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Platinum complexes of tertiary amine functionalised phosphines

Matthew L. Clarke [a,*], Alexandra M.Z. Slawin [b], J. Derek Woollins [b]

[a] School of Chemistry, Cantocks Close, University of Bristol, Bristol BS8 1TS, UK
[b] School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

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Abstract

The reaction of several tertiary amine functionalised phosphines with [Pt(COD)Cl_2] has been studied. Reactions with ratios of L:Pt = 2 proceeded cleanly to give either *cis* or *trans* complexes depending on the cone angle of the phosphines. The *trans* complexes could also be prepared by reaction with Zeise's salt. Reactions of [Pt(COD)Cl_2] with L:Pt = 1 are less straightforward, and a mixture of *cis* and *trans* monodentate complexes, and in one example, a chelate complex have been isolated. The X-ray crystal structures of [$PtCl_2(\eta^2$-$^i Pr_2PN(Me)CH_2CH_2NMe_2)$] and a monodentate complex [*trans*-$PtCl_2(\eta^1$-$^i Pr_2PNH$-*c*-$NC_5H_{10})_2$] are reported.

Keywords: Co-ordination chemistry; Platinum; Catalysis; Hemi-labile; Phosphines; Chelate ligands

1. Introduction

Hemilabile ligands continue to provide novel applications in catalysis and organometallic chemistry. Phosphorus-amine ligands have proved to be very useful in several reactions. For example, there are a large range of chiral P,N ligands that have been shown to provide excellent enantioselectivity in several asymmetric processes [1] the use of phosphine–imine ligands has proved fruitful in palladium catalysed C–C bond forming reactions [2] and pyridylphosphine palladium complexes catalyse the carbonylation of alkynes thousands of times more effectively than triphenylphosphine palladium catalysts [3]. This reaction is an industrially viable process.

In the last few years, several catalytic systems containing potentially hemilabile phosphine ligands have been developed that allow the Suzuki cross coupling reaction to be carried out using more readily available and less costly aryl chlorides. Two of the ligand types are shown in Fig. 1. The P,O chelate ligand **1** can catalyse the coupling of aryl chlorides (1 mol% $Pd_2dba_3 \cdot CHCl_3$, 105 °C) [4] while a more active catalytic system was simultaneously developed by Buchwald and co-workers, who demonstrated that palladium complexes of ligand **2** were particularly suited to this reaction [5]. Further study revealed that the more readily synthesised ligand **3** could be used at least as effectively, even at room temperature (it is possible that ligand **3** acts a phosphorus–arene–alkene chelate) [6].

It is thought that the catalytic reaction proceeds through palladium complexes that contain only one phosphine ligand, and are, therefore, very reactive in both oxidative addition and transmetallation steps. The ligands **2** and **3** have also shown utility in palladium catalysed amination and etherifications of aryl chlorides [7]. We envisaged that reaction of a di-amine with $^i Pr_2PCl$ or Cy_2PCl could deliver a range of P–N ligands that might be useful in this reaction. Work described in our preliminary communication established that palladium complexes prepared (in situ) from **4** and **5** are a cheap and readily available catalyst for the Suzuki reaction of aryl chlorides. Ligand **6** and an analogue of **5** that lacked the second N atom, gave much lower yields (Fig. 2, Scheme 1) [8].

Our initial attempts at isolating the catalytic intermediates in these reactions have not been successful. However, it seems reasonable that a difference in co-ordination chemistry is responsible for the differing catalytic activity seen from the various phosphino-amine ligands. In order to gain greater understanding of the

* Corresponding author. Fax: +44-117-929-0509
E-mail address: matt.clarke@bristol.ac.uk (M.L. Clarke).

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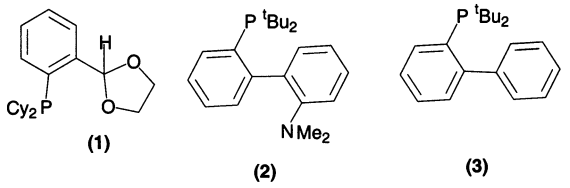


Fig. 1.

