

Platinum(II), palladium(II) and rhodium(I) complexes of *o*-, *m*- and *p*-Ph₂PC₆H₄PO(OEt)₂. PtCl₂–SnCl₂ Hydroformylation catalysts modified with phosphonated triarylphosphines

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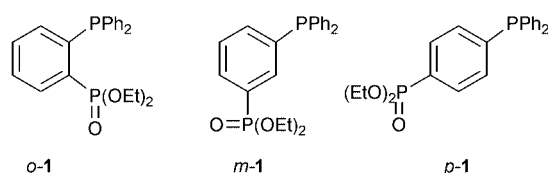
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An improved route to the bulky phosphine *o*-Ph₂PC₆H₄PO(OEt)₂ **o**-**1** has been elaborated. The isomers [PtCl₂L₂], L = *o*- (**2**), *m*- (**3**) or *p*- (**4**), were made by treatment of [PtCl₂(cod)] with the appropriate phosphine. Complex **2** has a *trans* configuration whereas the *m* and *p* isomers, **3** and **4** are *cis*, reflecting the greater bulk of the *o* isomer. Crystal structure analyses of **o**-**1** and its platinum complex **2** indicated normal dimensions for the tertiary phosphine in both and the considerable asymmetric steric bulk of *o*-**1**. Abstraction of the chloro ligands in **2** occurs upon addition of AgSbF₆ and the resulting dicationic bis P,O-chelate **5** has a *cis* geometry. The palladium complexes [PdCl₂L₂], L = *o*- (**6**), *m*- (**7**), or *p*- (**8**) were made by treatment of [PdCl₂(NCPh)₂] with the appropriate phosphine but, in contrast to the platinum analogues, the *o* isomer **6** has a *cis* configuration and the *m* and *p* isomers **7** and **8** are predominantly *trans*. Complex **6** is fluxional: variable temperature ³¹P NMR spectroscopy is consistent with hemilabile behaviour of the ligand with reversible co-ordination of the P=O of the phosphonate functionality. Treatment of [Rh₂Cl₂(CO)₄] with **o**-**1** gave the mononuclear chelate [RhCl(CO)(*o*-**1**)] (**9**) which upon addition of further *o*-**1** gave predominantly the fluxional species *trans*-[RhCl(CO)(*o*-**1**)₂]. The platinum complexes **2**, **3** and **4** when combined with SnCl₂ catalyse the hydroformylation of but-2-ene and but-1-ene.

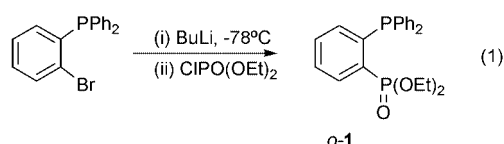
Introduction

Tertiary phosphines containing phosphonate ester functionalities have recently attracted attention as potentially hemilabile, P,O-chelating ligands^{1–5} and as precursors to water-soluble phosphines for two-phase catalysis.⁶ Here we show that the bulky *ortho*-phosphonated triphenylphosphine **o**-**1** forms P,O-chelates with platinum(II), palladium(II) and rhodium(I) and compare the hydroformylation catalytic activity of the platinum(II) complexes of isomeric ligands *o*-, *m*- and *p*-**1** in the presence of SnCl₂.



Results and discussion

The ligand **o**-**1** was made by the route shown in eqn. (1) which



has the advantage over the literature method⁶ of being simpler and higher yielding (see Experimental section). The bulkiness of the lithio intermediate and the product **o**-**1** presumably inhibits the further substitution at the phosphonate phosphorus in **o**-**1**. The ligands *m*- and *p*-**1** were made by the route reported by Knight and co-workers.⁶ Crystals of **o**-**1** suitable for X-ray diffraction study were grown from CDCl₃. The results of the

