Steric control over the formation of *cis* and *trans* bis-chelated palladium(II) complexes using a new series of flexible *N,P* pyridyl–phosphine ligands†‡

Deborah A. Clarke, Philip W. Miller, Nicholas J. Long* and Andrew J. P. White

Received 14th June 2007, Accepted 17th July 2007
First published as an Advance Article on the web 13th August 2007
DOI: 10.1039/b709032c

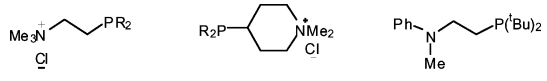
The deprotection of phosphonium chloride salts $[PR_2(CH_2OH)_2]^+Cl^-$ and subsequent condensation reaction with *N*-methyl-2-aminopyridine has been carried out to give a series of ligands of the form $PR_2CH_2N(CH_3)C_5H_4N$ (R = Ph **6**, Cy **7**, *t*-Bu **8**) which have been fully characterised either as the pure ligand (**6**) or the air stable borane adducts (R = Cy **7a**, *t*-Bu **8a**). The 1 : 1 reactions of **6**, **7** and **8** with $PdCl_2(COD)$ gave the *N,P* chelate complexes $[Pd\{PR_2CH_2N(CH_3)C_5H_4N\}Cl_2]$; the Cy (**10**) and *t*-Bu (**11**) complexes were characterised by X-ray crystallography. The bisligated species $[Pd\{PCy_2CH_2N(CH_3)C_5H_4N\}_2Cl_2]$ (**12**) was obtained when the reaction was carried out at higher temperatures and the ligands were found to be coordinated to the metal in a *trans* configuration through the phosphorus donors. Abstraction of the chlorides from the bis-ligated species **12**, using silver salts, resulted in the coordination of the pyridine ring forming the bis-chelate complex $[Pd\{PCy_2CH_2N(CH_3)C_5H_4N\}_2]^{2+}$ **13**. In comparison, the palladium bis-chelate complex of ligand **5** $[Pd\{PPh_2CH_2N(CH_3)C_5H_4N\}_2]^{2+}$ (**14**) was shown to form in a *cis* configuration and was fully characterised by X-ray crystallography.

Introduction

The chemistry of pyridylphosphines has been much developed in recent years owing to the versatility of these ligands in coordination chemistry and catalysis.[1–5] The most frequently used pyridylphosphine, 2-pyridyldiphenylphosphine (dppy), displays a variety of coordination modes to metal centres; most commonly *P*-coordination and *N,P* bridging are observed.[6] The formation of *N,P* metal chelate complexes are obviously difficult to achieve using dppy owing to ring strain in the resultant four-membered chelate; recently however a number of ligands with organic spacer groups between the nitrogen and phosphorus atoms have been synthesised and shown to display *N,P*-coordination to a variety of metals.[7–19] These bidentate ligands show a much greater potential for application to a range of catalytic reactions.

The interest in using bidentate *P,N* ligands for catalysis stems from their hemilability, an effect arising from having both hard and soft donor atoms in the same molecule.[20] The numerous modes of chelation, along with the strong coordinate bonding of the phosphorus to late transition metals results in the stabilisation of the metal centre in a variety of oxidation states and geometries. In addition, the chelate effect may impart stability on the active catalyst in the absence of a substrate, whilst in the presence of a substrate the harder nitrogen atom can dissociate to provide a vacant site for binding in a catalytic reaction.

The recent use and development of electron rich, bulky phosphine ligands for catalytic applications has been well documented.[21,22] Most notably, the use of these ligands in palladium catalysed cross-coupling reactions has been demonstrated to activate aryl chloride substrates even under mild conditions.[23–31] The ability of bulky alkyl phosphines to provide highly coordinatively unsaturated nucleophilic catalytic precursors is key to their effectiveness.[24] The combination of bulky electron rich phosphines with quaternised amine groups has been investigated most notably for aqueous phase cross-coupling reactions,[23,32] and ring opening[33] ring closing[34] metathesis polymerisation using the aminophosphine ligands **1–4** (Scheme 1). The effects of a hemilabile nitrogen donor using the aminophosphine ligand **5** for the promotion of aryl amination reactions has been demonstrated by Hii *et al.*[24]



1: R = Cy **2**: R = ^{t}Bu **3**: R = Cy **4**: R = ^{t}Bu **5**

Scheme 1 Some known examples of aminophosphine ligands.

We thought it would be interesting to extend the range of bulky electron rich aminophosphines that have the ability to act as hemilabile ligands to metal centres owing to their potential in catalytic applications. Herein we report the synthesis of a series of new *N,P* ligands (Scheme 2), based on a pyridine ring with a methylene amino spacer between the phosphorus donor, and their coordination chemistry to palladium(II).

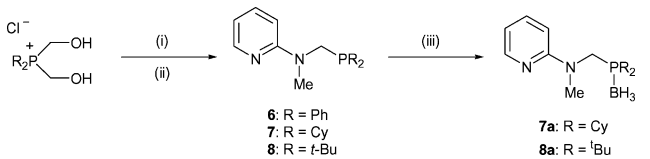
Results and discussion

The new *N,P* ligands **6**, **7** and **8** were prepared by the direct condensation of the appropriate PR_2CH_2OH precursor with *N*-methyl-2-aminopyridine (Scheme 2). Phosphonium chloride

Department of Chemistry, Imperial College London, South Kensington, London, UK SW7 2AZ. E-mail: n.long@imperial.ac.uk; Tel: +44 (0)20 7594 5781

† CCDC reference numbers 650212–650216. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709032c

‡ Electronic supplementary information (ESI) available: Additional crystal structure data. See DOI: 10.1039/b709032c



Scheme 2 Conditions: (i) NEt_3, methanol, reflux 2 h; (ii) *N*-methyl-2-aminopyridine, reflux 24 h; (iii) $BH_3S(CH_3)_2$·THF, diethyl ether, stirred at room temperature overnight.

precursor salts were prepared from their corresponding diphenyl or dialkyl phosphine, in high yield, according to established literature procedures.[35] The chloride salt was deprotected *in situ* using triethylamine, forming hydroxymethyl-diphenylphosphine or hydroxymethyl-dialkylphosphine prior to reaction with *N*-methyl-2-aminopyridine. Subsequent precipitation with diethyl ether and removal of the base salt gave the required ligand.

Ligand **6** was obtained in high yield as a white air stable solid, the $^{31}P\{^1H\}$ NMR spectrum showed a single peak at −21.3 ppm. A similar ligand synthesised by Durran *et al.*[6] shows a peak at −17.4 ppm. Ligands **7** and **8** were obtained as viscous, air sensitive oils in crude yields of *ca.* 70%—the bulky alkyl Cy and ^{t}Bu phosphine groups appeared to hinder this condensation reaction compared to the Ph derivative. NMR spectroscopic data for these ligands and their phosphine precursors are summarised in Tables 1 and 2.

The air sensitive ligands **7** and **8** were isolated as their corresponding borane salts following reaction with borane dimethyl sulfide in THF (Scheme 2).[36] The borane adducts **7a** and **8a** were obtained as air stable white crystalline solids after flash column chromatography. Their $^{31}P\{^1H\}$ NMR spectra showed expected downfield shifts, relative to the unprotected ligands (Table 1), and coupling to spin active ^{10}B and ^{11}B nuclei. There was no significant change to the proton spectra of either ligand when coordinated to boron.

Crystals of the borane adduct **7a** suitable for single crystal X-ray diffraction were obtained by recrystallisation from hot ethanol. The crystal structure of **7a** (Fig. 1) shows the expected ligand structure with coordination of the borane occurring solely to the phosphorus atom and not to any of the potentially competing nitrogen atoms. The P–C(1)–N(2)–C(3) dihedral angle is *ca.* 107°.

The borane could be readily removed from **7a** and **8a** to give the purified ligands (in overall 10% and 9% yields respectively) by stirring overnight with fluoroboric acid dimethyl ether complex in THF.[37] ^{31}P NMR spectra showed single peaks for both ligands. The purity of the ligands was significantly improved compared to the crude products prior to the borane protection step.