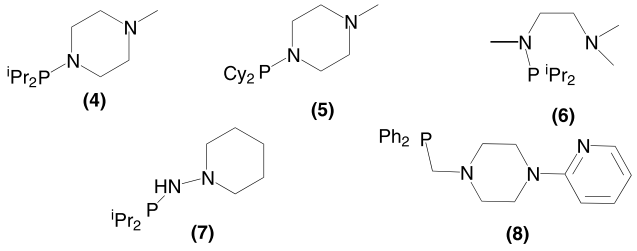


Fig. 2.

co-ordination chemistry of these types of P–N ligand, we have studied the reaction of a range of tertiary amine functionalised phosphines with well known platinum precursors. Platinum complexes derived from P–N ligands have been extensively studied [9]. However, these generally feature a phosphine that contains a more strongly co-ordinating sp^2 hybridised nitrogen donor. Late transition metals derived from P–N ligands in which the N atom is an sp^3 hybridised tertiary amine are far less common [10,11], thus, providing the impetus for the study described here.

2. Experimental

2.1. General

All manipulations were carried out under an atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropriate drying agent (THF, Et_2O, DCM) or obtained as anhydrous grade (Aldrich Chemical Co.). ^1H and ^{31}P NMR spectra were recorded using a 'Varian 2000' 300 MHz spectrometer. IR spectra were recorded as KBr discs (prepared in air) on a Perkin–Elmer PE2000 FTIR–RAMAN spectrometer. Ligands **4**, **6** and **8** have been reported elsewhere [8] [12]. $[Pt(COD)Cl_2]$ was prepared by literature methods [13].

2.2. X-ray crystallography

Crystal structure **12** was obtained using a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected using 0.3° or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures.

Crystal structure **13** was determined by a Ryder CCD diffractometer using Mo Kα radiation.

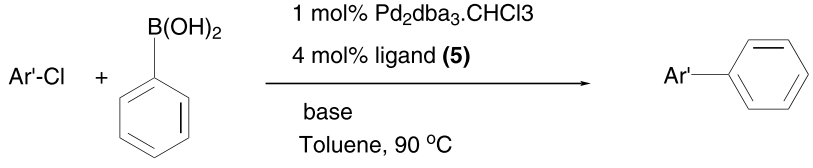
All data were corrected for Lorentz, polarisation and long term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by F^2 (SHELXTL) [14] for all data with $I > 3\sigma(I)$ (Table 1).

2.3. N-Di-isopropylphosphino-N′-aminopiperidine (7)

This ligand has not been reported previously and is prepared by a similar method to that used for the other phosphino-amines. Dropwise addition of neat di-isopropylchlorophosphine to a solution of *N*-amino-piperadine and triethylamine in diethylether gives a white precipitate of Et_3NHCl and a solution of the desired ligand within 1 h. Filtration (using a cannula or filter stick) and removal of solvent gave the desired ligand

Table 1
Crystal data for compounds **4** and **5**

	12	**13**
Empirical formula	$C_{11}H_{27}Cl_2N_2PPt$	$C_{22}H_{50}Cl_2N_4P_2Pt$
M	484.31	698.59
Crystal system	orthorhombic	triclinic
Space group	$Pna2_1$	$P\bar{1}$
a (Å)	20.5504(10)	7.976(2)
b (Å)	8.9428(5)	10.169(3)
c (Å)	9.1679(4)	10.234(3)
α (°)	90	70.952(11)
β (°)	90	81.716(14)
γ (°)	90	72.550(9)
U (Å^3)	1684.86(14)	747.5(4)
Z	4	1
μ (mm^{-1})	8.724	4.995
Reflections measured	6764	4606
Independent reflections	2361	3865
Final R_1	0.0.261	0.0249
WR_2 $[I > 2\sigma(I)]$	0.0523	0.0714



Scheme 1.

(colourless oil) in essentially pure form, and quantitative yield.

^{31}P NMR (121.4 MHz; $CDCl_3$): δ 62.9. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.0 (12H, m), 1.1–1.3 (4H, m), 1.6 (4H, m), 2.6 (4H, s, br.), 3.0 (1H, s, br.). M. S. (ES+) MH+req's 217.1833; Found: 217.1833.

2.4. Synthesis of trans complexes from Zeise's salt

A solution of ligand (2 equiv.) in CH_2Cl_2 was added dropwise to an acetone solution of Zeise's salt. After stirring for 5 min, the solvent was removed and the complex extracted with CH_2Cl_2, filtered through Celite and had solvent removed in vacuo. Triturating the pale yellow precipitate with Et_2O and drying in vacuo gave the desired complex in essentially quantitative yield.

