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Ether functionalised aminophosphines: synthesis and co-ordination chemistry of palladium(II) and platinum(II) complexes †

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Ether-functionalised aminophosphines Ph_2PNHR [R = $CH_2CH_2OCH_3$ **L**^{1}, $CH_2CH(OCH_3)_2$ **L**^{2}, $CH_2CH_2CH_2OCH_3$ **L**^{3} or $C_6H_4OCH_3$-2 **L**^{4}] were prepared from the reaction of Ph_2PCl and the amine RNH_2 in the presence of triethylamine. Reaction of **L**$^{1–4}$ with $[MCl_2(cod)]$ (M = Pd or Pt) or $[PtBr_2(cod)]$ gave the complexes $[MCl_2L_2]$ (**1**, M = Pd, L = **L**^{1}; **2**, M = Pd, L = **L**^{2}; **3**, M = Pd, L = **L**^{3}; **4**, M = Pd, L = **L**^{4}; **5**, M = Pt, L = **L**^{1}; **6**, M = Pt, L = **L**^{2}; **7**, M = Pt, L = **L**^{4}) and $[PtBr_2(\mathbf{L}^1)_2]$ **8**. X-Ray crystallographic analyses of complexes **1** and **2** indicated the presence of bifurcated hydrogen bonds between the NH protons and both the chloride ligands and the ether oxygen atoms. Reaction of **1**, **5** and **7** with two equivalents of $AgBF_4$ led to formation of *trans*-$[Pd(\mathbf{L}^1)_2][BF_4]_2$ **9** and *cis*-$[PtL_2][BF_4]_2$ (L = **L**^{1}; **10** or **L**^{4} **11**) containing bidentate P,O-co-ordinated ligands whereas reaction of **1** with one equivalent of $AgBF_4$ gave exclusively $[\{Pd(\mu\text{-}Cl)(\mathbf{L}^1)_2\}_2][BF_4]_2$ **12**, containing only unidentate aminophosphine ligands. Reaction of **5** and **8** with $NaNO_2$ led to formation of *cis*-$[PtX(NO_2)(\mathbf{L}^1)_2]$ (X = Cl **13** or Br **14**). Shielding of one of the NH protons with respect to **5** and **8** suggested loss of N–H · · · X hydrogen bonding and this was confirmed by an X-ray crystallographic analysis of **14**. Reaction of **L**$^{1–4}$ with $[\{M(dmba)(\mu\text{-}Cl)\}_2]$ (M = Pd or Pt; Hdmba = *N*,*N*-dimethylbenzylamine) gave [M(dmba)ClL] (**16**, M = Pd, L = **L**^{1}; **17**, M = Pd, L = **L**^{2}; **18**, M = Pd, L = **L**^{3}; **19**, M = Pd, L = **L**^{4}; **20**, M = Pt, L = **L**^{1}; **21**, M = Pt, L = **L**^{2}; **22**, M = Pt, L = **L**^{4}). The crystal structure of **16** reveals a similar bifurcated hydrogen bond to those observed in **1** and **2**, whereas the structure of **18** shows the N–H · · · Cl interaction to be present but the N–H · · · O interaction absent. Reaction of **16**, **20** and **22** with $AgBF_4$ gave the bidentate P,O-co-ordinated complexes $[M(dmba)L]BF_4$ (**23**, M = Pd, L = **L**^{1}; **24**, M = Pt, L = **L**^{1}; **25**, M = Pt, L = **L**^{4}). Displacement of the co-ordinated ether oxygen was achieved by reaction of **24** and **25** with CO and of **25** with xylyl isocyanide and acetonitrile. Attempts to recrystallise **24** led instead to isolation of the dinuclear species $[\{Pt(dmba)(\mu\text{-}PPh_2O)\}_2]$ **30** which was characterised by X-ray crystallography.

Introduction

Phosphines lie at the heart of modern co-ordination and organometallic chemistry, with their transition metal complexes of primary importance as homogeneous catalysts for many processes. Although there now exists a huge body of work on the chemistry of both phosphines and phosphites, aminophosphines (or phosphinamines) containing P–N bonds instead of P–C or P–O bonds have been relatively neglected as ligands. One potential reason for the underdevelopment of this chemistry is that the P–N bond is envisaged as being susceptible to relatively easy cleavage,[1] although a similar lack of stability to hydrolysis has not prevented the widespread use of phosphites.[2] Despite the relative lack of development, there are indications of the potential utility of transition metal complexes of aminophosphines. For example, rhodium(I)[3] and platinum(II)[4] complexes of chiral aminophosphines have proved to be efficient catalysts for asymmetric hydrogenation and hydroformylation reactions respectively, and nickel complexes have been employed[5] in the cyclodimerisation of buta-1,3-diene. In addition, Woollins and co-workers have reported a number of examples of aminophosphines including those derived from 1,2-diaminobenzene[6] and $Ph_2PNHCOPh$,[7] and aminophosphines of the type $Ph_2PNHC_6H_4COR$ have also recently been reported.[8]

The chemistry of ether phosphines has received considerable attention, most notably from Lindner and co-workers,[9] and the hemilabile co-ordination by the ether oxygen in ligands such as $Ph_2PCH_2CH_2OCH_3$ to late transition metals has important catalytic implications.[10] In this paper we explore the synthesis and reactivity of aminophosphines that contain ether functionalities.

Results and discussion

(i) Ligand synthesis

Since NH bonds are generally more acidic than CH bonds, the synthesis of aminophosphines from Ph_2PCl requires milder conditions than the analogous synthesis of phosphines. Reaction of Ph_2PCl with an equimolar amount of the appropriate primary amine in the presence of triethylamine leads to good yields of the aminophosphines $Ph_2PNHCH_2CH_2OCH_3$ (**L**^{1}), $Ph_2PNHCH_2CH(OCH_3)_2$ (**L**^{2}), $Ph_2PNHCH_2CH_2CH_2OCH_3$ (**L**^{3}) and $Ph_2PNHC_6H_4OCH_3$-2 (**L**^{4}) with precipitation of NEt_3HCl the main driving force. Care needs to be taken during the syntheses to exclude water, in order to prevent the formation of $Ph_2PP(O)Ph_2$, which is catalysed by NEt_3.[11] The aminophosphines **L**$^{1–4}$ were isolated as colourless moisture-sensitive oils, and characterised on the basis of multinuclear NMR and IR spectroscopy (see Table 1) and microanalysis.

Compounds **L**$^{1–4}$ are susceptible to alcoholysis, the reaction with methanol leading to cleavage of the P–N bond and formation of Ph_2POMe. The influence of the alkyl and aryl substituents on this reaction was studied by comparing the relative rates of methanolysis of **L**^{1} and **L**^{4}. 20 equivalents of methanol

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b001436m/

Table 1 ^{31}P-{^{1}H} NMR data, IR data and δ(NH) from the ^{1}H NMR spectrum for ligands $\mathbf{L^{1-4}}$ and complexes **1**–**29**

Compound		δ(P)	^{1}J(Pt,P)/Hz	δ(NH)	$\tilde{\nu}$(NH)/cm^{-1}	Other data
$\mathbf{L^1}$	$Ph_2PNHCH_2CH_2OCH_3$	42.0	—	2.46	3370	
$\mathbf{L^2}$	$Ph_2PNHCH_2CH(OCH_3)_2$	42.9	—	2.23	3368	
$\mathbf{L^3}$	$Ph_2PNHCH_2CH_2CH_2OCH_3$	41.9	—	2.20	3370	
$\mathbf{L^4}$	$Ph_2PNHC_6H_4OCH_3$-*2*	27.2	—	5.32	3381	
cis-**1**	*cis*-[$PdCl_2(\mathbf{L^1})_2$]	59.0	—	4.40		
trans-**1**	*trans*-[$PdCl_2(\mathbf{L^1})_2$]	46.4	—	4.28	3351	
cis-**2**	*cis*-[$PdCl_2(\mathbf{L^2})_2$]	59.2	—	4.42		
trans-**2**	*trans*-[$PdCl_2(\mathbf{L^2})_2$]	46.9	—	4.29	3331	
cis-**3**	*cis*-[$PdCl_2(\mathbf{L^3})_2$]	58.8	—	4.47		
trans-**3**	*trans*-[$PdCl_2(\mathbf{L^3})_2$]	46.2	—	4.11	3332	
4	*trans*-[$PdCl_2(\mathbf{L^4})_2$]		—		3300	
5	*cis*-[$PtCl_2(\mathbf{L^1})_2$]	35.5	3940	4.08	3380, 3293	
6	*cis*-[$PtCl_2(\mathbf{L^2})_2$]	35.8	3940	4.09	3350, 3247	
7	*cis*-[$PtCl_2(\mathbf{L^4})_2$]	30.1	3934	6.82	3370, 3199	
8	*cis*-[$PtBr_2(\mathbf{L^1})_2$]	36.7	3904	3.97	3399, 3293	
9	*trans*-[$Pd(\mathbf{L^1})_2][BF_4]_2$	80.1	—	4.07	3316	
10	*cis*-[$Pt(\mathbf{L^1})_2][BF_4]_2$	39.6	4346	3.87	3326	
11	*cis*-[$Pt(\mathbf{L^4})_2][BF_4]_2$	27.7	4162	6.48	3296	
12	[{$Pd(\mu\text{-}Cl)_2(\mathbf{L^1})_2$}$_2$][$BF_4$]$_2$	61.4	—	4.39	3274	
13	*cis*-[$PtCl(NO_2)(\mathbf{L^1})_2$]	33.8	4115	4.40	3396, 3264	^{2}J(P,P) 24
		25.5	3186	3.50		
14	*cis*-[$PtBr(NO_2)(\mathbf{L^1})_2$]	33.8	4101	4.20	3397, 3311	^{2}J(P,P) 23
		25.5	3166	3.30		
15	*cis*-[$Pt(NO_2)_2(\mathbf{L^1})_2$]	26.8	3370	3.54		
16	[Pd(dmba)Cl($\mathbf{L^1}$)]	68.4	—	4.40	3285	
17	[Pd(dmba)Cl($\mathbf{L^2}$)]	68.4	—	4.48	3284	
18	[Pd(dmba)Cl($\mathbf{L^3}$)]	67.6	—	4.40	3303	
19	[Pd(dmba)Cl($\mathbf{L^4}$)]	59.7	—	6.60	3197	
20	[Pt(dmba)Cl($\mathbf{L^1}$)]	42.1	4460	4.23	3308	
21	[Pt(dmba)Cl($\mathbf{L^2}$)]	42.3	4470	4.24	3294	
22	[Pt(dmba)Cl($\mathbf{L^4}$)]	34.8	4464	6.37	3214	
23	[Pd(dmba)($\mathbf{L^1}$)]BF_4	75.2	—	3.40		
24	[Pt(dmba)($\mathbf{L^1}$)]BF_4	48.8	4396	3.15	3399	
25	[Pt(dmba)($\mathbf{L^4}$)]BF_4	60.9	4393	6.00	3390	
26	[Pt(dmba)($\mathbf{L^1}$)(CO)]BF_4	38.8	3666	3.57	3334	ν(CO) 2114
27	[Pt(dmba)($\mathbf{L^4}$)(CO)]BF_4	35.4	3696	5.90		ν(CO) 2105
28	[Pt(dmba)($\mathbf{L^4}$)(CNXyl)]BF_4	36.7	3897	5.85	3376	ν(NC) 2179
29	[Pt(dmba)($\mathbf{L^4}$)($NCCH_3$)]BF_4	38.5	4256	5.74	3370	

