Concise syntheses of tridentate PNE ligands and their coordination chemistry with palladium(II) : a solution- and solid-state study†

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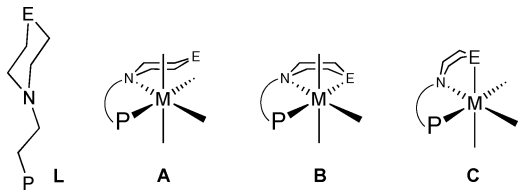
A straightforward methodology for the high-yielding synthesis of the di-functionalised phosphines {$Ph_2P(CH_2)_2NC_4H_8E$, E = NMe (**1**), O (**2**), S (**3**)} *via* base-catalysed Michael addition is described. Reaction of the functionalised tertiary phosphines **1–3** with $PdCl_2(MeCN)_2$ affords complexes in which the ligands are bound in a tridentate fashion, namely [PdCl(κ³-PNE)]Cl (**6a**, **8**) as the predominant products. A κ²-PN coordination mode was also identified crystallographically for ligand **1** following its reaction with $PdCl_2(MeCN)_2$, which afforded [$PdCl_2$(**1**-κ²-PN)] (**6b**) in *ca.* 5% yield. Conductivity studies of solutions of **6a** are consistent with an ionic formulation, however the poor solubility of **7** and **8** precluded their study in a similar fashion. Analysis of bulk samples of [$PdCl_2$(**1**)] (**6**) and [$PdCl_2$(**3**)] (**8**) by ^{15}N and ^{31}P NMR spectroscopy in the solid state as consistent with exclusive tridentate binding of the PNE ligands. An X-ray crystallographic study has probed the coordination of **1** in the unusual salt [PdCl(**1**-κ³-PNN)]$_2$[$Mg(SO_4)_2(OH_2)_4$] (**10**) prepared by treating a methanolic solution of **6** with excess $MgSO_4$. No data could be obtained to support the transformation of **6a** into **6b** on addition of excess chloride. In contrast, **6a** reacts regioselectively with the water-soluble phosphine $Cy_2PCH_2CH_2NMe_3Cl$ to afford the *cis*-diphosphine complex *cis*-[PdCl($Cy_2PCH_2CH_2NMe_3Cl$)(**1**-κ²-PN)]Cl_2 (**9**). Reaction of **1** with PdCl(Me)(COD) results in the formation of the κ²-PN dichloride complex [PdCl(Me)(**1**-κ²-PN)] (**11**). Attempts to prepare [Pd(Me)(MeCN)(**1**-κ²-PN)][PF_6] (**12**) through reaction of **11** with $NaPF_6$ in MeCN led to decomposition. Treatment of $PdMe_2$(TMEDA) with **1** at low temperature initially affords [$PdMe_2$(**1**-κ²-NN)], which isomerises to afford [$PdMe_2$(**1**-κ²-PN)] (**13**); at temperatures greater than 10 °C complex **13** decomposes rapidly.

Introduction

The entropic effects associated with the coordination of multidentate ligands have been long known to direct a metal's coordination number, stoichiometry, stereochemistry and hence reactivity.[1] The potential of such systems has been further extended by the development of so-called 'hybrid' ligands. These combine electronically (and often sterically) disparate binding sites within a single scaffold,[2] and offer significant control over reactions occurring at the metal centre to which they are bound.[3–6] Indeed, 'hybrid' ligand complexes have been exploited to considerable effect in a wide variety of homogeneously-catalysed processes, where their potential to provide a donor moiety that may dissociate/recoordinate in a reversible manner is advantageous.[7–10]



To further maximise the utility of 'hybrid' ligand frameworks, engendering high levels of control over the coordination behaviour of the various donor fragments is essential. One means of achieving this is to design metal scaffolds such as **L** that feature a third, pendant labile donor moiety E (potentially providing reversible coordinative unsaturation at M), *e.g.* **A** *vs.* **B**, in addition to the essential mixed-donor chelate (*e.g.* a κ²-PN unit) that provides electronic control at the metal centre. However, to gain maximum benefit from such ligands, it is crucial that the nature of the κ³-tridentate binding mode of the scaffold remains the same following each cycle of dissociation–reassociation, thereby avoiding the complication of isomerisation within the metal's coordination sphere. To ensure such control, geometric constraints can be imposed upon the system through the inclusion of 'double chelate linkages', such as those provided by piperazine (E = NH) for example, forcing *meridional* coordination **B** over the alternative *facial* geometry **C**.[11–17] Indeed, open-chain and macrocyclic tetraaza ligands that contain a piperazino moiety are known to show enhanced stability to demetallation, as a result of their rigid and pre-defined coordination.[18,19]

Here we report both the preparation of PNE ligands of type **L** and their coordination behaviour with a variety of Pd(II) fragments.

Results and discussion

Ligand syntheses

The acid- or base-catalysed Michael addition of an amine across a vinyl phosphine provides a concise methodology for

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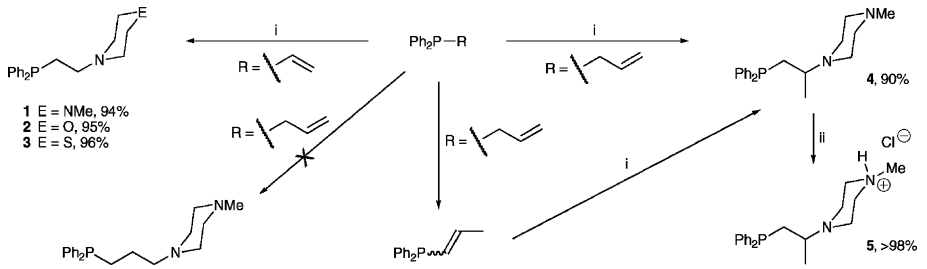


Scheme 1 Reagents and conditions: (i) HNC_4H_8E, cat. $NaNH_2$, THF, reflux, 24 h. (ii) HCl(g), Et_2O, RT.

the preparation of a diverse range of potentially chelating PN ligands.[20,21] Here, this approach has been extended to afford access to potentially tridentate scaffolds that comprise a PN-chelating core bearing a third donor site tethered through a double ethylene bridge.

The desired ligands were synthesised using an extension to Davies' method for the preparation of 2-diphenylphosphinoethylamines.[22] Reaction of diphenylvinylphosphine with an equimolar quantity of the appropriate heterocyclic secondary amine in the presence of a catalytic quantity of $NaNH_2$ in THF afforded the PNE derivatives **1–3** (E = NMe, O,[23] S, respectively) in near-quantitative isolated yields (*ca.* 95%) (Scheme 1). Each compound presents a single, characteristic resonance by ^{31}P NMR spectroscopy (Table 1). This approach is advantageous since it provides direct access to the desired P(III) phosphine-derived ligands, rather than necessitating initial preparation of the phosphine oxide followed by reduction.[21]

The room temperature ^1H NMR spectrum of **1** exhibits extreme line broadening for all methylene resonances (no appreciable line-sharpening was observed on warming the sample to 323 K), as a result of conformational changes and inversion at nitrogen within the heterocyclic ring system.[24] At 223 K ($CDCl_3$) the spectrum is somewhat simplified, but is clearly non-first-order comprising a complex set of five resonances assigned to the CH_2 protons and a singlet for the N–CH_3 group (in addition to phenyl resonances). The complexity of these spectra is enhanced by the asymmetric substitution of the piperazino moiety.[19]

The ambient temperature ^1H NMR spectra for both the morpholine and thiomorpholine derivatives, **2** and **3** respectively, are significantly less broadened than that of **1**, reflecting the differing geometric constraints imposed by each of the heteroatoms N, O and S. Again, neither spectrum is first-order; both compounds **2** and **3** present four sets of methylene resonances in addition to the expected phenyl signals.

The $^{13}C\{^1H\}$ NMR spectra for compounds **1–3** are as expected and unremarkable, each showing four sharp methylene carbon resonances. Although ^1H–^{13}C correlation spectra were acquired, they did not assist in the assignment of the ^1H NMR spectra.

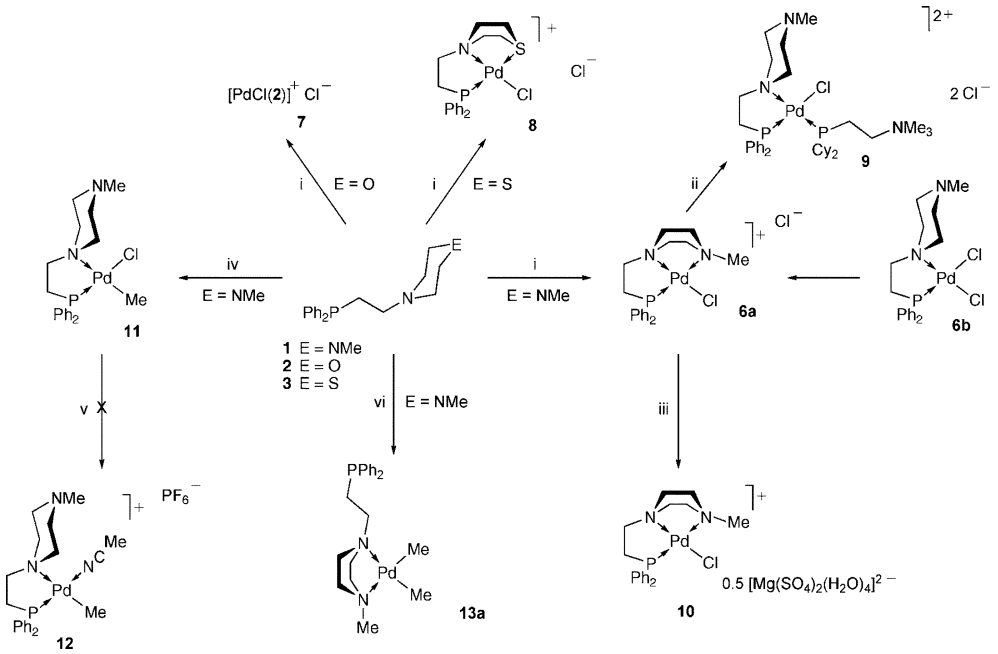
With a view to extending this Michael addition-based synthetic methodology to the preparation of compounds with a longer, potentially 1,3-PN-chelating scaffold, the reaction of allyldiphenylphosphine with *N*-methylpiperazine was undertaken using identical reaction conditions to those used above. However, rather than the desired 1,3-product, the methyl-branched compound **4** was obtained quantitatively (according to ^{31}P NMR spectroscopy). To facilitate purification and structural analysis of **4** (the aliphatic region of its ^1H NMR spectrum is severely broadened at room temperature), its hydrochloride was prepared through treatment of **4** with excess gaseous HCl. Salt **5** was isolated as a colourless solid, which was recrystallised from $CHCl_3$–Et_2O. The combination of ^1H and ^1H–^1H COSY NMR spectra (ambient temperature) readily established the structure of **5**, with a characteristic methyl resonance appearing at δ 1.05 (d, $^4J_{PH}$ = 6.4 Hz) ppm. Unambiguous confirmation of the regiochemistry of **5** was obtained from its X-ray structural analysis (*vide infra*). The formation of **4** is believed to result from initial base-catalysed isomerisation of the allyl- to the methylvinyl-phosphine, which then undergoes addition of the piperazino moiety, in accordance with comparable observations in the literature.[25,26] The coordination chemistry of **4** is entirely analogous to that of **1** and hence will be discussed elsewhere.[27]

Coordination of 1–3 with '$PdCl_2$'

The coordination chemistry of compounds **1–3** has been probed with Pd(II) and is summarised in Scheme 2. Compounds **1–3** react readily with 1 eq. $PdCl_2(MeCN)_2$ in CH_2Cl_2 with the rapid formation of a yellow precipitate in each case. Analysis of the resulting complexes **6–8** (>65% yield) confirms that they have empirical formulae that correspond to [$PdCl_2$(**1–3**)], each giving rise to $[M–Cl]^+$ ions by mass spectrometry with m/z = 455.0, 441.9 and 457.9, respectively. For each complex a significant high frequency coordination chemical shift ($\delta \approx +70$ ppm) was observed upon coordination of **1–3**, according to ^{31}P NMR spectroscopy (Table 1), indicative of P–Pd binding. The three complexes are poorly soluble in common solvents, with limited solubility only being achieved in polar media such as DMSO, water or MeOH. This behaviour is suggestive of tridentate κ^3-PNE coordination of ligands **1–3**, following chloride ion dissociation, and the resultant formation of a salt.