2.5. Trans-dichloro-bis-(N-Di-isopropylphosphino-N-methylpiperazine)platinum(II) (**9**)

Yellow powder. *Anal*. Calc. for $C_{22}H_{50}N_4P_2Pt_1Cl_2$: C, 37.82; H, 7.21; N, 8.02. Found: C, 38.05; H, 7.16; N, 7.86%. IR(ν_{max} cm^{-1}) 2968, 2932, 2841, 2786, 1604, 1453, 1370, 1288, 1256, 1217, 1288, 1147, 1098, 1002, 961, 924, 884, 784, 696, 673, 635, 583, 498, 406, 338. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 77.3 ($^1J_{P-Pt} = 2678$ Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.2 (12H, m), 2.25, (3H, s), 2.42 (4H, s, br.), 2.75 (2H, m), 3.42 (4H, s, br.). M. S. (ES+) MH+req's 698.2614; Found: 698.2619.

2.6. Trans-dichloro-bis-(N-Di-isopropylphosphino-NN′N″-trimethylethylenediamine)platinum(II) (**10**)

This complex, which is very soluble was isolated by cooling a hexane solution in the freezer overnight to give yellow crystals. *Anal*. Calc. for $C_{22}H_{54}N_4P_2Pt_1Cl_2$: C, 37.61; H, 7.76; N, 7.97. Found: C, 38.20; H, 8.29; N, 7.80%. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 82.2 ($^1J_{P-Pt} =$ 2641 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.25 (12H, m), 2.14 (6H, s), 2.45 (2H, t, app., $J = 7$ Hz), 2.65 (2H, m), 2.80 (2H, t, $J = 4.3$ Hz), 2.22 (3H, br.). M. S. (ES+) MH+req's 702. 2927; Found: 702.2938.

2.7. Cis-[(8)$_2$PtCl$_2$] (**11**)

Addition of CH_2Cl_2 to a schlenk tube containing 2 equiv. of ligand **8** and 1 equiv. of [Pt(COD)Cl_2] and stirring for 1 h gives quantitative conversion to the *cis* complex. Removal of solvent to near dryness, and addition of diethylether produces a white precipitate that was collected on a frit (in air), washed with diethyl ether, and dried in vacuo.

Anal. Calc. for $C_{44}H_{48}N_6P_2Pt_1Cl_2 \cdot 0.5\ CH_2Cl_2$: C, 51.83; H, 4.79; N, 8.15. Found: C, 52.46; H, 5.07; N, 7.86%. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 1.2 ($^1J_{P-Pt} =$ 3641 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ: 2.45 (4H, s, br.), 3.25 (4H, s, br.), 3.7 (2H, s, br.), 5.3 (0.7H, s CH_2Cl_2), 6.58 (2H, m), 7.12 (4H, t, $J = 7.0$ Hz), 7.25 (2H, m), 7.44 (1H, t, $J = 7.4$ Hz), 7.70 (4H, t, $J = 8.6$ Hz), 8.13 (1H, d, $J = 3.9$ Hz). M. S. (ES+) (M−Cl)+ req's 952. 2752; Found: 952.2753.

Addition of 1 or 2 equiv. of $AgBF_4$ to this compound provides a new species which shows a ^{31}P NMR spectrum that strongly suggests the piperazine nitrogen is co-ordinated to the platinum as shown in structure **14**. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ −9.1 ($^1J_{P-Pt} = 3252$ Hz; satellites weak and slightly broad), −61.1 ($^1J_{P-Pt} =$ 3140 Hz; satellites weak and slightly broad).

2.8. Cis-dichloro-(N-Di-isopropylphosphino-N,N′N″-trimethylethylenediamine, P,N)platinum(II) (**12**)

Addition of a dichloromethane solution containing 1 equiv. of N-Di-isopropylphosphino-*N*,*N*′*N*″-trimethylethylenediamine to a dichloromethane suspension of [Pt(COD)Cl_2] gave initially a mixture of products. The major species had the following NMR spectrum typical of a *cis* chelate complex.

^{31}P NMR (121.4 MHz; $CDCl_3$): δ 61.8 ($^1J_{P-Pt} = 4001$ Hz). M.S. 449 $(M-Cl)^+$ Recrystallisation by slow diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the mixture gave a few crystals of **12**. There was only enough pure material for a X-ray crystallography and elemental analysis. *Anal*. Calc. for $C_{11}H_{27}N_2P_1Pt_1Cl_2$: C, 27.28; H, 5.62; N, 5.78. Found: C, 27.63; H, 5.63; N, 5.60%.