Table 1 $^{31}P\{^1H\}$ NMR shifts for the intermediates and products of the reaction shown in Scheme 2

	$^{31}P\{^1H\}$ NMR (ppm) [$CDCl_3$]		
Ligand	PR_2CH_2OH	Ligand	Borane adduct
6: R = Ph	−10.1	−21.3	—
7: R = Cy	1.4	−10.1	41.9
8: R = ^{t}Bu	20.3	17.2	25.0

Table 2 $^{31}P\{^1H\}$ NMR and aromatic proton chemical shifts for the free ligands and palladium complexes **9**, **10** and **11**

		$^{1}H\}$ NMR (ppm)							$^{1}H\}$ NMR (ppm)					
Ligand	$^{31}P\{^1H\}$NMR (ppm)	a	b	c	d	e	f	Complex	$^{31}P\{^1H\}$	a	b	c	d	e	f
6: R = Ph	−21.3	8.21	6.56	7.42	6.52	4.51	2.93	**9**: R = Ph	26.0	9.32	6.89	7.74	6.95	3.53	2.94
7: R = Cy	−10.1	8.12	6.53–6.46	7.40	6.53–6.46	3.95	3.05	**10**: R = Cy	50.0	9.20	6.95–6.88	7.74	6.95–6.66	2.99	3.06
8: R = ^{t}Bu	17.2	8.15	6.57–6.43	7.40	6.57–6.43	4.10	3.08	**11**: R = ^{t}Bu	64.1	9.17	6.88	7.74	6.93	3.22	3.29

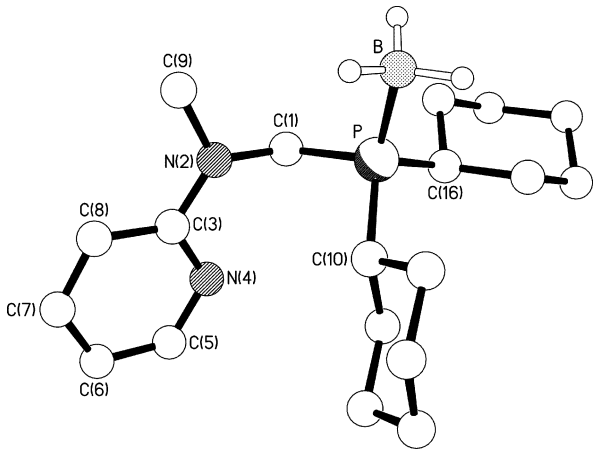
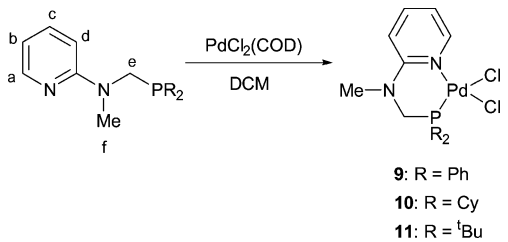


Fig. 1 The molecular structure of borane adduct **7a**.

Coordination to palladium(II)

To investigate the chelating ability of ligands **6**, **7** and **8**, they were stoichiometrically reacted with $PdCl_2(COD)$ affording the Pd(II) species as shown in Scheme 3. In each case the ligand chelated to the metal centre to form the expected six-membered chelate rings. This was evidenced by the characteristic downfield shifts observed in the $^{31}P\{^1H\}$ NMR spectra of all three complexes **9**, **10** and **11** upon coordination to the palladium centre. Coordination of the pyridine nitrogen of the ligands to palladium was observed in the ^1H NMR spectra of the complexes. The proton *ortho* to the pyridine nitrogen was significantly shifted downfield relative to that of the free ligand owing to donation of electron density from the aromatic ring to the metal centre. The $^{31}P\{^1H\}$ NMR and ^1H NMR chemical shifts of the free ligands and complexes are summarised in Table 2.



Scheme 3 Coordination of ligands to palladium(II).

Notably, there is a considerable upfield chemical shift, of approximately 1 ppm, for the methylene protons of all three ligands upon complexation to palladium. This may be explained by the increase in shielding of these protons by the lone pair on the nitrogen as a result of chelation to palladium. In the free ligand there is greater rotational freedom about the N–CH_2P bond which would result in decreased shielding and explain their downfield chemical shift relative to the complex.

Single crystals suitable for X-ray diffraction analysis of complex **10** were obtained by layering a dichloromethane (DCM) solution of **10** with diethyl ether. The crystal structure of **10** (Fig. 2, Table 3) shows the expected chelating mode of the ligand bonding to the palladium *via* the pyridyl nitrogen and phosphine group.

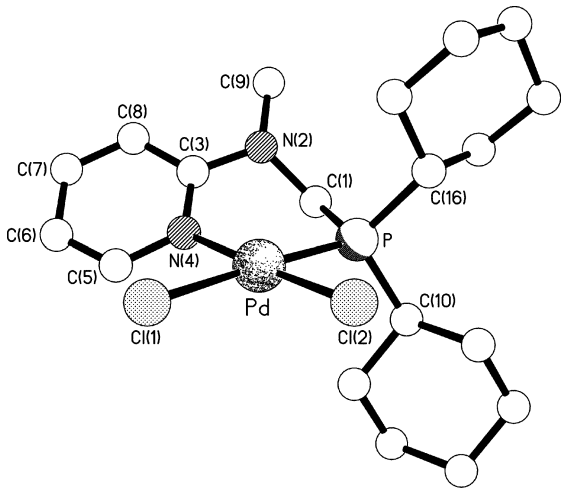


Fig. 2 The molecular structure of complex **10**.

In order to chelate to the palladium centre the ligand has twisted about the C(1)–N(2) bond such that the P–C(1)–N(2)–C(3) dihedral angle is *ca.* 83°, *cf.* 107° in the free ligand **7a** (*vide supra*). The six-membered chelate ring has a twisted boat conformation, {C(1),P,Pd,N(4)} being coplanar to within *ca.* 0.04 Å with N(2) and C(3) lying *ca.* 1.07 and 0.73 Å respectively out of this plane on the same side. Interestingly, the coordination of the metal to the pyridyl nitrogen N(4) is noticeably distorted, the metal lying *ca.* 0.83 Å out of the pyridyl ring plane such that the N(4)–Pd vector is inclined by *ca.* 22° to the plane of the ring. Both the conformation of the six-membered ring and the distorted pyridyl coordination are features also seen in the closely related structure *cis*-dichloro-(*N*-(cyclohexyl)-*N*-((diphenylphosphino)methyl)pyridine-2-amine-*N*′,*P*)-palladium(II).[17]

Single crystals of complex **11** suitable for X-ray diffraction were obtained by dissolution of the compound in hot DCM and subsequent slow cooling. The crystal structure of the *t*-butyl complex **11** (Fig. 3, Table 3) is similar to that of its cyclohexyl counterpart **10** (Fig. 2), though notable differences can be seen in the angles at the metal centre. In particular, the P–Pd–Cl(2) angle differs by more than 5° between the two complexes, though there is no obvious reason for this. The ligand is again twisted

Table 3 Comparative selected bond lengths (Å) and angles (°) for **10** and **11**

	10	**11**		**10**	**11**
Pd–P	2.2092(5)	2.2460(3)	Pd–Cl(1)	2.4132(5)	2.3945(4)
Pd–Cl(2)	2.2935(5)	2.2869(4)	Pd–N(4)	2.0995(15)	2.1024(11)
P–Pd–Cl(1)	175.700(17)	177.781(13)	P–Pd–Cl(2)	85.759(19)	91.044(15)
P–Pd–N(4)	92.55(4)	91.80(3)	Cl(1)–Pd–Cl(2)	90.013(19)	87.817(15)
Cl(1)–Pd–N(4)	91.70(4)	89.47(3)	Cl(2)–Pd–N(4)	177.91(4)	175.16(3)

