DALTON
FULL PAPER

The preparation and coordination chemistry of phosphorus(III) derivatives of dialkyl hydrazines

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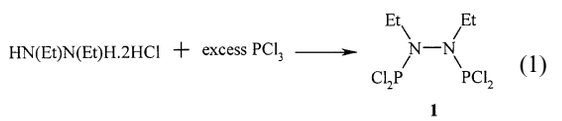
The formation of the new inorganic hydrazine based ligands $R_2PNR'NR'PR_2$ [R′ = Et, R = Cl, Ph, OPh, CH_2Ph, *o*-$MeOC_6H_4$: R′ = Me, R = *o*-MeC_6H_4, *o*-$MeOC_6H_4$] is reported. These ligands have been complexed at Pd(II) and Pt(II) centres and demonstrative X-ray structures have been determined. When R = *o*-$MeOC_6H_4$ the oxygen atoms of two of the OMe groups coordinate pseudo axially.

Since the discovery of bis(dihalophosphino)amines, $X_2PN(R)PX_2$,[1–3] extensive research has been carried out on the main group and transition metal/organometallic chemistry of this type of ligand system.[1–16] This is in sharp contrast to the corresponding studies of the dinitrogen-bridged diphosphines, bis(dihalophosphino)hydrazines, $X_2PN(R)N(R)PX_2$, which, until recent work by Reddy and Katti,[17–19] has been limited to a few reports.[20,21] The development of the chemistry of bis(dihalophosphino)hydrazine ligands is of particular significance because they have a similar chain length to that of dppe, a ligand which has proved adept at forming five-membered chelate rings and has demonstrated significant applications in catalytic systems. The reactivity of the halide substituents on these ligands may also be utilised in the development of a wide range of $R'_2PN(R)N(R)PR'_2$-type derivatives, allowing excellent control of the steric and electronic properties of any subsequent ligands. The studies reported by Reddy and Katti have centred on the synthesis and coordination chemistry of derivatives of bis(dichlorophosphino)dimethylhydrazine, $Cl_2PN(Me)N(Me)PCl_2$. We have studied the dimethyl and diethylhydrazine, and here report on the effects changes in the substituent groups have on the coordination chemistry of such ligands. We have also synthesised a number of derivatives of $Cl_2PN(Me)N(Me)PCl_2$ containing phenyl groups with OMe in the *ortho* position to investigate the possibility of these substituents occupying sites above and below metal centres in complexes, thus limiting the available approach routes of reactants in catalytic systems.

Results and discussion

As mentioned above Katti has reported the synthesis of $Cl_2PN(Me)N(Me)PCl_2$ from the reaction of 1,2-dimethylhydrazine dihydrochloride and phosphorus trichloride.[17] Employing a similar technique we were able to synthesise the analogous diphosphine, $Cl_2PN(Et)N(Et)PCl_2$ **1**, from the reaction of 1,2-diethylhydrazine dihydrochloride and phosphorus trichloride [eqn. (1)].



(1)

1

Dropwise addition of PCl_3 to a finely ground sample of 1,2-diethylhydrazine dihydrochloride results in the formation of a viscous orange suspension. The reaction mixture is then heated under reflux for 96 hours and the excess PCl_3 removed *in vacuo* to leave a viscous orange oil. Kugelrohr distillation of the crude product leaves **1** as a colourless oil in good yield (72%). The $^{31}P-\{^1H\}$ NMR spectrum of **1** shows a singlet at δ(P) 156, an upfield shift of approximately 4 ppm from the value reported for $Cl_2PN(Me)N(Me)PCl_2$,[17] and FAB^+ mass spectrometry shows the expected parent-ion peak (*m*/*z* 290 $[M]^+$). Elemental analysis is in good agreement with the calculated values and the IR spectrum shows a band at 952 cm^{-1} that can be assigned to ν(PN). Having successfully synthesised $Cl_2PN(Et)N(Et)PCl_2$ we were then able to use this compound as a chloro precursor in nucleophilic substitution reactions and reactions with Grignard reagents to produce a range of aryloxy- and aryl-substituted phosphorus(III) hydrazides.

Reaction of $Cl_2PN(Et)N(Et)PCl_2$ with four equivalents of PhOH in the presence of Et_3N in hexane proceeds smoothly to yield the aryloxy-functionalised ligand $(PhO)_2PN(Et)N(Et)P(OPh)_2$ **2**. Dropwise addition of a hexane solution of phenol and triethylamine to a stirred hexane solution of $Cl_2PN(Et)N(Et)PCl_2$ results in the immediate precipitation of $[NEt_3H]Cl$ as the reaction proceeds. Stirring is continued for a further 12 hours. Removal of the ammonium salt by suction filtration and removal of the solvent *in vacuo* leaves **2** as a colourless viscous oil in good yield (81%). The $^{31}P-\{^1H\}$ NMR spectrum of **2** consists of a single resonance at δ(P) 139, the difference in chemical shift between it and **1** (17 ppm) being comparable to that observed between $Cl_2PN(Me)N(Me)PCl_2$ and $(PhO)_2PN(Me)N(Me)P(OPh)_2$.[17,18] Elemental analysis is in agreement with calculated values and FAB^+ mass spectrometry shows the expected parent-ion peak (*m*/*z* 520 $[M]^+$). The IR spectrum of **2** shows bands which can be assigned to ν(PN) and ν(PO) (930 and 1030 cm^{-1} respectively).

Reaction of $Cl_2PN(Et)N(Et)PCl_2$ **1** with four equivalents of RMgBr (R = Ph or CH_2Ph), in diethyl ether yields the diphosphines $Ph_2PN(Et)N(Et)PPh_2$ **3** and $(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2$ **4** as colourless and pale yellow solids in good yields (70 and 74% respectively). FAB^+ mass spectrometry shows peaks corresponding to the parent-ion peaks $[M]^+$ (*m*/*z* 456 for **3** and 512 for **4**) and the IR spectra contain bands which can be assigned to ν(PN) (970 for **3** and 962 cm^{-1} for **4**) The $^{31}P-\{^1H\}$ NMR spectra of the two compounds show singlets at δ(P) 64.2 and 64.8 respectively, significantly further upfield than the value for **2** due to the lack of highly electronegative oxygen atoms close to the phosphorus centres. Elemental analyses are in good agreement with calculated values.