2.9. Trans-dichloro-bis-(N-Di-isopropylphosphino-N′-aminopiperidine)platinum(II) (**13**)

Addition of a solution of N-Di-isopropylphosphino-*N*′-aminopiperidine in CH_2Cl_2 to a suspension of [Pt(COD)Cl_2] in CH_2Cl_2 yields a yellow solution, which when analysed by ^{31}P NMR shows several peaks with one major product ($\delta = 59$, $^1J_{P-Pt} = 2485$ Hz). Slow diffusion (in air) of Et_2O to a concentrated CH_2Cl_2 solution of this mixture reproducibly gave a few large yellow blocks of the *trans* complex. This complex was also prepared in high yield by the reaction of ligand **7** with Zeise's salt in 2:1 ratio.

Anal. Calc. for $C_{22}H_{54}N_4P_2Pt_1Cl_2$: C, 37.82; H, 7.21; N, 8.02. Found: C, 38.15; H, 7.03; N, 7.92%. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 59.1 ($^1J_{P-Pt} = 2485$ Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ: 1.31 (12H, m), 1.55 (6H, s, br), 2.68 (4H, m, br.), 3.48 (1H, s, v.br.), 4.75 (2H, m, br.). M. S. (FAB+): 697 (M+), 663, (M−Cl+). This compound was additionally characterised by X-ray crystallography.

3. Results and discussion

The amino-phosphine ligands **4**, **6** and **7** are obtained in essentially pure form by the slow addition of neat di-isopropyl-chlorophosphine to an Et_2O solution of the corresponding diamine and triethylamine. The reactions are typically complete in about 1 h. All of the ligands are air and moisture sensitive liquids or oils, and were characterised by multinuclear NMR, IR and high resolution mass spectroscopies and were described in communication form. Ligand **7**, which still contains an NH functionality, does not react further with $^{i}Pr_2PCl$ to give a PNP type ligand. Ligand **8** has been reported elsewhere [12].

The reaction of Zeises salt with diisopropylphosphino-*N*-methylpiperazine, **4** gave the P-monodentate *trans*-(η^1-L)$_2$PtCl$_2$ compound (**9**) (100% conversion). Analytically pure material was obtained after extraction with DCM, filtration, and precipitation with diethyl ether.

Reaction of diisopropylphosphino-*N*,*N*′,*N*″-trimethylethylenediamine, **10** with Zeises salt also gave a P-monodentate complex in 100% conversion. Ligand **6** has three very flexible alkyl groups, and consequently its platinum complex is significantly more soluble than **9**. Crystals of *trans*-(η^1-L)$_2$PtCl$_2$ (**10**) could be obtained by cooling a hexane solution in the freezer over night. Complex **13** can also be prepared by the reaction of di-isopropylphosphino-*N*-amino-piperidine, **7** and Zeise's salt (2:1 ratio).

These complexes show the expected singlet with satellites in their ^{31}P NMR spectrum. The magnitude of $^{1}J_{P-Pt}$ (2678, 2642 and 2485 Hz, respectively) is typical for alkyl phosphines located *trans* to each other. The FAB mass spectra of the two complexes supports the formulation suggested by the microanalytical data by showing peaks due to MH+, M−Cl and M−2Cl as the highest mass ions present.

