The synthesis and co-ordination chemistry of new functionalised pyridylphosphines derived from Ph₂PCH₂OH⁺

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Condensation of Ph₂PCH₂OH with H₂NC₅H₃(OH)N in methanol/toluene gave the new "hybrid" ligand Ph₂PCH₂N(H)C₅H₃(OH)N **Ia**, which upon phosphorylation with either ClP(O)R₂ (R = Ph, OPh) or ClPR₂ afforded Ph₂PCH₂N(H)C₅H₃(X)N [X = OP(O)Ph₂ **II**; OP(O)(OPh₂ **III**; OPPh₂ **IV**]. Oxidation of **Ia** with aqueous H₂O₂ in thf gave Ph₂P(O)CH₂N(H)C₅H₃(OH)N **V**. The dichloroplatinum(II) complexes **1–4** were prepared from [PtCl₂(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(μ -Cl)-(η^6 -*p*-cymene)}₂], [{RuCl(μ -Cl)(η^6 -C₆Me₆)}₂] or [{MCl(μ -Cl)(η^5 -C₅Me₅)}₂] (M = Rh, Ir) with **Ia**–**IV** afforded either monometallic [MCl₂(L)(PR₃)] **6–11** (M = Ru, Rh or Ir; L = η^6 -*p*-cymene, η^5 -C₅Me₅; PR₃ = **Ia**, **II** or **III**) or *P*,*P'*-bridged bimetallic [{MCl₂(L)}₂ **IV**] **12–15** (M = Ru, Rh or Ir; L = η^6 -*p*-cymene, η^6 -C₆Me₆, η^5 -C₅Me₅) complexes. The neutral ruthenium(II) complexes [RuCl₂(η^6 -*p*-cymene){*P*-Ph₂PCH₂N(H)C₅H₃(X)}] (X = OH **6a**; X = H **6b**) undergo isomerisation in CDCl₃ to give [RuCl(η^6 -*p*-cymene){*P*,*N*(pyridyl)-Ph₂PCH₂N(H)C₅H₃(X)N}]Cl (X = OH **6c**; X = H **6d**). In contrast aged solutions (*ca*. 40 d) of **7–15** show no evidence (by ³¹P{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-C₅H₄N)PPh₂ (dppy).² This ligand displays numerous ligating modes ranging from P-co-ordination, P,Nchelation 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 positions³ with respect to the P centre or constitute the linker^{4,5} between two -PR₂ moieties. Examples of multifunctional P/N(pyridyl)/X (X = $N_{,6}^{6}$ O, 7 C⁸) or chiral pyridylphosphines in which the chirality can be located either at P⁹ or in the backbone¹⁰ have also been documented.



Several groups have recently reported various catalytic applications with pyridylphosphine complexes¹¹ and elegant work by Drent *et al.*¹² amply illustrates this point. These workers found efficient alkoxycarbonylation catalysts are generated

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from Pd(OAc)₂/dppy/CH₃SO₃H and noted high catalytic activity and selectivity. Moreover this mechanism¹³ and aspects of co-ordination chemistry pertinent to this process¹⁴ 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 reactivites¹⁵ 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 Ph₂PCH₂OH was prepared from Ph₂PH and (CH₂O)_n according to a literature method ¹⁷ as were the metal complexes [PtCl₂(cod)] (cod = cycloocta-1,5-diene),¹⁸ [{MCl(μ -Cl)(η^5 -C₅Me₅)}₂] (M = Rh, Ir),¹⁹ [{Ru-Cl(μ -Cl)(η^6 -*p*-cymene}₂],²⁰ [{RuCl(μ -Cl)(η^6 -C₆Me₆)}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

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

spectrometer, ¹H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with chemical shifts (δ) in ppm to high frequency of SiMe₄ and coupling constants (J) in Hz, ³¹P{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% H₃PO₄ and coupling constants (J) in Hz. All NMR spectra were measured in CDCl₃ 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