were added to $\mathbf{L^1}$ and $\mathbf{L^4}$ in $CDCl_3$ and the solutions monitored by ^{31}P-{^{1}H} NMR spectroscopy. $\mathbf{L^1}$ reacted slowly, with the reaction taking 24 h to reach completion, whereas in contrast $\mathbf{L^4}$ was fully converted into Ph_2POMe after 30 min. These results were somewhat surprising since it has previously been reported that aminophosphines with aryl substituents such as $(Ph_2PNH)_2C_6H_4$-1,2 are air-stable indefinitely.[6]

(ii) Palladium(II) and platinum(II) complexes [MCl_2L_2]

The reaction of two equivalents of $\mathbf{L^{1-4}}$ with [$PdCl_2$(cod)] in dichloromethane gave virtually quantitative yields of [$PdCl_2L_2$] (L = $\mathbf{L^1}$ **1**, $\mathbf{L^2}$ **2**, $\mathbf{L^3}$ **3** or $\mathbf{L^4}$ **4**). The ^{31}P-{^{1}H} NMR spectra of the palladium complexes **1**–**3** showed two phosphorus resonances which were assigned to the *cis* and *trans* isomers (Table 1). In accordance with this, two sets of resonances were also observed in the ^{1}H NMR spectra. Crystallisation of the mixture of geometric isomers gave exclusively *trans*-[$PdCl_2L_2$] in the solid state (see below). The formation of an equilibrium mixture of the *cis* and *trans* isomers was followed by observing the slow isomerisation of the crystallographically characterised isomers *trans*-[$PdCl_2(\mathbf{L^1})_2$] and *trans*-[$PdCl_2(\mathbf{L^2})_2$] over a period of 24 hours. In both cases there was a 1 : 1 mixture of the *cis* and *trans* isomers at equilibrium in $CDCl_3$. These studies enabled the ^{31}P-{^{1}H} and ^{1}H resonances for the two isomers to be assigned. The complex [$PdCl_2${$PPh_2NHP(O)Ph_2$}$_2$] also exists in the *trans* form in the solid state and as a *cis–trans* mixture in solution, though in this case there is a 1 : 3.7 ratio of the *cis* and *trans* isomers at equilibrium in $CDCl_3$.[12] The complex [$PdCl_2(\mathbf{L^4})_2$] **4** proved to be insoluble in common solvents so could not be characterised using NMR spectroscopy. However, the IR spectrum showed one ν(NH) band as observed for **1**–**3** suggesting that **4** also exists in the solid state as the *trans* isomer.

The reaction of two equivalents of $\mathbf{L^1}$, $\mathbf{L^2}$ or $\mathbf{L^4}$ with [$PtCl_2$(cod)] in dichloromethane gave virtually quantitative yields of *cis*-[$PtCl_2L_2$] (L = $\mathbf{L^1}$ **5**, $\mathbf{L^2}$ **6** or $\mathbf{L^4}$ **7**). In the ^{31}P-{^{1}H} NMR spectra of complexes **5**–**7** ^{1}J(Pt,P) is *ca.* 3940 Hz (Table 1), typical for phosphorus *trans* to chloride. The IR spectra for the *cis* complexes **5**–**7** all show two bands for ν(NH), in contrast to the *trans* complexes **1**–**4** which show only one band. Reaction of $\mathbf{L^1}$ with [$PtBr_2$(cod)] in an analogous manner gave *cis*-[$PtBr_2(\mathbf{L^1})_2$] **8**.

Complexes **1** and **2** were recrystallised from dichloromethane–diethyl ether as yellow needle-shaped crystals, suitable for single crystal X-ray analyses. The crystal structures confirmed the *trans* orientation of the ligands; selected bond lengths and angles are given in Table 2 and the molecular structures are shown in Figs. 1 and 2. In both cases the asymmetric unit contains only half the molecule, with the remaining half being generated by inversion through a centre of symmetry on which the palladium atom resides with half-site occupancy. The palladium(II) centres are distorted square-planar, with *cis* angles of 88.49(4) and 91.51(4)° in **1** and 88.23(4) and 91.77(4)° in **2**. The Pd–P and Pd–Cl bond distances in **1** and **2** are unremarkable. The P–N distances [1.643(3) Å for **1**, 1.644(4) Å for **2**] are shorter than the generally accepted range for P–N single bonds (*e.g.* 1.689–1.727 Å in *N*-piperidinophosphines[13]), suggesting a degree of double bond character. This is generally observed in complexes of aminophosphines, and a search of the Cambridge Structural Database[14] revealed the average P–N distance for aminophosphines of the type Ph_2PNHR (R = alkyl or aryl), unconstrained by chelation, to be 1.67 Å (range 1.63–1.73 Å). The sums of angles around the nitrogen atoms in **1** and **2**

Table 2 Selected bond lengths (Å) and angles (°) for complexes *trans*-**1** and *trans*-**2**

	trans-**1**	*trans*-**2**
Pd(1)–Cl(1)	2.2963(10)	2.2957(12)
Pd(1)–P(1)	2.3158(10)	2.3304(12)
P(1)–N(1)	1.643(3)	1.644(4)
N(1)–C(13)	1.464(5)	1.456(5)
Cl(1)–Pd(1)–P(1)	91.51(4)	88.23(4)
Cl(1)–Pd(1)–P(1)′	88.49(4)	91.77(4)
N(1)–P(1)–Pd(1)	111.59(13)	111.31(14)
C(13)–N(1)–Pd(1)	127.6(3)	127.9(3)

Primed atoms generated by symmetry operations $-x, -y, -z + 1$ (*trans*-**1**), $-x, -y, -z$ (*trans*-**2**).

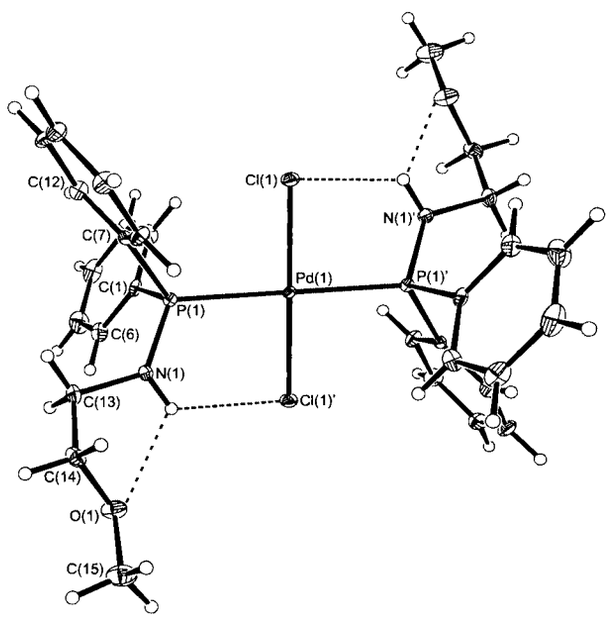

Fig. 1 Molecular structure of *trans*-$[PdCl_2(\mathbf{L}^1)_2]$ **1** with thermal ellipsoids at the 30% probability level. Unprimed atoms represent those in the asymmetric unit.

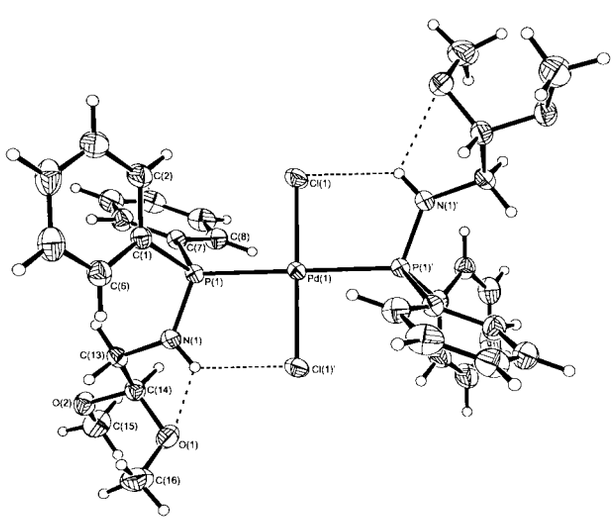

Fig. 2 Molecular structure of *trans*-$[PdCl_2(\mathbf{L}^2)_2]$ **2**. Details as in Fig. 1.

are 354 and 360° respectively, consistent with significant sp^2 character.

