Late transition metal complexes of a new P–N ligand $Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$: synthesis and structural studies

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Received (in Cambridge, UK) 19th October 2000, Accepted 19th December 2000
First published as an Advance Article on the web 22nd February 2001

A new functionalised pyridylphosphine $Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$ **1** has been synthesized from Ph_2PCH_2OH and 2-$H_2NC_5H_3(Cl\text{-}5)N$. Reaction of **1** with aqueous H_2O_2 gave $Ph_2P(O)CH_2N(H)C_5H_3(Cl\text{-}5)N$ **2**. The crystal structures of **1** and **2** reveal, in both cases, dimer pair formation through $N\text{–}H\cdots N_{pyridyl}$ or $N\text{–}H\cdots OP$ intermolecular hydrogen bonding respectively. Chloro bridge cleavage of either $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\}_2]$, $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ or $[\{Pd(C_{12}H_{12}N)(\mu\text{-}Cl)\}_2]$ with two equivalents of **1** gave the mononuclear complexes $[RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\mathbf{1}]$ **3**, $[RhCl_2(\eta^5\text{-}C_5Me_5)\mathbf{1}]$ **4** or $[PdCl(C_{12}H_{12}N)\mathbf{1}]$ **5** (P *trans* to N) respectively. The chloro complexes $[AuCl(\mathbf{1})]$ **6**, $[PtCl_2(\mathbf{1})_2]$ **7** and $[PdCl_2(\mathbf{1})_2]$ **8** were prepared by substitution of tht (tetrahydrothiophene) (or cod) from $[AuCl(tht)]$ or $[MCl_2(cod)]$ (M = Pt or Pd). In **3**–**8** only *P*-ligation of **1** was observed. Chloride abstraction from either **3**–**5** or **7**, **8** using $Ag[BF_4]$ gave the cationic complexes $[RuCl(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}][BF_4]$ **9**, $[RhCl(\eta^5\text{-}C_5Me_5)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}][BF_4]$ **10**, $[Pd(C_{12}H_{12}N)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}][BF_4]$ **11** and *cis*-$[M\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}_2][BF_4]_2$ (M = Pt **12** or Pd **13**) in which **1** chelates through both P and $N_{pyridyl}$ donor atoms. All complexes were characterised by a combination of multinuclear NMR, IR spectroscopy and elemental analyses. Furthermore the crystal structures of **5**–**7** and **12** have been determined and reveal several types of $N\text{–}H\cdots X$ (X = N, F or Cl; inter- or intra-molecular) hydrogen bonding contacts. The structure of **12** represents an extremely rare, crystallographically characterised, M–P–C–N–C–N six-membered metallacyle.

Introduction

Pyridylphosphines continue to engender much interest as excellent ligands for use in co-ordination and organometallic chemistry.[1,2] Their extreme versatility stems principally from the ease of synthesis which can influence dramatically ligand and complex behaviour. One frequently encountered pyridylphosphine is $(2\text{-}C_5H_4N)PPh_2$ (dppy)[3] which displays several ligating modes to transition metals (*e.g.* P-co-ordination, P,N-chelation and P,N-bridging). Recently there has been considerable interest in the development of bidentate ligand systems in which a pyridyl group may adopt exocyclic positions[4] with respect to the phosphorus centre or constitute the spacer[5,6] between two PR_2 moieties. Examples of multifunctional P/N(pyridyl)/X (X = N,[7] O [8] or C [9]) and even chiral ligand systems in which the chirality can be located either at P [10] or in the backbone[11] have also been documented.

The co-ordination chemistry of pyridylphosphines is diverse[1] with several complexes finding important catalytic applications, most significantly the alkoxycarbonylation of alkynes.[12,13] The mechanism and aspects of the co-ordination chemistry relevant to this process have been studied in detail by the groups of Matteoli[14] and Edwards.[15] Recently the hydrogenation of arenes using rhodium pyridylphosphine complexes anchored to a silica-supported palladium heterogeneous catalyst was described.[16] Herein we report the synthesis of a new pyridylphosphine, prepared by simple condensation and a study of its ligation behaviour towards several late transition-metal precursors. Some similarities in reactivity have previously been noted with $Ph_2PCH_2NHC_5(H)_3N(OH)$ and furthermore, the hydroxy group has been shown to undergo further reactions.[17] The incorporation of a suitably disposed halogeno group offers, amongst others, two attractive possibilities: (i) further functionalisation and (ii) the potential for hydrogen bonding or other secondary interactions. The crystal structures of six compounds have been determined and a propensity for intramolecular or intermolecular hydrogen bonding is observed. The formation of dimer pairs *via* $N\text{–}H\cdots X$ (X = N, O or Cl) is especially prevalent.

Experimental

General

Standard Schlenk techniques were used for ligand syntheses whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. The ligand Ph_2PCH_2OH was prepared from Ph_2PH and $(CH_2O)_n$ according to a literature method[18] as were the metal complexes $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2\}]$,[19] $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$,[20] $[\{Pd(C_{12}H_{12}N)(\mu\text{-}Cl)\}_2]$,[21] $[AuCl(tht)]$ (tht = tetrahydrothiophene)[22] and $[MCl_2(cod)]$ (M = Pd or Pt; cod = cycloocta-1,5-diene).[23,24] All other chemicals were obtained from commercial sources and used directly without further purification.