The reaction of simple mono- and di- phosphines with [Pt(COD)Cl$_2$] is a tried and tested method to form *cis* platinum complexes [LPtCl$_2$] or [L$_2$PtCl$_2$]. The products are often formed in quantitative yields and purity after removal of cyclo-octadiene (COD). An examination of the literature reveals that ligands that are significantly more bulky than triphenylphosphine (Tolman cone angle [15] $\theta = 145°$) will generally selectively give *trans* L$_2$PtCl$_2$ complexes. It is likely that the formation of the *trans* complexes is predominantly due to steric factors as no *cis* complexes are observed when electron rich Cy_3P ($\theta = 170°$) [16] or electron poor (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$P ($\theta = 170°$) [17] are reacted with [Pt(COD)Cl$_2$]. However, these reactions are also sensitive to electronic effects as more complicated reactions are generally observed with bulky electron rich ligands: a mixture of *cis* or *trans*-binuclear complexes, *trans* mononuclear complexes and unidentified products can be formed depending on the reactions conditions. It is noteworthy that *cis* and *trans* L$_2$PtCl$_2$ complexes have not been efficiently prepared from [Pt(COD)Cl$_2$] using either $^{i}Pr_3P$, Cy_3P and $^{t}Bu_3P$ as ligands. We estimate that the cone angles of ligands **4**, **6** and **7** to be similar to the parent tri-isopropylphosphine ($\theta = 160°–170°$). Ligand **8**, on the other hand is likely to be considerably less sterically demanding ($\theta = 135°–145°$). P–N type ligands have been observed to give *cis* or *trans*-[(η^1-L)$_2$PtCl$_2$], *cis*-[(η^1-L)(η^2-L) PtCl$_2$], or *cis*-[(η^2-L)$_2$Pt]·2Cl complexes depending on choice of ligand [9,10]. It was, therefore, of interest to determine how ligands **4**–**8** react with this well known precursor.

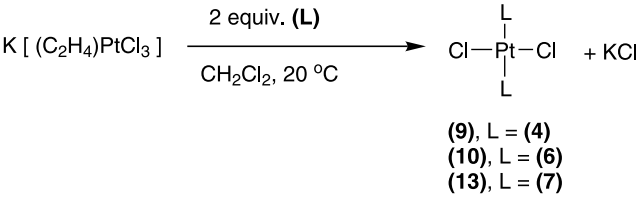
The reaction of ligands **4** and **6** with [Pt(COD)Cl$_2$] in a 2:1 ratio gives the *trans* complexes **9** and **10** (100% conversion by ^{31}P NMR), which had also been prepared from Zeises salt (Schemes 2 and 3). The reaction of **8** with [Pt(COD)Cl$_2$] in a 2:1 ratio gives a quantitative yield of the *cis* complex **11**. The magnitude of $^{1}J_{P-Pt}$ (3641 Hz) is typical of a *cis* phosphine complex. In each case, there is no evidence of nitrogen co-ordination within the complexes. Ligand **7** gave a mixture of products, in which the proportion of *trans*-[L$_2$Pt Cl$_2$] increases over time. None of the peaks observed in the ^{31}P NMR spectrum show $^{1}J_{P-Pt}$ coupling constants diagnostic for P *trans* chloride.

We have also studied the reactions of these ligands and [Pt(COD)Cl$_2$] in an equimolar ratio.

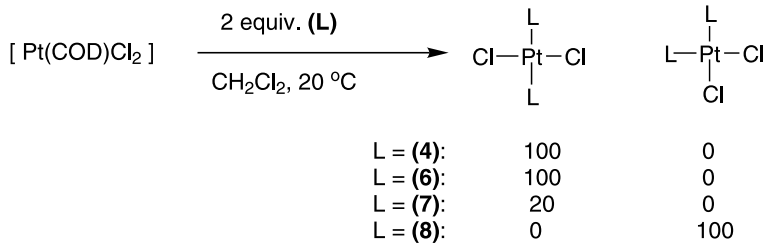
When diisopropylphosphino-*N*-methylpiperazine, **4** was reacted with [Pt(COD)Cl$_2$] in a 1:1 ratio, a complex mixture of products is formed. One of these is assumed to be *trans*-L$_2$PtCl$_2$, **9** as it shares a similar ^{31}P NMR spectrum. We have not been able to separate any new complexes from this mixture.

The situation is somewhat different with diisopropylphosphino-*N*, *N*′,*N*″-trimethylethylenediamine, **6**. Although the reaction does not proceed cleanly, there is clearly a major product present. It was possible to isolate a small sample of this complex in pure form by recrystallisation from dichloromethane–Et_2O. The magnitude of $^{1}J_{P-Pt}$ (4001 Hz) is strongly indicative of a phosphorus positioned *trans* to chloride and a complex of formula [**(6)**PtCl$_2$] is supported by chemical analyses (Scheme 4).

