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Complexes of tert-butyl diphenylphosphinomethyl ketone *N*-phenylhydrazone, *Z*-$PPh_2CH_2C(Bu^t)$=NNHPh, with molybdenum, palladium or platinum: crystal structure of *cis*-$[PdCl_2\{Z\text{-}PPh_2CH_2C(Bu^t)=NNHPh\}_2]$

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Abstract

tert-Butyl diphenylphosphinomethyl ketone *N*-phenylhydrazone, *Z*-$PPh_2CH_2C(Bu^t)$=NNHPh (**1**), was prepared by heating the phosphino *N,N*-dimethylhydrazone, *Z*-$PPh_2CH_2C(Bu^t)$=$NNMe_2$ with $PhNHNH_2$ in ethanol in the presence of acetic acid as catalyst. This phosphine was converted into the corresponding phosphine oxide **2a** and phosphine sulfide **2b**. Treatment of $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) with 1 equiv. of **1** gave the tetracarbonylmolybdenum(0) complex $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNHPh\}]$ (**3**) in which **1** is bidentate; $[Mo(CO)_4(nbd)]$ with 2 equiv. of **1** gave the bis(phosphine)molybdenum(0) complex *cis*-$[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNHPh\}_2]$ (**4**) in which **1** is monodentate through P. Treatment of $[PdCl_2(NCPh)_2]$ or $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) with 2 equiv. of **1** gave the complexes *cis*-$[MCl_2\{PPh_2CH_2C(Bu^t)=NNHPh\}_2]$ (M = Pd (**5a**), Pt (**5b**)). The crystal structure of **5a** was determined. Treatment of $[PtCl_2(NCMe)_2]$ with 2 equiv. of the phosphine **1** gave *trans*-$[PtCl_2\{PPh_2CH_2C(Bu^t)=NNHPh\}_2]$ (**5c**). Dehydrochlorination of the platinum(II) dichloride **5b** or **5c** with Et_3N gave the neutral *cis*-$[Pt\{PPh_2CH_2C(Bu^t)=NNPh\}_2]$ (**6**), containing two six-membered chelate rings. Treatment of the π-2-methylallyl complex $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$ with 2 equiv. of the phosphine **1** gave the neutral complex $[(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\{PPh_2CH_2C(Bu^t)=NNHPh\}]$ (**7**) in which **1** is monodentate through P. Dehydrochlorination of **7** with aqueous NaOH solution gave the π-methylallylpalladium(II) chelate complex $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd\{PPh_2CH_2C(Bu^t)=NNPh\}]$ (**8**) containing an amide–palladium bond. Treatment of **1** with $LiBu^n$ followed by PPh_2Cl gave the diphosphine *Z*-$PPh_2CH_2C(Bu^t)$=$NN(Ph)PPh_2$ (**9**) which with 0.5 equiv. of $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$ followed by NH_4PF_6 gave the π-methylallylpalladium(II) PF_6 salt $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd\{PPh_2CH_2C(Bu^t)=NN(Ph)PPh_2\}]PF_6$ (**10**). Crystals of **5a** are monoclinic, space group $P2_1/c$, with $a = 12.900(2)$, $b = 40.083(6)$, $c = 10.8779(11)$ Å, $\beta = 111.891(7)°$ and $Z = 4$, final $R = 0.0535$ for 7558 observed reflections with $F > 4.0\sigma(F)$.

Keywords: Crystal structures; Molybdenum complexes; Palladium complexes; Platinum complexes; Bidentate P–N ligand complexes

1. Introduction

There is increasing interest in the use of bidentate (P–N) ligands to generate new coordination, organometallic or catalytic chemistry [1–14]. Some examples include *o*-$PPh_2C_6H_4(CH_2)_nNMe_2$ ($n = 0$, 1) [7,8], $PPh_2(CH_2)_nNMe_2$ ($n = 2$, 3) [8], *o*-$PPh_2C_6H_4NH_2$ [9], *o*-$PPh_2C_6H_4NHR$ (R = Et or CH_2Ph) [10], $PPh_2(CH_2)_2(2\text{-}C_5H_4N)$ [11] and *o*-$PPh_2C_6H_4CH$=NR (R = Et, Pr^n, Pr^i or Bu^t) [12,13]. We have described the dimethylhydrazone phosphine *Z*-$PPh_2CH_2C(Bu^t)$=$NNMe_2$ and converted it into the corresponding hydrazone phosphine *Z*-$PPh_2CH_2C(Bu^t)$=NNH_2 by treating it with hydrazine in the presence of acetic acid as catalyst for the exchange process [15]. We have reported on the behaviour of these P,N-donors as ligands for Group 6 metal carbonyls [15], palladium and platinum [16], and rhodium and iridium [17]. We have also described some coordination chemistry of chiral *N,N*-dimethylhydrazone-, imine- or azine-P,N-donor ligands derived from (1*R*)-(+)-camphor [18,19] or (1*R*)-(−)-fenchone [20].

In view of the interest in these bidentate (P–N) ligands and our extensive studies of the dimethylhydrazone phosphine ligands and hydrazone phosphine ligands referred to above, it was of interest to study a related ligand in which the donor power of the nitrogen was reduced so that, although there was still the possibility of P,N-chelation, there was also the possibility of the N–metal bond breaking and the ligand becoming monodentate through P only. We considered a

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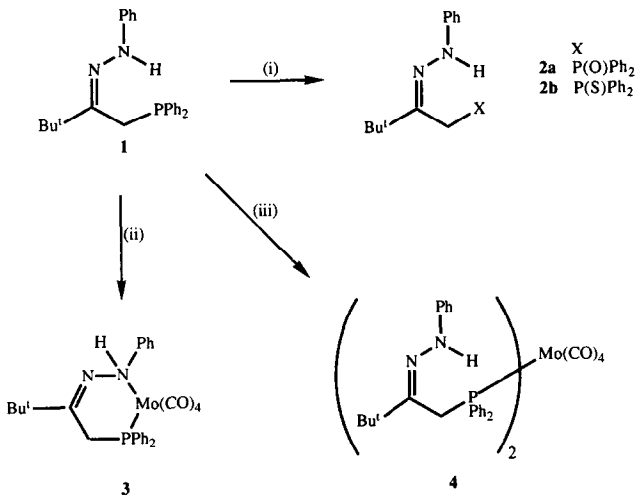