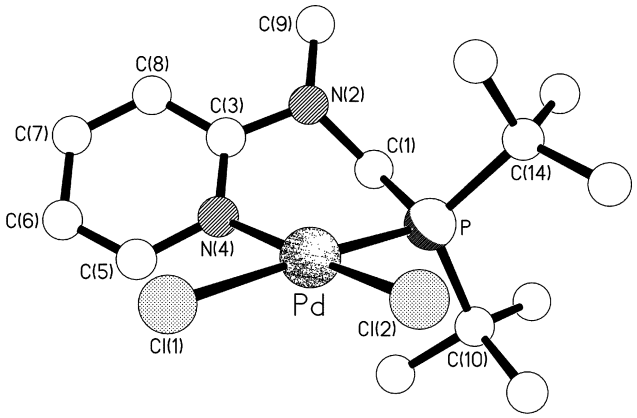


Fig. 3 The molecular structure of complex **11**.

about the C(1)–N(2) bond compared to **7a**, the P–C(1)–N(2)–C(3) dihedral angle being *ca.* 84°, *cf.* 107° in **7a** and 83° in **10**. As was seen in the structure of **10**, the six-membered C_2N_2PPd chelate ring has a twisted boat conformation, {C(1),P,Pd,N(4)} being coplanar to within *ca.* 0.08 Å with N(2) and C(3) lying *ca.* 1.13 and 0.76 Å respectively out of this plane on the same side. The pyridyl coordination is likewise similar, the palladium atom lying *ca.* 0.99 Å out of the pyridyl ring plane (the N(4)–Pd vector is inclined by *ca.* 27° to the plane of the ring).

When the reaction of cyclohexyl ligand **7** (Scheme 4) with $PdCl_2(COD)$, in a 1 : 1 ratio, was carried out at room temperature two peaks were observed in the $^{31}P\{^1H\}$NMR. One peak was a minor product at 50.0 ppm, the chelated product **10**, while a second peak appeared at 17.5 ppm and was suspected to be the non-chelated bis-ligated complex formed by the coordination of two ligands *via* the softer phosphine groups. An approximate bis/mono ligated ratio of 1 : 3 was obtained by integration of the $^{31}P\{^1H\}$ spectrum. Repeating this reaction at a lower temperature of −10 °C gave only the chelate complex **10**; no evidence of a second peak at 17.5 ppm was seen in the ^{31}P NMR spectrum. This suggests that the kinetic product of the reaction is complex **10**, formed at the lower temperature, while a second product, the thermodynamic product, forms when the temperatures are higher. This new complex (**12**) was isolated in its pure form from the reaction mixture as a yellow crystalline solid by layering a DCM solution with diethyl ether. The proton NMR spectrum of **12** showed no changes in chemical shift of the pyridyl protons or of the methylene protons from the free ligand, this indicated that the pyridyl ring remained uncoordinated to the Pd centre. Further evidence for the bis-ligated complex was corroborated by comparing the ^{31}P NMR chemical shift of **12** with the related *trans* complexes $Pd(PCy_3)_2Cl_2$ and $Pd(PCy_2\{allyl\})_2Cl_2$ which have $^{31}P\{^1H\}$ NMR chemical shifts of 24.8 ppm[38] and 19 ppm[39] respectively. Single crystal X-ray analysis of **12** (Fig. 4) confirmed the suspected *trans* bis-ligated complex.

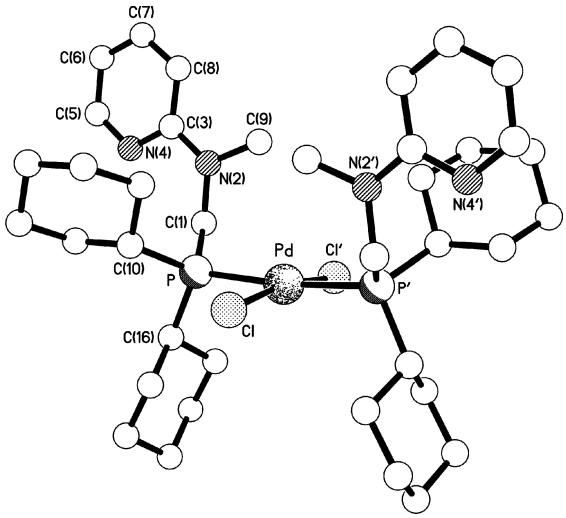
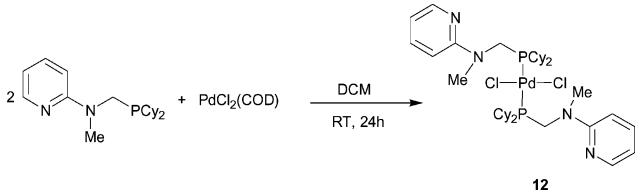


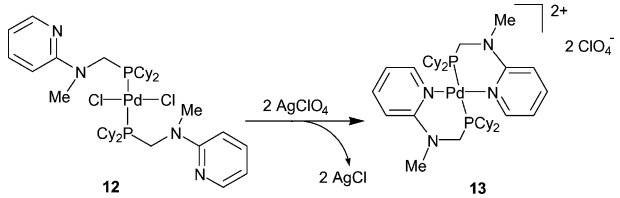
Fig. 4 The molecular structure of the C_2-symmetric complex **12**. Selected bond lengths (Å) and angles (°); Pd–P 2.3376(5), Pd–Cl 2.3048(5); P–Pd–Cl 89.649(18), P–Pd–P′ 173.907(17), P–Pd–Cl′ 90.870(18), Cl–Pd–Cl′ 170.23(2).

Unlike the chelating coordination modes seen in the structures of complexes **10** and **11**, here ligand **7** acts in a monodentate fashion coordinating only *via* the phosphorus donor (Fig. 4). The two ligands are oriented *trans* to each other, presumably a consequence of the steric bulk of the cyclohexyl groups, and it is notable that the Pd–P bond length [2.3376(5) Å] is longer than those seen in the mono-ligated complexes **10** and **11** where the ligand is bidentate [2.2092(5) and 2.2460(3) Å respectively]. The complex has crystallographic C_2 symmetry about an axis that passes through the metal centre perpendicular to the Cl_2P_2Pd plane. This square plane is noticeably distorted, the {Pd,Cl,P} and {Pd,Cl′,P′} planes being twisted with respect to each other by *ca.* 12°. Not being forced into a chelate ring, the P–C(1)–N(2)–C(3) dihedral angle is enlarged to *ca.* 124°. This is even larger than that seen in the crystal structure of borane adduct **7a** [107°], and may in part be associated with a short intermolecular C–H · · · π approach to the pyridyl ring from a methyl proton on C(9) of an adjacent molecule [see ESI‡ for more details].

When the bis-ligated complex **12**, which has two free uncoordinated pyridyl groups, was reacted with two equivalents of silver perchlorate, the two chloride ions were abstracted from the palladium centre resulting in the coordination of the pyridyl groups to the metal centre (Scheme 5). Evidence for the coordination of the pyridyl groups was given by the IR stretching frequency of the pyridyl ring which displayed a characteristic



Scheme 4 Formation of the bis-ligated complex **12**.



Scheme 5 Formation of the bis-chelate complex **13**.

