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New pyridyl modified phosphines: Synthesis and late transition-metal coordination studies

Sean E. Durran [a], Martin B. Smith [a,*], Sophie H. Dale [b], Simon J. Coles [c], Michael B. Hursthouse [c], Mark E. Light [c]

[a] Department of Chemistry, Loughborough University, Loughborough, Leics, LE11 3TU, UK
[b] School of Natural Sciences (Chemistry), Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
[c] EPSRC X-ray Crystallography Service, Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK

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This article is dedicated to Brian James on the special occasion of his 70th birthday. His enthusiasm for pyridylphosphine chemistry prompted much of our ongoing work in this field.

Abstract

Using a phosphorus based Mannich condensation reaction the new pyridylphosphines $\{5\text{-Ph}_2\text{PCH}_2\text{N(H)}\}\text{C}_5\text{H}_3(2\text{-Cl})\text{N}$ (**1-Cl**) and $\{2\text{-Ph}_2\text{PCH}_2\text{N(H)}\}\text{C}_5\text{H}_3(5\text{-Br})\text{N}$ (**1-Br**) have been synthesised in good yields (60% and 88%, respectively) from $\text{Ph}_2\text{PCH}_2\text{OH}$ and the appropriate aminopyridine. The ligands **1-Cl** and **1-Br** display variable coordination modes depending on the choice of late transition-metal complex used. Hence P-monodentate coordination has been observed for the mononuclear complexes AuCl(**1-Cl**) (**2**), AuCl(**1-Br**) (**3**), RuCl_2(*p*-cymene)(**1-Cl**) (**4**), RuCl_2(*p*-cymene)(**1-Br**) (**5**), $\text{RhCl}_2(\text{Cp}^*)$(**1-Cl**) (**6**), $\text{RhCl}_2(\text{Cp}^*)$(**1-Br**) (**7**), $\text{IrCl}_2(\text{Cp}^*)$(**1-Cl**) (**8**), $\text{IrCl}_2(\text{Cp}^*)$(**1′-Cl**) (**8′**), $\text{IrCl}_2(\text{Cp}^*)$(**1-Br**) (**9**), *cis-*/*trans*-$\text{PdCl}_2(\mathbf{1\text{-}Cl})_2$ (**10**), *cis-*/*trans*-$\text{PdCl}_2(\mathbf{1\text{-}Br})_2$ (**11**), *cis*-$\text{PtCl}_2(\mathbf{1\text{-}Cl})_2$ (**12**) and *cis*-$\text{PtCl}_2(\mathbf{1\text{-}Br})_2$ (**13**). Reaction of Pd(Me)Cl(cod) (cod = cycloocta-1,5-diene) with either 1 equiv. of **1-Br** or the known pyridylphosphines **1′-Cl**, **1-OH** or **1-H** gave the P/N-chelate complexes Pd(Me)Cl(**1-Br**–**1-H**) (**14**)–(**17**). All new compounds have been fully characterised by spectroscopic and analytical methods. Furthermore the structures of **4**, **5**, **10** and **16** · $(\text{CH}_3)_2\text{SO}$ have been elucidated by single crystal X-ray crystallography. A crystal structure of the dinuclear metallocycle *trans*,*trans*-$[\text{PdCl}_2\{\mu\text{-P/N-}\{\text{Ph}_2\text{PCH}_2\text{N(H)}\}\text{C}_5\text{H}_4\text{N}\}]_2 \cdot \text{CHCl}_3$, **18** · CHCl_3, has also been determined. Here **1-H** bridges, using both P and pyridyl N donors, two dichloropalladium centres affording a 12-membered ring with the PdCl_2 units adopting a head-to-tail arrangement.

Keywords: Phosphines; Transition-metals; X-ray crystallography; Multinuclear NMR; Chelate complexes; Bridging ligands

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1. Introduction

Pyridylphosphines are an important class of functionalised phosphine containing both P- and N-donor centres [1]. Many studies [2] have focused on simple pyridylphosphines most notably Ph_2PPy, PhPPy_2 and PPy_3 (Py = 2-pyridyl). These phosphines have been shown to display various coordination modes [2], serve as useful building blocks for di- [3a] and polynuclear compounds [3b] and have catalytic applications [4]. Recent work, using classical synthetic procedures in phosphorus chemistry [5], has shown that numerous other new pyridylphosphines [6–17] can be synthesised. These include PN-bidentate [6], mixed OPN- [7], PNP- [8], CNP-terdentate [9], chiral [10], phosphine oxide [11], and sulfide [12] based pyridyl modified ligands. James and co-workers [18] have made important contributions in this field with the synthesis of new bis(pyridylphosphines), and furthermore demonstrated a range of coordination modes for this novel ligand class. More recently this group have also investigated related *ortho*-*N*,*N*-dimethylanilinyl functionalised

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[*] Corresponding author. Tel.: +44 0 1509 222553; fax: +44 0 1509 223925.
E-mail address: m.b.smith@lboro.ac.uk (M.B. Smith).

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phosphines and shown that they can support homobimetallic and heterobimetallic complexes [19].

We describe here the synthesis of two new pyridylphosphines from a simple condensation reaction using Ph_2PCH_2OH. This methodology has proven extremely versatile in the past and we have applied this approach to the synthesis of a range of hybrid phosphines [20–25]. Furthermore we also show that a rich coordination chemistry exists with these new pyridylphosphine ligands including P-monodentate, P/N-chelate and P/N-bridging modes. All new compounds have been verified by spectroscopic and X-ray crystallographic techniques.

2. Experimental

2.1. Materials

Standard Schlenk techniques were used for the synthesis of **1-Cl** and **1-Br** whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. The ligands **1′-Cl**, **1-OH** and **1-H** have been reported elsewhere [20,21] and the metal complexes AuCl(tht) (tht = tetrahydrothiophene) [26], $\{RuCl_2(p\text{-cymene})\}_2$ [27], $\{MCl_2(Cp^*)\}_2$ (M = Rh, Ir; Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl) [28], $MCl_2(cod)$ (M = Pd, Pt) [29,30] and Pd(Me)Cl(cod) [31] were prepared according to known procedures. All other chemicals were obtained from commercial suppliers and used directly without further purification.

