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FULL PAPER

Amine-functionalised aminophosphines: synthesis, reversible co-ordination to platinum and use in heteronuclear dimer formation

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Amine functionalised aminophosphines $Ph_2PN(R)CH_2CH_2NMe_2$ (R = H **L**^{1} or Me **L**^{2}) were prepared from the reaction of PPh_2Cl with $NHRCH_2CH_2NMe_2$ in the presence of the base *n*-butyllithium (**L**^{1}) or triethylamine (**L**^{2}). Reaction of two equivalents of **L**^{1,2} with $[PtCl_2(cod)]$ gave the complexes *cis*-$[PtCl_2L_2]$ (L = **L**^{1} **1** or **L**^{2} **2**), which were shown to be fluxional with one of the amine groups reversibly co-ordinating to displace a chloride. Removal of a chloride in **1** by metathesis gave *cis*-$[PtCl(\mathbf{L}^1\text{-}P)(\mathbf{L}^1\text{-}P,N)]PF_6$ **3** which was not fluxional on the NMR timescale. Reaction of one equivalent of **L**^{2} with $[PtCl_2(cod)]$ gave the complex *cis*-$[PtCl_2(\mathbf{L}^2\text{-}P,N)]$ **4** in which **L**^{2} is acting as a bidentate ligand. The reaction of **L**^{2} with $[\{Pt(dmba)(\mu\text{-}Cl)\}_2]$ (Hdmba = *N*,*N*-dimethylbenzylamine) gave [Pt(dmba)-Cl(**L**^{2})] **5**, which exists as a mixture of the two geometric isomers. Reaction of **5** with $TlPF_6$ gave $[Pt(dmba)(\mathbf{L}^2\text{-}P,N)]$-$PF_6$ **6** as a single isomer in which the phosphorus atom is co-ordinated *trans* to the *N*,*N*-dimethylbenzylamine nitrogen atom. Complex **2** reacts with $CoCl_2{\cdot}6H_2O$ and $ZnCl_2$ to give *cis*-$[(\mathbf{L}^2\text{-}P,N)ClPt(\mu\text{-}\mathbf{L}^2)MCl_3]$ (M = Co **7** or Zn **8**). The zwitterionic structure of **7** was confirmed by a single-crystal X-ray analysis, which showed no metal–metal interaction between the platinum and cobalt centres.

Introduction

Aminophosphines of general formula $R_2PNR'R''$ have been relatively neglected as ligands, despite a number of potentially attractive features. The mild conditions required for formation of the P–N bond allow facile incorporation of additional functionalities, and problems caused by the sensitivity of this bond to hydrolysis are often eliminated on co-ordination.[1] In recent years there has been a growing interest in developing functionalised aminophosphines, and ligands incorporating ketones,[2–4] ethers,[1] phosphinites[5,6] and additional aminophosphines[7–11] have been prepared and studied. As far as nitrogen-donor functionalities are concerned, pyridines[12,13] and imines[14,15] have been incorporated into these ligands, though amines[16] have received less attention. In this paper we report the synthesis and platinum co-ordination chemistry of tertiary amine functionalised aminophosphines. The potential of these ligands to display hemilabile co-ordination and bridge heteronuclear metal centres is demonstrated.

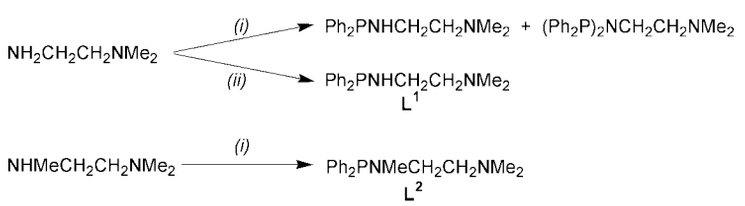
Results and discussion

(i) Ligand synthesis

The amine-functionalised aminophosphines $Ph_2PN(R)CH_2CH_2NMe_2$ (R = H **L**^{1} or Me **L**^{2}) were prepared in good yield from PPh_2Cl and $NHRCH_2CH_2NMe_2$ in the presence of base (Scheme 1) and characterised on the basis of multinuclear NMR spectroscopy and microanalysis. For **L**^{2}, triethylamine was used as the base, as in the synthesis of ether-functionalised aminophosphines such as $Ph_2PNHCH_2CH_2OMe$.[1] However, the reaction of PPh_2Cl with $NH_2CH_2CH_2NMe_2$ in the presence of NEt_3 gave, in addition to **L**^{1}, appreciable amounts of $(Ph_2P)_2NCH_2CH_2NMe_2$, from which it proved difficult to isolate **L**^{1}. Using the alternative synthetic strategy of low temperature amine deprotonation with BuLi, followed by reaction of the lithiated amine with PPh_2Cl, the desired product was formed without contamination by $(Ph_2P)_2NCH_2CH_2NMe_2$, and from this route it proved possible to isolate **L**^{1} in reasonable yield. As with the ether-functionalised aminophosphines, care needs to be taken to exclude water from the reaction mixtures to prevent formation of $Ph_2PP(O)Ph_2$.[1]

