3-Diphenylphosphino-(1*R*)-(+)-camphor Dimethylhydrazone Complexes with Platinum(II) and Palladium(II)†

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Treatment of the *Z-exo*-phosphine $PPh_2C_{10}H_{15}NNMe_2$ **1a** with $[PdCl_2(NCPh)_2]$ or $Na_2[PdCl_4]\cdot 4H_2O$ gives the compound $[PdCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2a** with the PPh_2 group *exo* and the $C{=}NNMe_2$ configuration *Z*, *i.e.* a six-membered ring chelate complex. The corresponding platinum complex **2d** was made from **1a** and $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene). Metathesis of complex **2a** or **2d** with LiBr, or **2a** with NaI, gave the corresponding bromides or iodide. Treatment of **2d** with $AgNO_3$ gave the mononitrato complex $[PtCl(ONO_2)(PPh_2C_{10}H_{15}NNMe_2)]$ **2f**. Treatment of $[PtMe_2(cod)]$ with **1a** gave $[PtMe_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2g**. The *exo*-phosphine **1a** when treated with acetic acid or hot sodium ethoxide solution was partially converted into a mixture with the corresponding *endo*-phosphine **1b**. Treatment of $[PtCl_2(cod)]$ with the **1a–1b** mixture gave a mixture of the *Z-exo-/endo*-chelate complexes $[PtCl_2(PPh_2C_{10}H_{15}NNMe_2)]$; similar treatment of $[PdCl_2(NCPh)_2]$ or $[PtMe_2(cod)]$ gave the corresponding *exo-/endo*-complexes. Treatment of **2d** with hydrogen chloride gave a new (protonated) species which with ethanol gave the *exo-/endo*-mixture **2d–3a**. The palladium complex **2a** with hydrogen chloride followed by methanol gave **2a–3b**. and another complex formulated as *E-exo*-$[PdCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **5**. Treatment of **2d** with an excess of LiMe gave a new species formulated as an anion $[PtMe_2(PPh_2C_{10}H_{14}NNMe_2)]^-$ **4**, which with methanol gave the *exo-/endo*-mixture **2g–3c**. Proton, ^{13}C-{^1H} and ^{31}P-{^1H} NMR data are given and discussed in some detail particularly regarding the determination of the stereochemistry at C(3) on the camphor residue. Crystals of compound **2a** are orthorhombic, space group $P2_12_12_1$ with a = 1165.1(2), b = 1272.5(2), c = 2106.1(5) pm and Z = 4; final R factor 0.0421 for 2812 observed reflections. The structure shows that the co-ordinated PPh_2 group is on the 3-*exo* position whilst the $C{=}NNMe_2$ moiety is co-ordinated through the NMe_2 nitrogen giving a six-membered co-ordinated ring. The arrangement around C=N is *Z*.

In a previous paper[1] we showed that treatment of (1*R*)-(+)-camphor (bornan-2-one) dimethylhydrazone with butyllithium, followed by PPh_2Cl, gave the 3-*exo*-diphenylphosphino-derivative **1a** with the hydrazone in the *Z* configuration. We went on to make some derivatives of Group 6 metal carbonyls in which the co-ordinated PPh_2 group remained *exo* but the $C{=}NNMe_2$ group could be either *Z* (six-membered chelate ring) or *E* (five-membered chelate ring). In a subsequent paper[2] we showed that the molybdenum tetracarbonyl complex of *exo*-3-diphenylphosphino-(1*R*)-camphor dimethylhydrazone $[Mo(CO)_4(PPh_2C_{10}H_{15}NNMe_2)]$ underwent a facile redox–fission reaction with hydrogen chloride to give a molybdenum(II) imine complex, $[Mo(CO)_3Cl_2(PPh_2C_{10}H_{15}NH)]$, which with sodium tetrahydroborate–carbon monoxide gave $[Mo(CO)_4(PPh_2C_{10}H_{15}NH)]$ with an *exo*-PPh_2 group. In the present paper we describe the chemistry of some palladium and platinum complexes with the *Z-exo*-phosphine **1a** and the *Z-endo*-phosphine **1b**. For the convenience of the reader, the various reactions and compounds formed are summarized in Scheme 1. Microanalytical data for the new compounds are in the Experimental section, IR and ^{31}P NMR data in Table 1 and ^1H- and ^1H-{^{31}P} NMR data in Table 2.

Results and Discussion

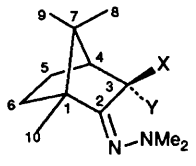
Treatment of the *Z-exo*-phosphine **1a** with $[PdCl_2(NCPh)_2]$ or $Na_2[PdCl_4]\cdot 4H_2O$ gave the chelate complex $[PdCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2a** in good yields; details are in the Experimental section. The complex was characterized by elemental analysis (C, H, N and Cl) a singlet ^{31}P-{^1H} NMR resonance (Table 1), an IR band at 1670 cm^{-1} assigned to ν(C=N) and two IR bands at 330 and 275 cm^{-1} (Table 1) assigned to ν(Pd–Cl), indicative of a *cis*-$PdCl_2$ arrangement. Similar ν(Pd–Cl) frequencies have been reported for complexes

Table 1 ^{31}P-{^1H} NMR data[a] and IR data[b]

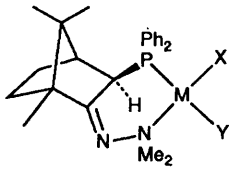
Complex	δ(P)	^1J(PtP)	ν(C=N)[c]	ν(M–Cl)[d]
1a	1.1		1655	
1b	−10.1		1655	
2a	38.7		1670	330, 275
2b	36.9[e]		1680	
2c	38.0		1675	
2d	14.7	4055	1675	340, 285
2e	12.8	3944	1675	
2f[f]	16.8	4438	1670	340
2g	45.2[g]	2155[g]	1655	
3a	10.8	4026	1665	335, 285
3b	34.4		1665	330, 280
3c	41.0[g]	2169[g]		
5	60.5		1620	330, 280

[a] Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated, ^1J(PtP) in Hz. [b] In cm^{-1}, all IR bands are of medium intensity. [c] KBr disc. [d] Nujol mulls. [e] In CH_2Cl_2. [f] IR bands due to ONO_2 group are at 1535s, 1280s and 995s cm^{-1}. [g] In C_6D_6.