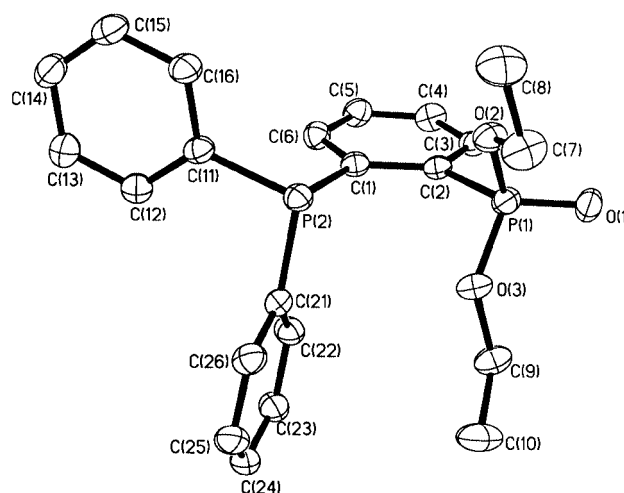


Fig. 1 Molecular structure of compound **o**-**1**. Selected atoms are labelled and all hydrogens are omitted for clarity.

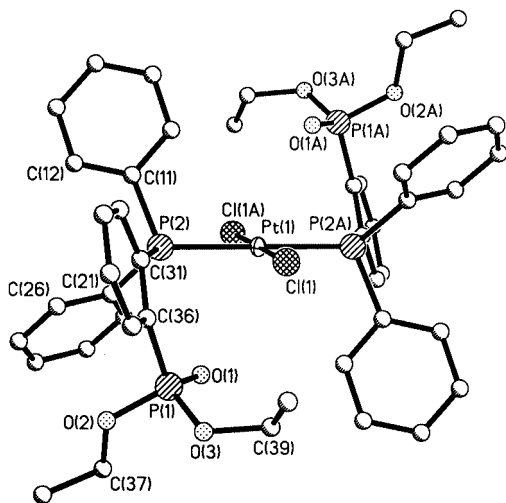
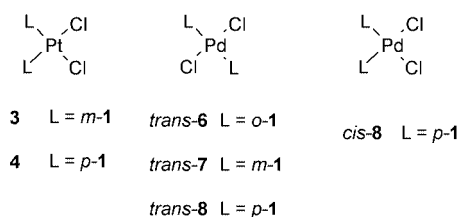
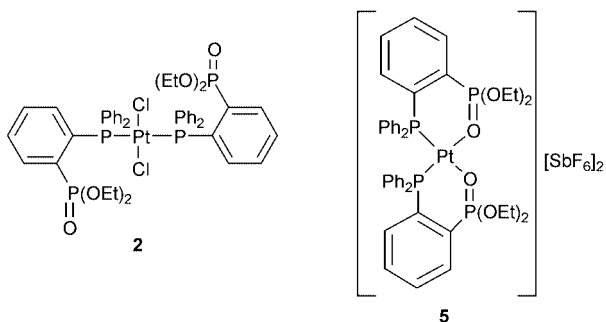
structure analysis are given in Fig. 1 which shows the molecular structure and atom labelling scheme, and Table 1 which lists important molecular dimensions. In common with other diaryl substituted phosphines,⁷ the two phenyl groups are twisted with respect to each other in an alternating face-edge arrangement. The two phosphorus atoms lie in the plane of the phenylene backbone. As expected, the P=O bond length is shorter than those of the ethoxy P–O groups. The conformation of the phosphonate ester group has the P=O oxygen atom *anti* to the phosphine phosphorus atom (torsion angle C(1)–C(2)–P(1)–O(1) 173.9(3)°).

Dichloroplatinum(II) chemistry

Treatment of [PtCl₂(cod)] with 1 or 2 equivalents of **o**-**1** gave the *trans* complex **2**, as the only phosphorus-containing

Table 1 Selected bond lengths (Å) and bond angles (°) for compound **o-1**

P(1)–O(1)	1.468(3)	P(1)–O(2)	1.565(2)
P(1)–O(3)	1.579(3)	P(1)–C(2)	1.793(3)
P(2)–C(21)	1.831(3)	P(2)–C(11)	1.832(4)
P(2)–C(1)	1.842(4)		
O(1)–P(1)–O(3)	113.31(14)	O(1)–P(1)–O(2)	116.59(15)
O(1)–P(1)–C(2)	111.96(16)	O(2)–P(1)–O(3)	102.55(14)
O(3)–P(1)–C(2)	108.72(15)	O(2)–P(1)–C(2)	102.74(14)
C(21)–P(2)–C(1)	101.34(15)	C(21)–P(2)–C(11)	101.28(16)
		C(11)–P(2)–C(1)	102.10(16)