Coordination of 1 with '$PdCl_2$'. In solution (D_2O),‡ **6** presented a static structure according to ^1H, ^{13}C and ^{31}P NMR spectroscopy. In contrast to unbound **1**, the proton resonance for the *N*–Me moiety of **6** shows coupling to phosphorus ($^4J_{PH} \approx 5$ Hz), in agreement with tridentate binding, **6a** (Scheme 2, Fig. 1). A combination of ROESY, ^1H–^{31}P HMQC and ^1H–^1H COSY spectra were used to aid spectral assignment. The protons of the P-to-N ethylene linkage appear as two non-first order resonances at δ 3.12 (H_a) and 3.37 (H_b) ppm, both coupling to phosphorus. The eight protons of the piperazino ring appear as four multiplet resonances

‡ Although complexes **6–8** are all poorly soluble, complex **6** is markedly more soluble in water, compared with **7** and **8**, which exhibit a greater solubility in DMSO compared to water.



Scheme 2 Reagents and conditions: (i) $[PdCl_2(MeCN)_2]$, CH_2Cl_2, RT, 12 h. (ii) $Cy_2PC_2H_4NMe_3Cl$, D_2O, RT, 0.5 h. (iii) $MgSO_4$, MeOH, RT, 12 h. (iv) [PdCl(Me)(COD)], CH_2Cl_2, RT, 18 h. (v) $NaPF_6$, MeCN, CH_2Cl_2, RT, 7 d. (vi) $[PdMe_2(TMEDA)]$, CH_2Cl_2, RT, 0.75 h.

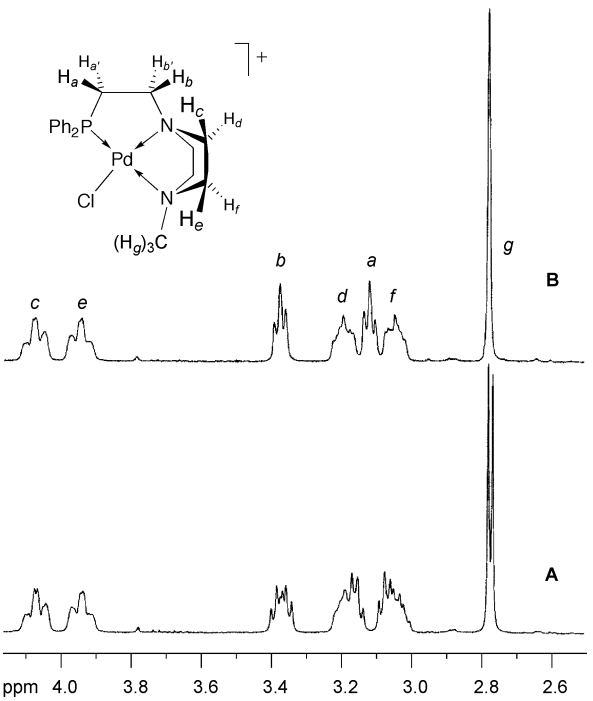


Fig. 1 ^1H (**A**) and $^1H\{^{31}P\}$ (**B**) NMR spectra of **6a** in D_2O (400.1 MHz).

at δ 3.05 (H_f), 3.19 (H_d), 3.95 (H_c), and 4.07 (H_c) ppm, none of which exhibit coupling to phosphorus. The $^{13}C\{^1H\}$ spectrum of **6a** was readily assigned, consisting of five non-phenyl resonances as expected.

Confirmation of the ionic nature of complex **6** in solution was obtained from conductivity studies. In MeOH (5×10^{-3} mol dm^{-3}) a molar conductance $\Lambda_M = 68\ \Omega\ cm^2\ mol^{-1}$ was obtained. This is consistent with **6** being a 1 : 1 electrolyte and hence, with κ^3-PNN binding of **1**, it adopts form **6a**.

Surprisingly, addition of excess magnesium sulfate to a suspension of **6a** in MeOH resulted in the complete dissolution of the palladium complex to yield a yellow solution, which after filtration and slow evaporation of the solvent, gave yellow crystals of the new complex $[PdCl(\mathbf{1}\text{-}\kappa^3\text{-PNN})]_2[Mg(SO_4)_2(H_2O)_4]$ (**10**) (*vide infra*) in 89% yield, presumably *via* loss of $MgCl_2$. As would be expected from the ionic structures of **6a** and **10**, the NMR spectroscopic data (d_4-MeOH) of their cations are identical; the aqua ligands of the anion of **10** could not be detected due to rapid exchange on the NMR timescale. Crystals of **10** were found to decompose rapidly out of the mother liquor to leave a weakly-coloured amorphous material of indeterminate composition. Consequently, the homogeneity of the sample of **10** could not be completely verified. However, the unit cells of several crystals were determined and were found to be identical. In direct support of the structure of **10**, conductimetry studies performed in MeOH solution ($\Lambda_M = 360\ \Omega\ cm^2\ mol^{-1}$) are consistent with **10** being a 1 : 2 electrolyte (with a monocationic metal centre). Attempts were made to characterise the anion of **10** by IR and Raman spectroscopies, however none of the expected bands for an *O*-sulfato ligand could be detected in the region 600–1200 cm^{-1}.[28] Despite repeated attempts, mass spectrometry (ES^-) was unable to identify the $[Mg(SO_4)_2(H_2O)_4]^{2-}$ anion intact, although the $[HSO_4]^-$ ion was observed on each attempt. In contrast, the $[PdCl(\mathbf{1}\text{-}\kappa^3\text{-PNN})]^+$ cation of **10** was readily observed by ES^+ analysis.

In the absence of $MgSO_4$, prolonged standing (days) of freshly prepared solutions of **6** in MeOH afford small quantities of pale yellow crystals of complex **6b** (~5% yield) in which **1** is bound in a bidentate κ^2-PN fashion (*vide infra*). Surprisingly, crystals of **6b** proved insoluble in both chloroform and dichloromethane, while their dissolution in polar solvents such as methanol, and

subsequent analysis by ^{1}H and ^{31}P NMR spectroscopies, merely gave spectra consistent with **6a**. Consequently, it proved impossible to characterise **6b** in solution spectroscopically. Disappointingly, **6b** could not be isolated in sufficient quantity for analysis by solid-state NMR spectroscopy, in order to probe the binding mode of **1** by ^{15}N NMR spectroscopy in the bulk sample (*vide infra*). Analysis of **6b** by ES^{+} mass spectrometry gave rise to the same [PdCl(**1**-κ^3-PNN)]$^{+}$ ion as was observed for **6a**.

Since both the κ^3-PNN (**6a**) and κ^2-PN (**6b**) forms of **6** have been isolated, it raises the question of whether these two binding modes of ligand **1** may interconvert in solution. Such behaviour would be consistent with that observed for related aminophosphine P–N chelates and the premise of so-called 'hemilability'.[2,29]

In order to explore this possibility both D_2O and d_4-MeOH solutions of **6a** were treated with increasing amounts of chloride ions in the form of NaCl (0.035–3.50 M, 1–100 eq.). The resulting solutions were monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopies. At chloride ion concentrations below 1.4 M no change in composition was detected spectroscopically, irrespective of the solvent. At higher Cl^{-} loadings the formation of an insoluble yellow powder became apparent, with complete precipitation of the palladium complex occurring on addition of *ca.* 100 equivalents of NaCl. The $^{31}P\{^{1}H\}$ NMR spectrum of the yellow precipitate, redissolved in fresh D_2O, was identical to that for **6a**. These observations reflect the inferior solubility of **6** compared with NaCl, the precipitation of the complex occurring as a result of 'salting-out'.

To try and circumvent the problem of precipitation, an alternative approach was adopted. A biphasic experiment was undertaken in which a yellow solution of **6** in D_2O was suspended above initially colourless $CDCl_3$. Addition of concentrations of NaCl $\geq$ 1.4 M ($\geq$ 40 eq.) resulted in the complete loss of colour in the aqueous phase and the yellow colouration of the lower organic phase. However, analysis of the $CDCl_3$ phase (in the presence of the upper aqueous phase, but with no mixing) by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopies only gave rise to spectra consistent with **6a**. Notably, removal of the aqueous phase led to complete precipitation of **6** and loss of colour from the $CDCl_3$ layer (consistent with the previously observed insolubility of **6b**). Identical results were obtained when nBu$_4$NCl was used in the place of NaCl.

Since the above experiments did not establish the chloride ion-dependent interconversion of the κ^3-PNN and κ^2-PN forms of **6**, a different strategy was sought for probing the lability of the N–Me donor moiety. Reaction of a D_2O solution of **6a** with a stoichiometric quantity of the water-soluble phosphine $Cy_2PCH_2CH_2NMe_3Cl$[30] led to the clean formation of the diphosphine complex **9** according to $^{31}P\{^{1}H\}$ NMR spectroscopy (Scheme 2, Table 1). The κ^2-PN coordination of **1** and the *cis*-P–P geometry are highlighted by the small magnitude of the $^{2}J_{PP}$ coupling constant (12.0 Hz) and are consistent with **9** being the thermodynamic product of this reaction (with P *trans* to N).[31]

Although the above observations (and those made by solid state NMR spectroscopy, *vide infra*) suggest that **6a** is the major product from the reaction of **1** with [$PdCl_2$(MeCN)$_2$], the origins of **6b** (isolated in low yield) remain obscure. Further study of the behaviour of **6b** was precluded by its insolubility in solvents other than methanol (in which it rapidly converts into **6a**). However, there is a notable preference for the formation of **6a** as evidenced by the reaction between [$PdCl_2$(MeCN)$_2$] and 2 eq. of **1** in CH_2Cl_2. This affords complex **6a** and unreacted **1** rather than the corresponding bis(phosphine) complex.

