

## Camphor-derived $\beta$ -Ketophosphine Complexes of Palladium(II) and Platinum(II)

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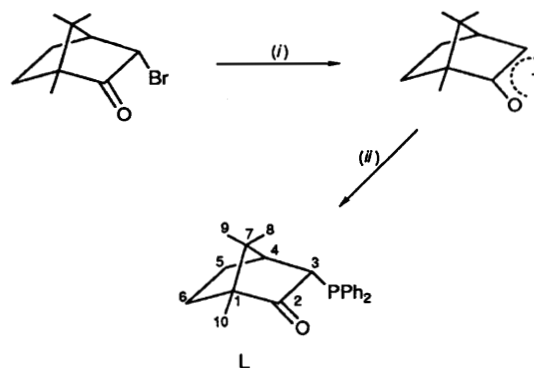
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Reaction of chlorodiphenylphosphine with the lithium enolate derived from the treatment of (1*R*)-endo-(+)-3-bromocamphor (camphor = bornan-2-one) with *n*-butyl-lithium gives (1*R*)-endo-(+)-3-diphenylphosphinocamphor (L). This new chiral  $\beta$ -ketophosphine ligand reacts with  $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$  to give *trans*- $[\text{PdL}_2\text{Cl}_2]$ , and in a 1 : 1 ratio to give the chloro-bridged dimer  $[\{\text{PdL}(\mu\text{-Cl})\text{Cl}_2\}]_2$ . The ligand L reacts with  $[\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2]$  to give *trans*- $[\text{PtL}_2\text{Cl}_2]$ . Thermolysis of  $[\text{ML}_2\text{Cl}_2]$  (M = Pd or Pt) in refluxing xylene gives mixed phosphine-phosphinite complexes with mutually *cis* chlorides. The complex  $[\text{PdL}_2\text{Cl}_2]$  reacts with an excess of  $\text{AgBF}_4$  to give  $[\text{PdL}_2][\text{BF}_4]_2$  which is shown to contain bidentate binding through the phosphorus and keto-oxygen atoms. All complexes are characterised by i.r.,  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy.

Although a wide range of chiral diphosphine ligands has been prepared and catalytic reactions demonstrating high enantioselectivities are known,<sup>1</sup> bidentate chiral ligands in which the donor set is P,O are relatively unusual and their co-ordination chemistry has been little explored.<sup>2</sup> This is somewhat surprising since functionalised phosphines of the type  $\text{R}_2\text{PCH}_2\text{C}(\text{O})\text{R}'$  or  $[\text{R}_2\text{PCH}=\text{C}(\text{O})\text{R}]^-$  have been used as ligands in e.g. the oligomerisation of ethene (SHOP process<sup>3</sup>) and the telomerisation of butadiene with  $\text{CO}_2$  to give lactones.<sup>4</sup> Ways in which the latter or related reactions, e.g. the dimerisation or oligomerisation of propene, could be carried out in a stereospecific manner would be extremely attractive. Following our recent studies of  $\beta$ -ketophosphonates with three chiral centres derived from the naturally occurring (+)-3-bromocamphor (camphor = bornan-2-one),<sup>5</sup> we have sought to prepare a chiral ligand containing a P,O donor set, also derived from (+)-3-bromocamphor. We now report the results of these studies, together with the thermal rearrangement of the 3-diphenylphosphinocamphor ligand to a new chiral bidentate phosphine-phosphinite complex. Braunstein and co-workers<sup>6</sup> have recently reported similar chemistry for the achiral  $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}$  ligand.

### Results and Discussion

(a) *Ligand*.—(1*R*)-endo-(+)-3-diphenylphosphinocamphor (L) was prepared by treatment of optically pure (1*R*)-endo-(+)-3-bromocamphor with *n*-butyl-lithium and subsequent treatment of the lithium enolate formed with chlorodiphenylphosphine (Scheme). Only one signal is observed in the  $^{31}\text{P}$  n.m.r. spectrum of the product and from an X-ray crystal structure obtained for a rhodium complex containing the ligand<sup>7</sup> we can confirm that the conformation of the ligand is *endo*. There is no evidence for attack at oxygen by phosphorus. 3-Diphenylphosphinocamphor is stable in air for several hours. An alternative synthesis of L was attempted, employing a common procedure for tertiary phosphine synthesis. Lithium diphenylphosphide and (1*R*)-endo-(+)-3-bromocamphor were allowed to react in tetrahydrofuran (thf) at  $-78^\circ\text{C}$  and a work-up procedure similar to that used for the successful synthesis of L was employed (see Experimental section). No 3-diphenylphosphinocamphor was isolated from the reaction but tetraphenyl-diphosphane was obtained in high yield, suggesting a possible lithium-halogen exchange reaction in which bromodiphenyl-



