The synthesis of *endo*-3-diphenylphosphino-(1*R*)-(+)-camphor (L) and some of its complexes with palladium(II), platinum(II) and rhodium(I); crystal structures of L and *cis*-$[PdCl_2L_2]$

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Abstract

Treatment of (1*R*)-(+)-camphor with $LiBu^n$, followed by Ph_2PCl gives, as the main product, *exo*-3-diphenylphosphino-(1*R*)-(+)-camphor (**3a**) together with some of the corresponding enolate anion **1**. However, on storage the *exo*-phosphine **3a** isomerises to the corresponding *endo*-phosphine **3b** which becomes the main product and was isolated in 70% yield. The crystal structure of **3b** was determined and detailed ^{13}C and proton NMR data are given. In chloroform solution, in the presence of acetic acid as catalyst, the *endo*-phosphine **3b** is partially converted back into the *exo*-isomer **3a** over 2 days. The *endo*-phosphine **3b** (L) with H_2O_2 gives the corresponding phosphine oxide **3c** and with monoclinic sulfur the corresponding phosphine sulfide **3d**. With $[PdCl_2(NCPh)_2]$ the *endo*-phosphine **3b** gives $[PdCl_2L_2]$ which exists as a *cis–trans* mixture **4a** and **4b** in solution. We have determined the X-ray crystal structure of the *cis*-form **4b**. Treatment of $[PtCl_2(COD)]$ with L, gives *cis*-$[PtCl_2L_2]$ (**4c**) but with $[PtCl_2(NCMe)_2]$ the corresponding *trans* complex *trans*-$[PtCl_2L_2]$ (**4d**) is formed. In compounds **4a–4d** the PPh_2 groups are *endo*. The complexes of type $[MCl_2L_2]$ (M = Pd or Pt) are also formed by treating the bis-camphorphosphine enolates $[M(PPh_2C_{10}H_{14}O)_2]$ with HCl. The complexes of type *cis*-$[Pt(C{\equiv}CR)_2(PPh_2C_{10}H_{15}O)_2]$ (R = Ph or C(Me)=CH_2) with HCl give exclusively *cis*-$[PtCl_2L_2]$. Treatment of $[Rh_2Cl_2(CO)_4]$ with the *endo*-phosphine **3b** (L) gives *trans*-$[RhCl(CO)L_2]$. ^1H, ^{31}P and some ^{13}C data are given. Crystals of *endo*-3-diphenylphosphino-(1*R*)-(+)-camphor (**3b**) are orthorhombic, space group $P2_12_12_1$ with $a = 778.6(1)$, $b = 1138.8(1)$, $c = 2128.9(3)$ pm and $Z = 4$, $R = 0.0329$ for 1674 observed reflections. The structure shows that the PPh_2 is *endo*. Crystals of **4b** are orthorhombic, space group $P2_12_12_1$, with $a = 1380.3(2)$, $b = 1785.1(3)$, $c = 1922.8(4)$ pm and $Z = 4$, $R = 0.0425$ for 4438 observed reflections. The structure shows that the PPh_2 groups are *endo* and that the phosphines are *cis*.

Introduction

In a previous paper [1] we described the preparation of the 3-diphenylphosphino-(1*R*)-(+)-camphor enolate anion (**1**), $[PPh_2C_{10}H_{14}O]^-$, formed by treatment of (1*R*)-(+)-camphor with lithium di-isopropylamide (lda), followed by one half mole equivalent of Ph_2PCl. We treated this phosphine enolate anion **1** with $Na_2PdCl_4 \cdot 4H_2O$ or with $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) to give the corresponding bis-chelate complexes $[M(PPh_2C_{10}H_{14}O)_2]$ (M = Pt (**2a**), Pd (**2b**)). Treatment of these bis-chelates with hydrogen chloride, or with terminal acetylenes (RC≡CH; R = Ph or C(Me)=CH_2) opened up the chelate rings to give complexes of the types $[MX_2(PPh_2C_{10}H_{15}O)_2]$ (X = Cl or C≡CR, M = Pd or Pt) but we did not fully determine the stereochemistries of these ring-opened products.

We also showed that treatment of lithiated (1*R*)-(+)-camphor, followed by an equivalent amount of PPh_2Cl gave some of the enolate anion **1** but the main product was formulated as the 3-*exo*-substituted camphor phosphine $[PPh_2C_{10}H_{15}O]$ (**3a**), together with some of the corresponding 3-*endo*-substituted isomer **3b**. However, over many hours in solution much of the *exo*-isomer isomerised to the *endo*-isomer, which then had become the major product. It is well established that treatment of (1*R*)-(+)-camphor with lda followed by an electrophile, e.g. MeI, invariably gives the *exo*-3-substituted derivative as the kinetic product but this isomerises on treatment with an acid or base catalyst, to give the *endo*-3-substituted derivative [2, 3]. We therefore assigned the 3-PPh_2 camphor derivatives as *exo*-(kinetic product) and *endo*-(thermodynamic product).

In the present paper we have confirmed these assignments by detailed proton and $^{13}C\{^1H\}$ NMR studies and by an X-ray crystal structural determination of the *endo*-isomer **3b** (see below). We have also determined the stereochemistries of the products formed by ring-opening reactions of bis-chelates of type **2** with hydrogen

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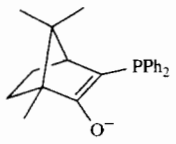
chloride or with terminal acetylenes. In a recent paper [4] we have shown that *exo*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone [5] and its complexes with platinum(II) or palladium(II) undergo acid or base-catalysed isomerisation to the corresponding *endo*-derivatives.



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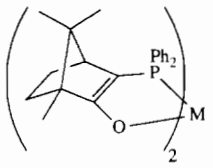
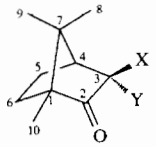
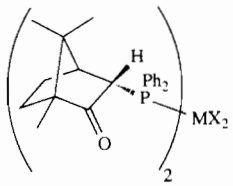


	M
2a *cis*	Pt
2b *cis*	Pd



	X	Y
3a	PPh_2	H
3b	H	PPh_2
3c	H	$P(O)Ph_2$
3d	H	$P(S)Ph_2$



		M	X
4a	*trans*	Pd	Cl
4b	*cis*	Pd	Cl
4c	*cis*	Pt	Cl
4d	*trans*	Pt	Cl
4e	*cis*	Pt	C≡CPh
4f	*cis*	Pt	C≡CC(Me)=CH_2

Experimental

The experimental techniques were the same as those used in other recent papers from this laboratory [6].

endo-3-Diphenylphosphino-(1R)-(+)-camphor (3b)

To a stirred solution of (1*R*)-(+)-camphor (16.0 g, 0.105 mol) in dry tetrahydrofuran (THF) (100 cm^3) at −70 °C was added dropwise a solution of Bu^nLi in hexane (68.0 cm^3, 1.6 mol dm^{-3}, 0.108 mol). After 1 h, a solution of Ph_2PCl (23.2 g, 18.9 cm^3, 0.105 mol) in dry THF (60 cm^3) was added at −70 °C. The resultant solution was stirred for 30 min and allowed to warm to room temperature. The ^{31}P $\{^1H\}$ NMR spectrum of this solution showed two singlets; one at 1.5 ppm (the *exo*-phosphine **3a**) and the other at −32.7 ppm (the enolate **1**) in the ratio *c.* 3:1. After two days at room temperature the solvent was removed under reduced pressure and the residue was extracted into degassed diethyl ether (100 cm^3). After removal of the solvent under reduced pressure, the residue was recrystallised from degassed ethanol (*c.* 40 cm^3) to give the required product **3b** as white microcrystals. The ^{31}P $\{^1H\}$ NMR spectrum of the ethanolic solution showed two singlets, one at 1.3 ppm **3a** and the other at −11.2 ppm, shown to be the *endo*-phosphine **3b**, in the ratio of *c.* 1:5 *exo:endo*. The yield of **3b** was 25.9 g, 72%, m.p. 187–188 °C, *m/z*, 336(M^+), $[\alpha]_D^{23} = +79.8°$ ($C = 2$ g per 100 cm^3, MeOH). *Anal.* Found: C, 78.3; H, 7.35. Calc. for $C_{22}H_{25}OP$: C, 78.55; H, 7.5%.

