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PAPER

Interplay of bite angle and cone angle effects. A comparison between *o*-$C_6H_4(CH_2PR_2)(PR'_2)$ and *o*-$C_6H_4(CH_2PR_2)(CH_2PR'_2)$ as ligands for Pd-catalysed ethene hydromethoxycarbonylation†‡

Tamara Fanjul,[a] Graham Eastham,[b] Joelle Floure,[a] Sebastian J. K. Forrest,[a] Mairi F. Haddow,[a] Alex Hamilton,[a] Paul G. Pringle,*[a] A. Guy Orpen[a] and Mark Waugh[b]

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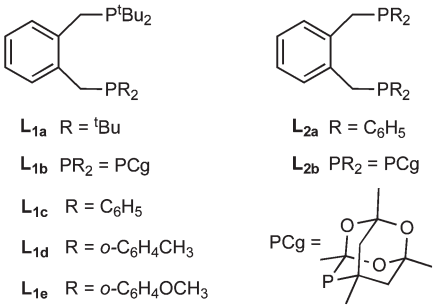
The following unsymmetrical diphosphines have been prepared: *o*-$C_6H_4(CH_2P^tBu_2)(PR_2)$ where R = P^tBu_2 (**L_{3a}**); PCg (**L_{3b}**); PPh_2 (**L_{3c}**); $P(o\text{-}C_6H_4CH_3)_2$ (**L_{3d}**); $P(o\text{-}C_6H_4OCH_3)_2$ (**L_{3e}**) and *o*-$C_6H_4(CH_2PCg)(PCg)$ (**L_{3f}**) where PCg is 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamant-6-yl. Hydromethoxycarbonylation of ethene under commercially relevant conditions has been investigated in the presence of Pd complexes of each of the ligands **L_{3a-f}** and the results compared with those obtained with the commercially used *o*-$C_6H_4(CH_2P^tBu_2)_2$ (**L_{1a}**). The Pd complexes of the bulkiest ligands **L_{3a}**, **L_{3b}** and **L_{3f}** are highly active catalysts but the Pd complexes of **L_{3c}**, **L_{3d}** and **L_{3e}** are completely inactive. The crystal structures of the complexes [$PtCl_2$(**L_{1a}**)] (**1a**) and [$PtCl_2$(**L_{3a}**)] (**2a**) have been determined and show that the crystallographic bite angles and cone angles are greater for **L_{1a}** than **L_{3a}**. Solution NMR studies show that the seven-membered chelate in **1a** is more rigid than the six-membered chelate in **2a**. Treatment of [PtCl(CH_3)(cod)] with **L_{3a-f}** gave [PtCl(CH_3)(**L_{3a-f}**)] as mixtures of 2 isomers **3a–f** and **4a–f**. The ratio of the products **4** : **3** ranges from 100 : 1 to 1 : 20, the precise proportion is apparently governed by a balance of two competing factors, steric bulk and the antisymbiotic effect. The palladium complexes [PdCl(CH_3)(**L_{3b}**)] (**5b**/**6b**) and [PdCl(CH_3)(**L_{3c}**)] (**5c**/**6c**) react with labelled ^{13}CO to give the corresponding acyl species [PdCl($^{13}COCH_3$)(**L_{3b}**)] (**7b**/**8b**) and [PdCl($^{13}COCH_3$)(**L_{3c}**)] (**7c**/**8c**). Treatment of [PdCl($^{13}COCH_3$)(L)] with MeOH gave $CH_3{}^{13}COOMe$ rapidly when L = **L_{3b}** but very slowly when L = **L_{3c}** paralleling the contrasting catalytic activity of the Pd complexes of these two ligands.

Introduction

The homogeneous palladium catalyst used for the first step (eqn (1)) of the Lucite Process is based on seven-membered chelates formed by the bulky *o*-diphosphinoxylene **L_{1a}**.[1] The bite angle[2] of the diphosphine backbone and the P-substituent stereoelectronic effects are key to the activity and chemoselectivity of the catalyst.[3–6] For example, while Pd catalysts based on **L_{1a}** give MeP efficiently in greater than 99.9% chemoselectivity, the catalyst based on **L_{2a}** sluggishly gives ethene/CO co-oligomers and polyketone.[7–9]

We recently reported that, in the case of *o*-diphosphinoxylenes, catalysts based on unsymmetrical ligands such as **L_{1b-e}** are comparable to the commercial catalysts based on **L_{1a}** in terms of activity and chemoselectively to MeP.[7,8] In addition, **L_{1c}** produces a longer-lived catalyst than **L_{1a}** and the catalyst based on **L_{1b}** outperformed, in terms of activity, both of its symmetrical analogues based on **L_{1a}** and **L_{2b}**.

(1)



The favourable properties of the Pd catalysts derived from symmetrical and unsymmetrical *o*-diphosphinoxylenes **L_{1a-e}**, and

[a]*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK. E-mail: paul.pringle@bristol.ac.uk*
[b]*Lucite International, Wilton Centre, Wilton, Redcar, Cleveland, TS10 4RF, UK*

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‡Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

$\mathbf{L_{2b}}$ prompted us to explore the performance of the analogous catalysts based on *o*-diphosphinotoluenes $\mathbf{L_{3a–f}}$ (Chart 1) which have a smaller bite angle. We report here that some of the *o*-diphosphinotoluenes produce outstandingly active and selective hydromethoxycarbonylation catalysts while others show no activity at all.

All of the *o*-diphosphinotoluenes $\mathbf{L_{3a–f}}$ are ditopic due to one donor being an aryl phosphine and the other a benzyl phosphine.

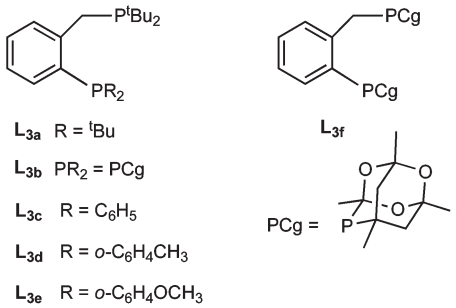


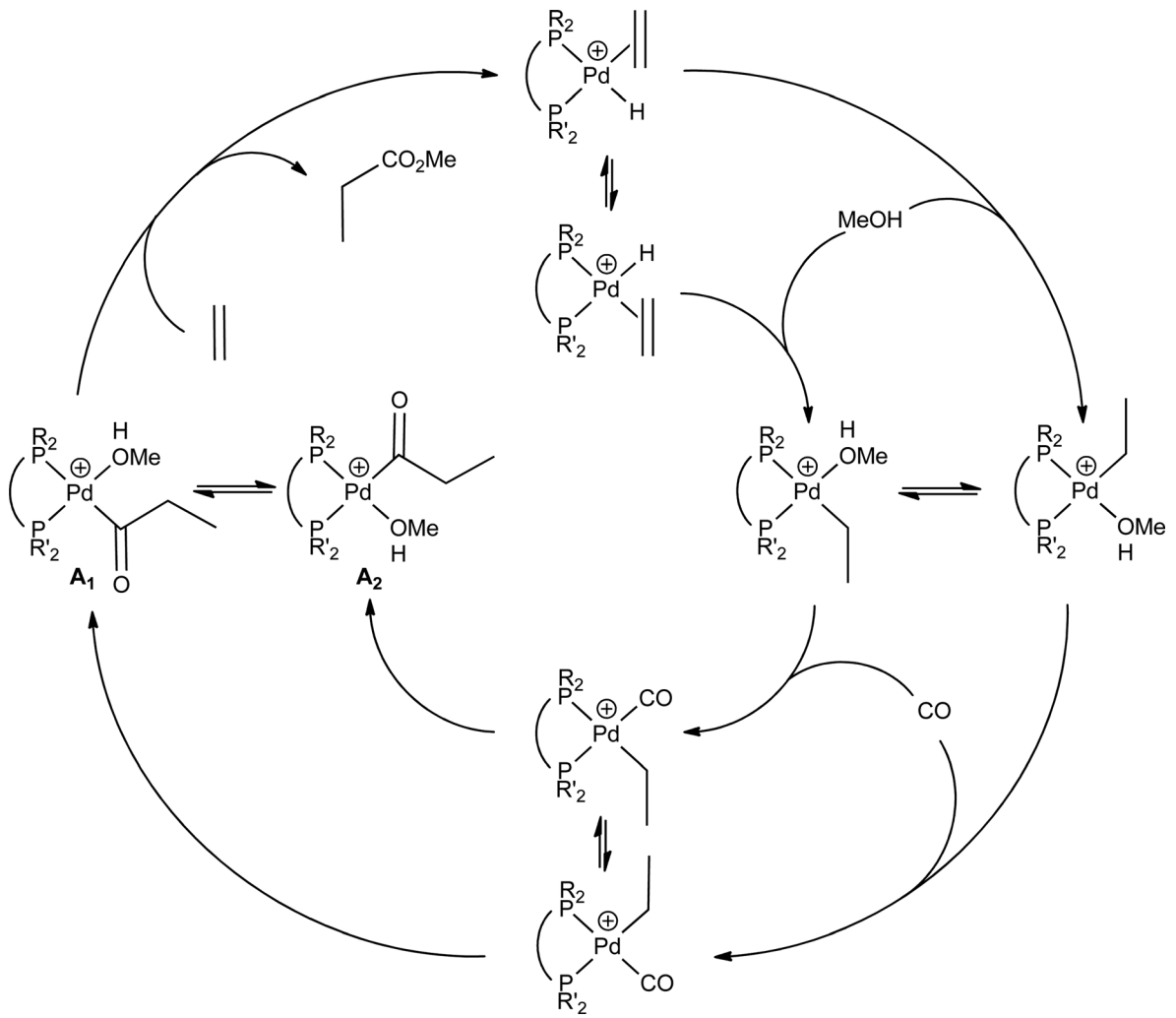
Chart 1

A general mechanism for the hydromethoxycarbonylation catalysed by Pd complexes of unsymmetrical diphosphines is given in Scheme 1. It shows that at each stage there is a potential bifurcation in the mechanism as a result of the geometric isomerism. In previous articles,[7,8] we have proposed that the high chemoselectivity of the catalysts derived from the unsymmetrical *o*-diphosphinoxylenes $\mathbf{L_{1b–e}}$ is due to the kinetic dominance of the intermediate $\mathbf{A_1}$ over its isomer $\mathbf{A_2}$ (Scheme 1). This proposition was supported by observations made on model palladium(II) and platinum(II) complexes. It was therefore of interest to investigate if the coordination chemistry of *o*-diphosphinotoluenes $\mathbf{L_{3a–f}}$ would provide insight into some of the sharply contrasting catalytic performances of the Pd complexes of these unsymmetrical ligands.

