DALTON
FULL PAPER

Uni-, bi- and ter-dentate complexes formed from $PPh_2CH_2C(R)$=NNHC(=O)Ph (R = Bu^t or Ph) and Pd or Pt: crystal structures of [PdCl{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}], [Pt{PPh_2CH=C(Ph)NN=C(Ph)O}{PPh_2CH_2C(Ph)=NNHC(=O)Ph}] and [Pd{PPh_2CH=$C(Bu^t)$NHNC(=O)Ph}$_2$]

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Treatment of the phosphino-*N*-benzoyl hydrazones $PPh_2CH_2C(R)$=NNHC(=O)Ph (R = Bu^t, **I**; R = Ph, **II**) with [$MCl_2(NCPh)_2$] (M = Pd or Pt) gave complexes of type [MCl{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (M = Pd, **1**; M = Pt, **2**) containing two fused five-membered chelate rings. Metathesis with LiBr or NaI gave [MX{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (X = Br or I; M = Pd or Pt). The complex [PtMe{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (**8**) was obtained by treating [$PtMe_2$(cod)] (cod = cycloocta-1,5-diene) with one equivalent of **I** in hot benzene. Treatment of [$PtMe_2$(cod)] with two equivalents of the phosphine **II** gave [PtMe{PPh_2CH_2C(Ph)=NNC(=O)Ph}{PPh_2CH_2C(Ph)=NNHC(=O)-Ph] (**11**), containing a six-membered chelate ring and a unidentate coordinated ligand **II**. Treatment of [$PtCl_2(NCMe)_2$] with two equivalents of **II** in the presence of triethylamine gave [Pt{PPh_2CH=C(Ph)N–N=C(Ph)O}-{PPh_2CH_2C(Ph)=NNHC(=O)Ph] (**12**), containing a terdentate (P,N,O-bonded) doubly deprotonated ene-hydrazone ligand and a unidentate ligand **II**. Prolonged treatment of [$PdCl_2(NCPh)_2$] with two equivalents of **I** in the presence of triethylamine gave [Pd{PPh_2CH=$C(Bu^t)$NHNC(=O)Ph}$_2$] (**13**), containing two chelated phosphino ene-hydrazide ligands forming six-membered rings. A similar platinum complex, [Pt{PPh_2CH=$C(Bu^t)$NHNC(=O)Ph}$_2$] (**14**), was synthesised. The terdentate complexes of [MX{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (M = Pd, Pt; X = Cl, Me) underwent base-promoted (NEt_3) Michael-type reactions with $MeO_2CC{\equiv}CCO_2Me$ to give terdentate complexes of the type [MX{PPh_2CH[$C(CO_2Me)$=$CH(CO_2Me)$]$C(Bu^t)$=NN=C(Ph)O}] (M = Pd, Pt; X = Cl, Me). The corresponding bromides and iodides were made by metathesis. The crystal structures of **1**, **12** and **13** have been determined.

In a previous paper, we showed that a new type of phosphine ligand, a phosphino-*N*-benzoyl hydrazone, $PPh_2CH_2C(Bu^t)$=NNHC(=O)Ph (**I**), generated novel chemistry with rhodium(I) and rhodium(III) carbonyls.[1] In these rhodium complexes, the monodeprotonated phosphino-*N*-benzoyl hydrazone, $PPh_2CH_2C(Bu^t)$=NN=$C(Ph)O^-$, acted as a terdentate ligand and was coordinated through P, N and O, giving two fused 5-membered chelate rings. Of the three donor atoms, one would expect phosphorus to be bonded the strongest to a metal such as rhodium, the amide oxygen to be the weakest bonded and an azine-type nitrogen to be somewhere between the two in its donor ability. One might also expect that such a phosphino *N*-benzoyl hydrazone might be induced to show terdentate (P,N,O-bonded), bidentate (P,N-bonded) and unidentate (P-bonded) bonding modes. We have now investigated the phosphino-*N*-benzoyl hydrazones, $PPh_2CH_2C(R)$=NNHC(=O)Ph (R = Bu^t or Ph) as ligands towards palladium and platinum and find that examples of terdentate (P,N,O) and bidentate (P,N) coordination are formed from the deprotonated phosphino-*N*-benzoyl hydrazone, and unidentate (P) coordination can occur from the undeprotonated form; 5- and 6-membered chelate rings have been obtained.

Results and discussion

The new ligand *Z*-PPh_2CH_2C(Ph)=NNHC(=O)Ph (**II**) was prepared by treating the keto-phosphine PPh_2CH_2C(=O)Ph with benzohydrazide in hot ethanol using acetic acid as catalyst. Preparative details are in the Experimental, along with characterising microanalytical, mass spectral and NMR data. We first investigated the coordinating ability of the deprotonated phosphino hydrazones $PPh_2CH_2C(Bu^t)$=NN=$C(Ph)O^-$ and PPh_2CH_2C(Ph)=NN=$C(Ph)O^-$ as terdentate ligands with palladium(II) and platinum(II); see Scheme 1. Where appropriate, for some of the syntheses described in this paper, we used ^{31}P-{^1H} NMR spectrocopy, with an external lock, to follow the progress of reactions in the reaction mixture.

Treatment of the phosphine **I** with one equivalent of [$PdCl_2(NCPh)_2$] in dichloromethane gave the chelate complex [PdCl{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (**1**) in 83% yield. This was characterised by elemental analysis, mass spectrometry and NMR spectroscopy, see Experimental. The infrared spectrum showed a band at 330 cm^{-1} due to ν(Pd–Cl). From the NMR data for **1**, we draw particular attention to the following—the ^{31}P-{^1H} NMR spectrum of complex **1** showed a singlet resonance at 32.2 ppm. The ^1H NMR spectrum of **1** showed a resonance due to the CH_2P protons as a doublet at 3.97 ppm, ^2J(PH) = 11.8 Hz. In the ^{13}C-{^1H} NMR spectrum, the carbon-13 chemical shift of 47.1 ppm is typical of a methylene carbon

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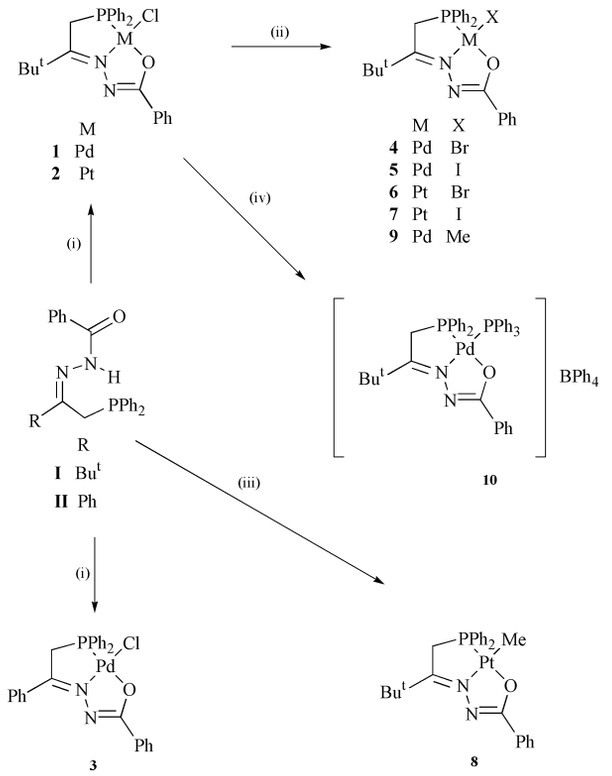


Scheme 1 (i) $[MCl_2(NCPh)_2]$ (M = Pd or Pt); (ii) LiBr or NaI; MeMgI for **9**; (iii) $[PtMe_2(cod)]$; (iv) PPh_3.

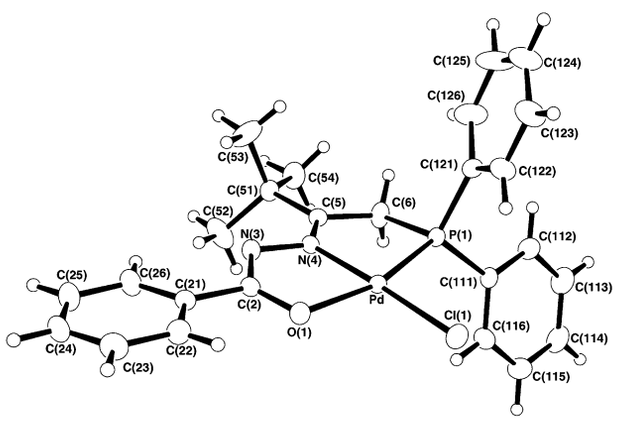


Fig. 1 Crystallographically determined molecular structure for $[PdCl\{PPh_2CH_2C(Bu^t)=NN=C(Ph)O\}]$ (**1**) drawn with 40% probability ellipsoids and with hydrogen atoms shown as circles of arbitrary radius.

attached to phosphorus in a five-membered chelate ring.[1–4] We also determined the crystal structure of the palladium complex **1** (Fig. 1); selected bond lengths and angles are given in Table 1. The structure shows that the mono-deprotonated phosphino-*N*-hydrazone $PPh_2CH_2C(Bu^t)=NN=C(Ph)O^-$ is terdentate (P,N,O-bonded) to palladium. The ligand atoms P, N, O and Cl are planar and there is nothing unusual in the bond lengths and angles. In the P(1)–C(6)–C(5)–N(4)–Pd ring, one hydrogen of the CH_2 group is pseudo-equatorial and the other pseudo-axial.