**Fig. 2** Molecular structure of complex **2**. Details as in Fig. 1.

product as shown by *in situ* ^{31}P NMR spectroscopy ($^1J(\text{PtP})$ 2876 Hz). Crystals of **2** suitable for X-ray diffraction study were grown by diffusion of a CH_2Cl_2 solution of $[\text{PtCl}_2(\text{cod})]$ into an acetone solution of **o-1**. The results of the structure analysis are given in Fig. 2 which shows the molecular structure and atom labelling scheme, and Table 2 which lists important molecular dimensions. The structure shows a *trans* arrangement of the ligands. While the phosphonate groups are not co-ordinated to platinum, the P=O groups point towards the metal and lie above the vacant axial sites at the platinum(II) centre $[\text{O}(1) \cdots \text{Pt}(1)$ 3.305(2) Å]. In contrast, the complex $[\text{PdBr}_2\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2\}_2]$ ⁸ has the P=O groups orientated away from the metal. The P–C bond lengths and C–P–C angles in **2** are similar to those of free

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **2·2Me₂CO**

Pt(1)–Cl(1)	2.3159(7)	Pt(1)–P(2)	2.3239(6)
P(1)–O(1)	1.4620(17)	P(1)–O(2)	1.5761(18)
P(1)–O(3)	1.5842(19)	P(1)–C(36)	1.804(2)
P(2)–C(21)	1.829(2)	P(2)–C(11)	1.835(2)
P(2)–C(31)	1.845(2)		
Cl(1)–Pt(1)–P(2)	91.91(2)	Cl(1)–Pt(1)–Cl(1a)	180.0
P(2)–Pt(1)–P(2a)	180.0	Cl(1a)–Pt(1)–P(2)	88.09(2)
O(1)–P(1)–O(3)	114.37(11)	O(1)–P(1)–O(2)	116.47(10)
O(1)–P(1)–C(36)	115.78(10)	O(2)–P(1)–O(3)	100.85(10)
O(3)–P(1)–C(36)	106.31(11)	O(2)–P(1)–C(36)	101.14(10)
C(21)–P(2)–C(31)	102.28(10)	C(21)–P(2)–C(11)	103.40(10)
C(21)–P(2)–Pt(1)	123.43(8)	C(11)–P(2)–C(31)	103.90(10)
C(31)–P(2)–Pt(1)	114.21(8)	C(11)–P(2)–Pt(1)	107.59(8)

o-1 as is usual for platinum complexes of triarylphosphines.⁹ The Pt–P and Pt–Cl bond lengths correspond well to literature values.¹⁰ The bond angles around the Pt atom are only slightly distorted from 90° (see Table 2). The cone angle¹¹ for ligand **o-1** in complex **2** is 185° which is comparable with the cone angle of PBUt_3 (186°) and much larger than that for PPh_3 (145°). The asymmetry of the ligand is such that one would expect a significant barrier to rotation about the Pt–P bond in **2**, given that the phosphonate group remains *gauche* to the metal in complexes of **o-1** (the Pt(1)–P(2)–C(31)–C(36) torsion angle in **2** is 72.8(2)°, *cf.* 34° for the corresponding (lone pair)–P–C–C angle in **o-1**). The conformation of the ligand in **2** differs from that in **o-1** in that the P=O group is now *gauche* to the phosphine function (O(1)–P(1)–C(36)–C(31) 22.3(2)°); this arrangement both brings the P=O group into the axial site of the Pt and avoids steric clashes involving the POEt groups.

Treatment of complex **2** with AgSbF_6 gave a new species assigned the bis chelate structure **5** on the basis of the ^{31}P NMR spectrum which showed two deceptively simple triplets for the PPh_2 and $\text{PO}(\text{OEt})_2$ signals with $^1J(\text{PtP})$ for the former of 4170 Hz, characteristic of a phosphine *trans* to an *O*-donor ligand.¹² Thus the conversion of **2** into **5** involves a *trans* to *cis* configuration change which is probably thermodynamically driven.¹³ The assignment of structure **5** is also supported by elemental analysis, mass spectrometry and ^1H NMR spectroscopy (see Experimental section).