To fully establish the structure of **12**, an X-ray crystal structure determination was carried out (Fig. 3, Table 2). This unambiguously confirms that the major product from the [Pt(COD)Cl$_2$]+1 equiv. Compound **6** is a 1:1



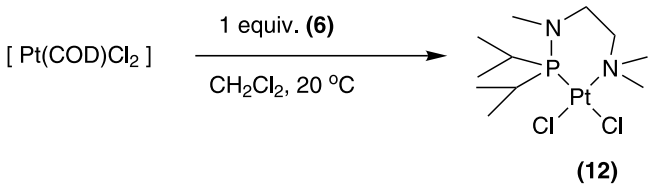
Scheme 2.



Scheme 3.

chelate complex. The platinum complex is of distorted square planar geometry with the P–Pt–N angle within the chelate ring enlarged to 98.0(2)°. The corresponding angle between the chloride ligands is reduced 85.70(10)°. As phosphorus ligands have higher *trans* influence than amines, the Pt–Cl bond *trans* to P is elongated by 0.077 Å compared with the chloride bound *trans* to N. The Pt–N bond lengths in **12** are similar to, but slightly longer, than those found in platinum P–N(sp^2 nitrogen) chelate structures [9]. If the structure is compared with the related structure, [Pt(Cl)(η^2-$Ph_2PN(Me)$–CH_2CH_2–NMe_2, *P*,*N*) ($Ph_2PN(Me)$–CH_2CH_2–NMe_2CoCl_3] reported by Burrows and co-workers [11] many of the parameters are similar. P–N and Pt–N bond lengths in the more electron rich phosphine complex, **12**, are 0.02(5) and 0.05(5) Å shorter, although this small variation could be ascribed to other factors not related to the ligand. The P–Pt–N angle is significantly smaller (90.85(13)°) in the Burrows structure, but this is most likely due to the more sterically crowded metal centre that contains an extra phosphine ligand.

It should be noted that the co-ordination behaviour of **6** in the presence of [Pt(COD)Cl_2] is very different from the phenyl substituted ligand. Whereas, the bulky ligand, **6** generates a *trans*-monodentate complex in the presence of 0.5 equiv. [Pt(COD)Cl_2], the Burrows ligand gave a complex of type *cis*-[(η^2-L-*P*,*N*)(η^1-L-*P*)PtCl]Cl which was in equilibrium with the *cis*-monodentate species. Meanwhile, equimolar reactions of diphenylphosphino-*N*,*N*′,*N*″-trimethylethylenediamine and [Pt(COD)Cl_2] occur cleanly to give the chelate complexes in high yield. It, therefore, appears that increasing steric bulk or basicity can reduce a ligands tendency to chelate. We favour the former explanation, and suggest that this may be due to an indirect effect:



Scheme 4.

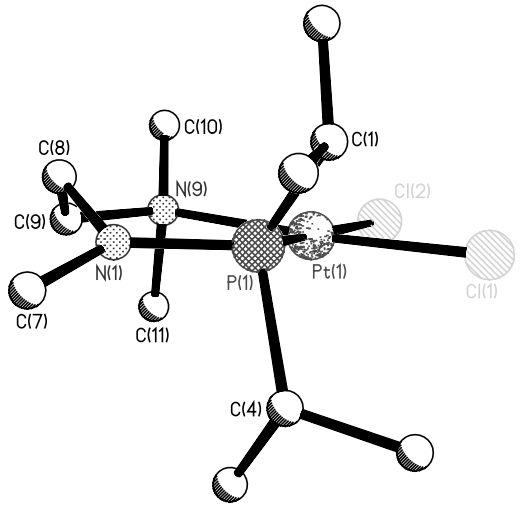


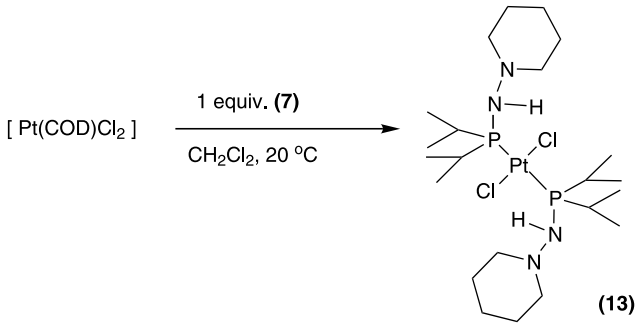
Fig. 3. Molecular structure of complex **12**.