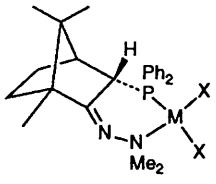
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



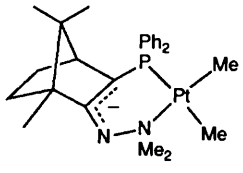
	X	Y
1a	PPh_2	H
1b	H	PPh_2



	M	X	Y
2a	Pd	Cl	Cl
2b	Pd	Br	Br
2c	Pd	I	I
2d	Pt	Cl	Cl
2e	Pt	Br	Br
2f	Pt	Cl	ONO_2
2g	Pt	Me	Me



	M	X
3a	Pt	Cl
3b	Pd	Cl
3c	Pt	Me



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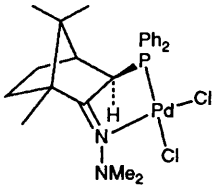

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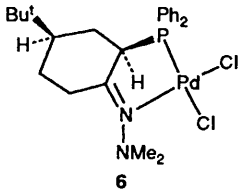

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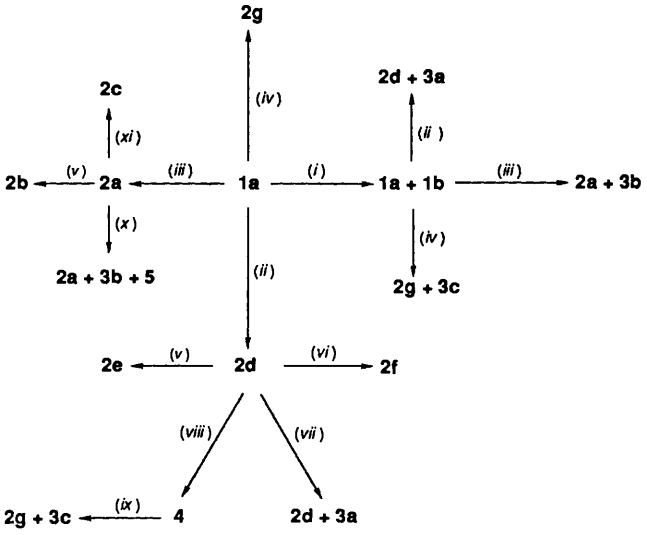

Scheme 1 (*i*) Acetic acid or NaOEt; (*ii*) $[PtCl_2(cod)]$; (*iii*) $[PdCl_2(NCPh)_2]$; (*iv*) $[PtMe_2(cod)]$; (*v*) LiBr; (*vi*) $AgNO_3$; (*vii*) dry HCl followed by EtOH; (*viii*) LiMe; (*ix*) MeOH; (*x*) dry HCl followed by MeOH; (*xi*) NaI

of the type *cis*-$[PdCl_2(NR_3)_2]$, *cis*-$[PdCl_2(py)_2]$ (py = pyridine) and *cis*-$[PdCl_2(PR_3)_2]$ (R = H or alkyl).[3,4] The ^1H NMR spectrum of **2a** showed that the NMe_2 methyl groups are non-equivalent (Table 2). We have determined the crystal structure of this complex (Fig. 1), see below for details; in particular the PPh_2 group is shown to be *exo* and the NMe_2 group is co-ordinated in a six-membered chelate ring, *i.e.* the configuration around C=N is *Z*. Treatment of the dichloro-complex **2a** with LiBr or NaI in acetone gave the corresponding dibromo- **2b** and diiodo-**2c** complexes. These were fully characterized.

We have also made the dichloro platinum complex **2d** by treating the ligand **1a** with $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene). It showed a singlet ^{31}P-$\{^1H\}$ NMR resonance, with satellites due to coupling with ^{195}Pt [$^1J(PtP)$ = 4055 Hz], and IR bands at 1675 [ν(C=N)] and 340, 285 cm^{-1} [ν(Pt–Cl)]. The proton NMR spectrum showed that both NMe_2 methyls are coupled to ^{195}Pt (Table 2) and that C(3)–H is also coupled to ^{195}Pt and to ^{31}P. The coupling constants of ^{195}Pt to the two NMe_2 methyls of 30.1 and 25.8 Hz are typical of a three-bond coupling and indicate that NMe_2 is co-ordinated to platinum in a six-membered ring and that the configuration around C=N is *Z*. Treatment of the dichloro-complex **2d** with LiBr gave the corresponding dibromide $[PtBr_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2e**.

Since a tertiary phosphine has a greater *trans* effect and *trans* influence than a tertiary amine, we anticipated that it might be possible to replace chlorine *trans* to phosphorus in **2d**, selectively. When an acetone solution of **2d** was treated with 1 mole equivalent of silver nitrate the monochloro mononitrato complex $[PtCl(ONO_2)(PPh_2C_{10}H_{15}NNMe_2)]$ **2f** was obtained. The ^{31}P-$\{^1H\}$ NMR spectrum showed that it was a single product with an exceptionally large ^{195}Pt–^{31}P coupling constant, $^1J(PtP)$ = 4438 Hz (Table 1). It is known that $^1J(PtP)$ for phosphorus in *trans* position to a nitrate ligand is larger than that of its chloride analogue.[6,7] The infrared spectrum showed only one band due to platinum–chlorine stretch, at 340 cm^{-1}. There were also strong bands at 1535, 1280 and 995 cm^{-1}, indicative of an ONO_2 group. Similar values have been reported for nitrato complexes of Ni, Pd and Pt.[8] The proton NMR spectrum showed two NMe_2 singlets with satellites, due to ^{195}Pt splitting, at δ 2.94 [$^3J(PtH)$ = 33.1] and 3.40 [$^3J(PtH)$ = 21.2 Hz]; these data confirmed that the platinum was co-ordinated by the NMe_2 group, *i.e.* the configuration around the C=N bond was *Z*. Treatment of the dichloride complex **2d** with 2 mol of $AgNO_3$ did not remove the second chloride.