The structure of complex **1** shows the presence of an intramolecular hydrogen bond between the N(1)–H(1) proton and the chloride ligand Cl(1) [N···Cl 3.170(3), H···Cl 2.54 Å, N–H···Cl 126°]. N–H···Cl hydrogen bonds have been observed in a number of other complexes containing mutually *cis* aminophosphine and chloride ligands,[12,15–20] and in these previous examples N···Cl distances range from 3.00 to 3.12 Å and H···Cl distances from 2.1 to 2.5 Å. The orientation of the ether chain suggests that the hydrogen bond is more accurately described as bifurcated, with the N–H···O interaction being the minor component of the 3-centre hydrogen bond. Vicinal intramolecular hydrogen bonding such as this is generally only observed in this manner due to the unfavourable angular geometry of the 5-membered hydrogen-bond ring, and the parameters [N···O 2.777(4), H···O 2.42 Å, N–H···O 104°] are similar to those observed for minor components of bifurcated hydrogen bonds in the crystal structures of nucleosides and nucleotides.[21,22] A similar intramolecular bifurcated hydrogen bond is observed in the structure of **2** [N···Cl 3.139(3), H···Cl 2.49 Å, N–H···Cl 131°; N···O 2.861(4), H···O 2.56 Å, N–H···O 100°].

Unlike the free ligands $\mathbf{L}^{1-4}$, complexes **1**–**7** do not readily react with methanol. The addition of an excess of wet methanol to a dichloromethane solution of **1** led to no change in the ^{31}P-$\{^1H\}$ NMR spectrum after 24 hours. The stabilisation of the aminophosphine ligands to methanolysis and hydrolysis on co-ordination is in direct contrast to diphosphazanes ($Ph_2PNRPPh_2$) for which the ligand is stable in methanol for several days at room temperature, but on co-ordination the P–N bond is readily cleaved.[18] Similarly, $Ph_2PNHP(O)Ph_2$ is activated to methanolysis on co-ordination to platinum.[16]

In order to examine the potential bidentate co-ordination of the ether functionalised aminophosphines, the complexes *trans*-$[PdCl_2(\mathbf{L}^1)_2]$ **1** and *cis*-$[PtCl_2L_2]$ (L = $\mathbf{L}^1$ **5** or $\mathbf{L}^4$ **7**) were treated with two equivalents of $AgBF_4$. Reaction in dichloromethane led to the rapid precipitation of silver chloride, and the products, *trans*-$[Pd(\mathbf{L}^1)_2][BF_4]_2$ **9** and *cis*-$[PtL_2][BF_4]_2$ (L = $\mathbf{L}^1$ **10** or $\mathbf{L}^4$ **11**), were characterised on the basis of multinuclear NMR spectroscopy and microanalysis. The platinum complexes **10** and **11** show a significant increase in $^1J(Pt,P)$, as expected on replacing chloride with a weaker *trans* influence ligand such as an ether oxygen. The ^1H NMR spectra too show evidence of co-ordination of the ether oxygen atoms, with a deshielding of the methoxy protons ($\Delta\delta = 0.43$ ppm for **9** with respect to **1**, 0.63 ppm for **10** with respect to **5**, 0.14 ppm for **11** with respect to **7**) and, for **9** and **10**, deshielding of the methylene protons, now attached to a 6-membered chelate ring. It is notable also that the NH protons become shielded on formation of the chelate rings in **9**, **10** and **11**. This is a likely consequence of the loss of hydrogen bonding to the NH proton.

Reaction of **1** with one equivalent of $AgBF_4$ led exclusively to the chloro-bridged dimer $[\{Pd(\mu\text{-}Cl)(\mathbf{L}^1)_2\}_2](BF_4)_2$ **12** which was characterised on the basis of multinuclear NMR spectroscopy, microanalysis and FAB-MS. Lindner and co-workers[23] have previously shown that a range of ether phosphines lead, under similar conditions, to complexes of the type $[PdClL_2]^+$ in which one phosphine is bidentate and P,O-co-ordinated, whereas the other is unidentate and P-co-ordinated. Only for ether phosphines in which the oxygen atom is less basic were dimers observed. In our case, it is likely to be the unfavorable formation of a 6-membered ring that favours the formation of **12** over $[PdCl(\mathbf{L}^1)_2]^+$.

(iii) Nitrito complexes

In order to probe further the N–H···X hydrogen bonding in this system, halide substitution reactions were carried out. The reaction of *cis*-$[PtX_2(\mathbf{L}^1)_2]$ (X = Cl **5** or Br **8**) with sodium nitrite in aqueous acetone was followed by ^{31}P-$\{^1H\}$ NMR spectroscopy, and showed that in both cases the formation of *cis*-$[PtX(NO_2)(\mathbf{L}^1)_2]$ (X = Cl **13** or Br **14**) reached a maximum yield after *ca.* 4 hours. Continuation of the reaction for 24 hours using an excess of sodium nitrite led to *cis*-$[Pt(NO_2)_2(\mathbf{L}^1)_2]$ **15** in both cases, though this complex was not isolated from the

Table 3 Selected bond lengths (Å) and angles (°) for complex **14**

Pt(1)–P(1)	2.2564(15)	P(2)–N(2)	1.661(5)
Pt(1)–P(2)	2.2684(14)	N(1)–C(13)	1.471(8)
Pt(1)–Br(1)	2.4889(8)	N(2)–C(28)	1.475(8)
Pt(1)–N(3)	2.150(6)	N(3)–O(1)	1.2235(14)
P(1)–N(1)	1.653(5)	N(3)–O(2)	1.2246(10)
N(3)–Pt(1)–P(1)	91.91(12)	N(1)–P(1)–Pt(1)	110.9(2)
N(3)–Pt(1)–P(2)	173.86(13)	C(13)–N(1)–P(1)	127.8(4)
N(3)–Pt(1)–Br(1)	83.19(12)	N(2)–P(2)–Pt(1)	110.1(2)
P(1)–Pt(1)–P(2)	93.78(5)	C(28)–N(2)–P(2)	126.6(4)
P(1)–Pt(1)–Br(1)	174.96(4)	O(1)–N(3)–O(2)	130.4(7)
P(2)–Pt(1)–Br(1)	91.07(4)		

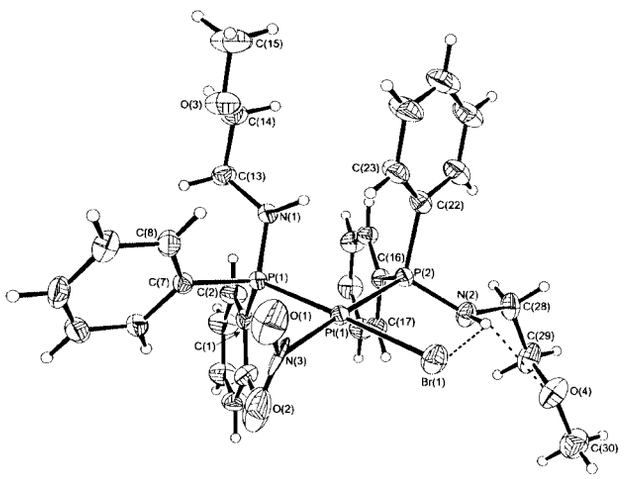

Fig. 3 Molecular structure of *cis*-[PtBr(NO_2)(L^1)$_2$] **14** with thermal ellipsoids at the 30% probability level.

reaction mixture. The ^{31}P-{^{1}H} NMR spectra of **13** and **14** show two sets of doublets, each with ^{195}Pt satellites, as expected for complexes containing two inequivalent phosphorus atoms. The doublets can be assigned on the basis of ^1J(Pt,P), the value of which is greater for the phosphorus atom *trans* to the halide. The effect of the different electronic effects of halide and nitrite on ^1J(Pt,P) is also reflected in the coupling constant for **15** which at 3370 Hz is 570 Hz less than that for **5**.

The ^{1}H NMR spectra of complexes **13** and **14** show two resonances for δ(NH), separated by approximately 0.9 ppm. Comparison of these spectra with those for **5** and **8** show that one of the amine hydrogen atoms has become significantly more shielded. This shielding is probably a consequence of the loss of the intramolecular N–H · · · X hydrogen bonding for this proton. The ^{1}H NMR spectrum of **15** shows that both amine hydrogen atoms are shielded with respect to the amine protons in **5** and **8**, thus δ(NH) provides a useful probe of intramolecular hydrogen bonding in these compounds.

In order to assess whether the same pattern was observed in the solid state, a single crystal X-ray analysis was carried out. Suitable crystals of complex **14** were grown from dichloromethane–hexane as colourless blocks. Selected bond lengths and angles are given in Table 3 and the molecular structure is shown in Fig. 3. The platinum(II) centre in **14** is distorted square planar with *cis* angles between 83.19(12) and 93.78(5)°. The Pt–P and Pt–Br distances are unremarkable, and as with the structures of **1** and **2** the P–N distances [1.653(5) and 1.661(5) Å] are shorter than would be expected for single P–N bonds. The sums of angles round the nitrogen atoms are 352 and 355° respectively, showing significant sp^2 character. An intramolecular hydrogen bond is observed between the N(2)–H(2A) proton and the bromine atom Br(1) [N(2) · · · Br(1) 3.175(4), H(2A) · · · Br(1) 2.48 Å, N(2)–H(2A) · · · Br(1) 128°], and as with **1** and **2** the orientation of the ether chain suggests that there is a significant N–H · · · O interaction as the minor component of a bifurcated hydrogen bond [N · · · O 2.791(7), H · · · O 2.67 Å, N–H · · · O 87°]. In contrast, no close contact is made by the amine hydrogen on the second aminophosphine ligand [N(1)–H(1A)] to either the nitrite or the ether oxygen atom, suggesting the solid state structure is the same as that observed in solution.