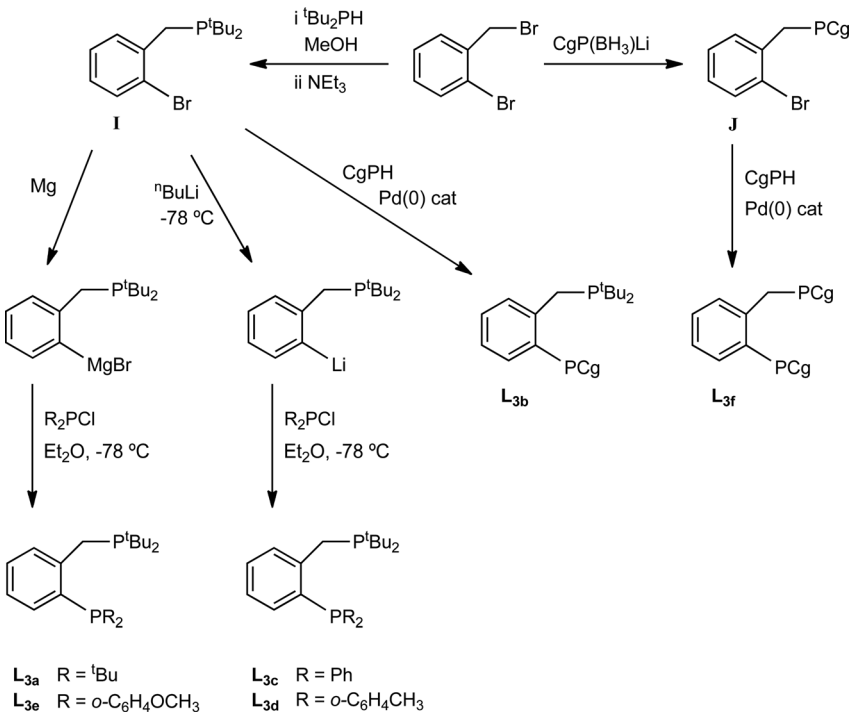
Results and discussion

Ligand synthesis

The diphosphines $\mathbf{L_{3a–f}}$ are readily obtained from *o*-α-dibromotoluene (2-bromobenzyl bromide) by the routes summarised in Scheme 2. Ligands $\mathbf{L_{3a–f}}$ are new and have been fully



Scheme 1



Scheme 2

characterised (see Experimental). The intermediate **I** is particularly versatile since it can be converted to organolithium or Grignard reagents or used in Pd-catalysed C–P coupling reactions allowing access to the range of diphosphines $\mathbf{L_{3a–e}}$. Compound **J** is a potentially useful intermediate to ditopic diphosphines although we have used it only to prepare $\mathbf{L_{3f}}$. Unlike the analogous *o*-diphosphinoxylenes, all of the *o*-diphosphinotoluenes have inequivalent P atoms, including $\mathbf{L_{3a}}$ and $\mathbf{L_{3f}}$. In general, two doublets were observed in the ^{31}P NMR spectra with $^{3}J_{PP}$ of the order of 5 Hz. Two diastereoisomers would be predicted for $\mathbf{L_{3f}}$ associated with the chirality of the PCg moiety[10] but only one set of singlets was observed in the ^{31}P NMR spectrum of the purified product, implying that only one diastereoisomer was present or that the signals for the two diastereoisomers are coincident.

Carbonylation catalysis

Ethene hydromethoxycarbonylation to give MeP (eqn (1)) was carried out with palladium catalysts derived from the *o*-diphosphinotoluenes $\mathbf{L_{3a–f}}$, under the conditions described in the Experimental section and the results are given in Table 1, along with those we previously reported[8] for the corresponding *o*-diphosphinoxylenes for comparison.

Two contrasting observations can be made from the catalysis data given in Table 1. (1) The *o*-diphosphinotoluenes $\mathbf{L_{3a}}$, $\mathbf{L_{3b}}$ and $\mathbf{L_{3f}}$ significantly outperform their *o*-diphosphinoxylene analogues in terms of relative rate and match them in their excellent chemoselectivity (compare Entries 1, 2 and 6T with 1, 2 and 6X). (2) The complexes derived from the mixed P^{t}Bu$_2$/PAr$_2$ ligands $\mathbf{L_{3c–e}}$ show no detectable catalytic activity which was unexpected in view of the high performance of their xylene analogues $\mathbf{L_{1c–e}}$ (compare Entries 3–5T with 3–5X). What the three successful *o*-diphosphinotoluenes have in common, is two, very bulky P-donors (P^{t}Bu$_2$ or PCg). Thus the effect on the catalysis of the smaller bite of the diphosphinotoluenes compared to the diphosphinoxylenes is non-linear: with relatively small PR$_2$ donors (as in $\mathbf{L_{3c–e}}$), the activity is zeroed whereas with bulky PR$_2$ donors (as in $\mathbf{L_{3a}}$, $\mathbf{L_{3b}}$ and $\mathbf{L_{3f}}$), the catalysts are the most efficient reported to date under these conditions.[11]

Platinum(II) and palladium(II) coordination chemistry

In order to gauge the stereoelectronic effects of the ligands in $\mathbf{L_{1a}}$ and $\mathbf{L_{3a}}$, the complexes [PtCl$_2$($\mathbf{L_{1a}}$)] (**1a**) and [PtCl$_2$($\mathbf{L_{3a}}$)] (**2a**) were prepared and the crystal structures of both determined (Fig. 1 and 2). The conformation of the 7-membered chelate in **1a** is similar to those of other diphosphinoxylene complexes, putting the phenylene ring almost orthogonal to the PtP$_2$ plane. The conformation of the 6-membered chelate in **2a** (and the others reported below) is approximately a half-chair and is defined by the P–M–P–C(1) torsion angle of 25°.

The crystallographically determined bite angle for $\mathbf{L_{1a}}$ in **1a** is 104° and for $\mathbf{L_{3a}}$ in **2a** is 97° and the cone angle for $\mathbf{L_{1a}}$ in **1a** is 276° and for $\mathbf{L_{3a}}$ in **2a** is 266°. It was noted that when the half cone angles (θ) around P(1) and P(2) in **2a** were measured, there was no significant difference between the benzyl-P^{t}Bu$_2$ and aryl-P^{t}Bu$_2$. The net effect of $\mathbf{L_{1a}}$ having a larger bite angle and larger cone angle than $\mathbf{L_{3a}}$ is the squeezing together of the adjacent ligands: the Cl···Cl distance is *ca.* 3.00 Å in **1a** and 3.16 Å in **2a**. It might be predicted that a benzyl-P^{t}Bu$_2$ would be a better σ-donor and therefore have a higher *trans* influence than an aryl-P^{t}Bu$_2$. Consistent with this, in the structure of **2a**, the Pt–Cl(1) distance is slightly longer than Pt–Cl(2). However the difference

Table 1 Pd-catalysed hydromethoxycarbonylation of ethene[a]

o-diphosphinotoluene					*o*-diphosphinoxylene analogue[8]				
Entry	Ligand	Selectivity/%	TON	Rel. rate	Entry	Ligand	Selectivity/%	TON	Rel. rate
1T	$\mathbf{L_{3a}}$	>99.9	29 600	1.7	1X	$\mathbf{L_{1a}}$	>99.9	17 900	1
2T	$\mathbf{L_{3b}}$	>99.9	67 300	3.8	2X	$\mathbf{L_{1b}}$	>99.9	25 600	1.4
3T	$\mathbf{L_{3c}}$	—	0	0	3X	$\mathbf{L_{1c}}$	99.5	16 300	0.9
4T	$\mathbf{L_{3d}}$	—	0	0	4X	$\mathbf{L_{1d}}$	99.5	32 200	1.8
5T	$\mathbf{L_{3e}}$	—	0	0	5X	$\mathbf{L_{1e}}$	99.5	3600	0.2
6T	$\mathbf{L_{3f}}$	>99.9	66 000	3.7	6X	$\mathbf{L_{2b}}$	>99.9	40 200	2.2

[a] The data given in this Table are the average of 2 or more runs. For reaction conditions, see Experimental. TON (in mol mol^{-1} Pd) were calculated from the mass gain after 3 h. The selectivity to MeP was measured by GC; the remainder was a mixture of co-oligomers. The relative rates are calculated from the TON after 3 h and are relative to the values for $\mathbf{L_{1a}}$.

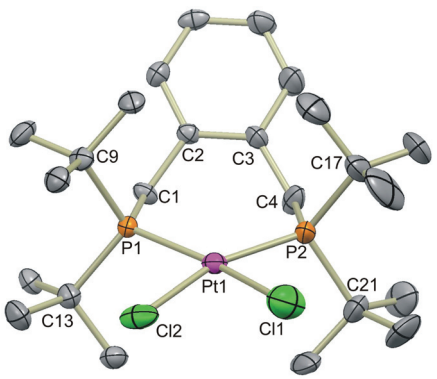


Fig. 1 Crystal structure of [$PtCl_2$($\mathbf{L_{1a}}$)] (**1a**). Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.267(3); Pt(1)–P(2) 2.304(2); Pt(1)–Cl(2) 2.321(4); Pt(1)–Cl(1) 2.362(3); P(1)–C(1) 1.826(12); P(1)–C(9) 1.902(13); P(1)–C(13) 1.909(12); P(2)–C(4) 1.872(10); P(2)–C(17) 1.882(10); P(2)–C(21) 1.920(10); P(1)–Pt(1)–P(2) 104.06(10); P(1)–Pt(1)–Cl(2) 87.24(14); P(2)–Pt(1)–Cl(1) 89.64(11); Cl(2)–Pt(1)–Cl(1) 79.51(14).

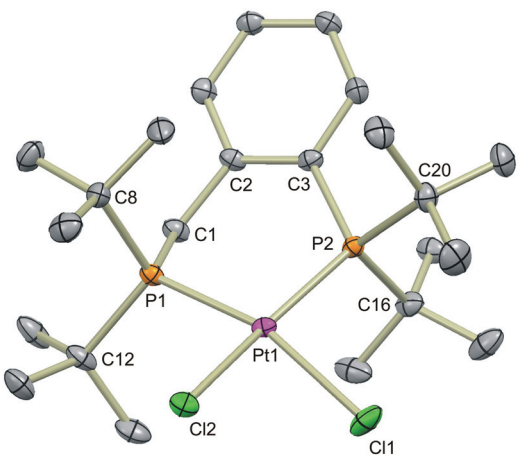


Fig. 2 Crystal structure of [$PtCl_2$($\mathbf{L_{3a}}$)] (**2a**). Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.2531(9); Pt(1)–P(2) 2.2895(8); Pt(1)–Cl(1) 2.3824(9); Pt(1)–Cl(2) 2.3627(8); P(1)–C(1) 1.823(3); P(1)–C(8) 1.878(4); P(1)–C(12) 1.913(3); P(2)–C(3) 1.848(3); P(2)–C(16) 1.906(3); P(2)–C(20) 1.922(4); P(1)–Pt(1)–P(2) 96.84(3); P(1)–Pt(1)–Cl(2) 89.52(3); P(2)–Pt(1)–Cl(1) 92.32(3); Cl(2)–Pt(1)–Cl(1) 83.65(3); torsion C(1)–P(1)–Pt(1)–P(2) 24.9.