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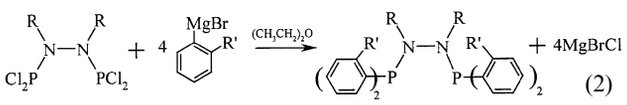
A series of ligands containing phenyl groups with substituents in the *ortho* position have also been successfully synthesised. Reaction of the chloro precursor **1** with the Grignard reagent *o*-anisylmagnesium bromide, *o*-$CH_3OC_6H_4MgBr$, generates $(o\text{-}C_6H_4OCH_3)_2PN(Et)N(Et)P(o\text{-}C_6H_4OCH_3)_2$ **5**, while reaction of $Cl_2PN(Me)N(Me)PCl_2$ with *o*-anisylmagnesium bromide or *o*-tolylmagnesium chloride, *o*-$CH_3C_6H_4MgCl$, yields $(o\text{-}C_6H_4OCH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4OCH_3)_2$ **6** and $(o\text{-}C_6H_4CH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4CH_3)_2$ **7** respectively [eqn. (2)].



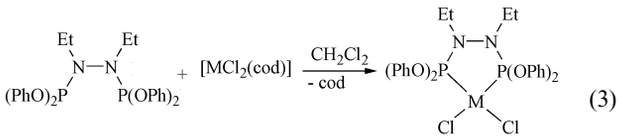
R = Et , R' = OMe (**5**); R= Me, R' = OMe(**6**), R= Me, R' = Me **7.**

The $^{31}P\text{-}\{^1H\}$ NMR spectra of **5** and **6** show singlets at δ(P) 40.5 and 42.6 respectively and the FAB^+ mass spectra contain peaks corresponding to $[M]^+$ (*m*/*z* 576 for **5** and 549 for **6**). The IR spectra of both compounds show a band which can be assigned to ν(PN) (933 for **5** and 969 cm^{-1} for **6**) and elemental analyses are in agreement with calculated values. As with **5** and **6** the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **7** indicates the presence of a single phosphorus species, represented by a singlet at δ(P) 47.2 and the FAB^+ mass spectrum shows a peak which corresponds to the parent-ion (*m*/*z* 485 $[M]^+$).

The $R_2PNR'NR'PR_2$ ligands described above are all stable in air as solids though the chloro starting material **1** hydrolyses rapidly in air.

Katti has reported the synthesis of various metal complexes in which diphosphine derivatives of $Cl_2PN(Me)N(Me)PCl_2$ act as *P*,*P*′ chelates.[17–19] Here we describe the synthesis of metal complexes containing derivatives of $Cl_2PN(Et)N(Et)PCl_2$ acting as *P*,*P*′ chelates, as well as further examples involving derivatives of $Cl_2PN(Me)N(Me)PCl_2$.

The reaction of $(PhO)_2PN(Et)N(Et)P(OPh)_2$ **2** with equimolar quantities of $[PtCl_2(cod)]$ or $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) in dichloromethane proceeds according to eqn. (3) to yield the five-membered, *P*,*P*′ chelates *cis*-$[PtCl_2\{(PhO)_2PN(Et)N(Et)P(OPh)_2\}]$ **8** and *cis*-$[PdCl_2\{(PhO)_2PN(Et)N(Et)P(OPh)_2\}]$ **9** respectively.



M = Pt (**8**), Pd (**9**)

The $^{31}P\text{-}\{^1H\}$ NMR spectra of **8** and **9** [δ(P) 92.3 and 116.6 respectively] exhibit an upfield shift of approximately 3 ppm when compared to the analogous dimethyl complexes *cis*-$[MCl_2\{(PhO)_2PN(Me)N(Me)P(OPh)_2\}]$.[19] The IR spectra of **8** and **9** both contain bands corresponding to ν(PN) and ν(PO) (968 and 1069 cm^{-1} respectively for **8** and 955 and 1070 cm^{-1} respectively for **9**) as well as two distinct ν(MCl) vibrations which are indicative of a *cis*-MCl_2 geometry. FAB^+ mass spectrometry shows the expected parent-ion peaks and peaks corresponding to the loss of a chloride ion and elemental analysis is in good agreement with calculated values. The solid state structure of **8** is shown in Fig. 1 and selected bond lengths and angles are shown in Table 1. The structure contains two crystallographically independent molecules although the two molecules are structurally similar. The five-membered chelate rings result in P–Pd–P angles of less than 90°. Both molecules are almost perfectly planar about the palladium [mean deviation

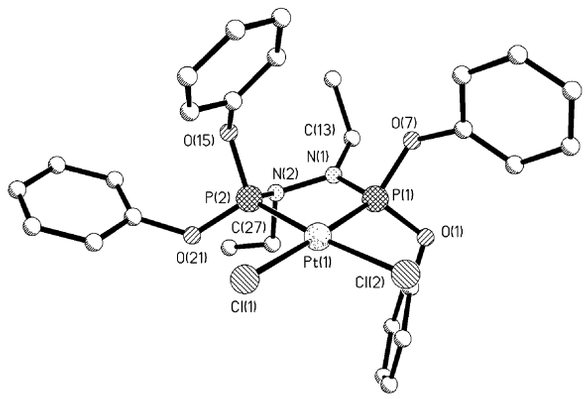
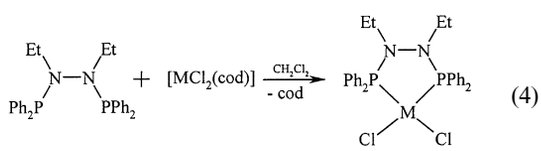


Fig. 1 The solid state structure of **8**.

from the PdP_2Cl_2 planes of 0.04 and 0.02 Å]. The PdP_2N_2 rings have a classic open envelope conformation. In the Pd(1)–P(1)–N(1)–N(2)–P(2) ring N(2) is out of the plane by 0.59 Å and in the Pd(2)–P(3)–N(3)–N(4)–P(4) ring N(3) and N(4) lie above the coordination plane by 0.41 and 0.72 Å respectively. The P–N, Pd–Cl and Pd–P bond lengths are similar to values previously reported for single bonds in the related chelate complex *cis*-$[PdCl_2\{(p\text{-}BrC_6H_4O)_2PN(Me)N(Me)P(OC_6H_4Br\text{-}p)_2\}]$,[19] although the P–N bond lengths are considerably shorter than those observed in **14** (*vide infra*) and the chelate urea based complexes we have previously reported.[22]

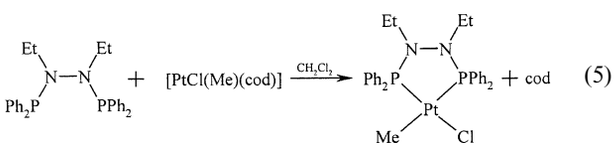
$Ph_2PN(Et)N(Et)PPh_2$ also reacts with equimolar quantities of $[PtCl_2(cod)]$ and $[PdCl_2(cod)]$ to yield five-membered *P*,*P*′ chelates [eqn. (4)] to give **10** and **11**.