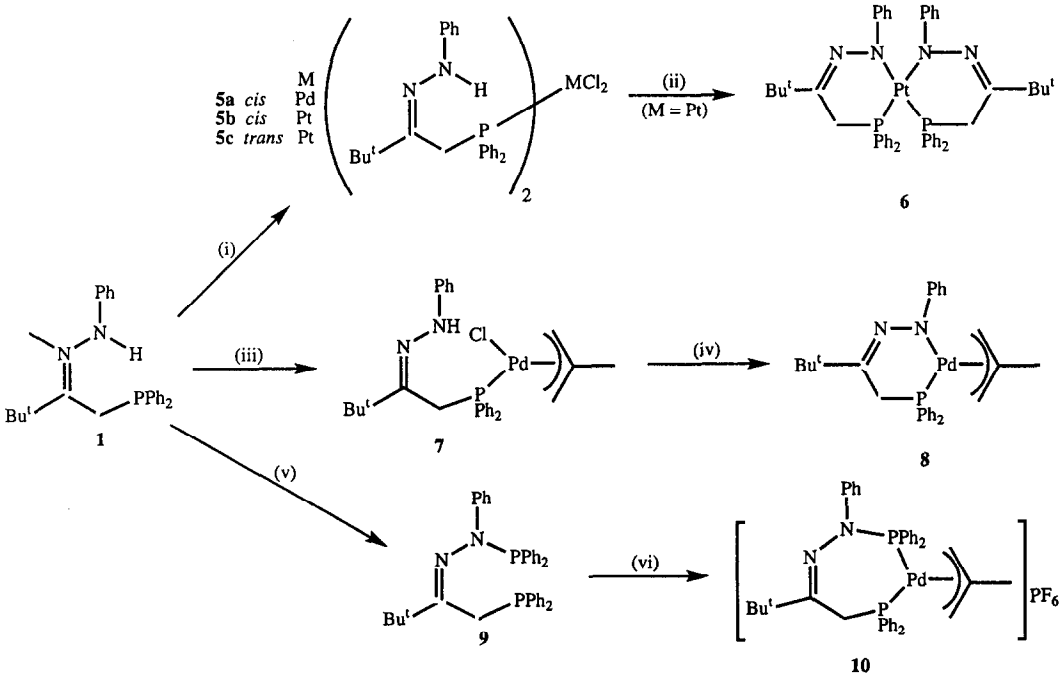
Scheme 1. (i) For **2a**, H_2O_2; for **2b**, monoclinic S; (ii) $[Mo(CO)_4(nbd)]$; (iii) 0.5 equiv. $[Mo(CO)_4(nbd)]$.

suitable ligand for such a study would be the phosphino *N*-phenylhydrazone, *Z*-$PPh_2CH_2C(Bu^t)$=NNHPh (**1**). Since the phenyl group is more electron-withdrawing than a methyl or hydrogen, we anticipated that the imine nitrogen (*N*HPh) would be a much poorer donor than the NR_2 (R = Me or H) of *Z*-$PPh_2CH_2C(Bu^t)$=NNR_2. This we have found to be the case and we report some chemistry with this new ligand.

2. Results and discussion

tert-Butyl diphenylphosphinomethyl ketone *N*-phenylhydrazone, *Z*-$PPh_2CH_2C(Bu^t)$=NNHPh (**1**), was obtained in 78% yield by the prolonged (12 h) heating of the phosphino *N,N*-dimethylhydrazone, $PPh_2CH_2C(Bu^t)$=$NNMe_2$ with $PhNHNH_2$ in ethanol in the presence of acetic acid. For the convenience of the reader the various reactions of **1** are summarised in Schemes 1 and 2. Elemental analytical, IR and some selected $^{13}C\{^1H\}$ NMR data are given in Section 3, and ^1H and $^{31}P\{^1H\}$ NMR data in Table 1. The ^{13}C spectra were assigned using attached proton tests and by comparison with published data [16,17]. The $^{31}P\{^1H\}$ NMR spectrum of this new phosphine showed a singlet at −20.8 ppm, and in the IR spectrum there was a band at 3320 cm^{-1} due to ν(N–H). The subsequent chemistry and in particular an X-ray crystallographic analysis of a palladium complex (see below) suggest that the phosphine **1** has the *Z*-configuration around the C=N bond. The phosphine **1**, on treatment with hydrogen peroxide, was converted into the corresponding phosphine oxide **2a** and treatment of **1** with monoclinic sulfur gave the phosphine sulfide **2b** (Scheme 1). The ^{31}P resonances were singlets at 32.6 (oxide) and 35.3 (sulfide) ppm. In the proton NMR spectrum, the resonance of the methylene protons of the phosphine oxide **2a** was a doublet with a large coupling constant $^2J(PH) = 15.1$ Hz, similarly the sulfide **2b** had $^2J(PH) = 15.6$ Hz, both much larger than the coupling to phosphorus(III) in **1** (1.2 Hz) (Table 1), as would be expected for phosphorus(V).

Treatment of $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) with 1 equiv. of phosphine **1**, in benzene for 4 days at 20 °C, gave the tetracarbonylmolybdenum(0) complex $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)$=NNHPh$\}]$ (**3**) (Scheme 1). The IR spectrum showed a band at 3320 cm^{-1} due to ν(N–H), and three strong absorption bands (at 2020, 1915 and 1860



Scheme 2. (i) For **5a**, 0.5 equiv. $[PdCl_2(NCPh)_2]$; for **5b**, 0.5 equiv. $[PtCl_2(cod)]$; for **5c**, $[PtCl_2(NCMe)_2]$; (ii) NEt_3; (iii) 0.5 equiv. $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$; (iv) 20% NaOH; (v) Bu^nLi, PPh_2Cl; (vi) 0.5 equiv. $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]/NH_4PF_6$.