Treatment of $[\text{PtCl}_2(\text{cod})]$ with *m*- and *p*-**1** gave the *cis* complexes **3** and **4** (see Experimental section for the characterising data) indicating that the *trans* geometry observed with **2** is most likely due to a steric effect of the *ortho*-substituent.

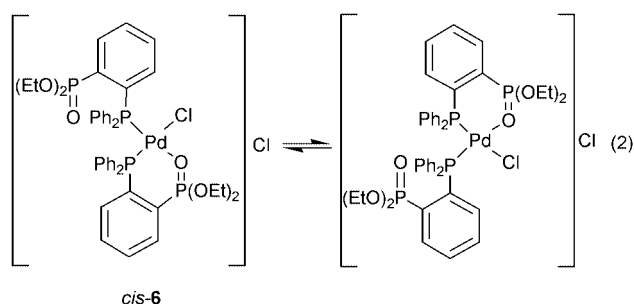
Dichloropalladium(II) chemistry

Palladium complexes whose elemental analyses were consistent with the formulae PdCl_2L_2 (**6**, **7** and **8** where L = *o*-, *m*- and *p*-**1** respectively) were made by treatment of $[\text{PdCl}_2(\text{NPh})_2]$ with the appropriate phosphonated phosphine.

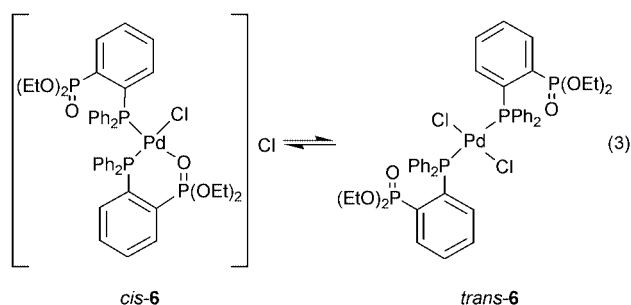
The ^{31}P NMR spectrum of the *meta* species **7** is simple and, by comparison of δ_{P} for the co-ordinated PPh_2 with literature values for co-ordinated triarylphosphines,¹⁴ is assigned the *trans* structure. The spectrum of **8**, derived from *p*-**1**, showed the presence of two species in the ratio of *ca.* 3:1 which were assigned to *trans*- and *cis*-**8** respectively. In the analogous platinum(II) chemistry with *m*- and *p*-**1**, only *cis*- $[\text{PtCl}_2\text{L}_2]$ were observed (see above) but the greater tendency for $[\text{PdCl}_2\text{L}_2]$ to be *trans* is well known.^{15,16} The greater proportion of *trans*- $[\text{PdCl}_2\text{L}_2]$ when L = *m*-**1** than when L = *p*-**1** reflects the greater bulk of *m*-**1**.

The solution behaviour of complex **6** was complicated. At +20 °C, the ^{31}P NMR spectrum showed two signals: a sharp singlet ($w_{1/2}$ 8 Hz) at δ 16.7 assigned to a co-ordinated PPh_2 group and a very broad singlet ($w_{1/2}$ 25 Hz) at δ 21.4 assigned to the $\text{PO}(\text{OEt})_2$ group. At –60 °C, the phosphonate signal was

resolved into two broad signals at δ 27.5 and 20.5 (ratio 1:1) and the phosphine signal was resolved into two singlets at δ 16.8 and 16.5 (ratio 1:1). We assign this species to *cis*-**6** and ascribe the fluxionality to the interchange of co-ordinated P=O groups, eqn. (2). Similar behaviour is observed with palladium(II)



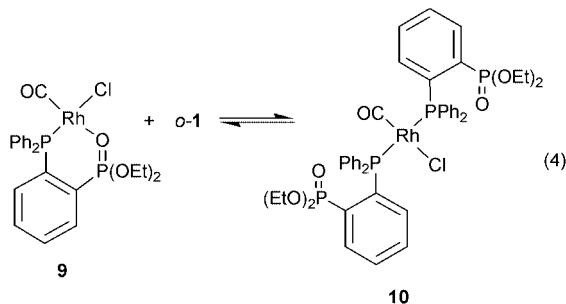
complexes of phosphino-alcohol¹⁷ and phosphino-ether¹⁸ hemilabile ligands. At -60°C a minor species (*ca.* 20%) was detected whose signals at δ 20.5 and 16.2 were sharp; when the solution was warmed to -40°C these signals remained sharp but diminished in intensity and at $+20^\circ\text{C}$ were undetectable. We assign these signals to *trans*-**6** which is in equilibrium with *cis*-**6**, eqn. (3); at low temperatures this equilibrium is shifted to the right.



