Diphenylphosphinomethyl t-butyl ketone *N*-diphenylphosphino-*N*-phenylhydrazone $PPh_2CH_2C(Bu^t)=N\text{–}N(Ph)PPh_2$ and its complexes with chromium(0), molybdenum(0), tungsten(0), palladium(II) and platinum(II)

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Abstract

The diphosphine $PPh_2CH_2C(Bu^t)=N\text{–}N(Ph)PPh_2$, which is of a new type, was prepared by treating methyl t-butyl ketone phenylhydrazone with two mole equivalents of $LiBu^n$, followed by PPh_2Cl. This diphosphine was converted to the corresponding dioxide **2a** and disulfide **2b**. Treatment of $[M(CO)_4(nbd)]$ (M = Mo, W or Cr; nbd = norbornadiene) with the diphosphine **1** gave the corresponding tetracarbonyl complexes $[M(CO)_4\{PPh_2CH_2C(Bu^t)=N\text{–}N(Ph)PPh_2\}]$ (M = Mo, **3a**; W, **3b**; Cr, **3c**) in which the diphosphine acts as a bidentate ligand. The corresponding palladium (**4a**) and platinum (**4b**) chelate complexes of type $[MCl_2\{PPh_2CH_2(Bu^t)=N\text{–}N(Ph)PPh_2\}]$ were prepared by treating **1** with $[PdCl_2(NCPh)_2]$, $[PtCl_2(cod)]$ or $[PtCl_2(NCPh)_2]$. $[PtMe_2\{PPh_2CH_2C(Bu^t)=N\text{–}N(Ph)PPh_2\}]$ (**4d**) was obtained from the reaction of **1** with $[PtMe_2(cod)]$. Methathesis of **4b** with NaI gave the corresponding iodide **4c**. Treatment of **4b** with concentrated solution of ammonia gave the salt, $[Pt(NH_3)_2\{PPh_2CH_2C(Bu^t)=N\text{–}N(Ph)PPh_2\}]Cl_2$ (**4e**). NMR spectral data are given and discussed in detail.

Introduction

In a previous paper [1] we showed that (1*R*)-(+) camphor-dimethylhydrazone could be converted to the 3-*exo*-diphenylphosphino derivative and the chemistry of this phosphine as a ligand for Group 6 metal carbonyls [1] and also platinum and palladium [2] was studied. We also extended this type of chemistry to a diphosphine generated from methyl t-butyl ketone azine [3].

There is increasing interest in the use of phosphorus donor ligands in chemistry including chelating diphosphines [4–8]. In the present paper we describe a new type of diphosphine prepared from a phenylhydrazone of methyl t-butyl ketone by dilithiation followed by treatment with PPh_2Cl. Although many types of ligands for transition metals have been derived from hydrazine or its derivatives [4] including hydrazones, this appears to be the first time that a bidentate diphosphorus ligand with one phosphorus bonded to nitrogen has been prepared from a hydrazone: many analogues of our ligand could probably be prepared. We described some complexes of this new ligand with chromium(0), molybdenum(0), tungsten(0), palladium(II) and platinum(II) and have also described the diphosphine dioxide and diphosphine disulfide (see Scheme 1).

Results and discussion

The various syntheses and reactions are summarized in Scheme 2. Diphenylphosphinomethyl t-butyl ketone *N*-diphenylphosphino-*N*-phenylhydrazone (**1**) was obtained in 84% yield by treating the phenylhydrazone of methyl t-butyl ketone with 2 equiv. of $LiBu^n$ at −15 °C followed by 2 equiv. of PPh_2Cl. The $^{31}P\{^1H\}$ NMR spectrum for this new diphosphine shows two singlet resonances; one at 60.0 (N-bonded) and the other at −16.9 (C-bonded) ppm (Table 1). The diphosphine **1** was converted into the corresponding dioxide **2a** and disulfide **2b** by reacting it with hydrogen peroxide or monoclinic sulfur, respectively. Their $^{31}P\{^1H\}$ resonances are singlets at 31.9, 23.6 (oxide) and 74.3, 34.3 (sulfide) ppm (Table 1). The methylene protons in the diphosphine **1** and its oxide **2a** and sulfide derivatives **2b** are doublets $^2J(PH) = 3.6$ Hz increasing to 15.4 (oxide) and 15.1 (sulfide) (Table 2). We have investigated this diphosphine **1** as a ligand for Group 6 metal carbonyls.