Conversion of the endo-phosphine 3b into the corresponding phosphine oxide 3c

An excess of hydrogen peroxide (0.4 cm^3, 30% wt./vol.) was added to a solution of the phosphine **3b** (0.6 g, 1.78 mmol) in acetone (15 cm^3). After 30 min, the solvent was removed and the residue crystallised from ethanol to give the required phosphine oxide **3c** as white needles. Yield 0.41 g, 65%. *Anal.* Found: C, 75.0; H, 7.2. Calc. for $C_{22}H_{25}O_2P$: C, 75.0; H, 7.15%.

Conversion of the endo-phosphine 3b into the corresponding phosphine sulfide 3d

A mixture of the phosphine **3b** (0.35 g, 1.0 mmol) and monoclinic sulfur (40 mg, 1.25 mmol) was heated under reflux in benzene (8 cm^3) for 2.5 h. The solution was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was recrystallised from ethanol to give the phosphine sulfide **3d** as white needles. Yield 0.19 g, 50%. *Anal.* Found: C, 71.25; H, 6.7. Calc. for $C_{22}H_{25}OPS$: C, 71.7; H, 6.85%.

trans-Bis{endo-3-diphenylphosphino-(1R)-(+)-camphor}dichloropalladium(II) (4a)

$[PdCl_2(NCPh)_2]$ (0.50 g, 1.3 mmol) was added to a solution containing the *endo*-phosphine **3b** (0.92 g, 2.7 mmol) in dichloromethane (15 cm^3). After 30 min, the solution was evaporated to a low volume under reduced pressure. Addition of methanol to the residue then gave the product **4a** as yellow microcrystals. Yield 0.93 g, 84%. *Anal.* Found: C, 61.6; H, 6.0; Cl, 8.6. Calc. for $C_{44}H_{50}Cl_2O_2P_2Pd$: C, 62.15; H, 5.95; Cl, 8.35%.

cis-Bis{endo-3-diphenylphosphino-(1R)-(+)-camphor}dichloroplatinum (4c)

$[PtCl_2(cod)]$ (0.40 g, 1.07 mmol) was added to a solution of the *endo*-phosphine **3b** (0.75 g 2.23 mmol) in dichloromethane (15 cm^3). After 15 min the solvent was removed and the residue recrystallised from dichloromethane/methanol to give the *cis*-dichloroplatinum complex **4c** as white microcrystals. Yield 0.77 g, 77%.

trans-Bis{endo-3-diphenylphosphino-(1R)-(+)-camphor}dichloroplatinum (4d)

$[PtCl_2(NCMe)_2]$ (0.14 g, 0.40 mmol) was added to a solution containing the *endo*-phosphine **3b** (0.277 g, 0.82 mmol) in dichloromethane (5 cm^3). After 30 min the solution was evaporated to a low volume (*c.* 1.5

cm^3) under reduced pressure and methanol (*c.* 1 cm^3) added to the residue. The *trans*-dichloroplatinum complex **4d** crystallised out as pale yellow needles. Yield 0.24 g, 63%. *Anal.* Found: C, 56.35; H, 5.5; Cl, 7.65. Calc. for $C_{44}H_{50}Cl_2O_2P_2Pt$: C, 56.25; H, 5.35; Cl, 7.55%.

Conversion of the trans-dichloro complex 4d into the bis-enolate complex 2a

The dichloro complex **4d** (0.25 g, 0.266 mmol) and an excess of NaH (0.10 g, 60% dispersion in mineral oil) in dry THF (10 cm^3) were heated under reflux for 20 h. The mixture was then filtered and the filtrate evaporated to dryness. The residue was extracted into dichloromethane (5 cm^3) and the extract washed with water and dried over anhydrous $MgSO_4$. Removal of solvent and recrystallisation of the residue from dichloromethane and methanol gave the bis-enolate complex **2a** as white microcrystals. Yield 0.21 g, 91%.

Conversion of the cis-dichloro complex 4c into the bis-enolate complex 2a

4c was converted into **2a** in 77% yield by a method similar to that given above.

Conversion of the cis-dichloroplatinum complex 4c into the trans-dichloroplatinum 4d

A solution containing the *cis*-dichloride **4c** (0.15 g, 0.16 mmol) in 1,4-dioxan (6 cm^3) was heated under reflux for 24 h. Removal of the solvent and recrystallisation of the residue from dichloromethane/methanol gave the *trans*-dichloride complex **4d** as yellow needles. Yield 0.90 g, 60%.

trans-Bis{endo-3-diphenylphosphino-(1R)-(+)-camphor}chloro(carbonyl)rhodium(I) (5)

Method a. The *endo*-phosphine **3b** (0.11 g, 0.32 mmol) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (30 mg, 0.077 mmol) in benzene (1.5 cm^3). After 30 min, the solution was filtered and evaporated to dryness under reduced pressure. The residue was triturated with methanol to give the chloro(carbonyl)rhodium complex **5** as yellow microcrystals. Yield 117 mg, 90%.

Method b. Carbon monoxide was bubbled through a solution of $RhCl_3 \cdot 3H_2O$ (1.0 g, 3.80 mmol) in boiling ethanol (25 cm^3) for 2.5 h. The resulting yellow solution was allowed to cool to room temperature, and argon was bubbled through it for 10 min to remove dissolved carbon monoxide. A solution containing the phosphine enolate **1** (8.0 mmol) in THF/hexane was added. After 2 h concentrated hydrochloric acid (2.5 cm^3) was added to give an orange solution, which gave the required product **5** as yellow microcrystals. Yield 2.45 g, 77%. An analytical sample was obtained from dichloromethane/ethanol. *Anal.* Found: C, 63.3; H, 5.85; Cl, 5.1. Calc. for $C_{45}H_{50}ClO_3P_2Ph \cdot 0.15CH_2Cl_2$: C, 63.65; H, 5.95; Cl, 5.4%.

X-ray diffraction analysis

All diffraction measurements were made at 200 K on a Stoe STADI4 diffractometer operating in the ω/θ scan mode using graphite monochromated X-radiation ($\lambda = 71.069$ pm) and, for compound **4b**, on-line profile fitting [7]. Crystal data are listed in Table 1 together with details of data collection and structure refinement. The data-sets were corrected for Lorentz and polarisation factors and also for absorption using azimuthal psi scans.

The structure of **3b** was solved by direct methods using SHELXS 86 [8] whilst that of **4b** was solved by standard heavy-atom techniques using SHELX 76 [9]. Both structures were refined by full-matrix least-squares using SHELX 76. In both cases all non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of the carbon and chlorine atoms of two disordered CH_2Cl_2 solvate molecules of **4b** which were refined with isotropic thermal parameters and 1/2 occupancy factors. All phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C = 139.5 pm). In both cases the hydrogen atoms were included in calculated positions (C–H = 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w^{-1} = \sigma^2(F) + g(F)^2$ was used for both complexes where g is a parameter which was adjusted so as to give a flat analysis of variance with increasing $\sin\theta$ and $[F/F_{max}]^{-1/2}$. In both cases refinement of the structure based on the L-form of camphor led to significantly higher R values. See also 'Supplementary material'.