Table 4 Selected bond lengths (Å) and angles (°) for complexes **16** and **18**

16		**18**	
Pd(1)–C(13)	1.955(6)	Pd(1)–C(17)	2.034(4)
Pd(1)–N(2)	2.141(5)	Pd(1)–N(2)	2.156(3)
Pd(1)–P(1)	2.247(2)	Pd(1)–P(1)	2.2472(8)
Pd(1)–Cl(1)	2.365(2)	Pd(1)–Cl(1)	2.3882(11)
P(1)–N(1)	1.616(6)	P(1)–N(1)	1.648(3)
N(1)–C(19)	1.470(8)	N(1)–C(13)	1.455(4)
C(13)–Pd(1)–N(2)	80.1(2)	C(17)–Pd(1)–N(2)	82.72(13)
C(13)–Pd(1)–P(1)	96.7(2)	C(17)–Pd(1)–P(1)	96.80(10)
N(2)–Pd(1)–P(1)	169.53(14)	N(2)–Pd(1)–P(1)	177.49(8)
C(13)–Pd(1)–Cl(1)	166.0(2)	C(17)–Pd(1)–Cl(1)	170.91(10)
N(2)–Pd(1)–Cl(1)	92.5(2)	N(2)–Pd(1)–Cl(1)	90.16(9)
P(1)–Pd(1)–Cl(1)	92.51(6)	P(1)–Pd(1)–Cl(1)	90.07(3)
N(1)–P(1)–Pd(1)	111.2(2)	N(1)–P(1)–Pd(1)	109.37(10)
C(19)–N(1)–P(1)	124.9(4)	C(13)–N(1)–P(1)	128.1(2)

(iv) Palladium(II) and platinum(II) complexes [M(dmba)ClL]

Complexes **9**–**11** were found readily to decompose in solution over several hours to give complex mixtures, so in an attempt to increase the stability of compounds containing $\mathbf{L}^{1-4}$ in a bidentate co-ordination mode complexes containing only one phosphine ligand were prepared. *N*,*N*-Dimethylbenzylamine (Hdmba) was used as a bidentate monoanionic C,N-donor ligand to block two co-ordination sites of the metal complex. The reaction of two equivalents of the appropriate phosphine with [{M(dmba)(μ-Cl)}$_2$] (M = Pd or Pt) gave the complexes [Pd(dmba)ClL] (L = $\mathbf{L}^1$ **16**, $\mathbf{L}^2$ **17**, $\mathbf{L}^3$ **18** or $\mathbf{L}^4$ **19**) or [Pt(dmba)ClL] (L = $\mathbf{L}^1$ **20**, $\mathbf{L}^2$ **21** or $\mathbf{L}^4$ **22**) in virtually quantitative yield.

The ^{31}P-{^{1}H} NMR spectra of complexes **16**–**19** showed single phosphorus resonances, suggesting that, in contrast to **1**–**3**, no isomerisation occurs in solution. The orientation of $\mathbf{L}^{1-4}$ *trans* to nitrogen can be inferred from the observation of ^4J(P,H) coupling constants in the dimethylbenzylamine methyl and methylene resonances. This arrangement of phosphine *trans* to nitrogen was also observed for the complex [Pd(dmba)ClL] (L = $PPh_2CH_2CO_2Et$)[24] and the non-observation of the other potential isomer was, in this case, ascribed to the lability of a phosphine *trans* to a σ-bonded carbon.

The ^{31}P-{^{1}H} NMR spectra of complexes **20**–**22** show single phosphorus resonances with ^1J(Pt,P) in the range 4460–4470 Hz. The high value is consistent with the phosphine *trans* to the nitrogen atom of the cyclometallated *N*,*N*-dimethylbenzylamine, and as for complexes **16**–**19**, the observation of ^4J(P,H) couplings also supports this. ^{31}P-{^{1}H} NMR spectra of crude samples of **20** showed the presence of an additional compound [δ 53.9, ^1J(Pt,P) 2170]. The lower magnitude of ^1J(Pt,P) is consistent with this compound being the isomer with the phosphorus atom *trans* to carbon. If the reaction mixture is left overnight this compound is converted into **20**. It has previously been demonstrated that the reaction of cyclometallated platinum chloro-bridged dimers with pyridines can give either *N*,*N*-*cis* or *N*,*N*-*trans* products, depending on substituents.[25]

Recrystallisation of complexes **16** and **18** from dichloromethane–pentane and dichloromethane–diethyl ether respectively produced single crystals suitable for X-ray analyses. Selected bond lengths and angles are given in Table 4 and the molecular structures are shown in Figs. 4 and 5. The palladium(II) centres in **16** and **18** are distorted square planar, with *cis* angles between 80.1(2) and 96.7(2)° and 82.73(13) and

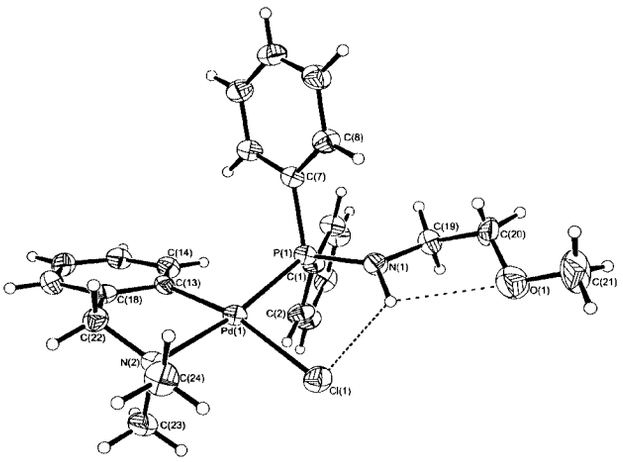

Fig. 4 Molecular structure of [Pd(dmba)Cl(**L**^{1})] **16**. Details as in Fig. 3.

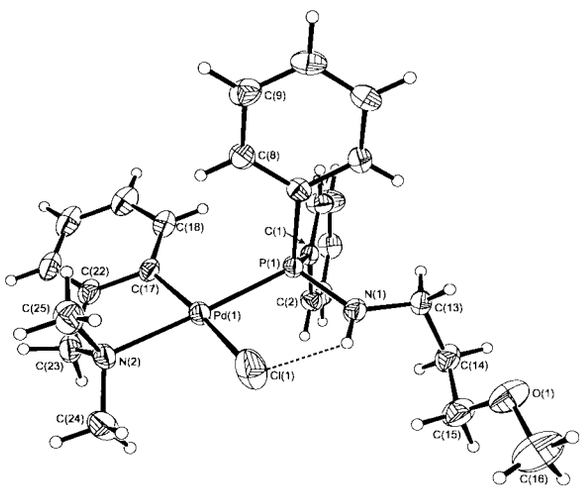

Fig. 5 Molecular structure of [Pd(dmba)Cl(**L**^{3})] **18**. Details as in Fig. 3.

96.80(10)° respectively. Complex **16** has a noticeable tetrahedral distortion, with Cl(1) and C(13) lying above (by 0.16 and 0.22 Å respectively) and P(1) and N(2) lying below (by 0.17 and 0.21 Å) the Pd(1)Cl(1)N(2)C(13)P(1) mean plane. The phosphine ligands in **16** and **18** are located *trans* to the amine nitrogen atom, consistent with the NMR data.

The Pd–P and Pd–Cl distances in complexes **16** and **18** are unremarkable, though as in **1** and **2** the P–N distances are shorter than might be expected for a single bond. Indeed, the P–N bond length in **16** [1.616(6) Å] is significantly shorter than those in **18** [1.648(3) Å], **1** [1.643(3) Å] and **2** [1.644(4) Å]. The sum of the angles around the nitrogen atom N(1) of the **L**^{1} ligand in **16** is 352° and the **L**^{3} ligand in **18** is 358°, also suggesting, as with **1** and **2**, a significant degree of sp^2 character in these compounds.

Again as in complexes **1** and **2**, the structure of **16** showed the presence of a bifurcated hydrogen bond between the N(1)–H(1) proton and both the chloride ligand Cl(1) and the ether oxygen atom O(1), with the major component to the chloride [N · · · Cl 3.087(6), H · · · Cl 2.42 Å, N–H · · · Cl 125°] and the minor component to the oxygen [N · · · O 2.904(8), H · · · O 2.53 Å, N–H · · · O 103°]. The structure of **18** shows the presence of a N–H · · · Cl interaction [N · · · Cl 3.087(3), H · · · Cl 2.43 Å, N–H · · · Cl 137°] but the ethoxy chain is orientated away from the NH group, so the N–H · · · O interaction is absent [N · · · O 3.626(4), H · · · O 3.39 Å, N–H · · · O 100°]. This is somewhat surprising, since an intramolecular 6-membered hydrogen-bonded ring might have been expected to be more favorable than a 5-membered hydrogen-bonded ring.

In order to examine the potential bidentate co-ordination mode of ligands **L**^{1} and **L**^{4}, complexes **16**, **20** and **22** were treated with $AgBF_4$. The reactions, in dichloromethane, occurred with rapid precipitation of silver chloride and formation of [Pd(dmba)(**L**^{1})]BF_4 **23** or [Pt(dmba)L]BF_4 (L = **L**^{1} **24** or **L**^{4} **25**). The ^{31}P-{^{1}H} NMR spectra for complexes **23**–**25** show single phosphorus resonances with, in the cases of **24** and **25**, ^1J(Pt,P) of 4396 and 4393 Hz respectively. Co-ordination of the ether oxygen atom leads to a slight deshielding of the methoxy protons and, in **23** and **24**, a larger deshielding of the aminophosphine methylene protons. There is significant shielding of the NH protons on formation of the 6-membered chelate ring ($\Delta\delta$ = −1.00 ppm for **23** with respect to **16**; −1.08 ppm for **24** with respect to **20**). As in **9** and **10**, this is a likely consequence of the loss of the N–H · · · Cl hydrogen bonding in **16** and **20**.

The co-ordinated ether oxygen atoms in complexes **23**–**25** are expected to be relatively labile.[26] In order to assess this, **24** and **25** were treated with CO, 2,6-dimethylphenyl (xylyl) isocyanide (CNXyl) and acetonitrile. Passage of CO gas through dichloromethane solutions of **24** and **25** led to no change in colour, but multinuclear NMR and IR spectroscopy indicated that reaction had occurred to give [Pt(dmba)(L)(CO)]BF_4 (L = **L**^{1} **26** or **L**^{4} **27**). The ^{31}P-{^{1}H} NMR spectra showed single phosphorus resonances with ^1J(Pt,P) of 3666 and 3696 Hz respectively. Observation of ^4J(P,H) coupling in the ^{1}H NMR spectrum for the methyl and methylene protons of the *N*,*N*-dimethylbenzylamine ligand suggests that the phosphine remains *trans* to the nitrogen atom. In the IR spectra, ν(CO) is observed at a high wavenumber (2114 and 2105 cm^{-1} for **26** and **27** respectively) suggesting relatively little backbonding to the carbonyl. Similar observations[26] have been reported for complexes of the type *trans*-[PtCl(CO)$(PR_3)_2$]$^+$.