We also made the dimethylplatinum complex **2g** by heating $[PtMe_2(cod)]$ with the *exo*-phosphine **1a** in benzene at 60 °C for 16 h.

We have examined the isomerization of the *exo*-phosphine **1a** to the *endo*-phosphine **1b** by ^{31}P-$\{^1H\}$ NMR spectroscopy. It is known that deprotonation of (1*R*)-(+)-camphor, followed by treatment with methyl iodide, gives a mixture (~4:1) of *exo*- and *endo*-(1*R*)-(+)-3-methylcamphor which, when treated with acid or base, is catalytically converted into a mixture of the *exo* and *endo* isomers in the proportion of ~1:9.[9] We have also observed the presence of both *exo* and *endo* isomers (~1:5) of (1*R*)-(+)-3-diphenylphosphinocamphor on storage for 16 h of a solution containing lithiated (1*R*)-(+)-camphor and 1 equivalent of PPh_2Cl.[10]

We have now treated the *exo*-phosphine **1a** in tetrahydrofuran (thf) with acetic acid and found partial conversion into **1b**. After 2 h the proportion of **1a** to **1b** was approximately 1:1.9 and did not change further with time, or on heating the solution to *ca.* 60 °C for 4 h. A similar ratio of **1a** to **1b** *viz.* 1:1.9 was obtained by heating to *ca.* 80 °C a solution of **1a** in propan-2-ol containing acetic acid for 3–4 h. We have also found that the isomerization of **1a** to **1b** could be catalysed by sodium ethoxide in ethanol. It was very slow at room temperature but, after heating **1a** in 0.4 mol dm^{-3} sodium ethoxide–ethanol–tetrahydrofuran solution at *ca.* 75 °C for 20 h, the proportion of **1a** and **1b** in the mixture was ≈1:1.5. We were not able to isolate a pure sample of the *endo* isomer **1b**. The proportions of **1a** and **1b** in the solid mixture varied between ≈1:1 and ≈1:1.5.

Since the pure *endo* isomer **1b** was not prepared it had to be characterized as a mixture with **1a**. Microanalytical data (C, H and N) were in agreement with a formula of $C_{24}H_{31}N_2P$ for the mixture, *i.e.* the two components are isomers (see Experimental

Table 2 Proton NMR data[a]

Compound	Camphor methyls	NMe_2	C^3H	C^4H
1a	0.73(s), 1.05(s), 1.07(s)	1.89 (6 H, s)	3.14 [d, ^2J(PH) 1.7]	1.61 [t, ^3J(HH) = ^3J(PH) 4.1][b]
1b	0.85(s), 0.91(s), 1.02(s)	1.81 (6 H, s, br)	3.76 [m, ^2J(PH) 1.8][b,c]	*d*
2a	−0.24(s), 0.73(s), 0.92(s)	3.01 (s), 3.66 (s)	2.71 [d, ^2J(PH) 14.8]	2.47 [dd, ^3J(HH) 3.2, ^3J(PH) 6.3]
2b	−0.24(s), 0.74(s), 0.93(s)	3.07 (s), 3.76 (s)	2.57 [d, ^2J(PH) 14.5]	2.49 [dd, ^3J(HH) 3.2, ^3J(PH) 6.1]
2c	−0.23(s), 0.73(s), 0.92(s)	3.09 (s), 3.83 (s)	2.51 [d, ^2J(PH) 14.0]	2.49 [dd, ^3J(HH) 3.2, ^3J(PH) 6.2]
2d	−0.11(s), 0.74(s), 0.91(s)	3.12 [s, ^3J(PtH) 30.1] 3.76 [s, ^3J(PtH) 25.8]	2.70 [d, ^2J(PH) 16.1][e]	2.48 [dd, ^3J(HH) 3.2, ^3J(PH) 6.5]
2e	−0.17(s), 0.74(s), 0.90(s)	3.23 [s, ^3J(PtH) 30.1] 3.89 [s, ^3J(PtH) 26.8]	2.69 [d, ^2J(PH) 16.1][f]	2.49 [dd, ^3J(HH) 3.2, ^3J(PH) 6.6]
2f	0.03(s), 0.74(s), 0.94(s)	2.94 [s, ^3J(PtH) 33.1] 3.40 [s, ^3J(PtH) 21.2]	2.43 [d, ^2J(PH) 15.9]	2.47 [m, ^3J(HH) 3.5][g]
2g[h]	0.06(s), 0.44(s), 0.96(s)	2.32 [s, ^3J(PtH) 15.9] 3.33 [s, ^3J(PtH) 16.2]	2.16 [d, ^2J(PH) 15.1]	*d*
3a	0.75(s), 0.92(s), 1.00(s)	3.30 [s, ^3J(PtH) 28.0] 3.84 [s, ^3J(PtH) 23.6]	*d*	2.17 (m, br)
3b	0.76(s), 0.81(s), 1.02(s)	3.12 (s), 3.70 (s)	3.03 (m)[i]	2.13 (m, br)
3c[j]	0.37(s), 0.57(s), 0.95(s)	2.59 [s, ^3J(PtH) 16.1] 3.38 [s, ^3J(PtH) 15.6]	*d*	*d*
5	−0.12(s), 0.74(s), 1.21(s)	2.94 (s), 3.06 (s)	3.97 [d, ^2J(PH) 15.8]	2.29 [dd, ^3J(HH) 3.0, ^3J(PH) 7.3]