M = Pt (**10**), Pd (**11**)

The $^{31}P\text{-}\{^1H\}$ NMR spectra of **10** and **11** show singlets at [δ(P) 100.4 and 132.2 respectively] with $J\{^{195}Pt\text{–}^{31}P\}$ of 4055 Hz for **10** in agreement with values previously reported for Pt(II) complexes containing the phosphorus, of a P–N ligand, *trans* to a chloride[23]—due to the lack of a highly electronegative oxygen next to the phosphorus atom, this value is significantly smaller than the $^1J\{^{195}Pt\text{–}^{31}P\}$ value in **8**. The FAB^+ mass spectrum of each compound displays the parent-ion peak and a peak corresponding to the loss of a chloride ion and the IR spectra show bands characteristic of ν(PN) stretches (997 cm^{-1} for **10** and **11**) indicating an increase in the bond order. The IR spectra of **10** and **11** also show two distinct ν(MCl) vibrations.

The reaction of $Ph_2PN(Et)N(Et)PPh_2$ with equimolar quantities of [PtCl(Me)(cod)] in dichloromethane proceeds according to eqn. (5) to give *cis*-$[PtMe(Cl)\{Ph_2PN(Et)N(Et)PPh_2\}]$ **12**.



The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **12** is an AX type spectrum due to the chemical inequivalence of the phosphorus centres, the phosphorus atom *trans* to the chloride ligand is assigned to the peak at δ(P) 96.8 due to the larger $^1J(^{195}Pt\text{–}^{31}P)$ coupling associated with it (4577 Hz) and the phosphorus *trans* to the methyl group is assigned to the peak at δ(P) 114.2 which has a smaller $^1J(^{195}Pt\text{–}^{31}P)$ coupling of 2016 Hz.

Table 1 Selected bond lengths (Å) and angles (°) for **8**, **9**, **14** and **15**

	8	**9**[a]	**14**	**15**
M(1)–Cl(1)	2.344(2)	2.343(2) [2.342(2)]	2.396(3)	2.393(6)
M(1)–Cl(2)	2.345(2)	2.341(2) [2.352(14)]	—	2.398(6)
M(1)–P(1)	2.182(2)	2.199(2) [2.207(2)]	2.221(4)	2.210(7)
M(1)–P(2)	2.177(2)	2.193(2) [2.194(2)]	—	2.207(7)
P(1)–N(1)	1.645(5)	1.654(4) [1.662(4)]	1.758(13)	1.70(2)
P(2)–N(2)	1.680(6)	1.684(4) [1.663(4)]	—	1.67(2)
N(1)–N(2)	1.440(7)	1.434(5) [1.432(5)]	1.37(2)	1.44(3)
Cl(1)–M(1)–Cl(2)	91.55(6)	93.20(6) [94.17(5)]	91.1(2)	91.0(2)
P(1)–M(1)–P(2)	82.55(6)	82.24(6) [81.46(5)]	84.9(2)	85.1(2)
M(1)–P(1)–N(1)	108.2(2)	107.9(2) [108.3(2)]	108.0(4)	107.9(8)
M(1)–P(2)–N(2)	110.6(2)	110.8(2) [110.0(2)]	—	108.2(8)
P(1)–N(1)–N(2)	119.6(4)	119.5(3) [119.4(3)]	114.2(4)	114.0(20)
P(2)–N(2)–N(1)	105.9(4)	105.7(3) [109.0(3)]	—	115.0(20)

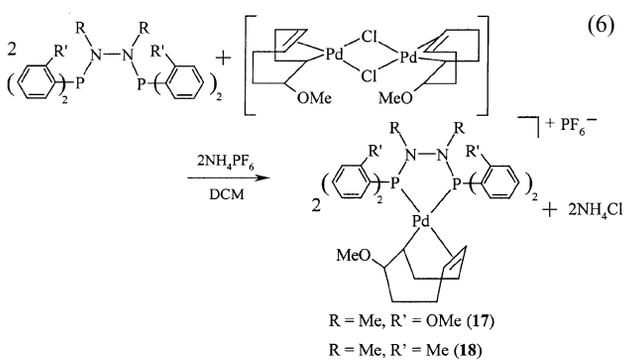
[a] The values in square brackets are for the second crystallographically independent molecule.

$(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2$ **4** reacts with $[PtCl_2(cod)]$ to give the five-membered metallacycle *cis*-$[PtCl_2\{(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2\}]$ **13** as a colourless solid in 84% yield. The ^{31}P-$\{^1H\}$ NMR spectrum shows a single resonance at δ(P) 108.3 with satellites [$^1J(^{195}Pt–^{31}P)$ 4033 Hz]. This represents a downfield shift of 44 ppm from the value recorded for the free ligand, which is comparable to the difference in shift observed between **3** and **10**.

The ligands containing *ortho* substituted phenyl groups, $(o\text{-}C_6H_4OCH_3)_2PN(Et)N(Et)P(o\text{-}C_6H_4OCH_3)_2$ **5**, $(o\text{-}C_6H_4OCH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4OCH_3)_2$ **6**, and $(o\text{-}C_6H_4CH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4CH_3)_2$ **7**, also react successfully with equimolar quantities of $[PtCl_2(cod)]$ to yield *P*,*P′* chelates **14**–**16**.

The ^{31}P-$\{^1H\}$ NMR spectra of all three products show singlets, at δ(P) 90.2, 88.5 and 110.3 respectively, representing downfield shifts of 45–65 ppm upon complexation. All show satellites from coupling to ^{195}Pt [$^1J(^{195}Pt–^{31}P)$ 4535 for **14**, 4438 for **15** and 4289 Hz for **16**] consistent with the values observed for **8**, **10**, and **13**, their relative magnitudes reflecting the nature of the substituents present, both in the *ortho* position in the ring and on the phosphorus atoms.

6 and **7** also react with the dimeric palladium species $[\{Pd(C_8H_{12}OCH_3)(\mu\text{-}Cl)\}_2]$ and NH_4PF_6 to yield the *cis*-*P*,*P′* chelates $[Pd(C_8H_{12}OCH_3)\{(o\text{-}C_6H_4OCH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4OCH_3)_2\}]PF_6$ **17**, and $[Pd(C_8H_{12}OCH_3)\{(o\text{-}C_6H_4CH_3)_2PN(Me)N(Me)P(o\text{-}C_6H_4CH_3)_2\}]PF_6$ **18** [eqn. (6)] in good yields (65 and 70% respectively).



The ^{31}P-$\{^1H\}$ NMR spectrum of each product shows an AX type pattern due to the phosphorus centres being chemically inequivalent, the FAB^+ mass spectra of the complexes correspond to the expected parent-cation. The IR spectra of both complexes show bands assigned to ν(PN) (950 for **17** and 948 cm^{-1} for **18**) and elemental analyses are in good agreement with calculated values.