Reaction of complex **25** with xylyl isocyanide gave [Pt(dmba)(**L**^{4})(CNXyl)]BF_4 **28**, which was characterised on the basis of multinuclear NMR and IR spectroscopy. Again, the ^{31}P-{^{1}H} NMR spectrum showed a single phosphorus resonance with ^1J(Pt,P) 3897 Hz, and observation of ^4J(P,H) suggests the phosphine remains *trans* to the amine nitrogen atom. In the IR spectrum, ν(NC) is observed at 2179 cm^{-1}, indicating as with **26** and **27** little backbonding. Reaction of **25** with acetonitrile gave the complex [Pt(dmba)(**L**^{4})$(NCCH_3)$]BF_4 **29**, which was also characterised on the basis of multinuclear NMR and IR spectroscopy. In this case ^1J(Pt,P) is 4256 Hz. Displacement of the ether oxygen atom from the platinum centre by a ligand such as acetonitrile clearly indicates how labile the Pt–O bond is in **25**. In contrast, the oxygen atom in the analogous complex [Pt(dmba){$PPh_2NC_4H_3(COCH_3$-2)}]$^+$ is not displaced by acetonitrile.[27]

Attempts to recrystallise complex **24** to obtain crystals suitable for X-ray analysis were unsuccessful, resulting in decomposition to a number of compounds, as observed in the ^{31}P-{^{1}H} NMR spectra. One of these compounds crystallised as colourless blocks suitable for a single crystal X-ray analysis. The analysis revealed it to be the dinuclear species [{Pt(dmba)(μ-PPh_2O)}$_2$] **30** (Fig. 6), for which selected bond lengths and angles are given in Table 5. Each of the two platinum(II) centres in **30** is co-ordinated to a bidentate cyclometallated *N*,*N*-dimethylbenzylamine ligand, a phosphorus atom and an oxygen atom. The two platinum centres both show distorted square-planar geometry, with *cis* angles between 82.1(7) and 98.9(6)° for Pt(1) and 82.6(8) and 98.7(7)° for Pt(2). The phosphorus atoms of the bridging PPh_2O^- ligands are arranged *trans* to the *N*,*N*-dimethylbenzylamine nitrogen atoms as in the starting material. The Pt(1)–O(1) and Pt(2)–O(2) bond distances, 2.116(11) and 2.098(11) Å, are similar to those in [$Pt_2Cl(PEt_3)_3$(μ-$PPh_2O)_2$],[28] [{Pd[PPh_2CH=C(O)Ph]-(μ-PPh_2O)}$_2$][29] and the cluster complex [Pt_3(μ$_3$-OH)(μ-$PPh_2O)_3$-$(PR_3)_3$]$^{2+}$,[30] all of which also contain bridging PPh_2O^- ligands, but shorter than those in [{Pt(PPh_3)(μ-PPh_2O)}$_2$] which contains a Pt–Pt bond, so straining the P–O bond.[30] The conform-

Table 5 Selected bond lengths (Å) and angles (°) for complex **30**

Pt(1)–C(13)	2.00(2)	Pt(2)–O(2)	2.098(11)
Pt(1)–O(1)	2.116(11)	Pt(2)–N(2)	2.15(2)
Pt(1)–N(1)	2.160(15)	Pt(2)–P(2)	2.217(5)
Pt(1)–P(1)	2.205(5)	P(1)–O(2)	1.531(13)
Pt(2)–C(34)	2.01(2)	P(2)–O(1)	1.556(12)
C(13)–Pt(1)–O(1)	170.4(7)	O(2)–Pt(2)–N(2)	88.8(8)
C(13)–Pt(1)–N(1)	82.1(7)	C(34)–Pt(2)–P(2)	98.7(7)
O(1)–Pt(1)–N(1)	88.9(5)	O(2)–Pt(2)–P(2)	89.9(4)
C(13)–Pt(1)–P(1)	98.9(6)	N(2)–Pt(2)–P(2)	176.2(4)
O(1)–Pt(1)–P(1)	90.1(3)	O(2)–P(1)–Pt(1)	115.4(5)
N(1)–Pt(1)–P(1)	179.0(4)	O(1)–P(2)–Pt(2)	115.5(5)
C(34)–Pt(2)–O(2)	171.3(8)	P(2)–O(1)–Pt(1)	126.1(7)
C(34)–Pt(2)–N(2)	82.6(8)	P(1)–O(2)–Pt(2)	128.6(7)

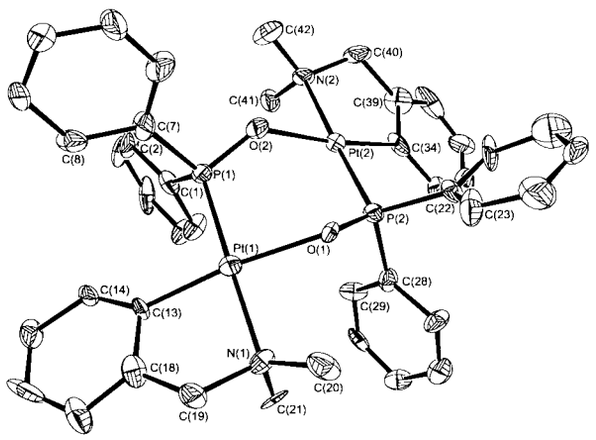

Fig. 6 Molecular structure of [{Pt(dmba)(μ-PPh_2O)}$_2$] **30** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and the CH_2Cl_2 of solvation have been omitted for clarity.

ation of the 6-membered ring in **30** can best be described as two distorted square planar units linked at an O···O hinge, with the angle between the Pt(1)–P(1)–O(1)–O(2) and Pt(2)–P(2)–O(1)–O(2) least squares planes being 48°. This conformation is in marked contrast to that observed in [{Pd[PPh_2CH=C(O)Ph]-(μ-PPh_2O)}$_2$] which is best described as a boat with the palladium atoms in the prows.[29]

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 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 and ^{31}P-{^{1}H} NMR spectra on a JEOL JNM-EX270 spectrometer operating at 270 MHz referenced to TMS and 109.4 MHz referenced to H_3PO_4, respectively, coupling constants are given in Hz and FAB mass spectra on a VG AutoSpec-Q spectrometer using 3-nitrobenzyl alcohol as the matrix. The complexes [PtX_2(cod)] (X = Cl or Br),[31] [$PdCl_2$(cod)],[32] and [{M(dmba)(μ-Cl)}$_2$] (M = Pd or Pt)[33] were prepared by standard literature methods. $\mathbf{L^{1\text{–}4}}$ were isolated in 80–90% yield, the palladium and platinum complexes in 70–90% yield unless noted otherwise below.

Syntheses

$Ph_2PNHCH_2CH_2OCH_3$ (L^1). Triethylamine (0.566 g, 5.5 mmol) and PPh_2Cl (1.23 g, 5.5 mmol) were added sequentially with stirring to a solution of 2-methoxyethylamine (0.41 g, 5.5 mmol) in THF (20 cm^3). The reaction mixture was stirred for 30 minutes and the solution filtered to remove NEt_3HCl, then evaporated under reduced pressure to give a pale yellow, viscous oil (Found: C, 69.3; H, 6.96; N, 5.15. $C_{15}H_{18}NOP$ requires C, 69.5; H, 7.00; N, 5.40%). ^{1}H NMR ($CDCl_3$): δ 7.47–7.40 (m, 4 H, Ar), 7.33–7.24 (m, 6 H, Ar), 3.32 (t, 2 H, CH_2O), 3.23 (s, 3 H, CH_3), 3.07 (dt, 2 H, CH_2N) and 2.46 (m, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 141.2 (d, ^1J(CP) 12, C_{ipso}), 130.8 (d, ^2J(CP) 20, C_{ortho}), 128.0 (s, C_{para}), 127.7 (d, ^3J(CP) 6, C_{meta}), 73.5 (d, ^3J(CP) 6, CH_2O), 58.1 (s, CH_3) and 45.3 (d, ^2J(CP) 14, CH_2N).

L^2. As for L^1 using NEt_3 (1.13 g, 11 mmol), PPh_2Cl (2.46 g, 11 mmol) and 2,2-dimethoxyethylamine (1.17 g, 11 mmol). Product extracted with diethyl ether at −78 °C (Found: C, 66.4; H, 6.86; N, 4.70. $C_{16}H_{20}NO_2P$ requires C, 66.4; H, 6.97; N, 4.84%). ^{1}H NMR ($CDCl_3$): δ 7.39–7.23 (m, Ar), 4.13 (t, 1 H, CH), 3.22 (s, 6 H, CH_3), 3.00 (m, 2 H, CH_2) and 2.23 (m, 1 H, NH). ^{13}C NMR (CD_2Cl_2): δ 141.4 (d, ^1J(CP) 12, C_{ipso}), 130.7 (d, ^2J(CP) 20, C_{ortho}), 127.8 (s, C_{para}), 127.6 (d, ^3J(CP) 6, C_{meta}), 104.3 (d, ^3J(CP) 6, CH), 53.0 (s, CH_3) and 47.2 (d, ^2J(CP) 14, CH_2).

L^3. As for L^1 using NEt_3 (1.11 g, 11 mmol), PPh_2Cl (2.41 g, 11 mmol) and 3-methoxypropylamine (0.98 g, 11 mmol). Product extracted with diethyl ether at −78 °C followed by hexane (Found: C, 70.8; H, 7.20; N, 4.67. $C_{16}H_{20}NOP$ requires C, 70.3; H, 7.38; N, 5.12%). ^{1}H NMR ($CDCl_3$): δ 7.52–7.46 (m, 4 H, Ar), 7.40–7.33 (m, 6 H, Ar), 3.44 (t, 2 H, CH_2O), 3.32 (s, 3 H, CH_3), 3.07 (m, 2 H, CH_2N), 2.20 (m, 1 H, NH) and 1.76 (q, 2 H, CH_2C_2). ^{13}C NMR ($CDCl_3$): δ 141.3 (d, C_{ipso}), 130.9 (d, ^2J(CP) 18, C_{ortho}), 127.8 (s, C_{para}), 127.7 (s, C_{meta}), 70.2 (s, CH_2O), 58.0 (s, CH_3), 43.1 (d, ^2J(CP) 11, CH_2N) and 32.1 (s, CCH_2C).