The corresponding chloroplatinum(II) complex $[PtCl\{PPh_2CH_2C(Bu^t)=NN=C(Ph)O\}]$ (**2**) was prepared by treating the phosphine **I** with one equivalent of $[PtCl_2(NCPh)_2]$. The ^{31}P-$\{^1H\}$ NMR spectrum of **2** showed a singlet at −0.1 ppm with satellites, $^1J(PtP) = 3992$ Hz. The large coupling is in agreement with phosphorus being *trans* to an electronegative (oxygen donor) ligand.[5,6]

The chloropalladium(II) complex $[PdCl\{PPh_2CH_2C(Ph)=NN=C(Ph)O\}]$ (**3**) was similarly prepared by treating the phosphine ligand **II** with one equivalent of $[PdCl_2(NCPh)_2]$. The ^{31}P-$\{^1H\}$ NMR spectrum of **3** showed a singlet at 35.1 ppm and the infrared spectrum a band at 330 cm^{-1} due to ν(Pd–Cl). In the ^1H NMR spectrum, the methylene protons (PCH_2) gave a broad resonance at 4.22 ppm. We were able to convert these chloropalladium(II), **1**, and chloroplatinum(II), **2**, complexes into the corresponding bromo or iodo complexes by metathesis. Treatment of the chloropalladium(II) complex **1** with an excess of lithium bromide in acetone gave the corresponding bromide **4**, or with sodium iodide in acetone, the corresponding iodide **5**. The bromoplatinum(II) complex **6** and iodoplatinum(II) complex **7** were prepared similarly. Characterisation data for these four complexes are given in the Experimental.

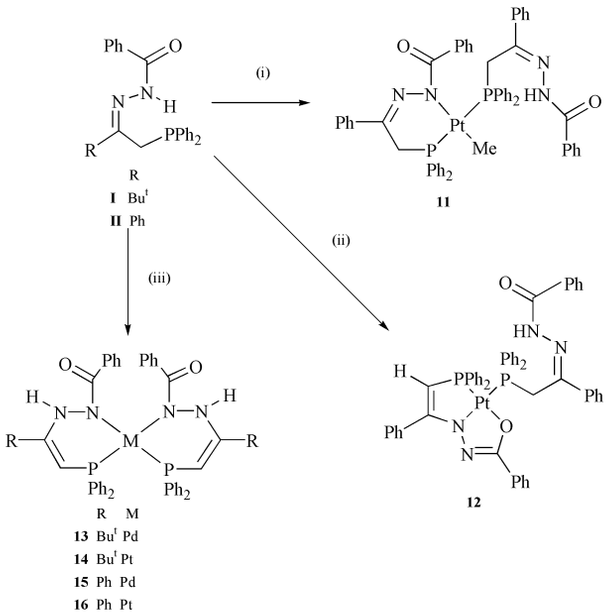
We synthesised the methylplatinum(II) complex $[PtMe\{PPh_2CH_2C(Bu^t)=NN=C(Ph)O\}]$ (**8**) by treating $[PtMe_2(cod)]$[7] with one equivalent of the phosphine **I** in hot benzene. The ^{31}P-$\{^1H\}$ NMR spectrum of **8** showed a singlet at 4.5 ppm with satellites, $^1J(PtP) = 4493$ Hz; this extremely large *J* value is characteristic of phosphorus *trans* to a highly electronegative (oxygen donor) and *cis* to a weakly electronegative (methyl) ligand.[6] We attempted to prepare the corresponding methylpalladium(II) complex $[PdMe\{PPh_2CH_2C(Bu^t)=NN=C(Ph)O\}]$ (**9**) by treating the chloropalladium(II) complex **1** with an excess of MeMgI, but we were unable to obtain the required product in an analytically pure form. However, the ^{31}P-$\{^1H\}$ NMR spectrum of the crude product showed a singlet at 33.4 ppm and the ^1H NMR spectrum showed two doublet resonances: one at 3.79 ppm $\{^2J(PH) = 11.0$ Hz$\}$ due to PCH_2, the other at 0.84 ppm with $^3J(PH) = 1.1$ Hz, due to $PdCH_3$, *i.e.* much of the required product **9** had probably been formed.

We found that a chloride ion was easily displaced from the chloropalladium(II) complex **1** by PPh_3, so that treatment of **1** with PPh_3 gave the cation $[Pd(PPh_3)\{PPh_2CH_2C(Bu^t)=NN=C(Ph)O\}]^+$, which we isolated as the BPh_4^- salt **10**. The ^{31}P-$\{^1H\}$ NMR spectrum of **10** showed an AB pattern with $^2J(PP) = 26$ Hz; this small value for $^2J(PP)$ shows that the phosphorus nuclei are mutually *cis*. In the ^1H NMR spectrum the resonance of the CH_2P protons was a double doublet at 3.89 ppm $\{^2J(PH) = 11.8$, $^4J(PH) = 1.4$ Hz$\}$.

We studied the reaction of $[PtMe_2(cod)]$ with two equivalents of the phosphine **II** in benzene. This gave $[PtMe\{PPh_2CH_2C(Ph)=NNC(=O)Ph\}\{PPh_2CH_2C(Ph)=NNHC(=O)Ph]$ (**11**) (see Scheme 2). This methylplatinum(II) complex contained a bidentate six-membered chelate ring formed from the deprotonated ligand and a unidentate phosphino-*N*-hydrazone ligand. The ^{31}P-$\{^1H\}$NMR spectrum of **11** at 36.2 MHz showed an AB pattern with satellites; $\delta P_A = 22.4$, $^1J(PtP) = 2898$ Hz; $\delta P_B = 52.2$, $^1J(PtP) = 3098$ Hz, with $^2J(P_AP_B) = 472$ Hz. The large value of $^2J(P_AP_B)$ shows that the P atoms are mutually *trans*. In the ^1H NMR spectrum of **11**, the methylene protons in the chelate ring gave a broad resonance at 3.92 ppm. The resonance of the methylene protons in the unidentate phosphine was a doublet at

Table 1 Interatomic distances (Å) and angles between interatomic vectors (°) for complex **1**, see Fig. 1; s.u.s are in parentheses

Pd–N(4)	1.9859(17)	Pd–O(1)	2.0666(14)
Pd–P(1)	2.1940(5)	Pd–Cl(1)	2.3095(5)
P(1)–C(111)	1.797(2)	P(1)–C(121)	1.808(2)
P(1)–C(6)	1.840(2)	O(1)–C(2)	1.297(3)
C(2)–N(3)	1.325(3)	C(2)–C(21)	1.492(3)
N(3)–N(4)	1.398(2)	N(4)–C(5)	1.300(3)
C(5)–C(6)	1.502(3)	C(5)–C(51)	1.531(3)
N(4)–Pd–O(1)	79.87(6)	N(4)–Pd–P(1)	84.55(5)
O(1)–Pd–P(1)	163.85(4)	N(4)–Pd–Cl(1)	177.32(5)
O(1)–Pd–Cl(1)	97.72(4)	P(1)–Pd–Cl(1)	97.94(2)
C(6)–P(1)–Pd	99.97(7)		
C(2)–O(1)–Pd	108.21(12)	O(1)–C(2)–N(3)	126.07(19)
C(2)–N(3)–N(4)	110.97(17)	C(5)–N(4)–N(3)	120.11(17)
C(5)–N(4)–Pd	125.29(15)	N(3)–N(4)–Pd	114.58(12)
N(4)–C(5)–C(6)	115.21(18)	C(5)–C(6)–P(1)	112.18(14)



Scheme 2 (i) $[PtMe_2(cod)]$; (ii) $[PtCl_2(NCMe)_2]$; (iii) 0.5 equiv. $[MCl_2(NCPh)_2]$ (M = Pd or Pt).

