(3) 167° and O(4)···O(1) 2.61, H(4O)···O(1) 1.79 Å; O(4)–H(4O)···O(1) 164°].

P-co-ordination chemistry

The co-ordination chemistry of **Ia**, **Ib** and **II**–**IV** was studied with several late transition-metal precurors of Ru(II), Rh(III), Ir(III), Pt(II) and Au(I). When 2 equivalents of **Ia**, **II** or **III** were reacted with $[PtCl_2(cod)]$ in dichloromethane at ambient temperature the new dichloroplatinum(II) complexes **1**–**3**



X = $OP(O)Ph_2$ **2**
X = $OP(O)(OPh)_2$ **3**



4

Table 4 Selected bond distances (Å) and angles (°) for compound **2**

Pt(1)–Cl(1)	2.3534(17)	Cl(1)–Pt(1)–P(1)	85.05(6)
Pt(1)–Cl(2)	2.3482(16)	Cl(1)–Pt(1)–Cl(2)	86.58(6)
Pt(1)–P(1)	2.2543(18)	Cl(2)–Pt(1)–P(3)	90.48(6)
Pt(1)–P(3)	2.2489(19)	P(1)–Pt(1)–P(3)	98.24(7)
P(2)–O(1)	1.617(5)	Cl(2)–Pt(1)–P(1)	170.86(7)
P(4)–O(3)	1.601(5)	Cl(1)–Pt(1)–P(3)	173.17(7)
P(2)–O(2)	1.463(6)	O(1)–P(2)–O(2)	116.2(3)
P(4)–O(4)	1.468(6)	O(3)–P(4)–O(4)	117.1(3)

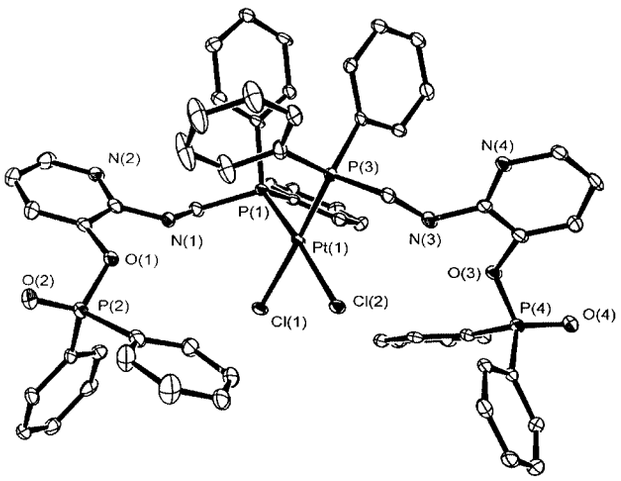


Fig. 2 Crystal structure of **2** (solvent omitted for clarity). Displacement ellipsoids are shown at the 30% probability level.

respectively were isolated in good yields (*ca.* 70%). Reaction of 1 equivalent of **IV** with [$PtCl_2$(cod)] gave the eight-membered *P*,*P*′-chelate complex **4**. Selected spectroscopic data are given in Table 2 and the Experimental section. For **1** a new phosphorus resonance at δ(P) 3.5 was observed along with a *J*(PtP) of 3550 Hz. The magnitude of this coupling suggests a *cis* configuration although the apparent absence of two ν_{PtCl} stretches in the IR spectrum infers *P*,*N*(pyridyl)-co-ordination of **Ia** rather than a monodentate *P*-mode of bonding. Hence we tentatively assign an ionic structure for **1** in which **Ia** functions as a *P*,*N*(pyridyl)-chelating ligand. The solution conductivity of **1** in water–methanol (90 : 10) is close to that expected for a 1 : 2 salt. For the platinum(II) complex **4** the inequivalent P nuclei gave two well resolved P resonances at δ(P) 18.6 [*J*(PtP) 3559 Hz] and 105.9 ppm [*J*(PtP) 4188 Hz] with a small *J*(PP) coupling of 20 Hz. Like **4** the complexes **2** and **3** are neutral [$PtCl_2(PR_3)_2$] species and furthermore, the $\delta(P_O)$ similar to that observed in the uncomplexed ligands [$\delta(P_O)$ 33.4 for **2**, −16.3 for **3**; 34.6 for **II**, −15.0 for **III**] indicating no Pt–O=P interaction.