Table 1
$^{31}P\{^1H\}$ [a] and proton NMR [b] data

	δP	δ(Bu^t)	δ(CH$_2$)	Others
1	−20.8	1.17(9H, s) [c]	2.94[2H, d, ^2J(PH) 1.2] [c]	[d]
2a	32.6	0.83(9H, s)	3.41[2H, d, ^2J(PH) 15.1]	10.40(1H, s, br, NH) [e]
2b	35.3	0.88(9H, s)	3.82[2H, d, ^2J(PH) 15.6]	9.44(1H, s, br, NH) [e]
3	51.8	0.84(9H, s)	2.79[1H, dd, ^2J(PH) 7.1, ^2J(HH) 14.1] 3.81[1H, dd, ^2J(PH) 10.2, ^2J(HH) 14.1]	6.39(1H, d, ^3J(PH) 6.8, NH] [e]
4	26.0	0.51(18H, s)	3.47(4H, br)	[d]
5a [f]	22.7	0.52(18H, s)	2.98[2H, t, br, ^2J(PH) 15, ^2J(HH) 15] 4.76[2H, dd, br, ^2J(PH) 12, ^2J(HH) 15]	9.27(2H, s, br, NH) [e]
5b [f]	2.7(3834)	0.51(18H, s)	3.07[2H, dd, br, ^2J(PH) 11, ^2J(HH) 15] 4.74[2H, dd, br, ^2J(PH) 12, ^2J(HH) 15]	9.17(2H, s, br, NH) [e]
5c	3.6(2538)	0.81(18H, s)	3.88[4H, N = 8.6, ^3J(PtH) 22.8] [g]	7.92(2H, s, br, NH) [e]
6 [f]	15.5(3089)	1.01(18H, s)	2.86[2H, m, ^2J(HH) 16] [h] 3.24[2H, m, ^2J(HH) 16] [h]	
7 [i]	9.4	0.81(9H, s)	3.75[1H, m, ^2J(PH) 7.6, ^2J(HH) 14.2] 3.84[1H, m, ^2J(PH) 7.2, ^2J(HH) 14.2]	1.70(3H, s, *Me*C$_3$H$_4$) 2.54(1H, s, H$_{anti}$ *trans* to Cl) 2.81[1H, d, ^4J(HH) 2.5, H$_{syn}$ *trans* to Cl] 3.33[1H, d, ^3J(PH) 10.5, H$_{anti}$ *trans* to P] 4.43[1H, dd, ^3J(PH) 5.0, ^4J(HH) 2.5, H$_{syn}$] 8.94[1H, s, br, NH] [e]
8 [i]	62.0	0.81(9H, s)	2.86[1H, t, ^2J(PH) 12, ^2J(HH) 12] 2.96[1H, t, ^2J(PH) 12, ^2J(HH) 12]	1.24(3H, s, *Me*C$_3$H$_4$) 1.73(1H, s, H$_{anti}$ *trans* to N) 2.61[1H, d, ^4J(HH) 2.4, H$_{syn}$ *trans* to N] 3.23[1H, d, ^{3}J(PH) 10.5, H$_{anti}$ *trans* to P] 3.73[1H, dd, ^3J(PH) 7.5, ^4J(HH) 2.4, H$_{syn}$]
9	60(s) −16.9(s)	0.99(9H, s)	2.50[2H, d, ^2J(PH) 3.6]	
10 [i]	81.9(d) [j] 30.9(d) [j]	0.96(9H, s)	3.90[1H, t, ^2J(PH) 11.9, ^2J(HH) 12.4] 4.29[1H, t, ^2J(PH) 11.9, ^2J(HH) 12.4]	1.59(3H, s, *Me*C$_3$H$_4$) 3.10[1H, d, ^3J(PH) 10.0, H$_{anti}$] 3.48[1H, d, ^3J(PH) 10.0, H$_{anti}$] 3.56[1H, m, ^4J(HH) 2.4, H$_{syn}$] [k] 4.44[1H, m, ^4J(HH) 2.4, H$_{syn}$] [k]

[a] Recorded at 36.2 MHz, chemical shifts δ relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated, ^1J(PtP) (Hz) in parentheses.
[b] Recorded at 100 MHz, chemical shifts δ relative to $SiMe_4$, solvent $CDCl_3$ unless otherwise stated, coupling constants J in Hz; s = singlet, d = doublet, dd = doublet of doublets, br = broad, m = multiplet, t = triplet.
[c] In C_6D_6.
[d] Resonance due to NH proton was not observed.
[e] Exchanged with D_2O.
[f] At −50 °C.
[g] $N = |^2J(PH) + {}^4J(PH)|$.
[h] Couplings to phosphorus and platinum were not resolved.
[i] At 250 MHz.
[j] $^2J(PP) = 51$ Hz.
[k] Couplings to phosphorus atoms were not resolved.

cm^{-1} for $\nu(C{\equiv}O)$), as expected and as found for the analogous tetracarbonyl–*Z*-$PPh_2CH_2C(Bu^t){=}NNMe_2$ and –*Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ complexes [15]. In the ^1H NMR spectrum, the NH proton resonance was a broad doublet at δ 6.39 with $^3J(PH) = 6.8$ Hz and the NH proton exchanged with deuterium on contact with D_2O. The $J(PH)$ value of 6.8 Hz shows that it is the NHPh nitrogen which is coordinated to the molybdenum atom, giving a six-membered chelate ring; a very similar value for $J(PH)$ was found for the *Z*-$PPh_2CH_2C(Bu^t){=}NNH_2$ complexes [15], i.e. it is a three-bond coupling; if the other nitrogen (C=N) had been coordinated then $J(PH)$ would be a four-bond coupling and be too small to observe (< 1 Hz). As expected, the CH_2P protons were not equivalent and resonated at δ 2.79 (dd, $^2J(PH) = 7.1$, $^2J(HH) = 14.1$ Hz) and 3.81 (dd, $^2J(PH) = 10.2$, $^2J(HH) = 14.1$ Hz). The ^{13}C NMR spectrum (Section 3) showed a doublet at δ 24.7 with $^1J(PC) = 5.6$ Hz for the CH_2P carbon; this chemical shift is typical of a methylene carbon in a six-membered chelate ring [16,17,20,21]. In the carbonyl region, four doublets were observed for the carbonyl ligands of which the doublet at 212.2 ppm with a large $^2J(PC)$ value of 37.1 Hz was assigned to the carbonyl carbon *trans* to P [20–22]. Treatment of $[Mo(CO)_4(nbd)]$ with 2 equiv. of the phosphine **1** gave the bis(phosphine) complex $[Mo(CO)_4\{PPh_2CH_2C(Bu^t){=}NNHPh\}_2]$ (**4**) in which each phosphine ligand is monodentate through phosphorus. In contrast, treatment of $[Mo(CO)_4(nbd)]$ with 2 equiv. of either *Z*-PPh_2-

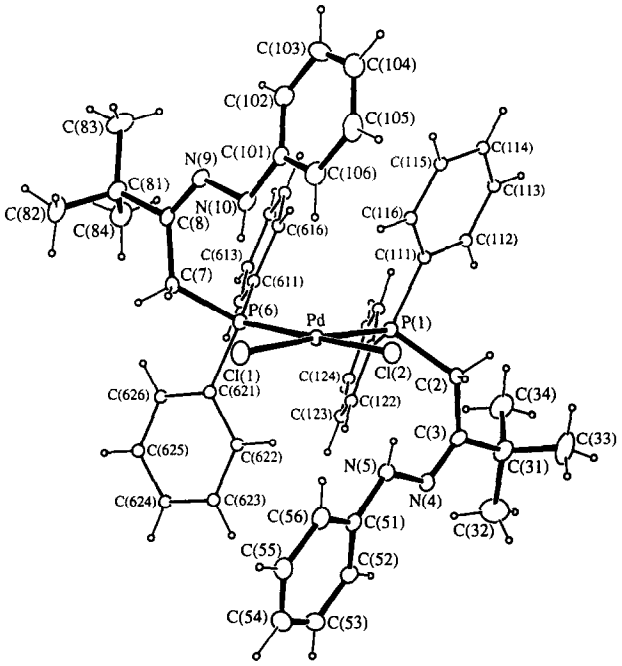


Fig. 1. ORTEP representation of the molecular structure of compound **5a**. Ellipses are shown at 50% probability level. In the interests of clarity both phosphine phenyl carbon atoms and hydrogen atoms are drawn as circles, each with an arbitrary small radius.