Results and discussion

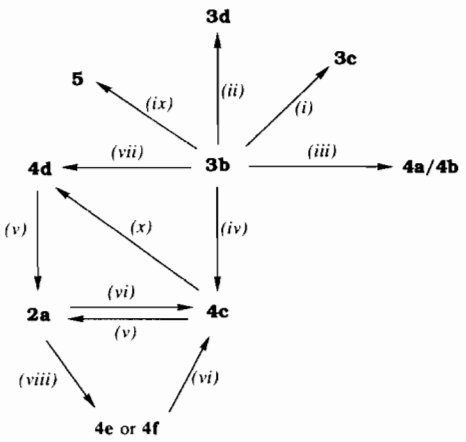
For the convenience of the reader the results discussed in this paper are summarised in Scheme 1.

Treatment of a tetrahydrofuran solution of (1*R*)-(+)-camphor with one equivalent of $LiBu^n$ at −70 °C, followed by one equivalent of PPh_2Cl, gave, from $^{31}P\{^1H\}$ NMR evidence, a mixture of the *exo*-phosphine **3a** ($\delta P = 1.5$ ppm) and the enolate ion **1** ($\delta P = -32.7$ ppm) in the ratio of *c.* 3:1. However, on storage, and as we have described previously, the proportion of the *exo*-phosphine **3a** decreased and after sixteen hours to two days the *endo*-phosphine **3b**, characterised by $\delta P = -10.5$ ppm became the major product. After two days the solvent was removed and the product taken up into the ethanol; the ethanol solution showed two singlets in its $^{31}P\{^1H\}$ NMR spectrum; these were due to the *exo*-phosphine **3a** ($\delta P = 1.3$ ppm) and the *endo*-

TABLE 1. Crystallographic data for compounds **3b** and **4b**[a]

	3b	**4b**
Crystal data		
Formula	$C_{22}H_{25}OP$	$C_{44}H_{50}Cl_2O_2P_2Pd \cdot CH_2Cl_2$
Molecular weight	336.41	935.09[b]
Crystal dimensions (mm)	0.85×0.3×0.15	0.5×0.4×0.25
a (pm)	778.6(1)	1380.3(2)
b (pm)	1138.8(1)	1785.1(3)
c (pm)	2128.9(3)	1922.8(4)
U (nm^{-3})	1.8876(4)	4.7377(14)
D_x (g cm^{-3})	1.18	1.31
$F(000)$	720	1928
μ (cm^{-1})	1.453	7.12
Data collection		
Scan mode	ω/θ	ω/θ
Scan width	1.05°+α-doublet splitting	[c]
Scan speeds (°min^{-1})	1.5–8.0	[c]
2θ: min., max. (°)	4.0, 50.0	4.0, 50.0
No. data collected	2056	4665
No. data observed[d]	1674	4438
Refinement		
ρ_{max}, ρ_{min} (e Å^{-3})	0.20, −0.18	0.82, −0.39
Δ/σ_{max}	0.25	0.17
R[e]	0.0329	0.0425
R'[f]	0.0406	0.0551
Weighting parameter, g[g]	0.0003	0.0004
No. parameters	203	495

[a]Common to both compounds: orthorhombic, space group $P2_12_12_1$, $Z=4$, $4.0<2\theta<50.0°$. [b]Includes CH_2Cl_2 solvate. [c]Scan divided into 30 steps, scan width and step sizes calculated from a learnt profile, scan speeds 0.4–1.5 s per step. [d]Criterion for observed reflection, $|F_o|>4.0\sigma(|F_o|)$. [e]$R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. [f]$R'=\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2$. [g]$w=[\sigma^2(|F_o|)+g(|F_o|)^2]^{-1}$.



Scheme 1. (i) H_2O_2; (ii) S; (iii) $[PdCl_2(NCPh)_2]$; (iv) $[PtCl_2(cod)]$; (ν) NaH; (vi) HCl; (vii) $[PtCl_2(NCMe)_2]$; (viii) RC≡CH; (ix) $[Rh_2Cl_2(CO)_4]$; (x) Δ.

phosphine **3b** ($\delta P = -11.2$ ppm) in the ratio of *c.* 1:5. When the ethanol solution was cooled to −15 °C the pure, crystalline, *endo*-phosphine **3b** was obtained in 72% yield. This *endo*-phosphine **3b** was fully characterised, see 'Experimental' for elemental analytical data on this and other new compounds. It showed a strong IR band at 1725 cm^{-1} due to ν(C=O) (Table 2).

TABLE 2. $^{31}P\{^1H\}$ NMR data[a] and IR data[b]

	δ(P)	^1J(MP)	ν(C=O)[c]	ν(M–Cl)[d]
2a[e]	4.6	3645		
2b[e]	31.6			
3b	−12.0[f]		1725	
3c	28.0[f]		1735	
3d	41.1[f]		1735	
4a	18.6[f]		1725	360
4b	30.6[f, g]			
4c[e]	6.4	3879	1725	285, 305
4d	14.5[f]	2577[f]	1735	350
4e[e]	13.1	2327	1730	
4f[e]	13.5	2314	1730	
5[h]	32.2	127	1725	300

[a]Recorded at 36.2 MHz, chemical shifts (δ) are in ppm relative to 85% H_3PO_4, ^1J(MP) values are in Hz. [b]In cm^{-1}. [c]KBr disc, all carbonyl bands are strong. [d]Nujol mulls. [e]From ref. 1. [f]In $CDCl_3$. [g]Tentative assignment. [h]In C_6D_6, $\nu(C\equiv O)=1985$ cm^{-1}.

Analysis of the ^1H (Table 3) and $^{13}C\{^1H\}$ (Table 4) NMR spectra of the compound allowed us to assign its stereochemistry unequivocally.

In the proton spectrum the H(3) *exo*-proton and H(4) proton were assigned using two-dimensional

TABLE 3. Proton NMR data[a]

	Camphor methyls	H(3)	H(4)
2a	0.67s, 1.03s, 1.13s		2.00(s, br)
2b	0.68s, 1.08s, 1.10s		1.93(s, br)
3b[b]	0.92(9H, s)	3.42[m, ^3J(HH) 4.5, ^2J(PH) ~ 0][c]	1.90[m, ^3J(HH) 4.6][c]
3c	0.90s, 0.92s, 0.95s	3.56[ddd, ^3J(HH) 4.4, ^4J(HH) 1.7, ^2J(PH) 14.9]	2.36(m)
3d	0.91s, 0.93s, 0.95s	3.83[ddd, ^3J(HH) 4.3, ^4J(HH) 1.6, ^2J(PH) 16.6]	2.45(m)
4a	0.79s, 0.93s, 0.96s	4.38[m, ^3J(HH) 4.0]	2.98(m)
4c	0.79s, 0.88(6H, s)	5.76[m, ^3J(HH) 3.7, ^2J(PH) 18.9]	2.34(m)
4d	0.80s, 0.92s, 0.97s	4.31[m, ^3J(HH) 4.3]	3.02(m)
4e	0.50s, 0.64s, 0.79s	4.35[m, ^3J(HH) 3.9]	3.21(m)
4f	0.67s, 0.80s, 0.87s	4.26[m, ^3J(HH) 4.1]	3.23(m)
5[d]	0.59s, 0.74(6H, s)	4.77[m, ^3J(HH) 4.0, ^4J(HH) 1.8]	3.11(m)

[a]Recorded at 100 MHz, chemical shifts (δ) are in ppm ($\pm$0.01 ppm) relative to $SiMe_4$, solvent $CDCl_3$ unless otherwise stated, coupling constants J are in Hz, s = singlet, m = multiplet, ddd = doublet of doublet of doublets, br = broad. [b]At 400 MHz. [c]Obtained by double resonance experiments at 400 MHz. [d]In C_6D_6.