4.92 ppm, ^2J(PH) = 14.7 Hz with satellites, ^3J(PtH) = 29.3 Hz. The methyl protons of the methylplatinum group gave a triplet resonance at 0.16 ppm, ^3J(PH) = 7.3 Hz with satellites, ^2J(PtH) = 70.9 Hz. The NH proton gave a broad resonance at 9.46 ppm. In the ^{13}C-{^{1}H} NMR spectrum, the PtMe carbon resonated as a triplet at −19.4 ppm, ^2J(PC) = 6.7 Hz, with satellites, ^1J(PtC) = 576 Hz.

In view of this interesting result from treating $[PtMe_2(cod)]$ with two equivalents of **II**, we treated $[PtCl_2(NCMe)_2]$ with two molar equivalents of the phosphino-*N*-hydrazone **II** in dichloromethane in the presence of an excess of Et_3N (without Et_3N the results were complicated). The result of treatment at 40 °C for a short time (10 min) gave [Pt{PPh_2CH=C(Ph)NN=C(Ph)O}-{PPh_2CH_2C(Ph)=NNHC(=O)Ph}] (**12**), containing a (P,N,O) terdentate ligand derived from **II** *via* loss of *two* protons (*i.e.* one NH proton and one methylene proton). The ^{31}P-{^{1}H} NMR spectrum of **12** at 36.2 MHz showed an AB pattern with satellites, δP_A 3.4, ^1J(PtP) = 3108 Hz for phosphorus *trans* to nitrogen and δP_B 8.0, ^1J(PtP) = 3557 Hz for phosphorus *trans* to an oxygen donor ligand. The value ^2J(PP) = 14 Hz shows that the two phosphorus donor atoms are *cis* to each other. The infrared spectrum showed a band at 3460 cm^{-1} due to ν(N–H). In the ^{1}H NMR spectrum, both the CH_2P protons, at 3.93 ppm, and the =CHP proton, at 4.81 ppm, gave doublet resonances with satellites {^2J(PH) = 10.0, ^3J(PtH) = 38.3 and ^2J(PH) = 10.5, ^3J(PtH) = 18.9 Hz, respectively}.

The crystal structure of complex **12** is shown in Fig. 2, with selected bond lengths and angles in Table 2. The four atoms coordinated to platinum are essentially coplanar. One of the phosphino hydrazone ligands **II** is doubly deprotonated and coordinated in a terdentate manner, through phosphorus, nitrogen and oxygen, giving two adjacent five-membered chelate rings. The undeprotonated phosphine ligand **II** is coordinated in a unidentate fashion through phosphorus. The C=C double bond length C(2)–C(3) is 1.374(4) Å, which is considerably shorter than the corresponding C–C single bond [C(7)–C(8) 1.509(4) Å] in the monodentate ligand.

We treated $[PdCl_2(NCPh)_2]$ with two equivalents of the phosphino-*N*-hydrazone **I** in dichloromethane in the presence of triethylamine for 3 h and obtained the deprotonated bis-(chelate)palladium(II) complex [Pd{PPh_2CH=C(Bu^t)NHNC-(=O)Ph}$_2$] (**13**), containing two six-membered chelate rings (Scheme 2). The ^{31}P-{^{1}H} NMR spectrum of **13** showed a singlet at 5.2 ppm. In the ^{1}H NMR spectrum, the resonance of the NH proton at 8.63 ppm was broad and was lost immediately on

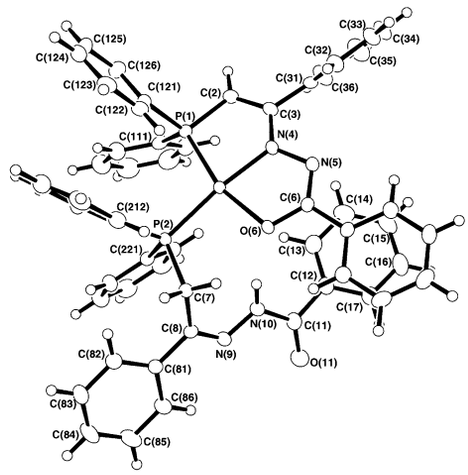


Fig. 2 Crystallographically determined molecular structure for [Pt-{PPh_2CH=C(Ph)NN=C(Ph)O}{PPh_2CH_2C(Ph)=NNHC(=O)Ph}] (**12**) drawn with 40% probability ellipsoids and with hydrogen atoms shown as circles of arbitrary radius.

contact of the CD_2Cl_2 solution with D_2O. The resonance of the =CHP proton was a doublet of doublets at 3.68 ppm, with coupling to both phosphorus and the NH proton. In the ^{1}H-{^{31}P} NMR spectrum of **13**, the =CHP proton gave a doublet resonance, ^4J(HH) = 1.3 Hz. In the presence of D_2O, the resonance of the =CHP proton in the ^{1}H-{^{31}P} NMR spectrum of **13** collapsed to a singlet and, in the ^{1}H NMR spectrum, a doublet with ^2J(PH) = 2.0 Hz. In the ^{13}C-{^{1}H} NMR spectrum, the =CHP carbon gave a doublet resonance at 62.3 ppm, ^1J(PC) = 73.6 Hz.

We determined the crystal structure of the bis(chelate)palladium(II) complex **13** and this is shown in Fig. 3, with selected

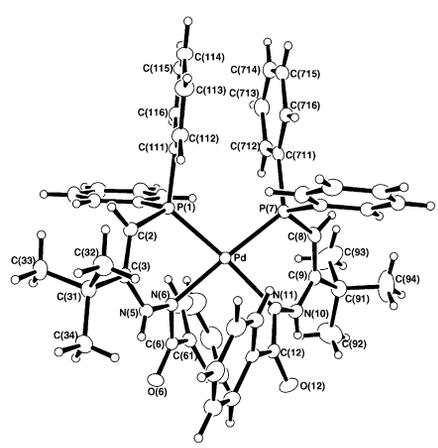


Fig. 3 Crystallographically determined molecular structure for [Pd-{PPh_2CH=C(Bu^t)NHNC(=O)Ph}$_2$] (**13**) drawn with 40% probability ellipsoids and with hydrogen atoms shown as circles of arbitrary radius.

bond lengths and angles in Table 3. It shows that the palladium is coordinated by two six-membered chelate rings formed from the hydrazone ligand **I**, with mono-deprotonation of a methylene group to give two C=CHP moieties with C(2)–C(3) 1.364(4) and C(8)–C(9) 1.365(4) Å. The two equivalent six-membered rings are puckered. There is essentially planar coordination around the palladium, with the phosphorus atoms mutually *cis*.

The corresponding platinum and palladium complexes [Pt{PPh_2CH=C(Bu^t)NHNC(=O)Ph}$_2$] (**14**), [Pd{PPh_2CH=C-(Ph)NHNC(=O)Ph}$_2$] (**15**) and [Pt{PPh_2CH=C(Ph)NHNC(=O)-Ph}$_2$] (**16**) were prepared by treating platinum or palladium sources {$[PtCl_2(cod)]$ or $[PdCl_2(NCPh)_2]$} with two equivalents of phosphines **I** or **II** in the presence of NEt_3 for several hours. The NMR data for **14**, **15** and **16** indicate that they have *cis*-bis

Table 2 Interatomic distances (Å) and angles between interatomic vectors (°) for complex **12**; s.u.s in parentheses

Pt–N(4)	1.985(2)	Pt–O(6)	2.050(2)
Pt–P(1)	2.2332(8)	Pt–P(2)	2.2609(8)
P(1)–C(2)	1.777(3)	C(2)–C(3)	1.374(4)
C(3)–N(4)	1.365(4)	C(3)–C(31)	1.489(4)
N(4)–N(5)	1.389(4)	N(5)–C(6)	1.299(4)
C(6)–O(6)	1.346(4)	C(6)–C(61)	1.472(4)
C(61)–C(62)	1.395(4)	P(2)–C(7)	1.872(3)
C(7)–C(8)	1.509(4)	C(8)–N(9)	1.287(4)
N(9)–N(10)	1.371(4)	N(10)–C(11)	1.381(4)
N(10)–H(10)	0.85(4)	C(11)–O(11)	1.218(4)
N(4)–Pt–O(6)	78.79(9)	N(4)–Pt–P(1)	83.62(8)
O(6)–Pt–P(1)	162.42(6)	N(4)–Pt–P(2)	173.28(8)
O(6)–Pt–P(2)	94.70(6)	P(1)–Pt–P(2)	102.88(3)
C(2)–P(1)–Pt	100.21(11)	C(7)–P(2)–Pt	109.61(10)
C(3)–C(2)–P(1)	115.9(2)	N(4)–C(3)–C(2)	118.0(3)
C(3)–N(4)–N(5)	121.3(2)	C(3)–N(4)–Pt	121.6(2)
N(5)–N(4)–Pt	116.57(18)	C(6)–N(5)–N(4)	111.0(2)
N(5)–C(6)–O(6)	124.3(3)	C(6)–O(6)–Pt	109.34(18)
C(8)–C(7)–P(2)	116.0(2)	N(9)–C(8)–C(81)	115.3(3)
N(9)–C(8)–C(7)	124.9(3)		
C(8)–N(9)–N(10)	120.2(3)	N(9)–N(10)–C(11)	118.2(3)
N(9)–N(10)–H(10)	123.0(3)	C(11)–N(10)–H(10)	118.0(3)
O(11)–C(11)–N(10)	123.0(3)	O(11)–C(11)–C(12)	122.5(3)