A number of attempts were made to abstract a chloride ion from both **6** and **10** using $NaPF_6$, $NaBPh_4$ and $AgBF_4$. Irrespective of the solvent (MeOH, CH_3CN) or the stoichiometry (1 : 1 or 1 : 2) reactions with the silver salt led to decomposition signified by the precipitation of 'palladium black', while no reaction at all was observed with the sodium salts.

Coordination of 2 and 3 with 'PdCl$_2$'. Confirmation of the coordination mode of the morpholine (**2**) and thiomorpholine (**3**) ligands with $PdCl_2$ was hampered by the poor solubility of the complexes **7** and **8**, which are only very sparingly soluble in MeOH, H_2O and DMSO.‡ The bulk composition of both **7** and **8** was probed by solid-state NMR spectroscopy (*vide infra*).

In solution (d_6-DMSO), both complexes **7** and **8** present a single slightly broadened resonance by $^{31}P\{^{1}H\}$ NMR spectroscopy ($\nu_{\frac{1}{2}} \sim 25$ Hz) at δ +50.4 and +49.8 ppm (300 K), respectively, comparable to the shifts recorded for **6a** (Table 1). No changes were observed on warming. Similarly, the ^{1}H NMR spectra (300 K) of **7** and **8** are broadened which, combined with their non-first-order nature, hindered structural assignment.

As was the case for **6**, complexes **7** and **8** are not amenable to anion exchange. Reactions with $AgBF_4$ in either MeOH or MeCN

Table 1 ^{31}P NMR spectroscopic data of compounds **1–5** and complexes **6–8** and **10–14**

Compound		$\delta^{31}P\{^{1}H\}$[a]
$Ph_2PC_2H_4N(C_2H_4)_2NMe$	**1**	−19.1[b,c]
$Ph_2PC_2H_4N(C_2H_4)_2O$	**2**	−18.2[b]
$Ph_2PC_2H_4N(C_2H_4)_2S$	**3**	−18.3[b]
$Ph_2PCH_2CH(Me)N(C_2H_4)_2NMe$	**4**	−18.6
$Ph_2PCH_2CH(Me)N(C_2H_4)_2NMe{\cdot}HCl$	**5**	−17.3
[PdCl(**1**-κ^3-PNN)]Cl	**6a**	+45.7[d]; +46.5[d]
[PdCl(**2**-κ^3-PNN)]Cl	**7**	+50.4 ($\nu_{\frac{1}{2}}$ = 24 Hz)[f]
[PdCl(**3**-κ^3-PNN)]Cl	**8**	+49.8 ($\nu_{\frac{1}{2}}$ = 27 Hz)[f]
[PdCl(**1**-κ^2-PN)($Cy_2PCH_2CH_2NMe_3Cl$)]Cl	**9**	+54.8 ($^{2}J_{PP}$ = 12.0 Hz)[g] +44.1 ($^{2}J_{PP}$ = 12.0 Hz)[g]
[PdCl(**1**-κ^3-PNN)]$_2$[$Mg(SO_4)_2(H_2O)_4$]	**10**	+46.5[e]
[PdCl(Me)(**1**-κ^2-PN)]	**11**	+45.7[h]
[$PdMe_2$(**1**-κ^2-NN)]	**13a**	+16.5[h]
[$PdMe_2$(**1**-κ^2-PN)]	**13b**	+43.8

[a] 121.4 MHz, $CDCl_3$, RT. [b] 202.3 MHz, $CDCl_3$, RT. [c] 223 K. [d] D_2O. [e] d_4-MeOH. [f] d_6-DMSO. [g] 81.0 MHz, $CDCl_3$, RT. [h] d_8-toluene.

solution led to rapid decomposition of the starting complexes with concomitant formation of 'palladium black'. No reactions were evident using either $NaPF_6$ or $NaBPh_4$.

Coordination of 1 with 'PdCl(Me)' and 'PdMe$_2$'

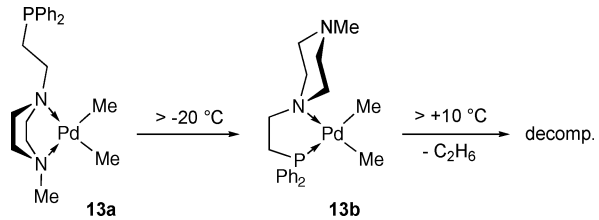
Compound **1** reacts cleanly with 1 eq. of [PdCl(Me)(COD)] to afford the air/moisture sensitive organometallic complex [PdCl(Me)(**1**-κ^2-PN)] (**11**) as a single regioisomer according to $^{31}P\{^1H\}$ NMR spectrosocopy, δ +45.7 (s) ppm (Scheme 2). Together, the solubility and conductivity data ($\Lambda_M = < 5\,\Omega\,cm^2\,mol^{-1}$) for **11** in CH_2Cl_2, are consistent with a bidentate coordination of **1**. Confirmation of this binding mode was obtained by ^1H NMR spectroscopy: upon saturation of the Pd–Me resonance at δ 0.51 ppm, a single NOE response (positive) was observed for the resonance at δ 7.64 ppm due to the *ortho*-phenyl protons, in the NOE difference spectrum of **11**. These data also substantiate the *trans*-P–Cl geometry expected on thermodynamic grounds for **11**.[3] The absence of phosphorus coupling to the NMe proton resonance is again consistent with κ^2-PN ligation of **1**.

The preference for bi- rather than tri-dentate coordination of **1** with the PdCl(Me) fragment (*cf.* **6a**) is readily explained. The strong *trans*-influence of the methyl ligand (*cf.* Cl^- in **6a**) causes an elongation of the *trans* Pd–N bond of **11**, which forces the piperazino moiety away from the palladium centre. This, combined with the geometric constraints imposed by the 6-membered piperazino ring fragment, prevents close approach of the NMe donor unit to the palladium centre, favouring κ^2-PN coordination of **1**.[32]

Attempts to abstract the chloride ion from **11** through reaction with a variety of salts of weakly-coordinating anions {*i.e.* $AgBF_4$, nBu_4NPF_6, $NaPF_6$, and $NaB[3,5\text{-}(CF_3)_2\text{-}C_6H_3]_4$[33]} to afford complexes **12** proved unproductive. All reactions undertaken in CH_2Cl_2 resulted in rapid decomposition, signified by precipitation of 'palladium black'. This behaviour has been tentatively attributed to a lack of intramolecular cation stabilisation by **1**, as a consequence of the electronic constraints imposed by the methyl ligand that prevents κ^3-PNN binding (*vide supra*). With a view to trying to 'trap' the cation generated following halide loss, identical reactions were performed in the coordinating solvent MeCN (Scheme 2). However, in these cases no reactions at all were observed with the $[PF_6]^-$ salts, while use of $NaB[3,5\text{-}(CF_3)_2C_6H_3]_4$ and $AgBF_4$ led to decomposition and the formation of Pd(0).

In order to probe this decomposition pathway further and to assess whether it would be possible to prepare complexes of **1** in which the two nitrogen atoms of the piperazino ring bind in preference to the P–N chelate, the reaction of **1** with the strongly *trans*-influencing *cis*-$PdMe_2$ fragment was undertaken.[34,35]

Treatment of [$PdMe_2$(TMEDA)] with 1 eq. **1** at low temperature led to the rapid formation of a new *cis*-dimethyl complex [$PdMe_2$(**1**-κ^2-NN)] (**13a**), stable at 253 K, which exhibits two methyl resonances by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and a single resonance at δ +16.5(s) ppm in its $^{31}P\{^1H\}$ NMR spectrum. As the temperature of the sample was slowly increased, a new resonance at δ +43.8 (s) ppm gradually started to appear (>253 K), which continued to grow in intensity at the expense of the resonance for **13a**, according to $^{31}P\{^1H\}$ NMR spectroscopy. This second signal has been assigned to the κ^2-PN *cis*-dimethyl complex [$PdMe_2$(**1**-κ^2-PN)] (**13b**) (*c.f.* ^{31}P NMR: δ +55.0 and +44.9 ppm for [$PdMe_2$(DPPE)][36] and **11**, respectively). At temperatures >283 K the onset of decomposition is rapid with concomitant precipitation of Pd(0) and loss of a signal by ^{31}P NMR spectroscopy. This process is accompanied by the formation of ethane, demonstrated by the appearance of a singlet resonance at δ 0.83 ppm by ^1H NMR spectroscopy. These data are consistent with **13b** decomposing in an exactly analogous manner to that established previously for certain *cis*-[$PdMe_2L_2$] complexes, namely *via* thermally induced elimination of ethane following reductive elimination.[34] Collectively, these observations are in agreement with the initial formation of a κ^2-NN dimethyl complex **13a**, which isomerises slowly to the κ^2-PN complex **13b** (Scheme 3), possibly as a result of the greater stability of the P–N chelate over that of the strained N–N binding of the doubly-chelating piperazino moiety.



Scheme 3 Proposed isomerisation of **13a** to **13b**.

Molecular structures

The molecular structures of **1** and **5** are shown in Fig. 2, with relevant geometric parameters listed in Table 2. The piperazino moiety adopts the expected chair conformation in both the neutral and protonated systems, with equatorial orientation of the substituents at both nitrogen atoms in each case. In agreement with the spectroscopic and analytical data, protonation of **4** occurs uniquely at the sterically less hindered N(4) atom. The cation and anion of **5** are linked by a strong N(4)–H...Cl hydrogen bond (N...Cl 3.002(4) Å) into an ionic pair. In the solid state the N(1)C(7)C(8)P chains of both **1** and **5** adopt a *gauche* conformation, with convergent P and N(1) lone pairs.

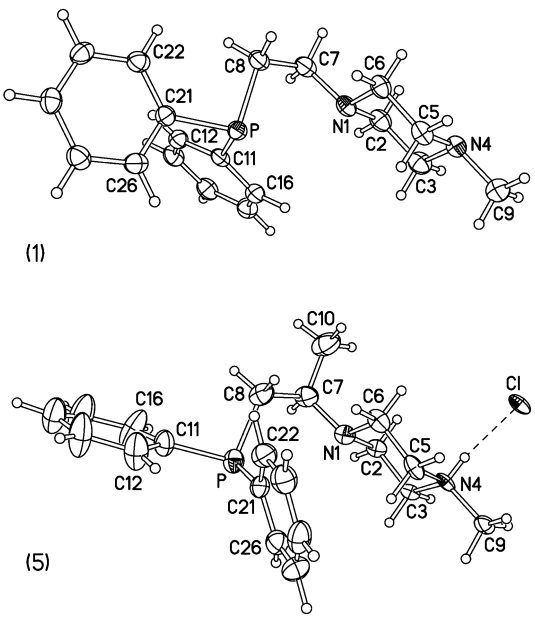


Fig. 2 Molecular structures of **1** (50% thermal ellipsoids) and **5** (30% thermal ellipsoids).