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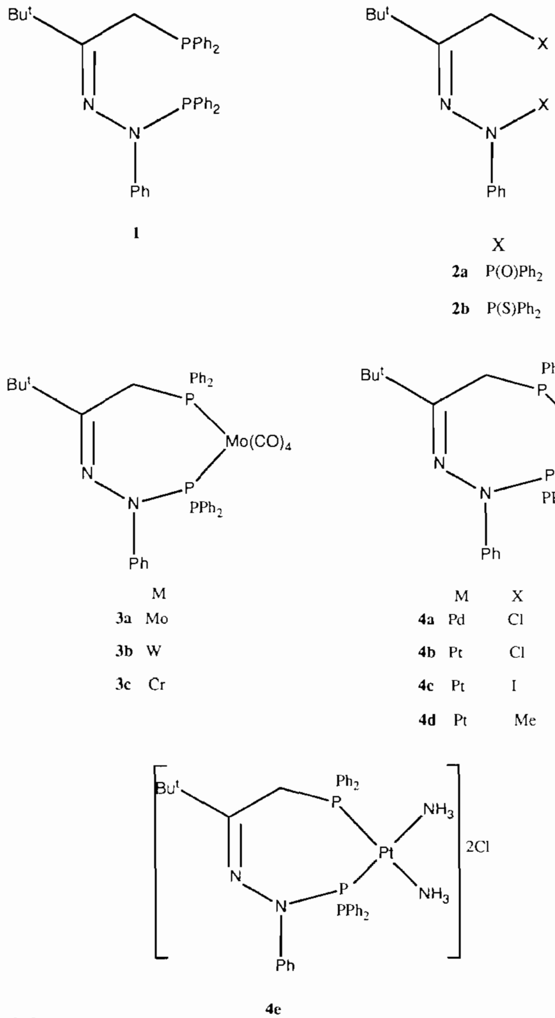
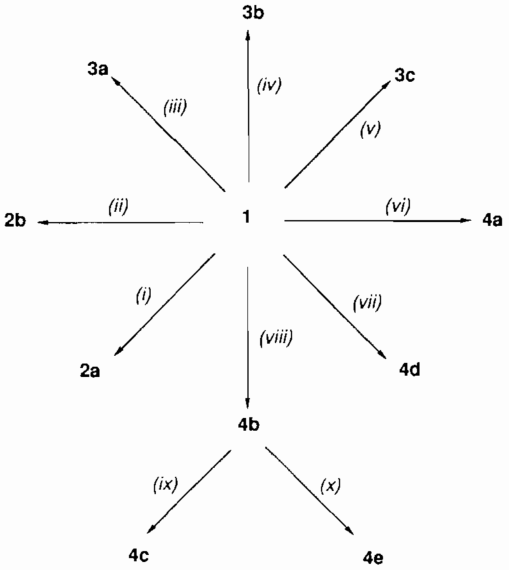


Scheme 1.



Scheme 2. (i) H_2O_2, (ii) monoclinic S, (iii) $[Mo(CO)_4(nbd)]$, (iv) $[W(CO)_4(nbd)]$ or $[W(CO)_6]$, (v) $[Cr(CO)_4(nbd)]$, (vi) $[PdCl_2(NCPh)_2]$, (vii) $[PtMe_2(cod)]$, (viii) $[PtCl_2(cod)]$ or $[PtCl_2(NCPh)_2]$, (ix) NaI, (x) ammonia solution.

TABLE 1. $^{31}P\{^1H\}$ NMR data[a]

	$\delta(P_A)$[b]	$\delta(P_B)$	$^2J(PP)$	$^1J(PtP_A)$	$^1J(PtP_B)$	$^1J(WP_A)$	$^1J(WP_B)$
1	60	−16.9					
2a	31.9	23.6					
2b	74.3	34.3					
3a	99.1	36.4	33				
3b	77.6	17.7	31			266	248
3c	118.2	54.8	46				
4a[c]	74.7	36.1	44				
4b[c]	51.1	13.3		4096	3297		
4c[d]	46.6	6.3		3889	3571		
4d	75.4	20.7	15	2152	1941		
4e[e]	88.6	55.0	26	3572	3897		

[a] Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4. In $CDCl_3$ unless stated otherwise. [b] N-bonded phosphorus. [c] In CD_2Cl_2. [d] In CD_3COCD_3. [e] In EtOH.