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets in the range 4000–200 cm^{-1} on a Perkin–Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (250 or 400 MHz) on Bruker AC250 FT or DPX-400 FT spectrometers 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 JEOL FX90Q or Bruker DPX-400 FT spectrometers with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4. 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.

2.3. Syntheses

2.3.1. Preparation of 1-Cl

A mixture of Ph_2PCH_2OH (0.895 g, 4.14 mmol) and 5-$H_2NC_5H_3$(2-Cl)N (0.531 g, 4.13 mmol) in methanol (15 ml) and toluene (25 ml) was refluxed under a nitrogen atmosphere for ca. 6 d. The volume was reduced to 3–4 ml whereupon a white solid deposited. After the addition of diethyl ether (10 ml) the solid was collected by suction filtration, washed with cold methanol (5 ml) and dried in vacuo. Yield: 0.806 g, 60%. The bromo compound $\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-Br})N$ (**1-Br**) was prepared in a similar manner (88%). For **1-Cl**, $C_{18}H_{16}N_2PCl$ requires: C, 66.15; H, 4.95; N, 8.57. Found: C, 66.09; H, 4.89; N, 8.27%. For **1-Br**, $C_{18}H_{16}N_2PBr$ requires: C, 58.23; H, 4.35; N, 7.55. Found: C, 58.44; H, 4.22; N, 7.09%.

2.3.2. Preparation of 2 and 3

To a stirred solution of AuCl(tht) (0.059 g, 0.184 mmol) in CH_2Cl_2 (10 ml) was added **1-Cl** (0.060 g, 0.184 mmol) as a solid in one portion. After stirring the solution for ca. 15 min the volume was concentrated in vacuo to 1–2 ml and petroleum ether (60–80 °C, 15 ml) added. The white solid **2** was collected by suction filtration and dried in vacuo. Yield: 0.072 g, 70%. The gold(I) compound $AuCl\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-Br})N\}$ (**3**) was prepared in a similar manner (87%). For **2**, $C_{18}H_{16}N_2PAuCl_2$ requires: C, 38.66; H, 2.88; N, 5.01. Found: C, 38.80; H, 3.10; N, 4.90%. For **3**, $C_{18}H_{16}N_2PBrAuCl \cdot 0.5CH_2Cl_2$ requires: C, 34.40; H, 2.65; N, 4.34. Found: C, 35.00; H, 2.70; N, 4.40%.

2.3.3. Preparation of 4–9

An illustrative example is given here for $RhCl_2(Cp^*)\{\{5\text{-}Ph_2PCH_2N(H)\}C_5H_3(2\text{-Cl})N\}$ (**6**). To a stirred solution of $\{RhCl_2(Cp^*)\}_2$ (0.088 g, 0.142 mmol) in CH_2Cl_2 (10 ml) was added **1-Cl** (0.094 g, 0.288 mmol) as a solid in one portion. After stirring the solution for ca. 15 min the volume was concentrated in vacuo to 1–2 ml and diethyl ether (15 ml) added. The red/orange solid was collected by suction filtration and dried in vacuo. Yield: 0.165 g, 90%. The rhodium(III) compound $RhCl_2(Cp^*)\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-Br})N\}$ (**7**) was prepared in a similar manner (77%). The iridum(III) analogues $IrCl_2(Cp^*)\{\{5\text{-}Ph_2PCH_2N(H)\}C_5H_3(2\text{-Cl})N\}$ (**8**), $IrCl_2(Cp^*)\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-Cl})N\}$ (**8′**) and $IrCl_2(Cp^*)\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-Br})N\}$ (**9**) were likewise prepared in 88%, 77% and 82% yields, respectively. The ruthenium(II) complexes $RuCl_2(Cp^*)\{\{5\text{-}Ph_2PCH_2N(H)\}C_5H_3(2\text{-Cl})N\}$ (**4**) (88%) and $RuCl_2(Cp^*)\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-Br})N\}$ (**5**) (89%) have also been prepared by bridge cleavage of the dimer $\{RuCl_2(p\text{-cymene})\}_2$ with either **1-Cl** or **1-Br**. For **4**, $C_{28}H_{30}N_2PRuCl_3 \cdot CHCl_3$ requires: C, 45.50; H, 4.10; N, 3.72. Found: C, 45.61; H, 4.01; N, 3.02%. For **5**, $C_{28}H_{30}N_2PRuBrCl_2$ requires: C, 49.65; H, 4.46; N, 4.14. Found: C, 49.10; H, 4.37; N, 3.75%. For **6**, $C_{28}H_{31}N_2PRhCl_3$ requires: C, 52.89; H, 4.92; N, 4.41. Found: C, 52.40; H, 4.78; N, 4.13%. For **7**, $C_{28}H_{31}N_2PRhBrCl_2 \cdot 0.5CH_2Cl_2$ requires: C, 48.13; H, 4.49; N, 3.85. Found: C, 48.27; H, 4.40; N, 4.21%. For **8**, $C_{28}H_{31}N_2PIrCl_3$ requires: C, 46.37; H, 4.32; N, 3.86. Found: C, 46.26; H, 4.22; N, 3.78%. For **8′**, $C_{28}H_{31}N_2PIrCl_3$ requires: C, 46.37; H, 4.32; N, 3.86. Found: C, 45.84; H, 4.32; N, 3.86%. For **9**, $C_{28}H_{31}N_2PIrBrCl_2$ requires: C, 43.69; H, 4.07; N, 3.64. Found: C, 43.27; H, 3.84; N, 3.16%.