Table 2 Selected bond distances (Å) and angles (°) for compounds **1**, **5** and complexes **6b**, **10** and **14**[a]

	1	5	6b	10	14
Pd–P	—	—	2.2024(6)	2.2243(5)	—
Pd–N(1)	—	—	2.118(2)	2.033(1)	2.041(2)
Pd–N(4)	—	—	—	2.143(1)	2.066(2)
Pd–Cl(1)	—	—	2.3903(6)	—	2.3107(7)
Pd–Cl(2)	—	—	2.3056(5)	2.2897(5)	2.3055(6)
P–C(Ph)[b]	1.839(3)	1.835(5)	1.807(2)	1.810(2)	—
P–C(8)	1.859(3)	1.851(6)	1.823(2)	1.832(2)	—
N(1)–C[b]	1.460(4)	1.464(7)	1.501(2)	1.497(2)	1.488(2)
N(4)–C(3,5)[b]	1.460(4)	1.492(6)	1.457(3)	1.486(2)	1.492(2)
N(4)–C(9)	1.465(4)	1.473(6)	1.457(3)	1.472(2)	1.478(3)
C–P–C[b,c]	100.7(2)	101.7(3)	107.9(1)	106.6(1)	—
C–N(1)–C[b,c]	111.5(3)	112.2(4)	107.9(1)	110.8(1)	109.1(2)
C–N(4)–C[b,c]	110.2(3)	112.4(4)	109.6(1)	110.4(1)	110.0(1)
N(1)–C(7)–C(8)–P	42.5(3)	54.4(6)	54.2(2)	47.4(2)	—

[a] In parentheses: e.s.d.s for individual values, σ for averages. [b] Average. [c] Individual e.s.d.s in parentheses (σ is meaningless due to systematic differences between the angles).

In complex **6b** (Fig. 3) the piperazino ring retains a chair conformation and the equatorial orientation of the methyl substituent, whereas the $Ph_2PCH_2CH_2$ moiety is pushed into an axial position upon coordination to Pd. The pendent N(4) atom has the lone pair in a *syn*-orientation with respect to the Pd atom. The latter has a distorted square-planar coordination; the Cl(1) and Cl(2) atoms deviate by 0.21 and −0.12 Å from the P–Pd–N(1) plane, which forms a 5.8° angle with the $PdCl_2$ plane. The Pd–Cl(1) bond is 0.085 Å longer than Pd–Cl(2), consistent with the stronger *trans*-influence of the P atom.

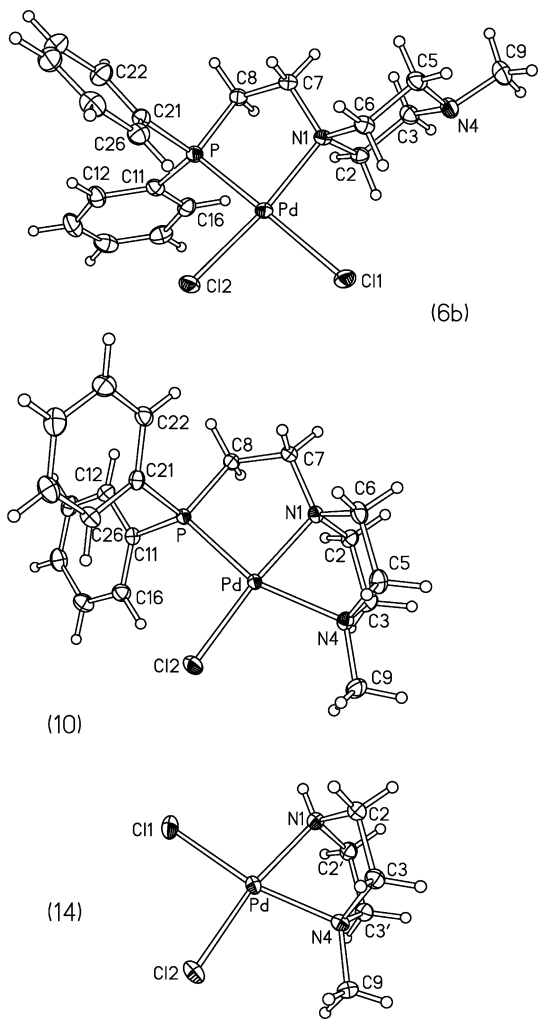


Fig. 3 Molecular structures (showing 50% thermal ellipsoids) of **6b**, the cation of **10**, and **14** (primed atoms are generated by the mirror plane).

The asymmetric unit of **10** contains one $[PdCl_2(\mathbf{1}\text{-}\kappa^3\text{-PNN})]^+$ cation (Fig. 3), three water molecules of crystallisation and half of the $[Mg(SO_4)_2(H_2O)_4]^{2-}$ dianion (Fig. 4) with monodentate *O*-sulfato ligands and *trans* octahedral coordination geometry about the magnesium atom, which lies at a crystallographic inversion centre. Whereas such anions exist in the minerals leonite,[37] $K_2Mg(SO_4)_2{\cdot}4H_2O$, and bloedite[38] (alias astrakhanite[39]), $Na_2Mg(SO_4)_2{\cdot}4H_2O$, they have not been previously observed in man-made solids. Indeed, the Cambridge Structural Database[40]

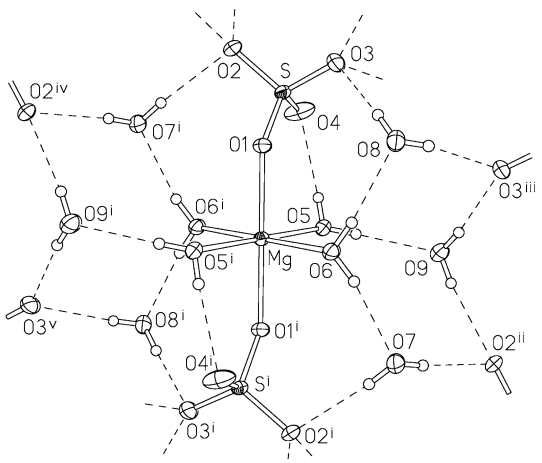


Fig. 4 An anion and water molecules of crystallisation in structure **10** (showing 50% thermal ellipsoids). Symmetry operations: (i) $1-x, 1-y, 1-z$; (ii) $x, 1/2-y, 1/2+z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, 1/2+y, 1/2-z$; (v) $x, y+1, z$. Selected bond distances (Å) and angles (°): Mg–O(1) 2.048(1), Mg–O(5) 2.100(1), Mg–O(6) 2.052(1), S–O(1) 1.473(1), other S–O (av.) 1.473(4); O(1)–Mg–O(5) 90.17(5), O(1)–Mg–O(6) 90.16(5), O(5)–Mg–O(6) 92.02(5), Mg–O(1)–S 137.64(8).

lists only one structure with magnesium–sulfate coordination of any kind, namely *cis*-$Mg(SO_4)(H_2O)\{OC(NH_2)_2\}_4$.[41]

The anion and water molecules of **10** are linked by hydrogen bonds into 2D layers, parallel to the (1 0 0) plane. The cations, which take no part in hydrogen bonding, form parallel (hydrophobic) layers, which alternate with the hydrophilic anion layers (see ESI†). In the cation, **1** binds in a tridentate fashion, as suggested by its solution-state behaviour, the piperazino ring having switched from a chair to a boat conformation, binding to the metal *via* both nitrogen atoms. As in **6b**, the fourfold coordination sphere of palladium is not quite planar, the Cl and N(4) atoms deviate from the P–Pd–N(1) plane by 0.17 and −0.24 Å, respectively. The Pd–N(4) bond is 0.11 Å longer than Pd–N(1), through the combined effect of the P-donor *trans*-influence and the strain of the chelating system. The P–Pd–N(1) 'bite' angle in **10** [87.35(4)°] is comparable to that in **6b** [86.27(4)°], while the N(1)–Pd–N(4) angle of 72.29(6)° is almost identical to the angle of 72.16(8)° found in **14** (*vide infra*), but much smaller than the corresponding angle Cl(1)–Pd–N(1) in **6b** [94.02(4)°]. The geometric constraints imposed by κ³-PNN coordination of **1** in complex **10** result in significant deviation from the ideal linear P–Pd–N(4) arrangement, imposing an angle of 158.57(4)°.

The $PdNC_2P$ metallacycles in both **6b** and **10** adopt a twist-conformation; the C(7) and C(8) atoms are displaced to opposite sides of the PdN(1)P plane, by −0.34 and 0.40 Å in **6b** and −0.20 and 0.46 Å in **10**. The N(1)–C(7)–C(8)–P torsion (Table 2) is broadly similar to that in uncoordinated **1** and **5**, hence the P…N distances are also similar, *viz.* 2.958(3) Å in **1** and 3.044(5) Å in **5**, against 2.955(2) Å in **6b** and 2.943(2) Å in **10**. Upon coordination to palladium the P–C bonds contract and the C–P–C angles widen, in comparison with the free ligand **1**. In contrast, the N–C bonds lengthen on coordination, and the C–N–C angles either decrease or remain the same (Table 2).

The molecule of **14** (Fig. 3) lies on a crystallographic mirror plane that passes through the Pd, both Cl and both N atoms. Thus, the metal coordination in **14** is rigorously planar, whereas its related, symmetrical analogue [$PtCl_2$(*N*,*N*-dimethylpiperazine-κ²-NN)] shows a small (*ca.* 3°) pseudo-tetrahedral twist between the PtN_2 and $PtCl_2$ planes.[32] In **14** the NH group forms an awkwardly bifurcated, and rather weak, hydrogen bond with both Cl(1) and Cl(2) atoms of a molecule related *via* the *a* glide plane: N…Cl distances 3.311(2) and 4.186(2) Å, N–H–Cl angles 124(3)° and 171(3)°, respectively.

Solid-state NMR spectroscopic studies

In order to probe the nature of the ligand coordination mode in a bulk sample of **6** (**1**-κ²-PN, **1**-κ³-PNN or a mixture), a combination of solid-state ^{31}P, ^{13}C and natural abundance ^{15}N NMR spectroscopic studies were undertaken.[42] Both the ^{31}P and ^{15}N NMR spectral data (Table 3) are consistent with a single coordination mode of **1**, with two distinct nitrogen environments being observed (δ −342.7 and −331.2 ppm), as expected. Both the ^{31}P and ^{13}C NMR data are entirely analogous to those obtained in solution for complexes **6a** and **10** (Table 1). Comparable ^{31}P and ^{15}N NMR data, δ +55.1 and −329.9 ppm, respectively, were obtained for the thiomorpholine-based complex **8**, again consistent with a single coordination environment in the solid state.