Treatment of $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) with the diphosphine **1** gave the hoped for tetracarbonyl product **3a** with the ligand chelating both phosphoruses in a seven-membered ring. The $^{31}P\{^1H\}$ NMR spectrum of **3a** showed an AX pattern (Table 1). The small value of $^2J(PP)$ (33 Hz) is typical of a cisoid arrangement.

In the $^{13}C\{^1H\}$ NMR spectrum of **3a** (see 'Experimental') the Bu^t group appears as two singlets, at 28.1 ppm for the methyl carbons and at 40.0 ppm for the quaternary carbon. The methylene carbon resonance at 32.4 ppm is a doublet ($^1J(PC) = 10.6$ Hz). The carbon atom of the C=N group also couples only to one phosphorus ($^2J(PC) = 5.9$ Hz). The resonance due to two carbonyl groups (*cis* to both phosphorus groups) overlap with each other and the other two carbonyl groups (both *trans* to phosphorus) are well separated (see 'Experimental').

In the ^1H NMR spectrum the methylene protons in **3a** are equivalent with $^2J(PH) = 11.4$ Hz and $^4J(PH) = 1.0$ Hz. The carbonyl frequencies in the IR spectrum (Table 3) and successive loss of one, three and four carbonyl groups from the parent molecular ion in the mass spectrum of the complex are in agreement with a tetracarbonyl. This tetracarbonyl complex **3a** was also made by heating molybdenum hexacarbonyl with **1**. The absence of formation of any five-membered chelate ring (coordination of the $-CH_2PPh_2$ group and nitrogen atom in the C=N group) in this reaction could be evidence that the configuration around the C=N in the ligand **1** is probably *Z*, as shown in Scheme 2. We have already shown by spectral and X-ray and crystallographic data that 3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone also has the *Z*-configuration around C=N in both ligand and its six-membered ring chelate, and *E*-configuration in its five-membered ring chelates (coordination of C=N nitrogen) [1].

TABLE 2. Proton NMR data[a]

	δ(Bu^t)	δ(CH$_2$)
1	0.99 (9H, s)	2.5 (2H, d, ^2J(PH) 3.6)
2a	0.98 (9H, s)	3.5 (2H, d, ^2J(PH) 15.4)
2b	0.87 (9H, s)	3.6 (2H, d, ^2J(PH) 15.1)
3a	0.85 (9H, s)	4.0 (2H, d, ^2J(PH) 11.4, ^4J(PH) 1.0)
3b	0.84 (9H, s)	4.2 (2H, d, ^2J(PH) 11.4)
3c	0.82 (9H, s)	3.9 (2H, dd, ^2J(PH) 11.7, ^4J(PH) 1.0)
4a[b]	0.94 (9H, s)	3.6 (2H, dd, ^2J(PH) 14.4, ^4J(PH) 1.9)
4b[b, c]	0.90 (9H, s)	3.9 (2H, dd, ^2J(PH) 14.2, ^4J(PH) 1.2)
4c[d]	0.79 (9H, s)	3.7 (2H, dd, ^2J(PH) 14.4, ^4J(PH) 1.1)
4d[e]	0.82 (9H, s)	4.1 (2H, br, ^2J(PH) 14.4)
4e[f]	0.83 (9H, s)	4.17 (2H, dd, ^2J(PH) 13.8, ^4J(PH) 1.2)

[a] Recorded at 100 MHz. Chemical shifts in ppm relative to SiMe$_4$. Solvent CDCl$_3$, unless stated otherwise. s = singlet, d = doublet, dd = doublet of doublets, br = broad. [b] In CD$_2$Cl$_2$. [c] $^3J(Pt\text{–}CH_2) = 36.1$ Hz. [d] $^3J(Pt\text{–}CH_2) = 37.1$ Hz. [e] $^3J(Pt\text{–}CH_2) = 36.8$ Hz, δ 0.7, 1.0 ppm (Pt*Me*) ^3J(PMe) = 7.5, 5.6 Hz, $^2J(PtCH_3) = 60.0$, 56.2 Hz. [f] $^3J(Pt\text{–}CH_2) = 36$ Hz; the NH$_3$ groups gave a broad singlet at δ = 2.9 ppm.