Scheme. Method for the preparation of L from 3-bromocamphor. (i)  $\text{LiBu}^\text{n}$ ,  $-78^\circ\text{C}$ ; (ii)  $\text{PPh}_2\text{Cl}$

phosphine is first formed but then reacts with lithium diphenylphosphide to give the diphosphane.

The i.r. and  $^{31}\text{P}$  n.m.r. data for the ligand L are given in Table 1 and the  $^1\text{H}$  n.m.r. data in Table 2. The  $^1\text{H}$  n.m.r. spectra for both ligand and complexes are complex and the spectrum of the free ligand was fully assigned using two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  correlation spectroscopy (COSY) and comparison with the spectrum of (1*R*)-endo-(+)-bromocamphor. Atom H(3) occurs as a singlet at  $\delta$  3.1 with  $J(\text{PH}) \approx 0$  Hz and this is not uncommon for free  $\beta$ -ketophosphine ligands;<sup>8</sup> H(4) occurs as a doublet of doublets at  $\delta$  1.93 and for the corresponding methylphosphonium salt (1) undergoes a large downfield shift to  $\delta$  5.15. This phenomenon has been attributed to a specific orientation of the phenyl rings, due to a change in geometry on the phosphorus atom, resulting in a deshielding effect on H(4) caused by the ring-current effect. This effect also occurs in complexes (2)–(6), but is not observed for e.g. (1*R*)-endo-(+)-3-(diethoxyphosphoryl)camphor or its molybdenum complexes<sup>9</sup> confirming that the phenyl rings and four-coordinate phosphorus atom are required for this downfield shift. Related interactions account for the high-field shift of the H(5) *endo* proton in the phosphonium salt (1) and the complexes (2)–(6) since models indicate that this proton sits directly above the centre of one of the phenyl rings on phosphorus.

In the  $^{13}\text{C}$  n.m.r. spectrum of L (see Experimental section), there is a remarkably large four-bond P–C coupling [22.9 Hz to

**Table 1.** I.r. and  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. data for new complexes

Complex	I.r. ( $\text{cm}^{-1}$ ) <sup>a</sup>		$^{31}\text{P}$ ( $\delta/\text{p.p.m.}$ ) <sup>b</sup>
	C=O	M—Cl	
L	1 719		0.1
(1)	1 735		20.3
(2)	1 734	355	18.0
(3)	1 734		16.8
(4)	1 730	348, 250	29.8
(5)	1 734	333	15.0, <sup>c</sup> $^1J(\text{PtP}) = 2\ 581$
(6) <i>cis</i>	1 651		45.8 <sup>c</sup>
<i>trans</i>	1 651		56.6 <sup>c</sup>
(7) <sup>d</sup>		310, 290	3.3, 121.9, $J(\text{PP}) = 7.3$
(8) <sup>e</sup>		310, 290	−21.5, $^1J(\text{PtP}) = 3\ 280$ 92.9, $^1J(\text{PtP}) = 4\ 081$ , $J(\text{PP}) = 7.3$

<sup>a</sup> Recorded as Nujol mulls between CsI plates. <sup>b</sup> Spectra recorded in  $\text{CDCl}_3$  unless otherwise stated. Shifts are to high frequency of external 85%  $\text{H}_3\text{PO}_4$ ,  $J$  values in Hz. <sup>c</sup> Recorded in  $\text{CD}_2\text{Cl}_2$ . <sup>d</sup>  $\nu(\text{C}=\text{C})$  1 592  $\text{cm}^{-1}$ . <sup>e</sup>  $\nu(\text{C}=\text{C})$  1 596  $\text{cm}^{-1}$ .