Chlorocarbonylrhodium(I) chemistry

When $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ was treated with 2 equivalents of *o*-**1** a complex formed which had a large $^1J(\text{RhP})$ value of 166 Hz. Elemental analysis is consistent with the formulation $[\text{RhCl}(\text{CO})\text{L}]$ and solution molecular weight measurement suggests that it is the mononuclear chelate species **9**. *des Abbayes* and co-workers⁵ have recently reported a related phosphine-phosphonate chelate of rhodium(I).

Addition of 1 equivalent of *o*-**1** to a solution of complex **9** led to a ^{31}P NMR spectrum at $+22^\circ\text{C}$ which showed the presence of three species in approximately equal proportions: sharp signals for the two starting materials *o*-**1** and **9** and broad signals for a new rhodium-containing product. At -80°C all the signals were sharp and the new product constituted *ca.* 90% of the signal intensity. We assign the structure **10** to this product ($^1J(\text{RhP})$ 131 Hz) and suggest that the equilibrium (4) is present



in solution which shifts to the right at low temperatures. The broadening of the signals for **10** at ambient temperatures is not due to ligand exchange, since the signals for *o*-**1** and **9** remain

Table 3 Hydroformylation of 1-butene and *cis*-butene^a

Entry	Ligand	Substrate	Conversion (%)	n:iso ^b	TOF ^c
1	PPh_3	1-Butene	60	6.3	213
2	<i>o</i> - 1		13	2.5	48
3	<i>m</i> - 1		47	3.0	94
4	<i>p</i> - 1		91	6.8	272
5	PPh_3	<i>cis</i> -2-Butene	14	0.6	63
6	<i>o</i> - 1		4	1.0	31
7	<i>o</i> - 1 ^d		12	0.7	37
8	<i>o</i> - 1 ^e		4	1.2	36
9	<i>m</i> - 1		28	0.5	71
10	<i>p</i> - 1		44	0.6	143

^a See Experimental section for detailed reaction conditions. Unless otherwise stated the Pt:ligand ratio was 1:1, Pt:Sn 1:5, Pt:substrate 1:1000, temperature 120°C , and pressure 80 bar. Product yields were calculated by GC (accuracy 1%). ^b Ratio of linear aldehyde to branched aldehydes. ^c Turnover frequency defined as the moles of butene converted per mol of Pt per hour. ^d At 100°C . ^e Using ligand:Pt of 2:1.

sharp, and is most likely due to fluxionality analogous to that detected in the palladium(II) species **6** (see above).

Hydroformylation catalysis with Pt/Sn systems modified by phosphonated phosphines

Monophosphine complexes of platinum(II) in the presence of an excess of SnCl_2 are well known hydroformylation catalysts¹⁹ although there remains uncertainty as to the role of the SnCl_2 and the mechanism of the reactions.^{20–25} We have screened the phosphonated phosphines for Pt–Sn hydroformylation catalysis under the conditions described²⁵ and compared the results with those for PPh_3 under the same conditions.

The results are collected in Table 3. As expected,²³ the terminal alkene substrate (entries 1–4) is more reactive than the internal alkene (entries 5–10). The order of hydroformylation conversion and activity for both substrates is *p*-**1** > $\text{PPh}_3 \approx m$ -**1** > *o*-**1**. We ascribe the low activity of the catalyst with *o*-**1** to its bulkiness and/or inhibition by P=O co-ordination. The significantly greater efficiency of the catalyst with *p*-**1** may be a function of the electron-withdrawing nature of the phosphonate group in the *para* position. This hypothesis is worthy of further investigation since, to our knowledge, ligand electronic effects have not been reported for the Pt/Sn/ PR_3 catalyst system.

Experimental

General methods were similar to those used in recent work from this laboratory.²⁶ All the experiments were carried out in an atmosphere of nitrogen. The ligands *m*- and *p*-**1** were made as previously described.⁶ The ^{31}P (162), ^1H (400) and ^{13}C (100 MHz) NMR spectra were measured at $+22^\circ\text{C}$ in CDCl_3 using a JEOL GX400 spectrometer.