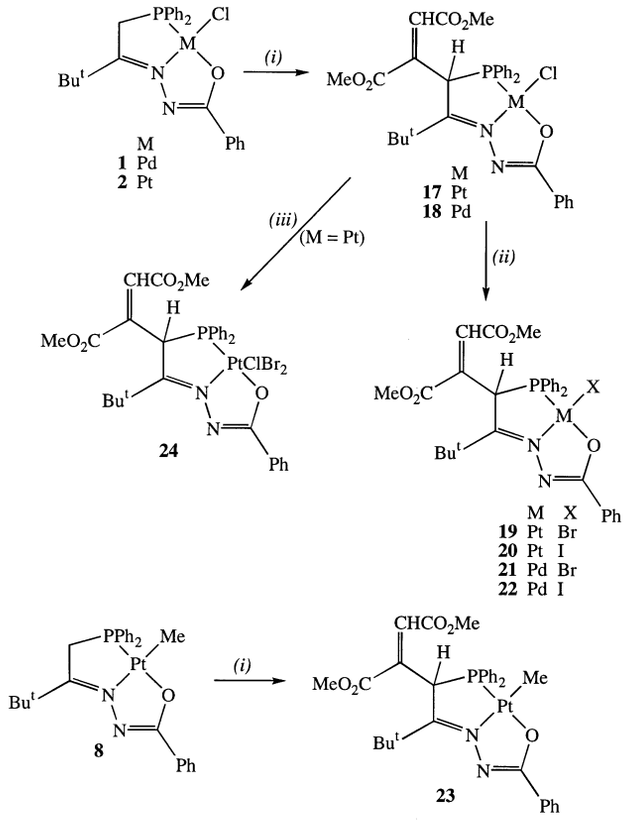
Table 3 Interatomic distances (Å) and angles between interatomic vectors (°) for complex **13**; s.u.s are in parentheses

Pd–N(6)	2.117(2)	Pd–N(11)	2.127(2)
Pd–P(1)	2.2605(7)	Pd–P(7)	2.2633(7)
P(1)–C(2)	1.748(3)	C(2)–C(3)	1.364(4)
C(3)–N(5)	1.333(3)	N(5)–N(6)	1.394(3)
N(5)–H(5)	0.79(3)	N(6)–C(6)	1.360(3)
O(6)–C(6)	1.247(3)	P(7)–C(8)	1.755(3)
C(8)–C(9)	1.365(4)	O(12)–C(12)	1.246(3)
C(9)–N(10)	1.337(4)	N(10)–N(11)	1.395(3)
N(10)–H(10)	0.79(3)	N(11)–C(12)	1.355(3)
N(6)–Pd–N(11)	94.64(8)	N(6)–Pd–P(1)	80.94(6)
N(11)–Pd–P(1)	174.71(6)	N(6)–Pd–P(7)	174.78(6)
N(11)–Pd–P(7)	82.31(6)	P(1)–Pd–P(7)	102.31(3)
		C(2)–P(1)–Pd	108.08(9)
C(3)–C(2)–P(1)	127.5(2)	N(5)–C(3)–C(2)	124.2(2)
N(5)–C(3)–C(31)	116.3(2)	C(2)–C(3)–C(31)	119.5(2)
C(3)–N(5)–N(6)	123.0(2)	C(3)–N(5)–H(5)	121.0(2)
N(6)–N(5)–H(5)	115.0(2)	C(6)–N(6)–N(5)	110.2(2)
C(6)–N(6)–Pd	122.59(18)	N(5)–N(6)–Pd	118.99(16)
O(6)–C(6)–N(6)	123.2(3)	N(10)–N(11)–Pd	118.08(16)
C(8)–P(7)–Pd	106.88(10)	C(9)–C(8)–P(7)	128.1(2)
N(10)–C(9)–C(8)	124.2(3)	O(12)–C(12)–N(11)	123.4(3)
C(12)–N(11)–Pd	124.38(18)	C(9)–N(10)–N(11)	123.9(2)
N(11)–N(10)–H(10)	117.0(2)	C(12)–N(11)–Pd	124.38(18)

chelate structures analogous to that of **13**. The ^{31}P-{^{1}H} NMR spectrum of **14** showed a singlet at −17.1 ppm with satellites, ^{1}J(PtP) = 3274 Hz. This intermediate value is consistent with phosphorus *trans* to nitrogen.[8,9]

In our previous study of the products formed by $PPh_2CH_2C(Bu^t)$=NNHC(=O)Ph (**I**) on rhodium,[1] we showed that $MeO_2CC{\equiv}CCO_2Me$ (dmad) reacted with the activated CH_2 adjacent to the coordinated phosphorus to give Michael-type addition. We have now studied the action of dmad on the complexes of type **1** and **2**. The various reactions are summarized in Scheme 3.

When we treated the chloroplatinum(II) complex [PtCl{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (**2**) with an excess of dmad in the presence of triethylamine, it caused a base-promoted Michael-type addition to the backbone of **2**, to give the product [PtCl{PPh_2CH[$C(CO_2Me)$=$CH(CO_2Me)$]$C(Bu^t)$=NN=C(Ph)O}] (**17**). The isolated solid product **17** was characterized by NMR spectroscopy, including assignments made based on a two-dimensional COSY experiment, infrared, mass spectrometry, elemental analysis (C, H, N) and a molecular weight determination (see Experimental). The ^{31}P-{^{1}H} NMR spectrum of **17** showed a singlet at 21.3 ppm with satellites, ^{1}J(PtP) = 4089 Hz, a high value is consistent with phosphorus *trans* to an oxygen donor ligand.[5,6] In the ^{1}H NMR spectrum of **17**, the methylene CHP proton gave a doublet resonance at 5.56 ppm, ^{2}J(PH) = 13.6 Hz with satellites, ^{3}J(PtH) = 38.4 Hz. The resonance of the C=C*H*(CO_2Me) alkenyl proton was a doublet at 6.58 ppm, ^{4}J(PH) = 4.3 Hz. The CO_2Me protons resonated at 3.22 and 3.68 ppm as singlets. A two-dimensional ^{1}H–^{13}C-{^{1}H}COSY experiment showed that there was a correlation between the proton at 5.56 ppm to the carbon at 57.5 ppm (*i.e.* a CHP moiety) and a correlation between the proton at 6.58 ppm and the carbon resonating at 131.2 ppm, *i.e.* a =C*H*(CO_2Me) moiety. In the ^{13}C-{^{1}H} NMR spectrum of **17**, the two singlets at 52.3 and 52.8 ppm were assigned to the resonances for the OMe carbons. Two signals at 173.1 and 180.6 ppm were due to the resonances for the *C*O_2Me carbons. The infrared spectrum of **17** showed bands at 345m and 1730s cm^{-1}, due to ν(Pt–Cl) and ν(C=O), respectively. In the mass spectrum of **17**, we observed the parent ion peak at 775 ([M + 1]$^{+}$) and a peak at 738 corresponding to the loss of a HCl molecule ([M − HCl]$^{+}$). The elemental analytical data are in agreement with the composition $C_{31}H_{33}ClN_2O_5PPt$, as required for the proposed structure of the chloroplatinum(II) complex **17**. The molecular



Scheme 3 (i) $MeO_2CC{\equiv}CCO_2Me$; (ii) LiBr or NaI; (iii) Br_2.

weight determination (osmometric) in chloroform solution for **17** gave a value of 767 Daltons, in satisfactory agreement with the molecular formula $C_{31}H_{33}ClN_2O_5PPt$ (774 Daltons).

The analogous palladium(II) complex **18** was prepared similarly by treatment of **1** with an excess of dmad in the presence of NEt_3. The ^{31}P-{^1H} NMR spectrum of **18** showed a singlet at 52.1 ppm. Mass spectral, infrared and NMR spectroscopic data were analogous to those of the chloroplatinum(II) complex **17**. We thus think that this complex has the analogous structure **18**.