2.3.4. Preparation of 10 and 11

To a stirred solution of $PdCl_2(cod)$ (0.040 g, 0.140 mmol) in CH_2Cl_2 (10 ml) was added **1-Cl** (0.091 g, 0.281 mmol) in one portion. After stirring the solution for ca. 15 min the volume was concentrated in vacuo to 1–2 ml and petroleum ether (60–80 °C, 15 ml) added. The yellow solid **10** was collected by suction filtration and dried in vacuo. Yield: 0.095 g, 82%. The dichloropalladium compound $PdCl_2$-$\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-}Br)N\}_2$ (**11**) was prepared in a similar manner (77%). For **10**, $C_{36}H_{32}N_4P_2PdCl_4$ requires: C, 52.00; H, 3.90; N, 6.70. Found: C, 52.40; H, 4.10; N, 6.64%. For **11**, $C_{36}H_{32}N_4P_2PdBr_2Cl_2$ requires: C, 47.00; H, 3.50; N, 6.10. Found: C, 46.90; H, 3.80; N, 5.90%.

2.3.5. Preparation of 12 and 13

To a stirred solution of $PtCl_2$(cod) (0.060 g, 0.160 mmol) in CH_2Cl_2 (10 ml) was added **1-Cl** (0.105 g, 0.321 mmol) in one portion. After stirring the solution for ca. 15 min the volume was concentrated in vacuo to 1–2 ml and diethyl ether (15 ml) added. The white solid **12** was collected by suction filtration and dried in vacuo. Yield: 0.124 g, 84%. The dichloroplatinum compound $PtCl_2\{\{2\text{-}Ph_2PCH_2\text{-}N(H)\}C_5H_3(5\text{-}Br)N\}_2$ (**13**) was prepared in a similar manner (89%). For **12**, $C_{36}H_{32}N_4P_2PtCl_4 \cdot 0.5CH_2Cl_2$ requires: C, 45.57; H, 3.46; N, 5.82. Found: C, 46.00; H, 3.88; N, 5.22%. For **13**, $C_{36}H_{32}N_4P_2PtBr_2Cl_2$ requires: C, 42.87; H, 3.20; N, 5.56. Found: C, 43.18; H, 3.30; N, 5.11%.

2.3.6. Preparation of 14–17

Preparation of $Pd(Me)Cl\{\{2\text{-}Ph_2PCH_2N(H)\}C_5H_3(5\text{-}Br)N\}$ (**14**). To a stirred solution of Pd(Me)Cl(cod) (0.068 g, 0.256 mmol) in CH_2Cl_2 (10 ml) was added **1-Br** (0.095 g, 0.256 mmol) as a solid in one portion. After stirring the solution for ca. 15 min the volume was concentrated in vacuo to 1–2 ml and diethyl ether (15 ml) added. The pale yellow solid was collected by suction filtration and dried in vacuo. Yield: 0.126 g, 93%. The palladium compounds **15** (93%), **16** (82%) and **17** (93%) were also synthesised. For **14**, $C_{19}H_{19}N_2PBrClPd$ requires: C, 43.21; H, 3.63; N, 5.31. Found: C, 42.85; H, 3.41; N, 5.34%. For **15**, $C_{19}H_{19}N_2PCl_2Pd$ requires: C, 47.18; H, 3.97; N, 5.79. Found: C, 46.59; H, 3.73; N, 5.60%. For **16**, $C_{19}H_{20}N_2OPClPd$ requires: C, 49.05; H, 4.34; N, 6.02. Found: C, 48.53; H, 4.11; N, 6.12%. For **17**, $C_{19}H_{20}N_2PClPd$ requires: C, 50.79; H, 4.50; N, 6.24. Found: C, 50.10; H, 4.26; N, 6.06%.

2.4. X-ray crystallography

The compounds **4**, **5** and **10** were obtained by vapour diffusion of Et_2O into either $CDCl_3$ or CH_2Cl_2 solutions over several days. Compound **16** · $(CH_3)_2SO$ was obtained by slow diffusion of Et_2O into a $CDCl_3$/dmso solution. A few X-ray quality crystals of **18** · $CHCl_3$ were obtained by slow diffusion of Et_2O into a $CDCl_3$/dmso solution of **17** over an extended period. Data were recorded at 120 K (or 150 K for **16** · $(CH_3)_2SO$), using a Nonius Kappa CCD area-detector diffractometer mounted at the window of a rotating anode FR591 generator with a molybdenum anode (0.71073 Å). φ and ω scans (2° increments) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs DIRDIF, DIRAX, COLLECT and DENZO and an empirical absorption correction was applied using SORTAV [32]. The structures were solved by direct methods and refined on F^2 values for all unique data by full-matrix least-squares. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms except NH were placed in calculated positions and refined using a riding model $[U_{iso}(H) = 1.2U_{eq}(C, N)$ for aryl,

Table 1
Crystallographic data for **4**, **5**, **10**, **16** · $(CH_3)_2SO$ and **18** · $CHCl_3$

Compound	**4**	**5**	**10**	**16** · $(CH_3)_2SO$	**18** · $CHCl_3$
Empirical formula	$C_{28}H_{30}Cl_3N_2PRu$	$C_{28}H_{30}BrCl_2N_2PRu$	$C_{36}H_{32}Cl_4N_4P_2Pd$	$C_{21}H_{26}ClN_2O_2PPdS$	$C_{19}H_{18}Cl_5N_2PPd$
Formula weight	632.93	677.39	830.80	543.32	588.97
Crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.5918(15)	7.6637(15)	28.989(6)	9.1177(18)	9.7546(3)
b (Å)	10.300(2)	10.391(2)	10.663(2)	10.762(2)	10.2608(3)
c (Å)	18.188(4)	18.072(4)	23.718(5)	12.624(3)	12.8523(4)
α (°)	78.77(3)	79.07(3)		100.16(3)	95.519(1)
β (°)	87.76(3)	86.31(3)	101.75(3)	106.78(3)	104.740(1)
γ (°)	69.93(3)	69.52(3)		101.56(3)	114.268(2)
Volume (Å^3)	1309.7(5)	1323.7(6)	7178(2)	1125.1(5)	1104.33(6)
Z	2	2	8	2	2
T (K)	120(2)	120(2)	120(2)	150(2)	120(2)
D_{calc} (Mg/m^3)	1.605	1.700	1.538	1.604	1.771
Absorption coefficient (mm^{-1})	0.987	2.385	0.937	1.127	1.527
Crystal	block; orange	plate; orange	needle; yellow	block; colourless	block; yellow
Crystal size (mm^3)	0.04 × 0.05 × 0.08	0.08 × 0.12 × 0.30	0.02 × 0.04 × 0.24	0.08 × 0.10 × 0.14	0.10 × 0.20 × 0.30
θ Range (°)	2.93–27.40	2.98–27.47	3.04–27.50	1.99–27.50	3.09–25.02
Reflections collected	17877	17292	30408	16994	8364
Independent reflections [R_{int}]	5741 [0.098]	5800 [0.071]	8017 [0.091]	5040 [0.044]	3760 [0.070]
Final R_1 ($F^2 > 2\sigma(F^2)$)[a], wR_2 (all data)[b]	0.052, 0.109	0.038, 0.097	0.046, 0.096	0.030, 0.074	0.036, 0.096