C(9)]. Since C(9), C(7), C(4), C(3), and P form an almost planar W arrangement, we attribute this high coupling to overlap of  $\sigma$  orbitals across the base of the W. High four-bond H—H couplings are sometimes observed if the H atoms are similarly related by a planar W geometry.<sup>10</sup> The P—C coupling drops to zero in the methyl phosphonium salt, the phosphine oxide, and 3-diethoxyphosphoryl camphor.<sup>9</sup>

(b) *Synthesis of Complexes.*—Addition of 2 equivalents of L to a suspension of  $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$ <sup>11</sup> in degassed ethanol results in the rapid precipitation of a bright yellow complex  $[\text{PdL}_2\text{Cl}_2]$  (2). A value of 1 734  $\text{cm}^{-1}$  for  $\nu(\text{C}=\text{O})$  implies that the keto group is unco-ordinated and the ligand is binding in a unidentate fashion. Metathesis of (2) with lithium bromide gives an orange complex  $[\text{PdL}_2\text{Br}_2]$  (3), and the disappearance of only one absorption peak at 355  $\text{cm}^{-1}$  in the far-i.r. spectrum of (3) due to  $\nu(\text{M}—\text{Cl})$  indicates that (2) is *trans*- $[\text{PdL}_2\text{Cl}_2]$  (Table 1). The *trans* configuration also follows from the appearance of a virtual triplet pattern due to H(3) in the  $^1\text{H}$  n.m.r. spectrum of (2) with  $^2J(\text{PH}) + ^4J(\text{PH}) = 8.6$  Hz (Table 2). One equivalent of L reacts with  $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$  in ethanol to give an orange complex (4) for which microanalytical and i.r. data suggest that the chloro-bridged dimer is formed.

When  $[\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2]$  is treated with 2 equivalents of L in ethanol a pale yellow powder is formed which has been characterised as  $[\text{PtL}_2\text{Cl}_2]$  (5). From  $^{31}\text{P}$  and  $^1\text{H}$  n.m.r. data (Tables 1 and 2) it can be seen that only one isomer is present.

The  $^{31}\text{P}$  n.m.r. spectrum shows a singlet with  $^{195}\text{Pt}$  satellites,  $J(\text{PtP}) = 2\ 581$  Hz, which suggests the *trans* configuration for the complex. This value is typical for a *trans* P—Pt—P arrangement.<sup>12</sup> In the  $^1\text{H}$  n.m.r. spectrum for the complex H(3) also occurs as a virtual triplet with  $^2J(\text{PH}) + ^4J(\text{PH}) = 8.1$  Hz. As for complex (2), the i.r. spectrum shows a strong absorption at 1 734  $\text{cm}^{-1}$  indicative of an unco-ordinated ketone group.

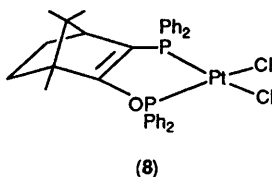
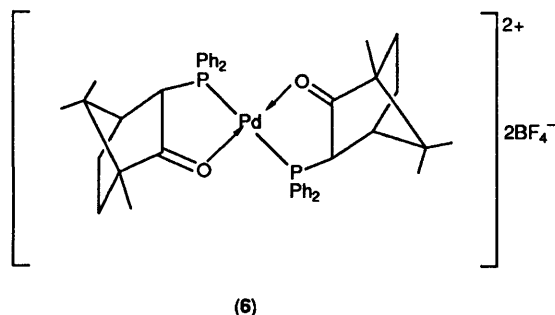
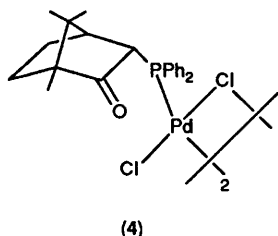
Addition of an excess of silver tetrafluoroborate to a solution of (2) in dichloromethane results in chloride abstraction from the complex and formation of the cationic complex  $[\text{PdL}_2]^+[\text{BF}_4]^-$  (6). The i.r. spectrum shows a fall in the  $\nu(\text{C}=\text{O})$  stretching frequency from 1 734 to 1 651  $\text{cm}^{-1}$  and indicates co-ordination of both keto-oxygen atoms to the metal centre. The  $^{31}\text{P}$  n.m.r. spectrum contains two singlets at 56.6 and 45.8 p.p.m. which have been assigned as the *trans* and *cis* isomers respectively occurring in a 3:2 ratio (based on integration of the  $^1\text{H}$  n.m.r. spectrum). The significant shift downfield from 18.0 p.p.m. for (2) is in keeping with the formation of a five-membered chelate-ring structure.<sup>13</sup> The *trans* isomer occurs at a higher chemical shift than the *cis* isomer and this is consistent with other P,O chelate complexes recently reported by Pringle and co-workers.<sup>14</sup> The  $^1\text{H}$  n.m.r. spectrum of (6) is complex with many signals obscured. The H(3) proton for the *trans* isomer again occurs as a virtual triplet with  $^2J(\text{PH}) + ^4J(\text{PH}) = 8.6$  Hz and the H(3) proton for the *cis* isomer is not observed. Some of the proton shifts are arbitrarily assigned although the three methyl groups for both isomers are separate and easily identified. In the *trans* isomer one methyl group on each ligand resonates to very high field ( $\delta < 0$ ). Models indicate that methyl group 10 sits directly above the centre of a phenyl ring on the phosphorus atom of the other ligand so we assign the high-field resonance to this methyl group.