Ligand **L**^{1} gave a ^{31}P chemical shift of δ 41.6, very close to those observed for both $Ph_2PNHCH_2CH_2OMe$ (δ 42.0)[1] and $Ph_2PNHPPh_2$ (δ 42.1).[17] The chemical shift for **L**^{2} was observed downfield of this, at δ 65.4. A similar chemical shift was observed for the diphosphine $Ph_2PN(CH_2Ph)CH_2CH_2N(CH_2Ph)PPh_2$ (δ 65.9)[9] suggesting that the difference in δ(P) is primarily due to the presence of an alkyl group rather than a hydrogen atom on the aminophosphine nitrogen atom. ^1H NMR spectra for **L**^{1} and **L**^{2} were as expected, with the NH proton in **L**^{1} observed as a broad multiplet at δ 2.49.

The diphosphine $(Ph_2P)_2NCH_2CH_2NMe_2$ was observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 64.2. The reaction of $NH_2CH_2CH_2NMe_2$ with two equivalents of PPh_2Cl in the presence of NEt_3 led to an increase in the proportion of $(Ph_2P)_2NCH_2CH_2NMe_2$ formed, though this diphosphine was not



Scheme 1 (*i*) PPh_2Cl, NEt_3, THF, (*ii*) PPh_2Cl, BuLi, THF, −78 °C.

Table 1 ^{31}P-{^{1}H} NMR data for $\mathbf{L}^{1,2}$ and complexes **1**–**6**, **8** and **9**

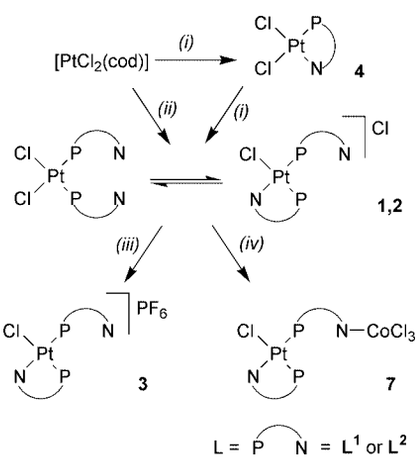
Compound	$\delta(^{31}P)$	^{1}J(P,Pt)/Hz	^{2}J(P,P)/Hz
$\mathbf{L}^1$ $Ph_2PNHCH_2CH_2NMe_2$	41.6		
$\mathbf{L}^2$ $Ph_2PNMeCH_2CH_2NMe_2$	65.4		
1 *cis*-[$PtCl_2(\mathbf{L}^1)_2$]	36.0 [a]	3954	
	38.4, 29.9 [b]	3953, 3601	18
2 *cis*-[$PtCl_2(\mathbf{L}^2)_2$]	50.1 [a]	3904	
	49.6, 46.9 [c]	4209, 3202	[d]
3 *cis*-[PtCl($\mathbf{L}^1$-*P*)($\mathbf{L}^1$-*P*,*N*)]PF_6	40.3, 33.2 [e]	4038, 3587	20
4 *cis*-[$PtCl_2(\mathbf{L}^2$-*P*,*N*)]	32.8	4175	
5a [Pt(dmba)Cl($\mathbf{L}^2$)]	66.4	4618	
5b	80.3	2126	
6 [Pt(dmba)($\mathbf{L}^2$-*P*,*N*)]PF_6	51.2 [e]	4880	
8 *cis*-[($\mathbf{L}^2$-*P*,*N*)ClPt(μ-$\mathbf{L}^2$)$ZnCl_3$]	47.6, 45.4	4196, 3476	[d]
9 [$Pt(O_2C_6H_3Bu^t)(\mathbf{L}^2)_2$]	55.4, 54.5	3796, 3800	27

[a] Recorded at 25 °C. [b] Additional features observed at −50 °C. [c] Additional features observed at −40 °C. [d] Could not be determined due to broadness. [e] Septet at δ −143.5 also observed [^{1}J(P,F) 711 Hz, PF_6^-].

isolated from the reaction mixture. Formation of diphosphines was not observed from the reaction of aminoethers with one equivalent of PPh_2Cl,[1] so it is possible that the increased basicity of the tertiary amine group aids deprotonation of the aminophosphine nitrogen atom.

(ii) Platinum(II) complexes

The reaction of two equivalents of $\mathbf{L}^1$ or $\mathbf{L}^2$ with [$PtCl_2$(cod)] in dichloromethane gave the complexes *cis*-[$PtCl_2L_2$] (L = $\mathbf{L}^1$ **1** or $\mathbf{L}^2$ **2**) (Scheme 2), which were isolated in reasonable yield and



Scheme 2 (*i*) L (1 equivalent), (*ii*) L (2 equivalents), (*iii*) $TlPF_6$, (*iv*) $CoCl_2$.