TABLE 3. IR data[a]

	ν(C=N)	ν(C≡O)	ν(M–Cl)
1	1590s		
2a[b]	1600s		
2b	1600m		
3a	1585m	2025, 1825sh, 1800	
3b	1590m	2015, 1815sh, 1800	
3c	1580m	2010, 1820sh, 1800	
4a	1585m		300, 285
4b	1600m[c]		325, 300
4c	1600m[c]		
4d	1600m[c]		
4e	1600m[c]		

[a] In cm^{-1} in CH$_2$Cl$_2$, unless stated otherwise. [b] ν(P=O) = 1200 (Nujol). [c] KBr disc.

The corresponding tungsten complex **3b** was prepared in a similar manner, from [W(CO)$_4$(nbd)] or [W(CO)$_6$] and the chromium complex **3c** from [Cr(CO)$_4$(nbd)]. The formation of a similar seven-membered ring chelate [W(CO)$_4${PPh$_2$CH$_2$C(Ph)=N–N(H)PPh$_2$}] by means of a four- to seven-membered expansion has already been achieved in this laboratory through a different route by reacting W(CO)$_4${Ph$_2$PCH(COPh)PPh$_2$}] with hydrazine hydrate [9].

We have also prepared some complexes of ligand **1** with palladium(II) and platinum(II). Treatment of diphosphine **1** with [PdCl$_2$(NCPh)$_2$] gave the chelate complex [PdCl$_2${PPh$_2$CH$_2$C(Bu^t)=N–N(Ph)PPh$_2$] (**4a**) in high yield; details are given in 'Experimental'. This palladium complex was characterized by elemental analysis (C, H, N and Cl), the ^{31}P{^{1}H} NMR spectrum, which showed an AX pattern ^2J(PP) = 44 Hz (Table 1); and an IR band at 1585 cm^{-1} assigned to ν(C=N) and two bands at 300 and 285 cm^{-1} assigned to ν(Pd–Cl) (Table 3) indicative of a *cis*-PdCl$_2$ arrangement.

In the ^{1}H NMR spectrum of **4a**, the methylene protons gave doublet of doublets centered at 3.6 ppm (^2J(PH) = 14.4 Hz, ^4J(PH) = 1.9 Hz) (Table 2). We have also made the dichloro-platinum complex **4b** by treating ligand **1** with either [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) or [PtCl$_2$(NCPh)$_2$]. The IR spectrum showed two bands due to ν(Pt–Cl), at 325 and 300 cm^{-1}. Although the ^{31}P{^{1}H} NMR spectrum showed two singlet resonances, this must be because ^2J(PP) is very close to zero; the two values for ^1J(Pt–P) are 4096 and 3297 Hz. The ^{13}C{^{1}H) and ^{1}H NMR spectra clearly show the formation of a seven-membered chelate ring. In the proton NMR spectrum the methylene protons show coupling to both phosphoruses (^2J(PH) = 14 Hz, ^4J(PH) = 1 Hz) (Table 2). The ^{13}C{^{1}H} NMR spectrum (see 'Experimental'), shows a methylene carbon doublet (^1J(PC) = 34.2 Hz) and the C=N carbon couples with both phosphorus nuclei to give a doublet of doublets (^2J(PC) = 7.4, ^3J(PC) = 5.2 Hz). Treatment of the dichloro complex **4b** with NaI gave the diiodo complex **4c**. The spectral data for **4c** were very similar to those of the dichloro complex **4b**. When the ligand **1** was treated with PtMe$_2$(cod) the hoped for chelate PtMe$_2${PPh$_2$CH$_2$C(Bu^t)=N–N(Ph)PPh$_2$} (**4d**) was formed. The ^{31}P{^{1}H} NMR spectrum of this dimethylplatinum(II) complex showed an AX pattern with ^2J(PP) = 15 Hz and the ^{195}Pt–^{31}P coupling constants were ^1J(Pt–P) = 2092 and 1881 Hz, indicative of a *cis*-PtMe$_2$ arrangement. Treatment of the dichloro-platinum complex **4b** with ammonia gave [Pt(NH$_3$)$_2$-{PPh$_2$CH$_2$C(Bu^t)=N–N(Ph)PPh$_2$]Cl$_2$ (**4e**) which on addition of dilute hydrochloric acid was converted back to the starting chelate **4b**. The ^{31}P{^{1}H} NMR spectrum of this complex **4e** shows an AX pattern with ^2J(PP) = 26 Hz. The Pt–P coupling constants ^1J(Pt–P) were 1518 and 1192 Hz. In the ^{1}H NMR spectrum the methylene protons couple to both phosphorus nuclei (^2J(PH) = 13.8 Hz, ^4J(PH) = 1.2 Hz) (Table 2).