L^4. As for L^1 using NEt_3 (1.13 g, 11 mmol), PPh_2Cl (2.46 g, 11 mmol) and *o*-anisidine (1.38 g, 11 mmol). Product extracted with diethyl ether at −78 °C (Found: C, 73.3; H, 6.11; N, 4.95. $C_{19}H_{18}NOP$ requires C, 74.2; H, 5.90; N, 4.56%). ^{1}H NMR ($CDCl_3$): δ 7.70–7.64 (m, 4 H, Ar), 7.55–7.44 (m, 6 H, Ar), 7.02 (m, 2 H), 6.93 (m, 2 H), 5.32 (d, 1 H, ^2J(PH) 7, NH) and 3.93 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 147.3 (d, ^3J(CP) 4, C2), 139.8 (d, ^2J(CP) 12, C_{ipso}), 135.7 (d, ^2J(CP) 18, C1), 130.6 (d, ^2J(CP) 21, C_{ortho}), 128.5 (s, C_{para}), 128.0 (d, ^3J(CP) 7, C_{meta}), 120.7 (s, C5), 118.3 (s, C4), 113.6 (d, ^3J(CP) 21, C6), 109.6 (s, C3) and 54.9 (s, CH_3).

[$PdCl_2(L^1)_2$] 1. The complex [$PdCl_2$(cod)] (0.100 g, 0.35 mmol) was added with stirring to a solution of L^1 (0.182 g, 0.70 mmol) in dichloromethane (40 cm^3). After 30 min the solution was concentrated under reduced pressure, and diethyl ether added to give yellow crystals of complex **1** (Found: C, 50.9; H, 5.20; N, 3.87. $C_{30}H_{36}Cl_2N_2O_2P_2Pd\cdot\frac{1}{4}CH_2Cl_2$ requires C, 50.7; H, 5.13; N, 3.91%). ^{1}H NMR ($CDCl_3$): *trans* isomer, δ 7.85–7.75 (m, Ar), 7.47–7.36 (m, Ar), 4.26 (m (br), 1 H, NH), 3.22 (s, 3 H, CH_3), 3.22 (t, 2 H, CH_2O) and 2.76 (m, 2 H, CH_2N); *cis* isomer, δ 7.8–7.3 (m, Ar), 4.45 (m (br), 1 H, NH), 3.28 (t, 2 H, CH_2O), 3.16 (s, 3 H, CH_3) and 2.55 (m, 2 H, CH_2N). FAB-MS: *m*/*z* 697, [M + H]$^+$; and 661, [M − Cl]$^+$.

Complex 2. As for complex **1** using [$PdCl_2$(cod)] (0.100 g, 0.35 mmol) and L^2 (0.203 g, 0.70 mmol) (Found: C, 50.6; H, 5.31; N, 3.68. $C_{32}H_{40}Cl_2N_2O_4P_2Pd$ requires C, 50.8; H, 5.33; N, 3.71%). ^{1}H NMR ($CDCl_3$): *trans* isomer, δ 7.90–7.82 (m, 4 H, Ar), 7.53–7.44 (m, 6 H, Ar), 4.29 (m (br), 1 H, NH), 4.05 (t, 1 H, CH), 3.25 (s, 6 H, CH_3) and 2.75 (m, 2 H, CH_2N); *cis* isomer, δ 7.94–7.86 (m, Ar), 7.58–7.35 (m, Ar), 4.42 (m, 1 H, NH), 4.02 (m, 1 H, CH), 3.23 (s, 6 H, CH_3) and 2.52 (m, 2 H, CH_2N). FAB-MS: *m*/*z* 756, [M + H]$^+$; and 721, [M − Cl]$^+$. Yield 0.177 g (67%).

Complex 3. As for complex **1** using [$PdCl_2$(cod)] (0.103 g, 0.36 mmol) and L^3 (0.198 g, 0.73 mmol) (Found: C, 53.0; H, 5.58; N, 3.82. $C_{32}H_{40}Cl_2N_2O_2P_2Pd$ requires C, 53.1; H, 5.57; N, 3.87%). ^{1}H NMR ($CDCl_3$): *cis–trans* mixture, δ 7.86–7.80 (m, Ar), 7.60–7.36 (m, Ar), 7.31–7.25 (m, Ar), 4.49 (br, NH), 4.11 (br, NH),

3.32 (t, CH_2O), 3.25 (m, CH_2O), 3.23 (s, CH_3), 3.19 (s, CH_3), 2.73 (m, CH_2N), 2.48 (m, CH_2N), 1.58 (q, CH_2C_2) and 1.50 (q, CH_2C_2).

Complex 4. As for complex **1** using [$PdCl_2$(cod)] (0.100 g, 0.35 mmol) and $\mathbf{L^4}$ (0.216 g, 0.70 mmol) (Found: C, 57.3; H, 4.66; N, 3.46. $C_{38}H_{36}Cl_2N_2O_2P_2Pd$ requires C, 57.6; H, 4.58; N, 3.54%).

Complex 5. As for complex **1** using [$PtCl_2$(cod)] (0.100 g, 0.27 mmol) and $\mathbf{L^1}$ (0.138 g, 0.53 mmol). Colourless crystals (Found: C, 44.2; H, 4.57; N, 3.37. $C_{30}H_{36}Cl_2N_2O_2P_2Pt\cdot\frac{1}{2}CH_2Cl_2$ requires C, 44.3; H, 4.51; N, 3.39%). ^{1}H NMR ($CDCl_3$): δ 7.57 (m, 4 H, Ar), 7.43 (m, 2 H, Ar), 7.30 (m, 4 H, Ar), 4.08 (m (br), 1 H, NH), 3.14 (s, 3 H, CH_3), 3.09 (t, 2 H, CH_2O) and 2.52 (m, 2 H, CH_2N). FAB-MS: *m*/*z* 785, $[M + H]^+$; and 749, $[M - Cl]^+$.

Complex 6. As for complex **1** using [$PtCl_2$(cod)] (0.136 g, 0.36 mmol) and $\mathbf{L^2}$ (0.210 g, 0.73 mmol). Colourless crystals (Found: C, 44.1; H, 4.72; N, 3.07. $C_{32}H_{40}Cl_2N_2O_4P_2Pt\cdot\frac{1}{2}CH_2Cl_2$ requires C, 44.0; H, 4.66; N, 3.16%). ^{1}H NMR ($CDCl_3$): δ 7.56 (m, 4 H, Ar), 7.45 (m, 2 H, Ar), 7.32 (m, 4 H, Ar), 4.09 (m (br), 1 H, NH), 3.93 (t, 1 H, CH), 3.14 (s, 6 H, CH_3) and 2.45 (m, 2 H, CH_2).

Complex 7. As for complex **1** using [$PtCl_2$(cod)] (0.100 g, 0.27 mmol) and $\mathbf{L^4}$ (0.164 g, 0.53 mmol). Colourless crystals (Found: C, 50.1; H, 4.09; N, 2.72. $C_{38}H_{36}Cl_2N_2O_2P_2Pt\cdot\frac{1}{2}CH_2Cl_2$ requires C, 50.1; H, 4.04; N, 3.03%). ^{1}H NMR ($CDCl_3$): δ 7.62 (m, 4 H, Ar), 7.46 (m, 2 H, Ar), 7.30 (m, 4 H, Ar), 6.82 (m, 1 H, NH), 6.74 (m, Ar), 6.72 (m, Ar), 6.33 (m, Ar), 6.07 (d, 1 H, Ar) and 3.65 (s, 3 H, CH_3). FAB-MS: *m*/*z* 880, $[M]^+$; 844, $[M - Cl]^+$; and 808 $[M - 2Cl]^+$.

Complex 8. As for complex **1** using [$PtBr_2$(cod)] (0.100 g, 0.21 mmol) and $\mathbf{L^1}$ (0.112 g, 0.43 mmol). Colourless crystals (Found: C, 40.3; H, 4.01; N, 2.75. $C_{30}H_{36}Br_2N_2O_2P_2Pt\cdot\frac{1}{2}CH_2Cl_2$ requires C, 40.0; H, 4.07; N, 3.06%). ^{1}H NMR ($CDCl_3$): δ 7.62 (m, 4 H, Ar), 7.45 (m, 2 H, Ar), 7.35 (m, 4 H, Ar), 3.97 (m (br), 1 H, NH), 3.16 (s, 3 H, CH_3), 3.12 (t, 2 H, CH_2O) and 2.55 (m, 2 H, CH_2N).

Reaction of complex 1 with $AgBF_4$ giving $[Pd(L^1)_2][BF_4]_2$ 9. The salt $AgBF_4$ (0.093 g, 0.48 mmol) was added to a solution of complex **1** (0.150 g, 0.22 mmol) in dichloromethane (30 cm^3) and the mixture stirred in darkness for 1 hour. 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 **9** as an orange solid. ^{1}H NMR ($CDCl_3$): δ 7.59 (m, Ar), 7.39 (m, Ar), 4.07 (m (br), 1 H, NH), 3.93 (m, 2 H, CH_2O), 3.65 (s, 3 H, CH_3) and 3.20 (m, 2 H, CH_2N).

Complex 10. As for complex **9** using $AgBF_4$ (0.060 g, 0.31 mmol) and **5** (0.100 g, 0.13 mmol). Recrystallisation from dichloromethane–hexane gave colourless microcrystals (Found: C, 38.1; H, 4.15; N, 2.56. $C_{30}H_{36}B_2F_8N_2O_2P_2Pt\cdot CH_2Cl_2$ requires C, 38.3; H, 3.94; N, 2.88%). ^{1}H NMR ($CDCl_3$): δ 7.61 (m, Ar), 7.52 (m, Ar), 7.35 (m, Ar), 4.20 (m, 2 H, CH_2O), 3.87 (m (br), 1 H, NH), 3.77 (s, 3 H, CH_3) and 3.22 (m, 2 H, CH_2N).

