Camphor-derived β-Ketophosphine Complexes of Palladium(II) and Platinum(II)

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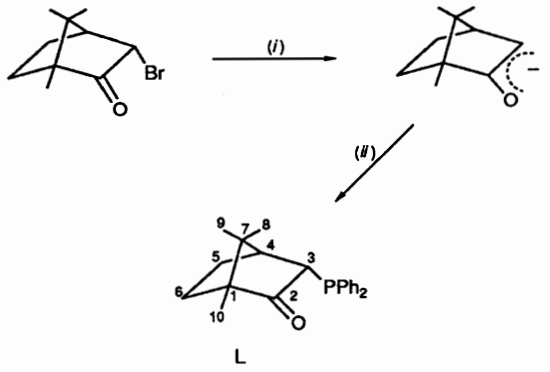
Reaction of chlorodiphenylphosphine with the lithium enolate derived from the treatment of (1*R*)-*endo*-(+)-3-bromocamphor (camphor = bornan-2-one) with n-butyl-lithium gives (1*R*)-*endo*-(+)-3-diphenylphosphinocamphor (L). This new chiral β-ketophosphine ligand reacts with $[Pd(CH_3CN)_2Cl_2]$ to give *trans*-$[PdL_2Cl_2]$, and in a 1:1 ratio to give the chloro-bridged dimer $[\{PdL(\mu\text{-}Cl)Cl\}_2]$. The ligand L reacts with $[Pt(CH_3CN)_2Cl_2]$ to give *trans*-$[PtL_2Cl_2]$. Thermolysis of $[ML_2Cl_2]$ (M = Pd or Pt) in refluxing xylene gives mixed phosphine–phosphinite complexes with mutually *cis* chlorides. The complex $[PdL_2Cl_2]$ reacts with an excess of $AgBF_4$ to give $[PdL_2][BF_4]_2$ which is shown to contain bidentate binding through the phosphorus and keto-oxygen atoms. All complexes are characterised by i.r., ^1H and ^{31}P n.m.r. spectroscopy.

Although a wide range of chiral diphosphine ligands has been prepared and catalytic reactions demonstrating high enantioselectivities are known,[1] bidentate chiral ligands in which the donor set is P,O are relatively unusual and their co-ordination chemistry has been little explored.[2] This is somewhat surprising since functionalised phosphines of the type $R_2PCH_2C(O)R'$ or $[R_2PCH{=}C(O)R']^-$ have been used as ligands in *e.g.*. the oligomerisation of ethene (SHOP process[3]) and the telomerisation of butadiene with CO_2 to give lactones.[4] 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 β-ketophosphonates with three chiral centres derived from the naturally occurring (+)-3-bromocamphor (camphor = bornan-2-one),[5] 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[6] have recently reported similar chemistry for the achiral $Ph_2PCH_2C(O)Ph$ 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}P n.m.r. spectrum of the product and from an *X*-ray crystal structure obtained for a rhodium complex containing the ligand[7] 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 °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 tetraphenyldiphosphane was obtained in high yield, suggesting a possible lithium–halogen exchange reaction in which bromodiphenylphosphine is first formed but then reacts with lithium diphenylphosphide to give the diphosphane.



Scheme. Method for the preparation of L from 3-bromocamphor. (*i*) $LiBu^n$, −78 °C; (*ii*) PPh_2Cl

The i.r. and ^{31}P n.m.r. data for the ligand L are given in Table 1 and the ^1H n.m.r. data in Table 2. The ^1H n.m.r. spectra for both ligand and complexes are complex and the spectrum of the free ligand was fully assigned using two-dimensional ^1H–^{13}C correlation spectroscopy (COSY) and comparison with the spectrum of (1*R*)-*endo*-(+)-bromocamphor. Atom H(3) occurs as a singlet at δ 3.1 with $J(PH) \approx 0$ Hz and this is not uncommon for free β-ketophosphine ligands;[8] H(4) occurs as a doublet of doublets at δ 1.93 and for the corresponding methylphosphonium salt (**1**) undergoes a large downfield shift to δ 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[9] confirming that the phenyl rings and four-co-ordinate 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}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}P-{^{1}H} n.m.r. data for new complexes