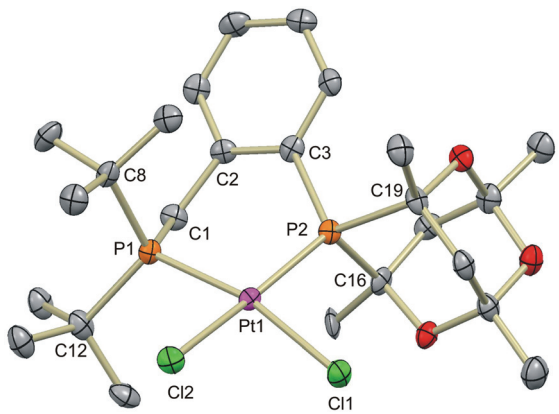
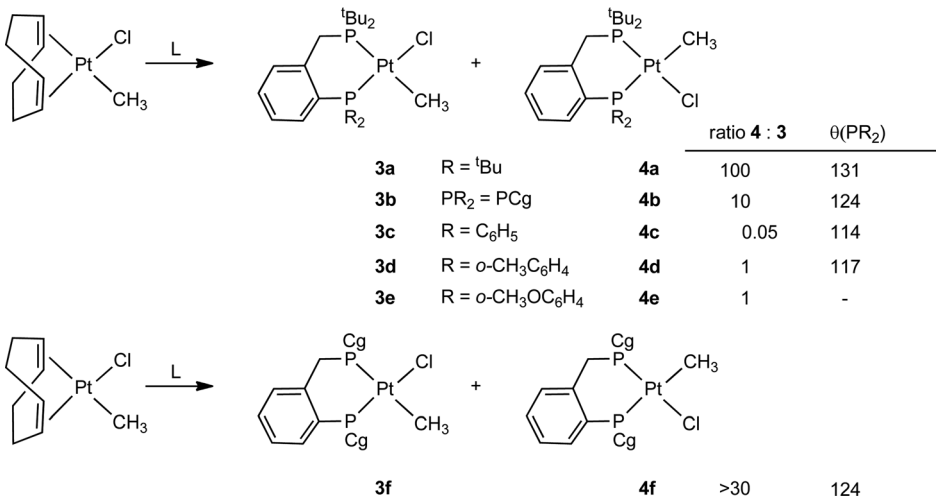


Fig. 3 Crystal Structure of [$PtCl_2$($\mathbf{L_{3b}}$)] (**2b**). Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.2562(16); Pt(1)–P(2) 2.2683(15); Pt(1)–Cl(1) 2.3574(16); Pt(1)–Cl(2) 2.3525(15); P(1)–C(1) 1.836(6); P(1)–C(8) 1.877(6); P(1)–C(12) 1.907(6); P(2)–C(3) 1.849(6); P(2)–C(16) 1.892(6); P(2)–C(19) 1.896(5); P(1)–Pt(1)–P(2) 94.07(6); P(1)–Pt(1)–Cl(2) 88.19(6); P(2)–Pt(1)–Cl(1) 95.87(6); Cl(2)–Pt(1)–Cl(1) 82.87(6); torsion C(1)–P(1)–Pt(1)–P(2) 20.9.

(*ca.* 0.02 Å) is less than the difference between the ostensibly equivalent Pt–Cl bond lengths in **1a** (*ca.* 0.04 Å).

A previously reported feature of the coordination chemistry of $\mathbf{L_{1a}}$ was the chelate ring conformation and its fluxionality.[8,9] It is clear from Fig. 1 and 2 that the *z*-coordinates of the backbone phenylene group render the CH_2 protons and the ^{t}Bu substituents inequivalent in both **1a** and **2a**. The ^{1}H NMR spectra of both complexes show broad signals for the CH_2 and ^{t}Bu protons at ambient temperatures and from the coalescence temperatures, estimated from variable temperature studies (see Experimental for details), the calculated values for $\Delta G^{\ddagger}$ are 13 kcal mol^{-1} for **1a** and 11 kcal mol^{-1} for **2a** indicating that the 7-membered chelate is more rigid than the 6-membered chelate.

Ligand $\mathbf{L_{3b}}$ produced a more efficient catalyst than $\mathbf{L_{3a}}$ (Table 1) and therefore the complex [$PtCl_2$($\mathbf{L_{3b}}$)] (**2b**) was prepared and its crystal structure determined (Fig. 3) in order to draw structural comparisons with **2a**.[12] The Pt–P distances and the Pt–Cl distances in **2a** and **2b** are very similar to each other. We have previously argued that RPCg is a significantly poorer σ-donor than RP^tBu_2[10] but this difference is apparently too subtle to be evident from the crystal structures of **2a** and **2b**. The



Scheme 3

Cl–Pt–Cl angles and Cl....Cl distances in **2b** (83°, 3.12 Å) and **2a** (84°, 3.16 Å) are similar which implies that the steric compression by the PCg group is at least as great as the P^{t}Bu$_2$ group.

The isomers of [PtCl(CH$_3$)(P–P′)], where P–P′ = a chelating unsymmetrical diphosphine can be viewed as models for key intermediates **A$_1$**/**A$_2$** (Scheme 1) since they contain a strong σ-donor (CH$_3$) and a relatively weak σ-donor (Cl). Thus the complexes [PtCl(CH$_3$)(**L$_{3a–f}$**)] (**3a–f**/**4a–f**) were prepared according to Scheme 3. The geometric isomers were readily distinguished from the characteristic chemical shifts and $^1J_{PtP}$ coupling constants; *e.g.* δ_P for coordinated P^{t}Bu$_2$ is in the +20 to +40 ppm region and $^1J_{PtP}$ for the P *trans* to CH$_3$ is less than 2000 Hz and *trans* to Cl was over 4000 Hz. The ^{31}P NMR spectrum of the **3d**/**4d** mixture showed the presence of 2 sets of similar signals for each component which is presumed to be due to conformers associated with restricted rotation about the P–C(*o*-tolyl) bond[13] (see Experimental). The ratios of the *o*-diphosphinotoluene complexes given in Scheme 3 were estimated from integration of the ^{31}P signals of mixtures that had been allowed to equilibrate for at least 24 h. It is notable that the 3 ligands that produce the most active carbonylation catalysts also produce the highest proportions of isomer **4** with the CH$_3$ *cis* to the benzyl-P^{t}Bu$_2$ donor.

The crystal structures of the major isomers of the complexes [PtCl(CH$_3$)(*o*-diphosphinotoluene)] **4a**, **4b**, **4f** and the co-crystallised mixtures **3c**/**4c** and **3d**/**4d** have been determined and are shown in Fig. 4–8. The half cone angles (θ) have been measured in each of the structures; the θ values for the P^{t}Bu$_2$ donors are very similar (131° ± 2°) in all of the structures and the θ values for the other PR$_2$ groups (given in Scheme 3) vary from 114° for PPh$_2$ to 124° for PCg. Caution should be exercised when crystallographic cone angles are used as an indicator of the bulk of a PR$_2$ donor because small differences in the conformation of the P–R substituent can lead to significant differences in the values of θ. This is especially true of PAr$_2$ groups, since changing the orientation of the P–Ar can be a low energy process allowing θ to compress or expand in response to, for example, the bulk of adjacent ligands and solvation effects. Note that P^{t}Bu$_2$ and PCg have much less capacity to respond sterically to their environment because of the rotational symmetry about the P–^{t}Bu bond and the rigidity of the PCg.

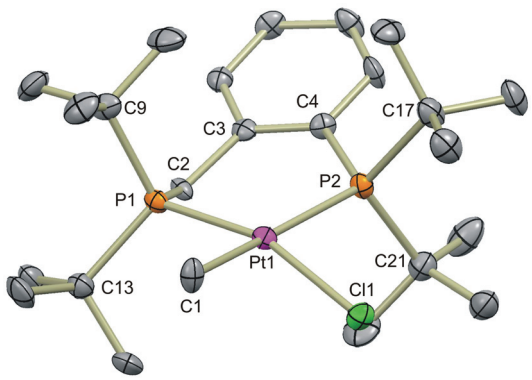


Fig. 4 Crystal Structure of [PtCl$_2$(**L$_{3a}$**)] (**4a**). Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 2.123(6); Pt(1)–P(1) 2.2307(17); Pt(1)–P(2) 2.3926(15); Pt(1)–Cl(1) 2.4015(16); P(1)–C(2) 1.832(6); P(1)–C(9) 1.880(7); P(1)–C(13) 1.904(7); P(2)–C(4) 1.840(6); P(2)–C(21) 1.902(6); P(2)–C(17) 1.927(6); C(1)–Pt(1)–P(1) 91.11(18); C(1)–Pt(1)–P(2) 168.32(19); P(1)–Pt(1)–P(2) 97.41(5); C(1)–Pt(1)–Cl(1) 80.24(18); P(1)–Pt(1)–Cl(1) 161.75(6); P(2)–Pt(1)–Cl(1) 93.66(5); torsion C(2)–P(1)–Pt(1)–P(2) 23.4.

We have previously suggested[7] that the ratio of the geometric isomers of the complexes [PtCl(CH$_3$)(*o*-diphosphinoxylene)] is largely controlled by steric effects; CH$_3$ is slightly larger than Cl[14] and therefore occupies the less congested of the two sites on the metal. The crystal structure of **2a** suggests there is no significant difference in the steric congestion at the ditopic sites *trans* to the P-donors. Thus the observed ratio for **3a** : **4a** of 1 : 100 appears to be due to an electronic effect, namely the anti-symbiotic effect[15] whereby the strong σ-donor CH$_3$ has a preference to be *trans* to the weaker aryl-P^{t}Bu$_2$ donor. Similar stereoelectronic arguments could rationalise the greater proportions of **4c–f** over **3c–f** compared to the analogous *o*-diphosphinoxylene complexes.[7,8] A fine balance of steric and electronic effects would explain the near parity observed for the ratios **3d** : **4d** and **3e** : **4e**.

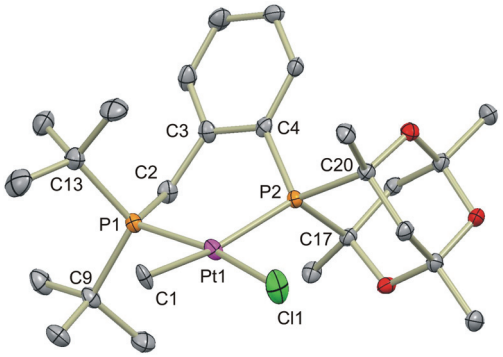


Fig. 5 Crystal Structure of $[PtCl_2(\mathbf{L_{3b}})]$ (**4b**). The thermal ellipsoid of Cl1(A/B) was found to be very elongated and so this was modelled as lying over two positions. Only one of these positions is shown for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 2.131(2); Pt(1)–P(1) 2.2372(7); Pt(1)–Cl(1B) 2.30(2); Pt(1)–P(2) 2.3478(7); Pt(1)–Cl(1A) 2.386(4); P(1)–C(2) 1.850(3); P(1)–C(13) 1.898(3); P(1)–C(9) 1.898(3); P(2)–C(4) 1.850(3); P(2)–C(20) 1.890(3); P(2)–C(17) 1.903(3); C(1)–Pt(1)–P(1) 89.80(7); C(1)–Pt(1)–Cl(1B) 77.5(5); P(1)–Pt(1)–Cl(1B) 167.1(5); C(1)–Pt(1)–P(2) 165.86(8); P(1)–Pt(1)–P(2) 95.33(2); Cl(1B)–Pt(1)–P(2) 97.5(5); C(1)–Pt(1)–Cl(1A) 80.78(12); P(1)–Pt(1)–Cl(1A) 163.50(8); Cl(1B)–Pt(1)–Cl(1A) 11.7(3); P(2)–Pt(1)–Cl(1A) 97.02(9); torsion C(2)–P(1)–Pt(1)–P(2) 12.3.