^1H–^{13}C correlation spectroscopy at 400 MHz. The H(3)*exo*-proton gave rise to a multiplet at 3.42 ppm, any coupling to phosphorus and H(4) were resolved by double resonance experiments (^2J(PH) ~ 0 Hz and ^3J(HH) = 4.5 Hz). Very weak 'W' ^4J(HH) coupling to H(5) *exo*-proton was observed. We have previously observed a weak (2.3 Hz) 'W' coupling to the H(5) *exo*-proton in *endo*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone [4]. The stereochemistry of the C(3) position follows from the ^3J(HH) coupling with the H(4) proton which depends on the dihedral angle between the two C–C–H planes, as predicted by the Karplus relationship [10]. There are several examples in the literature which show that for camphor derivatives or related species, ^3J(HH) between the H(3) *endo*-proton and the H(4) proton, is zero or very small (< 1 Hz) whereas ^3J(HH) between H(3) *exo*-proton and the H(4) proton is about 4 Hz. Examples from the literature which illustrate this include norcamphor [11], several derivatives of 3-methyl-camphor [3], other rigid bicyclic compounds, related to camphor [10], and our previous results with *exo*- and *endo*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazones [4] and their metal complexes [4, 12]. Moreover, as described below, we have determined the crystal structure of this camphor phosphine and confirmed that it is the *endo*-isomer **3b** (see Fig. 1 and below).

In a recent paper [14] it has been reported that treatment of (1*R*)-*endo*-(+)-3-bromocamphor with LiBu^n followed by PPh_2Cl gives (1*R*)-(+)-3-diphenylphosphinocamphor to which the *endo*-configuration was assigned. However, it is clear from the published $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR data that this phosphine is the *exo*-isomer **3a** (the H(3) proton gave rise to a *singlet* at 3.10 ppm, i.e. ^3J(HH) = 0 Hz). The assignment of the *endo*-configuration was based upon $^{13}C\{^1H\}$ NMR evidence, and the crystal structure of an unspecified rhodium complex. Although, as discussed below, $^{13}C\{^1H\}$ NMR data do provide evidence of stereochemistry, they support our reassignment of this phosphine as the *exo*-isomer **3a** and presumably under the conditions used to prepare the rhodium complex, the phosphine isomerised to the *endo*-configuration.

The $^{13}C\{^1H\}$ NMR spectra, which we have assigned by C–H correlation spectroscopy and by comparison with published data for (1*R*)-(+)-camphor [15, 16], help to establish the stereochemistry of these phosphines. Quin *et al.* reported [17] the $^{13}C\{^1H\}$ NMR spectra of a series of 2-norbornyl-phosphorus(III) and phosphorus(V) compounds. They showed that the pattern of coupling constants for the carbons in the norbornyl group is characteristic for the *exo*- and *endo*-phosphorus substituents. In particular, the resonance for C(5) in the camphor phosphines is expected to show a large coupling (> 20 Hz) to a phosphorus(III) in the *endo*-position but a smaller coupling (< 8 Hz) to a phosphorus(III) in the *exo*-position. As can be seen from Table 4, the spectrum of the *endo*-phosphine **3b**, has the resonance for C(5) with a coupling ^3J(PC) of 20.2 Hz; by comparison the *exo*-phosphine **3a** shows a corresponding coupling $^3J\{PC(5)\}$ of 2.4 Hz [14]. Additionally, we have measured the phosphorus(III)–carbon-13 couplings on the *exo*- and *endo*-isomers of 3-diphenylphosphinocamphor dimethylhydrazone; we find ^3J(PC) for C(5) is 15 Hz for the *endo*-phosphine and approximately zero for the *exo*-phosphine [4].

We have examined the acid/base catalysed isomerisation of the *endo*-phosphine **3b** to the *exo*-phosphine **3a**. As show by $^{31}P\{^1H\}$ NMR spectroscopy, a solution of the *endo*-phosphine **3b** in $CDCl_3$ containing acetic acid (0.01 M) was slowly isomerised to an *endo*-/*exo*-

TABLE 4. $^{13}C\{^1H\}$ NMR data[a]

Compound	Camphor carbons										Phosphine phenyls				Others
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C_i	C_o	C_m	C_p	
2a	57.8t[b] (6.0)	201.3t (10.5)	91.9m (80.1)	48.0s	27.3s	32.8s	56.4t[b] (16.2)	20.8s	20.8s	9.7s	131.5m (66.9)	132.7t (11.8)	127.8t (11.2)	130.1s	
											129.2m (65.0)	132.0t (10.8)	127.6t (11.3)	129.6s	
2b[c]	57.7t[b] (4.8)	201.6t (11.7)	89.5m (56.6)	48.5t (5.9)	27.5s	32.7s	56.6t[b] (18.5)	20.8s	20.5s	9.5s	131.5m (57.5)	132.7t (12.6)	128.0t (10.5)	130.1s	
											129.4m (70.7)	132.1t (11.3)	127.8t (8.9)	129.7s	
3b	59.5d (1.6[d])	217.6d (8.0[e])	50.3d (20.5[f])	47.7d (5.1[e])	23.2d (20.2[d])	30.3s	47.3d (2.4[d])	19.6s	19.0d (1.4[g])	9.7s	138.4d (14.2[f])	134.5d (21.0[e])	128.5d (7.7[d])	129.3s	
											136.9d (13.4[f])	133.0d (18.7[e])	128.0d (6.5[d])	128.1s	
3c	59.4d (1.7[d])	211.2d (3.3[e])	52.5d (69.2[f])	46.6d (2.2[e])	22.8d (5.5[d])	29.0s	47.1d (11.8[d])	19.2s	18.8s	9.7s	133.6d (29.4[f])	131.2d (9.5[e])	128.3d (11.8[d])	131.4d (2.6[g])	
											132.6d (29.1[f])	130.7d (9.5[e])	128.0d (12.1[d])	131.2d (3.2[e])	
4a	59.8s	212.6t (3.6)	49.1t (22.9)	48.9t (2.6)	24.0t (6.5)	29.1s	47.7t (10.7)	19.3s	18.8s	9.7s	131.5t (48.6)	136.2t (12.6)	128.0t (10.6)	130.7s	
											126.3t (45.0)	133.8t (12.8)	127.4t (10.8)	130.1s	
4b	60.1s	[h]	[h]	49.4s	[h]	[h]	47.7m [i]	19.4s	18.6s	9.6s	129.4m (43.7)	135.7m (8.1)	128.6m (12.5)	131.9s	
											[h]	133.2m (10.7)	127.7m (12.4)	[h]	
4c	59.9t (2.6)	212.0s	55.6m (40.5)	49.0t (5.8)	21.2s	29.8s	48.3m (10.8)	19.4s	18.8s	9.7s	129.3m (60.4)	137.5t (11.9)	128.2t (11.7)	131.9s	
											123.4m (60.1)	132.4t (11.9)	128.1t (10.8)	129.8s	
4d	59.9s	212.8t (3.6)	48.5t (29.5)	48.8s	24.0t (6.1)	29.4s	47.6t (10.8)	19.4s	18.9s	9.7s	131.2t (57.3)	136.0t (12.3)	128.0t (10.9)	130.6s	
											125.3t (52.6)	134.2t (12.8)	127.3t (10.9)	130.2s	
4e	60.0s	213.4t (4.4)	54.3m (34.5)	49.5s	23.6s	29.1s	46.9m (10.5)	19.2s	18.5s	9.6s	133.0m (55.1)	135.1t (11.6)	128.2t (10.7)	130.2s	100.0dd[j] (148.8[d], 21.9[d])
											125.7m (46.4)	135.0t (11.6)	127.2t (10.4)	130.0s	107.7m[k] (33.3)
															127.7s, 131.3s
															127.2s, 125.2s
4f	60.1s	213.7t (5.1)	54.5m (34.6)	49.5s	23.7s	29.2s	46.9m (10.5)	19.4s	18.6s	9.7s	132.1m (55.7)	135.3t (11.7)	128.2t (10.7)	130.1s	98.2dd[j] (148.9[d], 21.8[d])
											125.8m (44.8)	135.0t (11.8)	127.1t (10.2)	130.0s	108.8m[k] (33.2)
															130.2s, 116.8s
															24.1s