The X-ray structure of **2** (Fig. 2, Table 4) reveals an approximate square-planar co-ordination of the platinum [P(1)–Pt(1)–Cl(1) 85.05(6); Cl(1)–Pt(1)–Cl(2) 86.58(6); P(3)–Pt(1)–Cl(2) 90.48(6); P(1)–Pt(1)–P(3) 98.24(7)°]. The two "hybrid" ligands adopt a *cis* configuration with typical Pt–P [2.2543(18) and 2.2489(19) Å] and Pt–Cl bond distances [2.3534(17) and 2.3482(16) Å].[33] The P(2)–O(2) [1.463(6) Å] and P(4)–O(4) [1.468(6) Å] bond distances in **2** are indicative of appreciable double bond character[30–32] and shorter than those of the phenoxy P(2)–O(1) and P(4)–O(3) groups. There are two intramolecular N–H · · · Cl_{coord} hydrogen bonds [N(1) · · · Cl(1) 3.36, H(1n) · · · Cl(1) 2.58 Å; N(1)–H(1n) · · · Cl(1) 132° and N(3) · · · Cl(2) 3.13, H(3n) · · · Cl(2) 2.58 Å; N(3)–H(3n) · · · Cl(2) 123°] which may account for the orientation of the P=O groups away from the metal.

Reaction of 1 equiv. of **Ia** with [AuCl(tht)] gave the new gold(I) complex [AuCl{$Ph_2PCH_2N(H)C_5H_3(OH)N$}] **5** the $^{31}P\{^1H\}$ NMR and IR spectra of which are in full agreement with *P*-co-ordination of the pyridylphosphine ligand.

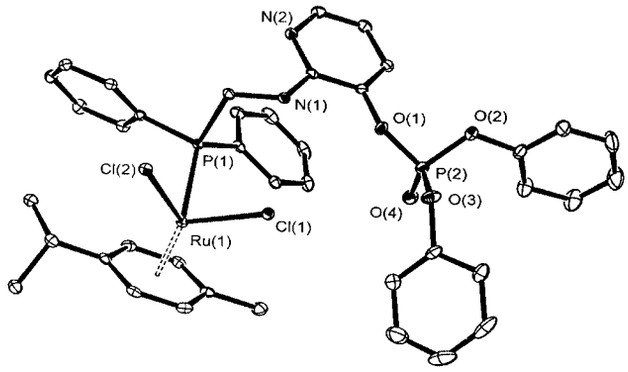
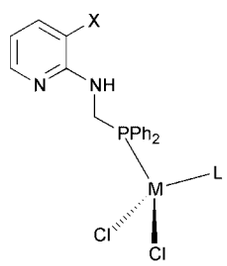


Fig. 3 Crystal structure of **8**. Displacement ellipsoids are shown at the 30% probability level.

Bridge cleavage of the dimers [{RuCl(μ-Cl)(η^6-*p*-cymene}$_2$] or [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] with **Ia**, **Ib**, **II** or **III** gave the mononuclear complexes **6a**–**11** as air stable, orange solids.



M = Ru, L = *p*-cymene, X = OH	**6a**
M = Ru, L = *p*-cymene, X = H	**6b**
M = Ru, L = *p*-cymene, X = $OP(O)Ph_2$	**7**
M = Ru, L = *p*-cymene, X = $OP(O)(OPh)_2$	**8**
M = Rh, L = C_5Me_5, X = OH	**9**
M = Rh, L = C_5Me_5, X = $OP(O)Ph_2$	**10**
M = Rh, L = C_5Me_5, X = $OP(O)(OPh)_2$	**11**

Reaction of [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] with 2 equiv. of **Ia** in CH_2Cl_2 at ambient temperature gave, after workup, an orange solid **9** whose $^{31}P\{^1H\}$ NMR spectrum indicated the presence of two species. The major species at δ(P) 22.4 [*J*(RhP) 136 Hz] is tentatively assigned to [$RhCl_2$(η^5-C_5Me_5)(**Ia**)] whilst the minor species at δ(P) 26.2 [*J*(RhP) 141 Hz] is thought to be [RhCl-(η^5-C_5Me_5){*P*,*N*(pyridyl)-**Ia**}]Cl and in an approximate ratio of 2.8 : 1, respectively. After allowing a $CDCl_3$ solution of **9** to stand for *ca.* 40 d, the ratio diminished slightly to 2.2 : 1. No *P*,*O*-chelation was infered by a lack of reactivity of [$RhCl_2$-(η^5-C_5Me_5)(**Ia**)] with bases (*e.g.*, NEt_3, Bu^tOK) in which deprotonation would be anticipated to give a *P*,*O*-chelating alkoxide.