Complex	I.r. (cm^{-1})[a] C=O	M–Cl	^{31}P (δ/p.p.m.)[b]
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,[c] ^{1}J(PtP) = 2 581
(6) *cis*	1 651		45.8[c]
trans	1 651		56.6[c]
(7)[d]		310, 290	3.3, 121.9, J(PP) = 7.3
(8)[e]		310, 290	−21.5, ^{1}J(PtP) = 3 280 92.9, ^{1}J(PtP) = 4 081, J(PP) = 7.3

[a] Recorded as Nujol mulls between CsI plates. [b] Spectra recorded in $CDCl_3$ unless otherwise stated. Shifts are to high frequency of external 85% H_3PO_4, J values in Hz. [c] Recorded in CD_2Cl_2. [d] ν(C=C) 1 592 cm^{-1}. [e] ν(C=C) 1 596 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 σ 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.[10] The P–C coupling drops to zero in the methyl phosphonium salt, the phosphine oxide, and 3-diethoxyphosphoryl camphor.[9]

(*b*) *Synthesis of Complexes.*—Addition of 2 equivalents of L to a suspension of $[Pd(CH_3CN)_2Cl_2]$[11] in degassed ethanol results in the rapid precipitation of a bright yellow complex $[PdL_2Cl_2]$ (**2**). A value of 1 734 cm^{-1} for ν(C=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 $[PdL_2Br_2]$ (**3**), and the disappearance of only one absorption peak at 355 cm^{-1} in the far-i.r. spectrum of (**3**) due to ν(M–Cl) indicates that (**2**) is *trans*-$[PdL_2Cl_2]$ (Table 1). The *trans* configuration also follows from the appearance of a virtual triplet pattern due to H(3) in the ^{1}H n.m.r. spectrum of (**2**) with ^{2}J(PH) + ^{4}J(PH) = 8.6 Hz (Table 2). One equivalent of L reacts with $[Pd(CH_3CN)_2Cl_2]$ in ethanol to give an orange complex (**4**) for which microanalytical and i.r. data suggest that the chloro-bridged dimer is formed.

When $[Pt(CH_3CN)_2Cl_2]$ is treated with 2 equivalents of L in ethanol a pale yellow powder is formed which has been characterised as $[PtL_2Cl_2]$ (**5**). From ^{31}P and ^{1}H n.m.r. data (Tables 1 and 2) it can be seen that only one isomer is present. The ^{31}P n.m.r. spectrum shows a singlet with ^{195}Pt satellites, J(PtP) = 2 581 Hz, which suggests the *trans* configuration for the complex. This value is typical for a *trans* P–Pt–P arrangement.[12] In the ^{1}H n.m.r. spectrum for the complex H(3) also occurs as a virtual triplet with ^{2}J(PH) + ^{4}J(PH) = 8.1 Hz. As for complex (**2**), the i.r. spectrum shows a strong absorption at 1 734 cm^{-1} indicative of an unco-ordinated ketone group.

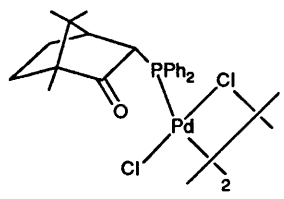
Addition of an excess of silver tetrafluoroborate to a solution of (**2**) in dichloromethane results in chloride abstraction from the complex and formation of the cationic complex $[PdL_2][BF_4]_2$ (**6**). The i.r. spectrum shows a fall in the ν(C=O) stretching frequency from 1 734 to 1 651 cm^{-1} and indicates co-ordination of both keto-oxygen atoms to the metal centre. The ^{31}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}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.[13] 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.[14] The ^{1}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 ^{2}J(PH) + ^{4}J(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 (δ < 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*-$[ML_2Cl_2]$ (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 ν(CO) and the appearance of a strong band at 1 592 cm^{-1} due to the newly formed carbon–carbon double bond. The ^{31}P n.m.r. spectrum shows a typical AX pattern with a doublet at 121.9 p.p.m. due to P_A and a doublet at 3.3 p.p.m. due to P_B [$J(P_AP_B)$ = 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}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[a]