[a]Spectra recorded in $CDCl_3$ solution at an operating frequency of 100.6 MHz unless stated otherwise. Assignments of resonances to carbon atoms C(8) and C(9) are arbitrary. Figures in parentheses are coupling constants, in hertz, to ^{31}P and are a measure of *N* unless otherwise stated. s = singlet, d = doublet, t = triplet, m = multiplet. [b]Tentative assignment. [c]Recorded at an operating frequency of 75 MHz. [d] $^3J(PC)$. [e] $^2J(PC)$. [f] $^1J(PC)$. [g] $^4J(PC)$. [h]Resonance not observed. [i]Resonance obscured. [j]Pt–*C*≡C. [k]Pt–C≡*C*.

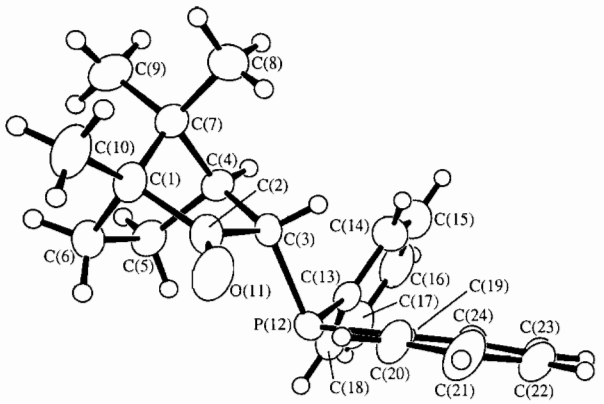


Fig. 1. ORTEP [13] representation of the crystal structure of **3b**.

mixture; equilibrium being reached after 2 days at 20 °C (ratio *endo*:*exo* 5.4:1). Treatment of a tetrahydrofuran solution of **3b** with one equivalent of $LiBu^n$ caused complete conversion to the enolate ion **1**, which, with methanol, gave a mixture of **3a** and **3b** ($^{31}P\{^1H\}$ NMR evidence).

We treated the *endo*-phosphine **3b** with H_2O_2 or with monoclinic sulfur to give the corresponding phosphine oxide, **3c**, or phosphine sulfide, **3d**. The phosphine oxide, **3c**, showed for the H(3) a ^3J-coupling to H(4) of 4.4. Hz indicative of a 3-*exo* proton and also a 'W'-coupling to *exo*-H(5) of 1.7 Hz (Table 3). Similar values were obtained with the phosphine sulfide **3d**, i.e. for both **3c** and **3d** the phosphorus substituent is in the *endo*-position. Corroboration for this assignment came from the $^{13}C\{^1H\}$ NMR spectrum of **3c**. Again referring to the study of 2-norbornyl phosphorus compounds [17], $^3J(PC)$ for the resonance for C(7) is expected to be very small (*c.* zero) for *exo*-P(V) and >10 Hz for *endo*-P(V); for **3c** $^3J(PC)$ for the C(7) resonance is 11.8 Hz (Table 4). In all the metal complexes described below, we have found that $|^3J(PC)+{}^5J(PC)|$ for the C(7) resonance is greater than 10 Hz, which again suggests *endo*-stereochemistry for these compounds.

We have made palladium, platinum and rhodium complexes from the *endo*-phosphine **3b**. Treatment of $[PdCl_2(NCPh)_2]$ with two equivalents of **3b** gave $[PdCl_2(PPh_2C_{10}H_{15}O)_2]$ which showed a very strong IR band at 360 cm^{-1} indicating a *trans*-configuration. In the ^1H and $^1H\{^{31}P\}$ NMR spectra (Table 3) the coupling between H(3) and H(4) clearly indicated an *exo*-configuration for H(3), i.e. PPh_2 is *endo*. However, in the $^{31}P\{^1H\}$ NMR spectrum we observed two resonances (at δ 18.6 and 30.6) in a ratio of ~10:1 which we tentatively assigned to two isomeric forms. The presence of two forms in solution was confirmed by the $^{13}C\{^1H\}$ NMR spectrum which again showed major and minor forms in ~10:1 ratio. The resonances for the phosphine phenyl C_{ipso}s and camphor C(3) atoms in the major form appeared as limiting 'virtual' triplets (see Fig. 2)