The X-ray structure of **8** (Fig. 3, Table 5) displays a classic "piano-stool" geometry formed by an η^6-*p*-cymene ligand and the three legs are the two chlorides and the phosphorus donor atom of **III**. The ligand **III** is exclusively *P*-co-ordinating with no interaction between the ruthenium(II) centre and either the pyridyl nitrogen or phosphoryl oxygen donor atoms. There is also an intramolecular N–H · · · Cl_{coord} H-bond [N(1) · · · Cl(1) 3.20, H(1) · · · Cl(1) 2.52 Å; N(1)–H(1) · · · Cl(1) 145°].

Ruthenium(II) *P*,*N*(pyridyl)-chelate chemistry

When $CDCl_3$ solutions of **6a** (or **6b**) are allowed to stand at ambient temperatures for several days isomerisation occurs to give the *P*,*N*(pyridyl)-chelate complexes [RuCl(η^6-*p*-cymene)-{*P*,*N*(pyridyl)-**Ia**}]Cl **6c** and [RuCl(η^6-*p*-cymene){*P*,*N*(pyridyl)-**Ib**}]Cl **6d**, respectively. No attempts to prepare **6c**, **6d** or other *P*,*N*(pyridyl)-chelate complexes using AgX as chloride abstractor have been made. The $^{31}P\{^1H\}$ NMR spectra show

Table 5 Selected bond distances (Å) and angles (°) for compounds **6c**, **6d** and **8**

	6c	6d	8
Ru(1)–Cl(1)	2.385(2)	2.382(2)	2.4305(6)
Ru(1)–P(1)	2.306(2)	2.296(2)	2.3396(6)
Ru(1)–N(1)	2.160(6)	2.158(6)	
Ru(1)–Cl(2)			2.4149(5)
P(2)–O(1)			1.5763(16)
P(2)–O(2)			1.5843(18)
P(2)–O(3)			1.5672(18)
P(2)–O(4)			1.4480(19)
Ru(1)–C range	2.184(7)–2.274(7)	2.184(7)–2.268(7)	2.185(2)–2.249(2)
Cl(1)–Ru(1)–P(1)	87.89(7)	88.06(8)	87.05(1)
Cl(1)–Ru(1)–N(1)	83.7(2)	84.0(2)	
N(1)–Ru(1)–P(1)	89.7(2)	89.3(2)	
Cl(2)–Ru(1)–P(1)			83.91(1)
Cl(1)–Ru(1)–Cl(2)			87.60(1)
C–Ru(1)–C range	34.7(3)–80.1(3)	35.6(3)–80.2(3)	35.75(9)–78.70(9)

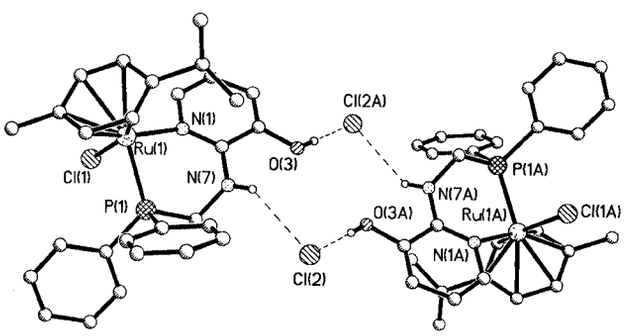
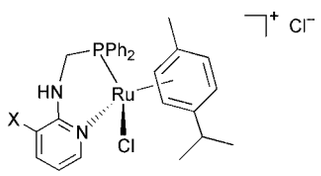


Fig. 4 Crystal structure of **6c** (solvent omitted for clarity).