Table 4 Chemical shifts of complexes **12**, **13** and **14**

		^{1}H NMR (ppm)					
Complex	^{31}P{^{1}H} NMR	a	b	c	d	e	f
12	17.5	8.18	6.65–6.51	7.48	6.65–6.51	4.48	3.29
13	55.9	7.38	6.62	7.81	7.26	3.70	3.31
14	30.8	7.86	6.64	7.73	7.06	4.45	3.22

shift to higher wavenumbers[40,41] (1605 cm^{-1}) compared to the free ligand (1594 cm^{-1}). The ^{31}P NMR spectrum (Table 4) showed a distinct downfield chemical shift from 17.5 ppm (complex **12**) to 55.9 ppm for the phosphine resonance upon ligation of the pyridyl groups. The ^{1}H NMR spectrum of the bis-chelate complex **13** displayed characteristic downfield chemical shifts for the pyridyl protons except for a marked and unexpected upfield chemical shift for the *ortho* protons (7.38 ppm) relative to the free ligand (8.12 ppm). This upfield shift of the *ortho* pyridyl protons can be explained by the increase in electron density on the palladium centre resulting from the coordination of two electron rich dicyclohexyl phosphine groups. The methylene protons resonance of the bis-chelate complex **13** are noticeably broadened at ambient temperature compared to the monochelate palladium dichloride complex **10** which show a sharp doublet resulting from coupling to the phosphorus atom. The broadening of the methylene protons in **13** indicates a fluxional conformation change of these protons occurring on the NMR timescale. Variable temperature ^{1}H NMR (Fig. 5) of complex **13** revealed an approximate coalescence temperature of 273 K, which corresponds to a Gibbs free energy of activation of 48.7 kJ mol^{-1} for this process from the Eyring equation. Further cooling of the sample revealed the splitting of this signal into two pseudo triplets (overlapping dd) at 3.8 ppm and 3.2 ppm which are the result of the 'freezing-out' of two distinct chemical environments for these methylene protons. A marked upfield chemical shift of the pyridyl *ortho* protons from 7.38 ppm at 293 K to 7.07 at 193 K was also observed which further supports a conformation change.

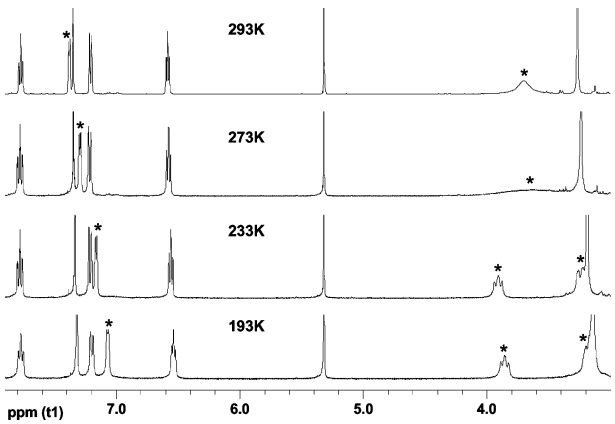
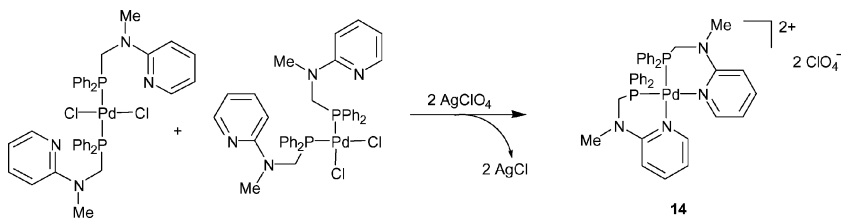


Fig. 5 Variable temperature (293 K to 193 K) ^{1}H NMR of complex **13** run in CD_2Cl_2. * indicates that these protons behave fluxionally and that the peaks change with temperature.

The attempted preparation of the analogous complex L_2PdCl_2 complex using the diphenylphosphino ligand **6** resulted in the formation of a mixture of *cis* and *trans* isomers, as might be expected,[42] appearing at 25.6 ppm and 10.0 ppm respectively in the ^{31}P{^{1}H} NMR ($CDCl_3$) spectrum. An approximate *cis* : *trans* ratio of 5 : 1 was obtained based on ^{31}P{^{1}H} NMR integration which showed no change when heated (50 °C) in a sealed NMR tube for 24 h; confirming a thermodymanic equilibrium. Abstraction of the chlorides using silver perchlorate initially gave a mixture of isomers; evaporation of the sample followed by recrystallisation from hot DCM resulted in the isolation of the *cis* isomer of the bis-chelate complex (Scheme 6). This was indicated by a single resonance in the ^{31}P NMR spectrum that was markedly shifted downfield to 30.8 ppm, relative to the non-chelated *cis* complex. The ^{1}H NMR spectrum of the bis-chelate complex **14** again showed distinct changes in the pyridyl proton resonances, relative to the free ligand, indicating coordination of the pyridyl ring. There was a general downfield shift of the pyridyl resonances on coordination except for the *ortho* proton (a), which again was unexpectedly shifted to an upfield position (7.86 ppm) compared to the free ligand (8.21 ppm). The IR spectrum, again, undoubtedly confirmed coordination of the pyridyl ring which displayed a characteristic stretch at 1608 cm^{-1} compared to the free ligand 1593 cm^{-1}. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution.

Single crystal X-ray diffraction of crystals of **14** showed the expected bis-chelate dicationic complex having two *N,P* ligands coordinating to a square planar palladium centre (Fig. 6, Table 5). The square plane is distorted, the two {Pd,P,N} coordination planes being twisted with respect to each other by *ca.* 11°. The complex has approximate C_2 symmetry about an axis that passes through the metal centre and bisects the P(1)–Pd–P(31) and



Scheme 6 Formation of the bis-chelate complex **14**.

Table 5 Selected bond lengths (Å) and angles (°) for **14**

Pd–P(1)	2.2319(7)	Pd–N(4)	2.100(2)
Pd–P(31)	2.2411(7)	Pd–N(34)	2.112(2)
P(1)–Pd–N(4)	81.06(7)	P(1)–Pd–P(31)	99.73(3)
P(1)–Pd–N(34)	168.09(7)	N(4)–Pd–P(31)	172.93(7)
N(4)–Pd–N(34)	90.76(9)	P(31)–Pd–N(34)	89.46(6)

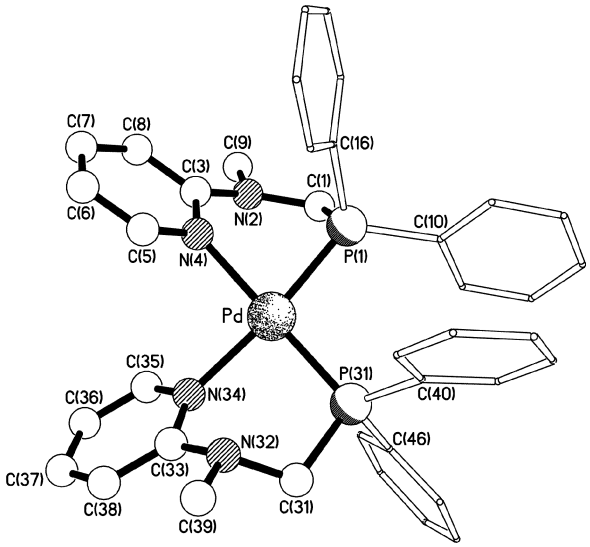


Fig. 6 The molecular structure of the dication in **14**.

N(4)–Pd–N(34) angles. The main departure from C_2 symmetry is in the two six-membered C_2N_2PPd chelate rings. The P(1)/N(4) ring has a twisted boat conformation, {P(1),C(1),N(2),C(3)} being coplanar to within *ca.* 0.02 Å with N(4) and Pd lying *ca.* 0.59 and 1.79 Å respectively out of this plane on the same side. The conformation of the P(31)/N(34) chelate ring is much nearer to an ideal boat; {Pd,N(32),C(33),N(34)} is coplanar to within *ca.* 0.08 Å with P(31) and C(31) lying *ca.* 1.33 and 1.49 Å respectively out of this plane on the same side. In fact, these two atoms are almost coplanar with the metal and N(32), the maximum deviation from planarity for {Pd,P(31),C(31),N(32)} being *ca.* 0.16 Å. This difference in conformation can be readily seen by comparing the P–C–N–C dihedral angles; the P(1)–C(1)–N(2)–C(3) dihedral angle is *ca.* 3° whilst that for P(31)–C(31)–N(32)–C(33) is *ca.* 79°. Whilst the latter is comparable to those seen in **10** and **11** [83 and 84° respectively] the former is vastly different to those seen in any of the other structures.