To provide a comparable, readily accessible reference for a palladium-bound *N*-Me moiety, a sample of the previously unknown C_s-symmetric complex *cis*-[$PdCl_2$(*N*-methylpiperazine-κ²-NN)] (**14**) was prepared and fully characterised in the solid state (*vide supra*) and in solution. Its natural abundance ^{15}N NMR spectrum showed two resonances at −362.5 and −350.2 ppm, which have been assigned to the palladium-bound *N*–H and *N*–Me units, respectively, with the aid of a dipolar dephasing experiment.

The resonance for the central palladium-bound *N*-atom of ligands **1** and **3** can readily be assigned from comparison of the ^{15}N NMR data from complexes **6** and **8**, appearing at *ca.* δ −330 ppm. The second ^{15}N NMR resonance observed for **6** (δ−342.7 ppm) has been assigned to a palladium-coordinated *N*–Me fragment by comparison with the similar chemical shift observed for the metal-bound *N*–Me from **14** (δ −350.2 ppm). Together these data are consistent with κ³-PNN coordination of **1** in complex **6** in the

Table 3 Selected solid-state ^{31}P, ^{15}N and ^{13}C NMR spectral data for complexes **6–8** and **14**[a]

Complex	Nucleus	δ ($\Delta\nu_{\frac{1}{2}}$/Hz)	Assignment
6	^{31}P[b]	55.1(1.5)	Ph_2P
	^{15}N[c]	−331.2(25)	$CH_2N(CH_2CH_2)_2$
		−342.7(20)	NMe
	^{13}C[d]	32.9	PCH_2
		45.0	NMe[e]
		47.9	CH_2
		49.4	CH_2
		56.1	CH_2
		63.8	PCH_2CH_2N
7	^{31}P[b]	55.8, 53.5, 51.9, 48.6[g]	Ph_2P
	^{15}N[c]	−290.4, −312.8, −332.3, −338.9	$CH_2N(CH_2CH_2)_2$
8	^{31}P[b]	51.1 (2.0)	Ph_2P
	^{15}N[c]	−329.9 (20)	$CH_2N(CH_2CH_2)_2$
14	^{15}N[c]	−350.2 (33)	NMe
		−362.5 (51)	NH
	^{13}C[d]	60.2	CH_2[f]
		51.5	NMe[e]

[a] Ambient probe temperature. [b] 121.4 MHz. [c] 30.4 MHz. [d] 75.4 MHz. [e] Confirmed by dipolar dephasing with a 40.00 μs delay. [f] Resonances coincident. [g] Overlapping resonances.

solid state. Consequently, a similar κ^3-PNS binding for ligand **3** with the $PdCl_2$ fragment has been assigned to **8**.

In contrast, the ^{31}P and ^{15}N NMR spectra for the morpholine-derived complex **7** each consisted of four resonances (Table 3). The composition of **7** is clearly more complicated in the solid state, despite its analytical data being consistent with the empirical formula [$PdCl_2$(**2**)] (*vide supra*). From the ^{31}P NMR data it is clear that the phosphine component of **2** is bound to palladium in each case, however. The different behaviour observed for **7** compared with that for complexes **6** and **8** is likely to be due to the presence of the harder *O*-donor moiety, favouring κ^2-PN and intermolecular ligation rather than κ^3-PNO binding to the soft palladium centre. A similar bidentate coordination has been proposed previously for ligand **2** in the rhodium complex [RhCl(CO)(**2**-κ^2-PN)].[23]

Conclusions

The Michael addition of piperazine, morpholine and thiomorpholine with diphenylvinylphosphine provides easy access to potentially tridentate PNE (E = N, O, S) donor ligands **1**–**3** in near-quantitative yields. Similar reactions undertaken with allyldiphenylphosphine gave rise to the methyl-branched ethane derivative rather than the 1,3-P–N compound, as a result of base-catalysed isomerisation of the allyl phosphine.

Ligands **1** and **3** favour *meridional*, κ^3-PNE coordination to the $PdCl_2$ fragment, affording complexes **6a** and **8**, respectively, following chloride ion displacement, both in solution and the solid state. However, it is apparent that the *N*–Me donor moiety of **1** is labile since it can be displaced by the phosphine $Cy_2PCH_2CH_2NMe_3Cl$. In contrast to the situation with **1** and **3**, the precise mode of binding of the PNO ligand **2** is less clear-cut, something attributed to weak O–Pd ligation.

It is clear that ligands **1**–**3** can adopt a variety of different coordination modes in response to the nature of the metal fragment to which they are bound. This is highlighted by the bidentate binding of **1** with both the PdCl(Me) and $PdMe_2$ fragments affording complexes **11** and **13**, respectively. Here, the presence of the strongly *trans*-influencing methyl group precludes tridentate binding of **1** as a consequence of elongation of the Pd–N bond of the middle *N*-atom. Such 'responsive' behaviour may prove beneficial in catalytic applications, where the electronic and steric demands of the metal centre are constantly changing.

An exploration of the coordination chemistry of phosphines **1**–**3** with a range of metal-containing fragments is on-going. The utility of such systems in a number of catalytic applications is being investigated actively.

Experimental

General considerations

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a Saffron Scientific nitrogen-filled glove box, unless stated otherwise. All NMR-scale reactions were conducted using NMR tubes fitted with J. Young tap valves. Bulk solvents were purified using an Innovative Technologies SPS facility and degassed prior to use. $CDCl_3$ and d_8-toluene were distilled from P_2O_5. Anhydrous d_4-MeOH and d_6-DMSO (Apollo) were used as received. D_2O (Apollo) was purged with dry nitrogen. Deuterated solvents were stored and handled under nitrogen.

Palladium dichloride was used on loan from Johnson Matthey. *N*-Methylpiperazine, morpholine, thiomorpholine, vinyl Grignard, and $NaNH_2$ were purchased from Aldrich and used as received. Ph_2PCl (Aldrich) was distilled under vacuum prior to use. Allyl Grignard was prepared from allyl chloride (Aldrich) in Et_2O using standard conditions.[43] The starting materials [$PdCl_2(MeCN)_2$],[44] [PdCl(Me)(COD)],[45] [$PdMe_2$(TMEDA)],[34,35] NaB[3,5-$(CF_3)_2$-$C_6H_3]_4$,[33] and $Cy_2PC_2H_4NMe_3Cl$[30] were prepared according to literature procedures or slight modifications thereof.

Routine solution phase NMR spectra were collected on a Varian Unity 300, Varian Mercury 400 or Varian Inova 500 at ambient probe temperatures (~290 K). Variable temperature and NOE spectra were collected on a Bruker AMX400. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (^1H), ^{13}C shift of the solvent (^{13}C), or to external aqueous 85% H_3PO_4 (^{31}P). Solvent proton shifts (ppm): $CDCl_3$ (s), 7.27 (s); d_4-MeOH (s), 3.31; d_6-DMSO (sept.), 2.50; d_8-toluene (sept.), 2.36; D_2O (s), 4.79. Solvent carbon shifts (ppm): $CDCl_3$, 77.2 (t); d_4-MeOH, 49.0; d_6-DMSO, 39.5; d_8-toluene (sept.), 21.4. In ^1H NMR spectra, ^{31}P coupled resonances were verified by running ^1H {^{31}P} experiments. ^{13}C NMR spectra were assigned with the aid of DEPT 90, DEPT 135 and ^1H–^{13}C correlation experiments. Chemical shifts are reported in ppm and coupling constants in Hz.

Solid-state NMR spectra were obtained on a Varian UNITY Inova 300 MHz spectrometer (5.0 mm probe) at ambient probe temperature; acquisition parameters are collected in Table 4. Chemical shifts were referenced to tetramethylsilane (^{13}C) by setting the high-frequency signal from adamantane to 38.4 ppm; to nitromethane (^{15}N) by setting the nitrate signal from solid ammonium nitrate to −5.1 ppm; and to H_3PO_4 (^{31}P) by setting the signal from $CaHPO_4{\cdot}2H_2O$ (Brushite) to 1.4 ppm.

Mass spectra were recorded either in Durham (ES: Micromass Autospec; MALDI ToF: Applied Biosystems Voyager-DE STR) or by the EPSRC National Mass Spectrometry Service at the University of Wales, Swansea, (ES: Waters ZQ-4000) and are reported in (*m*/*z*). The isotope distributions for all parent ion peaks for metal complexes were verified *via* comparison with a theoretical isotope pattern. Elemental analyses were performed by The Analytical Services Department of the Chemistry Department, Durham University. Infrared spectra were collected on a Perkin Elmer 1600 spectrophotometer using KBr discs or a Golden Gate ATR cell. Conductimetry measurements were made at 22.5 °C using 5×10^{-3} mol dm^{-3} solutions with a Jenway 4310 dip-in probe.

Table 4 Selected solid-state NMR acquisition parameters for complexes **6**–**8** and **14**

Complex	Nucleus	Recycle/s	Contact time/ms	Spin rate/kHz
6	^{31}P	3.0	5.00	5.73
	^{15}N	3.0	10.00	5.00
	^{13}C	3.0	1.00	4.62
7	^{31}P	20.0	3.00	8.00
	^{15}N	10.0	20.00	5.09
8	^{31}P	10.0	10.00	8.00
	^{15}N	5.0	5.00	5.06
14	^{15}N	5.0	20.00	5.08
	^{13}C	5.0	1.00	5.04

Preparations

Synthesis of diphenylvinylphosphine. A solution of chlorodiphenylphosphine (7.35 cm^3, 4.01 × 10^{-2} mol) in THF (50 cm^3) was allowed to cool to −78 °C and a solution of vinyl magnesium chloride (30 cm^3, 1.6 mol dm^{-3} solution in THF) added dropwise with stirring over the course of 0.5 h. The resulting mixture was allowed to stir at −78 °C for a further 0.5 h before being allowed to warm slowly to room temperature and stirred for a further 16 h. The THF was then removed *in vacuo*, replaced with hexane and the resulting solution filtered *via* a glass frit. The hexane was removed *in vacuo* to afford diphenylvinylphosphine as a colourless oil following vacuum distillation (5.53 g, 65%). ^{1}H NMR (499.8 MHz, $CDCl_3$) δ ppm: 5.49 (m, 1H, CH_2=CH–P), 5.77 (m, 1H, CH_2=CH–P), 6.50 (m, 1H, CH_2=CH–P), 7.16 (m, 6H, *m-/p*-PhH), 7.28 (m, 4H, *o*-PhH); ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$) δ ppm: 128.6 (d, $^3J_{CP}$ = 7.0 Hz, *m*-PhC), 128.8 (s, *p*-PhC), 129.6 (d, $^1J_{CP}$ = 24.0 Hz, CH_2=CH), 133.3 (d, $^2J_{PC}$ = 19.0 Hz, *o*-PhC), 136.9 (d, $^2J_{PC}$ = 14.0 Hz, CH_2=CH), 137.7 (d, $^1J_{PC}$ = 9.5 Hz, *i*-PhC); ^{31}P{^{1}H} (162.0 MHz, $CDCl_3$) δ ppm: −10.7 (s); MS (ES^+) *m/z*: 213.1 (MH^+).