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

methine, methylene and NH hydrogen atoms; $U_{iso}(H) = 1.5U_{eq}(C, O)$ for methyl and hydroxy hydrogen atoms; $U_{iso}(NH)$ freely refined in **10**]. NH hydrogen atoms were located in a difference Fourier map, and in compounds **4**, **5**, **16** · $(CH_3)_2SO$ and **18** · $CHCl_3$, their positions were refined using distance restraints [target N–H bond length = 0.88 Å]. Programs used were Bruker SHELXTL for structure solution and refinement, Diamond for molecular graphics, and local programs [33–38].

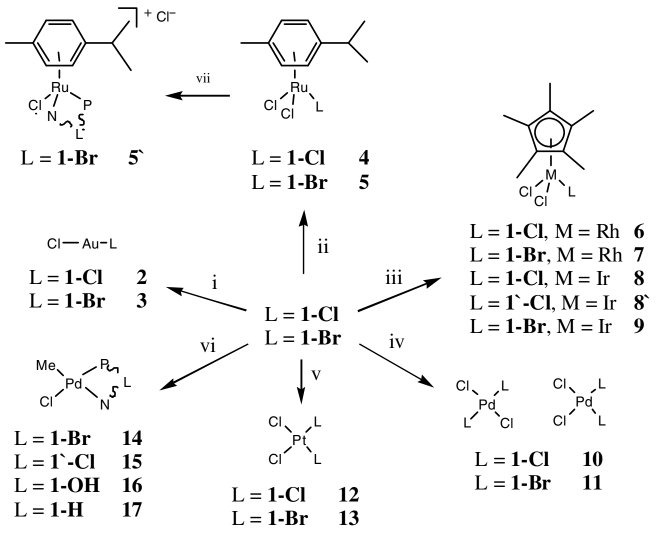
3. Results and discussion

3.1. Ligand syntheses

Using an established method [20–25] for C–N bond formation the new ligands **1-Cl** and **1-Br** were synthesised, as colourless solids, by condensation of Ph_2PCH_2OH with either 5-amino-2-chloropyridine or 2-amino-5-bromopyridine in MeOH/toluene under refluxing conditions (Scheme 1). The isomeric ligand **1′-Cl** has previously been reported [21] in our group along with **1-OH** [20] and **1-H**. Both **1-Cl** and **1-Br** display a characteristic phosphorus resonance at around δ(P) −19 ppm (in $CDCl_3$) shifted upfield by ca. 9 ppm with respect to that observed for Ph_2PCH_2OH [−9.9 ppm in $CDCl_3$]. Solutions of **1-Cl** and **1-Br** showed evidence for oxidation when left exposed in air for periods up to 5 d. The ^1H NMR spectra confirmed only mono substitution since a broad NH resonance was observed at 4.61 ppm (for **1-Cl**) and 4.52 ppm (for **1-Br**). In addition the ^1H NMR spectra showed a resonance at 3.80 (for **1-Cl**) and 4.04 (for **1-Br**) ppm assigned to the methylene protons. Characteristic weakly absorbing stretching vibrations of ν_{NH} in addition to ν_{CN}(pyridyl) were observed around 3200 and 1590 cm^{-1}, respectively. Selected microanalytical data can be found in Section 2.

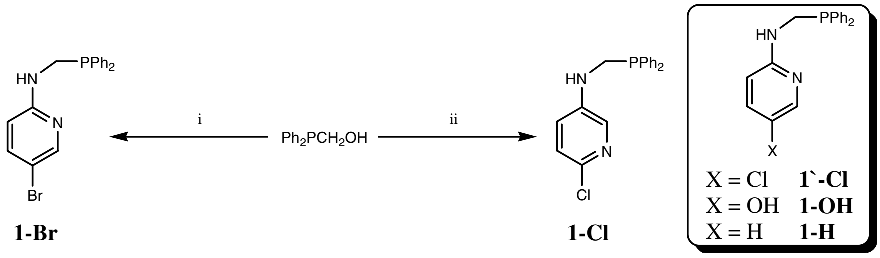
3.2. Coordination studies

In order to probe the coordination chemistry of the new pyridylphosphines **1-Cl** and **1-Br** we explored their reactivity towards various late transition-metals. Ligand displacement of tht from AuCl(tht) or cod from MCl_2(cod) (M = Pd, Pt) in CH_2Cl_2 at ambient temperature gave the gold (**2**, **3**), palladium (**10**, **11**) and platinum (**12**, **13**) complexes in 70–89% (Scheme 2). In all cases downfield ^{31}P resonances were observed in comparison to the free ligands **1-Cl** and **1-Br**. Hence for **2** and **3** single δ(P) resonances at 25.7 and 27.1 ppm were observed (Table 2) whilst the platinum(II) complexes **12** [δ(P) 6.2 ppm] and **13** [δ(P) 7.6 ppm] showed additional ^1J(PtP) coupling constants of ca. 3700 Hz indicative of a *cis* arrangement of pyridylphosphine ligands [20]. The palladium complexes **10** [δ(P) 26.0, 14.0 ppm] and **11** [δ(P) 29.8, 15.4 ppm], in $CDCl_3$ solution, exist as a mixture of *cis* and *trans* isomers whilst, in the solid state, only the *cis* isomer was observed as confirmed by IR spectroscopy (ν_{PdCl} 308 and 284 cm^{-1} for **10**; 319 and 281^{-1} for **11**).