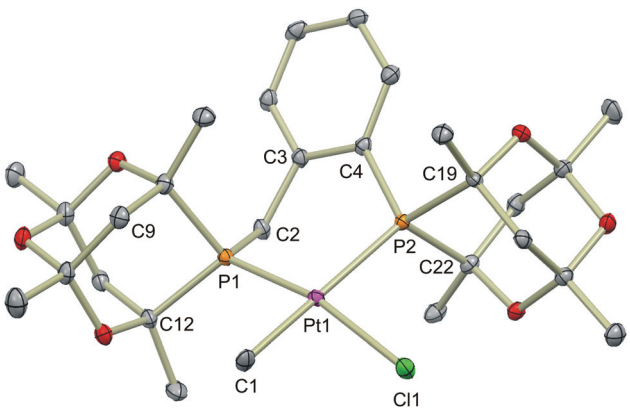


Fig. 6 Crystal Structure of $[PtCl_2(\mathbf{L_{3f}})]$ (**4f**). Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 2.093(3); Pt(1)–P(1) 2.2082(9); Pt(1)–P(2) 2.3754(9); Pt(1)–Cl(1) 2.3775(9); P(1)–C(2) 1.838(2); P(1)–C(9) 1.867(3); P(1)–C(12) 1.889(3); P(2)–C(4) 1.844(2); P(2)–C(19) 1.887(3); P(2)–C(22) 1.889(3); C(1)–Pt(1)–P(1) 90.96(9); C(1)–Pt(1)–P(2) 173.20(9); P(1)–Pt(1)–P(2) 93.27(4); C(1)–Pt(1)–Cl(1) 82.81(8); P(1)–Pt(1)–Cl(1) 166.87(3); P(2)–Pt(1)–Cl(1) 94.08(4); torsion C(2)–P(1)–Pt(1)–P(2) 29.5.

In order to probe the reasons for the disparate behaviour of the Pd catalysts derived from $\mathbf{L_{3b}}$ and $\mathbf{L_{3c}}$ (see Table 1), the palladium coordination chemistry with model complexes of these ligands was explored. Treatment of $[PdCl(CH_3)(cod)]$ with $\mathbf{L_{3b}}$ and $\mathbf{L_{3c}}$ gave the complexes **5b**/**6b** and **5c**/**6c** (Scheme 4). We tentatively assign the structures of the major isomers as **6b** and **5c** based on the ratios of the isomers observed for **5b**/**6b** (1 : 40) and **5c**/**6c** (25 : 1) being similar to those of the unambiguously assigned Pt analogues **3b**/**4b** (1 : 10) and **3c**/**4c** (20 : 1).

When solutions containing **5b**/**6b** or **5c**/**6c** were stirred under an atmosphere of ^{13}CO, the isotopic label enabled the

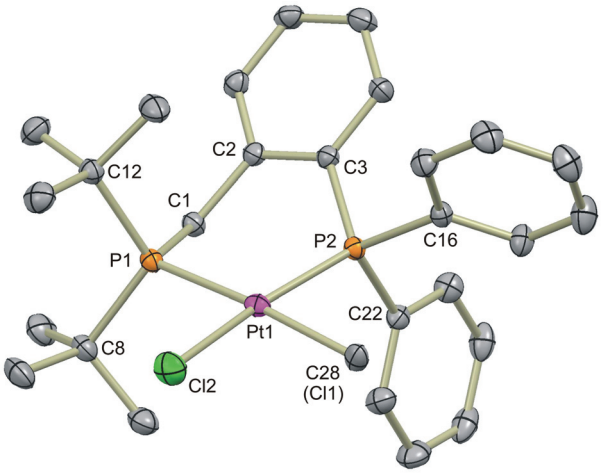


Fig. 7 Crystal structure of $[PtCl(CH_3)(\mathbf{L_{3c}})]$ (**3c**/**4c**). The crystal structure was found to be a solid solution of **3c** and **4c** with Cl/Me disorder at the C28 positions, is a ratio of Me : Cl of 0.87 : 0.13 (note, in solution the ratio was found to be 20 : 1). Selected bond lengths (Å) and angles (°): Pt(1)–C(28) 2.136(8); Pt(1)–P(2) 2.2085(7); Pt(1)–Cl(1) 2.21(2); Pt(1)–P(1) 2.3131(8); Pt(1)–Cl(2) 2.3658(8); P(2)–C(16) 1.823(3); P(2)–C(22) 1.827(3); P(2)–C(3) 1.827(3); P(1)–C(1) 1.846(3); P(1)–C(12) 1.880(3); P(1)–C(8) 1.900(3); C(28)–Pt(1)–P(2) 85.28(17); P(2)–Pt(1)–Cl(1) 91.9(4); P(2)–Pt(1)–P(1) 94.26(3); C(28)–Pt(1)–Cl(2) 86.04(17); Cl(1)–Pt(1)–Cl(2) 79.4(4); P(1)–Pt(1)–Cl(2) 94.72(3); torsion C(2)–P(1)–Pt(1)–P(2) 14.1.

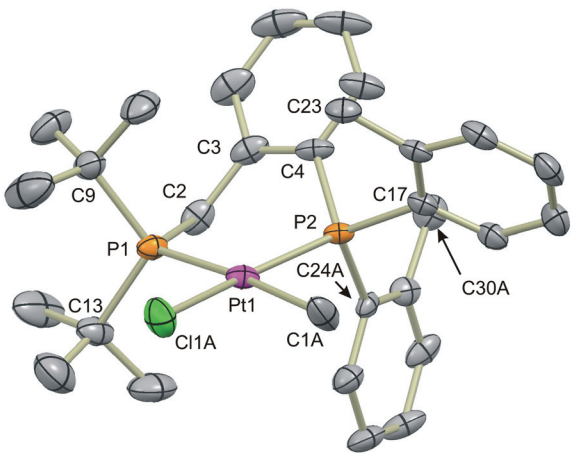
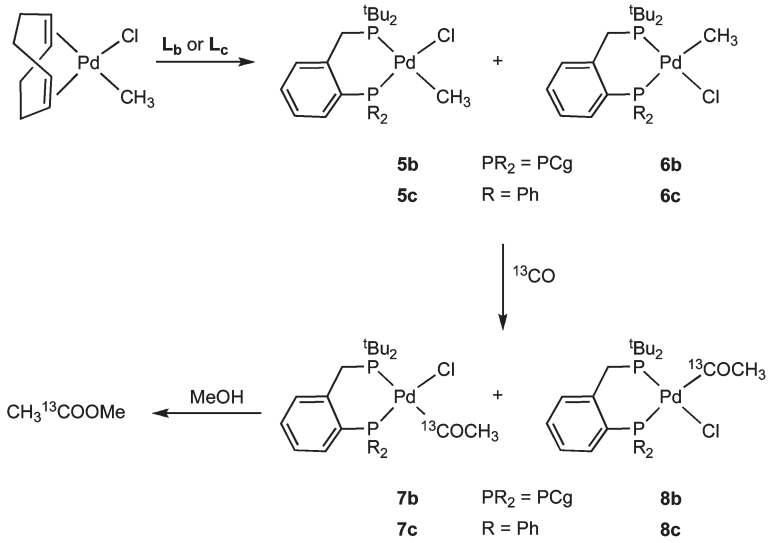


Fig. 8 Crystal structure of $[PtCl(CH_3)(\mathbf{L_{3d}})]$ (**3d**/**4d**). The chloride and methyl groups are disordered over the two positions. The individual positions of the methyl and chloride groups could not be modelled satisfactorily so they were considered to lie on the same position, although this description is clearly inaccurate. The occupancy of C1A at the position shown is 0.59. The tolyl group at C24 is also disordered over two positions. Only the major component (0.65) is shown. Selected bond lengths (Å) and angles (°): Pt(1)–P(2) 2.2692(13); Pt(1)–C(1A) 2.283(3); Pt(1)–P(1) 2.2932(14); Pt(1)–Cl(1A) 2.313(2); P(1)–C(2) 1.850(6); P(1)–C(9) 1.891(6); P(1)–C(13) 1.904(6); P(2)–C(17) 1.832(5); P(2)–C(4) 1.832(5); P(2)–C(24A) 1.852(6); P(2)–C(24B) 1.861(10); P(2)–Pt(1)–C(1A) 92.34(8); P(2)–Pt(1)–P(1) 93.63(5); C(1A)–Pt(1)–Cl(1A) 77.68(10); P(1)–Pt(1)–Cl(1A) 96.46(7); torsion C(2)–P(1)–Pt(1)–P(2) 8.2.

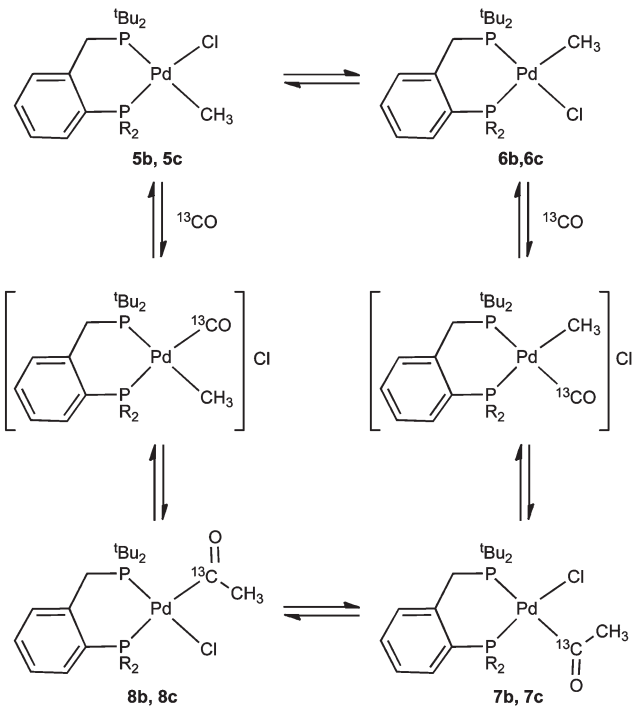


Scheme 4

unambiguous assignment from the ^{31}P NMR spectra of the geometric isomers of the products that formed. For example, in **7c**, the P^{t}Bu$_2$ signal at δ 39.2 has a J_{PC} of 120 Hz which is large and typical of a *trans* coupling and the PPh$_2$ signal at δ 14.6, has a J_{PC} of 16 Hz which is typical of a *cis* coupling. It was thus concluded that mixtures of the acyl complexes **7b**/**8b** (1 : 4) or **7c**/**8c** (9 : 1) were formed. The reactions did not go to completion after 20 min and decomposition to Pd metal occurred after prolonged reaction. Therefore the acyl products were characterised in solution only by ^{31}P and ^{13}C NMR and IR spectroscopy.

The CO insertion reactions (Scheme 4) are not very stereospecific since they have given mixtures of geometric isomers of the acyl complexes in ratios that are quite different from the alkyl complex precursors 1 : 40 → 1 : 4 for the complexes of **L$_{3b}$** and 25 : 1 → 9 : 1 for the complexes of **L$_{3c}$**. The mechanism for the CO insertion reaction proposed in Scheme 5 is based on literature precedent[7,8,16,17] and predicts inversion of stereochemistry at Pd. However, it is likely that the insertion reaction is under thermodynamic control because of equilibration of the acyl products; equilibration of this type has been shown to occur rapidly in acylpalladium *o*-diphosphinoxylene complexes.[17]

Addition of 1 equivalent of MeOH to a CH_2Cl_2 solution of a **7b**/**8b** mixture gave quantitative formation of $CH_3{}^{13}COOMe$ (δ_c 176.6 ppm) within the 3 min required to acquire the NMR spectrum. By contrast, a **7c**/**8c** mixture under similar conditions reacted slowly with MeOH even upon addition of a 5-fold excess. This contrast in the kinetics of the methanolysis of the complexes of **L$_{3b}$** and **L$_{3c}$** matches the contrast in the catalytic performance of these two ligands. A plausible mechanism for the methanolysis involves MeOH displacement of the Cl ligand, loss of a proton and the subsequent reductive elimination of the ester. The fact that the major isomers have different geometries (**8b** and **7c**) might be significant although it is likely that equilibration with the minor isomers would be rapid.[17] It is likely that the reductive elimination of the ester would be promoted by adjacent bulky groups and the two very bulky P-donors of ligand **L$_{3b}$** thus facilitate the methanolysis. In the catalytic system, no halide ligands are present but the methanolysis step



Scheme 5

has been proposed to be rate-limiting[6,16] and therefore similar steric-promotion factors are likely to be key to the success of the catalyst.