Due to the oily nature/air sensitivity of this product, satisfactory CHN analysis could not be obtained. Since the product gave satisfactory NMR spectra, it was used without further purification.

Synthesis of 1-(2-diphenylphosphino-ethyl)-4-methyl-piperazine, 1. To a solution of diphenylvinylphosphine (1.40 g, 6.60 × 10^{-3} mol) in THF (50 cm^3) was added *N*-methylpiperazine (0.80 cm^3, 7.26 × 10^{-3} mol) and a catalytic quantity of $NaNH_2$ (1.0 cm^3 of a suspension in toluene) under a flow of nitrogen. The resulting mixture was heated at reflux for 24 h, before being allowed to cool to room temperature and the $NaNH_2$ quenched by addition of NH_4Cl (20 cm^3, aq, 10%, degassed). The solution was extracted with CH_2Cl_2 (3 × 30 cm^3), the organic fractions combined and dried over $MgSO_4$. The drying agent was removed by filtration *via* a glass frit and, following removal of the CH_2Cl_2 under vacuum, **1** was obtained as a viscous yellow-orange oil (yield 1.94 g, 94%), which on prolonged standing (weeks) affords very pale yellow crystals suitable for X-ray diffraction studies, 1.50 g, 73%, (calc.: $C_{14}H_{25}N_2P$ C, 73.04; H, 8.08; N, 8.97. Found: C, 73.00; H, 7.88; N, 8.74. ^{1}H NMR: (499.8 MHz, 223 K, $CDCl_3$) δ ppm: 2.07 (m, 4H, NC_2H_4N), 2.23 (m, 5H, NC_2H_4N and CH_3N), 2.41 (m, 2H, NC_2H_4N), 2.72 (m, 2H, PC_2H_4), 2.82 (m, 2H, PC_2H_4), 7.24 (m, 6H, *m-/p*-PhH), 7.36 (m, 4H, *o*-PhH); ^{13}C{^{1}H} (125.7 MHz, 223 K, $CDCl_3$) δ ppm: 24.9 (d, $^1J_{PC}$ = 12.0 Hz, Ph_2PCH_2), 45.1 (s, CH_3N), 52.0 (s, $MeN(CH_2CH_2)_2$), 54.1 (s, $MeN(CH_2CH_2)_2$), 54.3 (s, $Ph_2PCH_2CH_2N$), 127.5 (d, $^3J_{PC}$ = 7.0 Hz, *m*-PhC), 127.7 (s, *p*-PhC), 131.8 (d, $^2J_{PC}$ = 19.0 Hz, *o*-PhC), 137.6 (d, $^1J_{PC}$ = 13.0 Hz, *i*-PhC); ^{31}P{^{1}H} (202.3 MHz, $CDCl_3$) δ ppm: −19.1 (s); MS (ES^+) *m/z*: 313.2 (MH^+).

If a clean ^{31}P NMR spectrum of **1** was obtained, it was used without further purification.

Synthesis of 1-(2-diphenylphosphino-ethyl)-4-methyl-morpholine, 2. An analogous procedure to that used for the preparation of **1** was employed, with diphenylvinylphosphine (2.00 g, 9.44 × 10^{-3} mol) in THF (50 cm^3), morpholine (0.9 cm^3, 10.38 × 10^{-3} mol) and a catalytic quantity of $NaNH_2$ (1.0 cm^3 of a suspension in toluene), yield 2.68 g, 95%. ^{1}H NMR: (499.8 MHz, $CDCl_3$) δ ppm: 2.18 (m, 2H, PC_2H_4), 2.34 (br, $\nu_{\frac{1}{2}}$ = 13.9 Hz, 4H, NC_2H_4O), 2.40 (m, 2H, PC_2H_4), 3.58 (m, 4H, NC_2H_4O), 7.23 (m, 6H, *m-/p*-PhH), 7.34 (m, 4H, *o*-PhH); ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$) δ ppm: 24.5 (d, $^1J_{PC}$ = 12.0 Hz, PCH_2), 52.3 (s, NCH_2CH_2O), 54.5 (d, $^2J_{PC}$ = 23.0 Hz, PCH_2CH_2N), 65.8 (s, CH_2O), 127. 4 (d, $^3J_{PC}$ = 7.0 Hz, *m*-PhC), 127.6 (s, *p*-PhC), 131.7 (d, $^2J_{PC}$ = 19.0 Hz, *o*-PhC), 137.3 (d, $^1J_{PC}$ = 13.0 Hz, *i*-PhC); ^{31}P{^{1}H} (202.3 MHz, $CDCl_3$) δ ppm: −18.2 (s); MS (ES^+) *m/z*: 300.0 (MH^+).

If a clean ^{31}P NMR spectrum of **2** was obtained, it was used without further purification.

Synthesis of 1-(2-diphenylphosphino-ethyl)-4-methyl-thiomorpholine, 3. A slight modification of the procedure used for the preparation of **1** was employed, with diphenylvinylphosphine (1.51 g, 7.10 × 10^{-3} mol) in THF (50 cm^3), thiomorpholine (0.7 cm^3, 7.10 × 10^{-3} mol) and a catalytic quantity of $NaNH_2$ (1.0 cm^3 of a suspension in toluene), yield 2.15 g, 96%. ^{1}H NMR: (499.8 MHz, $CDCl_3$) δ ppm: 2.16 (m, 2H, PC_2H_4N), 2.42 (m, 2H, PC_2H_4N), 2.51 (m, 4H, NC_2H_4S), 2.59 (m, 4H, NC_2H_4S), 7.21 (m, 6H, *m-/p*-PhH), 7.33 (m, 4H, *o*-PhH); ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$) δ ppm: 24.7 (d, $^1J_{PC}$ = 13.0 Hz, PCH_2), 25.6 (s, PCH_2CH_2N), 27.2 (s, NCH_2CH_2S), 54.0 (s, NCH_2CH_2S), 55.2 (d, $^2J_{PC}$ = 22.5 Hz, NCH_2CH_2S), 127.8 (d, $^3J_{PC}$ = 7.0 Hz, *m*-PhC), 128.0 (s, *p*-PhC), 132.0 (d, $^2J_{PC}$ = 19.0 Hz, *o*-PhC), 137.7 (d, $^1J_{PC}$ = 12.5 Hz, *i*-PhC); ^{31}P{^{1}H} (202.3 MHz, $CDCl_3$) δ ppm: −18.3 (s); MS (ES^+) *m/z*: 316.1 (MH^+).

If a clean ^{31}P NMR spectrum of **3** was obtained, it was used without further purification.

Synthesis of allyldiphenylphosphine. This was prepared in an analogous fashion to that used for the preparation of vinyldiphenylphosphine from diphenylchlorophosphine (3.7 cm^3, 2.02 × 10^{-2} mol) in THF (50 cm^3) and allyl magnesium chloride (30 cm^3, 0.8 mol dm^{-3} solution in THF). Following purification by vacuum transfer, allyldiphenylphosphine was isolated as a colourless oil, yield 2.94 g, 64% (calc.: $C_{15}H_{15}P$ C, 73.62; H, 6.70. Found: C, 73.35; H, 6.72). ^{1}H NMR: (499.8 MHz, $CDCl_3$) δ ppm: 3.00 (dd, $^1J_{HH}$ = 1.0 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 5.12 (m, 2H, PCH_2), 5.93 (m, 1H, CH), 7.42 (m, 6H, *m-/p*-PhH), 7.56 (m, 4H, *o*-PhH); ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$) δ ppm: 34.1 (d, $^3J_{PC}$ = 14.0 Hz, CH_2), 117.8 (d, $^1J_{PC}$ = 14.0 Hz, Ph_2PCH_2), 128.7 (d, $^3J_{PC}$ = 7.0 Hz, *m*-PhC), 129.0 (s, *p*-PhC), 133.2 (d, $^2J_{PC}$ 18.0 Hz, *o*-PhC), 133.5 (d, $^2J_{PC}$ = 9.0 Hz, CH), 138.5 (d, $^1J_{PC}$ = 15.0 Hz, *i*-PhC); ^{31}P{^{1}H} (202.3 MHz, $CDCl_3$) δ ppm: −14.7 (s); MS (ES^+) *m/z*: 227.2 (MH^+).

Reaction of allyldiphenylphosphine with *N*-methyl piperazine; syntheses of 4 and 5. Using analogous conditions to those employed for the preparation of **1**, allyldiphenylphosphine (1.51 g, 6.68 × 10^{-3} mol) was reacted with *N*-methylpiperazine (3.0 cm^3, 2.70 × 10^{-2} mol) in the presence of $NaNH_2$ (1.0 cm^3 of a suspension in toluene). Following heating at reflux for 24 h, **4** was isolated as a viscous pale brown oil (yield 1.96, 90%). ^{1}H NMR: (499.7 MHz, $CDCl_3$, 223 K) δ ppm: 1.10 (d, $^4J_{PH}$ = 6.0 Hz, 3H, $CH_2CH(CH_3)N$), 1.97 (m, 2H, $N(C_4H_8)N$), 2.11 (m, 1H, $N(C_4H_8)N$), 2.26 (s, 3H, $N(C_4H_8)NCH_3$), 2.36 (m, 1H, $N(C_4H_8)N$), 2.45 (m, 2H, $N(C_4H_8)N$), 2.55 (overlapping m, 3H, $N(C_4H_8)N$ and Ph_2PCH_2CH), 2.72 (m, 2H, Ph_2PCH_2CH), 7.25–7.42 (m, 8H, *o-/m*-PhH), 7.45 (m, 2H, *p*-PhH); ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$) δ ppm: 14.6 (d, $^3J_{CP}$ = 7.5 Hz, $CH_2CH(CH_3)N$), 31.8 (d, $^1J_{CP}$ = 13.0 Hz, Ph_2PCH_2CH),

44.9 (s, $N(C_4H_8)NCH_3$), 46.5 (s, $N(CH_2CH_2)_2NCH_3$), 54.1 (s, $N(CH_2CH_2)_2NCH_3$), 55.8 (d, $^2J_{CP} = 16.0$ Hz, Ph_2PCH_2CH), 127.2 (d, $^3J_{CP} = 7.0$ Hz, *m*-Ph*C*), 127.3 (d, $^3J_{CP} = 7.0$ Hz, *m*-Ph*C*), 127.4 (s, *p*-Ph*C*), 127.5 (s, *p*-Ph*C*), 131.8 (d, $^2J_{CP} = 15.0$ Hz, *o*-Ph*C*), 131.8 (d, $^2J_{CP} = 15.0$ Hz, *o*-Ph*C*), 138.1 (d, $^1J_{CP} = 14.0$ Hz, *i*-Ph*C*), 138.4 (d, $^1J_{CP} = 14.0$ Hz, *i*-Ph*C*); $^{31}P\{^1H\}$ (121.4 MHz, $CDCl_3$) δ ppm: −18.6 (s); MS (ES^+) *m*/*z*: 327.2 (MH^+).