$CH_2C(Bu^t)=NNH_2$ or *Z*-$PPh_2CH_2C(Bu^t)=NNMe_2$ gave the corresponding chelate complex $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNR_2\text{-}P,N\}]$ (R = Me or H) and 1 equiv. of unreacted phosphine. The elemental analytical data are in agreement with the composition $C_{52}H_{54}MoN_4O_4P_2$, as required for the proposed structure $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNHPh\}_2]$ (**4**). The IR spectrum showed a band at 3320 cm^{-1} due to ν(N–H) and strong absorption bands at 2020, 1925 and 1885 cm^{-1} for ν(C≡O) [15]. The $^{31}P\{^1H\}$ NMR spectrum of **4** showed a singlet at δ 26.0, i.e. a downfield shift of ~47 ppm when compared to the ^{31}P chemical shift (−20.8) of the free phosphine **1**, and an upfield shift of ~26 ppm when compared to the ^{31}P chemical shift (51.8) of the chelate complex **3**, in which the phosphorus is in a six-membered chelate ring. In the ^1H NMR spectrum the methylene proton resonance of **4** was a broad peak, even at −50 °C.

We have also studied the coordination chemistry of the phosphine **1** with more electropositive metals such as palladium and platinum (Scheme 2). Treatment of $[PdCl_2(NCPh)_2]$ with 2 equiv. of the phosphine **1** gave the bis(phosphine)palladium(II) complex *cis*-$[PdCl_2\{PPh_2CH_2C(Bu^t)=NNHPh\}_2]$ (**5a**); the molecular structure of which was determined by X-ray crystallography (Fig. 1, see below). The structure showed that: (i) the geometry at the palladium atom is *cis*; (ii) the phosphines are monodentate; (iii) each chlorine atom is calculated to be unusually close to two hydrogens which are taken to be hydrogen bonded to it, e.g. Cl(1) is close to H(7b) and H(10), with Cl···HCP ~2.6 Å and Cl···HN ~2.6 Å, and Cl(2) is similarly close to H(2b) and H(5). In contrast to the behaviour of **1**, we found previously that treatment of $[PdCl_2(NCPh)_2]$ with 2 equiv. of the phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ gave the dicationic bis(chelate) palladium(II) complex *cis*-$[Pd\{PPh_2CH_2C(Bu^t)=NNH_2\text{-}P,N\}_2][2Cl]$ in essentially quantitative yield [16]. The IR spectrum of **5a** showed a band at 3220 cm^{-1} due to ν(N–H) and two bands due to ν(Pd–Cl) at 280 and 305 cm^{-1}. In the ^1H NMR spectrum, the NH proton resonance was at δ 9.27 as a broad peak which disappeared when the $CDCl_3$ solution was shaken with D_2O. At 20 °C the resonances for the CH_2P protons were broadened by a fluxional process but at −50 °C, the CH_2P protons were non-equivalent, and the $^1H\{^{31}P\}$ NMR spectrum showed an AB pattern with δ values at 2.98 and 4.76, $^2J(HH)$ = 15 Hz. Inequivalence of these methylene protons with a large chemical shift difference ($\Delta\delta_H \sim 1.8$ ppm) is unusual and we suggest this large difference is due to the presence of a hydrogen bond between the chlorine and one of the methylene protons, i.e. the one giving the resonance at δ 4.76. Treatment of $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) with 2 equiv. of the phosphine **1** gave the analogous platinum(II) complex **5b** which showed similar NMR properties to the dichloropalladium(II) complex **5a**, with the coupling constant $^1J(PtP)$ = 3834 Hz close to values reported for similar complexes with phosphorus *trans* to chlorine [16,19,22]. In contrast, treatment of $[PtCl_2(NCMe_2)]$ with 2 equiv. of the phosphine **1** gave the *trans*-dichloroplatinum(II) complex **5c**, which showed a single ^{31}P resonance at δ 3.6 with ^{195}Pt satellites ($^1J(PtP)$ = 2538 Hz) indicating that the phosphorus atoms are *trans* to each other [22]. The IR spectrum showed bands at 3250 and 335 cm^{-1} due to ν(N–H) and ν(Pt–Cl), respectively. In the ^1H NMR spectrum the CH_2P protons showed a 'virtual triplet' with $N = |^2J(PH) + {}^4J(PH)| = 8.6$ Hz and $^3J(PtH)$ = 22.8 Hz, as expected for complexes containing mutually *trans* phosphine ligands [23]. Dehydrochlorination of **5b** or **5c** with Et_3N in dichloromethane gave the bis(chelate)platinum(II) complex **6** containing the deprotonated phosphine ligand in a six-membered chelate ring. The $^{31}P\{^1H\}$ NMR spectrum of complex **6** showed a singlet at δ 15.5 with $^1J(PtP)$ = 3089 Hz, indicative of phosphorus *trans* to nitrogen [16,24–29]. At 20 °C the resonances due to CH_2P protons were broad and at −50 °C the $^1H\{^{31}P\}$ NMR spectrum showed an AB pattern with $^2J(HH)$ = 16 Hz. The ^{13}C NMR spectrum showed a triplet at δ 25.9, characteristic of a CH_2P carbon in a six-membered chelate ring; with an N–doublet separation of 33.2 Hz ($^1J(PC) + {}^3J(PC)$).

We have also studied the interaction of the ligand **1** with $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$. Treatment of the phosphine **1** with 0.5 equiv. of $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$ gave the neutral η^3-methylallylpalladium(II) complex $[(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\{PPh_2CH_2C(Bu^t)=NNPh\}]$ (**7**) in which the phosphine **1** is monodentate through phosphorus. Electrical conductivity measurements of **7** at 20 °C in acetone solution showed it to be a non-electrolyte (molar conductivity, $\Lambda_m = 0.77\ \Omega^{-1}\ mol^{-1}\ cm^2$) [30]. The IR spectrum showed

a band at 3240 cm^{-1} for ν(N–H), and the $^{31}P\{^1H\}$ NMR spectrum showed a singlet at δ 9.4. In the ^1H NMR spectrum, one two *syn*-proton (H_{syn}) of the allyl group absorbed at δ 2.81 (d, $^4J(H_{syn}H_{syn})$ 2.5 Hz) and the other at 4.43 (dd, $^3J(PH)$ 5.0, $^4J(H_{syn}H_{syn})$ 2.5 Hz) whilst one of the *anti*-protons gave a singlet at δ 2.54 and the other (*trans* to phosphorus) a doublet at δ 3.33 with $^3J(PH) = 10.5$ Hz. In the $^1H\{^{31}P\}$ NMR spectrum the CH_2P protons gave an AB pattern with $^2J(HH) = 14.2$ Hz. Dehydrochlorination of this methylallylpalladium(II) chloride **7** with sodium hydroxide gave the neutral chelating complex $[(\eta^3\text{-}2\text{-}MeC_3H_4)\text{-}Pd\{PPh_2CH_2C(Bu^t)=NNPh\}]$ (**8**), containing the deprotonated phosphino *N*-phenylhydrazone ligand. The ^{31}P resonance was a singlet at δ 62.0 with a chelate ring shift ($\Delta\delta \sim$ 53 ppm) when compared to the ^{31}P chemical shift (9.4) of **7**, and the 2-methylallyl group showed similar ^1H NMR properties to that of **7** (see Table 1).