Another difference between this structure and the structures of **10** and **11** is the coordination behaviour of the pyridyl rings. Here in **14** the metal is much closer to being coplanar with the pyridyl rings, being *ca.* 0.32 Å out of the N(4) ring plane [N–Pd vector inclined by *ca.* 8° to the plane of the ring] and *ca.* 0.45 Å out of the N(34) ring plane [N–Pd vector inclined by *ca.* 12° to the plane of the ring]; in **10** and **11** the vectors were inclined by *ca.* 22 and 27° respectively. In the structure of the related literature species bis((5-chloropyrid-2-ylaminomethyl)diphenylphosphine-*N,P*)-platinum(II) bis(tetrafluoroborate) the two six-membered chelate rings have very similar sofa conformations with the phosphorus folded out of the C_2N_2Pt plane in each case.[14]

In summary a series of new *N,P* ligands have been synthesised and shown to chelate to a palladium(II) by both the phosphorus and the nitrogen atoms. The sterically demanding dicyclohexylphosphino ligand **7** was demonstrated to form both mono-chelate and *P*-bound bis-ligated mondentate Pd(II) complexes depending on the reaction temperature. A novel bis-chelate complex **13** was formed when the chloride ions were abstracted from the dicyclohexyl bis-ligated complex **12** resulting in coordination of the pyridyl groups to the Pd(II) centre. A *trans* geometry was assigned to complex **13** based on the geometry of the precursor **12** and chemical shifts of comparable *trans* cyclohexylphosphino Pd(II) complexes found in the literature. The synthesis of related bis-chelate complex **14** using the diphenylphosphino ligand **6** gave exclusively the *cis* isomer, as characterised by X-ray crystallography. The well documented steric interactions of the much bulkier cyclohexylphosphino ligand are the likely cause of the predominance of the *trans* isomer for complex **13**. We are currently investigating the role of these ligands for creating heterogeneous mixed metal species and in catalytic C–C, C–N and C–O bond forming reactions.

Experimental

General considerations

All preparations were carried out using standard Schlenk line techniques under an inert atmosphere of N_2 unless otherwise stated. Solvents were dried over standard drying agents and freshly distilled under nitrogen before use. All starting materials were of reagent grade, purchased from either Aldrich Chemical Company or Acros Organics. Chromatographic separations were carried out on Kieselgel 60 SiO_2. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Jeol JNM-Ex 270 MHz FT spectrometer or on Bruker Av-400, DRX-400, Av-500 spectrometers. Variable temperature ^1H NMR spectra were run on a Bruker DRX-400 MHz spectrometer. Chemical shifts are reported in ppm using the residual proton impurities in the solvents. Pseudo-triplets which occur as a result of identical *J*-value coupling to two chemically inequivalent protons are assigned as dd and are recognised by the inclusion of only one *J*-value. Positive-ion FAB and electron ionisation mass spectra were recorded on a Micromass Autospec Q spectrometer using a 3-nitrobenzyl alcohol matrix. Electron ionisation was carried out at 70 eV. Infrared spectra were recorded on a Perkin-Elmer 983G spectrophotometer equipped with a Perkin-Elmer 3700 data station and recorded as either KBr pressed discs or Nujol mulls. Elemental analyses were carried out by Mr Stephen Boyer of the Department of Health and Human Sciences, London Metropolitan University. X-Ray diffraction analysis was carried out by Dr Andrew White of the Department of Chemistry at Imperial College London.

Synthesis of [(diphenylphosphino)methyl]-methyl-pyridin-2-ylamine, 6

To a solution of bis(hydroxymethyl)phosphonium chloride (0.5 g, 1.76 mmol) in methanol (10 ml) was added trimethylamine (234 µl, 1.76 mmol) and 2-(methylamino)pyridine (180 µl, 1.76 mmol) and brought to reflux for 1 h. After this time, methanol was removed *in vacuo* and diethyl ether added (20 ml) to extract the product.

The ether solution was filtered, *via* cannula, into a separate flask and the ether removed *in vacuo* to yield a white solid (0.50 g, 93%). Anal.: Calc. for $C_{19}H_{19}N_2P$: C, 74.5; H, 6.3; N, 9.1. Found: C, 74.6; H, 6.3; N, 9.1%. IR (ν/cm^{-1}) KBr: 1593 s (Py). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.21 (dd, 1H, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 2.0$ Hz), 7.62–7.52 (m, 3H, Ar–*H*), 7.42 (ddd, 1H, $^3J_{HH} = 8.6$ Hz, $^3J_{HH} = 7.2$ Hz $^4J_{HH} = 1.9$ Hz, Ar–*H*), 7.40–7.31 (m, 7 H, Ar–*H*), 6.56 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 4.9$ Hz, Ar–*H*), 6.52 (d, 1H, $^3J_{HH} = 8.7$ Hz, Ar–*H*), 4.51 (d, 2 H, $^2J_{PH} = 3.94$ Hz, C*H*$_2$P), 2.93 (s, 3H, C*H*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 109 MHz): δ −21.3. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 158.0 (s, Ar *C*), 147.7 (s, Ar *C*H), 137.6 (d, $^1J_{PC} = 15.2$ Hz, Ar *C*), 136.9 (s, Ar *C*H), 133.1 (d, $^2J_{PC} = 17.7$ Hz, Ar *C*H), 128.6 (s, Ar *C*H), 128.3 (d, $^3J_{PC} = 7.0$ Hz), 111.7 (s, Ar *C*H), 106.2 (s, Ar *C*H), 52.4 (d, $^1J_{PC} = 10.2$ Hz, *C*H$_2$), 37.3 (d, $^3J_{PC} = 3.5$ Hz, *C*H$_3$). EI-MS: *m*/*z* (%): 121 (100) [$C_7H_9N_2^+$], 322 (10) [$C_{19}H_{19}N_2PO^+$].

Synthesis of dicyclohexylphosphinomethyl-methyl-pyridin-2-ylamine, 7

To a Schlenk flask was added dicyclohexyl(hydroxymethyl)-phosphonium chloride (0.25 g, 0.85 mmol) and dry, degassed methanol (7 ml). Et_3N was added (0.118 ml, 0.85 mmol) and the mixture heated under reflux for 2 h. After cooling, *N*-methyl-2-aminopyridine (0.087 ml, 0.85 mmol) was added and the mixture heated under reflux overnight. Following this, the solvents were removed *in vacuo* and dry, degassed diethyl ether added (50 ml) to dissolve the ligand. Following cannula filtration under N_2 into another Schlenk flask the ether was removed *in vacuo* to give a viscous colourless oil. The ^{31}P{^{1}H} NMR spectrum of this crude product contained a mixture of the desired compound **7** and dicyclohexylphosphinomethanol starting material. The borane protection and purification steps are described below.

Synthesis of di-*tert*-butylphosphinomethyl-methyl-pyridin-2-yl-amine, 8

Procedure was analogous to that described for compound **7**.

Synthesis of the borane adduct of dicyclohexylphosphinomethyl-methyl-pyridin-2-yl-amine, 7a

The borane protection procedure described here is similar to that used by Hii *et al.*[36] To a solution of the ligand in dry, degassed diethyl ether (60 ml) was added borane–dimethyl sulfide complex (4.12 ml, 8.24 mmol) drop-wise and the mixture stirred overnight. The ether was removed *in vacuo* to give a viscous oil. Following flash column chromatography (2 : 1 petroleum ether 40–60 °C–diethyl ether) and recrystallisation from hot ethanol, the product was obtained as colourless crystals (0.50 g, 22%), Anal.: Calc. for $C_{15}H_{30}PBN_2$: C, 64.30; H, 10.79; N, 10.00. Found: C, 64.45; H, 10.69; N, 10.07%. IR (ν/cm^{-1}) (Nujol): 2364, 2339 ($\nu_{B\text{-}H}$). ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.15 (d, 1H, $^2J_{HH} = 2.97$ Hz, Ar–*H*), 7.47 (dd, 1H, $^2J_{HH} = 6.89$ Hz, Ar–*H*), 6.67–6.52 (m, 2H, Ar–*H*), 4.56 (d, 2 H, $^2J_{PH} = 3.21$ Hz, C*H*$_2$P), 3.12 (s, 3H, C*H*$_3$), 1.30 (d, 18 H, $^3J_{PH} = 12.1$ Hz, ^{t}Bu-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 158.2 (s, Ar *C*), 147.3 (s, Ar *C*H), 137.5 (s, Ar *C*H), 112.3 (s, Ar *C*H), 105.8 (s, Ar *C*H), 40.0 (d, $^1J_{PC} = 37.7$ Hz, *C*H$_2$), 38.5 (s, *C*H$_3$), 31.2 (d, $^1J_{PC} = 29.7$ Hz, Cy *C*H), 26.9 (m, Cy *C*H$_2$), 26.0 (s, Cy *C*H$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ 41.9 (m). EI-MS: *m*/*z* 121 (100) [$C_7H_9N_2^+$], 332 (9) [$C_{19}H_{34}N_2PB^+$].