Complex 11. As for complex **9** using $AgBF_4$ (0.117 g, 0.60 mmol) and **7** (0.213 g, 0.30 mmol). Recrystallisation from dichloromethane–hexane gave yellow microcrystals (Found: C, 46.4; H, 3.79; N, 2.48. $C_{38}H_{36}B_2F_8N_2O_2P_2Pt$ requires C, 46.4; H, 3.69; N, 2.85%). ^{1}H NMR (CD_2Cl_2): δ 7.44 (m, Ar), 7.22 (m, Ar), 6.82 (m, 2 H, Ar), 6.48 (d, ^2J(PH) 8, NH), 6.40 (m, 2 H, Ar) and 3.79 (s, 3 H, CH_3). Yield 0.076 g (32%).

Complex 12. As for complex **9** using $AgBF_4$ (0.030 g, 0.15 mmol) and **1** (0.107 g, 0.15 mmol) (Found: C, 47.1; H, 4.83; N, 3.66. $C_{60}H_{72}B_2Cl_2F_8N_4O_4P_4Pd_2\cdot\frac{1}{2}CH_2Cl_2$ requires C, 47.3; H, 4.79; N, 3.65%). ^{1}H NMR ($CDCl_3$): δ 7.35 (m, Ar), 4.39 (br, NH), 3.32 (t, CH_2O), 3.26 (s, CH_3) and 2.72 (t, CH_2N). FAB-MS: *m*/*z* 1407, $[M - BF_4]^+$; 1321, $[M - 2BF_4]^+$; and 660, $[PdCl(\mathbf{L^1})_2]^+$.

$[PtCl(NO_2)(L^1)_2]$ 13. A solution of $NaNO_2$ (0.070 g, 1.0 mmol) in water (4 cm^3) was added with stirring to a solution of complex **5** (0.150 g, 0.19 mmol) in acetone (20 cm^3). The mixture was stirred for 4 hours, after which the solvent was removed under reduced pressure, the product extracted with dichloromethane (3×20 cm^3) and recrystallised from dichloromethane–diethyl ether, followed by dichloromethane–hexane to give colourless crystals (Found: C, 42.2; H, 4.24; N, 4.82. $C_{30}H_{36}ClN_3O_4P_2Pt\cdot CH_2Cl_2$ requires C, 42.3; H, 4.35; N, 4.77%). ^{1}H NMR ($CDCl_3$): δ 7.68–7.28 (m, br, Ar), 4.40 (m, br, NH), 3.50 (m, br, NH), 3.20–3.17 (m, CH_2O/CH_3O), 2.72 (m, CH_2N) and 2.58 (m, CH_2N).

Complex 14. As for complex **13** using $NaNO_2$ (0.300 g, 4.35 mmol) and **8** (0.377 g, 0.43 mmol). Recrystallisation from dichloromethane–hexane gave colourless crystals (Found: C, 42.8; H, 4.34; N, 4.92. $C_{30}H_{36}BrN_3O_4P_2Pt$ requires C, 42.9; H, 4.32; N, 5.01%). ^{1}H NMR ($CDCl_3$): δ 7.60 (m, Ar), 7.43 (m, Ar), 7.32 (m, Ar), 4.20 (m, NH), 3.30 (m, NH), 3.21 (s, CH_3), 3.19 (s, CH_3), 3.16 (m, CH_2O), 2.73 (m, CH_2N) and 2.56 (m, CH_2N). FAB-MS: *m*/*z* 793, $[M - NO_2]^+$; and 712, $[M - NO_2 - Br]^+$. Yield 0.162 g (45%).

$[Pd(dmba)Cl(L^1)]$ 16. The complex [{Pd(dmba)(μ-Cl)}$_2$] (0.400 g, 0.75 mmol) was added to a solution of $\mathbf{L^1}$ (0.375 g, 1.45 mmol) in dichloromethane (30 cm^3). The solution was stirred for 1 hour, after which it was concentrated under reduced pressure, filtered and pentane added, to give yellow crystals of **16** (Found: C, 53.5; H, 5.66; N, 5.19. $C_{24}H_{30}ClN_2OPPd$ requires C, 53.8; H, 5.65; N, 5.23%). ^{1}H NMR ($CDCl_3$): δ 7.85 (m, Ar), 7.35 (m, Ar), 6.93 (d, Ar), 6.82 (t, Ar), 6.53 (m, Ar), 4.41 (m, br, NH), 3.91 (m, br, CH_2N (dmba)), 3.23 (m, br, CH_2O/CH_3O) and 2.76 (m, NCH_2, CH_3N). FAB-MS: *m*/*z* 535, $[M + H]^+$; and 499, $[M - Cl]^+$.

Complex 17. As for complex **16** using [{Pd(dmba)(μ-Cl)}$_2$] (0.200 g, 0.36 mmol) and $\mathbf{L^2}$ (0.210 g, 0.73 mmol). Recrystallisation from dichloromethane–pentane gave yellow crystals (Found: C, 52.4; H, 5.61; N, 4.80. $C_{25}H_{31}ClN_2O_2PPd$ requires C, 53.2; H, 5.54; N, 4.96%). ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 4 H, Ar), 7.42 (m, 6 H, Ar), 6.95 (d, 1 H, Ar), 6.82 (m, 1 H, Ar), 6.55 (m, 2 H, Ar), 4.48 (m, 1 H, NH), 4.14 (t, 1 H, CH), 3.93 (s, 2 H, CH_2N (dmba)), 3.25 (s, 6 H, CH_3O), 2.78 (d, J(CP) 3, 6 H, CH_3N) and 2.74 (m, 2 H, CH_2).

Complex 18. As for complex **16** using [{Pd(dmba)(μ-Cl)}$_2$] (0.100 g, 0.18 mmol) and $\mathbf{L^3}$ (0.099 g, 0.36 mmol). Recrystallisation from dichloromethane–diethyl ether gave yellow crystals (Found: C, 54.2; H, 5.85; N, 5.01. $C_{25}H_{32}ClN_2OPPd$ requires C, 54.7; H, 5.87; N, 5.10%). ^{1}H NMR ($CDCl_3$): δ 7.80 (m, Ar), 7.40 (m, Ar), 6.89 (d, 1 H, Ar), 6.78 (m, 1 H, Ar), 6.50 (m, 2 H, Ar), 4.40 (m, 1 H, NH), 3.89 (s, 2 H, CH_2N (dmba)), 3.30 (t, 2 H, CH_2O), 3.19 (s, 3 H, CH_3O), 2.74 (m, CH_2N/CH_3N) and 1.57 (m, 2 H, CH_2C_2).

Complex 19. As for complex **16** using [{Pd(dmba)(μ-Cl)}$_2$] (0.275 g, 0.90 mmol) and $\mathbf{L^4}$ (0.247 g, 0.45 mmol). Recrystallisation from dichloromethane–pentane gave yellow microcrystals (Found: C, 49.9; H, 4.53; N, 3.91. $C_{28}H_{30}ClN_2OPPd\cdot\frac{3}{2}CH_2Cl_2$ requires C, 49.9; H, 4.68; N, 3.94%). ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 4 H, Ar), 7.39 (m, 7 H, Ar), 6.98 (m, 1 H, Ar), 6.88 (m, 1 H, Ar), 6.71 (m, 2 H, Ar), 6.59 (m, 2 H, Ar), 6.42 (m, 1 H, Ar), 6.30 (d, ^2J(PH) 8, 1 H, NH), 3.94 (d, ^4J(PH) 2, 2 H, CH_2N (dmba)), 3.81 (s, 3 H, CH_3O) and 2.77 (d, 6 H ^4J(PH) 3, CH_3N).

Table 6 Crystallographic data for complexes **1**, **2**, **14**, **16**, **18** and **30**

	1	**2**	**14**	**16**	**18**	**30**
Empirical formula	$C_{30}H_{36}Cl_2N_2O_2P_2Pd$	$C_{32}H_{40}Cl_2N_2O_4P_2Pd$	$C_{30}H_{36}BrN_3O_4P_2Pt$	$C_{24}H_{30}ClN_2OPPd$	$C_{25}H_{32}ClN_2OPPd$	$C_{43}H_{46}Cl_2N_3O_2P_2Pt_2$
M	695.84	755.90	839.56	535.32	549.35	1145.84
T/K	150(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$Pbca$	$P2_1/c$	$P2_1/c$
a/Å	10.456(2)	8.396(2)	9.576(2)	14.070(2)	16.835(2)	13.877(5)
b/Å	7.553(1)	10.146(2)	24.119(5)	17.080(3)	8.3350(9)	20.984(7)
c/Å	19.935(2)	10.849(3)	14.306(2)	18.899(4)	19.590(2)	15.345(5)
α/°		94.97(2)				
β/°	100.641(13)	111.01(2)	105.09(2)		111.922(2)	107.09(3)
γ/°		94.71(2)				
U/Å^3	1547.3(4)	853.1(4)	3190.2(10)	4541.7(14)	2550.1(5)	4271(3)
Z	2	1	4	8	4	4
μ/mm^{-1}	0.906	0.832	5.790	1.024	0.914	6.781
Reflections collected	6352	3413	5596	3785	14866	6620
Independent reflections	2395 [R(int) = 0.0904]	2973 [R(int) = 0.0537]	5587 [R(int) = 0.0329[a]]	3715 [R(int) = 0.002]	5207 [R(int) = 0.0385]	6620 [R(int) = 0.0267[a]]
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0383, 0.1084	0.0518, 0.1298	0.0325, 0.0887	0.0534, 0.1366	0.0392, 0.0942	0.0715, 0.1449
(all data)	0.0451, 0.1098	0.0620, 0.1458	0.0454, 0.0949	0.0874, 0.1446	0.058, 0.1028	0.1541, 0.1776

[a] Pre DIFABS.