Complex	H(3)	H(4)	H(5x)	H(5n)	H(6x)	H(6n)	CH_3(8)	CH_3(9)	CH_3(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)[b]	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)[c]	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)	*d*	1.48 (dt)	*d*	0.77 (s)	1.25 (s)	0.94 (s)	7.2—8.0
(4)	3.05 (s, br)	4.38 (d)[e]	1.95[f]	0.65 (m)	1.53 (dt)	1.95[f]	0.90 (s)	0.99 (s)	0.80 (s)	7.2—7.9
(5)[g]	3.05 (t)[h]	4.30 (br)	2.04 (m)	*d*	1.65 (dt)	2.30 (m)	0.93 (s)	1.06 (s)	0.84 (s)	7.3—8.2
(6)[g] (*cis*)	*d*	5.0—5.6[i]	1.6 (m, br)[j]	*d*	1.90 (m)[j]	*d*	0.93 (s)	1.32 (s)	1.14 (s)	7.1—8.2
(*trans*)	2.35 (t)	5.0—5.6[i]	2.1 (m, br)[j]	0.75 (m)	1.90 (m)[j]	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[f]	0.3 (dt)	1.4—1.7[f]	1.4—1.7[f]	0.60 (s)	0.99 (s)	0.68 (s)	7.2—7.9
(8)		2.30 (s, br)	1.20[j]	0.2 (dt)	1.4—1.7[f,j]	1.4—1.7[f,j]	0.55 (s)	0.96 (s)	0.67 (s)	7.0—7.8

[a] Recorded in $CDCl_3$ at 298 K unless otherwise stated; x = exo, n = endo. For assignments, see Scheme. [b] ^{3}J(PH) = 21 Hz. [c] ^{2}J(PH) + ^{4}J(PH) = 8.6 Hz. [d] Signal not observed. [e] ^{3}J(PH) = 17.1 Hz. [f] Overlapping multiplets. [g] Recorded in CD_2Cl_2. [h] ^{2}J(PH) + ^{4}J(PH) = 8.1 Hz. [i] Signal obscured by solvent peak. [j] Assignments are arbitrary.



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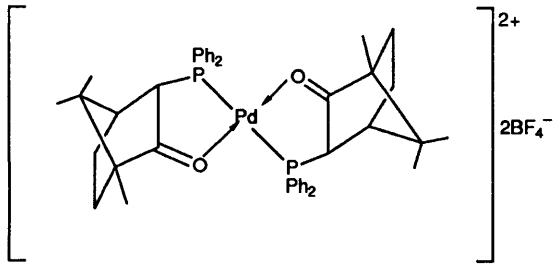

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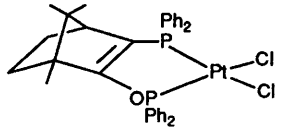

(8)

(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 cm^{-1} indicate *cis* chlorides. A similar thermal transformation has recently been reported by Braunstein and co-workers[6] for *cis*-$[PdCl_2(Ph_2PCH_2COPh)_2]$ 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*-$[ML_2Cl_2]$ 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 1 330 (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 ^{31}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_2 (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^{2+}-on-silica column) by standard Schlenk-line and catheter-tubing techniques.