Ph₂PCH₂N(H)C₅H₃(OH)N Ia. A mixture of Ph₂PCH₂OH (0.50 g, 2.31 mmol) and H₂NC₅H₃(OH)N (0.254 g, 2.31 mmol) in methanol (8 cm³) and toluene (13 cm³) 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 cm³. Addition of diethyl ether (15 cm³) 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 $v_{\rm NH/OH}$ cm^{-1.} ¹H NMR [(CD₃)₂SO]: δ 9.70 (OH), 7.57–6.40 (arom. H), 5.61 [³J(PH) 12.5 Hz, NH], 4.23 (CH₂). EI MS: *m/z* 308 (M⁺). In a similar manner Ph₂PCH₂N(H)C₅H₄N **Ib** was also prepared (79%). Selected data: IR: 3223 $v_{\rm NH}$ cm^{-1.} ¹H NMR: δ 8.12–6.40 (arom. H), 4.50 (NH), 4.08 (CH₂).

Ph2PCH2N(H)C5H3{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 cm³) at 0 °C was added dropwise over 15 min a toluene (10 cm³) 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 [HNEt₃]Cl and the solution concentrated in vacuo to ca. 1-2 cm³. Addition of diethyl ether (15 cm³) gave a white solid **III** which was collected by suction filtration and dried in vacuo. Yield: 0.452 g, 79%. Selected data: IR: 3374 $v_{\rm NH}$, 1298 $v_{\rm P-O}$ cm⁻¹. ¹H NMR: δ 8.00–6.51 (arom. H), 4.79 (NH), 4.19 (CH₂). In a similar manner the ligands $Ph_2PCH_2N(H)C_5H_3\{OP(O)Ph_2\}N$ II and Ph₂PCH₂N(H)C₅H₃(OPPh₂)N IV were prepared although an analytically pure sample of IV could not be obtained. Selected data for II: IR: 3360 $v_{\rm NH}$, 1232 $v_{\rm P=0}$ cm⁻¹. ¹H NMR: & 7.87-6.37 (arom. H), 4.89 (NH), 4.24 (CH₂). Selected data for IV: IR: 3431 $v_{\rm NH}$ cm⁻¹. ¹H NMR: δ 7.80–6.42 (arom. H), 4.91 (NH), 4.22 (CH₂).

Ph₂P(O)CH₂N(H)C₅H₃(OH)N V. To a solution of **Ia** (0.100 g, 0.324 mmol) in thf (2 cm³) was added aqueous H₂O₂ (30% w/w, 0.2 cm³). The solution was stirred for *ca*. 34 h, decanted to remove some insoluble material and diethyl ether (15 cm³) added. The off-white solid was collected by suction filtration and dried *in vacuo*. Yield: 0.051 g, 48%. Selected data: IR: 3418 v_{NH}, 1150 v_{PO} cm⁻¹. ¹H NMR: δ 7.84–6.45 (arom. H), 6.10 (NH), 4.51 (CH₂). Crystals of V suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a CDCl₃ solution over the course of several days.

[Pt{Ph₂PCH₂N(H)C₅H₃(OH)N}₂]Cl₂ 1. To a stirred solution of [PtCl₂(cod)] (0.050 g, 0.13 mmol) in CH₂Cl₂ (10 cm³) 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 cm³ and diethyl ether (15 cm³) added. The white solid 1 was filtered and dried *in vacuo*. Yield: 0.18 g, 77%. Selected data: IR: 3402, 3231 $v_{\rm NH/OH}$ cm⁻¹. The following dichloroplatinum(II) complexes were also prepared: *cis*-[PtCl₂{Ph₂-PCH₂N(H)C₅H₃{OP(O)Ph₂}N₂] 2 (79%). Selected data: IR:

3398 $v_{\rm NH}$, 1244 $v_{\rm P=0}$, 316, 290 $v_{\rm PtCl}$ cm⁻¹. ¹H NMR: δ 8.16–6.33 (arom. H), 4.72 [²J(PH) 6.9 Hz, CH₂]. FAB MS: *m/z* 1247 (M – Cl). *cis*-[PtCl₂{Ph₂PCH₂N(H)C₅H₃{OP(O)(OPh)₂}N}₂] **3** (67%). Selected data: IR: 3396 $v_{\rm NH}$, 1299 $v_{\rm P=0}$, 315, 283 $v_{\rm PtCl}$ cm⁻¹. ¹H NMR: δ 7.53–6.40 (arom. H), 6.04 (NH), 4.77 [²J(PH) 5.6 Hz, CH₂]. FAB MS: *m/z* 1311 (M – Cl). *cis*-[PtCl₂-{Ph₂PCH₂N(H)C₅H₃(OPPh₂)N}] **4** (94%) using 1 equiv. of **IV**. Selected data: IR: 3217 $v_{\rm NH}$, 321, 298 $v_{\rm PtCl}$ cm⁻¹. Crystals of **2** suitable for X-ray crystallography were grown by slow diffusion of light petroleum (bp 60–80 °C) into a CDCl₃ solution over the course of several days.

[AuCl{Ph_PCH_N(H)C_5H_3(OH)N}] 5. To a stirred solution of [AuCl(tht)] (0.050 g, 0.153 mmol) in CH₂Cl₂ (10 cm³) 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 cm³. 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 $v_{NH/OH}$, 325 v_{AuCl} cm⁻¹.