Pringle and co-workers have recently reported [24] on the use of P–X–P ligands as catalysts for polyketone synthesis. They noted some interesting effects on reaction rate as a consequence of *ortho* substitution of the phenyl rings, with alkyl or OMe substituents being beneficial. The X-ray structures of **8**, **9**, **14** and **15** (Table 1, Figs. 1–5) enable some comparisons to be made in

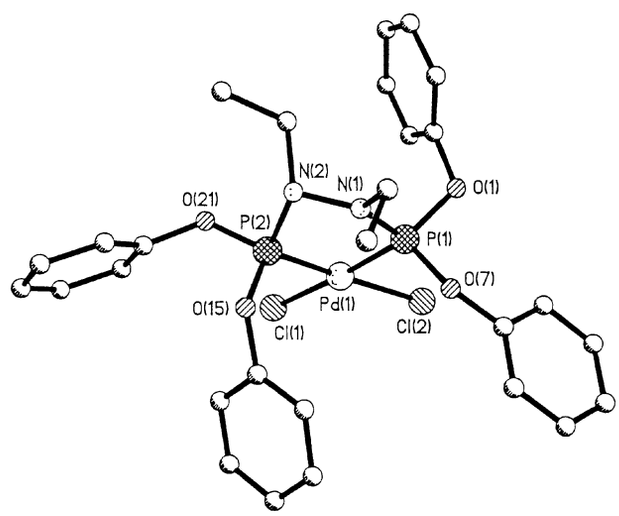


Fig. 2 The solid state structure of one of the independent molecules in *cis*-$[PdCl_2\{(PhO)_2PN(Et)N(Et)P(OPh)_2\}]$ **9**.

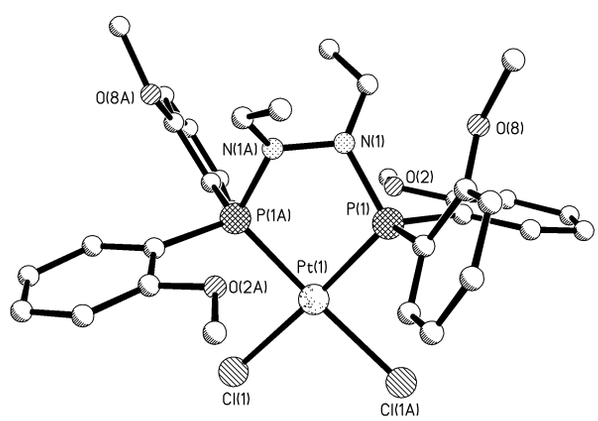


Fig. 3 The solid state structure of **14**.

the hydrazide case. All four structures reveal the expected square planar geometry at the metal centre with slightly puckered five-membered MP_2N_2 rings. Furthermore the influence of the electron withdrawing OPh group (in comparison to

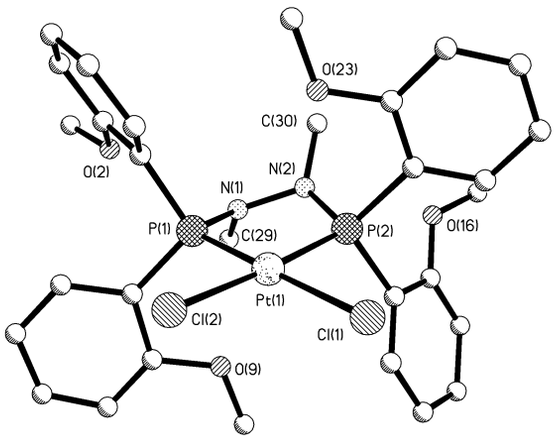


Fig. 4 The solid state structure of **15**.

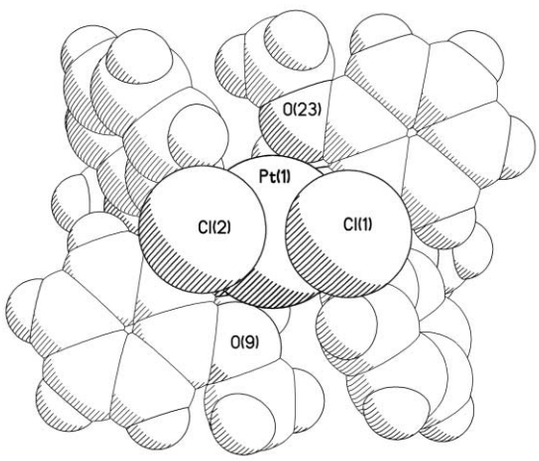


Fig. 5 Space filling representation of **15** illustrating the steric shielding of the metal centre.

the *o*-$MeOC_6H_4$ group) is noticeable in the shortening of the M–P bonds in the OPh containing complexes (Table 1). The most interesting feature is that in **14** and **15** two of the OMe groups arrange themselves in close to pseudo-octahedral geometries. [**14** Pt ··· O(2) 3.47, O ··· Pt ··· O angle 133°; **15** Pt ··· O(9) 3.37 Å, Pt ··· O(23) 3.40 Å, O ··· Pt ··· O 129°] which results in significant congestion above and below the coordination plane and this may limit the mechanistic pathways available during the catalytic process.

Experimental

General experimental conditions and instrumentation are as described previously.[25] 1,2-Diethylhydrazine dihydrochloride was crushed using a pestle and mortar prior to use. $[\{Pd(C_8H_{12}OCH_3)(\mu\text{-}Cl)\}_2]$ was prepared using the literature procedure.[26] Phenol, phosphorus trichloride, PhMgBr, $PhCH_2MgCl$ and *o*-$CH_3C_6H_4MgCl$ were used without further purification.

Syntheses

$Cl_2PN(Et)N(Et)PCl_2$ 1. Phosphorus trichloride (10.00 g, 72.7 mmol) was added to a finely crushed sample of 1,2-diethylhydrazine dihydrochloride (1.00 g, 6.2 mmol) at room temperature under an atmosphere of nitrogen. The reaction mixture was heated under reflux for 96 h. The excess phosphorus trichloride was removed *in vacuo* to leave a viscous orange oil. Distillation of the resulting oil *in vacuo* left compound **1** as a viscous, colourless oil. Yield: 1.3 g, 72%. Microanalysis: Found (Calc. for $C_4H_{10}Cl_4N_2P_2$) C, 17.0 (16.6); H, 3.5 (3.9); N, 9.7 (9.8)%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ(P) 156.3. IR (neat, cm^{-1}): 2978s, 2935s, 2555s, 2260s, 1451vs, 1379vs, 1355s, 1187vs, 1148vs, 1074vs, 1016vs, 952vs, 858w, 818w, 782w, 761w, 729vs, 612w, 507vs, 436vs, 404vs and 225w. FAB mass spectrum: *m*/*z* 289, $[M^+]$.