Synthesis of the borane adduct of di-*tert*-butylphosphinomethyl-methyl-pyridin-2-yl-amine, 8a

To a stirred solution of compound **8** (0.49 g, 1.70 mmol) in EtOH (15 ml) was added borane–dimethyl sulfide complex in THF (0.85 ml, 1.70 mmol) drop-wise. The mixture was stirred overnight and the solvent removed *in vacuo*. A white solid formed (0.27 g, 53%) which was recrystallised from hot ethanol to give white needle-like crystals (0.163 g, 32%). Anal.: Calc. for $C_{19}H_{34}PBN_2$: C, 68.68; H, 10.31; N, 8.43. Found: C, 68.75; H, 10.38; N, 8.55%. IR (ν/cm^{-1}) (Nujol): 2383, 2352 ($\nu_{B\text{-}H}$). ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.11 (d, 1H, $^3J_{HH} = 3.21$ Hz, Ar–*H*), 7.47 (dd, 1H, $^3J_{HH} = 7.8$ Hz, Ar–*H*), 6.54–6.50 (m, 2H, Ar–*H*), 4.30 (d, 2 H, $^2J_{H\text{-}P} = 3.0$ Hz, C*H*$_2$P), 3.12 (s, 3H, C*H*$_3$), 1.99–1.14 (m, 22H, Cy-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 158.4 (s, Ar *C*), 147.2 (s, Ar *C*H), 137.6 (s, Ar *C*H), 112.3 (s, Ar *C*H), 106.5 (s, Ar *C*H), 39.8 (d, $^1J_{PC} = 35.7$ Hz, *C*H$_2$), 38.4 (s, *C*H$_3$), 32.5 (d, $^1J_{PC} = 24.1$ Hz, *t*-Bu *C*), 28.2 (s, *t*-Bu *C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ 25.0 (m). EI-MS: *m*/*z* 279 (100) [$C_{15}H_{26}N_2PB^+$].

Deprotection of borane salts

Procedure as described by Trost *et al.*[37] Fluoroboric acid dimethyl ether complex (0.7 ml, 5.83 mmol) was added to a stirred solution of the borane salt **7a** (0.25 g, 0.76 mmol) in dry, degassed DCM (15 ml) at −15 °C. The reaction mixture was stirred overnight and allowed to warm to ambient temperature. The reaction mixture was diluted with dry, degassed DCM (15 ml), and degassed saturated $NaHCO_3$ solution (25 ml). Following a further 20 min of vigorous stirring, the aqueous phase was extracted twice with degassed DCM (2 × 20 ml), and the combined organic extracts washed with brine and dried over $MgSO_4$. The solvents were evaporated to give ligand **7** as a viscous air sensitive colourless oil (0.13 g, 55%) ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.12 (dd, 1H, $^3J_{HH} = 4.7$ Hz, $^4J_{HH} = 1.8$ Hz, Ar–*H*), 7.40 (td, 1H, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.9$ Hz, Ar–*H*), 6.53–6.46 (m, 2H, Ar–*H*), 3.95 (d, 2 H, $^2J_{PH} = 2.70$ Hz, C*H*$_2$P), 3.05 (s, 3H, C*H*$_3$), 1.80–1.20 (m, 22H, Cy–*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ −10.1.

The deprotection of borane salt **8a** was carried out using the same method to give ligand **8** as a viscous air sensitive colourless oil (0.21 g, 38%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.15 (dd, 1H, $^3J_{HH} = 4.9$ Hz, $^4J_{HH} = 1.5$ Hz, Ar–*H*), 7.40 (td, 1H, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 2.0$ Hz, Ar–*H*), 6.57–6.43 (m, 2H, Ar–*H*), 4.10 (d, 2 H, $^2J_{PH} = 1.7$ Hz, C*H*$_2$P), 3.08 (s, 3H, C*H*$_3$), 1.17 (d, 18 H, $^3J_{PH} = 10.9$ Hz, ^{t}Bu-*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ 17.2.

Synthesis of [(diphenylphosphino)-methyl]-methyl-pyridin-2-yl-amine palladium dichloride, 9

To a solution of ligand **6** (0.4 g, 1.30 mmol) in dichloromethane (5 ml) was added a solution of $PdCl_2$(COD) (0.37 g, 1.30 mmol) in dichloromethane (20 ml) and stirred for 1 h at room temperature. Dichloromethane was removed under reduced pressure to yield a yellow solid (0.61 g, 97%). Anal.: Calc. for $C_{19}H_{19}Cl_2N_2PPd$: C, 47.18; H, 3.96; N, 5.79. Found: C, 47.25; H, 3.95; N, 5.70%. IR (ν/cm^{-1}) KBr: 1603 s (Py). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 9.32 (dd, 1H, $^3J_{HH} = 6.2$ Hz, $^4J_{HH} = 1.7$ Hz, Ar–*H*), 8.02–7.92 (m,

4H, Ar–*H*), 7.74 (ddd, 1H, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HH}$ = 7.2 Hz $^{4}J_{HH}$ = 1.9 Hz, Ar–*H*), 7.62–7.45 (m, 6H, Ar–*H*), 6.95 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz, Ar–*H*), 6.89 (dd, 1H, $^{2}J_{HH}$ = 5.9 Hz, Ar–*H*), 3.53 (d, 2 H, $^{2}J_{PH}$ = 3.7 Hz, CH_2P), 2.94 (s, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 109 MHz): δ 26.0. FAB-MS: *m*/*z* (%) : 121 (100) [$C_7H_9N_2^+$], 447 (30) [$C_{19}H_{19}ClN_2PPd^+$].

Synthesis of [dicyclohexylphosphinomethyl-methyl-pyridin-2-yl-amine] palladium dichloride, 10

To a Schlenk flask was added $PdCl_2$(COD) (0.12 g, 0.42 mmol) and a magnetic stirrer bar. DCM (10 ml) was added and the mixture stirred until the palladium complex had dissolved. This solution was transferred by cannula into a second Schlenk flask containing ligand **7** (0.12 g, 0.42 mmol) at −10 °C. The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* yielding a yellow solid. Following recrystallisation from DCM–diethyl ether, yellow block crystals were obtained (81.5 mg, 0.16 mmol, 42%). Anal.: Calc. for $C_{19}H_{31}N_2PPdCl_2$: C, 46.03; H, 6.30; N, 5.65. Found: C, 45.07; H, 6.50; N, 5.24%. IR (ν/cm^{-1}) (Nujol): 1606 (ν_{Py}). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 9.20 (dd, 1H, $^{3}J_{HH}$ = 6.0 Hz, $^{4}J_{HH}$ = 1.5 Hz, Ar–*H*), 7.74 (td, 1H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.9 Hz, Ar–*H*), 6.95–6.88 (m, 2H, Ar–*H*), 3.06 (s, 3H, CH_3), 2.99 (d, 2 H, $^{2}J_{PH}$ = 3.9 Hz, CH_2P), 2.38–1.26 (m, 22H, Cy-*H*). ^{13}C {^{1}H} NMR ($CDCl_3$, 400 MHz): δ 162.2 (s, Ar *C*), 155.1 (s, Ar *C*H), 140.4 (s, Ar *C*H), 117.0 (s, Ar *C*H), 112.7 (s, Ar *C*H), 41.8 (s with fine, *C*H_2), 41.4 (s, *C*H_3), 33.5 (d, $^{1}J_{PC}$ = 26.9 Hz, Cy *C*H), 28.1 (d, J_{PC} = 14.9 Hz, Cy *C*H_2), 26.6 (t, J_{PC} = 11.7 Hz, Cy *C*H_2), 25.8 (s, Cy *C*H_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ 50.0. FAB MS: *m*/*z* 121 (100) [$C_7H_9N_2^+$], 461 (87) [$C_{19}H_{31}N_2$-$PPdCl^+$].