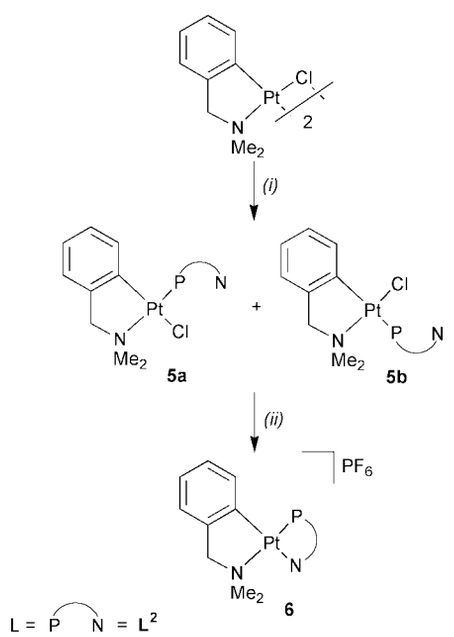
characterised by NMR and IR spectroscopy and microanalysis. The room temperature ^{31}P-{^{1}H} NMR spectra of **1** and **2** consisted of broad singlets with δ(P) 36.0 and 50.1 respectively. In both cases the magnitude of the ^{1}J(Pt,P) coupling constant, 3954 Hz for **1** and 3904 Hz for **2**, is typical for a phosphine ligand *trans* to chloride. The broadness of the signals suggested the presence of fluxionality, and on recording the spectra at −40 or −50 °C two distinct resonances each with ^{195}Pt satellites were observed in addition to the singlet observed at room temperature (Table 1). These additional features are indicative of a structure in which the two phosphorus atoms are no longer equivalent. This is also supported by the observation of ^{2}J(P,P) coupling for **1**, though due to the broadness of the resonances analogous coupling was not observed for **2**. The inequivalence of the phosphorus nuclei is consistent with the presence of structures in which one ligand is unidentate *P*-co-ordinated and the other is bidentate *P*,*N*-co-ordinated, suggesting that the species *cis*-[$PtCl_2$(L-*P*)$_2$] and *cis*-[PtCl(L-*P*)(L-*P*,*N*)]Cl are both present in solution at low temperature and that exchange between them is slow on the NMR timescale, as is exchange between the phosphines in *cis*-[PtCl(L-*P*)(L-*P*,*N*)]Cl. The ^{1}H NMR spectra of **1** and **2** were broad and uninformative both at room temperature and at −50 °C.

These observations for ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ are in contrast to those previously reported for the phosphines $Ph_2PCH_2CH_2CH_2NMe_2$ ($\mathbf{L}^3$) and $Ph_2PCH_2CH_2NMe_2$ ($\mathbf{L}^4$).[18] Reaction of $\mathbf{L}^3$ with [$PtCl_2$(cod)] gave *cis*-[$PtCl_2(\mathbf{L}^3)_2$], for which no fluxionality was reported despite the potential formation of a 6-membered chelate ring analogous to those in **1** and **2** at low temperature. In contrast, reaction of $\mathbf{L}^4$ with [$PtCl_2$(cod)] gave only *cis*-[PtCl($\mathbf{L}^4$-*P*)($\mathbf{L}^4$-*P*,*N*)]Cl. The differences between $\mathbf{L}^3$ and $\mathbf{L}^4$ can be related to the relative stabilities of 6- and 5-membered chelate rings.

Further evidence for the presence of *cis*-[PtCl(L-*P*)(L-*P*,*N*)]$^+$ (L = $\mathbf{L}^1$ or $\mathbf{L}^2$) in solution came from the reaction of complex **1** with $TlPF_6$ which yielded *cis*-[PtCl($\mathbf{L}^1$-*P*)($\mathbf{L}^1$-*P*,*N*)]PF_6 **3**. The chemical shifts and the coupling constants in the ^{31}P-{^{1}H} NMR spectrum were comparable to those in the low temperature spectra of **1** (Table 1) suggesting similar ligand arrangements. However, in contrast to **1**, the spectra of **3** were sharp confirming that removal of the chloride anion prevents the fluxional processes from occurring. The chloride can also be abstracted using NH_4PF_6 or $NaBF_4$, though it has not proved possible to substitute the second halide to afford complexes of the type *cis*-[$Pt(\mathbf{L}^1$-*P*,*N*$)_2]^{2+}$. Similar observations were made with the phosphine $\mathbf{L}^3$, where *cis*-[PtCl($\mathbf{L}^3$-*P*)($\mathbf{L}^3$-*P*,*N*)]BF_4 was the only product from the reaction of *cis*-[$PtCl_2(\mathbf{L}^3)_2$] with an excess of $AgBF_4$.[18]

The reaction of [$PtCl_2$(cod)] with one equivalent of $\mathbf{L}^2$ gave the complex *cis*-[$PtCl_2(\mathbf{L}^2$-*P*,*N*)] **4** in which the aminophosphine ligand is bidentate (Scheme 2). Complex **4** was characterised on the basis of ^{31}P and ^{1}H NMR spectroscopy and microanalysis. The formation of **4** again illustrates the difference in behaviour between $\mathbf{L}^2$ and $\mathbf{L}^3$, as the reaction of $\mathbf{L}^3$ with [$PtCl_2$(cod)] gave only *cis*-[$PtCl_2(\mathbf{L}^3)_2$], with no evidence for *cis*-[$PtCl_2(\mathbf{L}^3$-*P*,*N*)].[18] As with the results above, this indicates the easier formation of a 6-membered chelate ring in which the phosphorus atom is bonded to an sp^2 hybridised nitrogen atom as opposed to a sp^3 hybridised carbon atom.