DOI: 10.1039/b008502m

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 MHz) on a Bruker AC250 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $SiMe_4$, $^{31}P\text{-}\{^1H\}$ NMR spectra on a JEOL FX90Q (36.2 MHz) spectrometer with chemical shifts (δ) 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) (Table 1) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Preparations

$Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$, 1. A CH_3OH (15 mL)–toluene (25 mL) solution of Ph_2PCH_2OH (1.00 g, 4.62 mmol) and 2-amino-5-chloropyridine (0.595 g, 4.63 mmol) was heated to ≈65 °C for *ca.* 6 d. The volume was reduced to ≈3–4 mL whereupon a white solid deposited. The solid was collected by suction filtration, washed with cold CH_3OH (5 mL) and dried *in vacuo.* Additional crops of compound **1** could be isolated from the filtrate. Yield: 1.311 g, 87%. IR: 3219 ν_{NH}, 1593 cm^{-1} $\nu_{CN(pyridyl)}$. EI MS: *m/z* 326 (M^+).

$Ph_2P(O)CH_2N(H)C_5H_3(Cl\text{-}5)N$, 2. To a CH_2Cl_2 (5 mL) solution of $Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$ (0.094 g, 0.288 mmol) was added aqueous H_2O_2 (30% w/w, ≈1 mL). After stirring the two-phase system for 1 h, anhydrous $MgSO_4$ was added and the $MgSO_4$ removed by filtration. The solvent was evaporated to dryness under reduced pressure and triturated with diethyl ether (10 mL). The product was collected by suction filtration and dried *in vacuo.* Yield: 0.058 g, 59%. IR: 3249 ν_{NH}, 1596 $\nu_{CN(pyridyl)}$, 1174 cm^{-1} ν_{PO}. EI MS: *m/z* 342 (M^+). Crystals of compound **2** suitable for X-ray crystallography were obtained by slow evaporation of the filtrate from the reaction of $[Pd(OAc)_2]$ with two equivalents of **1**.

$[RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}]$, 3. To a CH_2Cl_2 (20 mL) solution of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\}_2]$ (0.100 g, 0.163 mmol) was added $Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$ (0.107 g, 0.328 mmol). The solution was stirred for ≈15 min, reduced *in vacuo* to *ca.* 1–2 mL and diethyl ether (10 mL) added. The solid was collected by suction filtration and dried *in vacuo.* Yield: 0.190 g, 92%. IR: 3252 ν_{NH}, 1595 cm^{-1} $\nu_{CN(pyridyl)}$. FAB MS: *m/z* 634 (M^+).

In a similar manner the following complexes were prepared: $[RhCl_2(\eta^5\text{-}C_5Me_5)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}]$ **4** (79%) and $[PdCl(C_{12}H_{12}N)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}]$ **5** (84%). IR: 3277 ν_{NH}, 1596 cm^{-1} $\nu_{CN(pyridyl)}$; FAB MS: *m/z* 598 (M-Cl). IR: 3384 ν_{NH}, 1595 cm^{-1} $\nu_{CN(pyridyl)}$; FAB MS: *m/z* 603 (M − Cl).

Table 1 Microanalytical data for compounds **1–13**[a]

	Analysis (%)		
Compound	C	H	N
1	65.64(66.15)	4.76(4.95)	8.37(8.57)
2	63.00(63.07)	4.70(4.71)	7.89(8.17)
3	52.41(53.12)	4.87(4.79)	4.65(4.43)
4[b]	51.95(52.15)	4.69(5.01)	4.30(4.35)
5	56.26(56.39)	4.48(4.43)	6.41(6.58)
6	38.79(38.66)	2.94(2.88)	4.85(5.01)
7	47.46(47.02)	3.78(3.51)	5.84(6.09)
8	51.85(52.04)	3.91(3.88)	6.43(6.74)
9	48.71(49.14)	4.50(4.43)	3.73(4.09)
10[c]	47.28(47.09)	4.49(4.81)	3.69(3.92)
11[c]	50.28(50.23)	3.94(4.37)	5.58(5.86)
12	42.36(42.30)	3.17(3.16)	5.38(5.48)
13	46.36(46.32)	3.65(3.46)	5.08(6.00)

[a] Calculated values in parentheses. [b] Contains $0.5H_2O$. [c] Contains $1.5H_2O$.

$[AuCl\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}]$, 6. To a CH_2Cl_2 (10 mL) solution of [AuCl(tht)] (0.078 g, 0.243 mmol) was added $Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$ (0.078 g, 0.242 mmol) as a solid in one portion. The solution was stirred for ≈15 min and reduced *in vacuo* to *ca.* 1 mL. Addition of diethyl ether (15 mL) and light petroleum (bp 60–80 °C, 15 mL) gave a white solid which was collected by suction filtration and dried *in vacuo.* Yield: 0.113 g, 84%. IR: 3242 ν_{NH}, 1597 $\nu_{CN(pyridyl)}$, 323 cm^{-1} ν_{AuCl}. FAB MS: *m/z* 1083 (M_2 − Cl) (dimer pair).

$[PtCl_2\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}_2]$, 7. To a CH_2Cl_2 (10 mL) solution of $[PtCl_2(cod)]$ (0.050 g, 0.134 mmol) was added $Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N$ (0.087 g, 0.266 mmol) to give a colourless solution. After stirring for *ca.* 15 min the volume was concentrated to 1–2 mL under reduced pressure and Et_2O (20 mL) added. The mixture was stirred for 1 h, filtered under suction filtration and dried *in vacuo* overnight. Yield: 0.086 g, 70%. IR: 3373, 3319 ν_{NH}, 1596 $\nu_{CN(pyridyl)}$, 310, 284 cm^{-1} ν_{PtCl}. FAB MS: *m/z* 883 (M − Cl).

In a similar manner $[PdCl_2\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}_2]$ **8** was isolated in 85%. IR: 3371, 3306 ν_{NH}, 1596 $\nu_{CN(pyridyl)}$, 306, 282 cm^{-1} ν_{PdCl}. FAB MS: *m/z* 795 (M − Cl).