Scheme 2. (i) AuCl(tht); (ii) $\{RuCl_2(p\text{-cymene})\}_2$; (iii) $\{MCl_2(Cp^*)\}_2$ (M = Rh, Ir); (iv) $PdCl_2$(cod); (v) $PtCl_2$(cod); (vi) Pd(Me)Cl(cod); (vii) r.t., $CDCl_3$.

Bridge cleavage reactions of Ru, Rh and Ir dimers [2c,20] have been shown to be an excellent method for synthesising piano-stool half sandwich complexes. Accordingly when **1-Cl** or **1-Br** were reacted with $\{RuCl_2(p\text{-cymene})\}_2$ or $\{MCl_2(Cp^*)\}_2$ (M = Rh, Ir) the new ruthenium (**4**, **5**), rhodium (**6**, **7**) and iridium (**8**, **9**) complexes were isolated as orange solids (Scheme 2). Characterising data for these new compounds are given in Table 2. The $^{31}P\{^1H\}$ NMR data implies only P-coordination to the metal centre as indicated by the downfield shifts. We have previously shown that related ligands (**1′-Cl**, **1-OH** and **1-H**) can undergo P/N-chelation either upon standing at room



Scheme 1. (i) $2\text{-}H_2NC_5H_3(5\text{-Br})N$, CH_3OH/C_7H_8; (ii) $5\text{-}H_2NC_5H_3(2\text{-Cl})N$, CH_3OH/C_7H_8.

Table 2
Selected spectroscopic data for **1-Cl**, **1-Br** and **2**–**17**

Compound	^{31}P (ppm)	^{1}H (ppm)	ν_{NH}	ν_{CN}	ν_{MCl}[a]	*m*/*z*
1-Cl	−19.3	7.75–6.89 (arom. H); 4.61 (NH); 3.80 (CH_2)	3234, 3152	1590		327 (M)
1-Br	−18.1	8.11–6.28 (arom. H); 4.52 (NH); 4.04 (CH_2)	3217, 3123	1585		371 (M)
2	25.7	7.74–6.97 (arom. H); 4.24 (CH_2)[b]	3322	1586	318	559 (M)
3	27.1	8.05–6.37 (arom. H); 4.87 (NH); 4.63 (CH_2)	3245	1591	323	604 (M)
4	19.7	7.89–6.46 (arom. H); 4.82 (NH); 4.44 (CH_2)[c]	3251	1576		
5	19.3[d]	7.86–5.94 (arom. H); 5.60 (NH); 4.74 (CH_2)[c]	3255	1590		643 (M–Cl)
6	24.5 (146)	7.96–6.61 (arom. H); 5.37 (NH); 4.52 (CH_2); 1.39 ^3J(PH) 3.5 (C_5Me_5)	3272	1578		
7	24.4 (145)	7.89–6.09 (arom. H); 6.14 (NH); 4.85 (CH_2); 1.39 ^3J(PH) 3.5 (C_5Me_5)	3278	1592		
8	−6.3	7.84–6.62 (arom. H); 5.40 (NH); 4.60 (CH_2); 1.39 ^3J(PH) 2.0 (C_5Me_5)	3286	1577		725 (M)
8′	−6.5[e]	7.82–6.13 (arom. H); 6.10 (NH); 4.98 (CH_2); 1.39 ^3J(PH) 4.0 (C_5Me_5)	3294	1595		690 (M–Cl)
9	−6.5[f]	7.78–6.10 (arom. H); 5.09 (NH); 4.98 (CH_2); 1.39 ^3J(PH) 2.4 (C_5Me_5)	3293	1591		734 (M–Cl)
10	26.0, 14.0[g,h]	7.75–6.68 (arom. H); 4.83 (NH); 4.30 (CH_2)	3316	1585	308, 284	
11	29.8, 15.4[h]	8.00–6.16 (arom. H); 5.60 (NH); 4.69 (CH_2)	3331, 3207	1590	319, 281	
12	6.2 (3699)	7.52–6.67 (arom. H); 4.95 (NH); 4.23 (CH_2)	3324	1585	312, 288	
13	7.6 (3678)	7.94–6.52 (arom. H); 5.95 (NH); 4.66 (CH_2)	3371, 3322	1590	311, 284	
14	35.4[g]	9.32–6.69 (arom. H); 7.86 (NH); 4.11 (CH_2); 0.51, ^3J(PH) 2.8 (Pd–CH_3)	3265	1603		493 (M–Cl)
15	35.4[g]	9.25–6.70 (arom. H); 7.84 (NH); 4.11 (CH_2); 0.51, ^3J(PH) 2.8 (Pd–CH_3)	3264	1609		448 (M–Cl)
16	33.7[g]	10.50 (OH); 8.78-6.48 (arom. H); 6.93 (NH); 4.11 (CH_2); 0.55, ^3J(PH) 2.8 (Pd–CH_3)	3366, 3198, 3150[i]	1617		429 (M–Cl)
17	35.5[g]	9.16–6.51 (arom. H); 4.03 (CH_2); 0.47, ^3J(PH) 2.8 (Pd–CH_3)	3260	1614		

[a] M = Au, Pd or Pt.
[b] NH resonance not observed.
[c] *p*-Cymene resonances at 5.30–5.19, 2.58, 1.89, 0.92 (for **4**) and 5.27–5.20, 2.56, 1.87, 0.94 (for **5**).
[d] After ca. 30 d ratio of **5**:**5′** was 3.5:1.
[e] After ca. 20 d ratio of **8**:**8′** was 9:1.
[f] After ca. 20 d ratio of **9**:**9′** was 6:1.
[g] Recorded in $(CD_3)_2SO$.
[h] Mixture of *cis* and *trans* isomers.
[i] ν(NH)/ν(OH).

temperature in chlorinated solvent or use of a chloride abstractor such as Ag[BF_4] [20,21]. This behaviour is also observed here when solutions of **5**, **8′** and **9** are left to stand. Hence when a $CDCl_3$ solution of **5** is left for ca. 30 d an additional new species [δ(P) 34.0 ppm] gradually forms and can confidently be assigned to the cationic P/N-chelate complex **5′** [20].