$(PhO)_2PN(Et)N(Et)P(OPh)_2$ 2. A solution of phenol (1.30 g, 13.8 mmol) and triethylamine (1.39 g, 1.9 cm^3, 13.8 mmol) in hexane (20 cm^3) was added dropwise over a period of 30 min to a solution of $Cl_2PN(Et)N(Et)PCl_2$ (1.00 g, 3.4 mmol) in hexane (20.0 cm^3) at room temperature. The reaction mixture was stirred for 12 h during which time triethylamine hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness *in vacuo* to give a viscous, colourless oil. Yield: 1.45 g, 81%. Microanalysis: Found (Calc. for $C_{28}H_{30}N_2O_2P_2$) C, 70.0 (69.6); H, 5.5 (5.8); N, 5.4 (5.2)%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ(P) 139.0. IR (neat, cm^{-1}): 2978vs, 2940s, 2350s, 1589s, 1444s, 1372vs, 1349s, 1170vs, 1111s, 1030s, 1009s, 930vs, 818w, 773w, 758m, 608w, 515s, 446m, 395s and 217w. FAB mass spectrum: *m*/*z* 520, $[M]^+$.

$Ph_2PN(Et)N(Et)PPh_2$ 3. A solution of **1** (1.00 g, 3.4 mmol) in diethyl ether (20.0 cm^3) was added dropwise over a period of 30 min to a stirred solution of 1 M PhMgBr in diethyl ether (2.50 g, 14.0 cm^3, 13.6 mmol) at 0 °C and the reaction mixture stirred for 18 h. Deionized water (20.0 cm^3) was added slowly over 10 min and stirring continued for a further 1 h, after which the reaction mixture was transferred to a separatory funnel and the layers separated. The ether layer was dried over $MgSO_4$ and the drying agent then removed by suction filtration. The filtrate was evaporated to dryness *in vacuo* to give a white solid product. Yield: 1.1 g, 70%. Microanalysis: Found (Calc. for $C_{28}H_{30}N_2P_2$) C, 73.9 (73.7); H, 6.5 (6.6); N, 5.9 (6.1)%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ(P)64.2. IR (KBr disc, cm^{-1}): 2973w, 1651s, 1484w, 1434vs, 1362s, 1320w, 1172vs, 1124s, 1057s, 1024s, 970s, 826s, 759s, 698s, 608w, 575s, 528w, 483w, 333s, 240vs and 230vs. FAB mass spectrum: *m*/*z* 456, $[M]^+$.

$(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2$ 4. A solution of **1** (1.00 g, 3.4 mmol) in diethyl ether (20.0 cm^3) was added dropwise over a period of 30 min to a stirred solution of 2 M $PhCH_2MgCl$ in diethyl ether (2.10 g, 6.8 cm^3, 13.7 mmol) at 0 °C and the reaction mixture stirred for 12 h. Deoinized water (20.0 cm^3) was added slowly over 10 min and stirring continued for a further 1 h, after which the reaction mixture was transferred to a separatory funnel and the layers separated. The ether layer was dried over $MgSO_4$ and the drying agent then removed by suction filtration. The filtrate was evaporated to dryness *in vacuo* to give a pale yellow, solid product. Yield: 1.3 g, 74%. Microanalysis: Found (Calc. for $C_{32}H_{38}N_2P_2$) C, 74.3 (74.9); H, 7.4 (7.5); N, 5.2 (5.5)%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ(P) 64.8. IR (KBr disc, cm^{-1}): 3025w, 1600s, 1493vs, 1451vs, 1376s, 1210s, 1092s, 1062s, 1028s, 962s, 933s, 906s, 850vs, 823s, 764s, 697s, 585s, 569w, 497s, 478s, and 230vs. FAB mass spectrum: *m*/*z* 512, $[M]^+$.

$(o\text{-}C_6H_4OCH_3)_2PN(Et)N(Et)P(o\text{-}C_6H_4OCH_3)_2$ 5. A solution of *o*-bromoanisole (4.90 g, 3.3 cm^3, 26.5 mmol) in diethyl ether (80.0 cm^3) was added dropwise to a slurry of magnesium turnings (1.43 g, 59.0 mmol) and iodine (1 crystal) in diethyl ether (20.0 cm^3) and the reaction mixture stirred for 2.5 h. 60.0 cm^3 of the reaction solution was transferred to a round bottomed flask and a solution of $Cl_2PN(Et)N(Et)PCl_2$ (1.00 g, 3.4 mmol) in diethyl ether (25.0 cm^3) added dropwise over a period of 30 min. After stirring for 24 h, deionized water (25.0 cm^3) was added slowly over 10 min and stirring continued for a further 1 h, after which the reaction mixture was transferred to a separatory funnel and the layers separated. The ether layer was dried over $MgSO_4$ and the drying agent then removed by suction filtration. The filtrate was evaporated to dryness *in vacuo* to give a colourless oil. The product was washed with light petroleum

(bp 60–80 °C) to give a solid product. Yield: 1.31 g, 67%. Microanalysis: Found (Calc. for $C_{32}H_{38}N_2O_4P_2$) C, 66.1 (66.6); H, 6.3 (6.6); N, 4.4 (4.8)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 40.5. IR (KBr disc, cm^{-1}): 3053m, 2941m, 2834m, 1655w, 1571s, 1472s, 1427vs, 1374w, 1270s, 1242vs, 1182m, 1160m, 1128m, 1099w, 1067w, 1027s, 933s, 793m, 757vs, 729w, 708w, 503w, 480w, 431w, 237vs and 218s. FAB mass spectrum: *m*/*z* 576, $[M]^+$.