(c) *Thermolysis of trans-[ML<sub>2</sub>Cl<sub>2</sub>]* (M = Pd or Pt).—When a solution of complex (2) in xylene is refluxed for 4 h the yellow colour of the solution disappears, and on cooling white microcrystals of (7) are formed. The i.r. spectrum shows the disappearance of  $\nu(\text{CO})$  and the appearance of a strong band at 1 592  $\text{cm}^{-1}$  due to the newly formed carbon—carbon double bond. The  $^{31}\text{P}$  n.m.r. spectrum shows a typical AX pattern with a doublet at 121.9 p.p.m. due to  $\text{P}_\text{A}$  and a doublet at 3.3 p.p.m. due to  $\text{P}_\text{B}$  [ $J(\text{P}_\text{A}\text{P}_\text{B}) = 7.3$  Hz]. These are typical values for co-ordinated phosphinite and phosphine ligands respectively. The relatively small coupling constant between the two phosphorus ligands confirms the *cis* geometry. The  $^1\text{H}$  n.m.r. data are shown in Table 2 and are unremarkable except for the fact that H(4) has moved to a lower chemical shift value (2.35) consistent with the proposition that the ring-current effect of one of the phenyl groups is causing the downfield shift of this proton in complexes

**Table 2.** Proton n.m.r. data<sup>a</sup>

Complex	H(3)	H(4)	H(5x)	H(5n)	H(6x)	H(6n)	CH <sub>3</sub> (8)	CH <sub>3</sub> (9)	CH <sub>3</sub> (10)	Phenyl
L	3.1 (s)	1.93 (dd)	2.1 (m)	1.55 (m)	1.8 (dt)	1.7 (m)	0.95 (s)	1.25 (s)	1.10 (s)	7.2—8.0
(1)	2.9 (s)	5.15 (d) <sup>b</sup>	1.85 (m)	0.85 (m)	1.63 (dt)	1.38 (m)	1.00 (s)	1.25 (s)	0.95 (s)	7.2—8.0
(2)	3.0 (t) <sup>c</sup>	4.35 (d, br)	1.92 (m)	0.60 (m)	1.55 (dt)	2.10 (m)	0.93 (s)	1.00 (s)	0.8 (s)	7.2—8.0
(3)	3.05 (s, br)	4.63 (d)	1.85 (m)	<i>d</i>	1.48 (dt)	<i>d</i>	0.77 (s)	1.25 (s)	0.94 (s)	7.2—8.0
(4)	3.05 (s, br)	4.38 (d) <sup>e</sup>	1.95 <sup>f</sup>	0.65 (m)	1.53 (dt)	1.95 <sup>f</sup>	0.90 (s)	0.99 (s)	0.80 (s)	7.2—7.9
(5) <sup>g</sup>	3.05 (t) <sup>h</sup>	4.30 (br)	2.04 (m)	<i>d</i>	1.65 (dt)	2.30 (m)	0.93 (s)	1.06 (s)	0.84 (s)	7.3—8.2
(6) <sup>g</sup> ( <i>cis</i> )	<i>d</i>	5.0—5.6 <sup>i</sup>	1.6 (m, br) <sup>j</sup>	<i>d</i>	1.90 (m) <sup>j</sup>	<i>d</i>	0.93 (s)	1.32 (s)	1.14 (s)	7.1—8.2
( <i>trans</i> )	2.35 (t)	5.0—5.6 <sup>i</sup>	2.1 (m, br) <sup>j</sup>	0.75 (m)	1.90 (m) <sup>j</sup>	2.42 (m)	0.78 (s)	1.05 (s)	−0.20 (s)	7.1—8.2
(7)		2.35 (s, br)	1.4—1.7 <sup>f</sup>	0.3 (dt)	1.4—1.7 <sup>f</sup>	1.4—1.7 <sup>f</sup>	0.60 (s)	0.99 (s)	0.68 (s)	7.2—7.9
(8)		2.30 (s, br)	1.20 <sup>j</sup>	0.2 (dt)	1.4—1.7 <sup>f,j</sup>	1.4—1.7 <sup>f,j</sup>	0.55 (s)	0.96 (s)	0.67 (s)	7.0—7.8