The platinum(II) complex **17** was stable in solution; possibly substitution of one of the methylene hydrogens in **1** by $C(CO_2Me)$=$CH(CO_2Me)$ caused the chelation to platinum to be stronger (an extension of the Thorpe–Ingold effect). We thus thought it might be possible to effect replacement of the chloride by bromide without causing further change. We found this to be so. Thus, treatment of **17** with an excess of lithium bromide in acetone solution gave the corresponding bromide **19** in satisfactory (57%) yield. This complex was characterised by elemental analysis, mass spectrometry, IR spectroscopy and NMR spectroscopy (see Experimental). We similarly prepared the corresponding iodo-complex **20**, and also the bromopalladium (**21**) and iodopalladium (**22**) complexes.

Treatment of the methylplatinum(II) complex [PtMe{$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}] (**8**) with an excess of dmad in the presence of Et_3N similarly induced Michael addition and gave the methylplatinum(II) complex [PtMe{$PPh_2CH[C(CO_2Me)$=$CH(CO_2Me)]C(Bu^t)$=NN=C(Ph)O}] **23**. This complex has similar NMR charateristics to those of the chloroplatinum(II) complex **17** with, additionally, a PtMe doublet resonance at 0.79 ppm, ^3J(PH) = 1.3 Hz with satellites, ^2J(PtH) = 71.6 Hz in the ^1H NMR spectrum.

When we treated the chloroplatinum(II) complex [PtCl{$PPh_2CH[C(CO_2Me)$=$CH(CO_2Me)]C(Bu^t)$=NN=C(Ph)O}] (**17**) with an excess of bromine solution in CCl_4, a single platinum(IV) adduct, [$PtClBr_2${$PPh_2CH[C(CO_2Me)$=$CH(CO_2Me)]$-$C(Bu^t)$=NN=C(Ph)O}] (**24**), was isolated as an orange solid and characterized. The ^{31}P-{^1H} NMR spectrum of **24** showed a singlet at 12.6 ppm with satellites ^1J(PtP) = 2504 Hz, which is consistent with the change of the oxidation state of the platinum from divalent to tetravalent.[10] In the ^1H NMR spectrum of **24**, the CHP proton gave a doublet resonance at 6.64 ppm, ^2J(PH) = 14.4 Hz with satellites, ^3J(PtH) = 10.2 Hz. The resonance for the C=C*H*(CO_2Me) proton could not be assigned since it was obscured by the resonances of the phenyl protons. It is likely that in the octahedral platinum(IV) complex **24**, the two bromine atoms have added mutually *trans* to the platinum.[11] There was no reaction when we treated the chloropalladium(II) complex **18** with bromine solution.

In our previous work[1] on the adducts of $MeO_2CC{\equiv}CCO_2Me$ (dmad) to the rhodium carbonyl complex [Rh(CO){$PPh_2CH_2C(Bu^t)$=NN=C(Ph)O}], in which the deprotonated $PPh_2CH_2C(Bu^t)$=N–N=C(Ph)$^-$ ligand was terdentate, *i.e.* P,N,O-bound, two dmad molecules added. One gave a 5-membered metallacycle ring $PPh_2CH[C(CO_2Me)$=$CH(CO_2Me)]Rh$, in which the $C(CO_2Me)$=$CH(CO_2Me)$ moiety had both CO_2Me groups *cis* on the C=C bond. The second $MeO_2CC{\equiv}CCO_2Me$ gave rise to a terminal $RhC(CO_2Me)$=$CH(CO_2Me)$ in which (again) both CO_2Me groups were *cis* on C=C. These *cis* orientations probably arose because reactions occured within the coordination sphere of the rhodium. However, the formation of **17** by attack by one acetylene carbon of dmad on the methine carbon formed by deprotonation of **1** might be followed by *exo*-protonation of the second (acetylenic) carbon, giving $PtC(CO_2Me)$=$CH(CO_2Me)$ in which the CO_2Me groups would be mutually *trans* with respect to C=C. This might also be the case for **18**. There are examples of olefins or acetylenes reacting within the coordination sphere of platinum(II) {or palladium(II)}, but there are also examples of *exo*-attack on unsaturated ligands attached to platinum(II) {or palladium(II)}, *e.g.* *exo*-attack by MeO^- on [MCl_2(cod)] (M = Pt or Pd),[12] vinyl ester exchange (palladium)[13] or attack by nucleophiles on coordinated allylic groups, *e.g.* with cations of the type [Pd(diphosphine)(allyl)]$^+$.[14] Thus, we have not specified the geometry around $C(CO_2Me)$=$CH(CO_2Me)$ in complexes **17**–**24**; only one geometric isomer is formed but we do not know whether it is *cis* or *trans* across C=C.

Experimental

All the reactions were carried out in an atmosphere of dry nitrogen. NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz, respectively), a JEOL FX-100 spectometer (operating frequencies for ^1H and ^{31}P were 99.5 and 40.25 MHz, respectively), or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C were 400.13, 161.9 and 100.6 MHz, respectively). ^1H and ^{13}C chemical shifts are in ppm relative to tetramethylsilane and for ^{31}P are relative to 85% phosphoric acid, coupling constants are in Hz. In the proton NMR spectra, the resonances due to phenyl protons appeared between 7.0 to 7.9 ppm. Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer (4000–600 cm^{-1}) or a Pye Unicam SP 2000 (4000–200 cm^{-1}). EI and FAB mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration. Molecular weights were determined on a Hitachi-Perkin Elmer model 115 apparatus in chloroform at 30 °C.

Syntheses

Z-$PPh_2CH_2C(Bu^t)$=NNHC(=O)Ph (**I**) was prepared according to our literature procedure.[1]

***Z*-PPh_2CH_2C(Ph)=NNHC(=O)Ph (II).** A solution of the keto-phosphine *Z*-PPh_2CH_2C(=O)Ph (4.4 g, 10.4 mmol), benzohydrazide (6.4 g, 47.0 mmol) and acetic acid (10 cm^3) in ethanol (60 cm^3) was heated under reflux for 12 h. This gave the required

phosphine **II** as a white crystalline solid. Yield 3.0 g, 68%. Found: C, 76.0; H, 5.35; N, 6.65; $C_{27}H_{23}N_2OP$ requires C, 76.75; H, 5.5; N, 6.65%. MS (EI) *m/z*: 422 (M^+). IR (cm^{-1}): *ν*(N–H) = 3360m and *ν*(C=O) = 1675s. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): −21.8 (s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 3.58 (2H, s, CH_2) and 9.23 (1H, br, NH, exchanges with D_2O).

[PdCl{PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}] (1). A solution containing **I** (1.1 g, 2.9 mmol) and [$PdCl_2(NCPh)_2$] (990 mg 0.26 mmol) in dichloromethane (20 cm^3) was put aside for 24 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **1** as a yellow solid. Yield 1.32 g, 83%. An analytical sample was crystallised from CH_2Cl_2–MeOH. Found: C, 54.7; H, 4.7; N, 5.1; $C_{25}H_{26}ClN_2OPPd\cdot0.1CH_2Cl_2$ requires C, 54.6; H, 4.8; N, 5.05%. MS (FAB) *m/z*: 543 ([M + 1]$^+$) and 507 (M–Cl). IR (cm^{-1}): *ν*(Pd–Cl) = 330m. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 32.2 (s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.51 (9H, s, Bu^t), 3.97 [2H, d, ^2J(PH)11.8, CH_2]. ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$) δ_C: 28.6 (3C, s, C*Me*$_3$), 38.3 (1C, d, ^3J(PC) 10.7, *C*Me$_3$), 47.1 [1C, d, ^1J(PC) 32.6, CH_2P], 173.2 (1C, s, C=N) and 177.4 (1C, s, C=N).

[PtCl{PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}] (2). A solution containing the phosphine **I** (760 mg, 1.9 mmol) and [$PtCl_2(NCPh)_2$] (890 mg 1.9 mmol) in sadichloromethane (20 cm^3) was put aside for 24 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **2** as a yellow solid. Yield 690 mg, 65%. A sample was recrystallised from CH_2Cl_2–MeOH. Found: C, 44.0; H, 3.5; N, 4.75; $C_{25}H_{26}ClN_2OPPt\cdot0.8CH_2Cl_2$ requires C, 44.3; H, 4.0; N, 4.0%. MS (FAB) *m/z*: 632 ([M + 1]$^+$) and 596 (M − Cl). IR (cm^{-1}): *ν*(Pt–Cl) = 325m. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): −0.14 (s), ^1J(PtP) = 3992. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.53 (9H, s, Bu^t) and 3.79 [2H, d, ^2J(PH) 11.3, ^3J(PtH) 10.2, CH_2].

[PdCl{PPh$_2$CH$_2$C(Ph)=NN=C(Ph)O}] (3). A solution containing the phosphine **II** (156 mg, 0.37 mmol) and [$PdCl_2(NCPh)_2$] (141 mg 0.36 mmol) in dichloromethane (10 cm^3) was put aside for 30 min. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **3** as a yellow solid. Yield 110 mg, 53%. Found: C, 57.4; H, 3.8; N, 5.7; $C_{27}H_{22}ClN_2OPPd$ requires C, 57.55; H, 4.1; N, 5.0%. MS (FAB) *m/z*: 563 ([M + 1]$^+$) and 527 (M − Cl). IR (cm^{-1}): *ν*(Pd–Cl) = 330m. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 35.1(s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 4.22 (2H, br, CH_2).