Synthesis of [di-*tert*butylphosphinomethyl-methyl-pyridin-2-yl-amine] palladium dichloride, 11

Procedure followed as for compound **10**. After the reaction mixture had been stirred overnight in DCM an insoluble precipitate had formed. Solvents were removed *in vacuo* to give a crude yellow solid (0.43 g). Recrystallisation from hot acetonitrile gave yellow cubic crystals on cooling (0.216 g, 53%). Anal.: Calc. for $C_{15}H_{27}N_2PCl_2Pd$: C, 40.61; H, 6.13; N, 6.31. Found: C, 40.59; H, 6.20; N, 6.39%. IR (ν/cm^{-1}): 1605.8. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 9.17 (dd, 1H, $^{3}J_{HH}$ = 6.0 Hz, $^{4}J_{HH}$ = 1.7 Hz, Ar–*H*), 7.74 (td, 1H, $^{3}J_{HH}$ = 1.7 Hz, $^{4}J_{HH}$ = 7.9 Hz, Ar–*H*), 6.93 (d, 1H, $^{3}J_{HH}$ = 8.5 Hz, Ar–*H*), 6.88 (td, 1H, $^{3}J_{HH}$ = 6.9 Hz $^{4}J_{HH}$ = 1.0 Hz, Ar–*H*), 3.22 (d, 2 H, $^{2}J_{PH}$ = 2.9 Hz, CH_2P), 3.11 (s, 3H, CH_3), 1.64 (d, 9H, $^{3}J_{PH}$ = 14.4 Hz, ^{t}Bu-*H*). ^{13}C {^{1}H} NMR ($CDCl_3$, 400 MHz): δ 163.0 (s, Ar *C*), 155.3 (s, Ar *C*H), 140.3 (s, Ar *C*H), 116.2 (s, Ar *C*H), 111.4 (s, Ar *C*H), 43.7 (d, $^{1}J_{PC}$ = 33.5 Hz, *C*H_2), 40.9 (s with fine, *C*H_3), 38.1 (d, $^{1}J_{PC}$ = 16.9 Hz, *t*-Bu *C*), 30.4 (s, *t*-Bu *C*H_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ 64.1. FAB MS: *m*/*z* 450 (100) [$C_{15}H_{27}N_2PCl_2Pd^+$], 407 [$C_{15}H_{27}N_2PClPd^+$].

Synthesis of bis[cyclohexylphosphinomethyl-methyl-pyridin-2-yl-amine] palladium dichloride, 12

Procedure followed as for compound **10** with stirring overnight at 40 °C. The product was obtained as yellow needle-like crystals by layering a DCM solution with diethyl ether (0.1 g, 0.12 mmol, 26%). Anal.: Calc. for $C_{38}H_{62}Cl_2N_4P_2Pd$: C, 56.1; H, 7.7; N, 6.9. Found: C, 55.9; H, 7.7; N, 6.7%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.18 (d, 2 H, $^{3}J_{HH}$ = 4.9 Hz, Ar–*H*), 7.48 (dd, 2 H, $^{3}J_{HH}$ = 7.4 Hz, Ar–*H*), 6.58–6.51 (m, 4H, Ar–*H*), 4.48 (s, 4H, CH_2), 3.29 (s, 6H, CH_3), 2.36, 0.85 (m, 44H, Cy-*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 270 MHz): δ 17.5. FAB MS: *m*/*z* 779 (50) [$C_{38}H_{62}N_4P_2ClPd^+$].

Synthesis of bis-chelate palladium complex [Pd{$PCy_2CH_2N(CH_3)C_5H_4N$}$_2$] [ClO_4]$_2$, 13

To a solution of complex **12** (50 mg, 0.06 mmol) in dichloromethane (3 ml) was added silver perchlorate (25 mg, 0.12 mmol) and stirred for 48 h at room temperature in darkness. The solution was then filtered through a pad of Celite and evaporated to dryness. Crystals were obtained after 2 d when a solution of the complex (0.03 M) in dichloromethane was layered with benzene. The crystals were collected, filtered off, washed with diethyl ether and dried *in vacuo* (41 mg, 72%). Anal.: Calc. for $C_{38}H_{62}Cl_2N_4O_8P_2Pd$: C, 48.44; H, 6.63; N, 5.95. Found: C, 48.34; H, 6.62; N, 5.91%. IR (cm^{-1}) KBr: 1605 m (py). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.81 (ddd, 2 H, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 7.3 Hz $^{4}J_{HH}$ = 1.7 Hz, Ar–*H*), 7.38 (d, 2 H, $^{3}J_{HH}$ = 4.0 Hz, Ar–*H*), 7.26 (d, 2 H, $^{3}J_{HH}$ = 8.7 Hz, Ar–*H*), 6.23 (dd, 2 H, $^{3}J_{HH}$ = 6.5 Hz, Ar–*H*), 3.70 (s, br, 4H, CH_2P), 3.31 (s, 6H, CH_3), 2.45–1.20 (m, 44H, Cy-*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2 162 MHz): δ 55.9. FAB-MS: *m*/*z* (%): 121 (100) [$C_7H_9N_2^+$], 743 (80) [$C_{38}H_{62}N_4P_2Pd^+$], 843 (10) [{$C_{38}H_{62}N_4P_2Pd(ClO_4)$}$^+$].

Synthesis of bis-chelate palladium complex [Pd{$PPh_2CH_2N(CH_3)C_5H_4N$}$_2$] [ClO_4]$_2$, 14

To a solution of the ligand **6** (200 mg, 0.64 mmol) in dichloromethane (5 ml) was added $PdCl_2$(COD) (92 mg, 0.32 mmol) in dichloromethane (5 ml) and stirred at room temperature for 1 h. Silver perchlorate (133 mg, 0.64 mmol) was then added and stirred for 48 h at room temperature in darkness. The solution was then filtered through a pad of Celite and evaporated to dryness (130 mg, 44%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution. Anal.: Calc. for $C_{38}H_{38}Cl_2N_4O_8P_2Pd$: C, 49.72; H, 4.17; N, 6.10. Found: C, 49.75; H, 4.12; N, 5.93%. IR (ν/cm^{-1}) KBr: 1608 s (py). ^{1}H NMR (CD_3CN, 400 MHz): δ 7.86 (d, 2 H, $^{3}J_{HH}$ = 5.9 Hz, Ar–*H*), 7.73 (ddd, 2 H, $^{3}J_{HH}$ = 8.8 Hz, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 1.7 Hz, Ar–*H*), 7.58–7.54 (m, 4H, Ar–*H*), 7.42–7.34 (m, 16H, Ar–*H*), 7.06 (d, 2 H, $^{3}J_{HH}$ = 8.8 Hz, Ar–*H*), 6.64 (dd, 2 H, $^{3}J_{HH}$ = 6.4 Hz, Ar–*H*), 4.45 (d, 4H, $^{2}J_{PH}$ = 5.6 Hz, CH_2P), 3.22 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (CD_3CN 162 MHz) δ 30.8. FAB-MS: *m*/*z* (%): 323 (100) [$C_{19}H_{19}N_2PO^+$], 719 (65) [$C_{38}H_{38}NP_2Pd^+$], 918 (10) [{$C_{38}H_{38}NP_2Pd(ClO_4)$}$^+$].

X-Ray crystallography

Table 6 provides a summary of the crystallographic data for compounds **7a**, **10**, **11**, **12** and **14**. Data were collected using Oxford Diffraction PX Ultra (**7a** and **14**) and Xcalibur 3 (**10**, **11** and **12**) diffractometers, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[43] The B–H protons in the structure of **7a** were found from ΔF maps and refined with free isotropic thermal parameters subject to a B–H distance constraint of 1.10 Å.