<sup>a</sup> Recorded in  $\text{CDCl}_3$  at 298 K unless otherwise stated; x = exo, n = endo. For assignments, see Scheme. <sup>b</sup>  $^3J(\text{PH}) = 21$  Hz. <sup>c</sup>  $^2J(\text{PH}) + ^4J(\text{PH}) = 8.6$  Hz. <sup>d</sup> Signal not observed. <sup>e</sup>  $^3J(\text{PH}) = 17.1$  Hz. <sup>f</sup> Overlapping multiplets. <sup>g</sup> Recorded in  $\text{CD}_2\text{Cl}_2$ . <sup>h</sup>  $^2J(\text{PH}) + ^4J(\text{PH}) = 8.1$  Hz. <sup>i</sup> Signal obscured by solvent peak. <sup>j</sup> Assignments are arbitrary.



(1)–(6). In complex (7), due to the  $sp^2$  geometry of C(3), the phenyl rings will undoubtedly be in a different orientation relative to H(4), and therefore the influence of the ring-current effect is removed. The corresponding platinum phosphine–phosphinite complex (8) was also obtained by refluxing a solution of (5) in xylene for 5 h. The i.r. spectrum is similar to the analogous palladium complex and strong absorptions at 290 and 310  $\text{cm}^{-1}$  indicate *cis* chlorides. A similar thermal transformation has recently been reported by Braunstein and co-workers<sup>6</sup> for *cis*-[PdCl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>COPh)<sub>2</sub>] and the mechanism proposed involves the intramolecular coupling between two *cis* ligands due to the thermolysis of a P–C bond of one ligand and deprotonation of the second by the base formed from the initial bond cleavage. We can show that this coupling also occurs in *trans*-[ML<sub>2</sub>Cl<sub>2</sub>] and this can be explained on the basis of a possible *trans*–*cis* isomerisation occurring in the formation of complexes (7) and (8).

## Experimental

Microanalyses were by the University of St. Andrews Microanalytical Services, i.r. spectra were recorded on Perkin-Elmer 1710 (Fourier transform) and 1330 (dispersion) spectrometers as Nujol mulls between CsI plates. N.m.r. spectra were recorded on a Varian CFT 20 spectrometer and a Bruker AM 300 spectrometer operating in the Fourier-transform mode with (for <sup>31</sup>P) proton-noise decoupling. Melting points were determined on an Electrothermal digital melting point apparatus in air and are uncorrected. Mass spectra were recorded on a Finnigan Mat INCOS 50 mass spectrometer. Optical rotations were measured with an Optical Activity AA-1000 automatic polarimeter. Solvents were dried by (a) distillation from sodium diphenylketyl [thf, diethyl ether, toluene, or light petroleum (b.p. 40–60 °C)] or (b) distillation from CaH<sub>2</sub> (dichloromethane). Chlorodiphenylphosphine was distilled under reduced pressure and stored under nitrogen at

–25 °C. Xylene was distilled from sodium prior to use. All manipulations were carried out under dry oxygen-free nitrogen (purified by passing over a Cr<sup>2+</sup>-on-silica column) by standard Schlenk-line and catheter-tubing techniques.