$[RuCl(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}][BF_4]$, 9. To a CH_2Cl_2 (30 mL) suspension of $Ag[BF_4]$ (0.032 g, 0.164 mmol) was added $[RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}]$ (0.096 g, 0.152 mmol) and the mixture stirred in the dark for 2 h. The AgCl was filtered off through a small Celite plug and the orange solution reduced *in vacuo* to *ca.* 1–2 mL. Addition of diethyl ether (15 mL) gave compound **9** which was collected by suction filtration, washed with diethyl ether (2 mL) and dried *in vacuo.* Yield: 0.096 g, 92%. IR: 3364 ν_{NH}, 1611 cm^{-1} $\nu_{CN(pyridyl)}$. FAB MS: *m/z* 597 (M − BF_4).

In a similar manner the following complexes were prepared: $[RhCl(\eta^5\text{-}C_5Me_5)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}][BF_4]$ **10** (77%) and $[Pd(C_{12}H_{12}N)\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}][BF_4]$ **11** (99%). IR: 3363 ν_{NH}, 1613 cm^{-1} $\nu_{CN(pyridyl)}$; FAB MS: *m/z* 599 (M − BF_4). IR: 3383 ν_{NH}, 1608 cm^{-1} $\nu_{CN(pyridyl)}$. FAB MS: *m/z* 603 (M − BF_4).

***cis*-$[Pt\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}_2][BF_4]_2$, 12.** To a CH_2Cl_2 (25 mL) suspension of $Ag[BF_4]$ (0.053 g, 0.272 mmol) was added $[PtCl_2\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\}_2]$ (0.100 g, 0.109 mmol) and the mixture stirred in the dark for 2 h. The AgCl was filtered off through a small Celite plug and the yellow solution evaporated to dryness. The residue was taken up in CH_2Cl_2 (2 mL) and addition of diethyl ether (15 mL) gave a pale yellow solid which was collected by suction filtration, washed with Et_2O and dried *in vacuo.* Yield: 0.078 g, 70%. IR: 3364 ν_{NH}, 1628, 1597 cm^{-1} $\nu_{CN(pyridyl)}$. FAB MS: *m/z* 935 (M − BF_4). In a similar manner $[Pd\{Ph_2PCH_2N(H)C_5H_3(Cl\text{-}5)N\text{-}P,N\}_2][BF_4]_2$ **13** was isolated in 55% yield. IR: 3350 ν_{NH}, 1623 cm^{-1} $\nu_{CN(pyridyl)}$. FAB MS: *m/z* 760 (M − $2BF_4$).

X-Ray crystallography

Crystals of compounds **1**, **6** and **7** suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a $CDCl_3$ solution over several days. For **5** crystals were grown by slow diffusion of diethyl ether–light petroleum (bp 60–80 °C) into a $CDCl_3$ solution over several days whilst in the case of **12** crystals were grown by vapour diffusion of diethyl ether into a CH_2Cl_2–CH_3OH solution over several days.

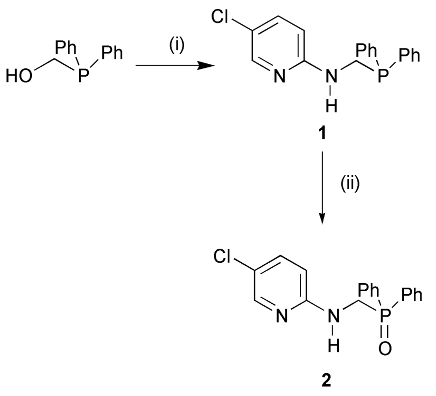
The crystal structures of compounds **1**, **2** and **5–7** were obtained using either a Bruker SMART diffractometer with graphite-monochromated (Mo-Kα) radiation ($\lambda = 0.710\,37$ Å) or a Rigaku AFC7S serial diffractometer with graphite-monochromated Cu-Kα radiation ($\lambda = 1.541\,78$ Å) and ω scans. Details of the crystal data collection and refinement are given in Table 3. All data were corrected for Lorentz-polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by empirical methods.[25] Structures were solved by direct methods and refined by full-matrix least squares against F (TEXSAN[26]) for data with $I > 2\sigma(I)$ or F^2 (SHELXTL[27]) for all data. A standard SHELXTL weighting scheme was used for **1** and **7** whilst in the case of **2**, **5** and **6** the weighting scheme for the Rigaku/TEXSAN was as previously reported.[28] All N–H protons were located (0.98 Å in **1**, **7**; 1.00 Å in **2**, **5** and **6**). Refinements converged to residuals given in Table 3. All calculations were made with programs from the SHELXTL or TEXSAN systems.

For compound **12** data were collected on a colourless plate on a Nonius Kappa CCD area detector diffractometer at the window of a rotating anode FR591 generator, with a molybdenum target [λ(Mo-Kα) = 0.710 69 Å] and controlled by the COLLECT[29] software package. Data were corrected for absorption using the empirical method employed in Sortav.[30] The structure was solved by direct methods (SHELXS 97[31]) and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL 97[31]). Non-hydrogen atoms were refined anisotropically with hydrogens included in idealised positions (C–H distance 0.97 Å) with thermal parameters riding on those of the parent atom. The presence of the N–H protons was confirmed in the difference map, however they were included in the model in calculated positions, riding on the coordinates of the parent atom.

CCDC reference number 440/253. See http://www.rsc.org/suppdata/nj/b008502m/ for crystallographic files in .cif format.