X = OH **6c**
X = H **6d**

small downfield shifts in δ(P) of *ca.* 10 ppm upon six-membered ring formation. The crystal structure of **6c** (Fig. 4, Table 5) shows a similar overall structure to **8** but here the ligand is clearly seen to adopt a *P*,*N*(pyridyl)-chelation mode. The Ru(1)–Cl(1) [2.385(2) Å] and Ru(1)–P(1) [2.306(2) Å] distances are similar to those found in **8** and **12** whereas the Ru(1)–N(1) [2.160(6) Å] bond length is similar to values previously reported for other ruthenium(II) pyridylphosphine complexes.[2c,5e,34] An interesting structural feature is the intermolecular O–H $\cdots$ Cl_{ion} [O(3) $\cdots$ Cl(2A) 3.00, H(3) $\cdots$ Cl(2A) 2.18 Å; O(3)–H(3) $\cdots$ Cl(2A) 177°] and N–H $\cdots$ Cl_{ion} H-bonding [N(7) $\cdots$ Cl(2) 3.31, H(7) $\cdots$ Cl(2) 2.63 Å; N(7)–H(7) $\cdots$ Cl(2) 137°] linking two molecules into a dimer pair. The structure of **6d** (Fig. 5, Table 5) is essentially similar to that of **6c**, with comparable Ru–N, Ru–P and Ru–Cl bond lengths. There is also an intermolecular N–H $\cdots$ Cl_{ion} contact with the chloride counter ion [N(7) $\cdots$ Cl(2) 3.18, H(7n) $\cdots$ Cl(2) 2.24 Å; N(7)–H(7n) $\cdots$ Cl(2) 147°]. To the best of our knowledge the structures of **6c** and **6d** constitute extremely rare examples of crystallographically characterised six-membered M–P–C–N–C–N metallacycles.[35]

P,*P*′-Bridge chemistry

Bridge cleavage of the dimers [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$], [{RuCl(μ-Cl)(η^6-C_6Me_6)}$_2$] or [{MCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (M = Rh, Ir) with 1 equiv. of **IV** gave the new bimetallic complexes **12**–**15** in 74–88% as air stable, brown, orange or yellow solids. With the exception of **15**, the phosphorus chemical shifts for P^{III}–C and P^{III}–O are observed typically at δ(P) *ca.* 25 and 120, respectively (Table 2). The ^{1}H NMR spectra of **12**–**15** show well resolved, separate resonances for the two inequivalent *p*-cymene, C_6Me_6 or C_5Me_5 ancillary ligands (Experimental section). The X-ray structures of **12** and **14** (Figs. 6 and 7, Table 6) both reveal a bimetallic complex in which **IV** *P*,*P*′-bridges two {$RuCl_2$(η^6-*p*-cymene)} or {$RhCl_2$(Cp*)} metal fragments, respectively. Within **14** the Rh–P [Rh(1)–P(1) 2.2944(11) and Rh(2)–P(2) 2.3136(11) Å] and Rh–Cl distances [Rh(1)–Cl(1)

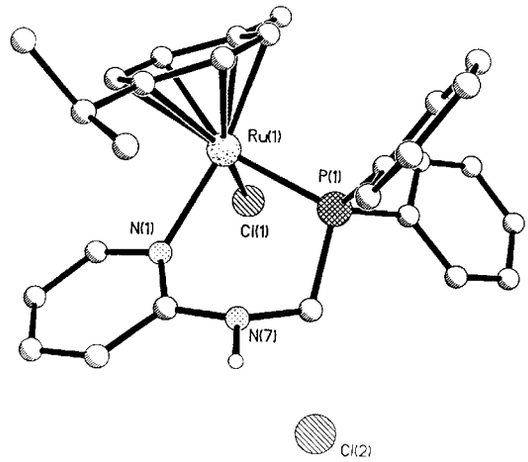


Fig. 5 Crystal structure of **6d** (solvent omitted for clarity).

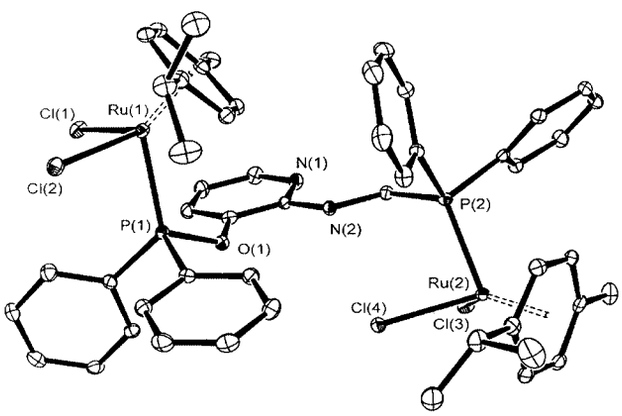
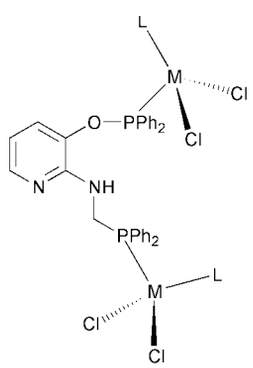


Fig. 6 Crystal structure of **12** (solvents omitted for clarity). Displacement ellipsoids are shown at the 30% probability level.