[a] Recorded at 100 MHz, chemical shifts are in ppm relative to $SiMe_4$, *J* values in Hz, solvent $CDCl_3$ unless otherwise stated. s = Singlet, m = multiplet, t = triplet, br = broad. [b] Obtained by double-resonance experiments at 400 MHz. [c] ^3J(HH) = 4.0 and ^4J(HH) = 2.3 Hz. [d] Not resolved. [e] ^3J(PtH) = 6.1 Hz. [f] ^3J(PtH) = 8.9 Hz. [g] Signal obscured by C^3H. [h] In C_6D_6, δ 1.35 [d, ^3J(PH) = 7.0, ^2J(PtH) = 69.8, PtMe] and 1.37 [d, ^3J(PH) = 7.5, ^2J(PtH) = 83.8 Hz, PtMe]. [i] Signal obscured by NMe_2 peaks. [j] In C_6D_6, δ 1.25 (PtMe) and 1.26 (PtMe).

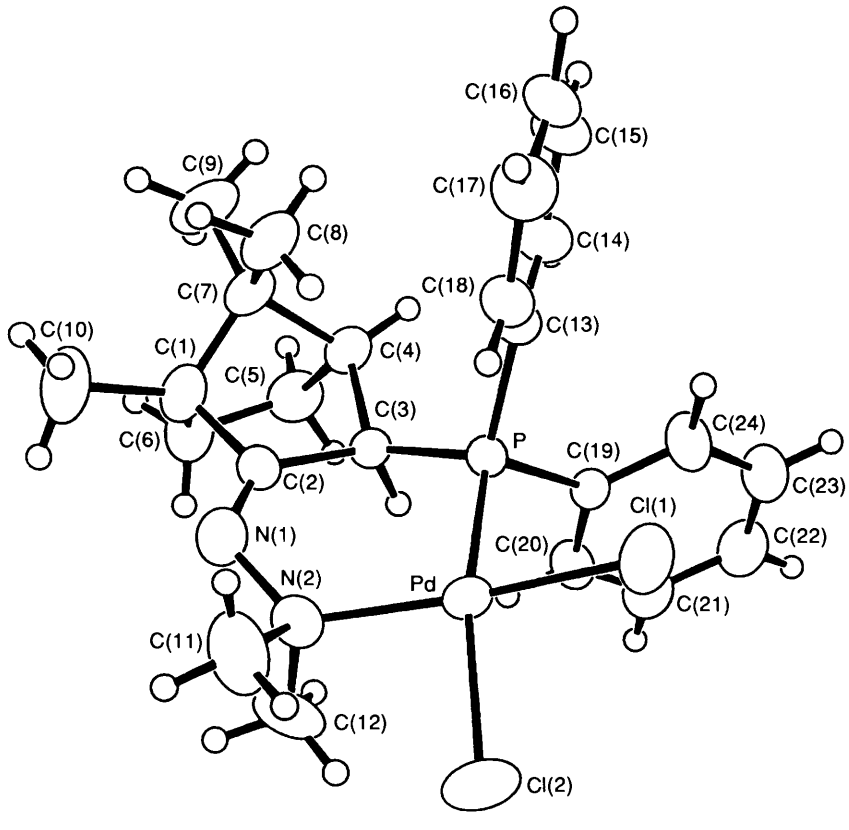

Fig. 1 An ORTEP drawing[5] of the molecular structure of $[PdCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2a**

section). The *endo*-phosphine **1b** showed a singlet $^{31}P\{^1H\}$ NMR resonance at δ −10.1 (Table 1) and in the proton spectrum the *exo*-hydrogen on C(3) was coupled to the methine hydrogen [^3J(HH) = 4.0 Hz] and to the *exo*-hydrogen on C(5), [^4J(HH) = 2.3 Hz], a 'W coupling'. The coupling to phosphorus was resolved by double-resonance experiments at 400 MHz [^2J(PH) = 1.8 Hz]. In contrast, the *endo*-hydrogen on C(3) in the *exo*-phosphine **1a** was only coupled to phosphorus [^2J(PH) = 1.7 Hz], as established by ^1H and $^1H\{^{31}P\}$ NMR experiments. There are several reports in the literature that the coupling constants ^3J(HH) between a 3-*endo* proton and a 4-bridgehead proton is zero for camphor derivatives such as **1a**: examples of this include (1*R*)-(+)-3-*exo*-methylcamphor,[9] (1*R*)-(+)-9-bromo-3-*exo*-methylcamphor,[9] (1*R*)-(+)-9,10-dibromo-3-*exo*-methylcamphor,[9] norcamphor[11] and Group 6 complexes of camphor phosphines,[1,2] whereas ^3J(HH) between a 3-*exo* proton and a 4-bridged proton is about 4.0–4.5 Hz.[9,11] In a range of rigid bicyclic compounds, ^3J(HH) between *endo* and bridgehead protons was found to be zero or < 1 Hz.[12]

Table 3 Selected bond lengths (pm) and angles (°) for compound **2a** with estimated standard deviations (e.s.d.s) in parentheses