Bubbling gaseous HCl through an ethereal solution of **4** (0.85 g, 2.60×10^{-3} mol) resulted in the immediate precipitation of the mono-hydrochloride salt **5** as a white solid, which was isolated in near-quantitative yield (0.93 g, 98%). Crystals of X-ray quality were grown from $CHCl_3/Et_2O$. (Calc.: $C_{20}H_{28}N_2PCl$ C, 66.19; H, 7.79; N, 7.72. Found: C, 66.36; H, 7.76; N, 7.92). ^1H NMR (499.7 MHz, $CDCl_3$) δ ppm: 1.05 (d, $^4J_{PH} = 6.4$ Hz, 3H, $CH_2CH(CH_3)NCH_3$), 1.90 (m, 1H, $N(C_4H_8)N$), 2.10–2.35 (m, 2H, $N(C_4H_8)N$), 2.45–2.85 (m, 6H, $N(C_4H_8)N$, Ph_2PCH_2CH), 2.95–3.34 (m, 5H, $N(C_4H_8)N$, $CH_3N(C_4H_8)N$, and Ph_2PCH_2CH), 7.18–7.32 (m, 8H, *o*-/*m*-Ph*H*), 7.41 (s, *p*-Ph*H*), 12.27 (br s, $\nu_{\frac{1}{2}} = 37.5$ Hz, 1H, NH^+); ^1H (499.7 MHz, $CDCl_3$, 223 K) δ ppm: 1.08 (s, 3H, $CH_2CH(CH_3)N$), 1.86–2.09 (m, 2H, Ph_2PCH_2CH and $N(C_4H_8)N$), 2.32–2.88 (m, 8H, Ph_2PCH_2CH, $N(C_4H_8)N$, $N(C_4H_8)NCH_3$, and Ph_2PCH_2CH), 3.07 (m, 3H, $N(C_4H_8)N$), 3.34 (m, 1H, $N(C_4H_8)N$), 7.26–7.41 (m, 8H, *o*-/*m*-Ph*H*), 7.50 (s, *p*-Ph*H*), 11.72 (br s, $\nu_{\frac{1}{2}} = 33.3$ Hz, 1H, NH^+); $^{13}C\{^1H\}$ (100.6 MHz, $CDCl_3$) δ ppm: 14.4 (d, $^3J_{PC} = 8.0$ Hz, $CH_2CH(CH_3)N$), 31.9 (s, Ph_2PCH_2CH), 42.7 (s, $N(C_4H_8)NCH_3$), 46.3 (s, $N(CH_2CH_2)_2NCH_3$), 52.0 (s, $N(CH_2CH_2)_2NCH_3$), 56.9 (s, Ph_2PCH_2CH), 127.4 (d, $^3J_{PC} = 7.5$ Hz, *m*-Ph*C*), 127.6 (d, $^3J_{PC} = 7.5$ Hz, *m*-Ph*C*), 127.7 (s, *p*-Ph*C*), 127.9 (s, *p*-Ph*C*), 131.5 (d, $^2J_{PC} = 19.5$ Hz, *o*-Ph*C*), 132.1 (d, $^2J_{PC} = 19.5$ Hz, *o*-Ph*C*), 137.5 (br s, *i*-Ph*C*); $^{31}P\{^1H\}$ (121.4 MHz, $CDCl_3$) δ ppm: −17.3 (s); MS (ES^+, MeOH) *m*/*z*: 343.4 $[M–Cl + Me]^+$.

Synthesis of [$PdCl_2$(1)], 6. To a Schlenk flask charged with $PdCl_2(MeCN)_2$ (0.11 g, 4.24×10^{-4} mol) was added **1** (0.13 g, 4.26×10^{-4} mol) and CH_2Cl_2 (20 cm^3). The mixture was stirred at room temperature for 12 h, which resulted in the formation of a fine yellow solid. The precipitate was isolated by cannula filtration, washed repeatedly with hexane and diethyl ether and dried *in vacuo* to afford **6** as a bright yellow powder (yield 0.14 g, 68%). (calc.: $C_{19}H_{25}N_2PPdCl_2$ C, 46.59; H, 5.16; N, 5.72. Found: C, 46.17; H, 5.15; N, 5.82). For spectroscopic assignments see Fig. 2. ^1H NMR (400.1 MHz, D_2O) δ ppm: 2.78 (d, $^4J_{PH} = 5.1$ Hz, 3H, H_g), 3.05 (m, 2H, H_f), 3.12 (m, 2H, H_a), 3.19 (m, 2H, H_d), 3.37 (m, 2H, H_b), 3.95 (m, 2H, H_e), 4.07 (m, 2H, H_c), 7.58 (m, 4H, *m*-Ph*H*), 7.64 (m, 2H, *p*-Ph*H*), 7.96 (m, 4H, *o*-(Ph*H*); $^{13}C\{^1H\}$ 100.6 MHz, D_2O) δ ppm: 35.0 (d, $^1J_{PC} = 32.0$ Hz, Ph_2PCH_2), 45.9 (s, CH_3N), 57.0 (s, CH_2), 57.6 (s, CH_2), 58.0 (s, $Ph_2PCH_2CH_2$), 126.0 (d, $^1J_{PC} = 52.5$ Hz, *i*-Ph*C*), 130.3 (d, $^3J_{PC} = 11.5$ Hz, *m*-Ph*C*), 133.8 (d, $^4J_{PC} = 7.0$ Hz, *p*-Ph*C*), 134.0 (d, $^2J_{PC} = 12.0$ Hz, *o*-Ph*C*); $^{31}P\{^1H\}$ (121.4 MHz, D_2O) δ ppm: +45.7 (s); $^{31}P\{^1H\}$ (121.4 MHz, CD_3OD) δ ppm: +46.5 (s); MS (MALDI ToF, Dithranol matrix) *m*/*z*: 455.0 (M–Cl^+); Λ_M (MeOH, 5×10^{-3} mol, 22.5 °C: 68 Ω cm^2 mol^{-1}).

Synthesis of [$PdCl_2$(2)], 7. An analogous procedure to that used for the preparation of **6** was adopted, involving reaction of $PdCl_2(MeCN)_2$ (0.17 g, 6.68×10^{-4} mol) with **2** (0.20 g, 6.68×10^{-4} mol) in CH_2Cl_2 (20 cm^3). This lead to the isolation of **7** as a dull yellow powder (yield 0.21 g, 67%) (calc.: $C_{18}H_{22}NOPPdCl_2$ C, 45.35; H, 4.66; N, 2.94. Found: C, 45.18; H, 4.57; N, 2.78). ^1H NMR (d_6-DMSO): the spectrum was so broad that assignment was impossible; limited solubility precluded acquisition of $^{13}C\{^1H\}$ NMR spectral data; $^{31}P\{^1H\}$ NMR (121.4 MHz, d_6-DMSO) δ ppm: +50.4 ($\nu_{\frac{1}{2}} = 24$ Hz); MS (ES^+) *m*/*z*: 441.9 (M–Cl^+).

Synthesis of [$PdCl_2$(3)], 8. An analogous procedure to that used for the preparation of **6** was adopted, involving reaction of $PdCl_2(MeCN)_2$ (0.16 g, 6.34×10^{-4} mol) with **3** (0.20 g, 6.34×10^{-4} mol) in CH_2Cl_2 (20 cm^3). This lead to the isolation of **8** as a yellow powder (0.25 g, 80%) (calc.: $C_{18}H_{22}NSPPdCl_2$ C, 43.87; H, 4.51; N, 2.84. Found: C, 43.93; H, 4.62; N, 2.82). ^1H NMR (299.9 MHz, d_6-DMSO) δ ppm: 2.80–3.45 (m, 8H, CH_2), 3.82 (m, 2H, CH_2), 4.34 (m, 2H, CH_2), 7.51 (m, 6H, *m*-/*p*-Ph*H*), 7.89 (m, 4H, *o*-Ph*H*); the low solubility of **8** precluded the acquisition of ^{13}C NMR spectra; ^{31}P NMR (121.4 MHz, d_6-DMSO) δ ppm: +49.8 ($\nu_{\frac{1}{2}} = 27$ Hz); MS (ES^+) *m*/*z*: 457.9 (M–Cl^+).

Synthesis of [$PdCl(Cy_2PC_2H_4NMe_3)(1\text{-}\kappa^2\text{-}PN)]Cl_2$, 9. A solution ($D_2O$) of **6** (0.018 g, 3.68×10^{-5} mol) was treated under N_2 with $Cy_2PC_2H_4NMe_3Cl$ (0.012 g, 3.68×10^{-5} mol). $^{31}P\{^1H\}$ NMR (81.0 MHz, D_2O) δ ppm: +54.8 (d, $^2J_{PP} = 12.0$ Hz), +44.1 (d, $^2J_{PP} = 12.0$ Hz).

Synthesis of [$PdCl_2(1\text{-}\kappa^3\text{-}PNN)]_2[Mg(SO_4)_2(H_2O)_4]$, 10. Under air, complex **6** (0.10 g, 2.08×10^{-4} mol) was treated with $MgSO_4$ (1.01 g, 8.352×10^{-3} mol) in methanol (10 cm^3) and the resulting mixture allowed to stir at room temperature for 36 h. The excess unreacted $MgSO_4$ and $MgCl_2$ by-product were removed by filtration and the solvent removed *in vacuo* to afford **10** as a vivid yellow powder (yield 0.22 g, 89%). Crystals of X-ray quality were grown by slow evaporation of a dilute methanolic solution of the product under air (CHN analyses proved unreliable as a result of desolvation and decomposition). For spectroscopic assignments see Fig. 2. ^1H NMR (299.9 MHz, CD_3OD) δ ppm: 2.67 (d, $^4J_{PH} = 5.0$ Hz, 3H, CH_3N), 2.95 (m, 4H, $MeNCH_2CH_2$), 3.08 (m, 4H, $MeNCH_2CH_2$), 3.83 (m, 2H, $Ph_2PCH_2CH_2$), 3.96 (m, 2H, $Ph_2PCH_2CH_2N$), 7.58 (m, 4H, *m*-Ph*H*), 7.60 (m, 6H, *p*-Ph*H*), 7.96 (m, 4H, *o*-Ph*H*) {*NB.* the resonance due to the solvent obscures a 2H multiplet}; $^{13}C\{^1H\}$ (100.6 MHz, CD_3OD) δ ppm: 34.4 (d, $^1J_{PC} = 12.0$ Hz, Ph_2PCH_2), 44.9 (d, $^2J_{PC} = 2.5$ Hz, CH_3N), 56.5 (s, $MeN(C_2H_4)_2$), 57.0 (s, $MeN(C_2H_4)_2$), 57.5 (d, $^2J_{PC} = 4.0$ Hz, $Ph_2PCH_2CH_2$), 126.5 (d, $^1J_{PC} = 53.0$ Hz, *i*-Ph*C*), 129.4 (d, $^3J_{PC} = 12.0$ Hz, *m*-Ph*C*), 132.6 (d, $^4J_{PC} = 2.5$ Hz, *p*-Ph*C*), 133.2 (d, $^2J_{PC} = 11.5$ Hz, *o*-Ph*C*); $^{31}P\{^1H\}$ (121.4 MHz, CD_3OD) δ ppm: +46.5; MS (ES^+, MeOH) *m*/*z*: 455.0 (M–Cl^+); MS (ES^-, MeOH) *m*/*z*: 97.0 ($[HSO_4]^-$); Λ_M (MeOH, 5×10^{-3} mol, 22.5 °C: 360 Ω cm^2 mol^{-1}).