Ligand $\mathbf{L}^2$ reacts with [{Pt(dmba)(μ-Cl)}$_2$] (Hdmba = *N*,*N*-dimethylbenzylamine), cleaving the halide bridges, to give [Pt(dmba)Cl($\mathbf{L}^2$)] **5** (Scheme 3). Complex **5** is formed as an approximately 1:1 mixture of the two potential isomers with the phosphorus atom *trans* to either the nitrogen (**5a**) or carbon



Scheme 3 (*i*) L; (*ii*) $TlPF_6$.

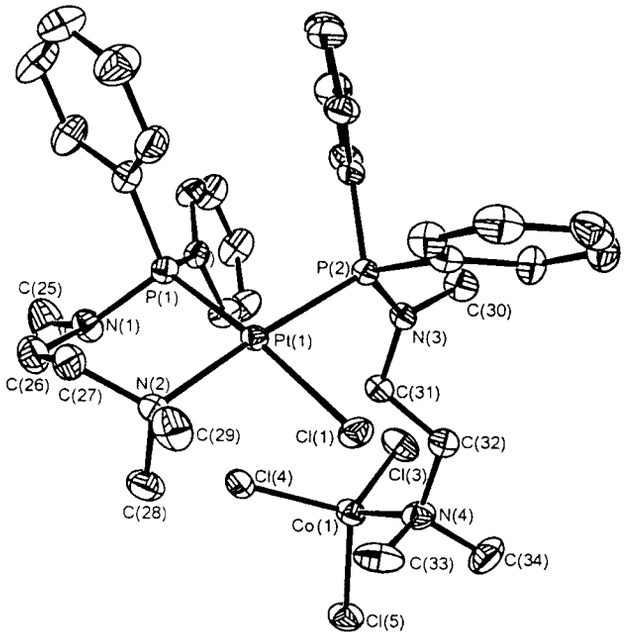


Fig. 1 Molecular structure of complex **7** with the thermal ellipsoids represented at the 30% probability level.

atom of the dmba ligand (**5b**). The ^{31}P-{^{1}H} signals can readily be assigned on the basis of the ^{1}J(Pt,P) coupling constants, which reflect the differing *trans* influences of the two donors. Thus **5a** is observed at δ 66.4 (^{1}J(Pt,P) = 4618 Hz) and **5b** at δ 80.3 (^{1}J(Pt,P) = 2126 Hz). These assignments are confirmed by observation of ^{4}J(P,H) coupling in the ^{1}H NMR spectrum [19] for the isomer with the larger ^{1}J(Pt,P) coupling constant, which can be isolated on recrystallisation. Reaction of complex **5** with $TlPF_6$ gave [Pt(dmba)(**L**^{2}-*P*,*N*)]PF_6 **6**, which was characterised on the basis of ^{31}P-{^{1}H} and ^{1}H NMR spectroscopy. Only one isomer of **6** was observed, and the value of ^{1}J(Pt,P) suggests that the compound has the phosphorus atom *trans* to the nitrogen atom of the dmba ligand (Scheme 3).

(iii) Mixed metal complexes

Since complexes **1**, **2** and **3** contain unco-ordinated amine nitrogen atoms they can potentially act as ligands to other metal centres, thus allowing formation of heteronuclear dimers through bridging aminophosphine ligands. In order to assess this **2** was treated with one equivalent of either $CoCl_2 \cdot 6H_2O$ or $ZnCl_2$ in acetone. Recrystallisation of the products from dichloromethane–hexane gave blue and colourless crystals respectively, that in the case of cobalt were suitable for a single crystal X-ray analysis. The X-ray study confirmed the identity of this compound as the zwitterionic complex *cis*-[(**L**^{2}-*P*,*N*)-ClPt(μ-**L**^{2})$CoCl_3$] **7** for which the platinum centre is formally cationic and the cobalt centre anionic. The asymmetric unit, shown in Fig. 1, demonstrates the different co-ordination modes of the two aminophosphine ligands, with one chelating to the platinum centre in a bidentate mode, and the other bridging between the platinum and cobalt centres. Selected bond lengths and angles are given in Table 2.