P–Pd	220.5(3)	Cl(1)–Pd	229.7(4)
Cl(2)–Pd	239.6(4)	N(2)–Pd	210.8(7)
C(3)–P	183.6(8)	C(13)–P	179.8(5)
C(19)–P	181.2(5)	C(2)–C(1)	148.9(10)
C(6)–C(1)	156.9(11)	C(7)–C(1)	154.7(11)
C(10)–C(1)	151.8(10)	C(3)–C(2)	151.9(10)
N(1)–C(2)	127.9(9)	C(4)–C(3)	155.9(9)
C(5)–C(4)	154.5(10)	C(7)–C(4)	158.4(9)
C(6)–C(5)	154.8(11)	C(8)–C(7)	153.0(11)
C(9)–C(7)	150.5(11)	N(2)–N(1)	147.9(8)
C(11)–N(2)	150.1(10)	C(12)–C(2)	149.0(10)
Cl(1)–Pd–P	85.3(2)	Cl(2)–Pd–P	164.4(1)
Cl(2)–Pd–Cl(1)	89.6(2)	N(2)–Pd–P	96.1(2)
N(2)–Pd–Cl(1)	172.1(2)	N(2)–Pd–Cl(2)	91.0(2)
C(3)–P–Pd	108.6(3)	C(13)–P–Pd	117.8(2)
C(13)–P–C(3)	110.8(3)	C(19)–P–Pd	108.2(2)
C(19)–P–C(3)	103.5(3)	C(19)–P–C(13)	106.8(3)
C(6)–C(1)–C(2)	104.5(6)	C(7)–C(1)–C(2)	101.5(6)
C(7)–C(1)–C(6)	102.1(7)	C(10)–C(1)–C(2)	116.2(7)
C(10)–C(1)–C(6)	112.8(7)	C(10)–C(1)–C(7)	117.9(7)
C(3)–C(2)–C(1)	107.2(6)	N(1)–C(2)–C(1)	120.2(6)
N(1)–C(2)–C(3)	132.5(6)	C(2)–C(3)–P	117.3(5)
C(4)–C(3)–P	121.7(5)	C(4)–C(3)–C(2)	101.4(5)
C(5)–C(4)–C(3)	103.5(6)	C(7)–C(4)–C(3)	103.9(6)
C(7)–C(4)–C(5)	101.0(6)	C(6)–C(5)–C(4)	103.0(6)
C(5)–C(6)–C(1)	104.0(6)	C(4)–C(7)–C(1)	93.4(5)
C(8)–C(7)–C(1)	110.6(7)	C(8)–C(7)–C(4)	115.3(6)
C(9)–C(7)–C(1)	116.0(7)	C(9)–C(7)–C(4)	112.4(7)
C(9)–C(7)–C(8)	108.7(6)	N(2)–N(1)–C(2)	120.6(6)
N(1)–N(2)–Pd	125.0(5)	C(11)–N(2)–Pd	104.5(5)
C(11)–N(2)–N(1)	102.0(6)	C(12)–N(2)–Pd	109.7(6)
C(12)–N(2)–N(1)	105.7(6)	C(12)–N(2)–C(11)	109.1(7)

We have measured the ^{13}C NMR spectrum of the *exo*-phosphine **1a** and assigned all the resonances of the $C_{10}H_{15}NNMe_2$ moiety using ^1H–^{13}C correlation spectroscopy and comparison with the published data for (1*R*)-(+)-camphor.[13,14] We have done similar ^{13}C NMR studies on the **1a**–**1b** mixture and were thus able to assign shifts and coupling constants for the *endo*-phosphine **1b**; see Experimental section for data. The subsequent chemistry of this *endo*-phosphine **1b** established the configuration around the C=N to be *Z* (see below).

We have made some metal complexes of the *exo*-/*endo*-phosphine mixture **1a** and **1b**. Thus, treatment of a *ca.* 1:1 mixture of these two chelating phosphines with $[PtCl_2(cod)]$ in dichloromethane gave a mixture of the two *cis*-dichloride isomers $[PtCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2d** and **3a**. The elemental analytical data (C, H, N and Cl) for the mixture were in agreement with the formulation $C_{24}H_{31}Cl_2N_2PPt{\cdot}CH_2Cl_2$ and the ^{31}P-$\{^1H\}$ NMR spectrum of the mixture showed the presence of the *exo*-phosphine complex, characterized by a singlet phosphorus resonance, δ(P) 14.7, with satellites $^1J(PtP)$ = 4055 Hz (Table 1) and an approximately equal amount of a complex characterized by a singlet phosphorus resonance at δ(P) 10.8, with satellites, $^1J(PtP)$ = 4026 Hz. The ^1H NMR spectrum of this mixture showed the presence of **2a** (data in Table 2) and two singlets with satellites due to the co-ordinated NMe_2 group of the second species, δ(H) 3.30 [$^3J(PtH)$ = 28.0] and 3.84 [$^3J(PtH)$ = 23.6 Hz]. We therefore formulate this second species as the *endo*-phosphine complex **3a**. A similar treatment of $[PdCl_2(NCPh)_2]$ with a *ca.* 1:1 mixture of the phosphines **1a** and **1b** gave a mixture of the two isomeric complexes **2a** and **3b**. We have also prepared a mixture of the dimethylplatinum complexes **2g** and **3c** by treating a mixture of **1a** and **1b** with $[PtMe_2(cod)]$. The mixture would not crystallize but we characterized it by ^{31}P-$\{^1H\}$ and proton NMR spectroscopy (see Tables 1 and 2).

When a solution of complex **2d** in dry thf was treated with an excess of methyllithium the resultant solution showed a single phosphorus-containing species absorbing at δ 12.2 with satellies, $^1J(PtP)$ = 2208 Hz. When we treated this solution with methanol a mixture of the complexes **2g** and **3c** in *ca.* 1:1 proportions, was formed. These were identified by ^{31}P-$\{^1H\}$ NMR spectroscopy. We suggest that the intermediate absorbing at δ 12.2 is the anion **4**.