Conclusions

The homogeneous catalytic performance of palladium complexes derived from ligands of the type *o*-$C_6H_4(CH_2PR_2)(PR'_2)$ for the hydromethoxycarbonylation of ethene is a sensitive function of the P-substituents. Some of the *o*-diphosphinotoluenes reported here produce catalysts that are the most active so far

reported, outstripping the commercialised Lucite catalyst based on *o*-$C_6H_4(CH_2P^tBu_2)_2$ in terms of relative rate by a factor of up to 3.8. On the other hand, complexes of some *o*-diphosphinotoluenes showed zero activity. A comparative study of the coordination chemistry of analogous *o*-diphosphinotoluenes and *o*-diphosphinoxylenes with Pd and Pt support the hypothesis that the smaller bite angle of *o*-diphosphinotoluenes can switch off the catalysis, perhaps by reducing the facility of intramolecular reactions such as migratory insertions or reductive eliminations. This negative effect of the smaller bite angle of *o*-diphosphinotoluene is counteracted by the presence of very bulky P^tBu_2 or PCg donors which not only restore the catalytic function but indeed lead to catalysts which surpass their *o*-diphosphinoxylene analogues.

Experimental

Unless otherwise stated, all reactions were carried out under a dry nitrogen atmosphere using standard Schlenk-line techniques. Dry N_2-saturated solvents were collected from a Grubbs system[18] in flame and vacuum-dried glassware. MeOH was dried over 3 Å molecular sieves, pentane was dried over 4 Å molecular sieves and both were deoxygenated by N_2 saturation. The complexes $[PtCl_2(cod)]$,[19] $[PtCl(CH_3)(cod)]$,[20] and $[PdCl(CH_3)(cod)]$[21] were prepared by literature methods. $^tBu_2PH$ in THF was obtained from JCI USA Inc. and $^tBu_2PH(BH_3)$ from Lucite International. CgPH and $CgPH(BH_3)$ were obtained as previously described.[13] All phosphines were stored under nitrogen at room temperature. All other reagents were used as received from Aldrich, Strem or Lancaster. NMR spectra were recorded on a Jeol Delta 270, Jeol Eclipse 300, Jeol Eclipse 400, Varian 400, Varian 500, or Lambda 300. Infrared spectroscopy was carried out on a Perkin Elmer 1600 Series FTIR. Mass spectra were recorded on a MD800 by the Mass Spectrometry Service, University of Bristol. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

Preparation of *o*-$BrC_6H_4CH_2P^tBu_2$ (I)[22]

1-Bromo-2-(bromomethyl)benzene (3.39 g, 13.6 mmol) was placed in a two-necked round-bottomed flask equipped with a condenser and dissolved in MeOH (20 mL). $^tBu_2PH$ (1.99 g, 2.52 mL, 13.6 mmol) was added dropwise to the solution at room temperature. The reaction mixture was heated to reflux and stirred overnight at that temperature. Then, the solution was cooled to room temperature and NEt_3 (1.38 g, 1.89 mL, 13.6 mmol) was added dropwise. The solution was stirred for 1 h and then the volatiles were removed under reduced pressure and the crude product was redissolved in pentane. The solution was filtered *via* canula and the solvent was removed under reduced pressure affording a colourless oil (3.95 g, 92%). $^{31}P\{^1H\}$ NMR (121 MHz, C_5H_{12}): δ 33.5 (s).

Preparation of *o*-$BrC_6H_4CH_2PCg$ (J)

$CgPH(BH_3)$ (7.75 g, 34.0 mmol) was dissolved in THF (100 mL). The solution was cooled to −78 °C and ^nBuLi (2.5M in hexanes, 13.6 mL, 34.0 mmol) was added. This solution was then immediately added to a solution of 2-bromobenzylbromide (8.50 g, 34.0 mmol) at −78 °C. The mixture was then stirred at −78 °C for 30 min before warming it to room temperature and stirring it for 16 h. The solvent was then removed at reduced pressure and the residue suspended in toluene (150 mL). Water (40 mL, N_2-saturated) was added followed by diethylamine (20 mL, N_2-saturated). The organic phase was then cannula transferred into a Schlenk tube and the aqueous residues washed with toluene (50 mL). The toluene extracts were combined and the solvent removed under reduced pressure to give an off-white solid (13.5 g, 96%, 95% pure). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −26.2 (s).

Preparation of *o*-$C_6H_4(CH_2P^tBu_2)(P^tBu_2)$ (L_{3a})

In a 500 mL Schlenk flask, magnesium ribbon (1.89 g, 78.0 mmol) was suspended in THF (150 mL) and iodine (4 crystals) and 1,2-dibromoethane (8 drops) were then added and the suspension was stirred at room temperature for 1 h. To this suspension was then added dropwise a solution **I** (12.3 g, 39.0 mmol) in THF (50 mL). The resultant colourless solution was then heated to reflux for 3 h. This gave a brown/orange solution with some unreacted magnesium. The Grignard solution was then added slowly to a 500 mL Schlenk flask containing $^tBu_2PCl$ (7.04 g, 39.0 mmol), CuI (0.717 g, 3.76 mmol) and LiBr (0.650 g, 7.49 mmol) and THF (100 mL) at 0 °C. The resultant solution was allowed to warm up to room temperature and stirred overnight. The solvent was then removed under reduced pressure and the residue suspended in diethyl ether (300 mL). Water (100 mL, N_2-saturated) was then added to give a biphasic solution. The upper (organic) phase was cannula transferred into a Schlenk tube and the aqueous residues washed with ether (200 mL). The ether extracts were then combined and then dried over Na_2SO_4. The ether solution was then cannula transferred into a Schlenk flask and then the solvent removed under reduced pressure to give an off-white solid crude product (14.2 g). The solid was suspended in methanol (50 mL) and heated to boiling which produced a colourless solution. The solution was then cooled to room temperature to give a white crystalline solid. The methanol solution was then removed by cannula and the white crystalline solid dried under vacuum and then manipulated in a glovebox (6.8 g, 46%, 95% pure). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 35.0 (d, J(PP) = 3 Hz), 14.0 (d, J(PP) = 3 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.85–7.81 (1 H, m), 7.68 (1 H, d, J(HH) = 7.7 Hz), 7.28–7.24 (1 H, m), 7.13–7.10 (1 H, m), 3.38 (CH_2, dd, J(HP) = 5.6 Hz, J(HP) = 3.8 Hz), 1.41 (3 H, d, J(HP) = 13.9 Hz), 1.21 (CH_3, 18 H, d, J(HP) = 11.6 Hz), 1.15 (CH_3, 18 H, d, J(HP) = 10.6 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 149.7 (*ipso C*, dd, J(CP) = 26.5 Hz, J(CP) = 12.5 Hz), 136.7 (*ipso C*, dd, J(CP) = 24.1 Hz, J(CP) = 3.1 Hz), 135.9 (d, J(CP) = 3.1 Hz), 131.4 (dd, J(CP) = 20.2 Hz, J(CP) = 4.7 Hz), 128.7 (s), 124.4 (d, J(CP) = 2.3 Hz), 33.2 ($C(CH_3)_3$, d, J(CP) = 23.7 Hz), 32.6 ($C(CH_3)_3$, d, J(CP) = 22.6 Hz), 31.1 ($PhC(CH_3)_3$, d, J(CP) = 14.8 Hz), 30.4 ($CH_2C(CH_3)_3$, d, J(CP) = 13.6 Hz), 30.4 ($CH_2C(CH_3)_3$, d, J(CP) = 13.2 Hz), 27.9 (CH_2, dd, J(CP) = 30.4 Hz, J(CP) = 21.8 Hz). Accurate mass spectrum: M_r = 381.2845 $(M + H)^+$ (calcd for $C_{23}H_{43}P_2$ 381.2835).

Preparation of *o*-$C_6H_4(CH_2P^tBu_2)(PCg)$ (L_{3b})

2-bromobenzylbromide (10.0 g, 40.0 mmol) was dissolved in MeCN (50 mL). To this solution was added $^tBu_2PH$ (8.0 mL, 43 mmol). The resultant solution was then stirred for 16 h. The solvent was then removed under reduced pressure to give a white solid. This was suspended in toluene (40 mL) and water (40 mL, N_2-saturated) was added. This was followed by diethylamine (10 mL) to give a white suspension. Ethanol (10 mL) was added and the resultant biphasic mixture separated. The upper (organic) phase was cannula transferred into a Schlenk tube and the solvent removed under reduced pressure to give a colourless oil (10.6 g). To this oil was added DABCO (9.52 g, 84.9 mmol), CgPH (8.25 g, 38.2 mmol) and $[Pd(PPh_3)_4]$ (1.0 g, 0.87 mmol). To this suspension was added *o*-xylene (50 mL, N_2-saturated) and the resultant suspension was then heated to 140 °C for 16 h. The orange suspension was then allowed to cool to 100 °C and was filtered at this temperature. The solution was reduced to 10 mL under reduced pressure and then methanol (40 mL) was added. The resultant yellow/orange oily material was heated to 60 °C for 20 min before cooling to room temperature. This resulted in the formation of a yellow crystalline material which was then allowed to stand for 16 h. The solid was then isolated by filtration and the dried under vacuum. The free flowing yellow solid product (7.5 g, 39%) was manipulated in a glove-box. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 35.8 (s), −41.6 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 8.46 (1 H, m), 8.12 (1 H, m), 7.15 (1 H, m), 7.05 (1 H, m), 4.35 (1H, CH_2Ar, ddd, *J*(HH) = 18.6 Hz, *J*(HP) = 9.0, 4.0 Hz), 2.57 (1H, d, CH_2Ar, *J*(HH) = 18.6 Hz), 2.00 (1H, m, CH_2), 1.67 (3H, m, CH_2), 1.47 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.31 (3H, s, CH_3), 1.18 (9H, d, CCH_3)$_3$, *J*(HP) = 6.0 Hz), 1.15 (9H, d, CCH_3)$_3$, *J*(HP) = 6.0 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.2 (dd, *J*(CP) = 24.0, 12.0 Hz), 133.5 (d, *J*(CP) = 3.0 Hz), 132.8 (dd, *J*(CP) = 26.2, 3.0 Hz), 131.4 (dd, *J*(CP) = 18.7, 5.1 Hz), 96.8 (s), 96.1 (s), 74.5 (d, *J*(CP) = 15.5 Hz), 73.5 (d, *J*(CP) = 37.5 Hz), 46.1 (d, *J*(CP) = 26.2 Hz), 36.2 (s), 33.3 (s), 32.9 (s), 31.3 (s), 31.0 (s), 30.1 (d, *J*(CP) = 14.8 Hz), 29.9 (d, *J*(CP) = 15.0 Hz), 27.2 (dd, *J*(CP) = 29.7, 22.5 Hz), 26.4 (d, *J*(CP) = 11.2 Hz). Elemental analysis (calcd for $C_{25}H_{38}O_3P_2$): C: 66.64 (66.63), H: 9.34 (8.95).