(1*R*)-endo-(+)-3-Diphenylphosphinocamphor (L).—To a solution of (1*R*)-endo-(+)-3-bromocamphor (1.16 g, 5 mmol) in thf (10  $\text{cm}^3$ ) was added dropwise at –78 °C a solution of *n*-butyl-lithium (3.44  $\text{cm}^3$ , 1 mol  $\text{dm}^{-3}$  in hexane, 5.5 mmol). After the mixture was stirred for 1 h at –78 °C, a solution of chlorodiphenylphosphine (0.9  $\text{cm}^3$ , 5 mmol) in thf (5  $\text{cm}^3$ ) was added *via* a catheter. The mixture was allowed to warm to room temperature and stirred for 72 h. The solvent was removed *in vacuo* and the residue extracted into diethyl ether. Removal of the solvent and recrystallisation from degassed ethanol afforded pure L as colourless prisms, m.p. 82–84 °C. Yield 0.62 g, 37% (Found: C, 78.1; H, 7.7. C<sub>22</sub>H<sub>25</sub>OP requires C, 78.6; H, 7.5%). Mass spectrum:  $m/z$  336 ( $M^+$ );  $\alpha = +17.04^\circ$  ( $c = 5$  g per 100  $\text{cm}^3$ , MeOH, 589.3 nm). <sup>13</sup>C-{<sup>1</sup>H} n.m.r. (CDCl<sub>3</sub>):  $\delta$  10.13 [s, C(10)], 20.60 [s, C(8)], 22.85 [d, C(9)], <sup>4</sup> $J$ (PC) = 22.9, 30.36 [s, C(6)], 30.57 [d, C(5)], <sup>3</sup> $J$ (PC) = 2.40, 47.06 [s, C(7)], 48.27 [d, C(4)], <sup>2</sup> $J$ (PC) = 2.59, 54.16 [d, C(3)], <sup>1</sup> $J$ (PC) = 28.42, 59.20 [s, C(1)], and 218.2 p.p.m. [d, C(2), <sup>2</sup> $J$ (PC) = 7.27 Hz].

(1*R*)-endo-(+)-3-Methyldiphenylphosphinocamphor Iodide (1).—To a solution of L (0.60 g, 1.79 mmol) in toluene (10  $\text{cm}^3$ ) was added an excess of iodomethane (0.25  $\text{cm}^3$ , 4 mmol). The mixture was stirred for 12 h and the resulting white crystals were filtered off, washed with diethyl ether, and dried *in vacuo*. M.p. 190–192 °C, yield 0.46 g (73%) (Found: C, 57.4; H, 5.8. C<sub>23</sub>H<sub>28</sub>IOP requires C, 57.8; H, 5.9%).

Dichlorobis[(1*R*)-endo-(+)-3-diphenylphosphinocamphor]-palladium(II) (2).—A solution of L (0.84 g, 2.5 mmol) in ethanol (*ca.* 10  $\text{cm}^3$ ) was added to a suspension of [Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>] (0.32 g, 1.25 mmol) in ethanol (*ca.* 25  $\text{cm}^3$ ). After stirring for 1 min a yellow precipitate appeared. The latter was filtered off and washed with diethyl ether. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–light petroleum afforded pure air-stable yellow crystals of (2). M.p. 192 °C, yield 1.00 g (94.1%) (Found: C, 62.2; H, 5.4. C<sub>44</sub>H<sub>50</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pd requires C, 62.5; H, 5.9%).

Dibromobis[(1*R*)-endo-(+)-3-diphenylphosphinocamphor]-palladium(II) (3).—An excess of lithium bromide (0.114 g, 1.31 mmol) was added to a solution of complex (2) (0.186 g, 0.22 mmol) in acetone (*ca.* 25  $\text{cm}^3$ ) and stirred overnight. The resulting orange solution was filtered and concentrated. Addition of light petroleum produced an orange powder which was washed with further portions of light petroleum and dried *in vacuo* to give air-stable complex (3). M.p. >130 °C (slow decomp.), yield 0.13 g (62.5%) (Found: C, 54.6; H, 5.6. C<sub>44</sub>H<sub>50</sub>Br<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pd requires C, 56.3; H, 5.4%).