Results and discussion

We recently reported the synthesis of some new, potentially multidentate, pyridylphosphines $Ph_2PCH_2N(H)C_5H_3N(OX)$ [X = H, PPh_2, $P(O)Ph_2$ or $P(O)(OPh)_2$] and demonstrated various co-ordination capabilities of these ligands.[17] The synthesis of the new 5-chloro substituted ligand $Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)$ **1** was readily accomplished by heating a CH_3OH–toluene solution of Ph_2PCH_2OH and $H_2NC_5H_3N(Cl\text{-}5)$ for *ca.* 6 d (Scheme 1). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** (Table 2 and for other characterisation data see Experimental) showed a single phosphorus resonance at δ(P) −17.4, an identical shift to that of the unsubstituted ligand $Ph_2PCH_2N(H)C_5H_4N$.[17] Further confirmation for the presence of only one "Ph_2PCH_2" group [as opposed to $(Ph_2PCH_2)_2NC_5H_3N(Cl\text{-}5)$ bearing two "Ph_2PCH_2" moieties] came from the ^1H NMR and IR spectra which showed a broad δ(NH) resonance at 4.71 and a sharp ν_{NH} vibration at 3219 cm^{-1} respectively. In the crystal structure of **1** (Fig. 1, Table 4) molecules of $Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)$ are arranged in dimer pairs by intermolecular $N\text{–}H\cdots N_{pyridyl}$ hydrogen bonds [N(14)···N(16A) 3.10(1), H(14n)···N(16A) 2.12 Å; N(14)–H(14n)···N(16A) 175°]. A similar observation was recently noted by Woollins and co-workers for $Ph_2PN(H)C_5H_4N$.[2a]



Scheme 1 (i) $H_2NC_5H_3N(Cl\text{-}5)$, (ii) aq. H_2O_2.

Oxidation of compound **1** with aqueous H_2O_2 gave $Ph_2P(O)CH_2N(H)C_5H_3N(Cl\text{-}5)$ **2** in 59% yield (Scheme 1). The downfield shift in δ(P) (29.7) and the observation of an intense ν_{PO} absorption at 1174 cm^{-1} are in accord with oxidation of the phosphorus(III) centre. The crystal structure of **2** (Fig. 2, Table 4) has been determined and confirms a tertiary phosphine oxide with a PO bond length of 1.489(2) Å consistent with appreciable double bond character.[32] Molecules of $Ph_2P(O)CH_2N(H)C_5H_3N(Cl\text{-}5)$ are linked into dimer pairs through intermolecular N–H···OP hydrogen bonding [N(14)···O(1A) 2.89(1), H(14n)···O(1A) 1.93 Å; N(14)–H(14n)···O(1A) 153°] forming a pseudo ten-membered ring. Previously NH···OP hydrogen-bonding has been observed in the mixed P^{III}/P^{V} ligand $Ph_2PN(H)P(O)Ph_2$[33] and the unusual platinum(II) complexes [Pt{P(O)(OMe)-

Table 2 Selected ^{31}P and ^{1}H NMR data for compounds **1–13**

Compound	δ(P)	^1J(PtP)	^1J(RhP)	δ(H) arom.	NH	CH₂
1	−17.4			8.05–6.34	4.71	4.05
2	29.7			8.00–6.39	5.25	4.37
3	19.0			7.90–5.97	5.58	4.74[a]
4	24.5		145	7.88–6.11	6.11	4.84[b]
5	38.7			8.10–6.23		4.75[c]
6	27.5			8.00–6.42	4.88	4.65
7	7.7	3682		7.90–6.48	5.80	4.64
8	29.7, 15.4[d]			8.22–6.57		4.80[e]
9	33.7			8.90–7.20		3.09, 4.68[a]
10	25.4		141	8.29–7.14		3.68, 4.51[b]
11	33.4			8.08–6.57		4.24[c]
12	2.0	3532[f]				
13	29.1[g]					

[a] $^iPrC_6H_4Me$ resonances at δ 5.28–5.19, 2.57, 1.88 and 0.95 (for **3**); 5.52–4.92, 2.01, 1.05 and 1.01 (for **9**). [b] C_5Me_5 resonance at δ 1.38 [J(PH) 3.5 Hz] (for **4**); 1.38 [J(PH) 3.5 Hz] (for **10**). [c] NMe_2 resonance at: δ 3.55 (for **5**); 3.15 [J(PH) 2.1 Hz] (for **11**). [d] *Ca.* 2.5 : 1 ratio of *cis* : *trans* isomers respectively in $CDCl_3$, *ca.* 17 : 1 ratio in $(CD_3)_2SO$. [e] Recorded in $(CD_3)_2SO$. [f] Recorded in $CDCl_3$–CH_3OH. [g] Recorded in CH_2Cl_2–C_6D_6.

Table 3 Details of the X-ray data collections and refinements for compounds **1**, **2**, **5**–**7** and **12**

	1	**2**	**5**	**6**	**7**	**12**
Empirical formula	$C_{18}H_{16}ClN_2P$	$C_{18}H_{16}ClN_2OP$	$C_{30}H_{28}Cl_2N_3PPd$	$C_{18}H_{16}AuClN_2P$	$C_{36}H_{32}Cl_4N_4P_2Pt$	$C_{36}H_{32}B_2Cl_2F_8N_4P_2Pt$
M	326.75	342.76	638.85	559.18	919.49	1022.21
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	13.3340(12)	9.226(2)	11.944(3)	9.849(3)	11.3466(2)	12.8214(1)
b/Å	5.8545(5)	12.365(6)	14.623(2)	11.647(3)	11.5291(2)	18.0482(2)
c/Å	21.617(2)	8.559(4)	16.140(2)	9.054(2)	16.0391(3)	17.5951(2)
α/°		98.90(4)		109.31(2)	65.574(1)	
β/°	90.761(2)	107.85(2)	91.36(2)	95.75(3)	89.056(1)	93.954(1)
γ/°		106.17(3)		102.41(3)	69.75	
U/Å^3	1687.3(3)	861.3(6)	2818.1(9)	940.6(5)	1831.71(6)	4061.87(7)
T/K	293(2)	293	293	293	293(2)	150(2)
Z	4	2	4	2	2	4
μ/mm^{-1}	0.319	0.32	0.92	8.17	4.24	3.73
Measured reflections	6101	3229	5437	3514	9342	45 264
Independent reflections (R_{int})	2325(0.2699)	3025(0.015)	5175(0.049)	3306(0.029)	5209(0.0279)	9139(0.0668)
Observed reflections ($I > 2.0\sigma(I)$)	1695	2160	2869	2436	4587	9139
Final R, R_w	0.088, 0.166	0.034, 0.033	0.037, 0.048	0.026, 0.025	0.026, 0.062	0.043, 0.118