The co-ordination geometry around the platinum centre is distorted square planar, with *cis* angles ranging from 84.53(6) to 97.44(6)°, whereas that around the cobalt is distorted tetrahedral with angles ranging from 104.8(2) to 115.7(1)°. The shorter Pt(1)–P(1) bond length relative to the Pt(1)–P(2) distance reflects the relative *trans* influence of the chloride and tertiary amine ligands, which is also mirrored in the ^{1}J(Pt,P) coupling constants for complex **3**. The two P–N bond distances are shorter than expected for a single bond, suggesting a degree of double bond character, in common with other aminophosphine ligands. This is also reflected in the sum of angles around

Table 2 Selected bond lengths (Å) and angles (°) for complex **7**

Pt(1)–N(2)	2.167(5)	Co(1)–Cl(3)	2.214(2)
Pt(1)–P(1)	2.247(2)	Co(1)–Cl(4)	2.246(2)
Pt(1)–P(2)	2.271(2)	Co(1)–Cl(5)	2.249(2)
Pt(1)–Cl(1)	2.365(2)	P(1)–N(1)	1.673(5)
Co(1)–N(4)	2.118(6)	P(2)–N(3)	1.657(5)
N(2)–Pt(1)–P(1)	90.85(13)	N(4)–Co(1)–Cl(3)	104.8(2)
N(2)–Pt(1)–P(2)	170.38(13)	N(4)–Co(1)–Cl(4)	108.7(2)
P(1)–Pt(1)–P(2)	97.44(6)	Cl(3)–Co(1)–Cl(4)	115.71(10)
N(2)–Pt(1)–Cl(1)	88.23(13)	N(4)–Co(1)–Cl(5)	106.9(2)
P(1)–Pt(1)–Cl(1)	169.30(6)	Cl(3)–Co(1)–Cl(5)	113.91(9)
P(2)–Pt(1)–Cl(1)	84.53(6)	Cl(4)–Co(1)–Cl(5)	106.44(8)

N(1) and N(2) which, at 354 and 360° respectively, show a high degree of sp^2 character. The two P–N bond lengths are similar, so involvement in the six-membered chelate ring has not significantly affected the P–N bond distance, though the P(1)–N(1)–C(26) angle within the chelate ring is reduced [119.1(5)°] relative to the equivalent angle in the *P*-bonded ligand [123.1(4)°]. Molecules of **7** stack along the *b* axis with intermolecular Pt · · · Co distances of 6.3 Å, similar to those observed within the individual molecules (6.0 Å). Closer intermolecular contact of the metal centres is prevented by the presence of the phenyl groups on the ligands.

Complex **7** dissolves in methanol to give a pale pink solution, suggesting that co-ordination of solvent molecules leads to octahedral geometry around the cobalt centre. This solvent co-ordination is reversible and on removal of methanol *in vacuo* the complex reverts to the initial blue colour. The molecular ion of **7** was not observed in the FAB mass spectrum; the highest molecular mass peak observed was at *m*/*z* 803, and can be assigned to [*M* − $CoCl_3$]$^+$. Microanalytical data suggest the zinc compound to be the isostructural species *cis*-[(**L**^{2}-*P*,*N*)ClPt(μ-**L**^{2})$ZnCl_3$] **8**. The ^{31}P-{^{1}H} NMR spectrum of **8** was broad, but both the chemical shifts and the coupling constants are similar to those observed in the low temperature spectrum of **2** suggesting similar geometries around the platinum centre, *i.e.* one bidentate and one unidentate **L**^{2} ligand and a chloride.

In order to investigate the possibility of both aminophosphine ligands bridging to the cobalt centre, giving species of general formula [X_2Pt(μ-**L**^{2})$_2$$CoCl_2$] it was decided to use a bidentate dianionic ligand in order to prevent halide transfer from platinum to cobalt. One potential ligand for this is a catecholate, and consequently [Pt($O_2C_6H_3Bu^t$)(**L**^{2})$_2$] **9** was prepared from the reaction between **L**^{2} and [Pt($O_2C_6H_3Bu^t$)(cod)], with the latter formed *in situ* from [$PtCl_2$(cod)], 4-*tert*-butylcatechol and the base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).[20] Complex **9** was isolated as an orange powder and characterised on the basis of microanalysis and ^{31}P-{^{1}H} and ^{1}H NMR spectroscopy. The ^{31}P-{^{1}H} NMR spectrum shows an AB system with ^{195}Pt satellites, the second order spectrum a result of the similar chemical environments of the two phosphorus atoms, which differ only due to the presence of the *tert*-butyl group on the catecholate. The reaction of **9** with $CoCl_2 \cdot 6H_2O$ gave a blue crystalline product, but this did not prove to be a doubly bridged species. Instead, the product was identified on the basis of microanalysis and IR spectroscopy as **7**. Hence, reaction of **9** with $CoCl_2 \cdot 6H_2O$ leads to displacement of catecholate by chloride.

Conclusion

The results described demonstrate that amine-functionalised aminophosphines can readily be prepared and can act as both uni- and bi-dentate ligands on platinum. Moreover, compounds containing *P*-bound ligands have unco-ordinated nitrogen atoms which can act as ligands to other metals thus affording heteronuclear bimetallic compounds such as **7**.

Experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen using dry dioxygen-free solvents unless noted otherwise. Microanalyses (C, H and N) were carried out by Mr Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet 510P spectrometer as KBr pellets, Nujol mulls or dichloromethane solutions in KBr cells. ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were recorded on a JEOL JNM-EX270 spectrometer operating at 270 MHz referenced to TMS, 67.8 MHz referenced to TMS and 109.4 MHz referenced to H_3PO_4, respectively. FAB mass spectra were recorded on a VG AutoSpec-Q spectrometer using 3-nitrobenzyl alcohol as the matrix. [$PtCl_2$(cod)][21] and [{Pt(dmba)(μ-Cl)}$_2$][22] were prepared by standard literature methods. ^{31}P-{^{1}H} NMR data are given in Table 1.

Syntheses

$Ph_2PNHCH_2CH_2NMe_2$ L^1. *n*-Butyllithium in hexane (6.96 cm^3, 1.6 M, 11 mmol) and PPh_2Cl (2.46 g, 11 mmol) were added sequentially with stirring to a solution of $NH_2CH_2CH_2NMe_2$ (0.980 g, 11 mmol) in THF (40 cm^3) at −78 °C. The reaction mixture was stirred for 2 hours and then slowly warmed to room temperature. The solvent was removed under reduced pressure and the product extracted with ice cold diethyl ether. The resulting solution was evaporated under reduced pressure to give a pale yellow moisture-sensitive oil. Yield 2.28 g (75%) (Found: C, 71.1; H, 7.68; N, 9.60. $C_{16}H_{21}N_2P$ requires C, 70.6; H, 7.77; N, 10.3%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 41.6. ^{1}H NMR ($CDCl_3$): δ 7.41–7.37 (m, 4 H, Ar), 7.30–7.15 (m, 6 H, Ar), 2.89 (dt, 2 H, ^{3}J(H,P) 14, ^{3}J(H,H) 6, CH_2NP), 2.49 (m, 1 H, NH), 2.24 (t, 2 H, ^{3}J(H,H) 6 Hz, CH_2N) and 2.08 (s, 6 H, CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 140.9 (d, ^{1}J(C,P) 13, C_{ipso}), 130.7 (d, ^{2}J(C,P) 20, C_{ortho}), 127.5 (d, ^{3}J(C,P) 7, C_{meta}), 127.3 (s, C_{para}), 60.3 (d, ^{3}J(C,P) 7, CH_2N), 44.6 (s, CH_3) and 42.3 (d, ^{2}J(C,P) 11 Hz, CH_2NP). IR (KBr, cm^{-1}): 3370 [m (br), ν(NH)].

$Ph_2PNMeCH_2CH_2NMe_2$ L^2. Triethylamine (1.13 g, 11 mmol) and PPh_2Cl (2.46 g, 11 mmol) were added sequentially with stirring to a solution of $NHMeCH_2CH_2NMe_2$ (1.14 g, 11 mmol) in THF (20 cm^3). The reaction mixture was stirred for 30 minutes and then filtered to remove NEt_3HCl. The resulting solution was evaporated under reduced pressure and the product extracted with diethyl ether at −78 °C. The resulting solution was evaporated under reduced pressure to give a colourless moisture-sensitive oil. Yield 2.37 g (76%) (Found: C, 71.1; H, 7.96; N, 9.31. $C_{17}H_{23}N_2P$ requires C, 71.3; H, 8.10; N, 9.78%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 65.4. ^{1}H NMR ($CDCl_3$): δ 7.41–7.34 (m, 4 H, Ar), 7.33–7.28 (m, 6 H, Ar), 3.22–3.12 (m, 2 H, CH_2NP), 2.52 (d, 3 H, ^{3}J(H,P) 6, CH_3NP), 2.35 (t, 2 H, ^{3}J(H,H) 7 Hz, CH_2N) and 2.17 (s, 6 H, CH_3N). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 139.0 (d, ^{1}J(C,P) 16, C_{ipso}), 131.5 (d, ^{2}J(C,P) 20, C_{ortho}), 127.8 (s, C_{para}), 127.6 (d, ^{3}J(C,P) 7, C_{meta}), 58.1 (d, ^{2}J(C,P) 6, CH_2N), 54.2 (d, ^{2}J(C,P) 29 Hz, CH_2NP), 45.3 (s, CH_3N) and 36.9 (s, CH_3NP).