Experimental

All the reactions were carried out in an atmosphere of dry nitrogen or argon. Tetrahydrofuran, benzene and toluene were distilled from sodium and benzophenone under argon. NMR spectra were recorded using a JEOL FX-90 Q spectrometer (operating frequencies for ^{1}H and ^{31}P of 89.5 and 36.2 MHz, respectively), a JEOL FX-100 spectrometer (operating frequencies for ^{1}H and ^{31}P of 99.5 and 40.25 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^{1}H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz, respectively). ^{1}H and ^{13}C shifts are relative to tetramethylsilane and

^{31}P shifts are relative to 85% phosphoric acid. Mass spectra were recorded using a VG Autospec with 8 kv acceleration. Microanalyses were carried out in the microanalytical laboratory of Leeds University chemistry department.

Preparation of $PPH_2CH_2C(Bu^t){=}N{-}N(Ph)PPh_2$ *(1)*

A solution of LiBu^n (65 cm^3, 0.10 mol) in n-hexane was added to a solution of $CH_3(Bu^t)C{=}NNHPh$ (9.5 g, 0.05 mol) in dry tetrahydrofuran (100 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 crystallized from methanol–ether (4:1) giving the required diphosphine **1** as colourless microcrystals (23.5 g, 84%), m.p. 140 °C. *Anal.* Found: C, 77.4; H, 6.6; N, 5.0. Calc. for $C_{36}H_{36}N_2P_2$: C, 77.45; H, 6.5; N, 5.0%. Mass spectrum (EI): *m/z* 558 (M^+).

Conversion of 1 into the corresponding diphosphine dioxide ***2d***

A suspension of **1** (0.56 g, 1 mmol) in acetone (8 cm^3) was treated with an excess of hydrogen peroxide (0.7 ml, 30% wt./vol.) at 0 °C. The solution was allowed to warm at room temperature and stirred for 30 min. The acetone was evaporated and the product was extracted into diethyl ether. The ether extract was washed with water and dried ($MgSO_4$). Evaporation of the solvent followed by crystallization of the residue from ethanol–hexane gave the corresponding dioxide **2a** (0.45 g, 76%). *Anal.* Found: C, 72.75; H, 6.35; N, 4.55. Calc. for $C_{36}H_{36}N_2O_2P_2$: C, 72.2; H, 6.15; N, 4.7%. Mass spectrum (EI): *m/z* 590 (M^+).

Conversion of 1 into the corresponding diphosphine disulfide ***2b***

A mixture of **1** (0.28 g, 0.5 mmol) and monoclinic sulfur (48 mg, 1.5 mmol) was refluxed in toluene (8 cm^3) for 1 h. Concentration of the solvent gave the required disulfide **2b** as white needles (0.28 g, 93%). *Anal.* Found: C, 69.35; H, 5.85; N, 4.4. Calc. for $C_{36}H_{36}N_2P_2S_2$: C, 69.4; H, 5.8; N, 4.5%. Mass spectrum (EI): *m/z* 622 (M^+).

Preparation of $[Mo(CO)_4\{PPH_2CH_2C(Bu^t){=}N{-}N(Ph)PPh_2\}]$ *(3a)*

(*i*) *From* $[Mo(CO)_4(nbd)]$. A solution of the hydrazone diphosphine **1** (0.22 g, 0.4 mmol) and $[Mo(CO)_4(nbd)]$ (0.12 g, 0.4 mmol) in benzene (7 cm^3) was refluxed for 15 min and then concentrated to a low volume (*c.* 2 cm^3). Addition of methanol then gave the required product **3c** as yellow microcrystals (0.29 g, 95%). *Anal.* Found: C, 62.55; H, 4.4; N, 3.45. Calc. for $C_{40}H_{36}N_2O_4MoP_2$: C, 62.6; H, 4.4; N, 3.6%. Mass spectrum (FAB): *m/z* 766 (M^+), 738 (*M*-CO), 682 (*M*-3CO) and 654 (*M*-4CO).