Since the complexes of type **2** have a lone pair on the uncoordinated nitrogen (C=N) we studied the effect of hydrogen chloride on the *exo*-phosphine–platinum dichloride complex **2d**, in an attempt to protonate this lone pair. In dichloromethane solution **2d** gave a phosphorus resonance, δ(P) 14.7 [$^1J(PtP)$ 4055 Hz] and when dry hydrogen chloride was bubbled through a solution of **2d** in dichloromethane it was completely converted into another species, characterized by δ(P) 7.9 [$^1J(PtP)$ = 3437 Hz]. We suggest this corresponds to a derivative of **2d** containing a $Me_2\overset{+}{N}NH_2C{=}CPPh_2$ moiety. Subsequent treatment of this solution with ethanol gave a mixture of **2d** and **3a** in the approximate proportions of 1:3, as shown by ^{31}P-$\{^1H\}$ and ^1H NMR spectroscopy. A similar treatment of the palladium complex **2a** with dry hydrogen chloride gave a new species, characterized by a singlet phosphorus resonance at δ(P) 30.2, again presumably a protonated complex; this solution, on addition of methanol, gave a mixture (*ca.* 1:2.4) of the *exo*- and *endo*-phosphine complexes **2a** and **3b** (proton and ^{31}P-$\{^1H\}$ NMR evidence). When we treated a mixture of **2a** and **3b** with dry hydrogen chloride the species absorbing at δ(P) 30.2 was reformed. The mother-liquor from this mixture gave a new complex in about 30% yield but contaminated with small amounts of **2a** and **3b**. This new complex was characterized by a singlet phosphorus resonance at δ(P) 60.5. We tentatively suggest that this is due to the five-membered chelate ring complex **5** and have made a similar five-membered ring chelate complex which also has δ(P) ≈60: 4-*tert*-butylcyclohexanone *N*,*N*-dimethylhydrazone was treated with lithium diisopropylamide or butyllithium, followed by PPh_2Cl, and the resultant (isolated) phosphine was treated with $[PdCl_2(NCPh)_2]$. This gave the chelate complex **6** the structure of which has been established by X-ray crystallography. This complex had δ(P) at 62.5.[15] Complex **5** showed a doublet for C(3)–H in the proton NMR spectrum at δ(H) 3.97, $^2J(PH)$ = 15.8 Hz (Table 2). These data are characteristic of C(3)–H being *endo* and therefore PPh_2 being in an *exo* position.

Crystal Structure of $[PdCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2a**.—The crystal structure of complex **2a** is shown in Fig. 1 and selected bond lengths and angles are shown in Table 3 and atom coordinates in Table 4. The structure shows that the PPh_2 group is in the *exo* position and that the palladium is co-ordinated to the NMe_2 nitrogen. The arrangement around the C=N bond is *Z*. The co-ordination around palladium is essentially square planar, the deviations being in part due to the restrictions imposed by the rigid camphor backbone. As would be expected, the Pd–Cl bond *trans* to phosphorus is longer [239.6(4) pm] than that *trans* to nitrogen [229.7(4) pm], due to the higher *trans* influence of phosphorus over nitrogen.

Experimental

The general methods and instruments were the same as in other recent publications from this laboratory.[16]

Preparations.—$[PdCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2a**. (*i*) From $[PdCl_2(NCPh)_2]$. A solution of the *exo*-phosphine **1a** (1.0 g, 2.6 mmol) in dichloromethane (15 cm^3) was added to a solution of $[PdCl_2(NCPh)_2]$ (1.0 g, 2.6 mmol) in dichloromethane (25 cm^3). Addition of ethanol (*ca.* 25 cm^3) to the resulting yellow solution gave the required product **2a** as yellow microcrystals. Yield 1.3 g, 90%.

Table 4 Atom coordinates ($\times 10^4$) for compound **2a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pd	−1607.0(5)	−4044.8(4)	−2778.6(2)
P	−3024(1)	−2905(1)	−2694(1)
Cl(1)	−2683(2)	−5078(2)	−2111(1)
Cl(2)	27(2)	−5140(2)	−2579(1)
C(1)	−2433(7)	−989(7)	−4181(3)
C(2)	−2006(6)	−1830(6)	−3751(3)
C(3)	−2624(6)	−1701(5)	−3121(3)
C(4)	−3527(6)	−840(5)	−3289(3)
C(5)	−2821(8)	188(6)	−3282(4)
C(6)	−2022(8)	61(6)	−3864(4)
C(7)	−3731(7)	−989(6)	−4027(3)
C(8)	−4280(8)	−2034(7)	−4220(4)
C(9)	−4421(10)	−106(8)	−4311(5)
C(10)	−2078(10)	−1075(8)	−4873(4)
N(1)	−1226(6)	−2465(5)	−3939(3)
N(2)	−707(6)	−3228(5)	−3493(3)
C(11)	−294(10)	−4072(8)	−3935(5)
C(12)	303(7)	−2683(9)	−3211(6)
C(13)	−4438(3)	−3329(4)	−2918(2)
C(14)	−5396(3)	−2701(4)	−2800(2)
C(15)	−6474(3)	−3008(4)	−3021(2)
C(16)	−6594(3)	−3944(4)	−3359(2)
C(17)	−5673(3)	−4573(4)	−3476(2)
C(18)	−4559(3)	−4266(4)	−3256(2)
C(19)	−3108(4)	−2483(4)	−1873(2)
C(20)	−2238(4)	−1853(4)	−1624(2)
C(21)	−2245(4)	−1587(4)	−981(2)
C(22)	−3122(4)	−1951(4)	−588(2)
C(23)	−3993(4)	−2581(4)	−837(2)
C(24)	−3986(4)	−2846(4)	−1480(2)

(*ii*) *From* $Na_2[PdCl_4]\cdot 4H_2O$. A warm solution of the *exo*-phosphine **1a** (0.30 g, 0.80 mmol) in ethanol (12 cm^3) was added to a solution of $Na_2[PdCl_4]\cdot 4H_2O$ (0.24 g, 0.75 mmol) in ethanol (12 cm^3). The resulting solution was heated to *ca.* 80 °C for 1 min and then allowed to cool. This gave the product **2a** (0.30 g, 73%) (Found: C, 51.45; H, 5.7; Cl, 13.0; N, 4.85. $C_{24}H_{31}Cl_2N_2PPd$ requires C, 51.85; H, 5.6; Cl, 12.75; N, 5.05%).