N(H)C(Ph)=NN(H)Me}(Cl)(PEt$_3$)] and [Pt{P(O)(OMe)N(H)-N(Me)C(Me)=NH}(Cl)(PEt$_3$)].[34]

P-Co-ordination studies

A brief study of the ligating ability of compound **1** was undertaken to ascertain the potential for P-co-ordination and P,N$_{pyridyl}$-chelation. First halogeno-bridge cleavage of either [{RuCl(μ-Cl)(η^6-*p*-MeC$_6$H$_4$Pr^i)], [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$] or [{Pd(C$_{12}$H$_{12}$N)(μ-Cl)}$_2$] with two equivalents, of **1** in CH$_2$Cl$_2$ gave the mononuclear complexes [RuCl$_2$(η^6-*p*-MeC$_6$H$_4$Pr^i)(**1**)] **3**, [RhCl$_2$(η^5-C$_5$Me$_5$)(**1**)] **4** or [PdCl-(C$_{12}$H$_{12}$N)(**1**)] **5** respectively (Scheme 2). Pertinent spectroscopic data are given in Table 2 and the Experimental. In all cases P-complexation was inferred by a downfield shift in δ(P)

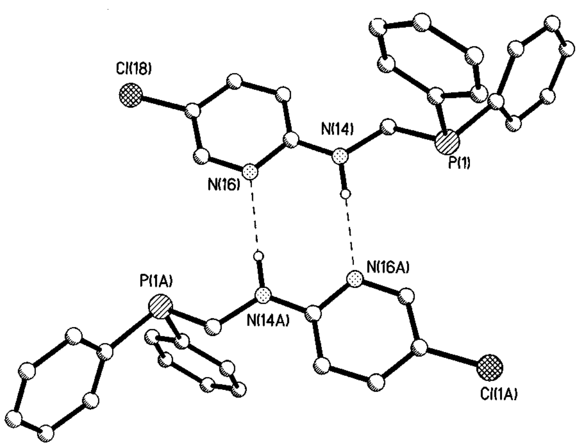


Fig. 1 Crystal structure of compound **1** showing the hydrogen bonded dimer pair.

Table 4 Selected bond distances (Å) and angles (°) for compounds **1** and **2**

	1	**2**
P(1)–C(1)	1.826(4)	1.800(2)
P(1)–C(7)	1.837(4)	1.792(2)
P(1)–C(13)	1.840(5)	1.811(2)
C(13)–N(14)	1.462(5)	1.443(3)
N(14)–C(15)	1.363(5)	1.364(3)
P(1)–O(1)		1.489(2)
C(1)–P(1)–C(7)	102.1(2)	107.3(1)
C(1)–P(1)–C(13)	102.1(2)	105.3(1)
C(7)–P(1)–C(13)	97.6(2)	106.8(1)
P(1)–C(13)–N(14)	111.6(3)	111.3(2)
C(13)–N(14)–C(15)	121.7(4)	122.2(2)
O(1)–P(1)–C(13)		112.6(1)

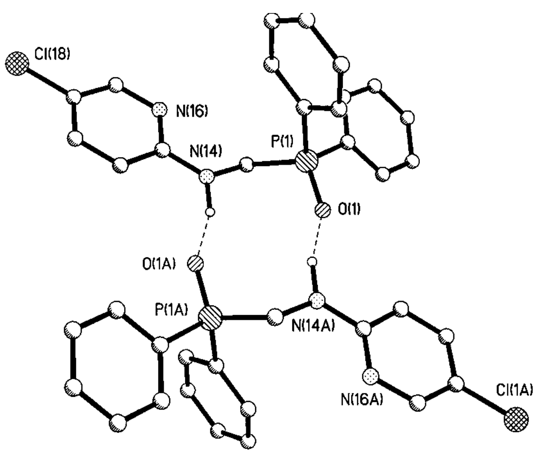
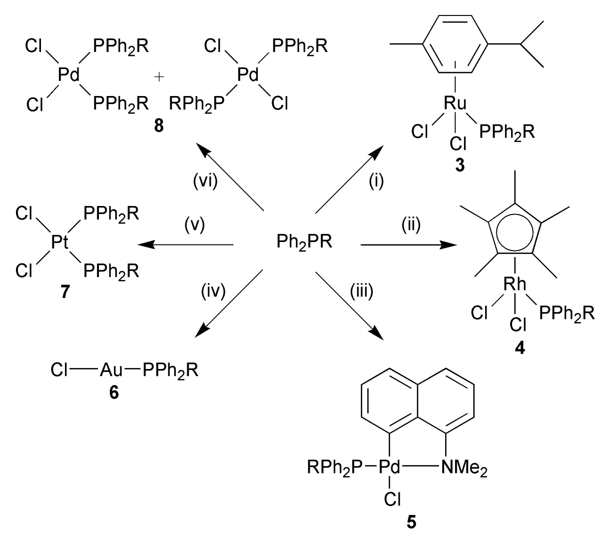


Fig. 2 Crystal structure of compound **2** showing the hydrogen bonded dimer pair.