(*o*-$C_6H_4OCH_3)_2$PN(Me)N(Me)P(*o*-$C_6H_4OCH_3)_2$ 6. A solution of *o*-bromoanisole (4.90 g, 3.3 cm^3, 26.5 mmol) in diethyl ether (80.0 cm^3) was added dropwise to a slurry of magnesium turnings (1.43 g, 59.0 mmol) and iodine (1 crystal) in diethyl ether (20.0 cm^3) and the reaction mixture stirred for 2.5 h. 60.0 cm^3 of the reaction solution was transferred to a round bottomed flask and a solution of $Cl_2PN(Me)N(Me)PCl_2$ (1.00 g, 3.8 mmol) in diethyl ether (25.0 cm^3) added dropwise over a period of 30 min. reaction. After stirring for 24 h, deionized water (25.0 cm^3) was added slowly over 10 min and stirring continued for a further 1 h, after which the reaction mixture was transferred to a separatory funnel and the layers separated. The ether layer was dried over $MgSO_4$ and the drying agent then removed by suction filtration. The filtrate was evaporated to dryness *in vacuo* to give a colourless oil. The product was washed with light petroleum (bp 60–80 °C) to give a solid product. Yield: 1.7 g, 81%. Microanalysis: Found (Calc. for $C_{30}H_{34}N_2O_4P_2$) C, 65.1 (65.7); H, 5.9 (6.3); N, 4.8 (5.1)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 42.6. IR (KBr disc, cm^{-1}): 3385s, 3059s, 3000s, 2935s, 2834s, 1583vs, 1571vs, 1460vs, 1429vs, 1268s, 1238s, 1159w, 1129s, 1092w, 1066s, 1042s, 969vs, 883w, 858w, 792s, 753vs, 692s, 611s, 574w, 498s, 472s, 428vs and 230vs. FAB mass spectrum: *m*/*z* 549, $[M]^+$.

(*o*-$C_6H_4CH_3)_2$PN(Me)N(Me)P(*o*-$C_6H_4CH_3)_2$ 7. A solution of $Cl_2PN(Me)N(Me)PCl_2$ (1.00 g, 3.8 mmol) in diethyl ether (25.0 cm^3) was added dropwise over a period of 30 min to a stirred solution of 1 M *o*-$CH_3C_6H_4MgCl$ in diethyl ether (2.30 g, 15.2 cm^3, 15.2 mmol) at 0 °C and the reaction mixture heated under reflux for 4 h. Deionized water (25.0 cm^3) was added slowly over 10 min and stirring continued for a further 1 h, after which the reaction mixture was transferred to a separatory funnel and the layers separated. The ether layer was dried over $MgSO_4$ and the drying agent then removed by suction filtration. The filtrate was evaporated to dryness *in vacuo* to give a yellow oil. The product was washed with light petroleum (bp 60–80 °C) to give a pale yellow solid. Yield: 1.2 g, 65%. Microanalysis: Found (Calc. for $C_{30}H_{34}N_2P_2$) C, 74.7 (74.4); H, 6.8 (7.1); N, 5.2 (5.8)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 47.2. IR (KBr disc, cm^{-1}): 3396w, 1815w, 1560s, 1520vs, 1439vs, 1377s, 1268w, 1198w, 1156s, 1130s, 1066s, 1030s, 956s, 897s, 845vs, 800s, 751s, 731vs, 718s, 607s, 562w, 487s, 455s, 396w, 292w and 230vs. FAB mass spectrum: *m*/*z* 485, $[M]^+$.

***cis*-[$PtCl_2${$(PhO)_2PN(Et)N(Et)P(OPh)_2$}] 8.** A solution of $(PhO)_2PN(Et)$ $N(Et)P(OPh)_2$ (0.175 g, 0.34 mmol) in dichloromethane (10.0 cm^3) was added dropwise to a solution of [$PtCl_2$(cod)] (0.130 g, 0.34 mmol) in dichloromethane (5.0 cm^3) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm^3 and diethyl ether (20.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.178 g, 65%. Microanalysis: Found (Calc. for $C_{28}H_{30}Cl_2N_2O_4P_2Pt$) C, 42.4 (42.7); H, 3.9 (3.8); N, 3.4 (3.6)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 92.3, $^1J(^{195}Pt–^{31}P)$ 5503 Hz. IR (KBr disc, cm^{-1}): 2991s, 1585vs, 1484vs, 1455vs, 1385s, 1348s, 1186vs, 1113vs, 1069vs, 1023s, 968vs, 822s, 763vs, 688s, 652s, 614w, 586s, 535w, 439w, 325s, 299m, 236vs and 227vs. FAB mass spectrum: *m*/*z* 786, $[M]^+$.

***cis*-[$PdCl_2${$(PhO)_2PN(Et)N(Et)P(OPh)_2$}] 9.** A solution of $(PhO)_2PN(Et)N(Et)P(OPh)_2$ (0.182 g, 0.35 mmol) in dichloromethane (10.0 cm^3) was added dropwise to a solution of [$PdCl_2$(cod)] (0.100 g, 0.35 mmol) in dichloromethane (5.0 cm^3) and the yellow solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm^3 and diethyl ether (20.0 cm^3) added. The yellow product was collected by suction filtration. Yield: 0.123 g, 50%. Microanalysis: Found (Calc. for $C_{28}H_{30}Cl_2N_2O_4P_2Pd$) C, 48.0 (48.2); H, 4.4 (4.3); N, 4.0 (4.0)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 116.6. IR (KBr disc, cm^{-1}): 2975s, 1585vs, 1484vs, 1455vs, 1377s, 1348w, 1177vs, 1119vs, 1070s, 1024s, 955vs, 822s, 763vs, 682s, 654s, 614w, 575s, 518w, 496w, 329s, 296s, 237vs and 225vs. FAB mass spectrum: *m*/*z* 698, $[M]^+$.

***cis*-[$PtCl_2${$Ph_2PN(Et)N(Et)PPh_2$}] 10.** To a solution of [$PtCl_2$(cod)] (0.040 g, 0.11 mmol) in dichloromethane (5.0 cm^3) was added solid $Ph_2PN(Et)N(Et)PPh_2$ (0.048 g, 0.11 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm^3 and diethyl ether (10.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.060 g, 78%. Microanalysis: Found (Calc. for $C_{28}H_{30}Cl_2N_2P_2Pt$) C, 47.7 (47.4); H, 4.4 (4.1); N, 3.4 (3.8)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 100.4, $^1J(^{195}Pt–^{31}P)$ 4055 Hz. IR (KBr disc, cm^{-1}): 3053s, 2972s, 1572vs, 1480vs, 1436vs, 1380s, 1311w, 1182vs, 1104vs, 1027w, 997s, 921w, 872w, 749vs, 720vs, 692s, 656s, 630w, 578s, 556w, 527s, 507vs, 493w, 471w, 314s, 233vs and 225vs. FAB mass spectrum: *m*/*z* 722, $[M]^+$.

***cis*-[$PdCl_2${$Ph_2PN(Et)N(Et)PPh_2$}] 11.** To a solution of [$PdCl_2$(cod)] (0.030 g, 0.11 mmol) in dichloromethane (15.0 cm^3) was added solid $Ph_2PN(Et)N(Et)PPh_2$ (0.048 g, 0.11 mmol) and the yellow solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm^3 and diethyl ether (20.0 cm^3) added. The yellow product was collected by suction filtration. Yield: 0.052 g, 78%. Microanalysis: Found (Calc. for $C_{28}H_{30}Cl_2N_2P_2Pd$) C, 52.8 (53.1); H, 4.6 (4.8); N, 4.2 (4.4)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 132.2. IR (KBr disc, cm^{-1}): 3053w, 2972s, 1618w, 1585w, 1479s, 1436vs, 1380s, 1312w, 1183w, 1118vs, 1101vs, 1026w, 997s, 918w, 750vs, 719vs, 691s, 654s, 609w, 574s, 522s, 490w, 292w and 225vs. FAB mass spectrum: *m*/*z* 634, $[M]^+$.