Deprotonation of the phosphino *N*-phenylhydrazone **1** with $LiBu^n$ and treatment of the resultant anion with 1 equiv. of PPh_2Cl gave the diphosphine $Z\text{-}PPh_2CH_2C(Bu^t)=NN(Ph)PPh_2$ (**9**) in 64% yield. This diphosphine **9** was previously prepared by dilithiating the phenylhydrazone of methyl tert-butyl ketone and treating the resultant dianion with 2 equiv. of PPh_2Cl [31]. Treatment of the diphosphine **9** with 0.5 equiv. of $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$ followed by NH_4PF_6 gave the PF_6 salt $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd\{PPh_2CH_2C(Bu^t)=NN(Ph)PPh_2\}]PF_6$ (**10**), which had a molar conductivity (Λ_m) of 141 Ω^{-1} mol^{-1} cm^2 in acetone at 20 °C, typical for a 1:1 electrolyte [30]. The $^{31}P\{^1H\}$ NMR spectrum showed an AB pattern with resonances at δ 81.9 and 30.9, $^2J(PP) = 51$ Hz. In the ^1H NMR spectrum, the two *syn*-protons (H_{syn}) of the allyl group absorbed at δ 3.56 and 4.44 with $^4J(H_{syn}H_{syn}) = 2.4$ Hz, whilst the *anti*-protons gave two doublets at δ 3.10 and 3.48 with $^3J(PH) = 10$ Hz for each proton (Fig. 2). The (CH_2P) methylene protons were non-equivalent and gave an AB pattern in the $^1H\{^{31}P\}$ NMR spectrum with δ 3.90 and 4.29, $^2J(HH) = 12.4$ Hz (Fig. 2). The ^{13}C NMR data agreed well with the proposed structure **10**.

2.1. *Crystal structure of cis-[PdCl$_2$(PPh$_2$CH$_2$C(Bu^t)=NNHPh)$_2$] (5a)*

The molecular structure of complex **5a** is shown in Fig. 1, with atom coordinates in Table 2, and selected bond lengths and angles in Table 3. The structure shows that the tertiary phosphine ligands are monodentate and coordinated to the palladium in mutual *cis*-positions with a P–Pd–P bond angle of 97.4°; the Cl–P–Cl angle is 87.5°. Inspection of the structure suggested that the hydrogen on N(10) was pointing towards Cl(1) and probably interacting with it and that one of the methylene hydrogens on C(7) was similarly interacting with Cl(1). Similar interactions between Cl(2) and H on N(5) and a methylene H on C(2) were also probably occurring. Calculations of H···acceptor (i.e. chlorine) distances using a literature method [32] gave H···Cl distances

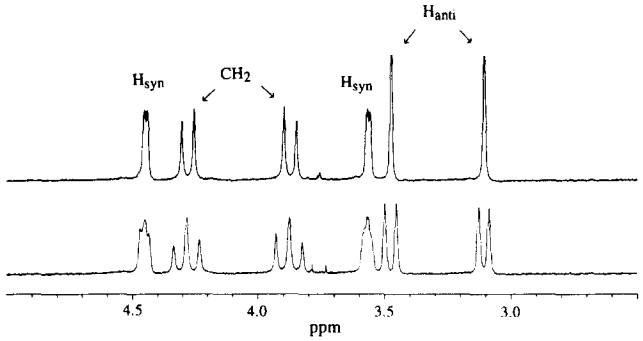


Fig. 2. Part of the proton NMR pattern of compound **10**. Upper, $^1H\{^{31}P\}$ pattern; lower ^1H pattern.

of 2.53···2.62 Å as shown in Table 3. The C–H···Cl and N–H···Cl angles were estimated to be N(5)–H(5)···Cl(2) 171°, N(10)–H(10)···Cl(1) 165°, C(2)–H(2B)···Cl(2) 129° and C(7)–H(7B)···Cl(1) 130°, i.e. two-centre (linear) H bonds are present (see Ref. [33]). Using van der Waals' radii for C, N, H and Cl of 1.70, 1.55, 1.20 and 1.75 Å [34] indicates that the H···Cl distances are 0.35 Å less that the sums of the van der Waals' radii, i.e. there is significant hydrogen bonding to chlorine.

3. Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. IR spectra were recorded using a Perkin-Elmer model 457 grating spectrometer. 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 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz, respectively), a Bruker ARX-250 (operating frequncies for ^1H and ^{13}C of 250.13 and 62.9 MHz, respectively), or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz, respectively). ^1H chemical shifts are relative to tetramethylsilane and ^{31}P shifts are relative to 85% phosphoric acid, and all coupling constants are in Hz. Electron impact and fast atom bombardment mass spectra were recorded on a VG mass spectrometer. For metal complexes m/z values are quoted for ^{35}Cl, ^{98}Mo, ^{106}Pd and ^{195}Pt. IR frequencies ν(C≡O) were determined in dichloromethane solution, ν(N–H) as KBr discs and ν(M–Cl) as Nujol mulls between polyethylene plates.

3.1. *Z-PPh$_2$CH$_2$C(Bu^t)=NNHPh (1)*

A solution containing the phosphino *N,N*-dimethylhydrazone $Z\text{-}PPh_2CH_2C(Bu^t)=NNMe_2$ (6.07 g 18.6 mmol), phenylhydrazine (2.0 cm^3, 2.10 g 19.0 mmol) and acetic acid (1.0 cm^3) in ethanol (25 cm^3) was heated under reflux for 12 h. The required phosphine **1** crystallised out as a white crystalline solid (4.97 g, 78%). *Anal.* Found: C, 76.9; H, 7.3; N, 7.5. Calc. for $C_{24}H_{27}N_2P$: C, 77.0; H, 7.3; N, 7.5%.