 $[RhCl_2(\eta^5-C_5Me_5){Ph_2PCH_2N(H)C_5H_3(OP(O)(OPh)_2N)]$ 11. To the solids $[{RhCl(\mu-Cl)(\eta^5-C_5Me_5)}_2]$ (0.030 g, 0.0485 mmol) and III (0.050 g, 0.0926 mmol, ca. 2 equiv.) was added CH_2Cl_2 (10 cm³). The solution was stirred for *ca*. 30 min and the volume reduced to ca. 1-2 cm³ by evaporation under reduced pressure. Addition of light petroleum (bp 60-80 °C, 10 cm³) gave 11 which was collected by suction filtration and dried in vacuo. Yield: 0.074 g, 90%. Selected data: IR: 3443, 3432 v_{NH}, 1303 $v_{P=0}$ cm⁻¹. ¹H NMR: δ 7.94–6.22 (arom. H), 5.91 (NH), 5.00 (CH₂), 1.38 [J(PH) 4.2 Hz, C₅Me₅]. FAB MS: m/z 813 (M - Cl). Using a similar procedure the following complexes were prepared: $[RuCl_2(\eta^6-p-cymene)] \{Ph_2PCH_2N(H)C_5H_3-$ (OH)N}] 6a (90%). Selected data: IR: 3474, 3416, 3235 v_{NH/OH} cm⁻¹. FAB MS: m/z 615 (M). [RuCl₂(η^6 -p-cymene){Ph₂- $PCH_2N(H)C_5H_4N$] **6b** (81%). Selected data: IR: 3298 v_{NH} cm⁻¹. ¹H NMR: δ 7.90–5.98 (arom. H), 5.37 (NH), 5.30–5.19 [CH₃C₆H₄CH(CH₃)₂], 4.75 (CH₂), 2.56 [CH₃C₆H₄CH(CH₃)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). [RuCl₂(η^6 -p-cymene){Ph₂PCH₂N(H)C₅H₃- $[OP(O)Ph_2]N$] 7 (77%). Selected data: IR: 3365 v_{NH} , 1235 $v_{P=O}$ cm⁻¹. ¹H NMR: δ 7.93–6.09 (arom. H), 5.63 (NH), 5.29–5.21 [CH₃C₆H₄CH(CH₃)₂], 4.90 (CH₂), 2.55 [CH₃C₆H₄CH(CH₃)₂], 1.84, [CH₃C₆H₄CH(CH₃)₂], 0.91 [CH₃C₆H₄CH(CH₃)₂]. FAB MS: m/z 815 (M). [RuCl₂(η^6 -p-cymene){Ph₂PCH₂N(H)C₅H₃-[OP(O)(OPh)₂]N}] 8 (77%). Selected data: IR: 3311 v_{NH}, 1295 $v_{P=0} \text{ cm}^{-1}$. ¹H NMR: δ 7.90–6.21 (arom. H), 5.45 (NH), 5.29– 5.18 [CH₃C₆H₄CH(CH₃)₂], 4.88 (CH₂), 2.56 [CH₃C₆H₄CH-(CH₃)₂], 1.88, [CH₃C₆H₄CH(CH₃)₂], 0.90 [CH₃C₆H₄CH(CH₃)₂]. FAB MS: m/z 847 (M). [RhCl₂(η^{5} -C₅Me₅){Ph₂PCH₂N(H)- $C_5H_3(OH)N$] 9. Selected data: IR: 3407, 3251 $v_{NH/OH}$ cm⁻¹. FAB MS: m/z 581 (M - Cl). [RhCl₂(η^{5} -C₅Me₅){Ph₂PCH₂-N(H)C₅H₃[OP(O)Ph₂]N}] **10** (85%). Selected data: IR: 3298 $\nu_{\rm NH}$, 1240 $\nu_{\rm P=0}$ cm⁻¹. ¹H NMR: δ 7.98–6.13 (arom. H), 6.08 (NH), 5.03 [J(PH) 5.1 Hz, CH₂], 1.41 [J(PH) 3.2 Hz, C₅Me₅]. 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: $[{RuCl_2(\eta^6-p-cymene)}_2{Ph_2PCH_2N(H)C_5H_3-(OPPh_2)N}]$ **12** (74%). Selected data: IR: 3407 v_{NH} cm⁻¹. ¹H NMR: δ 8.00–6.10 (arom. H), 6.05 (NH), 5.37–5.10 [CH₃C₆H₄-CH(CH₃)₂, CH₂], 2.69, 2.40 [CH₃C₆H₄CH(CH₃)₂], 1.87, 1.56 [CH₃C₆H₄CH(CH₃)₂], 1.06, 0.69 [CH₃C₆H₄CH(CH₃)₂]. FAB MS: *m*/*z* 1107 (M). [{RuCl₂(\eta⁶-C₆Me₆)}₂{Ph_2PCH_2N(H)C₅H₃-(OPPh₂)N}] **13** (81%). Selected data: IR: 3385 v_{NH} cm⁻¹. ¹H NMR: δ 8.15–6.00 (arom. H), 5.00 (CH₂), 1.83, 1.66 (C₆Me₆). ES MS: *m*/*z* 1127 (M – Cl). [{RhCl₂(η⁵-C₅Me₅)}₂{Ph_2PCH₂-N(H)C₅H₃(OPPh₂)N}] **14** (88%). Selected data: IR: 3422 v_{NH} cm⁻¹. ¹H NMR: δ 8.18–7.30 (arom. H), 6.14, 5.24 (CH₂, NH), 1.46 [*J*(PH) 3.5 Hz, C₅Me₅], 1.24 [*J*(PH) 4 Hz, C₅Me₅]. FAB MS: *m*/*z* 1073 (M – Cl). [{IrCl₂(η⁵-C₅Me₅)}₂{Ph_2PCH₂N(H)- $C_{s}H_{3}(OPPh_{2})N$] **15** (81%). Selected data: IR: 3426 v_{NH} cm⁻¹. ¹H NMR: δ 8.21–6.12 (arom. H), 5.40 (NH), 1.47 [*J*(PH) 2.2 Hz, $C_{5}Me_{s}$], 1.25 [*J*(PH) 2.4 Hz, $C_{5}Me_{s}$]. 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 CDCl₃ solution over the course of several days. A CDCl₃ 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-97²³ and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-97²³) 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-K α) radiation ($\lambda = 0.710$ 37 Å) or a Rigaku AFC7S serial diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.541$ 78 Å) and ω scans. Structures were solved by direct methods and refined by full-matrix least squares against *F* (TEXSAN²⁵) for data with $I > 3\sigma(I)$ or F^2 (SHELXTL²⁶) 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 CHCl₃ 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_2 -PCH₂OH C and commercially available $H_2NC_5H_3(OH)N$ in methanol/toluene (Scheme 1). An attempt to prepare the substi-