[PdBr{PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}] (4). A solution containing the chloropalladium(II) complex **1** (235 mg, 0.43 mmol) and LiBr (850 mg, 9.8 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **4** as a yellow solid. Yield 166 mg, 65%. Found: C, 50.85; H, 4.4; Br, 13.4; N, 4.8; $C_{25}H_{26}BrN_2OPPd$ requires C, 51.1; H, 4.45; Br, 13.6; N, 4.8%. MS (FAB) *m/z*: 589 (M^+). ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 34.6 (s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.53 (9H, s, Bu^t) and 3.98 [2H, d, ^2J(PH) 12.1, CH_2].

[PdI{PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}] (5). A solution containing the chloropalladium(II) complex **1** (205 mg, 0.38 mmol) and NaI (1.2 g, 7.9 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **5** as an orange solid. Yield 123 mg, 51%. A sample was recrystallised from CH_2Cl_2–MeOH. Found: C, 46.05; H, 3.95; I, 19.2; N, 4.2; $C_{25}H_{26}IN_2OPPd\cdot0.2CH_2Cl_2$ requires C, 46.42; H, 4.0; I, 19.4; N, 4.3%. MS (FAB) *m/z*: 635 ([M + 1]$^+$). ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 37.8 (s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.53 (9H, s, Bu^t) and 4.02 [2H, d, ^2J(PH) 12.1, CH_2].

[PtBr{PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}] (6). A solution containing the chloroplatinum(II) complex (**2**) (175 mg, 0.27 mmol) and LiBr (540 mg, 5.15 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **6** as a yellow solid. Yield 92 mg, 50%. A sample was recrystallised from CH_2Cl_2–MeOH. Found: C, 43.7; H, 3.6; Br, 11.5; N, 4.3; $C_{25}H_{26}BrN_2OPPt\cdot0.2CH_2Cl_2$ requires C, 43.6; H, 3.8; Br, 11.5; N, 4.0%. MS (FAB) *m/z*: 677 ([M + 1]$^+$). ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 0.88 (s), ^1J(PtP) = 3919. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.58 (9H, s, Bu^t) and 3.63 [2H, d, ^2J(PH) 11.3, ^3J(PtH) 9.9, CH_2].

[PtI{PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}] (7). A solution containing the chloroplatinum(II) complex **2** (155 mg, 0.24 mmol) and NaI (760 mg, 5.1 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **7** as an orange solid. Yield 118 mg, 68%. Found: C, 41.1; H, 3.35; I, 17.3; N, 3.9; $C_{25}H_{26}IN_2OPPt$ requires C, 41.5; H, 3.6; I, 17.55; N, 3.9%. MS (FAB) *m/z*: 724 ([M + 1]$^+$). ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 2.79 (s), ^1J(PtP) = 3676. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.55 (9H, s, Bu^t) and 3.80 [2H, d, ^2J(PH) 11.2, ^3J(PtH) 9.7, CH_2].

[PtMe{PPh$_2$CH$_2$C(Ph)=NN=C(Ph)O}] (8). A solution containing [$PtMe_2$(cod)] (57 mg, 0.17 mmol) and the phosphine **I** (69 mg, 0.17 mmol) in benzene (4 cm^3) was heated at 80 °C for 2 h. The solvent was then removed and methanol added to the residue to give **8** as a yellow solid. Yield 42 mg, 40%. Found: C, 50.95; H, 4.75; N, 4.5; $C_{26}H_{29}N_2OPPt$ requires C, 51.05; H, 4.8; N, 4.6%. MS (FAB) *m/z*: 612 (M^+). ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 4.5 (s), ^1J(PtP) = 4493. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 0.86 [3H, ^3J(PH) 1.3, ^2J(PtH) 71.8, PtMe], 1.51 (9H, s, Bu^t) and 3.78 [2H, d, ^2J(PH) 11.0, ^3J(PtH) 29.5, CH_2].

[Pd(PPh$_3$){PPh$_2$CH$_2$C(Bu^t)=NN=C(Ph)O}]BPh$_4$ (10). A solution containing the chloropalladium(II) complex **1** (106 mg, 0.19 mmol) and triphenylphosphine (52 mg, 0.19 mmol) in chloroform (5 cm^3) was put aside for 1 h. The solvent was then removed and the residue redissolved in methanol (2 cm^3), a solution of $NaBPh_4$ in methanol was added to give **10** as yellow crystalline solid. Yield 170 mg, 82%. Found: C, 73.25; H, 5.4; N, 2.35; $C_{67}H_{61}BN_2OP_2Pd$ requires C, 73.85; H, 5.65; N, 2.6%. MS (FAB) *m/z*: 769 ([M − BPh_4]$^+$). ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 24.9 (d), 37.8 (d), ^2J(PP) = 26. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.41 (9H, s, Bu^t) and 3.89 [2H, dd, ^2J(PH) 11.8, ^4J(PH) 1.4, CH_2].

[PtMe{PPh$_2$CH$_2$C(Ph)=NNC(=O)Ph}{PPh$_2$CH$_2$C(Ph)=NNHC(=O)Ph}] (11). A solution of the phosphine **II** (103 mg, 0.24 mmol) and [$PtMe_2$(cod)] (40 mg 0.12 mmol) in benzene (5 cm^3) was put aside for 25 min. The solvent was then evaporated to low volume under reduced pressure and *n*-hexane added to the residue to give **11** as an orange solid. Yield 111 mg, 87%. Found: C, 61.45; H, 4.45; N, 5.2; $C_{55}H_{48}N_4O_2P_2Pt\cdot CH_3OH$ requires C 61.9; H, 4.8; N, 5.15%. MS (FAB) *m/z*: 1054 ([M + 1]$^+$) and 1038 ([M − Me]$^+$). IR (cm^{-1}): *ν*(N–H) = 3050m. ^{31}P-{^1H}NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 22.4 (d), ^1J(PtP) = 2898; 52.2 (d), ^1J(PtP) = 3098 and ^2J(PP) = 472. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 0.16 [3H, t, ^3J(PH) 7.3, ^2J(PtH) 70.9, PtMe], 3.92 (2H, br, CH_2), 4.92 [2H, d, ^2J(PH) 14.7, ^3J(PtH) 29.3, CH_2] and 9.46 [1H, br, NH, exchanges with D_2O]. ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$) δ_C: −19.4 [1C, t, ^2J(PC) 6.7, ^1J(PtC) 576, PtMe], 26.2 [1C, d, ^1J(PC) 26.0, CH_2], 27.7 [1C, d, ^1J(PC) 21.8, CH_2], 147.4 (1C, s, C=N), 155.4 [1C, d, ^2J(PC) 6.2, C=N], 166.2 (1C, s, C=O) and 172.9 (1C, s, C=O).

[Pt{PPh_2CH=C(Ph)NN=C(Ph)O}{PPh_2CH_2C(Ph)=NNHC(=O)Ph}] (12). A solution containing the phosphine **II** (96 mg, 0.23 mmol) and [$PtCl_2(NCMe)_2$] (40 mg, 0.11 mmol) in dichloromethane (5 cm^3) was warmed for 10 min, then treated with triethylamine (0.1 cm^3) and put aside for 20 min. The solvent was then removed and methanol added to the residue to give (**12**) as an orange solid. Yield 66 mg, 58%. Found: C, 61.85; H, 4.1; N, 5.5; $C_{54}H_{44}N_4O_2P_2Pt\cdot CH_3OH$ requires C, 61.75; H, 4.5; N, 5.25%. MS (FAB) *m*/*z*: 1038 ([M + 1]$^+$). IR (cm^{-1}): ν(N–H) = 3460m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 3.4 (d), ^1J(PtP) = 3108; 8.0 (d), ^1J(PtP) = 3557 and ^2J(PP) = 14. ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 3.93 [2H, d, ^2J(PH) 10.0, ^3J(PtH) 38.3, CH_2] and 4.81 [1H, d, ^2J(PH) 10.5, ^3J(PtH) 18.9, PCH=].