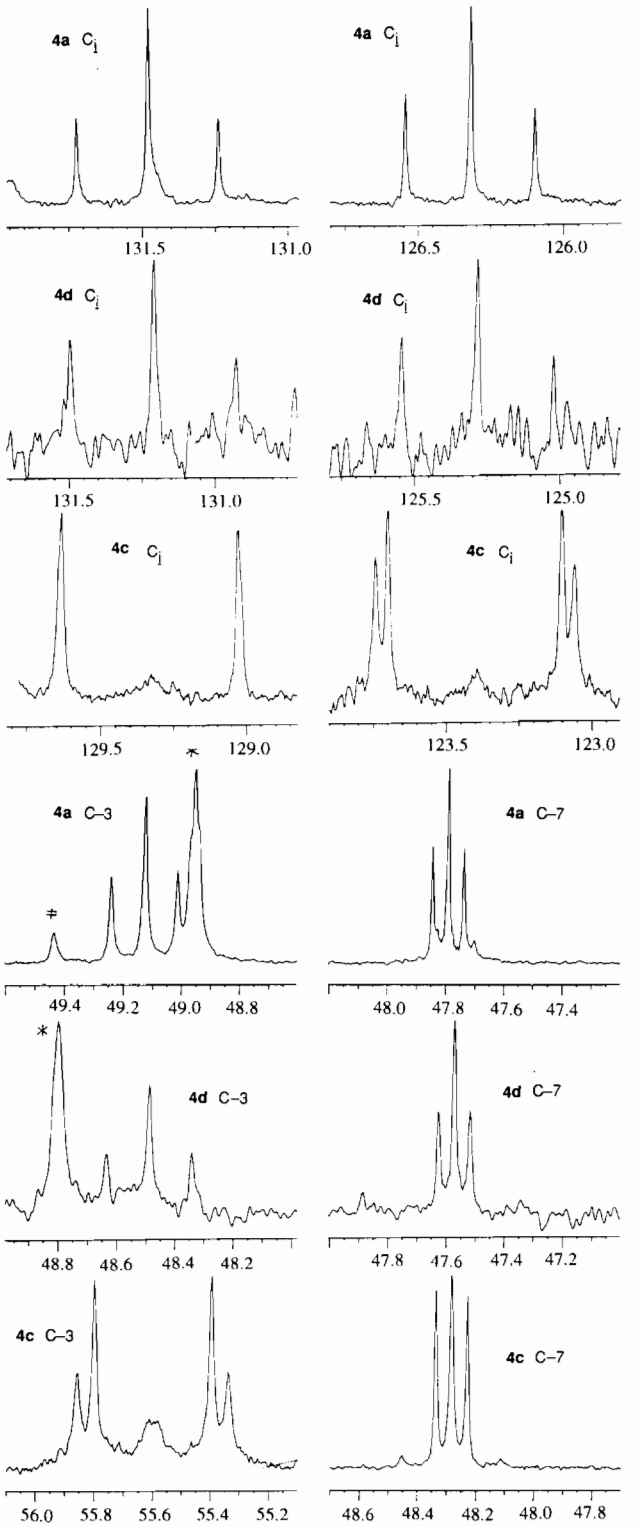


Fig. 2. Portions of the $^{13}C\{^1H\}$ NMR spectra of **4a**, **4d** and **4c**, recorded in $CDCl_3$ solution at 100.6 MHz. C_i resonances refer to the *ipso*-carbons of the non-equivalent phenyls attached to phosphorus. The resonances of the *trans*-complexes **4a** and **4d** are essentially limiting whereas those of the *cis*-complex **4c** are not. Peaks marked with an asterisk (*) arise from C-4 carbon resonances of **4a** and **4d** while the peak marked (‡) is assigned to the C-4 resonance of **4b**.

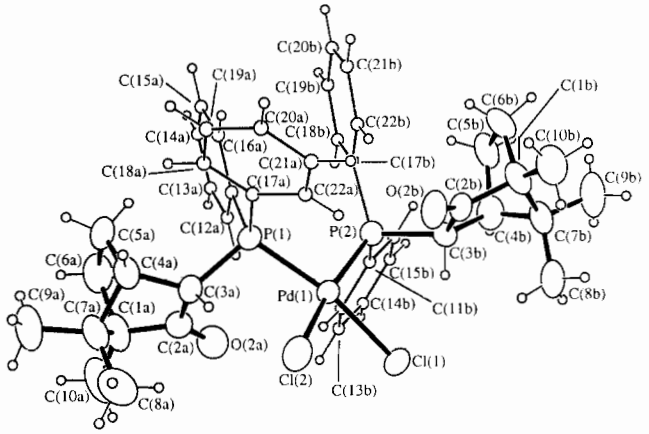


Fig. 3. ORTEP [13] representation of the crystal structure of **4b**. In the interests of clarity the phenyl carbon atoms and all hydrogen atoms have been drawn as circles with a small radius of arbitrary value.

TABLE 5. Bond lengths (pm) and angles (°) for compound **3b** with e.s.d.s in parentheses

C(3)–P(12)	187.9(5)	C(13)–P(12)	184.4(3)
C(19)–P(12)	185.4(3)	C(2)–C(1)	152.7(6)
C(6)–C(1)	155.3(6)	C(7)–C(1)	154.1(6)
C(10)–C(1)	151.8(6)	C(3)–C(2)	152.6(6)
O(11)–C(2)	120.9(5)	C(4)–C(3)	154.2(6)
C(5)–C(4)	154.7(6)	C(7)–C(4)	155.3(6)
C(6)–C(5)	154.4(6)	C(8)–C(7)	153.3(6)
C(9)–C(7)	152.9(6)		
C(13)–P(12)–C(3)	99.9(2)	C(19)–P(12)–C(3)	101.6(2)
C(19)–P(12)–C(13)	102.0(2)	C(6)–C(1)–C(2)	101.6(3)
C(7)–C(1)–C(2)	101.6(3)	C(7)–C(1)–C(6)	102.5(3)
C(10)–C(1)–C(2)	113.8(4)	C(10)–C(1)–C(6)	115.5(3)
C(10)–C(1)–C(7)	119.3(4)	C(3)–C(2)–C(1)	107.3(3)
O(11)–C(2)–C(1)	125.7(4)	O(11)–C(2)–C(3)	127.0(4)
C(2)–C(3)–P(12)	114.3(3)	C(4)–C(3)–P(12)	115.9(3)
C(4)–C(3)–C(2)	100.3(3)	C(5)–C(4)–C(3)	108.2(3)
C(7)–C(4)–C(3)	102.3(3)	C(7)–C(4)–C(5)	102.4(3)
C(6)–C(5)–C(4)	103.0(3)	C(5)–C(6)–C(1)	103.7(3)
C(4)–C(7)–C(1)	93.9(3)	C(8)–C(7)–C(1)	114.0(3)
C(8)–C(7)–C(4)	112.3(4)	C(9)–C(7)–C(1)	113.7(4)
C(9)–C(7)–C(4)	114.2(4)	C(9)–C(7)–C(8)	108.3(4)
C(14)–C(13)–P(12)	123.9(2)	C(18)–C(13)–P(12)	116.1(2)
C(20)–C(19)–P(12)	117.7(2)	C(24)–C(19)–P(12)	122.1(2)

suggesting that the phosphine ligands are mutually *trans* at the metal centre, i.e. **4a**. The resonances for the minor species in solution that could be identified, showed non-limiting second-order patterns typical of *cis*-positioning of the phosphines, i.e. **4b**. We have previously discussed the use of $^{13}C\{^1H\}$ NMR spectroscopy to determine the stereochemistry of tertiary phosphine-metal complexes [18]. We could not identify or assign ^1H resonances of this minor component presumably because they overlapped with the much stronger resonances of the major component **4a**.

TABLE 6. Non-hydrogen atomic coordinates ($\times 10^4$) for compound **3b** with e.s.d.s in parentheses

	x	*y*	*z*
P(12)	−2049.8(8)	−2379.3(6)	−8617.8(3)
C(1)	−3127(4)	−5115(2)	−9724(1)
C(2)	−2014(4)	−4665(2)	−9184(1)
C(3)	−3116(3)	−3822(2)	−8799(1)
C(4)	−4732(4)	−3758(2)	−9217(1)
C(5)	−4242(4)	−3126(2)	−9836(1)
C(6)	−3119(4)	−4045(2)	−10177(1)
C(7)	−4939(4)	−5054(3)	−9433(1)
C(8)	−6400(5)	−5205(3)	−9911(2)
C(9)	−5223(6)	−5927(3)	−8897(2)
C(10)	−2504(5)	−6265(3)	−10005(2)
O(11)	−520(3)	−4911(2)	−9097(1)
C(13)	−3943(2)	−1514(1)	−8377(1)
C(14)	−5208(2)	−1925(1)	−7968(1)
C(15)	−6590(2)	−1205(1)	−7806(1)
C(16)	−6707(2)	−73(1)	−8055(1)
C(17)	−5443(2)	338(1)	−8464(1)
C(18)	−4061(2)	−382(1)	−8626(1)
C(19)	−1015(2)	−2699(2)	−7852(1)
C(20)	250(2)	−3568(2)	−7837(1)
C(21)	1147(2)	−3789(2)	−7281(1)
C(22)	779(2)	−3142(2)	−6741(1)
C(23)	−486(2)	−2273(2)	−6756(1)
C(24)	−1383(2)	−2062(2)	−7311(1)

When we recrystallised a sample of the **4a:4b** mixture from CH_2Cl_2/MeOH we obtained crystals of quality suitable for an X-ray diffraction study (see below). However, the crystal structure (Fig. 3) (see below) proved to be the *cis*-isomer **4b**. Presumably the *cis* and *trans* forms equilibrate in solution, but the interconversion is slow on the NMR time scale. Complexes of type $[PdCl_2L_2]$ (L = tertiary phosphine) are labile and interconversion *cis* ↔ *trans* would be expected to occur at room temperature [19]. The product $[PdCl_2L_2]$ **4a:4b** was identical with the product we obtained previously by treating the bis-chelate **2b** with dry hydrogen chloride, the stereochemistry of which was not determined. In our previous paper we suggested that the stereochemistry of the enolate **2b** was *cis*, by analogy with the platinum complex **2a**, the stereochemistry of which was shown to be *cis* from the large value of $^1J(^{195}Pt^{31}P)$. We now report the $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b** (see Table 4) and the appearance of the resonances for the C_{ipso}s and camphor C(3) as non-limiting second-order patterns confirms our assignment of these compounds as *cis*.