Di- $\mu$ -chloro-dichlorobis[(1*R*)-endo-(+)-3-diphenylphosphinocamphor]dipalladium(II) (4).—A solution of L (0.423 g, 1.26 mmol) in ethanol (*ca.* 20  $\text{cm}^3$ ) was added to a suspension of [Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>] (0.327 g, 1.26 mmol) in ethanol (*ca.* 20  $\text{cm}^3$ ). After stirring for 5 min an orange precipitate appeared. The latter was filtered off and washed with diethyl ether. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–light petroleum afforded pure air-stable orange crystals of complex (4). M.p. >185 °C (slow decomp.), yield 0.65 g (83.7%) (Found: C, 51.5; H, 4.5. C<sub>44</sub>H<sub>50</sub>Cl<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub> requires C, 51.4; H, 4.9%).

Dichlorobis[(1*R*)-endo-(+)-3-diphenylphosphinocamphor]-platinum(II) (5).—A solution of L (0.73 g, 2.17 mmol) in ethanol (*ca.* 10  $\text{cm}^3$ ) was added to a suspension of [Pt(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>]



(0.38 g, 1.08 mmol) in ethanol (*ca.* 25 cm<sup>3</sup>). After stirring for 30 min a pale yellow precipitate appeared. The latter was filtered off and washed with diethyl ether. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–light petroleum afforded pure air-stable yellow crystals of (5). M.p. 240 °C, yield 0.64 g (63%) (Found: C, 56.1; H, 5.3. C<sub>44</sub>H<sub>50</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pt requires C, 56.3; H, 5.4%).

*Bis*[(1*R*)-endo-(+)-3-diphenylphosphinocamphor]palladium(II) Tetrafluoroborate (6).—An excess of AgBF<sub>4</sub> (0.43 g, 2.2 mmol) was added to a solution of complex (2) (0.85 g, 1 mmol) in dichloromethane (20 cm<sup>3</sup>). After stirring for 3 h the solution was filtered and concentrated. On standing for 2 d at room temperature, bright yellow needles of air-sensitive complex (6) were deposited, and were filtered off and dried *in vacuo*. This complex was also obtained by crystallisation from a CH<sub>2</sub>Cl<sub>2</sub>–light petroleum solution. (One equivalent of CH<sub>2</sub>Cl<sub>2</sub> was found to be present by <sup>1</sup>H n.m.r. spectroscopy, and could not be removed from the product.) M.p. >235 °C (decomp.), yield 0.6 g (63%) (Found: C, 53.3; H, 5.0. C<sub>45</sub>H<sub>52</sub>B<sub>2</sub>Cl<sub>2</sub>-F<sub>8</sub>O<sub>2</sub>P<sub>2</sub>Pd requires C, 52.1; H, 5.0%).

*Dichloro*(3-diphenylphosphino-2-diphenylphosphinoxo-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene)palladium(II) (7).—A solution of complex (2) (0.86 g, 1 mmol) in xylene (40 cm<sup>3</sup>) was refluxed for 4 h. Slow cooling resulted in the formation of white air-stable microcrystals of pure complex (7). The crystals were filtered off, washed with light petroleum, and dried *in vacuo*. M.p. >215 °C (decomp.), yield 0.3 g (43%) (Found: C, 58.5; H, 4.5. C<sub>34</sub>H<sub>34</sub>Cl<sub>2</sub>OP<sub>2</sub>Pd requires C, 58.5; H, 4.9%).

*Dichloro*(3-diphenylphosphino-2-diphenylphosphinoxo-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene)platinum(II).—A solution of complex (5) (1.44 g, 1.53 mmol) in xylene (*ca.* 40 cm<sup>3</sup>) was refluxed for 5 h. Slow cooling resulted in the formation of white air-stable crystals of pure (8). The crystals were filtered off, washed with light petroleum, and dried *in vacuo*. M.p. 288 °C, yield 0.68 g (57%) (Found: C, 52.1; H, 4.3. C<sub>34</sub>H<sub>34</sub>Cl<sub>2</sub>OP<sub>2</sub>Pt requires C, 51.9; H, 4.4%).

## Acknowledgements

We thank the S.E.R.C. for a studentship (to D. A. K.) and funds to purchase the medium-field n.m.r. spectrometer, and Johnson Matthey for the generous loan of palladium and platinum salts.

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Received 19th February 1990; Paper 0/00750A