Braunstein [6b] recently showed that phosphinitopyridine ligands form mononuclear tetrahedral nickel(II) complexes in which these ligands adopt a six-membered ring conformation. We wished to probe whether **1-Br** (or indeed **1′-Cl**, **1-OH** and **1-H**) could effectively function as P/N-chelating ligands at a palladium(II) metal centre. Reaction of **1-Br**, **1′-Cl**, **1-OH** or **1-H** with Pd(Me)Cl(cod) in a 1:1 molar ratio, in CH_2Cl_2, gave after work-up the new chelate complexes **14**–**17** in high yields (>80%). Two geometric isomers are possible for **14**–**17** yet ^{31}P{^{1}H} NMR spectroscopy showed one single resonance around δ(P) 35 ppm (Table 2). We believe this isomer to have the phosphine ($-PPh_2$) group *trans* to the chloride ligand [7,9b]. Additionally the ^{1}H NMR spectra clearly showed the presence of a methyl ligand within the coordination sphere since a doublet around 0.5 ppm [^1J(PH) 2.8 Hz] was observed for all four compounds. Interestingly, as documented by others [7], the pyridinic CH proton adjacent to the nitrogen experiences a significant downfield shift [δ(H) 8.78–9.32 ppm] upon P/N-chelation.

3.3. X-ray studies

The X-ray structures of **4**, **5**, **10**, **16** · $(CH_3)_2SO$ and **18** · $CHCl_3$ have each been determined and illustrate the flexible bonding nature of **1-Cl**, **1-Br**, **1-OH** and **1-H** ligands in accommodating P-monodentate, P/N-chelating and P/N-bridging coordination modes (see Table 3).

The structures of the ruthenium complexes **4** (Fig. 1) and **5** (Fig. 2) confirm a classic "piano-stool" geometry formed by the ancillary η^6-*p*-$MeC_6H_4{}^iPr$ ligand and the three "legs" being the two chlorides and the phosphorus donor of the P-monodentate pyridylphoshine. There are no significant differences observed in the Ru–P and Ru–Cl bond lengths for **4** and **5** and both are comparable to other previously reported compounds [2c,20,22]. There is an intramolecular N–H···Cl_{coord} hydrogen bond in **4** [N(1)···Cl(1) 3.162(4) Å, H(1n)···Cl(1) 2.35(2) Å; N(1)–H(1n)···Cl(1) 154(4)°] and

Table 3
Crystallographic data for **4**, **5**, **10**, **16** · $(CH_3)_2SO$ and **18** · $CHCl_3$

 M	**4** Ru	**5** Ru	**10** Pd	**16** · $(CH_3)_2SO$ Pd	**18** · $CHCl_3$ Pd
Bond length (Å)					
M(1)–P(1)	2.3443(15)	2.3426(12)	2.2778(10)	2.1864(10)	2.2497(10)
M(1)–P(2)			2.2694(10)		
M(1)–Cl(1)	2.4321(13)	2.4345(10)	2.3606(11)	2.4166(10)	2.2991(9)
M(1)–Cl(2)	2.4063(15)	2.4048(12)	2.3681(10)		2.2954(9)
M(1)–N(1)				2.2275(18)	2.113(3)
M(1)–C(1)				2.049(2)	
M(1)–C_{arene} range	2.177(4)–2.248(5)	2.187(3)–2.244(3)			
P(1)–$C_{methylene}$	1.875(4)	1.873(3)	1.843(3)	1.826(2)	1.858(4)
P(2)–$C_{methylene}$			1.845(4)		
$C_{methylene}$–N(1)	1.450(6)	1.445(4)	1.447(5)	1.452(3)	1.439(5)
$C_{methylene}$–N(3)			1.450(5)		
N(1)–$C_{aromatic}$	1.395(6)	1.371(4)	1.413(5)	1.372(3)	1.370(5)
N(3)–$C_{aromatic}$			1.410(5)		
C(15)–N(2)				1.338(3)	1.361(5)
Bond angles (°)					
P(1)–M(1)–Cl(1)	88.29(5)	89.01(4)	168.28(3)	172.43(2)	88.42(3)
P(1)–M(1)–Cl(2)	83.85(5)	83.64(4)	88.60(4)		92.67(3)
P(2)–M(1)–Cl(1)			89.86(4)		
P(2)–M(1)–Cl(2)			169.66(3)		
P(1)–M(1)–P(2)			96.63(4)		
Cl(1)–M(1)–Cl(2)	88.24(4)	88.55(3)	86.58(4)		175.18(4)
Cl(1)–M(1)–N(2)				93.13(6)	89.31(8)
Cl(2)–M(1)–N(2)					89.70(8)
Cl(1)–M(1)–C(1)				87.70(7)	
P(1)–M(1)–C(1)				86.16(7)	
N(2)–M(1)–C(1)				179.05(8)	
P(1)–M(1)–N				92.98(6)	177.43(8)
P(1)–Ru(1)–C_{arene} range	93.44(13)–160.39(15)	93.31(9)–160.59(11)			
P(1)–$C_{methylene}$–N(1)	112.3(3)	110.5(2)	115.5(3)	110.42(15)	109.8(3)
P(2)–$C_{methylene}$–N(3)			112.6(3)		
$C_{methylene}$–N(1)–$C_{aromatic}$	122.9(3)	123.2(2)	117.6(3)	119.22(19)	125.1(3)
$C_{methylene}$–N(3)–$C_{aromatic}$			119.3(3)		

5 [N(1)···Cl(1) 3.133(3) Å, H(1n)···Cl(1) 2.313(18) Å; N(1)–H(1n)···Cl(1) 154(3)°].