***cis*-[PtMe(Cl){$Ph_2PN(Et)N(Et)PPh_2$}] 12.** To a solution of [PtMe(Cl)(cod)] (0.038 g, 0.11 mmol) in dichloromethane (10.0 cm^3) was added solid $Ph_2PN(Et)N(Et)PPh_2$ (0.048 g, 0.11 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 1.0 cm^3 and diethyl ether (20.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.058 g, 79%. Microanalysis: Found (Calc. for $C_{29}H_{33}ClN_2P_2Pt$) C, 49.5 (49.6); H, 4.6 (4.7); N, 3.8 (3.9)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): $\delta(P_A$ *trans* to $CH_3)$ 114.2, $^1J(^{195}Pt–^{31}P_A)$ 2016 Hz, $\delta(P_B$ *trans* to Cl) 96.8, $^1J(^{195}Pt–^{31}P_B)$ 4577 Hz. IR (KBr disc, cm^{-1}): 3054s, 2970s, 2874s, 1671w, 1479s, 1436vs, 1377s, 1312w, 1180s, 1122vs, 1103vs, 997w, 750vs, 717vs, 693vs, 652s, 580s, 554s, 524vs, 492s, 301w, 242s and 210vs. FAB mass spectrum: *m*/*z* 702, $[M]^+$.

***cis*-[$PtCl_2${$(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2$}] 13.** To a solution of [$PtCl_2$(cod)] (0.050 g, 0.13 mmol) in dichloromethane (15.0 cm^3) was added solid $(PhCH_2)_2PN(Et)N(Et)P(CH_2Ph)_2$ (0.068 g, 0.13 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 2.0 cm^3 and diethyl ether (20.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.087 g, 84%. Microanalysis: Found (Calc. for $C_{32}H_{38}Cl_2N_2P_2Pt$) C, 48.8 (49.4); H, 4.7 (4.9); N, 3.1 (3.6)%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ(P) 108.3, $^1J(^{195}Pt–^{31}P)$ 4033 Hz, $^2J(^{31}P_A–^{31}P_B)$ 17 Hz. IR (KBr disc, cm^{-1}): 3026s, 2979s, 2926s, 1601s, 1495vs, 1452vs, 1386s, 1357w, 1260s, 1172vs, 1124s, 1073s, 988w, 917w, 857s, 838s, 808s, 790s,

Table 2 Details of X-ray data collection and refinement

Compound	**8**	**9**	**14**	**15**
Empirical formula	$C_{28}H_{30}Cl_2N_2O_4P_2Pt$	$C_{28}H_{30}Cl_2N_2O_4P_2Pd$	$C_{33.5}H_{43}Cl_5N_2O_5P_2Pt$	$C_{30.5}H_{35}Cl_3N_2O_5P_2Pt$
Formula weight	786.5	697.8	988.0	857.0
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
T/K	293(2)	293(2)	293(2)	298(2)
Space group	*Pbca*	$P2_1n$	*C*2/*c*	$P\bar{1}$
a/Å	8.7379(3)	22.2887(4)	24.3478(7)	10.2861(2)
b/Å	17.2627(5)	8.8062(2)	14.2665(3)	11.9149(1)
c/Å	40.8907(11)	32.0433(5)	14.7842(4)	15.9825(2)
α/°				95.546(1)
β/°		105.61(1)	111.458(1)	99.112(1)
γ/°				106.871(1)
V/Å^3	6168	6057	4779	1824
Z	8	8	4	2
D_c/Mg m^{-3}	1.69	1.53	1.37	1.56
Absorption coefficient/mm^{-1}	4.86	0.93	3.32	4.19
Observed independent reflections [$I > 2.0\sigma(I)$]	4399	8637	5501	5158
Final R, Rw	0.0339, 0.0631	0.0449, 0.0728	0.0875, 0.1953	0.0774, 0.2781

773s, 755vs, 695vs, 610w, 582s, 569w, 535w, 472w, 317s, 235s and 229vs. FAB mass spectrum: *m*/*z* 778, $[M]^+$.

***cis*-[PtCl$_2${(*o*-C$_6$H$_4$OCH$_3$)$_2$PN(Et)N(Et)P(*o*-C$_6$H$_4$OCH$_3$)$_2$}] 14.** To a solution of [PtCl$_2$(cod)] (0.100 g, 0.26 mmol) in dichloromethane (5.0 cm^3) was added solid (C$_6$H$_4$-*o*-OCH$_3$)$_2$PN(Et)N(Et)P(C$_6$H$_4$-*o*-OCH$_3$)$_2$ (0.154 g, 0.26 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 2.0 cm^3 and diethyl ether (20.0 cm^3) added. The white product was collected by suction filtration.Yield: 0.107 g, 70%. Microanalysis: Found (Calc. for C$_{32}$H$_{30}$Cl$_2$N$_2$O$_4$P$_2$Pt) C, 45.1 (45.6); H, 4.4 (4.5); N, 2.8 (3.3)%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ(P) 90.2, ^1J(^{195}Pt–^{31}P) 4535 Hz. IR (KBr disc, cm^{-1}): 3065w, 2937w, 2864w, 1588s, 1573s, 1477vs, 1463s, 1430vs, 1375w, 1282s, 1253s, 1182m, 1165m, 1109m, 1075m, 1045m, 1019s, 943w, 801s, 757s, 692m, 633m, 581m, 557m, 506m, 446w, 337w, 303w, 280w and 229s. FAB mass spectrum: *m*/*z* 842, $[M]^+$.