Preparation of *o*-$C_6H_4(CH_2P^tBu_2)(PPh_2)$ (L_{3c})

o-$BrC_6H_4CH_2P^tBu_2$ (1.00 g, 4.40 mmol) was placed in a two-necked round bottomed flask and dissolved in Et_2O (10 mL). A 1.6 M solution of ^{n}BuLi (2.75 mL, 4.40 mmol) in hexane was added dropwise over 5 min at −78 °C and stirred for 15 min at room temperature before Ph_2PCl (0.82 mL, 4.40 mmol) was added over 5 min at −78 °C. A white precipitate was observed and the orange solution was stirred overnight at room temperature. Water (10 mL) was added and the organic layer was separated, dried over $MgSO_4$ and filtered *via* canula. The volatiles were removed under reduced pressure and the residue was recrystallised from the minimum amount of boiling MeOH affording a white solid (0.45 g, 24%). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 32.3 (*P*$^tBu_2$, d, *J*(PP) = 4 Hz), −14.8 (*P*Ph_2, d, *J*(PP) = 4 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.91–7.87 (1 H, m), 7.39–7.29 (11 H, m), 7.08 (1 H, d, *J*(HH) = 7.5 Hz), 6.88 (1 H, dd, *J*(HH) = 4.2 Hz, *J*(HH) = 1.5 Hz), 3.06 (CH_2, 2 H, t, *J*(HP) = 3.7 Hz), 1.13 (CH_3, 18 H, d, *J*(HP) = 11.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 146.6 (*ipso* CCH_2PPh_2, dd, *J*(CP) = 23.8 Hz, *J*(CP) = 13.1 Hz), 137.5 (*ipso C*, d, *J*(CP) = 10.8 Hz), 136.9 (*ipso* C$CH_2P^tBu_2$, dd, *J*(CP) = 10.0 Hz, *J*(CP) = 3.1 Hz), 134.6 (d, *J*(CP) = 20.0 Hz), 133.8 (s), 131.2 (s), 131.2 (*C*H, s), 131.0 (s), 130.9 (s), 126.2 (d, *J*(CP) = 1.6 Hz), 32.5 (*C*(CH$_3$)$_3$, d, *J*(CP) = 22.3 Hz), 30.2 (C(*C*H$_3$)$_3$, d, *J*(CP) = 13.5 Hz), 30.1 (C(*C*H$_3$)$_3$, d, *J*(CP) = 13.5 Hz), 27.4 (*C*H$_2$, d, *J*(CP) = 23.8 Hz). Accurate mass spectrum: M_r = 421.2209 $(M + H)^+$ (calcd for $C_{27}H_{35}P_2$ 421.2209).

Preparation of *o*-$C_6H_4(CH_2P^tBu_2)(P\{o\text{-}CH_3C_6H_4\}_2)$ (L_{3d})

o-$BrC_6H_4CH_2P^tBu_2$ (0.76 g, 3.30 mmol) was placed in a two-necked round bottomed flask and dissolved in Et_2O (10 mL). A 1.6 M solution of ^{n}BuLi (2.00 mL, 3.30 mmol) in hexane was added dropwise over 5 min at −78 °C and stirred for 20 min at room temperature before a solution of (*o*-tolyl)$_2$PCl (0.83 g, 3.30 mmol) in Et_2O (3 mL) was added over 5 min at −78 °C. A white precipitate was observed and the yellow solution was stirred overnight at room temperature. Water (10 mL) was added and the organic layer was separated, dried over $MgSO_4$ and filtered *via* canula. The volatiles were removed under reduced pressure and the residue was recrystallised from the minimum amount of boiling MeOH affording a white solid (0.19 g, 13%). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 30.6 (*P*$^tBu_2$, d, *J*(PP) = 7 Hz), −30.5 (*P*Ar_2, d, *J*(PP) = 7 Hz). ^1H NMR (300 MHz, C_6D_6): δ 8.24 (1 H, quintuplet, *J*(HH) = 3.8 Hz), 7.28–6.94 (11 H, m), 3.27 (CH_2, 2 H, br s), 2.58 (CH_3Ph, 6 H, d, *J*(HP) = 0.9 Hz), 1.19 (C(CH_3)$_3$, 18 H, d, *J*(HP) = 10.8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 143.3 (d, *J*(CP) = 26.5 Hz), 135.6 (d, *J*(CP) = 10.7 Hz), 134.3 (s), 133.8 (s), 130.9 (d, *J*(CP) = 4.9 Hz), 129.5 (s), 127.0 (d, *J*(CP) = 0.6 Hz), 126.7 (d, *J*(CP) = 1.4 Hz), 32.4 (*C*(CH$_3$)$_3$, br d, *J*(CP) = 23.4 Hz), 30.3 (C(*C*H$_3$)$_3$, d, *J*(CP) = 13.9 Hz), 30.2 (C(*C*H$_3$)$_3$, d, *J*(CP) = 13.9 Hz), 27.4 (*C*H$_3$Ph, d, *J*(CP) = 1.2 Hz), 21.8 (*C*H$_2$, d, *J*(CP) = 21.9 Hz). Accurate mass spectrum: M_r = 449.2536 $(M + H)^+$ (calcd for $C_{29}H_{39}P_2$ 449.2522).

Preparation of *o*-$C_6H_4(CH_2P^tBu_2)(P\{o\text{-}CH_3OC_6H_4\}_2)$ (L_{3e})

Into a 500 mL Schlenk flask was added magnesium ribbon (3.30 g, 136 mmol). This was suspended in THF (100 mL) and iodine (4 crystals) was then added. The suspension was then heated in a hot water bath for 20 min. To this suspension was added a solution of **I** (21.5 g, 68.1 mmol) in THF (50 mL) dropwise over 1 h. The resultant colourless solution was then heated to reflux for 4 h to give a grey suspension which was then cooled to room temperature and stirred at room temperature for 3 d to give a brown/orange solution with some unreacted magnesium. This mixture was then refluxed for 2 h before being cooled to room temperature. The Grignard solution was then added slowly to a 500 mL Schlenk flask containing the di-*o*-methoxyphenylchlorophosphine (19.1 g, 68.1 mmol), CuI (1.3 g, 6.8 mmol), LiBr (1.1 g, 12 mmol) and THF (150 mL) at 0 °C. The resultant solution was allowed to warm up to room temperature and stirred for 16 h. The solvent was then removed

under reduced pressure and the residue suspended in diethyl ether (300 mL). Water (100 mL, N_2-saturated) was then added to give a biphasic mixture. The upper (organic) phase was cannula transferred into a Schlenk tube and the aqueous residues washed with ether (200 mL). The ether extracts were then combined and dried over Na_2SO_4. The ether solution was then cannula transferred into a Schlenk flask and the solvent removed under reduced pressure to give the yellow/white solid crude product. The solid was suspended in methanol (100 mL) and heated to reflux give a cloudy solution which was then cooled to room temperature and the methanol solution was removed by cannula. The white crystalline solid product (6.8 g, 20%, 95% pure) was then dried under vacuum and manipulated in a glovebox. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 33.7 (P^tBu_2, d, J(PP) = 3 Hz), −37.8 (PAr_2, d, J(PP) = 3 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.85–7.81 (1 H, m), 7.35 (2 H, t, J(HH) = 8.3 Hz), 7.30–7.26 (1 H, m), 7.01 (1 H, t, J(HH) = 7.4 Hz), 6.94 (2 H, dd, J(HH) = 7.8 Hz, J(HH) = 4.9 Hz), 6.86 (2 H, t, J(HH) = 7.3 Hz), 6.79 (1 H, dd, J(HH) = 7.1 Hz, J(HH) = 3.4 Hz), 6.69–6.66 (2 H, m), 3.73 (OCH_3, 6 H, s), 3.09 (CH_2, 2 H, br s), 1.15 ($C(CH_3)_3$, 18 H, d, J(HP) = 10.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 162.1 (d, J(CP) = 17.1 Hz), 146.8 (dd, J(CP) = 25.7 Hz, J(CP) = 12.5 Hz), 136.1 (d, J(CP) = 10.1 Hz), 134.6 (s), 133.6 (s), 130.8 (dd, J(CP) = 20.2 Hz, J(CP) = 3.9 Hz), 130.6 (s), 130.1 (d, J(CP) = 8.6 Hz), 128.6 (s), 127.5 (s), 125.9 (d, J(CP) = 1.6 Hz), 125.7 (d, J(CP) = 2.3 Hz), 125.3 (d, J(CP) = 13.2 Hz), 121.6 (s), 121.3 (s), 120.7 (s), 110.9 (s), 100.6 (s), 56.1 (OCH_3), 32.5 ($C(CH_3)_3$, d, J(CP) = 22.6 Hz), 30.2 ($C(CH_3)_3$, d, J(CP) = 13.2 Hz), 30.1 ($C(CH_3)_3$, d, J(CP) = 13.2 Hz), 26.6 (CH_2, dd, J(CP) = 26.5 Hz, J(CP) = 23.4 Hz). Accurate mass spectrum: M_r = 497.2386 $(M + O + H)^+$ (calcd for $C_{29}H_{39}O_3P_2$ 497.2369).

Preparation of *o*-$C_6H_4(CH_2PCg)(PCg)$ (L_{3f})

The intermediate **J** (13.5 g, 35.1 mmol) was dissolved in toluene (60 mL) and to this solution was added DABCO (9.93 g, 88.5 mmol), CgPH (7.57 g, 35.1 mmol) and $[Pd(PPh_3)_4]$ (1.0 g, 0.87 mmol). The resultant pale yellow solution was then heated to 140 °C for 16 h to give an orange/yellow suspension. The suspension was allowed to cool to 100 °C and was then filtered through a frit containing celite to give a red/orange solution which was concentrated under reduced pressure to 10 mL. Methanol (40 mL) was added and the resulting solution put aside for 16 h which led to the formation of a yellow/orange solid. The solution was cannula transferred into a Schlenk tube and the solvent removed under reduced pressure to give the crude solid product. The solid was purified by dissolving in boiling methanol (40 mL) and allowing the solution to cool to room temperature before placing in a freezer (−10 °C) overnight. The resulting yellow/orange crystalline material was isolated by cannula transfer of the methanol mother liquor followed by drying the solid product (2.6 g, 14%, 95% pure) under vacuum and manipulating it in a glovebox. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ −21.4 (CH_2PCg, d, J(PP) = 24 Hz), −41.9 (PCg, d, J(PP) = 24 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.18 (1 H, dt, J(HH) = 7.6 Hz, J(HH) = 1.8 Hz), 7.52–7.49 (1 H, m), 7.30 (1 H, td, J(HH) = 7.6 Hz, J(HH) = 1.5 Hz), 7.23–7.20 (1 H, m), 3.63 (CHH, 1 H, ddd, J(HH) = 14.6 Hz, J(HP) = 5.4 Hz, J(HP) = 4.7 Hz), 2.95 (CHH, 1 H, d, J(HH) = 14.6 Hz), 2.14 (CHH, 1 H, dd, J(HH) = 13.5 Hz, J(HH) = 2.5 Hz), 2.06 (CHH, 1 H, dd, J(HH) = 13.5 Hz, J(HH) = 3.9 Hz), 1.44–1.30 (CH_3, 18 H, m), 1.21 (CH_3, 3 H, d, J(HP) = 12.2 Hz), 1.11 (CH_3, 3 H, d, J(HP) = 12.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 146.7 (dd, J(CP) = 26.1 Hz, J(CP) = 9.3 Hz), 134.7 (dd, J(CP) = 2.7 Hz, J(CP) = 1.2 Hz), 133.1 (dd, J(CP) = 28.8 Hz, J(CP) = 2.7 Hz), 131.3 (dd, J(CP) = 11.3 Hz, J(CP) = 5.1 Hz), 129.9 (s), 126.6 (d, J(CP) = 2.3 Hz), 97.4 (CO_2CH_3, d, J(CP) = 0.8 Hz), 97.0 (CO_2CH_3, d, J(CP) = 0.8 Hz), 96.6 (CO_2CH_3, s), 96.5 (CO_2CH_3, s), 74.8 ($COCH_3$, dd, J(CP) = 8.2 Hz, J(CP) = 1.2 Hz), 74.9 ($COCH_3$, J(CP) = 24.1 Hz), 73.7 ($COCH_3$, d, J(CP) = 12.1 Hz), 73.1 ($COCH_3$, dd, J(CP) = 23.7 Hz, J(CP) = 2.7 Hz), 46.6 (CH_2, d, J(CP) = 19.1 Hz), 45.4 (CH_2, d, J(CP) = 15.6 Hz), 38.4 (CH_2, dd, J(CP) = 6.2 Hz, J(CP) = 1.6 Hz), 36.5 (CH_2, d, J(CP) = 1.6 Hz), 29.2 (CH_3, d, J(CP) = 4.7 Hz), 29.0 (CH_3, d, J(CP) = 4.7 Hz), 28.4 (CH_3, s), 28.2 (CH_3, s), 27.5 (CH_2P, dd, J(CP) = 26.1 Hz, J(CP) = 24.1 Hz), 27.5 (CH_3, s), 27.4 (CH_3, s), 27.0 (CH_3, s), 26.9 (CH_3, s). Accurate mass spectrum: M_r = 521.2239 $(M + H)^+$ (calcd for $C_{27}H_{39}O_6P_2$ 521.2216).