Table 2
Fractional non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for molecule **5a** with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} [a]
Pd	546.7(3)	6295.02(10)	5638.2(4)	18.35(12)
Cl(1)	−551.6(12)	6008.2(4)	6614.6(13)	32.2(3)
Cl(2)	1391.7(12)	6579.3(3)	7679.6(13)	28.8(3)
P(1)	1735.6(11)	6575.1(3)	4875.8(13)	20.9(3)
C(111)	1257(4)	7002.0(13)	4463(5)	25.1(12)
C(112)	1777(5)	7223.8(15)	3883(6)	37.5(15)
C(113)	1444(6)	7552(2)	3681(8)	48(2)
C(114)	608(5)	7670(2)	4071(8)	48(2)
C(115)	90(5)	7452(2)	4653(7)	43(2)
C(116)	400(5)	7121.8(14)	4822(6)	33.1(13)
C(121)	2042(4)	6387.8(14)	3531(5)	27.4(12)
C(122)	2516(5)	6069.5(15)	3759(6)	34.3(14)
C(123)	2837(6)	5915(2)	2808(8)	56(2)
C(124)	2674(6)	6074(2)	1637(7)	60(2)
C(125)	2181(6)	6384(2)	1390(6)	56(2)
C(126)	1856(5)	6543(2)	2322(6)	39(2)
C(2)	3169(4)	6662.0(13)	6129(5)	25.3(12)
C(3)	4094(5)	6409.5(15)	6374(5)	28.2(12)
C(31)	5128(5)	6516(2)	6104(7)	38.4(15)
C(32)	5922(7)	6223(2)	6274(10)	65(2)
C(33)	5724(6)	6785(2)	7112(9)	64(2)
C(34)	4814(6)	6658(2)	4694(8)	53(2)
N(4)	4126(4)	6126.7(12)	6907(5)	29.3(11)
N(5)	3229(4)	6038.3(12)	7256(5)	26.5(10)
C(51)	3288(4)	5734.7(13)	7896(5)	28.1(12)
C(52)	4042(5)	5487.6(14)	7890(6)	34.4(14)
C(53)	4047(6)	5189(2)	8509(7)	48(2)
C(54)	3311(6)	5128(2)	9150(7)	52(2)
C(55)	2555(6)	5370(2)	9144(6)	45(2)
C(56)	2535(5)	5675.2(15)	8517(5)	33.2(14)
P(6)	−420.6(11)	6009.1(3)	3728.0(13)	19.7(3)
C(611)	−519(4)	6182.1(14)	2156(5)	28.4(12)
C(612)	−252(5)	6001(2)	1212(5)	32.3(13)
C(613)	−426(6)	6136(2)	−23(6)	44(2)
C(614)	−853(6)	6458(2)	−313(6)	50(2)
C(615)	−1088(6)	6642(2)	613(6)	45(2)
C(616)	−918(5)	6508.0(14)	1843(5)	30.5(13)
C(621)	142(4)	5589.4(13)	3869(5)	23.5(11)
C(622)	1096(5)	5510.3(14)	4969(5)	28.8(12)
C(623)	1529(5)	5188.3(15)	5139(6)	35.6(14)
C(624)	1029(5)	4945.5(15)	4218(6)	38.6(15)
C(625)	75(5)	5019.4(15)	3122(6)	37.3(15)
C(626)	−352(5)	5339.8(14)	2947(5)	30.9(13)
C(7)	−1914(4)	5918.3(13)	3437(5)	23.7(11)
C(8)	−2819(4)	6163.6(14)	2650(6)	26.4(12)
C(81)	−3738(5)	6037(2)	1364(6)	34.4(14)
C(82)	−4378(5)	5759(2)	1745(7)	46(2)
C(83)	−4550(6)	6320(2)	723(7)	55(2)
C(84)	−3234(6)	5909(2)	393(6)	43(2)
N(9)	−2917(4)	6459.2(12)	3042(4)	26.8(10)
N(10)	−2127(4)	6572.1(12)	4227(5)	29.0(11)
C(101)	−2328(4)	6888.5(13)	4627(5)	25.2(12)
C(102)	−2974(5)	7123.1(15)	3728(6)	35.7(14)
C(103)	−3134(6)	7434(2)	4162(8)	48(2)
C(104)	−2661(6)	7520(2)	5484(7)	47(2)
C(105)	−2003(5)	7290(2)	6368(7)	44(2)
C(106)	−1820(5)	6976(2)	5963(6)	35.1(14)

[a] U_{eq} = 1/3 × trace of the orthogonalised U_{ij} matrix.

ν(N–H) = 3320 cm^{-1}. *m/z*: 374 (M^+). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C: 27.2 (1C, d, ^1J(PC) 23.1 CH_2P), 28.8 (3C, s, CMe_3), 38.9 (1C, s, CMe_3), 151.3 (1C, s, C=N).

3.2. *Z-P(=O)Ph$_2$CH$_2$C(Bu^t)=NNHPh (2a)*

A suspension of **1** (443 mg, 1.18 mmol) in acetone (8 cm^3) was treated with an excess of hydrogen peroxide (1.5 cm^3, 30% wt./vol.) at 0 °C, and the resulting solution was allowed to warm to room temperature. After 3 h, the solvent was removed under reduced pressure and n-hexane added to the residue to give the phosphine oxide **2a** as a white solid (423 mg, 91%). *Anal.* Found: C, 72.85; H, 6.6; N, 6.85. Calc. for $C_{24}H_{27}N_2OP$: C, 73.8; H, 6.95; N, 7.2%. ν(N–H) = 3320 cm^{-1}; ν(P=O) (KBr) = 1200 cm^{-1}. *m/z*: 390 (M^+). The carbon analysis was low, possibly due to the presence of water.

3.3. *Z-P(=S)Ph$_2$CH$_2$C(Bu^t)=NNHPh (2b)*

A mixture containing **1** (408 mg, 1.09 mmol) and monoclinic sulfur (56 mg, 1.76 mmol) was reflux in toluene (10 cm^3) for 1 h. The solution was then concentrated to ~2 cm^3 and the residue cooled to −30 °C. The required sulfide **2b** crystallised out as a white solid (364 mg, 81%). *Anal.* Found: C, 70.0; H, 6.8; N, 6.5. Calc. for $C_{24}H_{27}N_2PS$: C, 70.9; H, 6.7; N, 6.9%. ν(N–H) (KBr) = 3340 cm^{-1}. *m/z*: 406 (M^+).

3.4. *[Mo(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NNHPh}] (3)*

A solution containing **1** (916 mg, 2.44 mmol) and [Mo(CO)$_4$(nbd)] (734 mg 2.44 mmol) in benzene (10 cm^3) was put aside for 4 days. The required product **3** deposited as yellow microcrystals (345 mg, 73%). *Anal.* Found: C, 57.85; H, 4.8; N, 4.6. Calc. for $C_{28}H_{27}MoN_2O_4P$: C, 57.7; H, 4.65; N, 4.8%. ν(C≡O) = 2020, 1915, 1860 cm^{-1}; ν(N–H) = 3320 cm^{-1}. *m/z*: 584 (M^+), 528 (M−2CO), 472 (M−4CO). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C: 24.7 (1C, d, ^1J(PC) 5.6, CH_2P), 27.4 (3C, s, CMe_3), 39.4 (1C, s, CMe_3), 166.7 (1C, s, C=N), 207.6 (1C, d, ^2J(PC) 7.6, C≡O), 208.9 (1C, d, ^2J(PC) 10.2, C≡O), 212.2 (1C, d, ^2J(PC) 37.1, C≡O, *trans* to P), 222.1 (1C, d, ^2J(PC) 6.9, C≡O).