***cis*-[$PtCl_2(L^1)_2$] 1.** [$PtCl_2$(cod)] (0.332 g, 0.86 mmol) was added with stirring to a solution of L^1 (0.470 g, 1.73 mmol) in dichloromethane. After 30 min the solvent was removed *in vacuo* and the crude product recrystallised from dichloromethane–diethyl ether. Yield 0.50 g (70%) (Found: C, 47.1; H, 5.21; N, 6.41. $C_{32}H_{42}Cl_2N_4P_2Pt$ requires C, 47.4; H, 5.22; N, 6.91%). ^{1}H NMR (d^6-acetone): δ 7.80 (m, Ar), 7.57 (m, Ar), 7.50 (m, Ar), 4.69 (br, NH), 2.66 (br, CH_2), 2.25 (br, CH_2) and 2.12 (br, CH_3). IR (KBr, cm^{-1}): 3370 [m (br), ν(NH)].

***cis*-[$PtCl_2(L^2)_2$] 2.** As for complex **1** using [$PtCl_2$(cod)] (0.136 g, 0.36 mmol) and L^2 (0.214 g, 0.75 mmol). Recrystallised from THF–hexane. Yield 0.15 g (50%) (Found: C, 49.8; H, 5.99; N, 6.19. $C_{34}H_{46}Cl_2N_4P_2Pt\cdot C_4H_8O$ requires C, 50.1; H, 5.98; N, 6.15%). ^{1}H NMR (CD_2Cl_2, +25 °C): δ 7.46–7.20 (m, Ar), 3.20 (m (br), 2 H, CH_2NP), 2.68 (m (br), 2 H, CH_2N), 2.51 (d, 3 H, ^{3}J(H,P) 10 Hz, CH_3NP) and 2.39 (s (br), 6 H, CH_3N).

***cis*-[PtCl(L^1-*P*)(L^1-*P*,*N*)]PF_6 3.** $TlPF_6$ (0.260 g, 0.75 mmol) was added with stirring to a solution of complex **1** (0.200 g, 0.25 mmol) in dichloromethane. After 3 hours the solution was filtered, the solvent removed *in vacuo* and the product recrystallised from dichloromethane–pentane, then methanol–diethyl ether. Yield 0.16 g (69%) (Found: C, 41.6; H, 4.71; N, 5.84. $C_{32}H_{42}ClF_6N_4P_3Pt$ requires C, 41.8; H, 4.60; N, 6.09%). ^{1}H NMR (CD_2Cl_2): δ 7.73–7.58 (m, Ar), 7.47 (m, Ar), 7.34 (m, Ar), 3.47 (br, CH_2), 3.32 (m, NH), 3.07 (m (br), CH_2), 2.99 (m, ^{4}J(H,P) 3 Hz, CH_3NPt), 2.45 (m, CH_2), 2.26 (br, CH_2) and 2.06 (s, CH_3N). IR (KBr, cm^{-1}): 3367, 3212 [m, ν(NH)] and 840 [vs, $\nu(PF_6)$].

***cis*-[$PtCl_2$(L^2-*P*,*N*)] 4.** As for complex **1** using [$PtCl_2$(cod)] (0.228 g, 0.61 mmol) and L^2 (0.175 g, 0.61 mmol). Yield 0.25 g (75%) (Found: C, 37.1; H, 4.22; N, 4.85. $C_{17}H_{23}Cl_2N_2PPt$ requires C, 37.0; H, 4.20; N, 5.07%). ^{1}H NMR ($CDCl_3$): δ 7.83 (m, 4 H, Ar), 7.46 (m, 6 H, Ar), 3.32 (m (br), 2 H, CH_2), 3.27 (s (br), 2 H, CH_2), 3.12 (m (br), 6 H, CH_3N) and 2.38 (d, 2 H, ^{3}J(H,P) 8 Hz, CH_3NP).

[Pt(dmba)Cl(L^2)] 5. The complex [{Pt(dmba)(μ-Cl)}$_2$] (0.204 g, 0.28 mmol) was added to a solution of L^2 (0.160 g, 0.56 mmol) in dichloromethane (30 cm^3). The solution was stirred for 1 hour, after which it was concentrated under reduced pressure, filtered and diethyl ether added, to give **5**. Yield 0.34 g (93%, mixture of isomers) (Found: C, 48.1; H, 5.57; N, 6.87. $C_{26}H_{35}ClN_3PPt$ requires C, 48.0; H, 5.42; N, 6.45%). ^{1}H NMR (CD_2Cl_2): δ 7.85 (m, 4 H, Ar), 7.38 (m, 6 H, Ar), 7.10 (m, Ar), 6.97 (t, Ar), 6.69 (t, Ar), 4.05 (m, 2 H, ^{4}J(H,P) 3, CH_2N (dmba)), 3.38 (m, 2 H, CH_2NP), 2.95 (m, 6 H, ^{4}J(H,P) 3, CH_3N (dmba)), 2.75 (d, 3 H, ^{3}J(H,P) 11, CH_3NP), 2.49 (t, 2 H, ^{3}J(H,H) 8 Hz, CH_2N) and 2.14 (s, 6 H, CH_3N).