Carbonylation catalysis

$Pd(OAc)_2$ (22 mg, 0.10 mmol) and ligand $\mathbf{L_{3a–f}}$ (0.50 mmol) were dissolved in methanol (300 mL) and the solution was stirred for 30 min. The addition of methane sulfonic acid (2.92 mL, 45 mmol) completed the preparation of the catalyst solution. The catalyst solution was added to the pre-evacuated autoclave and heated to 100 °C, at which point the pressure generated by the solvent was 2.3 bar. The autoclave was then pressurised to 12.3 bar with CO : ethene (1 : 1) from a 10 L reservoir at higher pressure. A regulatory valve ensured that the pressure of the autoclave was maintained throughout the reaction at 12.3 bar through continual injection of gas from the reservoir. The pressure of the reservoir and the reactor temperature were logged throughout the reaction period of 3 h. The amount of product at any point in the reaction could be calculated from the drop in reservoir pressure by assuming ideal gas behaviour and 100% selectivity for methyl propionate, allowing reaction TON with the particular ligand to be estimated. After 3 h, the autoclave was cooled and vented. The reaction solution was collected from the base of the vessel and immediately placed under a N_2 atmosphere. The solution was weighed so that the TON could be calculated.

Preparation of $[PtCl_2(L_{1a})]$ (1)

A solution of $\mathbf{L_{1a}}$ (72 mg, 0.18 mmol) in CH_2Cl_2 (4 mL) was added to a stirred solution of $[PtCl_2(cod)]$ (65 mg, 0.17 mmol) in CH_2Cl_2 (4 mL) and the mixture was stirred for 96 h. The volatiles were then removed under reduced pressure, the residue washed with pentane and toluene respectively, and dried under reduced pressure to afford a white solid (105 mg, 83%). Crystals suitable for X-ray analysis were grown by slow vapour diffusion of pentane into a solution of the product in $CHCl_3$. $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2): δ 11.4 ($CH_2P^tBu_2$, s, J(PPt) =

3646 Hz). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.39–7.37 (2H, m), 7.23–7.21 (2H, m), 3.61 (CH_2 4H, br), 1.54 (CH_3, 36H, br, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 135.2 (s), 132.7 (s), 127.3 (s), 100.0 (CH_2, s), 32.0 (CCH_3, s), 30.9 (CCH_3, s). Accurate mass spectrum: M_r = 624.2256 $(M - Cl)^+$ (calcd for $C_{23}H_{42}P_2PtCl$ 624.2255). Elemental analysis (calcd for $C_{24}H_{44}Cl_2P_2Pt.2CHCl_3$): C: 35.44 (34.72) H: 5.15 (5.16).

Preparation of [$PtCl_2(L_{3a})$] (2a)

A solution of **L_{3a}** (79 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) was added to a stirred solution of [$PtCl_2$(cod)] (73 mg, 0.20 mmol) in CH_2Cl_2 (4 mL) and the mixture was stirred for 48 h. The volatiles were then removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure to afford a yellow solid (112 mg, 90%). Crystals suitable for X-ray analysis were grown by slow vapour diffusion of hexane into a solution of the product in CH_2Cl_2. $^{31}P\{^{1}H\}$ NMR (202.4 MHz, $CDCl_3$): δ 33.4 ($CH_2P^tBu_2$, d, J(PPt) = 3656 Hz, J(PP) = 15 Hz), 31.5 (P^tBu_2, d, J(PPt) = 3706 Hz, J(PP) = 15 Hz). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11–8.07 (1 H, m), 7.46–7.44 (2 H, m), 7.30–7.27 (1 H, m), 3.60 (CH_2, 2 H, d, J(HP) = 12.1 Hz. J(HPt) = 60.8 Hz), 1.65 (CH_3, 18 H, d, J(HP) = 14.9 Hz), 1.47 (CH_3, 18 H, d, J(HP) = 14.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 141.6 (dd, J(CP) = 9.7 Hz, J(CP) = 3.9 Hz), 134.5 (d, J(CP) = 1.8 Hz), 133.7 (d, J(CP) = 6.5 Hz), 1.33.6 (d J(CP) = 6.7 Hz), 131.5 (d, J(CP) = 2.3 Hz), 126.7 (dd, J(CP) = 6.9 Hz, J(CP) = 1.8 Hz), 40.6 ($C(CH_3)_3$, d, J(CP) = 25.5 Hz), 39.2 ($C(CH_3)_3$, d, J(CP) = 26.3 Hz), 33.3 ($C(CH_3)_3$, d, J(CP) = 2.6 Hz), 30.9 ($C(CH_3)_3$, d, J(CP) = 1.6 Hz), 27.8 (CH_2, dd, J(CP) = 26.9 Hz, J(CP) = 9.4 Hz). Accurate mass spectrum: M_r = 610.2114 $(M - Cl)^+$ (calcd for $C_{23}H_{42}P_2PtCl$ 610.2093). Elemental analysis (calcd for $C_{23}H_{42}Cl_2P_2Pt.CH_2Cl_2$): C: 38.86 (39.41), H: 5.61 (6.06).

Preparation of [$PtCl_2(L_{3b})$] (2b)

A solution of **L_{3a}** (126 mg, 0.280 mmol) in CH_2Cl_2 (2 mL) was added dropwise over 30 s to a stirred solution of [$PtCl_2$(cod)] (105 mg, 0.280 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for 1 h after which the volatiles were removed under reduced pressure and then Et_2O (60 mL) added to the residue to give a white solid product (174 mg, 87%) which was then filtered off, was washed with Et_2O and dried under reduced pressure. Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a solution of the product in CH_2Cl_2. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 46.9 (P^tBu_2, d, J(PPt) = 3425 Hz, J(PP) = 18 Hz), −12.4 (PCg, d, J(PPt) = 3698 Hz, J(PP) = 18 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75–7.36 (4 H, m), 4.95 (CH_2Ar, dd, 1H, J(HH) = 17.0 Hz J(HP) = 2.0 Hz), 3.98 (CH_2Ar, m, 1H), 3.52 (CH_2Ar, dd, 1H, J(HH) = 17.0 Hz J(HP) = 12.1 Hz), 1.94 (CH_3, 3H, d, J(HP) = 16.0 Hz), 1.70 ($C(CH_3)_3$, 9H, d, J(HP) = 16.0 Hz), 1.59 (CH_3, 3H, d, J(HP) = 16.0 Hz), 1.44 (CH_3, 3H, s), 1.31 (CH_3, 3H, s), 1.13 ($C(CH_3)_3$, 9H, d, J(HP) = 16.0 Hz). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 140.4 (m), 134.3 (m), 128.4 (d, J(CP) = 15 Hz), 124.5 (d, J(CP) = 15 Hz), 123.9 (d, J(CP) = 15 Hz), 97.1 (s), 96.6 (s), 77.5 (d, J(CP) = 37.5 Hz), 75.5 (d, J(CP) = 37.5 Hz), 53.5 (s), 43.5 (d, J(CP) = 7.5 Hz), 39.8 (d, J(CP) = 15 Hz), 39.6 (d, J(CP) = 7.5 Hz), 32.2 (s), 29.9 (s), 27.6 (s), 26.9 (s), 25.3 (d, J(CP) = 7.5 Hz). EI mass spectrum: M_r = 681 $(M - Cl)^+$, 646 $(M - 2Cl)^+$. Elemental analysis (calcd for $C_{25}H_{38}Cl_2O_3P_2Pt$), C: 41.03 (41.91), H: 5.52 (5.63).

Preparation of [$PtCl(CH_3)(L_{3a})$] (3a/4a)

A solution of **L_{3a}** (74 mg, 0.19 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 30 s to a stirred solution of [$PtCl(CH_3)$-(cod)] (64 mg, 0.18 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred overnight. The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording a white solid (91 mg, 81%). Crystals suitable for X-ray analysis were grown by slow vapour diffusion of hexane into a solution of the product in CH_2Cl_2. The product was obtained as a mixture of two isomers in a 1 : 100 ratio (**3a** : **4a**) at room temperature. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): For **3a**: δ 40.1 ($CH_2P^tBu_2$, d, J(PPt) = 4328 Hz, J(PP) = 17 Hz), 35.2 (P^tBu_2, d, J(PPt) = 1820 Hz, J(PP) = 17 Hz). For **4a**: δ 36.4 (P^tBu_2, d, J(PPt) = 4458 Hz, J(PP) = 15 Hz), 36.1 ($CH_2P^tBu_2$, d, J(PPt) = 1755 Hz, J(PP) = 15 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): For **3a**: δ 7.82–7.79 (1 H, m), 7.42–7.16 (3 H, m), 2.53–2.21 (CH_2, 2 H, m), 1.38 (CH_3, 18 H, d, J(HP) = 13.6 Hz), 1.24 (CH_3, 18 H, d, J(HP) = 12.7 Hz), 0.88 (CH_3-Pt, br t, J(HPt) not discernible, J(HP*trans*) = J(HP*cis*) = 6.2 Hz). For **4a**: δ 8.04–8.01 (1 H, m), 7.38–7.36 (2 H, m), 7.27–7.22 (1 H, m), 2.53–2.21 (CH_2, 2 H, m), 1.51 (CH_3, 18 H, d, J(HP) = 13.1 Hz), 1.31 (CH_3, 18 H, d, J(HP) = 13.2 Hz), 0.99 (CH_3-Pt, 3 H, br d, J(HPt) = 49.9 Hz, J(HP*trans*) = 4.9 Hz, J(HP*cis*) not resolved). $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2): δ 143.6 (dd, J(CP) = 14.0 Hz, J(CP) = 3.9 Hz), 136.8 (d, J(CP) = 1.6 Hz), 133.9 (s), 130.8 (d, J(CP) = 2.3 Hz), 127.5 (dd, J(CP) = 22.6 Hz, J(CP) = 3.9 Hz), 126.6 (dd, J(CP) = 4.7 Hz, J(CP) = 1.6 Hz), 39.6 ($C(CH_3)_3$, d, J(CP) = 13.2 Hz), 39.0 ($C(CH_3)_3$, d, J(CP) = 26.5 Hz), 38.9 ($C(CH_3)_3$, d, J(CP) = 26.5 Hz), 32.9 ($C(CH_3)_3$, d, J(CP) = 4.7 Hz), 31.1 ($C(CH_3)_3$, d, J(CP) = 2.3 Hz), 28.9 (CH_2, J(CP) = 26.5 Hz, J(CP) = 14.0 Hz). Accurate mass spectrum: M_r = 590.2661 $(M - Cl)^+$ (calcd for $C_{24}H_{45}P_2Pt$ 590.2639). Elemental analysis (calcd for $C_{24}H_{45}ClP_2Pt$): C: 45.58 (46.04), H: 7.01 (7.24).