The palladium complex **10** (Fig. 3) displays a *cis* configuration with respect to the phosphorus ligands, the palladium(II) centre being in a near square planar geometry [Cl(1)–Pd(1)–Cl(2) 86.58(4)°, P(1)–Pd(1)–Cl(2) 88.60(4)°, P(2)–Pd(1)–Cl(1) 89.86(4)°, P(2)–Pd(1)–P(1) 96.63(4)°]. The Pd–P and Pd–Cl bond distances are normal and there is an intermolecular N–H···Cl_{coord} hydrogen bond [N(1)···Cl(1) 3.310(4) Å, H(1N)···Cl(1) 2.65(4) Å; N(1)–H(1N)···Cl(1) 137(3)°; symm. code = 0.5 −*x*, 0.5 −*y*, 1 −*z*]. We recently reported [21] an X-ray structure determination of the platinum(II) complex $PtCl_2$(**1′-Cl**)$_2$ in which molecules are arranged into dimer pairs via intermolecular N–H···Cl H-bonding.

The X-ray structure of **16** · $(CH_3)_2SO$ (Fig. 4) clearly shows that **1-OH** adopts a P/N-chelating mode with the two additional coordination sites occupied by methyl and chloride ligands. The bond angles around palladium [P(1)–Pd(1)–C(1) 86.16(7)°, Cl(1)–Pd(1)–C(1) 87.70(7)°, P(1)–Pd(1)–N(2) 92.98(6)° and Cl(1)–Pd(1)–N(2) 93.13(6)°] confirm an approximate square-planar arrangement with the pyridyl nitrogen *trans* to the methyl group [9b]. The

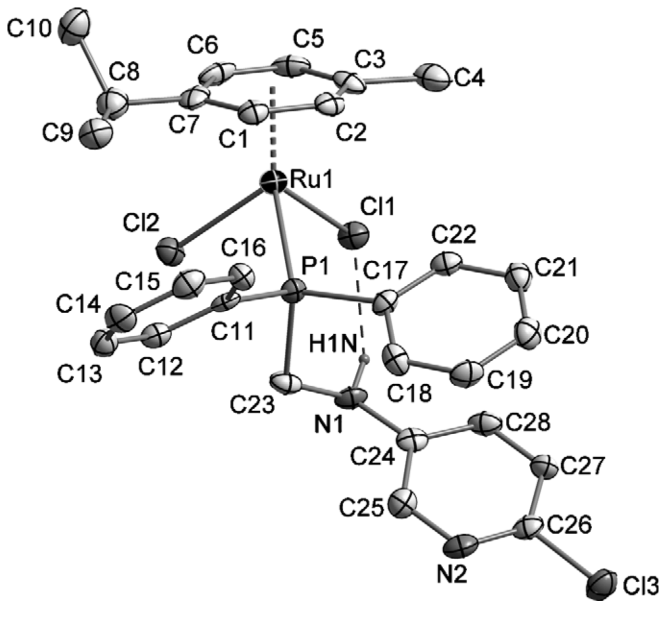


Fig. 1. X-ray structure of **4**. All hydrogens, except on N(1), have been omitted for clarity. The η^6-coordination is illustrated by a thick dashed line between Ru and the centroid of the aromatic ring of the *p*-cymene ligand. The H-bond is shown as a dashed line.

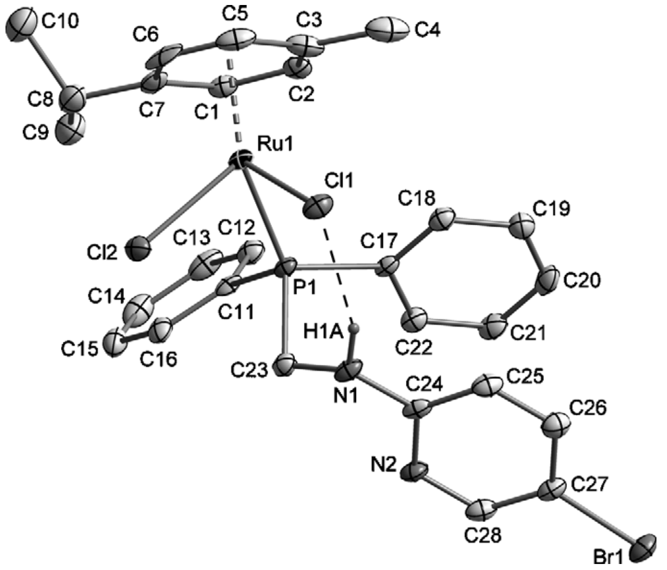


Fig. 2. X-ray structure of **5**. All hydrogens, except on N(1), have been omitted for clarity. The η^6-coordination is illustrated by a thick dashed line between Ru and the centroid of the aromatic ring of the *p*-cymene ligand. The H-bond is shown as a dashed line.

Pd–P, Pd–N, Pd–C and Pd–Cl bond lengths are all in the normal range [9b]. The Pd–P–C–N–C–N six-membered ring has a twist-boat conformation. The dihedral angle between the coordination plane and that of the pyridine ring in **16** is 33.24(8)°. There is an intramolecular N–H···O hydrogen bond to the neighbouring phenolic group [N(1)···O(1) 2.651(2) Å, H(1)···O(1) 2.23(2) Å; N(1)–H(1)···O(1) 109(2)°].