Preparations

1-Diethylphosphono-2-diphenylphosphinobenzene o-1. A solution of 1-bromo-2-diphenylphosphinobenzene (2.0 g, 5.9 mmol) in THF (15 cm^3) was added dropwise to a cooled (-78°C) and stirred solution of *n*-BuLi (3.7 cm^3 , 5.9 mmol, 1.6 M solution in hexane). Immediately after the addition was complete, diethyl chlorophosphate (0.90 cm^3 , 5.9 mmol) was added dropwise over 5 min and the stirred mixture then allowed to warm to room temperature. After 4 h, the solvent was removed *in vacuo* and diethyl ether (10 cm^3) added to precipitate the LiCl. Distilled water (10 cm^3) was then added and the two layers separated. The organic layer was dried over MgSO_4 and the volatiles were removed *in vacuo*. The residue was dissolved in diethyl ether (5 cm^3) and then pentane (20 cm^3) added. The

mixture was placed in a freezer (-10°C) overnight, and the resulting crystals collected, washed with pentane and dried *in vacuo* to give compound **o-1** (1.7 g, 73%). Elemental analysis, found (calc.): C, 66.6 (66.3); H, 6.0 (6.1%). EI mass spectrum: $m/z = 398$ (M^+). ^{31}P , ^{13}C and ^1H NMR data measured were similar to those reported.⁶ Single crystals were grown from a CDCl_3 solution by slow evaporation from an NMR tube.

trans-[PtCl₂{2-Ph₂PC₆H₄P(O)(OEt)₂}] 2. A solution of compound **o-1** (150 mg, 0.37 mmol) in dichloromethane (4 cm³) was added to a CH_2Cl_2 solution (6 cm³) of $[\text{PtCl}_2(\text{cod})]$ (70 mg, 0.19 mmol). The mixture was left to stir overnight, by which time a precipitate had formed. Collection of the pale yellow solid gave complex **2** (150 mg, 74%). Elemental analysis, found (calc.): C, 49.4 (49.7); H, 4.7 (4.6); Cl, 6.8 (6.7%). ^{31}P NMR: δ 19.6 (s, P=O) and 16.5 [s, PPh₂, $^1J(\text{PtP})$ 2876 Hz]. ^1H NMR: δ 0.99 [t, 6 H, CH₃, $^3J(\text{HH})$ 6.9 Hz], 3.64 [m, 2 H, CH₂], 3.78 [m, 2 H, CH₂], 7.25–7.38 [m, 10 H, aromatics] and 7.75–7.95 [m, 4 H, aromatics]. Single crystals of the sparingly soluble **2** were grown by careful layering of a 1:1 $\text{Me}_2\text{CO}-\text{CH}_2\text{Cl}_2$ solution of **o-1** over a CH_2Cl_2 solution of $[\text{PtCl}_2(\text{cod})]$ in an NMR tube; as the reaction slowly ensued, the crystalline product was formed.

cis-[PtCl₂{3-Ph₂PC₆H₄P(O)(OEt)₂}] 3. A solution of compound **m-1** (320 mg, 0.8 mmol) in dichloromethane (4 cm³) was added to a solution of $[\text{PtCl}_2(\text{cod})]$ (150 mg, 0.4 mmol) in dichloromethane (6 cm³). After 2 h, diethyl ether (25 cm³) was added and the white solid product **3** collected (260 mg, 61%). Elemental analysis, found (calc.): C, 49.5 (49.7); H, 4.5 (4.6%). ^{31}P NMR: δ 18.0 (s, P=O) and 16.0 [s, PPh₂, $^1J(\text{PtP})$ 3667 Hz]. ^1H NMR: δ 1.16 [t, 6 H, CH₃, $^3J(\text{HH})$ 7.1 Hz], 3.98 [m, 4 H, CH₂] and 7.19–7.75 [m, 14 H, aromatics].