***cis*-[PtCl$_2${(*o*-C$_6$H$_4$OCH$_3$)$_2$PN(Me)N(Me)P(*o*-C$_6$H$_4$OCH$_3$)$_2$}] 15.** To a solution of [PtCl$_2$(cod)] (0.075 g, 0.20 mmol) in dichloromethane (5.0 cm^3) was added solid (C$_6$H$_4$-*o*-OCH$_3$)$_2$PN(Me)N(Me)P(C$_6$H$_4$-*o*-OCH$_3$)$_2$ (0.110 g, 0.20 mmol) and the colourless solution stirred for *ca.* 2 h. The solution was concentrated under reduced pressure to *ca.* 2.0 cm^3 and diethyl ether (20.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.101 g, 57%. Microanalysis: Found (Calc. for C$_{30}$H$_{34}$Cl$_2$N$_2$O$_4$P$_2$Pt) C, 48.1 (48.8); H, 3.4 (3.9); N, 2.8 (3.2)%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ(P) 88.5, ^1J(^{195}Pt–^{31}P) 4438 Hz. IR (KBr disc, cm^{-1}): 3386s, 3067s, 2932s, 2833s, 1637w, 1587vs, 1571s, 1474vs, 1455vs, 1428vs, 1276s, 1251s, 1164w, 1136w, 1072w, 1016s, 965w, 800s, 762vs, 694w, 646s, 581s, 558s, 526w, 509w, 484w, 445s, 365w, 276w, 230s and 215vs. FAB mass spectrum: *m*/*z* 814, $[M]^+$.

***cis*-[PtCl$_2${(*o*-C$_6$H$_4$CH$_3$)$_2$PN(Me)N(Me)P(*o*-C$_6$H$_4$CH$_3$)$_2$}] 16.** To a solution of [PtCl$_2$(cod)] (0.070 g, 0.19 mmol) in dichloromethane (5.0 cm^3) was added solid (C$_6$H$_4$-*o*-CH$_3$)$_2$PN(Me)N(Me)P(C$_6$H$_4$-*o*-CH$_3$)$_2$ (0.090 g, 0.19 mmol) and the colourless solution stirred for *ca.* 1 h. The solution was concentrated under reduced pressure to *ca.* 2.0 cm^3 and diethyl ether (15.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.092 g, 69%. Microanalysis: Found (Calc. for C$_{30}$H$_{34}$Cl$_2$N$_2$P$_2$Pt) C, 47.5 (48.0); H, 4.3 (4.6); N, 3.5 (3.7)%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ(P) 110.3, ^1J(^{195}Pt–^{31}P) 4289 Hz. IR (KBr disc, cm^{-1}): 2894s, 1654w, 1591s, 1561s, 1447vs, 1379s, 1283s, 1203w, 1162w, 1133s, 1084s, 946w, 808s, 762vs, 723s, 684w, 576s, 554w, 531w, 515w, 494s, 455s, 420s, 303w, 286w, 235s and 230vs. FAB mass spectrum: *m*/*z* 714, $[M - Cl]^+$.

[Pd(C$_8$H$_{12}$OCH$_3$){(*o*-C$_6$H$_4$OCH$_3$)$_2$PN(Me)N(Me)P(*o*-C$_6$H$_4$OCH$_3$)$_2$}]PF$_6$ 17. To a stirred solution of [{Pd(C$_8$H$_{12}$OCH$_3$)(μ-Cl)}$_2$] (0.050 g, 0.09 mmol) in dichloromethane (10.0 cm^3) was added solid NH_4PF_6 (0.030 g, 0.18 mmol) and the reaction mixture stirred for a further 30 min. A solution of (C$_6$H$_4$-*o*-OCH$_3$)$_2$PN(Me)N(Me)P(C$_6$H$_4$-*o*-OCH$_3$)$_2$ (0.100 g, 0.18 mmol) in dichloromethane (10.0 cm^3) was then added dropwise to the reaction mixture over a period of 10 min and the resulting dark brown solution stirred for 2 h. The solution was concentrated under reduced pressure to *ca.* 5.0 cm^3 and diethyl ether (25.0 cm^3) added. The light brown product was collected by suction filtration. Yield: 0.109 g, 65%. Microanalysis: Found (Calc. for C$_{39}$H$_{49}$F$_6$N$_2$OP$_3$Pd) C, 53.8 (53.5); H, 5.6 (5.6); N, 3.1 (3.2)%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ(P) 104.8 and 92.1, ^2J(^{31}P–^{31}P) 66 Hz. IR (KBr disc, cm^{-1}): 2933w, 1586m, 1574m, 1515m, 1474s, 1431s, 1275s, 1245s, 1164m, 1135m, 1075w, 1043w, 1018m, 950m, 839s, 797m, 756m, 737w, 657w, 616m, 580w, 557m, 523w, 501w, 436w and 358w. FAB mass spectrum: *m*/*z* 794, $[M - PF_6]^+$.

[Pd(C$_8$H$_{12}$OCH$_3$){(*o*-C$_6$H$_4$CH$_3$)$_2$PN(Me)N(Me)P(*o*-C$_6$H$_4$CH$_3$)$_2$}]PF$_6$ 18. To a stirred solution of [{Pd(C$_8$H$_{12}$OCH$_3$)(μ-Cl)}$_2$] (0.130 g, 0.23 mmol) in dichloromethane (10.0 cm^3) was added solid NH_4PF_6 (0.075 g, 0.46 mmol) and the reaction mixture stirred for a further 30 min. A solution of (C$_6$H$_4$-*o*-CH$_3$)$_2$PN(Me)N(Me)P(C$_6$H$_4$-*o*-CH$_3$)$_2$ (0.222 g, 0.46 mmol) in dichloromethane (10.0 cm^3) was then added dropwise to the reaction mixture over a period of 10 min and the resulting dark brown solution stirred for 2 h. The solution was concentrated under reduced pressure to *ca.* 5.0 cm^3 and diethyl ether (25.0 cm^3) added. The light brown product was collected by suction filtration. Yield: 0.280 g, 70%. Microanalysis: Found (Calc. for C$_{39}$H$_{49}$F$_6$N$_2$OP$_3$Pd) C, 53.0 (53.5); H, 5.6 (5.6); N, 3.1 (3.2)%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 113.4 and 105.2, ^2J(^{31}P–^{31}P) 66 Hz. IR (KBr disc, cm^{-1}): 2924vs, 1624w, 1588s, 1523vs, 1448vs, 1381w, 1278s, 1186s, 1132s, 1081s, 1023s, 948w, 839vs, 806s, 757vs, 719s, 682w, 611w, 556vs, 538w, 508w, 488s, 469s, 280w, 242s and 229vs. FAB mass spectrum: *m*/*z* 730, $[M - PF_6]^+$.

Crystallography

Was performed using a Bruker SMART diffractometer; full hemisphere of data with 0.3° 'slices', room temperature, Mo-Kα radiation and empirical absorption corrections. All of the other non-hydrogen atoms were refined anisotropically with the hydrogen atoms being refined in idealised geometries. In **14** the hydrogen atoms of the solvate water were not included in the refinement. All calculations employed the SHELXTL program system.[27] Refinement and data collection details are summarised in Table 2.

CCDC reference numbers 168562–168564 and 168964.

See http://www.rsc.org/suppdata/dt/b1/b107072j/ for crystallographic data in CIF or other electronic format.

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