3.5. *[Mo(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NNHPh}$_2$] (4)*

A solution containing **1** (317 mg, 0.85 mmol) and [Mo(CO)$_4$(nbd)] (128 mg, 0.42 mmol) was put aside for 24 h. The required product **4** deposited as white microcrystals (210 mg, 52%). *Anal.* Found: C, 64.7; H, 5.7; N, 5.4. Calc. for $C_{52}H_{54}MoN_4O_4P_2$: C, 65.3; H, 5.7; N, 5.85%. ν(C≡O) = 2020, 1925, 1885 cm^{-1}; ν(N–H) = 3320 cm^{-1}. *m/z*: 903 (M+2–2CO), 872 (M−3CO), 844 (M−4CO).

Table 3
Selected bond lengths (Å), short non-bonded contacts (Å) and bond angles (°) for **5a** with e.s.d.s in parentheses

Pd–P(1)	2.2910(14)	Pd–P(6)	2.2924(14)
Pd–Cl(1)	2.3621(14)	Pd–Cl(2)	2.3690(13)
P(1)–C(111)	1.818(5)	P(6)–C(611)	1.805(5)
P(1)–C(121)	1.815(5)	P(6)–C(621)	1.816(5)
P(1)–C(2)	1.876(5)	P(6)–C(7)	1.867(5)
C(2)–C(3)	1.511(8)	C(7)–C(8)	1.522(8)
C(3)–N(4)	1.267(7)	C(8)–N(9)	1.281(7)
C(3)–C(31)	1.529(8)	C(8)–C(81)	1.544(8)
N(4)–N(5)	1.392(7)	N(9)–N(10)	1.388(6)
N(5)–C(51)	1.390(7)	N(10)–C(101)	1.396(7)
N(5)–H(5)	0.80(7)	N(10)–H(10)	0.89(7)
Cl(2)···H(5)	2.57(8)	Cl(1)···H(10)	2.60(7)
Cl(2)···H(2b)	2.615	Cl(1)···H(7b)	2.532
P(1)–Pd–P(6)	97.38(5)	P(1)–Pd–Cl(1)	147.88(5)
P(6)–Pd–Cl(1)	87.09(5)	P(1)–Pd–Cl(2)	88.14(5)
P(6)–Pd–Cl(2)	174.17(5)	Cl(1)–Pd–Cl(2)	87.49(5)
C(2)–P(1)–Pd	116.1(2)	C(7)–P(6)–Pd	115.4(2)
C(3)–C(2)–P(1)	120.2(4)	C(8)–C(7)–P(6)	119.7(4)
N(4)–C(3)–C(2)	124.7(5)	N(9)–C(8)–C(7)	124.1(5)
N(4)–C(3)–C(31)	117.1(5)	N(9)–C(8)–C(81)	117.8(5)
C(2)–C(3)–C(31)	117.9(5)	C(7)–C(8)–C(81)	117.9(5)
C(3)–N(4)–N(5)	117.7(5)	C(8)–N(9)–N(10)	118.8(5)
C(51)–N(5)–N(4)	117.6(5)	N(9)–N(10)–C(101)	115.4(4)
C(51)–N(5)–H(5)	114(5)	C(101)–N(10)–H(10)	115(4)
N(4)–N(5)–H(5)	122(5)	N(9)–N(10)–H(10)	118(4)

3.6. *Cis-[PdCl$_2${PPh$_2$CH$_2$C(Bu^t)=NNHPh}$_2$] (5a)*

A solution containing **1** (867 mg, 2.32 mmol) and [PdCl$_2$(NCPh)$_2$] (444 mg, 1.16 mmol) in dichloromethane (10 cm^3) was put aside for 1 min. This gave the required product **5a** as reddish orange microcrystals (894 mg, 84%). *Anal.* Found: C, 62.35; H, 5.8; Cl, 7.7; N, 6.1. Calc. for $C_{48}H_{54}Cl_2N_4P_2Pd$: C, 62.2; H, 5.9; Cl, 7.7; N, 6.05%. ν(Pd–Cl) (Nujol) = 280, 305 cm^{-1}; ν(N–H) (KBr) = 3220 cm^{-1}. *m/z*: 889 (*M* − Cl), 853 (*M* − Cl − HCl).

3.7. *Cis-[PtCl$_2${PPh$_2$CH$_2$C(Bu^t)=NNHPh}$_2$] (5b)*

A solution containing **1** (519 mg, 1.39 mmol) and [PtCl$_2$(cod)] (519 mg, 1.38 mmol) in dichloromethane (10 cm^3) was put aside for 4 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **5b** as yellow microcrystals (723 mg, 51%). *Anal.* Found: C, 57.05; H, 5.35; Cl, 7.2; N, 5.55. Calc. for $C_{48}H_{54}Cl_2N_4P_2Pt$: C, 56.8; H, 5.4; Cl, 7.0; N, 5.5%. ν(Pt–Cl) = 310, 290 cm^{-1}; ν(N–H) (KBr) = 3250 cm^{-1}. *m/z*: 979 (*M* − 1 − Cl), 942 (*M* − Cl − HCl).

3.8. *Trans-[PtCl$_2${PPh$_2$CH$_2$C(Bu^t)=NNHPh}$_2$] (5c)*

A solution containing **1** (534 mg, 1.39 mmol) and PtCl$_2$(NCMe)$_2$ (244 mg, 0.71 mmol) in dichloromethane (10 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 a yellow solid (499 mg, 70%). *Anal.* Found: C, 56.3; H, 5.25; Cl, 7.3; N, 5.45. Calc. for $C_{48}H_{54}Cl_2N_4P_2Pt$: C, 56.8; H, 5.4; Cl, 7.0; N, 5.5%. ν(Pt–Cl) = 335 cm^{-1}; ν(N–H) = 3250 cm^{-1}. *m/z*: 978 (*M* − Cl), 942 (*M* − Cl − HCl).

3.9. *Cis-[Pt{PPh$_2$CH$_2$C(Bu^t)=NNPh}$_2$] (6)*

A solution of **5b** or **5c** (303 mg, 0.29 mmol) in chloroform (10 cm^3) was treated with an excess of triethylamine (0.1 cm^3, 0.72 mmol) and put aside for 2 days. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give a brown solid (219 mg, 71%). *Anal.* Found: C, 59.45; H, 5.3; N, 5.35. Calc. for $C_{48}H_{52}N_4P_2Pt$: C, 61.2; H, 5.5; N, 5.9%. *m/z*: 941 (M^+). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C: 25.9 (2C, t, $^1J(PC) + {}^3J(PC)$ 33.2, CH_2P), 20.1 (6C, s, CMe_3), 45.3 (2C, s, CMe_3), 160.0 (2C, s, C=N).