Table 2
Selected bond lengths (Å) and angles (°) for **12**

Bond lengths			
Pt(1)–Cl(1)	2.295(2)	Pt(1)–Cl(2)	2.371(2)
Pt(1)–P(1)	2.224(2)	Pt(1)–N(9)	2.118(8)
P(1)–N(1)	1.650(5)		
Bond angles			
Cl(1)–Pt(1)–Cl(2)	85.7(1)	P(1)–Pt(1)–Cl(1)	87.02(8)
P(1)–Pt(1)–Cl(2)	172.3(2)	N(9)–Pt(1)–P(1)	98.0(2)
N(9)–Pt(1)–Cl(1)	174.1(6)	N(9)–Pt(1)–Cl(2)	89.1(2)
C(7)–N(1)–P(1)	132.0(8)	N(1)–P(1)–Pt(1)	113.2(3)
C(7)–N(1)–C(8)	113.1(7)		

The nitrogen in a *cis*-L_2PtCl_2 complex displaces a chloride ligand that is labilised by the strong *trans* influence of the P atom. The chloride ligands in *trans*-L_2PtCl_2 complexes formed from bulky ligands are bound more strongly to the platinum centre and less likely to dissociate and allow N co-ordination.

The different behaviour that ligands **4** and **6** show when reacted with Pt(COD)Cl_2 may well have some significance. Palladium complexes derived from di-isopropylphosphino-*N*,*N*′,*N*″-trimethylethylenediamine do not show any catalytic activity in the Suzuki coupling reaction of the tricky substrate chloro–toluene. It is



Scheme 5.

tempting to suggest that the formation of a strong P,N-chelate could deactivate the palladium complex towards oxidative addition or transmetallation steps. Di-isopropylphosphino-*N*-methylpiperazine, which does not yield an isolatable P–N chelate complex with platinum shows good catalytic activity in the Suzuki reaction. There is not sufficient evidence to make definite conclusions, but it does seem likely that a subtle difference in co-ordination strength is responsible for the differing catalytic behaviour.

Addition of 1 equiv. of di-isopropylphosphino-*N*-amino-piperidine to $[Pt(COD)Cl_2]$ does not proceed cleanly either. Fortunately, slow diffusion of Et_2O into DCM solutions of the resulting mixture repeatedly gives large yellow blocks of *trans*-L_2PtCl_2 as determined by ^{31}P NMR spectroscopy and chemical analyses (Scheme 5).

The crystal structure of **13** (Fig. 4, Table 3) confirmed our spectroscopic and analytical data that suggested a complex of type *trans*-L_2PtCl_2. The structure has slightly distorted square planar geometry at platinum, and a notable feature is the presence of two intermolecular hydrogen bonds between the NH moiety and a chloride ligand (N(1)–H···Cl = 2.37(5) Å; N(1)–Cl(1) = 3.098(3) Å. The Cl–Pt–P–N–H ring systems are symmetrical, and the angle Cl–Pt–P (91.18(3)° vs. 88.82(4)°) is slightly larger if the chloride and phosphorus ligands are part of the same hydrogen bonded ring. Hydrogen bonding between halide ligands and NH in phosphino-amine metal complexes is often observed, although most reports are of intramolecular hydrogen bonds [18,9]. It is possible the increased steric bulk of the ligand and the *trans* geometry of complex **13** favours the intermolecular hydrogen bonds observed here. The Pt–P distances within this complex are longer than those found in the P–N chelate structure as befits the greater *trans* influence of phosphorus over chloride. The Pt–Cl bond lengths lie in between the values found for the Cl *trans* P and Cl *trans* N in the chelate complex, and are in line with arguments that chloride is slightly more *trans* labilising than amine ligands. The presence of two heteroatom substituents on N(1) does not have any major effect on the P–N bond length (1.668(3) Å), which is planar at nitrogen in common with most phosphino-amines [9].

Reaction of ligand **8** with $[Pt(COD)Cl_2]$ in an equimolar ratio gives an equimolar mixture of $[Pt(COD)Cl_2]$ and *cis*[η^1-**(8)**$_2$$PtCl_2$, (**11**), strong evidence that ligand **8** strongly prefers monodentate *cis* co-ordination. However, when 1 or 2 equiv. of silver perchlorate were added to a NMR tube containing **11**, a new complex is formed quantitatively. Although we have not isolated this new complex, it is worthy of comment, as the ^{31}P NMR spectrum observed is highly