M = Ru, L = *p*-cymene **12**
M = Ru, L = C_6Me_6 **13**
M = Rh, L = C_5Me_5 **14**
M = Ir, L = C_5Me_5 **15**

Table 6 Selected bond distances (Å) and angles (°) for compounds **12** and **14**

	12 (M = Ru)	**14** (M = Rh)
M(1)–Cl(1)	2.4130(14)	2.4015(10)
M(1)–Cl(2)	2.4263(15)	2.4320(9)
M(2)–Cl(3)	2.4076(14)	2.4163(9)
M(2)–Cl(4)	2.4327(14)	2.3925(10)
M(1)–P(1)	2.3119(14)	2.2944(11)
M(2)–P(2)	2.3443(14)	2.3136(11)
P(1)–O(1)	1.644(4)	1.641(2)
M(1)–C range	2.191(6)–2.266(6)	2.167(3)–2.241(3)
M(2)–C range	2.184(5)–2.278(6)	2.158(3)–2.222(3)
Cl(1)–M(1)–P(1)	91.00(5)	87.89(3)
Cl(2)–M(1)–P(1)	85.39(5)	98.44(4)
Cl(1)–M(1)–Cl(2)	88.81(5)	88.50(4)
Cl(3)–M(2)–P(2)	83.38(5)	88.23(4)
Cl(4)–M(2)–P(2)	87.20(5)	85.15(3)
Cl(3)–M(2)–Cl(4)	86.49(5)	92.03(4)
M(1)–P(1)–O(1)	113.81(14)	116.93(8)

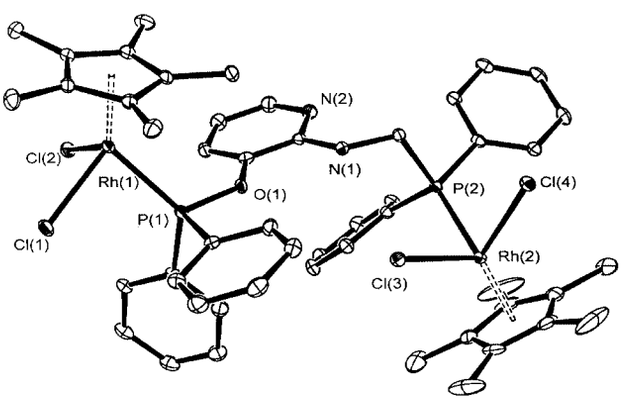


Fig. 7 Crystal structure of **14** (solvent omitted for clarity). Displacement ellipsoids are shown at the 30% probability level.

2.4015(10) and Rh(1)–Cl(2) 2.4320(9) Å; Rh(2)–Cl(3) 2.40163(9) and Rh(2)–Cl(4) 2.3925(20) Å] are similar for both metal fragments. Likewise the bimetallic ruthenium complex **12** shows similar Ru–Cl distances for both disparate ruthenium(II) groups. The P(1)–O(1) bond length [1.641(2) Å] in **14** is similar to that observed in **12** [1.644(4) Å]. There is also an intramolecular N–H $\cdots$ Cl_{coord} hydrogen bond [N(2) $\cdots$ Cl(4) 3.23, H(2n) $\cdots$ Cl(4) 2.41 Å; N(2)–H(2n) $\cdots$ Cl(4) 150° in **12**; N(1) $\cdots$ Cl(3) 3.15, H(1) $\cdots$ Cl(3) 2.48 Å; N(1)–H(1) $\cdots$ Cl(3) 136° in **14**] and a C–H $\cdots$ Cl_{coord} intermolecular hydrogen bond [C(2s) $\cdots$ Cl(1) 3.43, H(2s) $\cdots$ Cl(1) 2.52 Å; C(2s)–H(2s) $\cdots$ Cl(1) 151° in **12**; C(1s) $\cdots$ Cl(2) 3.57, H(1s) $\cdots$ Cl(2) 2.70 Å; C(1s)–H(1s) $\cdots$ Cl(2) 166° in **14**] with a $CHCl_3$ solvate.

In summary, straightforward preparative routes to new potentially multidentate pyridylphosphines have been developed. This facile method should bode well for the synthesis of new ligands bearing suitably disposed functionalities. From our complexation studies, using a range of late transition-metal precursors, variation of the substituent group in the 3-position can influence the ligand bonding mode *e.g.* *P*-co-ordination, *P*,*N*(pyridyl)-chelation, *P*,*P*′-chelation or *P*,*P*′-bridging. These interesting co-ordination properties may have useful implications in homogeneous catalysis. Further studies are currently in progress and will be reported in due course.

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