$[PdBr_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2b**. A solution of the dichloro-complex **2a** (0.15 g, 0.27 mmol) and an excess of lithium bromide (0.23 g, 2.7 mmol) in acetone (12 cm^3) was put aside for 24 h. The solution was then evaporated to dryness and the product extracted into dichloromethane. Crystallization from dichloromethane–acetone gave **2b** as yellow microcrystals; yield (0.15 g, 85%) (Found: C, 42.3; H, 4.75; N, 3.8. $C_{24}H_{31}Br_2N_2PPd\cdot 0.6CH_2Cl_2$ requires C, 42.45; H, 4.65; N, 4.0%).

$[PdI_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2c**. This was prepared from **2a** and isolated in an analogous manner to **2b**; yield 79% (Found: C, 39.05; H, 4.25; N, 3.7. $C_{24}H_{31}I_2N_2PPd$ requires C, 39.0; H, 4.25; N, 3.8%).

$[PtCl_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2d**. A solution containing the phosphine **1a** (1.0 g, 2.67 mmol) and $[PtCl_2(cod)]$ (1.0 g, 2.67 mmol) in dichloromethane (20 cm^3) was refluxed for 45 min. The required product was isolated as off-white microcrystals; yield (1.49 g, 86%) (Found: C, 44.5; H, 4.85; Cl, 10.9; N, 4.2. $C_{24}H_{31}Cl_2N_2PPt$ requires C, 44.7; H, 4.85; Cl, 11.0; N, 4.35%).

$[PtBr_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2e**. This was prepared and isolated in an analogous manner to complex **2b**, in 82% yield (Found: C, 39.0; H, 4.3; N, 3.7. $C_{24}H_{31}Br_2N_2PPt$ requires C, 39.3; H, 4.25; N, 3.8%).

$[PtCl(NO_3)(PPh_2C_{10}H_{15}NNMe_2)]$ **2f**. Silver nitrate (53 mg, 0.31 mmol) in the minimum amount of water was added to a solution containing the dichloro complex **2d** (0.20 g, 0.31 mmol) in acetone (15 cm^3). The precipitate of silver chloride was filtered off and the filtrate was evaporated to dryness. The resultant residue was recrystallized from dichloromethane–ethanol to give the mononitrato complex **2f** as white microcrystals; yield (0.16 g, 77%) (Found: C, 42.55; H, 4.6; Cl, 4.9; N, 6.1. $C_{24}H_{31}ClN_3O_3PPt$ requires C, 42.95; H, 4.65; Cl, 5.2; N, 6.25%).

$[PtMe_2(PPh_2C_{10}H_{15}NNMe_2)]$ **2g**. A solution containing $[PtMe_2(cod)]$ (66 mg, 0.20 mmol) and the phosphine **1a** (76 mg, 0.20 mmol) in benzene (1.5 cm^3) was heated at *ca.* 60 °C for 15 h. The resulting yellow solution was evaporated to dryness and then triturated with ethanol to give the required product **2g** as white microcrystals; yield (35 mg, 29%) (Found: C, 51.7; H, 6.0; N, 4.65. $C_{26}H_{37}N_2PPt$ requires C, 51.75; H, 6.2; N, 4.65%).

Isomerization of exo-*Phosphine* **1a** *to* endo-*Phosphine* **1b**.—A mixture of the *exo*-phosphine **1a** (1.0 g, 2.77 mmol) and acetic acid (1.3 cm^3) was refluxed in propan-2-ol (15 cm^3) for 4 h. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the mixture showed it to comprise of **1a** and **1b** in the ratio of ≈1:1.9 (see Discussion). The solvent was removed under reduced pressure and the residue recrystallized from ethanol to give a white crystalline solid (0.77 g, 77%). It was found to be a mixture of **1a** and **1b** in the ratio *ca.* 1:1.5 (see Discussion) (Found: C, 76.3; H, 8.1; N, 7.6. $C_{24}H_{31}N_2P$ requires C, 76.15; H, 8.25; N, 7.4%). *exo*-Phosphine **1a**: $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 11.5 (s, C^{10}), 19.4 (s, C^8), 21.9 [d, ^4J(PC) 21.1, C^9], 30.4 (s, C^5), 32.1 (s, C^6), 45.7 (s, NMe_2), 45.8 [d, ^1J(PC) 27.8, C^3], 47.1 [d, ^3J(PC) 1.6, C^7], 48.0 [d, ^2J(PC) 1.8, C^4], 53.1 [d, ^3J(PC) 3.2, C^1] and 184.1 [d, ^2J(PC) 6.7 Hz, C^2]. *endo*-Phosphine **1b**: $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz) δ 12.5 (s, C^{10}), 18.4 (s, C^8), 19.5 (s, C^9), 23.0 [d, ^3J(PC) 15.7, C^5], 33.2 (s, C^6), 41.9 [d, ^1J(PC) 18.8, C^3], 45.7 (s, NMe_2), 48.2 [d, ^3J(PC) 1.9, C^7], 48.6 (s, C^4), 53.7 [d, ^3J(PC) 1.7, C^1] and 183.5 [d, ^2J(PC) 9.0 Hz, C^2].