Scheme 1 Reagents and conditions: (i) Ph₂PCH₂OH; (ii) aq. H₂O₂; (iii) ClP(O)Ph₂, ClP(O)(OPh)₂ or ClPPh₂, NEt₃.

tuted ditertiary phosphine $(Ph_2PCH_2)_2NC_5H_3(OH)N$ using 2 equiv. of C gave only Ia and unreacted C [³¹P{¹H} NMR evidence]. A similar procedure was recently employed for the construction of dendrimers terminally coated with $-N(CH_2PPh_2)_2$

| Compound | ٧ | 2 | 6c | 6d | 8 | 12 | 14 |
|-------------------------------------|---|--|--|--|---|---|---|
| Empirical formula M | C ₁₈ H ₁₇ N ₂ O ₂ P 324 31 | C ₆₀ H ₅₄ Cl ₂ N ₂ O ₅ P ₄ Pt 1777 93 | C _{28.50} H _{31.50} Cl _{3.50} N ₂ OPRu 674.17 | C ₂₉ H ₅₇ Cl ₅ N ₂ PRu 717 89 | $C_{40}H_{40}Cl_2N_2O_4P_2Ru$ 846.65 | C _{54.50} H _{66.50} Cl _{11.50} N ₂ O ₂ P ₂ Ru ₂ 1453 35 | C ₅₁ H ₅₇ Cl ₇ N ₂ OP ₂ Rh ₂ 1729 90 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | P1 8 7043(6) | P1 10 9899(5) | $P2_1/n$ 11 0689(7) | $P2_1/c$ 10 980(2) | PI 7 3753(3) | P1 11 2902(3) | P1 9 6851(3) |
| blÅ | 10.8681(8) | 15.8626(8) | 12.2999(8) | 12.228(3) | 12.8896(3) | 13.6623(4) | 16.4272(7) |
| $c/ m \AA$ | 17.2011(11) | 16.8562(11) | 23.989(2) | 24.193(3) | 20.6503(5) | 21.4044(7) | 16.6831(8) |
| al° | 90.024(4) | 81.161(3) | ~ | | 106.031(2) | 93.695(2) | 99.178(3) |
| βl° | 91.491(4) | 76.380(3) | 102.825(1) | 101.96(2) | 99.091(2) | 104.682(2) | 91.764(3) |
| | 100.7774 | 77.645(3) | | | 93.886(2) | 101.304(2) | 92.281(3) |
| Ū/ų | 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 | 7 | 4 | 4 | 6 | 2 | 7 |
| 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 |
| | | | | | | | |

| Compound | $\delta(\mathbf{P})$ | $\delta(P_0)$ | 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 <i>ª</i> | | 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>ⁱ</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 (CD₃)₂SO. ^{*b*} Tentative assignment. ^{*c*} One phosphorus resonance at $\delta(P) - 16.6$ (36.2 MHz). ^{*d*} OPPh₂ group, recorded in C₇H₈-C₆D₆ insert. ^{*e*} Recorded *in situ*. ^{*f*} CPPh₂ group. ^{*g*} Recorded in CDCl₃-CH₃OH. ^{*h*} $\delta(P)$ 31.6 for *P*,*N*(pyridyl)-chelate species **6c**. ^{*i*} $\delta(P)$ 33.0 for *P*,*N*(pyridyl)-chelate species **6d**. ^{*j*} Minor species at $\delta(P)$ 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, Me₂CO and Me₂SO], displays moderate solubility in CH₂Cl₂ and toluene and poor solubility in Et₂O. The ³¹P{¹H} NMR spectrum of **Ia** [(CD₃)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 (CDCl₃)]. Furthermore there is negligible change in δ (P) in comparison with Ph₂PCH₂N(H)-C₅H₄N **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)Ph₂ II; OP(O)(OPh)₂ III; OPPh₂ IV] were conveniently prepared from Ia upon stoichiometric reaction with ClP(O)Ph₂, ClP(O)(OPh)₂ or ClPPh₂ and NEt₃ 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 ³¹P{¹H} NMR spectrum of IV showed two equally intense P resonances at $\delta(P) - 15.2$ (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 coordination 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 $v_{P=0}$. Pringle and co-workers²⁹ recently described an isomeric series of phosphonated triarylphosphines, Ph2PC6H4P(O)(OEt)2, and demonstrated the hydroformylation activity of their platinum(II) complexes in the presence of SnCl₂.