Treatment of $[PtCl_2(cod)]$ with **3b** gave *cis*-$[PtCl_2(PPh_2C_{10}H_{15}O)_2]$, a white crystalline product identical with the product obtained previously by treating the bis-chelate **2a** with an excess of hydrogen chloride. The ^1H NMR data suggest an *endo*-position for the PPh_2 groups. The far IR spectrum showed two ν(Pt–Cl) bands at 285 and 305 cm^{-1} indicating the *cis*-config-

TABLE 7. Bond lengths (pm) and angles (°) for compound **4b** with e.s.d.s in parentheses

P(1)–Pd(1)	227.8(4)	P(2)–Pd(1)	228.4(4)
Cl(1)–Pd(1)	236.4(4)	Cl(2)–Pd(1)	235.7(4)
C(3a)–P(1)	184.4(9)	C(11a)–P(1)	181.9(6)
C(17a)–P(1)	181.8(5)	C(3b)–P(2)	188.8(9)
C(11b)–P(2)	183.0(6)	C(17b)–P(2)	182.8(6)
C(2a)–C(1a)	150.7(13)	C(6a)–C(1a)	155.8(15)
C(7a)–C(1a)	153.2(14)	C(10a)–C(1a)	148.5(12)
O(2a)–C(2a)	121.8(10)	C(3a)–C(2a)	149.5(11)
C(4a)–C(3a)	157.7(12)	C(5a)–C(4a)	153.4(14)
C(7a)–C(4a)	155.7(13)	C(6a)–C(5a)	153.1(14)
C(8a)–C(7a)	151.5(14)	C(9a)–C(7a)	152.1(13)
C(2b)–C(1b)	151.8(12)	C(6b)–C(1b)	156.4(13)
C(7b)–C(1b)	156.0(13)	C(10b)–C(1b)	146.1(12)
O(2b)–C(2b)	118.9(10)	C(3b)–C(2b)	153.0(12)
C(4b)–C(3b)	154.2(12)	C(5b)–C(4b)	152.1(14)
C(7b)–C(4b)	155.1(13)	C(6b)–C(5b)	153.2(14)
C(8b)–C(7b)	150.1(14)	C(9b)–C(7b)	151.4(13)
P(2)–Pd(1)–P(1)	98.8(2)	Cl(1)–Pd(1)–P(1)	169.5(1)
Cl(1)–Pd(1)–P(2)	88.1(2)	Cl(2)–Pd(1)–P(1)	87.1(2)
Cl(2)–Pd(1)–P(2)	166.9(1)	Cl(2)–Pd(1)–Cl(1)	87.8(2)
C(3a)–P(1)–Pd(1)	107.7(3)	C(11a)–P(1)–Pd(1)	117.6(3)
C(11a)–P(1)–C(3a)	105.8(4)	C(17a)–P(1)–Pd(1)	110.3(3)
C(17a)–P(1)–C(3a)	105.3(4)	C(17a)–P(1)–C(11a)	109.3(3)
C(3b)–P(2)–Pd(1)	104.6(3)	C(11b)–P(2)–Pd(1)	111.1(3)
C(11b)–P(2)–C(3b)	106.0(4)	C(17b)–P(2)–Pd(1)	119.7(3)
C(17b)–P(2)–C(3b)	107.8(4)	C(17b)–P(2)–C(11b)	106.8(3)
C(6a)–C(1a)–C(2a)	102.2(8)	C(7a)–C(1a)–C(2a)	102.6(7)
C(7a)–C(1a)–C(6a)	101.2(8)	C(10)–C(1a)–C(2a)	115.3(9)
C(10)–C(1a)–C(6a)	113.8(9)	C(10)–C(1a)–C(7a)	119.3(9)
O(2a)–C(2a)–C(1a)	127.4(9)	C(3a)–C(2a)–C(1a)	108.1(7)
C(3a)–C(2a)–O(2a)	124.5(9)	C(2a)–C(3a)–P(1)	115.9(6)
C(4a)–C(3a)–P(1)	126.1(6)	C(4a)–C(3a)–C(2a)	100.6(7)
C(5a)–C(4a)–C(3a)	108.4(7)	C(7a)–C(4a)–C(3a)	100.9(7)
C(7a)–C(4a)–C(5a)	101.3(8)	C(6a)–C(5a)–C(4a)	103.4(8)
C(5a)–C(6a)–C(1a)	104.0(8)	C(4a)–C(7a)–C(1a)	94.2(7)
C(8a)–C(7a)–C(1a)	111.5(9)	C(8a)–C(7a)–C(4a)	112.5(8)
C(9a)–C(7a)–C(1a)	116.0(9)	C(9a)–C(7a)–C(4a)	112.4(9)
C(9a)–C(7a)–C(8a)	109.6(9)	C(12a)–C(11a)–P(1)	117.2(3)
C(16a)–C(11a)–P(1)	122.5(3)	C(18a)–C(17a)–P(1)	122.9(3)
C(22a)–C(17a)–P(1)	117.0(3)	C(6b)–C(1b)–C(2b)	103.2(7)
C(7b)–C(1b)–C(2b)	100.6(7)	C(7b)–C(1b)–C(6b)	101.2(8)
C(10b)–C(1b)–C(2b)	113.8(8)	C(10b)–C(1b)–C(6b)	115.2(9)
C(10b)–C(1b)–C(7b)	120.4(8)	O(2b)–C(2b)–C(1b)	126.8(8)
C(3b)–C(2b)–C(1b)	106.5(7)	C(3b)–C(2b)–O(2b)	126.6(7)
C(2b)–C(3b)–P(2)	114.6(6)	C(4b)–C(3b)–P(2)	124.9(6)
C(4b)–C(3b)–C(2b)	101.2(7)	C(5b)–C(4b)–C(3b)	111.8(8)
C(7b)–C(4b)–C(3b)	99.9(7)	C(7b)–C(4b)–C(5b)	102.7(8)
C(6b)–C(5b)–C(4b)	103.0(8)	C(5b)–C(6b)–C(1b)	104.5(8)
C(4b)–C(7b)–C(1b)	93.7(7)	C(8b)–C(7b)–C(1b)	112.5(8)
C(8b)–C(7b)–C(4b)	115.4(8)	C(9b)–C(7b)–C(1b)	113.0(9)
C(9b)–C(7b)–C(4b)	114.2(8)	C(9b)–C(7b)–C(8b)	107.8(8)
C(12b)–C(11b)–P(2)	118.5(3)	C(16b)–C(11b)–P(2)	121.5(3)
C(18b)–C(17b)–P(2)	122.2(2)	C(22b)–C(17b)–P(2)	117.6(2)