Scheme 2 (i) [{RuCl(μ-Cl)(η^6-*p*-MeC$_6$H$_4$Pr^i)$_2$}], (ii) [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$], (iii) [{Pd(C$_{12}$H$_{12}$N)(μ-Cl)}$_2$], (iv) [AuCl(tht)], (v) [PtCl$_2$(cod)], (vi) [PdCl$_2$(cod)]. R = CH$_2$N(H)C$_5$H$_3$(Cl-5)N.

and further corroborated by very small changes in $\nu_{\mathrm{CN(pyridyl)}}$ (from IR) indicating a non-co-ordinated pyridyl ring. The ^{1}H NMR spectra showed the expected resonances for co-ordinated **1** in addition to the other spectator ligands. The CH_2 group was observed typically at *ca.* δ(H) 4.80, some 0.75 ppm downfield from that of non-complexed **1**. The crystal structure of **5** (Fig. 3, Table 5) shows an orthometallated $C_{12}H_{12}N$, Cl^- and $Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)$ ligands arranged in a *cis* disposition [*i.e.* P(1) *trans* to N(28)]. The geometry around the palladium(II) centre is essentially square-planar with bond angles in the range 83.3(2) [N(28)–Pd(1)–C(21)] to 94.1(2)° [P(1)–Pd(1)-C(21)]. The Pd–N, Pd–P and Pd–Cl bond distances are unexceptional. Unlike the intermolecular hydrogen-bonding pattern observed in **1** and **2**, the amine proton of the co-ordinated ligand in **5** is intramolecularly hydrogen bonded to an adjacent chloride [N(14)···Cl(1) 3.18(1), H(14n)···Cl(1) 2.60 Å; N(14)–H(14n)···Cl(1) 119°].

Reaction of [AuCl(tht)] or [MCl_2(cod)] (M = Pt or Pd) with one (or two) equivalent of **1** gave the chloro complexes [AuCl(**1**)] **6**, [$PtCl_2$(**1**)$_2$] **7** and [$PdCl_2$(**1**)$_2$] **8** respectively (Scheme 2). In the case of **7**, the ^{31}P-{^{1}H} NMR spectrum (Table 2) showed a single ^{31}P resonance flanked by ^{195}Pt satellites [^{1}J(PtP) 3682 Hz] indicative of the *cis* disposition of the tertiary phosphine ligands. In contrast complex **8** displays two singlets at δ(P) 29.7 and 15.4 consistent with both *cis* and *trans* isomers[35] present in $CDCl_3$ solution (*ca.* 2.5 : 1 ratio respectively). The ratio of these two isomers does not change significantly (*ca.* 3.5 : 1) even after allowing solutions to stand for 6 d. In the solid state the IR spectrum indicated only the *cis* isomer is present (ν_{PdCl} 306, 282 cm^{-1}). The crystal structures of **6** and **7** have both been determined. For **6** (Fig. 4, Table 5), the expected linear geometry is observed [Cl(1)–Au(1)–P(1) 174.96(7)°] and, reminiscent of the structure of **1**, forms a dimer pair arrangement through N–H···N_{pyridyl} hydrogen bonding [N(14)···N(16A) 3.07(1), H(14n)···N(16A) 2.14 Å; N(14)–H(14n)···N(16A) 167°]. No other secondary interactions (*i.e.* Au···Au, Cl···Cl) are observed between molecules of **6**. In contrast [AuCl{$Ph_2PN(H)C_5H_4N$}] forms an infinite 1-D chain through N–H···N_{pyridyl} hydrogen bonding[2a] and shows that by incorporating a methylene spacer between the Ph_2P and $N(H)C_5H_4N$ groups the gross solid state structure can be strongly influenced. The platinum complex **7** (Fig. 5, Table 5) shows a near square-planar geometry [P(1)–Pt(1)–Cl(2) 87.23(5), Cl(1)–Pt(1)–Cl(2) 87.69(5), P(2)–Pt(1)–Cl(1) 88.92(5) and P(1)–Pt(1)–P(2) 96.72(4)°] with two *cis* bonded $Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)$ and Cl^- ligands. The Pt lies 0.05 Å below the plane of its four donor substituents. The Pt–P and Pt–Cl bond distances are normal and compare well with those of *cis*-[$PtCl_2(Ph_2PCH_2OH)_2$].[36] Molecules of **7** are arranged into dimer pairs *via* N–H···Cl_{coord} hydrogen bonding [N(14)···Cl(1A) 3.39(1), H(14n)···Cl(1A) 2.52 Å; N(14)–H(14n)···Cl(1A) 147°; [N(34)···Cl(2A) 3.64(1), H(34n)···Cl(2A) 2.76 Å; N(34)–H(34n)···Cl(2A) 151°]. This is

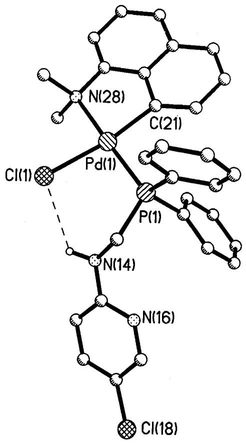


Fig. 3 Crystal structure of compound **5**.

Table 5 Selected bond distances (Å) and angles (°) for compounds **5**–**7**

	5	6	7
Pd(1)–Cl(1)	2.406(2)		
Pd(1)–P(1)	2.250(2)		
Pd(1)–N(28)	2.153(5)		
Pd(1)–C(21)	2.009(6)		
N(28)–Pd(1)–C(21)	83.3(2)		
Cl(1)–Pd(1)–N(28)	91.2(1)		
Cl(1)–Pd(1)–P(1)	92.15(6)		
P(1)–Pd(1)–C(21)	94.1(2)		
Cl(1)–Pd(1)–C(21)	171.4(2)		
P(1)–Pd(1)–N(28)	173.2(1)		
Au(1)–Cl(1)		2.294(2)	
Au(1)–P(1)		2.231(2)	
Cl(1)–Au(1)–P(1)		174.96(7)	
Pt(1)–Cl(1)			2.3500(13)
Pt(1)–Cl(2)			2.3594(13)
Pt(1)–P(1)			2.2572(12)
Pt(1)–P(2)			2.2494(12)
Cl(2)–Pt(1)–P(1)			87.23(5)
Cl(1)–Pt(1)–Cl(2)			87.69(5)
Cl(1)–Pt(1)–P(2)			88.92(5)
P(1)–Pt(1)–P(2)			96.72(4)
Cl(1)–Pt(1)–P(1)			169.90(4)
Cl(2)–Pt(1)–P(2)			174.75(5)