(*ii*) *From* $[Mo(CO)_6]$. A mixture of molybdenum hexacarbonyl (0.26 g, 1.0 mmol) and the diphosphine **1** (0.55 g, 1 mmol) in n-decane (10 cm^3) was refluxed for 30 min and then allowed to cool to *c.* 20 °C. The product **3a** was filtered off, yield 0.45 g (60%). $^{13}C\{^1H\}$ NMR data: δC ($CDCl_3$): 28.1 (3C, s, CMe_3), 32.4 (1C, d, ^1J(PC) 10.6 Hz, CH_2), 40.0 (1C, s, CMe_3), 180.5 (1C, d, ^2J(PC) 5.99 Hz, C=N), 208.5 (2C, broad multiplet, 2C≡O *cis* to both phosphorus groups), 213.3 (1C, dd, ^2J(PC) 26.2, 8.0 Hz, C≡O), 215.99 (1C, dd, ^2J(PC) 28.8, 9.1 Hz, C≡O).

Preparation of $[W(CO)_4\{PPh_2CH_2C(Bu^t){=}N{-}N(Ph)PPh_2\}]$ *(3b)*

(*i*) *From* $[W(CO)_4(nbd)]$. A solution of **1** (0.22 g, 0.4 mmol) in benzene (10 cm^3) was treated with $[W(CO)_4(nbd)]$ (0.16 g, 0.4 mmol) and the mixture refluxed for 4 h. The solution was then concentrated and diethyl ether added. The microcrystalline product (**3b**) was filtered off (yield 0.28 g, 82%). *Anal.* Found: C, 56.0; H, 4.05; N, 3.1. Calc. for $C_{40}H_{36}N_2O_4P_2W$: C, 56.25; H, 4.2; N, 3.3%. Mass spectrum (FAB): *m/z* 854 (M^+), 826 (*M*-CO), 798 (*M*-2CO), 770 (*M*-3CO), 742 (*M*-4CO).

(*ii*) *From* $[W(CO)_6]$. The above reaction was repeated using $W(CO)_6$ in n-decane (8 cm^3). The mixture was refluxed for 2 h. On cooling, the required product (**3b**) crystallized out and was filtered off and washed with light petroleum (b.p. 40–60 °C) etc. (yield 0.20 g, 64%).

Preparation of $[Cr(CO)_4\{PPh_2CH_2C(Bu^t){=}N{-}N(Ph)PPh_2\}]$ *(3c)*

A mixture of the hydrazonediphosphine (0.28 g, 0.5 mmol) and $[Cr(CO)_4(nbd)]$ (0.13 g, 0.5 mmol) in benzene (10 cm^3) was refluxed for 15 h. The solvent was then evaporated. Recrystallization of the residue from benzene–methanol gave the required product **3c** as microcrystals (yield 0.30 g, 83%). *Anal.* Found: C. 66.45; H, 5.0; N, 3.85 Calc. for $C_{40}H_{36}N_2O_4CrP_2$: C, 66.5, H, 5.0; N, 3.9%. Mass spectrum (FAB): *m/z* 722 (M^+), 638 (*M*-3CO), 610 (*M*-4CO).

Preparation of $[PdCl_2\{PPh_2CH_2C(Bu)^t{=}N{-}N(Ph)PPh_2\}]$ *(4a)*

A solution of the hydrazone-diphenylphosphine **1** (0.22 g, 0.4 mmol) in dichloromethane (10 cm^3) was mixed with a solution of $[PdCl_2(NCPh)_2]$ (0.16 g, 0.4 mmol) in dichloromethane (10 cm^3) and the mixture stirred for 15 min. The solution was then concentrated by evaporation to *c.* 3 cm^3). Addition of ether (5 cm^3) to the residue gave the required product **4a** as yellow microcrystals (0.26 g, 88%), *Anal.* Found: C, 58.9; H, 5.1; Cl, 9.65; N, 3.85. Calc. $C_{36}H_{36}Cl_2N_2PPd$: C, 58.75;

H, 4.95; Cl, 9.65; N, 3.8%. Mass spectrum (EI): *m/e* 700 (*M*-Cl), 665 (*M*-2Cl).