Table 3Selected 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) | O(1)–P(1)–C(1) | 112.19(14) |
|--------------|------------------------|--------------------|----------------------------|
| P(1)–C(1) | 1.807(3) | O(1)–P(1)–C(1) | [112.26(14)] 111.90(13) |
| P(1)-C(7) | [1.804(3)] 1.792(3) | O(1) - P(1) - C(1) | [110.90(12)] 111.62(12) |
| P(1) = C(12) | [1.801(3)] | P(1) = C(1) = V(1) | [111.19(12)] |
| P(1) = C(13) | [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 [PtCl₂(cod)] in dichloromethane at ambient temperature the new dichloroplatinum(II) complexes 1-3



| 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 [PtCl₂(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 $\delta(P)$ 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 v_{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(pyridy)chelating ligand. The solution conductivity of 1 in watermethanol (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 $\delta(P)$ 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 $\delta(P_0)$ similar to that observed in the uncomplexed ligands [$\delta(P_0)$ 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 ³¹P{¹H}</sup> 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 -C₅Me₅)}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 |
| $M = Rh, L = C_5 Me_5, X = OH$ | 9 |
| $M = Rh, L = C_5 Me_5, X = OP(O)Ph_2$ | 10 |
| $M = Rh, L = C_5 Me_5, X = OP(O)(OPh)_2$ | 11 |

Reaction of [{RhCl(μ -Cl)(η^5 -C₅Me₅)}₂] with 2 equiv. of **Ia** in CH₂Cl₂ at ambient temperature gave, after workup, an orange solid **9** whose ³¹P{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 [RhCl₂(η^5 -C₅Me₅)(**Ia**)] whilst the minor species at δ (P) 26.2 [*J*(RhP) 141 Hz] is thought to be [RhCl-(η^5 -C₅Me₅){*P*,*N*(pyridyl)-**Ia**}]Cl and in an approximate ratio of 2.8:1, respectively. After allowing a CDCl₃ 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 [RhCl₂(η^5 -C₅Me₅)(**Ia**)] with bases (*e.g.*, NEt₃, 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 CDCl₃ 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 ³¹P{¹H}</sup> NMR spectra show

| | 6с | 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) - | 2.184(7) - | 2.185(2)- |
| | 2.274(7) | 2.268(7) | 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) - | 35.6(3)- | 35.75(9)- |
| () | 80.1(3) | 80.2(3) | 78.70(9) |



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



small downfield shifts in $\delta(P)$ 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 · · · Cl_{ion} $H(7) \cdots Cl(2)$ 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····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 -C₆Me₆)}₂] or [{MCl(μ -Cl)(η^5 -C₅Me₅)}₂] (M =



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

CI(2)



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



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 ¹H NMR spectra of **12–15** show well resolved, separate resonances for the two inequivalent *p*-cymene, C₆Me₆ or C₅Me₅ 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 {RuCl₂(η⁶-*p*-cymene)} or {RhCl₂(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)

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····Cl_{coord} hydrogen bond [N(2)····Cl(4) 3.23, H(2n)···Cl(4) 2.41 Å; N(2)–H(2n)···Cl(4) 150° in **12**; N(1)····Cl(3) 3.15, H(1)····Cl(3) 2.48 Å; N(1)–H(1)····Cl(3) 136° in **14**] and a C–H····Cl_{coord} intermolecular hydrogen bond [C(2s)···Cl(1) 3.43, H(2s)···Cl(1) 2.52 Å; C(2s)– H(2s)···Cl(1) 151° in **12**; C(1s)···Cl(2) 3.57, H(1s)···Cl(2) 2.70 Å; C(1s)–H(1s)···Cl(2) 166° in **14**] with a CHCl₃ 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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