[Pd{PPh_2CH=C(Bu^t)NHNC(=O)Ph}$_2$] (13). A solution containing the phosphine **I** (110 mg, 0.27 mmol) and [$PdCl_2$(NCPh)$_2$] (50 mg, 0.14 mmol) in dichloromethane (2 cm^3) was treated with an excess of triethylamine (0.1 cm^3, 0.72 mmol) and then put aside for 3 h. The solvent was then removed and methanol added to the residue to give **13** as an orange solid. Yield 52 mg, 41%. Found: C, 65.75; H, 5.95; N, 6.4; $C_{50}H_{52}N_4O_2P_2Pd$ requires C, 66.05; H, 5.75; N, 6.15%. MS (FAB) *m*/*z*: 909 ([M + 1]$^+$). IR (cm^{-1}): ν(C=C) = 1605m and ν(N–H) = 3325m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 5.2(s). ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.16 (9H, s, Bu^t), 3.68 [1H, dd, ^2J(PH) 2.0, ^4J(HH) 1.3, PCH=] and 8.63 [1H, br, NH, exchanges with D_2O]. ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ_C: 29.8 (3C, s, CMe_3), 37.1 (1C, s, *C*Me_3), 62.3 [1C, d, ^1J(PC) 73.6, =CHP], 161.8 (1C, s, =CN) and 173.5 (1C, s, C=O).

[Pt{PPh_2CH=C(Bu^t)NHNC(=O)Ph}$_2$] (14). A solution containing the phosphine **I** (310 mg, 0.77 mmol) and [$PtCl_2$(cod)] (144 mg, 0.38 mmol) in dichloromethane (10 cm^3) was treated with an excess of triethylamine (0.1 cm^3, 0.72 mmol) and was put aside for 6 h. The solvent was then removed and methanol added to the residue to give **14** as a pale yellow solid. Yield 88 mg, 47%. Found: C, 58.9; H, 5.3; N, 5.4; $C_{50}H_{52}N_4O_2P_2Pt\cdot 2CH_3OH$ requires C, 58.8; H, 5.7; N, 5.25%. MS (FAB) *m*/*z*: 998 ([M + 1]$^+$). IR (cm^{-1}): ν(C=C) = 1595m and ν(N–H) = 3325m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): −17.1(s), ^1J(PtP) = 3274. ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.12 (9H, s, Bu^t), 3.78 [1H, dd, ^2J(PH) 2.14, ^4J(HH) 1.4, ^3J(PtH) 37.8, PCH=] and 8.20 [1H, br, ^3J(PtH) 23.1, NH, exchanges with D_2O]. ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ_C: 29.8 (3C, s, CMe_3), 37.1 (1C, s, *C*Me_3), 62.9 [1C, d, ^1J(PC) 81.3, =CHP], 161.3 (1C, s, =CN) and 173.2 (1C, s, C=O).

[Pd{PPh_2CH=C(Ph)NHNC(=O)Ph}$_2$] (15). A solution containing the phosphine **II** (109 mg, 0.26mmol) and [$PdCl_2$(NCPh)$_2$] (50 mg, 0.13 mmol) in dichloromethane (5 cm^3) was treated with triethylamine (0.1 cm^3, 0.7 mmol) and the mixture put aside for 12 h. The solvent was then removed and methanol added to the residue to give **15** as an orange solid. Yield 100 mg, 81%. Found: C, 67.75; H, 4.45; N, 5.9; $C_{54}H_{44}N_4O_2P_2Pd\cdot 0.2CH_2Cl_2$ requires C, 67.4; H, 4.6; N, 5.7%. MS (FAB) *m*/*z*: 949 ([M + 1]$^+$). IR (cm^{-1}): ν(C=C) = 1595m and ν(N–H) = 3325m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 5.7 (s). ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 4.10 [1H, dd, ^2J(PH) 2.7, ^4J(HH) 1.7, PCH=] and 8.09 [1H, br, NH, exchanges with D_2O].

[Pt{PPh_2CH=C(Ph)NHNC(=O)Ph}$_2$] (16). A solution containing the phosphine **II** (104 mg, 0.25 mmol) and [$PtCl_2$(NCPh)$_2$] (58 mg, 0.12 mmol) in dichloromethane (5 cm^3) was treated with triethylamine (0.1 cm^3) and then put aside for 20 h. The solvent was then removed and methanol added to the residue to give **16** as a pale yellow solid. Yield 96 mg, 78%. Found: C, 61.75; H, 4.0; N, 5.25; $C_{54}H_{44}N_4O_2P_2pt\cdot 0.2CH_2Cl_2$ requires C, 61.7; H, 4.2; N, 5.3%. MS (FAB) *m*/*z*: 1038 ([M + 1]$^+$). IR (cm^{-1}): ν(C=C) = 1595m and ν(N–H) = 3320m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): −16.6(s), ^1J(PtP) = 3311. ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 4.15 [1H, dd, ^2J(PH) 4.6, ^4J(HH) 1.3, ^3J(PtH) 37.8, PCH=] and 10.90 [1H, br, NH, exchanges with D_2O].

[PtCl{PPh_2CH[C(CO_2Me)=CH(CO_2Me]=C(Bu^t)N–N=C(Ph)O }] (17). A solution of the chloroplatinum(II) complex **2** (70 mg, 0.11 mmol) and dimethyl acetylenedicarboxylate (15 µl, 0.12 mmol) in chloroform (2 cm^3) was treated with triethylamine (15 µl) and then put aside for 12 h. The solvent was then removed and methanol added to the residue to give **17** as a pale pink solid. Yield 47 mg, 55%. Found: C, 47.8; H, 4.15; Cl, 4.7; N, 3.45; $C_{31}H_{33}ClN_2O_5PPt$ requires C, 48.05; H, 4.3; Cl, 4.6; N, 3.6%. MS (FAB) *m*/*z*: 775 ([M + 1]$^+$) and 738 (M–HCl). IR (cm^{-1}): ν(C=O) = 1730s and ν(Pt–Cl) = 345m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 21.3(s), ^1J(PtP) = 4089. ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.42 (9H, s, Bu^t), 3.22 (3H, s, OMe), 3.68(3H, s, OMe), 5.56 [1H, d, ^2J(PH) 13.6, ^3J(PtH) 38.4, PCH] and 6.58 [1H, d, ^4J(PH) 4.3, =$CHCO_2$]. ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ_C: 28.8 (3C, s, CMe_3), 39.3 [1C, d, ^3J(PC) 7.3, *C*Me_3], 52.3 (1C, s, OMe), 52.9 (1C, s, OMe), 57.5 [1C, d, ^1J(PC) 34.8, CHP], 131.2 (1C, s, =*C*HCO_2Me), 163.9 (1C, s, C=N), 165.3 [1C, d, *J*(PC) 2.8, C=N], 172.9 [1C, s, C=O] and 180.6 [1C, d, *J*(PC) 3.6, C=O). Molecular weight in chloroform = 767 Daltons; calc. for $C_{31}H_{33}ClN_2O_5PPt$ 775 Daltons.

[PdCl{PPh_2CH[C(CO_2Me)=CH(CO_2Me]=C(Bu^t)N–N=C(Ph)O}] (18). Compound **1** (710 mg, 1.3 mmol) and dimethyl acetylenedicarboxylate (0.27 ml, 2.2 mmol) in chloroform (10 cm^3) was treated with triethylamine (0.30 ml) and the solution put aside for 5 h. The solvent was then removed and methanol added to the residue to give **18** as a pale pink solid. Yield 0.45 g, 51%. Found: C, 53.95; H, 4.6; Cl, 5.3; N, 4.15; $C_{31}H_{33}ClN_2O_5PPd$ requires C, 54.3; H, 4.85; Cl, 5.1; N, 4.1%. MS (FAB) *m*/*z*: 685 (M^+) and 649 (M–HCl). IR (cm^{-1}): ν(C=O) = 1730s and ν(Pd–Cl) = 340m. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 52.1(s). ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.41 (9H, s, Bu^t), 3.26 (3H, s, OMe), 3.67 (3H, s, OMe), 5.60 [1H, d, ^2J(PH) 14.7, PCH] and 6.69 [1H, d, ^4J(PH)4.4, =$CHCO_2$]. ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ_C: 28.8 (3C, s, CMe_3), 39.5 [1C, d, ^3J(PC) 9.5, *C*Me_3], 52.3 (1C, s, OMe), 52.8 (1C, s, OMe), 57.4 [1C, d, ^1J(PC) 27.5, CHP], 130.9 (1C, s, =*C*HCO_2Me), 163.8 (1C, s, C=N), 165.1 [1C, d, *J*(PC) 3.1, C=N], 172.5 [1C, d, *J*(PC) 3.5, C=O] and 178.4 [1C, d, *J*(PC) 3.4, C=O].