Table 3
Selected bond lengths (Å) and angles (°) for **13**

Bond lengths			
Pt(1)–Cl(1)#	2.306(1)	Pt(1)–Cl(1)	2.306(1)
Pt(1)–P(1)	2.3272(8)	Pt(1)–P(1)#	2.3272(8)
P(1)–N(1)	1.668(3)	N(1)–N(7)	1.428(4)
N(1)–Cl(1)#	3.098(3)	NH(1)–Cl(1)	2.37(5)
Bond angles			
Cl(1)#–Pt(1)–Cl(1)	180.00(5)	Cl(1)#–Pt(1)–P(1)	91.18 (4)
Cl(1)–Pt(1)–P(1)	88.82(4)	Cl(1)#–Pt(1)–P(1)	88.83(4)
Cl(1)–Pt(1)–P(1)#	91.17(4)	P(1)–Pt(1)–P(1)#	180.0
N(7)–N(1)–P(1)	122.5	N(1)–N(7)–C(8)	110.0(3)
N(1)–P(1)–Pt(1)	109.5(1)		

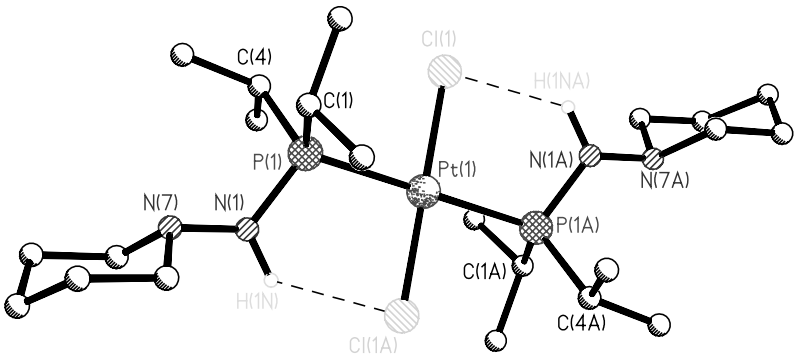
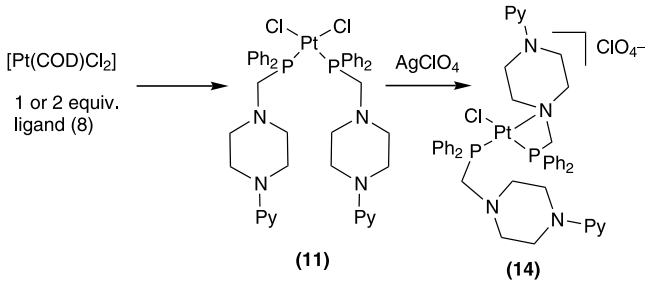


Fig. 4. Molecular structure of complex **13**.



Scheme 6.

distinctive of a particular co-ordination type. Two slightly broadened singlets with shortened Pt satellites (satellites were ca. 5–10% of the main peak area, possible due to relaxation effects) are observed in the ^{31}P NMR spectrum ($\delta_P = -9.1$, $^1J_{P-Pt} = 3252$ Hz; $\delta_p = -61.1$, $^1J_{P-Pt} = 3140$ Hz). There was no change in this spectrum when cooled to -60 °C. A shift of 60 ppm upfield, along with a reduction in the magnitude of $^1J_{P-Pt}$ suggests that a four membered phosphorus containing ring had formed [19,13]. This is most easily explained by structure **14**. The lack of P–P coupling is somewhat surprising but can be ascribed to the somewhat broad resonances. Addition of silver salts to other complexes described in this paper generally led to a complex mixture of products that could not be identified (Scheme 6).

4. Summary and conclusions

This study has highlighted the different co-ordination chemistry observed when bulky electron rich ligands are used in place of more common diphenylphosphino substituted ligands. We have also determined the propensity of the ligands **4**, **6**, **7** and **8** to form chelate complexes with platinum. It is clear that these ligands are far less willing to act as bidentate ligands with platinum than sp^2 nitrogen functionalised phosphines. Sp^2 nitrogen functionalised phosphines have been shown to readily form four, five and six membered chelate rings when added to [Pt(COD)Cl$_2$] or similar precursors [10]. Further applications of weakly chelating electron rich ligands in homogeneous catalysis will be reported in due course.

5. Supplementary data

Full crystallographic data has been deposited at the Cambridge crystallographic database and is available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request quoting deposition codes: CCDC 185583 and CCDC 185584.

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