cis-[PtCl₂{4-Ph₂PC₆H₄P(O)(OEt)₂}] 4. A solution of compound **p-1** (120 mg, 0.3 mmol) and $[\text{PtCl}_2(\text{cod})]$ (56 mg, 0.15 mmol) in dichloromethane (5 cm³) was stirred overnight. Diethyl ether (15 cm³) was added and the precipitate collected to give white solid **4** (80 mg, 50%). Elemental analysis, found (calc.): C, 49.5 (49.7); H, 4.5 (4.6%). ^{31}P NMR: δ 18.0 (s, P=O) and 16.0 [s, PPh₂, $^1J(\text{PtP})$ 3667 Hz]. ^1H NMR: δ 1.16 [t, 6 H, CH₃, $^3J(\text{HH})$ 7.1 Hz], 3.98 [m, 4 H, CH₂] and 7.19–7.75 [m, 14 H, aromatics].

Bis-chelate complex 5. To a slurry of complex **2** (90 mg, 0.085 mmol) in dichloromethane (5 cm³) was added a solution of AgSbF_6 (58 mg, 0.17 mmol) in acetone (1 cm³). The mixture was left to stir overnight, after which time the grey precipitate of AgCl was filtered off. Pentane (10 cm³) was added to the filtrate and the precipitate collected to give white solid product **5** (65 mg, 55%). Elemental analysis, found (calc.): C, 37.7 (38.1); H, 3.5 (3.5%). FAB mass spectrum: $m/z = 991$ [$\text{M}^+ - 2(\text{SbF}_6)$]. ^{31}P NMR: δ 18.5 [t, P=O, $J(\text{PP})$ ca. 40] and 1.7 [t, PPh₂, $^1J(\text{PtP})$ 4170 Hz]. ^1H NMR: δ 1.24 [t, 6 H, CH₃, $^3J(\text{HH})$ 6.2], 4.14 [br s, 3 H, CH₂], 6.74 [m, 1 H, CH₂] and 7.32–7.92 [m, 14 H, aromatics].

trans-[PdCl₂{3-Ph₂PC₆H₄P(O)(OEt)₂}] 7. A solution of compound **m-1** (370 mg, 0.9 mmol) and $[\text{PdCl}_2(\text{NCPh})_2]$ (180 mg, 0.46 mmol) in dichloromethane (10 cm³) was stirred for 2 h, after which time diethyl ether (25 cm³) was added. The resulting precipitate was collected to give yellow solid product, **7** (280 mg, 62%). Elemental analysis, found (calc.): C, 54.4 (54.3); H, 4.7 (5.0%). FAB mass spectrum: $m/z = 975$ [$\text{M}^+ + \text{H}$]. ^{31}P NMR: δ 17.3 (s, P=O) and 23.9 (s, PPh₂). ^1H NMR: δ 1.13 [t, 6 H, CH₃, $^3J(\text{HH})$ 7.0 Hz], 3.87–4.02 [m, 4 H, CH₂], 7.31–7.45 [m, 8 H, aromatics] and 7.62–7.97 [m, 6 H, aromatics].

[PdCl₂{4-Ph₂PC₆H₄P(O)(OEt)₂}] cis- and trans-8. A solution of compound **p-1** (230 mg, 0.58 mmol) and $[\text{PdCl}_2(\text{NCPh})_2]$

(110 mg, 0.29 mmol) in dichloromethane (6 cm³) was stirred overnight. Diethyl ether (30 cm³) was added, the mixture stirred for 3 h, and then orange **cis-8** (50 mg, 18%) precipitated. ^{31}P NMR: δ 16.5 (s, P=O) and 32.6 (s, PPh₂). The filtrate was concentrated to 5 cm³ and then pentane (10 cm³) was added to give yellow solid **trans-8** (75 mg, 27%). ^{31}P NMR: δ 17.5 (s, P=O) and 23.7 (s, PPh₂). Elemental analysis, found (calc.): C, 53.9 (54.3); H, 4.7 (5.0%). FAB mass spectrum of **cis-8** and **trans-8**: $m/z = 975$ [$\text{M}^+ + \text{H}$], 939 [$\text{M}^+ - \text{Cl}$] and 902 [$\text{M}^+ - 2\text{Cl}$].

Reaction between o-1 and [PdCl₂(NCPh)₂]. A solution of compound **o-1** (70 mg, 0.18 mmol) and $[\text{PdCl}_2(\text{NCPh})_2]$ (70 mg, 0.08 mmol) in CD_2Cl_2 (2 cm³) was stirred for 2 h, and then the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of the solution was measured (see Results and discussion for structure assignments).