3.10. *[(η^3-2-MeC$_3$H$_4$)PdCl{PPh$_2$CH$_2$C(Bu^t)=NNHPh}] (7)*

A solution containing **1** (825 mg, 2.20 mmol) and [{PdCl(η^3-2-MeC$_3$H$_4$)}$_2$] (434 mg, 1.10 mmol) in dichloromethane (10 cm^3) was put aside for 3 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **7** as yellow microcrystals (1.12 g, 87%). *Anal.* Found: C, 58.65; H, 5.8; Cl, 6.45; N, 5.15. Calc. for $C_{28}H_{34}ClN_2PPd$: C, 58.85; H, 6.0; Cl, 6.2; N, 4.9%. ν(N–H) = 3240 cm^{-1}. *m/z*: 571 (*M* + 1), 534 (*M* − HCl).

3.11. [(η^3-2-MeC_3H_4)Pd{$PPh_2CH_2C(Bu^t)$=NNPh}] (8)

A solution of **7** (105 mg, 0.18 mmol) in dichloromethane (5 cm^3) was shaken with an excess of aqueous sodium hydroxide (0.2 cm^3, 23% wt./wt.) and put aside for 1 h. The dichloromethane solution was then washed with water and dried over $MgSO_4$. The solvent was then evaporated to low volume under reduced pressure and n-hexane added to the residue to give a pale yellow solid (70 mg, 75%). *Anal.* Found: C, 62.55; H, 6.10; N, 5.45. Calc. for $C_{28}H_{33}N_2PPd$: C, 62.9; H, 6.30; N, 5.20%. *m/z*: 534 (M^+).

3.12. Z-$PPh_2CH_2C(Bu^t)$=NN(Ph)PPh_2 (9)

A solution of $LiBu^n$ (1.0 cm^3 1.60 mmol) in n-hexane was added to a solution of **1** (529 mg, 1.41 mmol) in dry tetrahydrofuran (10 cm^3) at −15 °C. After 1 h a solution of chlorodiphenylphosphine was added with stirring and the resultant solution was allowed to warm to room temperature. The solvent was then evaporated and the residue crystallised from methanol–ether (4:1) giving the required diphosphine **9** (556 mg, 64%). This diphosphine was identical to that described previously [31], which was prepared by a different method.

3.13. [(η^3-2-MeC_3H_4)Pd{$PPh_2CH_2C(Bu^t)$=NN-(Ph)PPh_2}]PF_6 (10)

A solution containing **9** (265 mg, 0.42 mmol) and [{PdCl(η^3-2-MeC_3H_4)}$_2$] (93 mg, 0.21 mmol) in dichloromethane (8 cm^3) was put aside for 40 min and NH_4PF_6 (0.12 g, 0.73 mmol) in methanol (4 cm^3) was added. The solvent was then removed under reduced pressure and water was added to the residue to give a pink solid (300 mg, 73%). *Anal.* Found: C, 54.55; H, 4.8; N, 3.1. Calc. for $C_{40}H_{43}F_6N_2P_3Pd$: C, 55.5; H, 5.0; N, 3.2%. *m/z*: 720 ($M-PF_6$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ_C: 21.8 (1C, s, *Me*C_3H_4), 27.3 (3C, s, C*Me*$_3$), 28.0 (1C, d, ^1J(PC) 19.8, CH_2P), 38.3 (1C, s, *C*Me_3), 75.9 (1C, d, ^2J(PC) 35.6, =CH_2), 74.7 (1C, d, ^2J(PC) 31.7, =CH_2), 138.2 (1C, s, ^2J(PC) 6.0 Hz, Me*C*Pd), 143.5 (1C, s, C=N).

3.14. Single crystal X-ray diffraction analysis of 5a

All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω scan mode using graphite monochromated Mo Kα X-radiation (λ = 71.069 pm). The data set was corrected for absorption using azimuthal ψ-scans (max. and min. transmission factors 0.4350 and 0.5946, respectively).

The structure was determined by heavy atom methods using SHELXS-86 [35] and was refined by full-matrix least-squares (based on F^2) using SHELXL-93 [36]. All data were used in the refinement. Three independent molecules of CH_2Cl_2 (of full, half and quarter occupancy, respectively) were located in the assymmetric part of the unit cell. All non-hydrogen atoms were refined with anisotropic thermal parameters apart from those of the 0.25 occupancy dichloromethane solvate molecule which were assigned isotropic thermal parameters. Restraints were applied to the phosphine phenyl groups so each group remained flat with overall C_{2v} symmetry. The amino hydrogen atoms were located on a Fourier difference synthesis. Their positional coordinates were free and each was assigned a fixed isotropic thermal parameter of $1.2U_{eq}$ of the parent nitrogen atom. All other hydrogen atoms were constrained to calculated positions (C–H = 0.93, 0.96, 0.97 and 0.99 Å for phenyl, methyl, methylene and methine hydrogen atoms, respectively) with fixed isotropic thermal parameters of nU_{eq} of the parent carbon atom where n was 1.5 for methyl hydrogens and 1.2 for all others. The weighting scheme $w=[\sigma^2(F_o^2)+(0.0390P)^2+33.7828P]^{-1}$ (where $P=(F_o^2+2F_c^2)/3$) was used. Apart from a small ripple close to one of the chlorine atoms of the 0.25 occupancy CH_2Cl_2 molecule, the final Fourier difference synthesis was flat and showed no features of chemical significance (max. and min. residual densities 1.509 and −0.914 e $Å^{-3}$). Final non-hydrogen atomic coordinates are given in Table 2. An ORTEP [37] diagram of **5a** is given in Fig. 1.

Crystal data. $C_{48}H_{54}Cl_2N_4P_2Pd \cdot 1.75CH_2Cl_2$, 0.76 × 0.61 × 0.49 mm, M = 1074.89 (includes solvate molecules), monoclinic, space group $P2_1/c$, a = 12.900(2), b = 40.083(6), c = 10.8779(11) Å, β = 111.891(7)°, V = 5219.1(12) $Å^3$, Z = 4, D_x = 1.368 Mg m^{-3}, μ = 0.375 mm^{-1}, $F(000)$ = 2214.

Data collection. $4.0 < 2\theta < 50.0°$; scan widths 1.05 + α-doublet splitting, scan speeds 1.0–8.0° min^{-1}. No. of data collected = 10 256; no. of unique data, n = 9188; no. with $F_o > 4.0\sigma(F_o)$ = 7558; $R_{int}\{=\Sigma|F_o^2-F_o^2(\text{mean})|/\Sigma[F_o^2]\}$ = 0.0543; $R_{sig}\{=\Sigma\sigma[F_o^2]/\Sigma[F_o^2]\}$ = 0.0227; T = 200 K.

Structure refinement. No. of parameters, p = 592; $R_1\{=\Sigma||F_o|-|F_c||/\Sigma|F_o|\}$ = 0.0535; $wR_2\{=(\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}\}$ = 0.1750; goodness of fit $s\{=\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}\}$ = 1.193; max. Δ/σ = 0.02, mean Δ/σ = 0.000.

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