A few crystals of **18** · $CHCl_3$ (Fig. 5) were obtained when a solution of **17** was allowed to stand for a prolonged period. X-ray crystallography confirmed that two pyridylphosphines **1-H** span both $PdCl_2$ units giving a 12-membered metallocycle and is essentially identical [39] to that previously reported (in this case as the CH_2Cl_2 solvate). Mak and co-workers [40] have shown that 2,6-bis(diphenylphosphino)pyridine can be used to synthesise a 12-membered dimethylplatinum(II) metallocycle in which only the two P-donors are coordinated. The two Pd–Cl bond lengths [2.2991(9) and 2.2954(9) Å] are similar to those previously reported [39] yet shorter than those found in **10** and **16** · $(CH_3)_2SO$ whilst the Pd–P distance [2.2497(10) Å] is longer than in **16** · $(CH_3)_2SO$. The difference in Pd–N(2) dis-

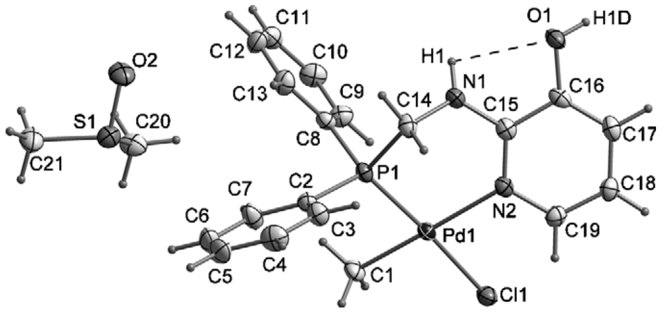


Fig. 4. X-ray structure of **16**.

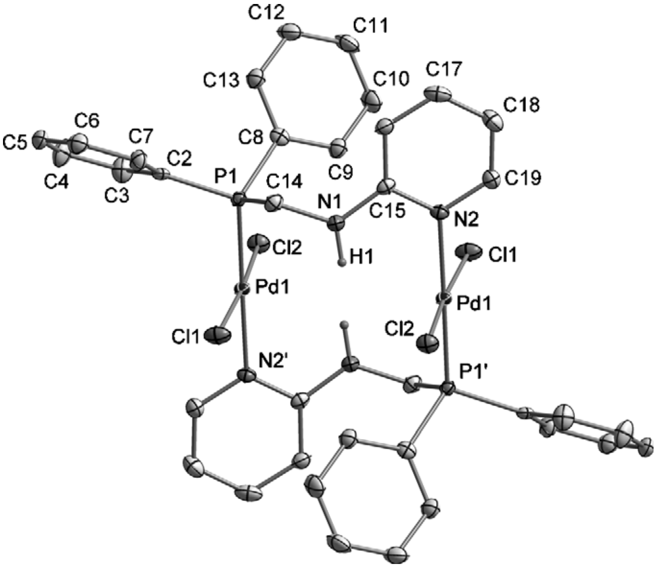


Fig. 5. X-ray structure of **18** · $CHCl_3$. All hydrogens, except on N(1), and the solvent have been omitted for clarity. Symmetry code = $1 - x$, $1 - y$, $1 - z$.

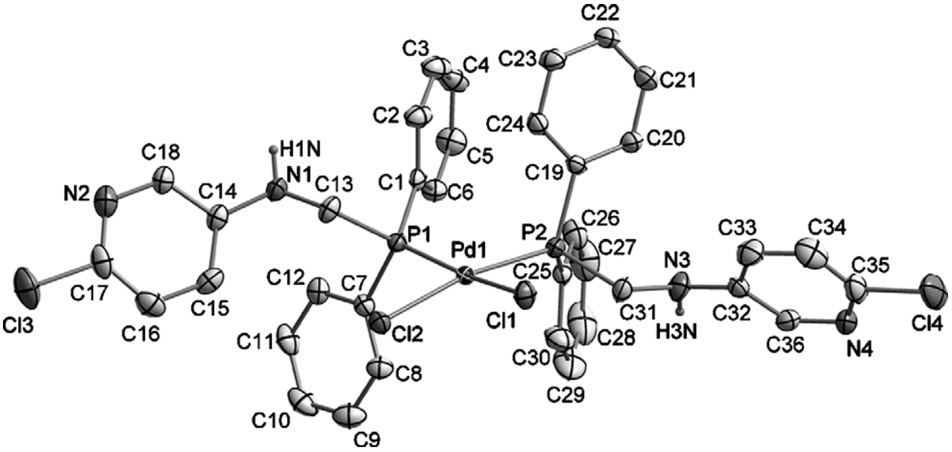


Fig. 3. X-ray structure of **10**. All hydrogens, except on N(1) and N(3), have been omitted for clarity.

tances can be attributed to the different *trans* groups [2.2275(18) Å (N(2) *trans* to C) in **16** · $(CH_3)_2SO$ versus 2.113(3) Å (N(2) *trans* to P) in **18** · $CHCl_3$]. The non-bonded Pd···Pd separation between $PdCl_2$ units in **18** · $CHCl_3$ is 4.6555(6) Å and can be compared with known homobimetallic Pd_2 complexes (4.594 Å [39], 4.710(1) Å [41], 5.261(2) Å [42] and 9.0239(5) Å [43]) using other pyridylphosphines as bridging ligands. Unlike Ph_2PPy and related pyridylphosphines, which have very rigid structures and have been used to synthesise hetero- and homonuclear metal complexes containing a metal–metal bond [6c,44], the inclusion of two flexible spacer atoms (carbon/nitrogen) disfavours any Pd···Pd interaction here. The dihedral angle between the coordination plane and that of the pyridine ring is 70.70(9)°.

4. Conclusions

Two new pyridylphosphines have been prepared and their coordination chemistry investigated with a range of late transition-metals. Functionalised phosphines continue to find considerable importance in many catalytic processes and this uniqueness can often be traced to the flexible ligating behaviour of many of these hybrid ligands.

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Appendix A. Supplementary data

A complete set of X-ray crystallographic structural data for compounds **4**, **5**, **10**, **16** · $(CH_3)_2SO$ and **18** · $CHCl_3$ (CCDC Nos. 289544, 289545, 289546, 217957 and 218017, respectively) is available at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition numbers. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.12.068.

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