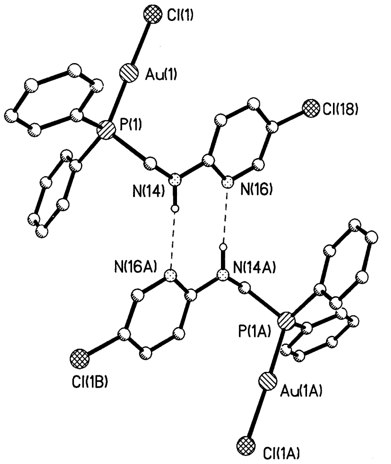


Fig. 4 Crystal structure of compound **6** showing the hydrogen bonded dimer pair.

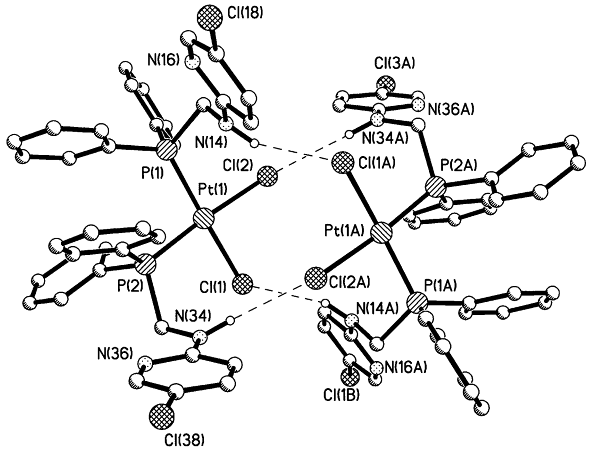
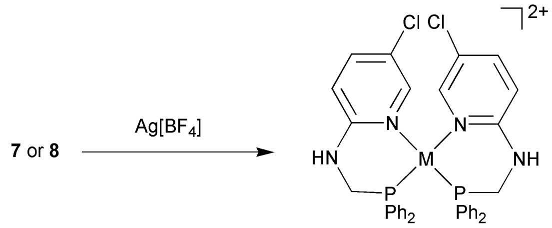


Fig. 5 Crystal structure of compound **7** showing the hydrogen bonded dimer pair.

further corroborated by two well resolved N–H vibrations (3373, 3319 cm^{-1}) in the IR spectrum of **7**.

P,*N*-Co-ordination studies

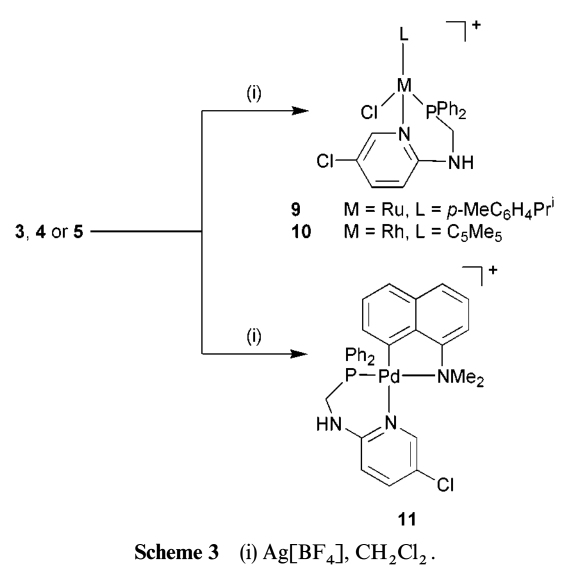
When a $\mathrm{CDCl_3}$ solution of **3** is allowed to stand for *ca.* 4 d a new phosphorus-containing species **9** [δ(P) 33.7] is formed, whose $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR shift is similar to that of $[\mathrm{RuCl}(\eta^6\text{-}p\text{-}\mathrm{MeC_6H_4Pr^i})\{\mathrm{Ph_2PCH_2N(H)C_5H_3N(OH)}\text{-}P,N\}]\mathrm{Cl}$ [δ(P) 31.6].[17] Hence we assign **9** as the isomerised cationic complex $[\mathrm{RuCl}(\eta^6\text{-}p\text{-}\mathrm{MeC_6H_4Pr^i})\{\mathrm{Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)}\text{-}P,N\}]\mathrm{Cl}$. Alternatively reaction of **3**, **4** or **5** with approximately one equivalent of $\mathrm{Ag[BF_4]}$ in $\mathrm{CH_2Cl_2}$ for 2 h gave the cationic complexes **9**, $[\mathrm{RhCl}(\eta^5\text{-}\mathrm{C_5Me_5})\{\mathrm{Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)}\text{-}P,N\}][\mathrm{BF_4}]$ **10** and $[\mathrm{Pd(C_{12}H_{12}N)}\{\mathrm{Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)}\text{-}P,N\}[\mathrm{BF_4}]$ **11** as their tetrafluoroborate salts (Scheme 3). The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectra show small downfield shifts [δ(P) 25.4, ^1J(RhP) 141 Hz for **10**; δ(P) 33.4 for **11**] with respect to those found for **4** and **5**. Further diagnostic confirmation for $\mathrm{P,N_{pyridyl}}$-chelation is seen in (i) the ^{1}H NMR spectra of **9**–**11** which show, in general, a downfield shift for H(6). (This feature has previously been documented for other complexes containing pyridylphosphines[37]), (ii) a shift to higher wavenumber for the pyridine ring vibration (*ca.* 1610 cm^{-1}).