Complex 20. As for complex **16** using [{Pt(dmba)(μ-Cl)}$_2$] (0.141 g, 0.19 mmol) and **L**^{1} (0.100 g, 0.39 mmol). Recrystallisation from dichloromethane–diethyl ether gave colourless crystals (Found: C, 45.9; H, 4.85; N, 4.34. $C_{24}H_{30}ClN_2OPPt$ requires C, 46.2; H, 4.85; N, 4.49%). ^{1}H NMR ($CDCl_3$): δ 7.86 (m, Ar), 7.40 (m, Ar), 6.98 (m, Ar), 6.86 (m, Ar), 6.75 (m, Ar), 6.52 (m, Ar), 4.23 (m, br, NH), 3.95 (m, CH_2N (dmba)), 3.28 (t, CH_2O), 3.25 (s, CH_3O), 2.89 (m, CH_3N) and 2.86 (m, CH_2N).

Complex 21. As for complex **16** using [{Pt(dmba)(μ-Cl)}$_2$] (0.189 g, 0.26 mmol) and **L**^{2} (0.150 g, 0.52 mmol). Recrystallisation from dichloromethane–hexane gave a pale yellow powder (Found: C, 46.0; H, 5.06; N, 4.21. $C_{25}H_{31}ClN_2O_2PPt$ requires C, 45.9; H, 4.93; N, 4.28%). ^{1}H NMR ($CDCl_3$): δ 7.88 (m, 4 H, Ar), 7.42 (m, 6 H, Ar), 7.02 (d, 1 H, Ar), 6.89 (t, 1 H, Ar), 6.78 (m, 1 H, Ar), 6.55 (m, 1 H, Ar), 4.24 (m, 1 H, NH), 4.18 (t, 1 H, CH), 3.99 (m, 2 H, CH_2N (dmba)), 3.28 (s, 6 H, CH_3O), 2.94 (m, 6 H, CH_3N) and 2.82 (m, 2 H, CH_2).

Complex 22. As for complex **16** using [{Pt(dmba)(μ-Cl)}$_2$] (0.257 g, 0.35 mmol) and **L**^{4} (0.217 g, 0.71 mmol). Recrystallisation from THF–hexane, followed by dichloromethane–hexane gave yellow microcrystals (Found: C, 46.6; H, 4.40; N, 3.64. $C_{28}H_{30}ClN_2OPPt\cdot\frac{3}{4}CH_2Cl_2$ requires C, 46.9; H, 4.32; N, 3.81%). ^{1}H NMR ($CDCl_3$): δ 7.88 (m, 4 H, Ar), 7.39 (m, 6 H, Ar), 7.27 (m, 1 H, Ar), 7.02 (m, 1 H, Ar), 6.88 (m, 2 H, Ar), 6.71 (m, 2 H, Ar), 6.58 (m, 1 H, Ar), 6.46 (m, 1 H, Ar), 6.37 (d, ^2J(PH) 8, 1 H, NH), 3.96 (m, ^3J(PtH) 28, ^4J(PH) 3, 2 H, CH_2N (dmba)), 3.80 (s, 3 H, CH_3O) and 2.90 (m, 6 H, ^3J(PtH) 23, ^4J(PH) 3, CH_3N). Yield 0.218 g (46%).

Reaction of complex 16 with $AgBF_4$ giving [Pd(dmba)(L^1)]BF_4 23. The salt $AgBF_4$ (0.122 g, 0.63 mmol) was added to a solution of complex **16** (0.200 g, 0.37 mmol) in dichloromethane (20 cm^3) and the mixture stirred in darkness for 30 min. The resulting solution was filtered, the residue washed with dichloromethane, and the filtrate and washings were combined. This solvent was then evaporated under reduced pressure to give **23** as a brown solid. ^{1}H NMR ($CDCl_3$): δ 7.79 (m, 4 H, Ar), 7.47 (m, 6 H, Ar), 6.94 (d, 1 H, Ar), 6.84 (t, 1 H, Ar), 6.43 (t, 1 H, Ar), 6.19 (t, 1 H, Ar), 4.01 (m, 2 H, CH_2N (dmba)), 3.85 (m, 2 H, CH_2O), 3.40 (br, 1 H, NH), 3.33 (m, 5 H, CH_3O/CH_2N) and 2.73 (d, 6 H, CH_3N).

Complex 24. As for complex **23** using $AgBF_4$ (0.052 g, 0.27 mmol) and **20** (0.100 g, 0.16 mmol). Recrystallisation from dichloromethane–pentane gave colourless crystals (Found: C, 42.9; H, 4.65; N, 3.96. $C_{24}H_{30}BF_4N_2OPPt$ requires C, 42.7; H, 4.48; N, 4.15%). ^{1}H NMR ($CDCl_3$): δ 7.83 (m, Ar), 7.48 (m, Ar), 6.92 (d, Ar), 6.77 (t, Ar), 6.32 (t, Ar), 6.15 (m, Ar), 4.11 (m, CH_2O), 4.02 (m, CH_2N (dmba)), 3.52 (s, CH_3O), 3.38 (s, CH_2N), 3.15 (m, br, NH) and 2.83 (m, CH_3N).

Complex 25. As for complex **23** using $AgBF_4$ (0.030 g, 0.16 mmol) and **22** (0.104 g, 0.16 mmol). ^{1}H NMR ($CDCl_3$): δ 7.70 (m, Ar), 7.10 (m, Ar), 6.50 (m, Ar), 6.40 (m, Ar), 6.00 (NH), 4.17 (s, CH_3O), 4.09 (CH_2) and 3.01 (CH_3N).

Reaction of complex 24 with CO giving [Pt(dmba)(L^1)(CO)]BF_4 26. Carbon monoxide was bubbled through a solution of complex **24** formed *in situ* from $AgBF_4$ (0.052 g, 0.27 mmol) and **20** (0.100 g, 0.16 mmol). Recrystallisation from dichloromethane–diethyl ether gave colourless crystals of **26** (Found: C, 42.6; H, 4.44; N, 3.95. $C_{25}H_{30}BF_4N_2O_2PPt\cdot\frac{1}{2}CH_2Cl_2$ requires C, 42.3; H, 4.51; N, 3.80%). ^{1}H NMR (CD_2Cl_2): δ 7.74 (m, Ar), 7.54 (m, Ar), 7.25 (m, Ar), 7.17 (m, Ar), 7.10 (m, Ar), 6.85 (m, Ar), 4.35 (m, CH_2N (dmba)), 3.57 (m, br, NH), 3.48 (t, CH_2O), 3.26 (m, CH_3O/CH_3N) and 3.20 (m, CH_2N).

Complex 27. As for complex **26** using $AgBF_4$ (0.052 g, 0.27 mmol) and **22** (0.100 g, 0.16 mmol). ^{1}H NMR (CD_2Cl_2): δ 7.86 (m, Ar), 7.57 (m, Ar), 7.31 (m, Ar), 7.18 (m, Ar), 6.88 (m, Ar), 6.73 (m, Ar), 5.90 (m, NH), 4.33 (m, CH_2), 3.76 (s, CH_3O) and 3.25 (m CH_3N).

Reaction of complex 25 with XylNC giving [Pt(dmba)(L^4)(CNXyl)]BF_4 28. The compound CNXyl (0.050 g, 0.38 mmol) was added to a solution of complex **25**, formed *in situ* from $AgBF_4$ (0.015 g, 0.08 mmol) and **22** (0.050 g, 0.08 mmol). ^{1}H NMR ($CDCl_3$): δ 7.86 (m, Ar), 7.45 (m, Ar), 7.17 (m, Ar), 6.82 (m, Ar), 5.85 (m, NH), 4.37 (d, CH_2, ^4J(PH) 3), 3.66 (s, CH_3O), 3.24 (d, CH_3N, ^4J(PH) 3) and 2.19 (s, CH_3C).

Reaction of complex 25 with acetonitrile giving [Pt(dmba)(L^4)(NCCH$_3$)]BF_4 29. An excess of acetonitrile (1 cm^3) was added to a solution of complex **25**, formed *in situ* from $AgBF_4$ (0.015 g, 0.08 mmol) and **22** (0.050 g, 0.08 mmol). ^{1}H NMR ($CDCl_3$): δ 7.76 (m, Ar), 7.49 (m, Ar), 7.10 (d, Ar), 7.01 (m, Ar), 6.89 (m, Ar), 6.73 (m, Ar), 5.74 (m, NH), 4.07 (m, CH_2), 3.77 (s, CH_3O), 2.98 (m, CH_3N) and 1.83 (s, CH_3CN).

Crystallography

Data for complexes **2**, **14**, **16** and **30** were collected on a CAD4 automatic 4-circle diffractometer, and for **1** and **18** on the EPSRC FAST system and a Bruker SMART 1000 CCD diffractometer, respectively. Hydrogen atoms were included in calculated positions on carbon centres for all structures. Hydrogens attached to nitrogen atoms were readily located throughout in the penultimate Fourier difference electron density maps, and included in the final stage of refinement with various restraints. In **1** the hydrogen attached to N(1) was refined at a fixed distance of 0.90 Å from the parent atom. The corresponding hydrogens in compounds **2**, **14** and **18** were treated similarly. In **16**, H(1A) and H(2A) were refined at a fixed distance of 0.98 Å from N(1) and N(2) respectively. In the structural refinement of complex **14** the maximum residual electron density peak was noted to be very close to the nitrite moiety, which points to possible disorder and librational effects in this region of the electron density map, given the large thermal vibration of the atoms therein. This disorder could not be successfully modelled and in the latter stages of refinement the N–O distances in the nitrite group were constrained to be similar to each other.

The crystal used for the structural determination of complex **30** was not a strong diffractor. This is exemplified by the statistics on the data and the larger than desirable ESDs for the geometric parameters associated with this crystal structure. In the final stages of the refinement the components of the anisotropic displacement parameters for atoms in the phenyl ring containing C(7) were refined subject to 'rigid bond' restraints. In addition the thermal parameters for C(5) and C(6) were treated similarly using SHELXL.[34]

An empirical absorption correction (DIFABS[35]) was applied to the data for compounds **14** and **30**. The associated maximum and minimum transmission factors for **14** were 1.000 and 0.860 respectively. The corresponding values for **30** were 1.000 and 0.219.

CCDC reference number 186/1924.

See http://www.rsc.org/suppdata/dt/b0/b001436m/ for crystallographic files in .cif format.

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