[RhCl(CO){2-Ph₂PC₆H₄P(O)(OEt)₂}] 9. To a solution of compound **o-1** (150 mg, 0.38 mmol) in dichloromethane (5 cm³) was added $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ (73 mg, 0.19 mmol) and the solution stirred overnight. Pentane (6 cm³) was added to the yellow solution, the mixture stirred for 30 min, and the pale yellow precipitate **9** collected (150 mg, 70%). Elemental analysis, found (calc.): C, 49.1 (48.9); H, 4.2 (4.3); Cl, 6.6 (6.3%). FAB mass spectrum: $m/z = 536$ [$\text{M}^+ - \text{CO}$] and 529 [$\text{M}^+ - \text{Cl}$]. ^{31}P NMR: δ 18.1 (d, P=O, $J(\text{PP})$ 22) and 39.3 [dd, PPh₂, $^1J(\text{RhP})$ 166 Hz]. ^1H NMR: δ 1.12 [t, 6 H, CH₃, $^3J(\text{HH})$ 14.1], 3.90–4.01 [m, 4 H, CH₂] and 7.05–7.84 [m, 14 H, aromatics]. Addition of more **o-1** to solutions of **9** gave a new rhodium-containing species (^{31}P NMR: δ 17.1 (s, P=O) and 27.7 [d, PPh₂, $^1J(\text{RhP})$ 131 Hz]) assigned structure **10** (see Results and discussion).

Standard procedure for the hydroformylation experiments

The hydroformylation experiments were performed in a 250 cm³ Hastelloy C Parr autoclave equipped with a substrate inlet vessel, a liquid sampling valve and a magnetically coupled Hastelloy C stirrer. The solution was stirred at 1000 rpm and the temperature controlled by an electronic heating mantle. In a typical experiment, SnCl_2 (189 mg, 1.0 mmol) was placed in the steel autoclave and the reactor sealed. Meanwhile, $[\text{PtCl}_2(\text{cod})]$ (75 mg, 0.2 mmol) and **o-1** (80 mg, 0.2 mmol) were stirred together in toluene (80 cm³) for 30–60 min, after which time the mixture was syringed into the reactor under a nitrogen atmosphere. The vessel was flushed with a 1:1 mixture of H_2 –CO three times and the stirrer switched on. The pressure was then increased to 40–50 bar with a 1:1 mixture of H_2 –CO and the mixture heated to the required temperature. Once the temperature had been reached, **cis-2-butene** (10 g) was flushed into the reactor and the pressure increased to 80 bar. The pressure was then kept constant for the duration of the reaction. The reactor was connected to a flow meter which enabled the syngas uptake to be monitored. Once the meter indicated the reaction had gone to completion, the autoclave was cooled to room temperature and the pressure slowly released. A sample was removed for GC analysis, using nonane as the internal standard.

X-Ray crystallography

Details of the structure determinations of compounds **o-1** and **2**· $2\text{Me}_2\text{CO}$ are given in Table 4. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints.

CCDC reference number 186/1785.

See <http://www.rsc.org/suppdata/dt/a9/a908963b/> for crystallographic files in .cif format.

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Table 4 Selected crystallographic details for the compounds **1** and **2·2Me₂CO**

	o-1	2·2Me₂CO
Empirical formula	C ₂₂ H ₂₄ O ₃ P ₂	C ₅₀ H ₆₀ Cl ₂ O ₈ P ₄ Pt
Formula weight	398.35	1178.85
Crystal system	Orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	8.5253(12)	9.2995(10)
<i>b</i> /Å	9.4993(17)	11.7240(11)
<i>c</i> /Å	25.999(4)	13.483(3)
<i>α</i> /°		64.608(12)
<i>β</i> /°		76.108(6)
<i>γ</i> /°		72.660(7)
<i>V</i> /Å ³	2105.5(6)	1256.9(3)
<i>T</i> /K	173(2)	173(2)
<i>Z</i>	4	1
<i>μ</i> /mm ^{−1}	0.225	3.077
Total reflections	9888	12712
Independent reflections	3694	5658
<i>R</i> _{int}	0.0412	0.0260
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0485	0.0203

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