(1R)-endo-(+)-3-*Diphenylphosphinocamphor* (L).—To a solution of (1*R*)-*endo*-(+)-3-bromocamphor (1.16 g, 5 mmol) in thf (10 cm^3) was added dropwise at −78 °C a solution of n-butyl-lithium (3.44 cm^3, 1 mol dm^{-3} in hexane, 5.5 mmol). After the mixture was stirred for 1 h at −78 °C, a solution of chlorodiphenylphosphine (0.9 cm^3, 5 mmol) in thf (5 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. $C_{22}H_{25}OP$ requires C, 78.6; H, 7.5%). Mass spectrum: *m/z* 336 (M^+); $\alpha = +17.04°$ (*c* = 5 g per 100 cm^3, MeOH, 589.3 nm). ^{13}C-{^1H} n.m.r. ($CDCl_3$): δ 10.13 [s, C(10)], 20.60 [s, C(8)], 22.85 [d, C(9), ^4J(PC) = 22.9], 30.36 [s, C(6)], 30.57 [d, C(5), ^3J(PC) = 2.40], 47.06 [s, C(7)], 48.27 [d, C(4), ^2J(PC) = 2.59], 54.16 [d, C(3), ^1J(PC) = 28.42], 59.20 [s, C(1)], and 218.2 p.p.m. [d, C(2), ^2J(PC) = 7.27 Hz].

(1R)-endo-(+)-3-*Methyldiphenylphosphinocamphor Iodide* (**1**).—To a solution of L (0.60 g, 1.79 mmol) in toluene (10 cm^3) was added an excess of iodomethane (0.25 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. $C_{23}H_{28}IOP$ requires C, 57.8; H, 5.9%).

Dichlorobis[(1R)-endo-(+)-3-*diphenylphosphinocamphor*]-*palladium*(II) (**2**).—A solution of L (0.84 g, 2.5 mmol) in ethanol (*ca.* 10 cm^3) was added to a suspension of $[Pd(CH_3CN)_2Cl_2]$ (0.32 g, 1.25 mmol) in ethanol (*ca.* 25 cm^3). After stirring for 1 min a yellow precipitate appeared. The latter was filtered off and washed with diethyl ether. Recrystallisation from CH_2Cl_2–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. $C_{44}H_{50}Cl_2O_2P_2Pd$ requires C, 62.5; H, 5.9%).

Dibromobis[(1R)-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 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. $C_{44}H_{50}Br_2O_2P_2Pd$ requires C, 56.3; H, 5.4%).

Di-μ-chloro-dichlorobis[(1R)-endo-(+)-3-*diphenylphosphinocamphor*]*dipalladium*(II) (**4**).—A solution of L (0.423 g, 1.26 mmol) in ethanol (*ca.* 20 cm^3) was added to a suspension of $[Pd(CH_3CN)_2Cl_2]$ (0.327 g, 1.26 mmol) in ethanol (*ca.* 20 cm^3). After stirring for 5 min an orange precipitate appeared. The latter was filtered off and washed with diethyl ether. Recrystallisation from CH_2Cl_2–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. $C_{44}H_{50}Cl_4O_2P_2Pd_2$ requires C, 51.4; H, 4.9%).

Dichlorobis[(1R)-endo-(+)-3-*diphenylphosphinocamphor*]-*platinum*(II) (**5**).—A solution of L (0.73 g, 2.17 mmol) in ethanol (*ca.* 10 cm^3) was added to a suspension of $[Pt(CH_3CN)_2Cl_2]$

(0.38 g, 1.08 mmol) in ethanol (*ca.* 25 cm^3). After stirring for 30 min a pale yellow precipitate appeared. The latter was filtered off and washed with diethyl ether. Recrystallisation from CH_2Cl_2–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. $C_{44}H_{50}Cl_2O_2P_2Pt$ requires C, 56.3; H, 5.4%).

Bis[(1R)-endo-(+)-3-*diphenylphosphinocamphor*]*palladium*(II) *Tetrafluoroborate* (**6**).—An excess of $AgBF_4$ (0.43 g, 2.2 mmol) was added to a solution of complex (**2**) (0.85 g, 1 mmol) in dichloromethane (20 cm^3). 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_2Cl_2–light petroleum solution. (One equivalent of CH_2Cl_2 was found to be present by ^1H 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. $C_{45}H_{52}B_2Cl_2F_8O_2P_2Pd$ 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^3) 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. $C_{34}H_{34}Cl_2OP_2Pd$ 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^3) 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. $C_{34}H_{34}Cl_2OP_2Pt$ requires C, 51.9; H, 4.4%).

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