Synthesis of [PdCl(Me)(2-κ^2-PN)], 11. To a Schlenk flask charged with PdClMe(COD) (8.40×10^{-2} g, 3.20×10^{-4} mol) was added **1** (0.100 g, 3.20×10^{-4} mol) in CH_2Cl_2 (10 cm^3). The resulting mixture was allowed to stir at room temperature for 18 h with all light excluded from the Schlenk flask. The solvent was then removed under vacuum, the product extracted with hexane and dried thoroughly *in vacuo* to afford a yellow powder (yield 0.11 g, 76%). ^1H NMR (499.8 MHz, $CDCl_3$, 223 K) δ ppm: 0.51 (s, 3H, $PdCH_3$), 2.21 (s, 3H, $CH_3N(C_4H_8)N$), 2.38–2.66 (m, 6H, $MeN(C_4H_8)N$, $Ph_2PCH_2CH_2$ and $MeN(C_4H_8)N$), 2.73–2.93 (m, 4H, $MeN(C_4H_8)N$ and $Ph_2PCH_2CH_2N$), 4.12 (m, 2H, $MeN(C_4H_8)N$), 7.41–7.56 (m, 6H, *m*-Ph*H* and *p*-Ph*H*), 7.64 (m, 4H, *o*-Ph*H*); $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$) δ ppm: 30.8 (d, $^1J_{PC} = 27.5$ Hz, $Ph_2PCH_2CH_2$), 46.5 (s, $CH_3N(CH_2CH_2)_2$),

49.3 (s, MeN(CH_2CH_2)$_2$N), 50.6 (s, PCH_2CH_2N), 53.9 (s, MeN(CH$_2$CH_2)$_2$N), 129.3 (d, $^3J_{PC}$ = 11.0 Hz, *m*-Ph*C*), 129.9 (s, *i*-Ph*C*), 131.6 (s, *p*-Ph*C*), 133.6 (d, $^2J_{PC}$ = 12.5 Hz, *o*-Ph*C*); ^{31}P{^{1}H} (202.3 MHz, $CDCl_3$) δ ppm: +45.7 (s); MS (ES$^+$) *m*/*z*: 433.0 [M–Cl]$^+$; MS (EI) *m*/*z*: 433.0 [M–Cl]$^+$; 454.3 [M–CH_3]$^+$.

Synthesis of [PdMe$_2$(1)], 13. To a Schlenk flask charged with PdMe$_2$(TMEDA) (0.15 g, 5.95 × 10^{-4} mol) in toluene (10 cm^3) was added a toluene solution of **1** (0.19 g, 5.95 × 10^{-4} mol, 10 cm^3). The resulting mixture was stirred at −20 °C with light excluded from the reaction vessel for 45 min by which time analysis by ^{31}P NMR spectroscopy showed the formation of the initial κ^2-NN product. The solvent was then removed under vacuum affording the product as a yellow-orange solid, which was stored at −30 °C to preserve the κ^2-NN coordination of the ligand (0.20 g, 74%). NMR analysis was undertaken by addition of d$_8$-toluene to a sample of **13** held at −196 °C in the absence of light. The frozen solution was transferred to the pre-cooled (−90 °C) probe of the NMR spectrometer and gradually warmed to ambient temperature in 10 °C increments.

[PdMe$_2$(1-κ^2-NN)], 13a. ^{1}H NMR (499.8 MHz, d$_8$-toluene, 253 K) δ ppm: 0.55 (s, 3H, PdCH_3), 1.05 (s, 3H, PdCH_3), 2.15 (m, 4H, MeN(C$_4H_8$)N), 2.21–2.28 (m, 5H, Ph$_2$PC$_2H_4$N and CH_3N(C$_4$H$_8$)N), 2.62 (m, 4H, MeN(C$_4H_8$)N), 2.90 (m, 2H, Ph$_2$PC$_2H_4$N), 7.22–7.27 (m, 8H, *o*-/*m*-Ph*H*), 7.79 (m, 2H, *p*-Ph*H*); ^{13}C{^{1}H} (125.7 MHz, d$_8$-toluene, 223 K) δ ppm: −2.3 (s, PdCH_3), 15.4 (s, PdCH_3), 26.6 (s, PCH_2CH_2), 51.4 (s, CH_3N(CH_2CH_2)$_2$N), 58.2 (s, MeN(CH_2CH_2)$_2$N), 60.5 MeN(CH$_2$CH_2)$_2$N), 63.8 (s, PCH$_2$CH_2N), 133.4 (s, *m*-Ph*C*), 133.6 (s, *p*-Ph*C*), 134.4 (s, *o*-Ph*C*), 138.6 (s, *i*-Ph*C*); ^{31}P{^{1}H} (202.3 MHz, d$_8$-toluene, 223 K) δ ppm: +16.5 (s); due to the thermal sensitivity of the complex, satisfactory MS and CHN data could not be obtained.

On gradual warming isomerisation to the κ^2-PN derivative was complete on attaining 10 °C, at which temperature the onset of rapid decomposition started to become apparent.

[PdMe$_2$(1-κ^2-PN)], 13b. ^{31}P{^{1}H} (202.3 MHz, d$_8$-toluene, 283 K): δ ppm: +43.8 (s, [PdMe$_2$(**1**-κ^2-PN)]).

Synthesis of [PdCl$_2$(*N*-methylpiperazine-κ^2-NN)]$_2$, 14. Initially, K_2PdCl_4 was prepared by treating an aqueous suspension of $PdCl_2$ (0.32 g, 1.80 × 10^{-3} mol) with KCl (0.27 g, 3.62 × 10^{-3} mol) in water (*ca.* 10 cm^3) under air. The resulting orange-brown solution was filtered and neat *N*-methylpiperazine (0.20 cm^3, 1.80 × 10^{-3} mol) added dropwise, under air, which resulted in the immediate precipitation of an orange solid. Complex **14** was isolated by filtration and subsequent washing with ice-cold water (2 × 1 cm^3), EtOH (2 × 10 cm^3), MeOH (2 × 10 cm^3), Et_2O (3 × 10 cm^3) and dried *in vacuo*, as an orange solid in 94% (0.47 g) yield. Crystals of X-ray quality were grown from a solution containing a small sample **14** in a minimum of water by cooling at 5 °C for 18 h (calc.: $C_5H_{12}Cl_2N_2Pd$ C, 21.64; H, 4.37; N, 10.10. Found: C, 21.33; H, 4.37; N, 9.82). ^{1}H NMR (400.1 MHz, D_2O) δ ppm: 2.49 (s, 3H, CH_3N), 2.55 (pseudo-d, J_{HH} = 7.6 Hz, 4H, CH_2), 3.80 (d, pseudo-d, J_{HH} = 7.6 Hz, 4H, CH_2); ^{13}C{^{1}H} NMR (100.6 MHz, d$_6$-DMSO) δ ppm: 46.0 (*C*H$_3$), 50.0 (HN(*C*H$_2$)$_2$), 54.8 (MeN(*C*H$_2$)$_2$); MS (ES$^+$, MeCN/DMSO) *m*/*z*: 283.2 [M–Cl + MeCN]$^+$, 316.2 [M–Cl + DMSO]$^+$

X-Ray crystallography

The X-ray single crystal data were collected on Bruker 3-circle diffractometers equipped with CCD area detectors SMART 1 K (**5** and **10**) and SMART 6 K (**1**, **6b**, **14**). Graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used. The crystals were cooled using Cryostream (Oxford Cryostreams) open-flow N_2 cryostats. Crystal data and other experimental details are given in Table 5. Semi-empirical absorption corrections[46] (based on

Table 5 Data collection and refinement parameters for compounds **1**, **5** and complexes **6b**, **10** and **14**

	1	**5**	**6b**	**10**	**14**
CCDC dep. No.	605821	605822	605823	605824	605825
Empirical formula	$C_{19}H_{25}N_2P$	$C_{20}H_{28}N_2PCl$	$C_{19}H_{25}Cl_2N_2PPd$	$[C_{19}H_{25}ClN_2PPd]_2[H_8MgO_{12}S_2]\cdot 6H_2O$	$C_5H_{12}Cl_2N_2Pd$
Formula weight	312.38	362.86	489.68	1305.05	277.47
T/K	120	120	120	120	120
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
Space group (No.)	$P2_1/c$ (#14)	*Fdd*2 (#43)	*P*-1 (#2)	$P2_1/c$ (#14)	*Pnma* (#62)
a/Å	7.183(1)	20.016(2)	7.938(1)	16.925(2)	11.055(1)
b/Å	7.348(1)	68.506(9)	9.597(1)	8.657(1)	8.1413(3)
c/Å	33.014(6)	5.9460(7)	13.675(1)	18.077(2)	9.399(1)
α/°	90	90	75.08(1)	90	90
β/°	90.10(1)	90	80.52(1)	92.94(1)	90
γ/°	90	90	88.71(1)	90	90
V/Å	1742.4(6)	8153.3(17)	992.7(2)	2645.3(5)	845.94(14)
Z	4	16	2	2	4
ρ_{calc}/ g cm^{-3}	1.191	1.182	1.638	1.638	2.179
μ(Mo Kα), mm^{-1}	0.16	0.27	1.29	1.00	2.75
Reflections: collected	16022	16540	16957	30538	11409
unique	4000	3952	5768	7011	1316
with $I > 2\sigma(I)$	3059	3234	4813	6194	1233
R_{int} (%)	8.2	5.2	4.7	3.4	2.2
Refined variables	200	225	228	355	81
R_1 and wR_2 (%)[a]	7.5, 20.1	7.1, 16.4	2.7, 6.1	2.5, 5.7	1.9, 4.8

[a] $R_1 = \sum\|F_c| - |F_o\|/\sum|F_o|$ for reflections with $I > 2\sigma(I)$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

Laue equivalents) were performed for **5**, **10** and **14**. Crystals of **1** grow as pseudo-merohedral twins with the approximate twin law of (−1 0 0/0 −1 0/0 0 1). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data using SHELXTL software.[47] All non-hydrogen atoms were refined in anisotropic approximation. All H atoms in **14** and those H atoms hydrogen-bonding in **5** (NH^+) and **10** (H_2O) were refined in isotropic approximation. Methyl groups were refined as rigid bodies, other H atoms were included as 'riding' on C atoms.

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