Table 6 Crystal data, data collection and refinement parameters for compounds **7a**, **10**, **11**, **12** and **14**[a]

	7a	**10**	**11**	**12**	**14**
Formula	$C_{19}H_{34}BN_2P$	$C_{19}H_{31}Cl_2N_2PPd$	$C_{15}H_{27}Cl_2N_2PPd$	$C_{38}H_{62}Cl_2N_4P_2Pd$	$[C_{38}H_{38}N_4P_2Pd](ClO_4)_2$
Solvent	—	CH_2Cl_2	—	—	CH_2Cl_2
Formula weight	332.26	580.65	443.66	814.16	1002.89
Colour, habit	Colourless prismatic needles	Yellow blocks	Yellow prisms	Yellow needles	Pale yellow blocks
Crystal size/mm	0.26 × 0.15 × 0.14	0.30 × 0.22 × 0.09	0.29 × 0.25 × 0.19	0.44 × 0.08 × 0.07	0.21 × 0.17 × 0.16
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a/Å	13.6292(13)	11.5230(13)	8.5961(13)	21.171(4)	9.8852(1)
b/Å	9.5466(7)	15.8628(19)	13.265(2)	20.345(4)	19.9719(1)
c/Å	15.4193(11)	13.3819(12)	16.3961(3)	9.4447(8)	21.56160(1)
β/°	90.817(7)	97.806(8)	105.141(5)	104.668(12)	98.528(1)
V/Å^3	2006.0(3)	2423.4(5)	1804.7(4)	3935.4(11)	4209.76(5)
Z	4	4	4	4[b]	4
D_c/g cm^{-3}	1.100	1.592	1.633	1.374	1.582
Radiation used	Cu-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Cu-Kα
μ/mm^{-1}	1.196	1.283	1.408	0.721	7.086
2θ max/°	141	64	64	64	143
No. of unique refln measured	3706	7934	5755	6437	8162
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	3060	6141	5342	4982	6763
No. of variables	221	254	192	214	566
R_1(obs), wR_2(all)[c]	0.039, 0.117	0.034, 0.096	0.021, 0.052	0.029, 0.076	0.031, 0.084

[a] Details in common: 173 K, graphite monochromated radiation, refinement based on F^2. [b] The molecule has crystallographic C_2 symmetry. [c] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Acknowledgements

We would like to thank the Wellcome Trust for providing a VIP award (PWM).

References

1 Z.-Z. Zhang and H. Cheng, *Coord. Chem. Rev.*, 1996, **147**, 1–39.
2 G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067–2089.
3 P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193**, 499–556.
4 A. Dervisi, P. G. Edwards, P. D. Newman and R. P. Tooze, *J. Chem. Soc., Dalton Trans.*, 2000, 523–528.
5 A. Dervisi, P. G. Edwards, P. D. Newman, R. P. Tooze, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1999, 1113–1120.
6 S. E. Durran, M. B. Smith, A. M. Z. Slawin and J. W. Steed, *J. Chem. Soc., Dalton Trans.*, 2000, 2771–2778.
7 S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2000, 2559–2575.
8 M. P. Anderson, C. C. Tso, B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, 1983, **22**, 3267–3275.
9 A. Del Zotto, G. Nardin and P. Rigo, *J. Chem. Soc., Dalton Trans.*, 1995, 3343–3351.
10 W. Seidel and H. Schoeler, *Z. Chem. (Stuttgart, Ger.)*, 1967, **7**, 431.
11 H. Brunner and H. Weber, *Chem. Ber.*, 1985, **118**, 3380–3395.
12 H. H. Wang, A. L. Casalnuovo, B. J. Johnson, A. M. Mueting and L. H. Pignolet, *Inorg. Chem.*, 1988, **27**, 325–331.
13 A. S. C. Chan, C. C. Chen, R. Cao, M. R. Lee, S. M. Peng and G. H. Lee, *Organometallics*, 1997, **16**, 3469–3473.
14 S. J. Coles, S. E. Durran, M. B. Hursthouse, A. M. Z. Slawin and M. B. Smith, *New J. Chem.*, 2001, **25**, 416–422.
15 H. Yang, N. Lugan and R. Mathieu, *Organometallics*, 1997, **16**, 2089–2095.
16 D. V. Griffiths, H. J. Groombridge, P. M. Mahoney, S. P. Swetnam, G. Walton and D. C. York, *Tetrahedron*, 2005, **61**, 4595–4600.
17 H.-B. Song, Z.-Z. Zhang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 2002, 1336–1346.
18 S. Kealey, N. J. Long, P. W. Miller, A. J. P. White, P. B. Hitchcock and A. Gee, *Dalton Trans.*, 2007, 2823.
19 M. J. Green, K. J. Cavell, P. G. Edwards, R. P. Tooze, B. W. Skelton and A. H. White, *Dalton Trans.*, 2004, 3251.
20 J. C. Jeffrey and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658–2666.
21 X. Y. Rueda and S. Castillón, *J. Organomet. Chem.*, 2007, **692**, 1628–1632.
22 A. Ochida, H. Ito and M. Sawamura, *J. Am. Chem. Soc.*, 2006, **128**, 16486–16487.
23 R. B. DeVasher, L. R. Moore and K. H. Shaughnessy, *J. Org. Chem.*, 2004, **69**, 7919–7927.
24 S. L. Parisel, L. A. Adrio, A. A. Pereira, M. M. Perez, J. M. Vila and K. K. Hii, *Tetrahedron*, 2005, **61**, 9822–9826.
25 J. H. Kirchhoff, C. Dai and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 1945–1947.
26 T. Hundertmark, A. F. Littke, S. L. Buchwald and G. C. Fu, *Org. Lett.*, 2000, **2**, 1729–1731.
27 J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 9550–9561.
28 U. Christmann, D. A. Pantazis, J. Benet-Buchholz, J. E. McGrady, F. Maseras and R. Vilar, *J. Am. Chem. Soc.*, 2006, **128**, 6376–6390.
29 T. Schareina and R. Kempe, *Angew. Chem., Int. Ed.*, 2002, **41**, 1521–1523.
30 M. an der Heiden and H. Plenio, *Chem. Commun.*, 2007, 972–974.
31 A. Tewari, M. Hein, A. Zapf and M. Beller, *Tetrahedron*, 2005, **61**, 9705–9709.
32 K. H. Shaughnessy and R. S. Booth, *Org. Lett.*, 2001, **3**, 2757–2759.
33 B. Mohr, D. M. Lynn and R. H. Grubbs, *Organometallics*, 1996, **15**, 4317–4325.
34 T. A. Kirkland, D. M. Lynn and R. H. Grubbs, *J. Org. Chem.*, 1998, **63**, 9904.
35 J. Fawcett, P. A. T. Hoye, R. D. W. Kemmitt, D. J. Law and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1993, 2563–2568.
36 H. Lam, X. Cheng, J. W. Steed, D. J. Aldous and K. K. Hii, *Tetrahedron Lett.*, 2002, **43**, 5875–5877.
37 B. M. Trost, B. Vidal and M. Thommen, *Chem.–Eur. J.*, 1999, **5**, 1055–1069.
38 A. M. Trzeciak, H. Bartosz-Bechowski, Z. Ciunik, K. Niesyty and J. J. Ziółkowski, *Can. J. Chem.*, 2001, **79**, 752–759.
39 T. Bartik and T. Himmler, *J. Organomet. Chem.*, 1985, **293**, 343–351.
40 N. S. Gill, R. H. Nuttall, D. E. Scaife and D. W. A. Sharpe, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79–87.
41 F. R. Hartley, S. G. Murray and A. Wilkinson, *Inorg. Chem.*, 1989, **28**, 549–554.
42 J. A. Rahn, M. S. Holt and J. H. Nelson, *Polyhedron*, 1989, **8**, 897–907.
43 *SHELXTL PC version 5.1*, Bruker AXS, Madison, WI, 1997; G. Sheldrick, *SHELX-97*, University of Göttingen, Göttingen, Germany, 1998.