[PtBr{PPh_2CH[C(CO_2Me)=CH(CO_2Me]=C(Bu^t)NN=C(Ph)O}] (19). A solution containing the chloroplatinum(II) complex **17** (118 mg, 0.15 mmol) and LiBr (415 mg, 4.8 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **19** as a yellow solid. Yield 70 mg, 57%. Found: C, 44.6; H, 3.8; N, 3.35; $C_{31}H_{33}BrN_2O_5PPt\cdot 0.3CH_2Cl_2$ requires C, 44.5; H, 4.0; N, 3.3%. MS (FAB) *m*/*z*: 820 (M − 1). IR (cm^{-1}): ν(C=O) = 1735s. ^{31}P-{^{1}H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 20.9(s), ^1J(PtP) = 4011. ^{1}H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.48(9H, s, Bu^t), 3.35 (3H, s, OMe), 3.71(3H, s, OMe), 5.67 [1H, d, ^2J(PH) 13.1, ^3J(PtH) 22.5, PCH] and 6.65 [1H, d, ^4J(PH) 4.3, =$CHCO_2$].

[PtI{PPh_2CH[C(CO_2Me)=CH(CO_2Me]=C(Bu^t)NN=C(Ph)O}] (20). A solution containing the chloroplatinum(II) complex **17** (111 mg, 0.14 mmol) and NaI (429 mg, 2.9 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **20** as an orange solid. This was recrystallised from CH_2Cl_2–MeOH. Yield 90 mg, 74%. Found: C, 41.7; H, 3.7; N, 3.8; $C_{31}H_{33}IN_2O_5PPt\cdot 0.5CH_2Cl_2$

Table 4 Selected crystallographic data for compounds **1**, **12** and **13**

Compound	**1**	**12**	**13**
Chemical formula	$C_{25}H_{26}ClN_2OPPd$	$C_{54}H_{44}N_4O_2P_2Pt{\cdot}CH_2Cl_2$	$C_{50}H_{52}N_4O_2P_2Pd{\cdot}CH_2Cl_2$
M	543.30	1122.89	994.22
Crystal system	Orthorhombic	Triclinic	Orthorhombic
a/Å	19.4346(8)	12.614(2)	25.162(2)
b/Å	9.6142(6)	13.671(2)	19.489(2)
c/Å	12.4346(4)	15.754(3)	19.329(2)
α/°		100.260(9)	
β/°		99.334(9)	
γ/°		110.682(7)	
Space group	$P2_12_12_1$	$P\bar{1}$	$Pbca$
Z	4	2	8
μ/mm^{-1}	1.003	1.538	0.616
No. data measured	5612	9673	8503
No. independent data	4110	8537	8341
R_{int}	0.0158	0.0221	0.0316
wR_2 (all data)	0.0424	0.0558	0.0792

requires C, 41.7; H, 3.7; N, 3.1%. MS (FAB) *m*/*z*: 866 (M^+). IR (cm^{-1}): ν(C=O) = 1735s. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 21.9 (s), ^1J(PtP) = 3910. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.51 (9H, s, Bu^t), 3.33 (3H, s, OMe), 3.72 (3H, s, OMe), 5.76 [1H, d, ^2J(PH) 13.2, ^3J(PtH) 21.8, PCH] and 6.68 [1H, d, ^4J(PH) 4.3, =$CHCO_2$].

[PdBr{PPh$_2$CH[C(CO$_2$Me)=CH(CO$_2$Me]=C(Bu^t)NN=C(Ph)O}] (21). A solution containing the chloropalladium(II) complex **18** (132 mg, 0.19 mmol) and LiBr (463 mg, 3.8 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **21** as a yellow solid. Yield 47 mg, 36%. Found: C, 50.0; H, 4.4; N, 3.5; $C_{31}H_{33}BrN_2O_5PPd{\cdot}CH_3OH$ requires C, 50.3; H, 4.8; N, 3.6%. MS (FAB) *m*/*z*: 731 (M − 1). IR (cm^{-1}): ν(C=C) = 1645m and ν(C=O) = 1735s. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 53.2(s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.42 (9H, s, Bu^t), 3.25 (3H, s, OMe), 3.68 (3H, s, OMe), 5.62 [1H, d, ^2J(PH) 14.8, PCH] and 6.71 [1H, d, ^4J(PH) 4.3, =$CHCO_2$].

[PdI{PPh$_2$CH[C(CO$_2$Me)=CH(CO$_2$Me]=C(Bu^t)NN=C(Ph)O}] (22). A solution containing the chloropalladium(II) complex **18** (142 mg 0.21 mmol) and NaI (800 mg, 5.40 mmol) in acetone (20 cm^3) was put aside for 15 h. The solvent was then removed and methanol added to the residue to give **22** as an orange solid. Yield 110 mg, 67%. Found: C, 47.6; H, 4.0; I, 16.4; N, 3.5; $C_{31}H_{33}IN_2O_5PPd$ requires C, 47.9; H, 4.3; I, 16.3; N, 3.6%. MS (FAB) *m*/*z*: 777 (M^+) and 649 (M − HI). IR (cm^{-1}): ν(C=C) = 1640m and ν(C=O) = 1735s. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 55.6(s). ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.43 (9H, s, Bu^t), 3.22 (3H, s, OMe), 3.68 (3H, s, OMe), 5.66 [1H, d, ^2J(PH) 14.8, PCH] and 6.71 [1H, d, ^4J(PH) 4.3, =$CHCO_2$]. Molecular weight in chloroform = 765 Daltons for calc. for $C_{31}H_{33}IN_2O_5PPd$ 777 Daltons.

[PtMe{PPh$_2$CH[C(CO$_2$Me)=CH(CO$_2$Me]=C(Bu^t)NN=C(Ph)O}] (23). A solution containing the methylplatinum(II) complex **9** (33 mg, 0.054 mmol) and dimethyl acetylenedicarboxylate (40 µl, 49 mg, 0.34 mmol) in chloroform (6 cm^3) was treated with an excess of triethylamine (50 µl, 35 mg, 0.34 mmol) and then put aside for 24 h. The solvent was then removed and methanol added to the residue to give **23** as a pale yellow solid. Yield 24 mg, 64%. Found: C, 50.85; H, 4.7; N, 3.5; $C_{32}H_{36}N_2O_5PPt$ requires C, 50.95; H, 4.8; N, 3.7%. MS (FAB) *m*/*z*: 753 (M − 1). IR (cm^{-1}): ν(C=C) = 1640m and ν(C=O) = 1730s. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 26.1 (s), ^1J(PtP) = 4823. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 0.79 [3H, d, ^1J(PH) 1.3, ^1J(PtH) 71.6, PtMe], 1.46 (9H, s, Bu^t), 3.33 (3H, s, OMe), 3.68 (3H, s, OMe), 5.62 [1H, d, ^2J(PH) 13.0, PCH] and 6.63 [1H, d, ^4J(PH) 4.2, =$CHCO_2$].

[PtBr$_2$Cl{PPh$_2$CH[C(CO$_2$Me)=CH(CO$_2$Me]=C(Bu^t)NN=C(Ph)O}] (24). A solution of bromine (0.22 mmol) in CCl_4 was added to a solution containing **17** (100 mg, 0.13 mmol) in $CHCl_3$ (5 cm^3) and was put aside for 5 min. The solvent was then removed and methanol added to the residue to give **24** as an orange solid. Yield 50 mg, 41%. Found: C, 36.95; H, 3.15; N, 2.6; $C_{31}H_{33}Br_2ClN_2O_5PPt{\cdot}CHCl_3$ requires C, 36.45; H, 3.25; N, 2.65%. MS (FAB) *m*/*z*: 775 ([M + 1 − 2Br]$^+$). IR (cm^{-1}): ν(C=C) = 1640m and ν(C=O) = 1735s. ^{31}P-{^1H} NMR (36.2 MHz, $CDCl_3$), δ_P (ppm): 12.6 (s), ^1J(PtP) = 2504. ^1H NMR (100 MHz, $CDCl_3$), δ_H (ppm): 1.64 (9H, s, Bu^t), 3.59 (3H, s, OMe), 3.67 (3H, s, OMe), 6.64 [1H, d, ^2J(PH) 14.4, ^3J(PtH) 10.2, PCH].

X-Ray crystallography

X-Ray diffraction experiments were carried out at 200 K on a Stoe STADI4 4-circle diffractometer with Mo-Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems open-flow N_2 gas cryostat, following a standard procedure. Semi-empirical absorption corrections based on psi-scans were applied to all three datasets. The structures were solved by direct methods (SHELXS 86[15]) and refined by full-matrix least squares (against F^2) using SHELXL 97.[16] All non-H atoms were refined with anisotropic displacement parameters, H atoms with isotropic displacement parameters. In the refinements, all the H atoms bonded to C atoms were allowed for as "riding" atoms. H atoms bonded to N in **12** and **13** were refined isotropically. Crystal data and experimental details are summarised in Table 4.

CCDC reference numbers 174213–174215.

See http://www.rsc.org/suppdata/dt/b1/b111079a/ for crystallographic data in CIF or other electronic format.

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