Preparation of *$[PtCl_2\{PPh_2CH_2C(Bu^t)=N-N(Ph)PPh_2\}]$ (**4b**)*

(*i*) *From* $[PtCl_2(cod)]$. A solution of **1** (0.22 g, 0.4 mmol) and $[PtCl_2(cod)]$ (0.15 g, 0.4 mmol) in chloroform (15 cm^3) was stirred at room temperature for 15 min. The solvent was then concentrated by evaporation and ethanol (10 cm^3) added. The resulting white microcrystals were filtered off (yield 0.31 g, 94%). *Anal.* Found: C, 47.1; H, 3.85; Cl, 18.1; N, 3.3. Calc. for $C_{36}H_{36}Cl_2N_2P_2Pt\cdot0.95CHCl_3$: C, 47.3; H, 3.95; Cl, 18.3; N, 2.98%. Mass spectrum (FAB): *m/z* 824 (M^+), 789 (*M*-Cl), 754 (*M*-2Cl).

(*ii*) *From* $[PtCl_2(NCPh)_2]$. A similar reaction was performed using $[PtCl_2(NCPh)_2]$ in CH_2Cl_2 (20 cm^3). Work up as above gave the required product **4b** in 91% yield. $^{13}C\{^1H\}$ NMR data: δC ($CDCl_3$): 28.4 (3C, s, CMe_3), 32.1 (1C, d, ^1J(PC) 34.2 Hz, CH_2), 39.6 (1C, d, ^3J(PC) 2.1 Hz, CMe_3), 180.0 (1C, dd, ^2J(PC) 7.4 Hz, ^3J(PC) 5.2 Hz, C=N).

Preparation of *$[PtI_2\{PPh_2CH_2C(Bu^t)=N-N(Ph)PPh_2\}]$ (**4c**)*

A solution of **4b** (0.16 g, 0.2 mmol) in acetone was treated with an excess of NaI (0.3 g, 2 mmol) at 20 °C for 1 h. The solvent was then evaporated and the residue extracted with chloroform. The extract was evaporated etc. to give the required product as yellow microcrystals (0.18 g, 89%) from acetone–ethanol. *Anal.* Found: C, 42.6; H, 3.45; N, 2.75. Calc. for $C_{36}H_{36}I_2N_2P_2Pt$: C, 42.9; H, 3.6; N, 2.8%. Mass spectrum (FAB): *m/z* 1007 (M^+), 881 (*M*-I), 755 (*M*-2I).

Preparation of *$PtMe\{PPh_2CH_2C(Bu^t)=N-N(Ph)PPh_2\}]$ (**4d**)*

A solution of the diphosphine **1** (0.22 g, 0.4 mmol) in CH_2Cl_2 (5 cm^3) was treated with $[PtMe_2(cod)]$ (0.13 g, 0.4 mmol) at room temperature for 30 min. The solvent was then concentrated by evaporation to *c.* 2 cm^3 and n-hexane (2 cm^3) was added. The resulting white microcrystals of the required product were filtered off (yield 0.26 g, 82%). *Anal.* Found: C, 58.35; H, 5.1; N, 3.85. Calc. for $C_{38}H_{42}N_2P_2Pt$: C, 58.2; H, 5.4; N, 3.6%. Mass spectrum (EI): *m/z* 783 (M^+), 768 (M-CH_3), 753 (M-$2CH_3$).

Preparation of *$[Pt(NH_3)_2\{PPh_2CH_2C(Bu)^t=N-N(Ph)PPh_2\}]$ (**4e**)*

A suspension of the dichloro complex **4b** (0.33 g, 0.4 mmol) in ethanol (15 cm^3) was treated with an excess of concentrated ammonia solution (0.2 cm^3, 35% wt./vol.) at 20 °C. The yellowish orange solution was then concentrated and cooled to give the required product **4e** as yellow–orange microcrystals (0.20 g, 50%). Mass spectrum (EI): *m/z* 823 (*M*-Cl), 788 (*M*-2Cl), 754 (M-2Cl-$2NH_3$). The corresponding tetrafluoroborate salt was obtained by addition of an ethanolic solution of ammonium tetrafluoroborate (0.25 mmol, 26 mg) to a solution of the dichloro complex (**4e**) (0.1 mmol, 86 mg) in ethanol (3 cm^3) at 20 °C. The required product was obtained (37 mg, 40%). The fluoroborate salt was purified by recrystallization using chloroform–ethanol (1:3). *Anal.* Found: C, 44.3; H, 3.7; N, 5.55. Calc. for $C_{36}H_{42}B_2F_8N_4P_2Pt\cdot0.4CHCl_3$: C, 44.3; H, 4.2; N, 5.55%.

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