TABLE 8. Non-hydrogen atomic coordinates ($\times 10^4$) for compound **4b** with e.s.d.s in parentheses

	x	*y*	*z*
Pd(1)	9173.9(4)	705.8(3)	7992.9(3)
P(1)	10260(1)	1640(1)	8204(1)
P(2)	9019(1)	255(1)	9099(1)
Cl(1)	8241(1)	−324(1)	7608(1)
Cl(2)	8956(2)	1239(2)	6883(1)
C(1a)	12621(6)	1364(5)	6980(5)
C(2a)	11690(6)	1071(4)	7286(4)
O(2a)	11474(5)	420(3)	7395(4)
C(3a)	11045(5)	1725(4)	7432(4)
C(4a)	11755(6)	2394(4)	7267(4)
C(5a)	12568(6)	2391(5)	7811(5)
C(6a)	13148(6)	1686(6)	7631(5)
C(7a)	12294(6)	2084(5)	6616(5)
C(8a)	11613(8)	1918(7)	6018(5)
C(9a)	13098(7)	2603(6)	6371(6)
C(10a)	13203(8)	806(6)	6587(7)
C(11a)	11074(3)	1527(3)	8940(2)
C(12a)	11631(3)	876(3)	8963(2)
C(13a)	12331(3)	786(3)	9479(2)
C(14a)	12474(3)	1348(3)	9973(2)
C(15a)	11917(3)	1999(3)	9950(2)
C(16a)	11217(3)	2089(3)	9434(2)
C(17a)	9639(3)	2535(2)	8274(2)
C(18a)	10127(3)	3220(2)	8276(2)
C(19a)	9604(3)	3888(2)	8290(2)
C(20a)	8594(3)	3872(2)	8300(2)
C(21a)	8106(3)	3188(2)	8298(2)
C(22a)	8629(3)	2519(2)	8284(2)
C(1b)	6211(6)	599(5)	9685(4)
C(2b)	7034(5)	746(4)	9179(4)
O(2b)	7137(4)	1284(3)	8822(3)
C(3b)	7684(5)	53(4)	9197(4)
C(4b)	7229(6)	−391(4)	9803(5)
C(5b	7352(7)	12(6)	10494(4)
C(6b)	6702(6)	703(6)	10411(4)
C(7b)	6139(6)	−272(5)	9640(5)
C(8b)	5814(7)	−536(5)	8936(5)
C(9b)	5460(7)	−603(6)	10176(6)
C(10b)	5356(7)	1064(6)	9564(6)
C(11b)	9636(4)	−646(2)	9195(3)
C(12b)	10165(4)	−924(2)	8633(3)
C(13b)	10648(4)	−1608(2)	8689(3)
C(14b)	10603(4)	−2014(2)	9308(3)
C(15b)	10075(4)	−1737(2)	9870(3)
C(16b)	9591(4)	−1054(2)	9814(3)
C(17b)	9391(3)	834(2)	9836(2)
C(18b)	10056(3)	585(2)	10331(2)
C(19b)	10259(3)	1025(2)	10913(2)
C(20b)	9797(3)	1713(2)	11000(2)
C(21b)	9132(3)	1962(2)	10505(2)
C(22b)	8929(3)	1523(2)	9923(2)

uration **4c** and the very large value of ^1J(PtP) (3829 Hz) also showed the *cis*-configuration. However, treatment of $[PtCl_2(NCMe)_2]$ with two equivalents of the *endo*-phosphine gave a yellow crystalline isomer $[PtCl_2(PPh_2C_{10}H_{15}O)_2]$ (**4d**) characterised by a singlet $^{31}P\{^1H\}$ resonance at 14.5 ppm with satellites ^1J(PtP) = 2577 Hz. This *J* value clearly indicates a *trans*-configuration. The resonances of H(3) and H(4) were multiplets suggesting an *endo*-configuration for the PPh_2s. The $^{13}C\{^1H\}$ NMR spectra confirmed our assignment of **4c** and **4d** as *cis* and *trans* isomers, respectively. The resonances due to the phenyl C_{ipso} and

the camphor C(3) and C(7) atoms, shown in Fig. 2 provide a good example of how, in a spin system AXX' changing the value of $J(XX')$ (i.e. $^2J(PP)$) from small (for the *cis* compound **4c**) to large (for the *trans* compound **4d**) increases the second-order character towards a limiting 'virtual' triplet.

We treated both the complexes **4c** and **4d** with NaH in mineral oil and obtained the enolate bis chelate **2a** in both cases. We also found that the *cis*-dichlorocomplex **4c** when heated in dioxan at 100 °C for 1 day was almost completely converted into the isomeric *trans*-dichloro complex **4d**.

We previously reported [1] that the enolate phosphine bis-chelate **2a**, when heated with HC≡CPh or HC≡CC(Me)=CH_2 gave the bis-acetylides $[Pt(C{\equiv}CR)_2(PPh_2C_{10}H_{15}O)_2]$ (**4e**) and (**4f**), respectively. We now show from the ^1H and $^1H\{^{31}P\}$ NMR data (Table 3) that H(3) is *exo* ($^3J(HH) \sim 4$Hz), i.e. the PPh_2s are *endo*. Additionally, from the $^{13}C\{^1H\}$ NMR spectra of **4e** and **4f** it is clear that both complexes are *cis*: the resonances for the α-acetylide carbon atoms being pseudo-first-order doublets of doublets ($^2J(PC_{trans}) = c.$ 149 Hz and $^2J(PC_{cis}) = c.$ 22 Hz), a situation which has been described for *cis*-diphosphine–dialkyl complexes of platinum [20]. We also find that treatment of these diacetylide complexes with dry HCl gives only the *cis*-dichloro complex **4c** and none of the *trans* complex **4d**.

We have also studied reactions between the *endo*-camphor phosphine, **3b** or the enolate ion **1** with rhodium chlorocarbonyl. Treatment of $[Rh_2Cl_2(CO)_4]$ with 4 equivalents of the *endo* phosphine, **3b** gave the expected chloro(carbonyl)rhodium(I) complex of type *trans*-$[RhCl(CO)L_2]$, (**5**), L = the *endo*-phosphine, **3b**, in 90% yield. This complex was fully characterised and the $^1H\{^{31}P\}$ NMR data showed that the phosphoruses were still *endo*, i.e. $^3J\{H(3)–H(4)\} = 4.0$ Hz (see Table 3). The same complex was obtained by treating rhodium chlorocarbonyl, prepared *in situ* from $RhCl_3 \cdot 3H_2O$ and carbon monoxide, with a solution of the phosphine enolate **1**, followed by treatment with hydrochloric acid.

Crystal structures of endo-3-diphenylphosphino-(1R)-(+)-camphor (3b) (L) and cis-$[PdCl_2L_2]$ (4b)

The crystal structure of the phosphine **3b** is shown in Fig. 1 and the bond lengths and angles are shown in Table 5 and atom coordinates in Table 6. The structure shows that the PPh_2 is *endo*. The crystal structure of the palladium dichloride complex **4b** is shown in Fig. 3 with bond lengths and angles shown in Table 7 and atom coordinates in Table 8. The structure shows that both phosphine ligands are *endo* and coordinated to palladium in a *cis* fashion.

Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises further details of data collection and structure refinement, non-hydrogen atomic coordinates, H atom coordinates and isotropic and anisotropic thermal parameters.

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