[Pt(dmba)(L^2-*P*,*N*)]PF_6 6. $TlPF_6$ (0.072 g, 0.21 mmol) was added to a solution of complex **5** (0.103 g, 0.16 mmol) in dichloromethane (10 cm^3) and the mixture stirred overnight. The resulting solution was filtered, the residue washed with dichloromethane and the filtrate and washings were combined. The solvent was then evaporated under reduced pressure to give a yellow solid, which was recrystallised from dichloromethane–hexane. Yield 0.049 g (41%). ^{1}H NMR (CD_2Cl_2): δ 7.85 (m, Ar), 7.48 (m, Ar), 6.82 (d, 1 H, Ar), 6.63 (t, 1 H, Ar), 6.40 (m, 1 H, Ar), 6.21 (t, 1 H, Ar), 3.99 (m (br), 2 H, CH_2N (dmba)), 3.26 (br, 4 H, CH_2N/CH_2NP), 2.90 (s, 6 H, CH_3N), 2.88 (m, 6 H, ^{4}J(H,P) 3, CH_3N (dmba)) and 2.44 (d, 2 H, ^{3}J(H,P) 9 Hz, CH_3NP).

***cis*-[(L^2-*P*,*N*)ClPt(μ-L^2)$CoCl_3$] 7.** $CoCl_2\cdot 6H_2O$ (0.069 g, 0.29 mmol) was added with stirring to a solution of complex **2** (0.244 g, 0.29 mmol) in acetone. After 30 min the solution was filtered, the solvent removed *in vacuo* and the product recrystallised from dichloromethane–diethyl ether. Yield 0.16 g (55%) (Found: C, 40.9; H, 4.76; N, 5.45. $C_{34}H_{46}Cl_4CoN_4P_2Pt\cdot {}^{1}/_{2}CH_2Cl_2$ requires C, 41.0; H, 4.69; N, 5.54%). FAB-MS: *m*/*z* 803, $[M - CoCl_3]^+$.

***cis*-[(L^2-*P*,*N*)ClPt(μ-L^2)$ZnCl_3$] 8.** As for complex **7** using $ZnCl_2$ (0.074 g, 0.54 mmol) and **2** (0.455 g, 0.54 mmol). Recrystallisation from dichloromethane–diethyl ether gave a colourless crystalline material (Found: C, 40.1; H, 4.60; N, 5.22. $C_{34}H_{46}Cl_4N_4P_2PtZn\cdot CH_2Cl_2$ requires C, 39.7; H, 4.56; N, 5.29%).

[Pt($O_2C_6H_3Bu^t$)(L^2)$_2$] 9. L^2 (0.306 g, 0.82 mmol) was added to a solution of [Pt($O_2C_6H_3Bu^t$)(cod)] formed *in situ* from [$PtCl_2$-

(cod)] (0.200 g, 0.53 mmol), 4-*tert*-butylcatechol (0.089 g, 0.53 mmol) and DBU (0.17 cm^3, 0.173 g, 1.14 mmol). The mixture was stirred for 30 minutes after which the solvent was removed under reduced pressure and the product extracted with hexane (40 cm^3). The solution was then cooled to −78 °C to precipitate the product as an orange powder. Yield 0.41 g (83%) (Found: C, 56.2; H, 6.34; N, 6.04. $C_{44}H_{58}N_4O_2P_2Pt$ requires C, 56.7; H, 6.27; N, 6.01%). ^{1}H NMR ($CDCl_3$): δ 7.60 (m, Ar), 7.38 (m, Ar), 7.22 (m, Ar), 6.85 (m, Ar), 6.71 (m, Ar), 6.56 (m, Ar), 3.34 (m (br), 2 H, CH_2NP), 2.83 (m, 3 H, CH_3NP), 2.43 (m, 2 H, CH_2N), 2.15 and 2.12 (s, 6 H, CH_3N) and 1.40 (s, 9 H, *t*-Bu).

Crystallography

Single crystals of complex **7** were prepared by recrystallisation from dichloromethane–diethyl ether. A crystal of approximate dimensions 0.18 × 0.18 × 0.15 mm was used for the data collection. $C_{34}H_{46}Cl_4CoN_4P_2Pt$, $M = 968.51$, monoclinic, space group $P2_1/c$, $T = 293(2)$ K, $a = 16.710(3)$, $b = 12.160(2)$, $c = 19.666(5)$ Å, $\beta = 104.82(2)°$, $U = 3863.1(14)$ Å^3, $Z = 4$, μ(Mo-Kα) = 4.436 mm^{-1}. 7270 reflections measured. 5156 F^2 data [$F_o > 4\sigma(F_o)$] gave $R1 = 0.0367$ and $wR2 = 0.0838$. Data were collected on an Enraf-Nonius CAD4 automatic four-circle diffractometer in the range $2.10 < \theta < 24.99°$ and corrected for Lorentz and polarisation effects, in addition to 12% decay of the sample in the X-ray beam. The structure solution and refinement were undertaken using SHELXS 86[23] and SHELXL 93[24] respectively. The plot of the asymmetric unit was produced using ORTEX.[25]

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See http://www.rsc.org/suppdata/dt/b0/b005899h/ for crystallographic files in .cif format.

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