Reactions between a Mixture (1:1) *of Phosphines* **1a** *and* **1b**.—*With* $[PtCl_2(cod)]$. The complex $[PtCl_2(cod)]$ (59 mg, 0.16 mmol) was added to a solution containing a mixture (≈1:1) of phosphines **1a** and **1b** (61 mg, 0.16 mmol) in dichloromethane (*ca.* 2 cm^3). After 2 h the solution was concentrated to a low volume under reduced pressure. Addition of methanol gave a mixture (≈1:1) of complexes **2d** and **3a** as a pale yellow crystalline solid; yield (71 mg, 69%) (Found: C, 41.1; H, 4.6; Cl, 19.1; N, 3.7. $C_{24}H_{31}Cl_2N_2PPt\cdot CH_2Cl_2$ requires C, 41.15; H, 4.55; Cl, 19.45; N, 3.85%).

With $[PdCl_2(NCPh)_2]$. Similarly, treatment of a mixture (≈1:1) of phosphines **1a** and **1b** with $[PdCl_2(NCPh)_2]$ (1 equivalent) in dichloromethane gave a mixture (≈1:1) of complexes **2a** and **3b** in 59% yield (Found: C, 47.95; H, 5.45; N, 4.45. $C_{24}H_{31}Cl_2N_2PPd\cdot 0.75CH_2Cl_2$ requires C, 48.0; H, 5.3; N, 4.5%).

With $[PtMe_2(cod)]$. A solution containing $[PtMe_2(cod)]$ (50 mg, 0.15 mmol) and a mixture (≈1:1) of phosphines **1a** and **1b** (58 mg, 0.15 mmol) in benzene (*ca.* 1.5 cm^3) was heated to *ca.* 60 °C for 22 h. Since the products failed to crystallize the solution was evaporated to dryness and redissolved in C_6D_6 for $^{31}P\text{-}\{^1H\}$, $^1H\text{-}\{^{31}P\}$ and ^1H NMR studies.

Reaction of Complex **2d** *with Dry Hydrogen Chloride*.—Dry hydrogen chloride was bubbled through a solution containing complex **2d** (0.31 g, 0.48 mmol) in dichloromethane (10 cm^3) for 90 s. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this solution showed only one phosphorus-containing species, which gave a singlet at δ 7.9 with ^{195}Pt satellites, ^1J(PtP) = 3437 Hz. After 1 h the solution was concentrated to a low volume (*ca.* 2 cm^3) under reduced pressure and ethanol (*ca.* 2 cm^3) added. A mixture (≈1:3) of the isomeric complexes **2d** and **3a** crystallized as pale yellow needles; yield (0.24 g, 77%).

Reaction of Complex **2a** *with Dry Hydrogen Chloride*.—Dry hydrogen chloride was bubbled through a solution containing complex **2a** (0.21 g, 0.37 mmol) in dichloromethane (10 cm^3) for 2 min. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of this solution showed only one phosphorus-containing species absorbing at δ 30.2.

After 15 min the solvent was removed under reduced pressure and the residue was crystallized from dichloromethane–methanol to give a mixture (≈1:2.4) of the isomeric complexes **2a** and **3b** as yellow microcrystals; yield (88 mg, 42%). The mother-liquor gave complex **5** as yellow microcrystals yield (72 mg, 34%), contaminated with small amounts of complexes **2a** and **3b** (see Discussion) (Found: C, 51.6; H, 5.55; Cl, 12.85; N, 4.9. $C_{24}H_{31}Cl_2N_2PPd$ **5** requires C, 51.85; H, 5.6; Cl, 12.75; N, 5.05%).

Reaction between Methyllithium and Complex **2d**.—An excess of LiMe (1.4 mol dm^{-3}) in diethyl ether (0.4 cm^3) was added to a suspension of complex **2d** (60 mg, 0.09 mmol) in dry thf (1.5 cm^3). The ^{31}P-{^1H} NMR spectrum of the resultant pale yellow solution after 3 h showed a single phosphorus-containing species at δ 12.2 {[J(PtP) = 2208 Hz]. A few drops of methanol were added to this solution. ^{31}P-{^1H} NMR spectroscopy showed after 1 h the presence of a mixture (≈1:1) of complexes **2g** and **3c**, absorbing at δ 45.0 [^1J(PtP) = 2169] and 40.5 [^1J(PtP) = 2177 Hz], respectively.

Single-crystal X-Ray Diffraction Analysis of Compound **2a**.—All crystallographic measurements were carried out at 290 K on a Nicolet P3/F diffractometer using graphite-monochromated Mo-Kα X-radiation (λ = 71.069 pm). The unit-cell parameters and their associated estimated standard deviations were obtained from a least-squares fit of the setting angles of 25 reflections in the range 20 < 2θ < 25°. Data were collected in the range 4.0 < 2θ < 50.0° over 171.4 h using ω–2θ scans with no significant variation in the intensities of three standard reflections. Lorentz and polarization corrections were applied to the data set together with a post structure-solution empirical absorption correction.[17]

The structure was determined *via* standard heavy-atom (for the Pd atom) and Fourier difference techniques and was refined by full-matrix least squares using the SHELX program system.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters except for the carbon and chlorine atoms of two disordered CH_2Cl_2 molecules which were refined isotropically. The phenyl groups were treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1}$ was used. Refinement of the enantiomeric structure (based on L-camphor) led to significantly higher values of R and R'.

Crystal data. $C_{24}H_{31}N_2PPd{\cdot}2CH_2Cl_2$, M = 725.69 (includes both solvent molecules), orthorhombic, space group $P2_12_12_1$, a = 1165.1(2), b = 1272.5(2), c = 2106.1(5) pm, U = 3.1223(10) nm^3, Z = 4, D_c = 1.54 Mg m^{-3}, μ = 10.77 cm^{-1}, F(000) = 1472. Crystal dimensions: 0.8 × 0.5 × 0.4 mm.

Data collection. Scan speeds 2.0–29.3° min^{-1}, ω scan widths 2.0° + α-doublet splitting, 4.0 < 2θ < 50.0°, 3884 data collected, 2812 with $I > 2.0\sigma(I)$ considered observed.

Structure refinement. Number of parameters = 307, R = 0.0421, R' = 0.0453.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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