12 M = Pt
13 M = Pd

(1)

Reaction of compound **7** (or **8**) with approximately two equivalents, of $\mathrm{Ag[BF_4]}$ in $\mathrm{CH_2Cl_2}$ gave the bis cationic complexes $[\mathrm{M}\{\mathrm{Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)}\text{-}P,N\}_2][\mathrm{BF_4}]_2$ **12** (M = Pt) and **13** (M = Pd) (Eqn. 1). The $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectrum of **12** showed a marginal shift in δ(P) (*ca.* 5 ppm) and a reduction in ^1J(PtP) of *ca.* 150 Hz (with respect to **7**) upon chelation through both P and $\mathrm{N_{pyridyl}}$ donor atoms. This was further supported by the absence of ν_{PtCl} vibrations and the tentative assignment of a ring stretching vibration of the co-ordinated pyridyl group at 1623 cm^{-1}. The crystal structure of **12** (Fig. 6, Table 6) establishes a near square-planar environment around Pt with two *cis* *P*,*N*-chelating $\mathrm{Ph_2PCH_2N(H)C_5H_3N(Cl\text{-}5)}$ ligands. The Pt–P bond distances are similar to those seen in **7** [2.2572(12) and 2.2494(12) Å] whilst the Pt–N bond lengths are comparable with those of other platinum pyridylphosphine complexes.[2c,38] The plane defined by Pt and the co-ordinated P atoms makes a dihedral angle of 17.65(11)° with the $\mathrm{PtN_2}$ mean plane. The Pt–P–C–N–C–N rings both adopt non-planar conformations presumably arising from steric and π–π interactions between the phenyl groups on the phosphorus atoms which forces these atoms out of the ring plane. There is an additional short N–H···F intermolecular hydrogen bond with a $[\mathrm{BF_4}]^-$ counter ion [N(3)···F(8) 2.87(1), H(3n)···F(8) 2.01 Å; N(3)–H(3n)···F(8) 172°]. The structure of **12** represents an extremely rare crystallographically characterised six-membered M–P–C–N–C–N metallacycle.[17,39] To date, the only other crystal structure containing this fragment is the cationic complex **A** reported by Schmidbaur and co-workers.[39]



9 M = Ru, L = p-MeC$_6$H$_4$Pr^i
10 M = Rh, L = C$_5$Me$_5$
11

Scheme 3 (i) $\mathrm{Ag[BF_4]}$, $\mathrm{CH_2Cl_2}$.

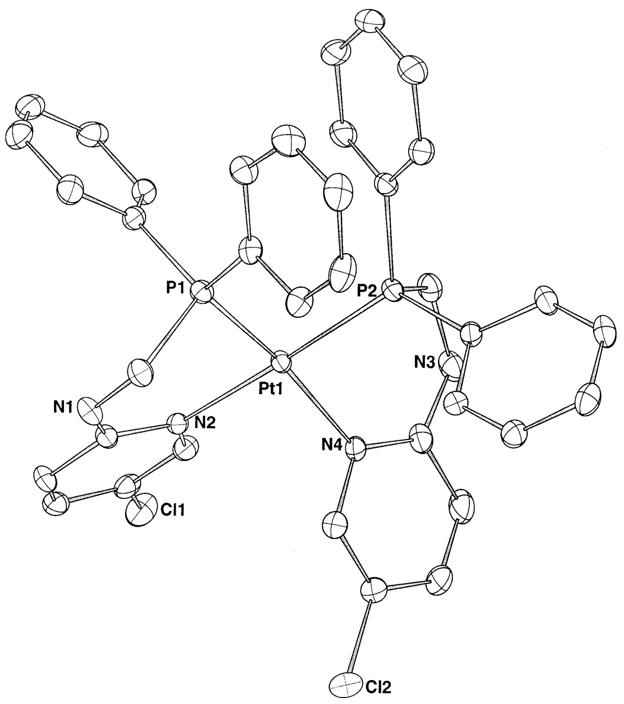
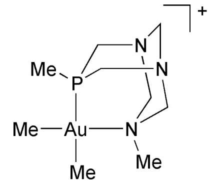


Fig. 6 Crystal structure of compound **12** ($[\mathrm{BF_4}]^-$ counter ion omitted for clairty).



A

In conclusion, we have shown that a new pyridylphosphine ligand is readily accessible and undergoes complexation to a range of late transition metals (Ru, Rh, Pd, Pt and Au). Furthermore both P- and $\mathrm{P,N_{pyridyl}}$-bonding modes have been observed and verified by spectroscopic and X-ray crystallographic studies. The crystal structures of several examples have been determined and illustrate a range of intra- and

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

Pt(1)–P(1)	2.2283(11)	Pt(1)–N(2)	2.140(4)
Pt(1)–P(2)	2.2321(10)	Pt(1)–N(4)	2.127(4)
P(2)–Pt(1)–N(4)	85.14(10)	P(1)–Pt(1)–P(2)	98.83(4)
P(1)–Pt(1)–N(2)	88.74(11)	P(1)–Pt(1)–N(4)	165.83(11)
N(2)–Pt(1)–N(4)	90.15(14)	P(2)–Pt(1)–N(2)	166.69(9)

inter-molecular hydrogen-bonding contacts (N–H···X where X = N, O, F or Cl). The chloro (and other halogeno) derivatives should serve as useful starting materials for further functionalisation and work along these lines is currently under investigation.

Acknowledgements

We would like to thank the EPSRC for support. The EPSRC Mass Spectrometery Service Centre at Swansea are also gratefully acknowledged. Precious metal salts were provided on loan by Johnson Matthey plc.

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