Preparation of [$PtCl(CH_3)(L_{3b})$] (3b/4b)

A solution of **L_{3b}** (101 mg, 0.23 mmol) in toluene (1.5 mL) was added dropwise over 30 s to a stirred solution of [$PtCl(CH_3)$-(cod)] (82 mg, 0.23 mmol) in toluene (1.5 mL). The mixture was stirred overnight. The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording an off-white solid (46 mg, 29%). Crystals suitable for X-ray analysis were grown by slow vapour diffusion of hexane into a solution of the product in CH_2Cl_2. The product was obtained as a mixture of two isomers in a 1 : 10 ratio (**3b** : **4b**). $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2): For **3b**: δ 50.2 (P^tBu_2, d, J(PPt) not discernible, J(PP) = 19 Hz), −8.2 (PCg, d, J(PPt) not discernible, J(PP) = 19 Hz). For **4b**: δ 47.5 (P^tBu_2, d, J(PPt) = 4252 Hz, J(PP) = 14 Hz), −5.5 (PCg, d, J(PPt) = 1539 Hz, J(PP) = 14 Hz). ^{1}H NMR (400 MHz,

CD_2Cl_2): δ 8.66–8.62 (1 H, m), 7.45–7.37 (2 H, m), 7.32–7.29 (1 H, m), 4.75 (CH*H*, 1 H, dd, *J*(HH) = 13.8 Hz, *J*(HP) = 3.1 Hz), 3.99 (C*H*HP, 1 H, td, *J*(HPt) = 89.9 Hz, *J*(HH) = 14.3 Hz, *J*(HP) = 5.7 Hz), 3.41 (CH*H*P, 1 H, dd, *J*(HPt) = 44.9 Hz, *J*(HH) = 14.3 Hz, *J*(HP) = 9.1 Hz), 1.79 (CH_3, 3 H, d, *J*(HP) = 13.8 Hz), 1.70 (C*H*H, 1 H, dd, *J*(HH) = 22.9 Hz, *J*(HH) = 13.8 Hz), 1.63–1.55 (CH_2, 2 H, m), 1.51 ($C(CH_3)_3$, 9 H, d, *J*(HP) = 13.4 Hz), 1.37 (CH_3, 6 H, s), 1.28 (CH_3, 3 H, s), 1.04 (CH_3-Pt, 3 H, dd, *J*(HPt) = 53.3 Hz, *J*(HP*trans*) = 7.1 Hz, *J*(HP*cis*) = 2.9 Hz), 1.03 ($C(CH_3)_3$, 9 H, d, *J*(HP) = 13.9 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 155.9 (*ipso C*, s), 141.5 (*ipso C*, dd, *J*(CP) = 13.8 Hz, *J*(CP) = 3.8 Hz), 134.8 (*C*H, d, *J*(CP) = 1.9 Hz), 134.2 (*C*H, dd, *J*(CP) = 7.3 Hz, *J*(CP) = 5.4 Hz), 130.9 (*C*H, br s), 128.5 (*C*H, dd, *J*(CP) = 4.8 Hz, *J*(CP) = 2.1 Hz), 97.4 (CO_2CH_3, d, *J*(CP) = 0.8 Hz), 96.7 (CO_2CH_3, d, *J*(CP) = 1.2 Hz), 78.7 ($COCH_3$, dd, *J*(CP) = 10.6 Hz, *J*(CP) = 1.3 Hz), 74.9 ($COCH_3$, d, *J*(CP) = 19.2 Hz), 43.9 (CH_2, d, *J*(CP) = 6.2 Hz), 40.1 (CH_2, s), 39.1 ($C(CH_3)_3$, dd, *J*(CP) = 24.2 Hz, *J*(CP) = 0.8 Hz), 38.7 ($C(CH_3)_3$, dd, *J*(CP) = 29.6 Hz, *J*(CP) = 1.2 Hz), 31.9 ($C(CH_3)_3$, d, *J*(CP) = 2.3 Hz), 30.9 (CH_2P, dd, *J*(CP) = 24.2 Hz, *J*(CP) = 14.6 Hz), 30.3 ($C(CH_3)_3$, d, *J*(CP) = 2.3 Hz), 29.7 (CH_3, d, *J*(CP) = 10.0 Hz), 28.1 (CH_3, s), 27.6 (CH_3, s), 25.5 (CH_3, d, *J*(CP) = 5.8 Hz), 2.3 (CH_3-Pt, dd, *J*(CP*trans*) = 88.6 Hz, *J*(CP*cis*) = 7.9 Hz). Accurate mass spectrum: M_r = 660.2348 $(M - Cl)^+$ (calcd for $C_{26}H_{43}O_3P_2Pt$ 660.2330).

Preparation of [PtCl(CH_3)(L_{3c})] (3c/4c)

A solution of $\mathbf{L_{3c}}$ (66 mg, 0.16 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 30 s to a stirred solution of [PtCl(CH_3)(cod)] (55 mg, 0.16 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred overnight. The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording a white solid (46 mg, 54%). Crystals suitable for X-ray analysis were grown by slow vapour diffusion of hexane into a solution of the product in CH_2Cl_2. The product was obtained as a mixture of two isomers in a 20 : 1 ratio (**3c** : **4c**) at room temperature. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): For **3c**: δ 49.8 (P^tBu_2, d, *J*(PPt) = 1797 Hz, *J*(PP) = 21 Hz), −14.4 (PPh_2, d, *J*(PPt) = 4307 Hz, *J*(PP) = 21 Hz). For **4c**: δ 51.0 (P^tBu_2, d, *J*(PPt) not discernible, *J*(PP) = 21 Hz), −14.1 (PPh_2, d, *J*(PPt) not discernible, *J*(PP) = 21 Hz). ^1H NMR (270 MHz, CD_2Cl_2): For **3c**: δ 7.54–7.11 (13 H, m), 6.75–6.67 (1 H, m), 3.20–3.03 (CH_2, 2 H, br m), 1.29 ($C(CH_3)_3$, 18 H, d, *J*(HP) = 12.9 Hz), 0.28 (CH_3-Pt, 3 H, dd, *J*(HPt) = 53.6 Hz, *J*(HP*trans*) = 6.9 Hz, *J*(HP*cis*) = 4.3 Hz). For **4c**: δ Peaks obscured by **3c** signals, 0.99 (CH_3-Pt, 3 H, dd, *J*(HPt) not discernible, *J*(HP*trans*) = 7.4 Hz, *J*(HP*cis*) = 1.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 142.5 (d, *J*(CP) = 10.8 Hz), 135.0 (d, *J*(CP) = 16.1 Hz), 134.7 (d, *J*(CP) = 11.5 Hz), 133.1 (dd, *J*(CP) = 8.5 Hz, *J*(CP) = 4.6 Hz), 133.8 (d, *J*(CP) = 2.3 Hz), 129.1 (s), 128.9 (d, *J*(CP) = 11.5 Hz), 128.7 (d, *J*(CP) = 10.0 Hz), 127.7 (d, *J*(CP) = 8.5 Hz), 37.7 ($C(CH_3)_3$, d, *J*(CP) = 13.1 Hz), 30.4 ($C(CH_3)_3$, d, *J*(CP) = 3.8 Hz), 26.1 (CH_2, dd, *J*(CP) = 16.9 Hz, *J*(CP) = 10.0 Hz), 14.3 (CH_3-Pt, dd, *J*(CP*trans*) = 92.2 Hz, *J*(CP*cis*) = 5.4 Hz). Accurate mass spectrum: M_r = 630.2014 $(M - Cl)^+$ (calcd for $C_{28}H_{37}P_2Pt$ 630.2013). Elemental analysis (calcd for $C_{28}H_{37}ClP_2Pt$): C: 50.07 (50.49), H: 5.61 (5.60).

Synthesis of [PtCl(CH_3)(L_{3d})] (3d/4d)

A solution of $\mathbf{L_{3d}}$ (60 mg, 0.13 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 30 s to a stirred solution of [PtCl(CH_3)(cod)] (47 mg, 0.13 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred overnight. The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording a white solid (37 mg, 41%). Crystals suitable for X-ray analysis were grown from a saturated solution of the product in CH_2Cl_2. The product was obtained as a mixture of four isomers in a 2 : 2 : 3 : 1 ratio (**3d** : **3d′** : **4d** : **4d′**) at room temperature. $^{31}P\{^1H\}$ NMR (121 MHz, $C_2D_2Cl_4$): For **3d**: δ 52.6 (P^tBu_2, d, *J*(PPt) = 1842 Hz, *J*(PP) = 20 Hz), 14.9 (PAr_2, d, *J*(PPt) = 4392 Hz, *J*(PP) = 20 Hz). For **3d′**: δ 46.9 (P^tBu_2, d, *J*(PPt) = 1766 Hz, *J*(PP) = 20 Hz), 0.0 (PAr_2, d, *J*(PPt) = 4213 Hz, *J*(PP) = 20 Hz). For **4d**: δ 48.8 (P^tBu_2, d, *J*(PPt) = 4222 Hz, *J*(PP) = 18 Hz), 12.5 (PAr_2, d, *J*(PPt) = 1593 Hz, *J*(PP) = 18 Hz). For **4d′**: δ 53.1 (P^tBu_2, d, *J*(PPt) = 4278 Hz, *J*(PP) = 18 Hz), 18.4 (PAr_2, d, *J*(PPt) = 1695 Hz, *J*(PP) = 18 Hz). ^1H NMR (300 MHz, CD_2Cl_2, 0 °C): δ 8.94 (td, *J*(HH) = 18.6 Hz, *J*(HH) = 7.1 Hz), 7.47–6.32 (m), 6.04 (s), 3.81–3.40 (CH_2), $CH_3(C_6H_5)$: 2.97 (s), 2.87 (s), 2.62 (s), 2.34 (s), 1.47–1.05 ($C(CH_3)_3$, m), 0.27 (CH_3-Pt, *J*(HPt) = 54.6 Hz, *J*(HP*trans*) = 6.4 Hz, *J*(HP*cis*) = 4.4 Hz), 0.12 (CH_3-Pt, *J*(HPt) = 38.4 Hz, *J*(H*P*trans) = 7.1 Hz, *J*(H*P*cis) = 5.0 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 134.0–130.3 (br), 127.6–125.5 (br), 113.6 (br s), 84.2 (s), 37.5–36.8 (br), 32.1 (s), 31.9 (s), 31.7 (s), 30.6–29.4 (br), 28.2 (br s), 25.2–24–9 (br), 24.1–23.6 (br), 0.8 (s). Accurate mass spectrum: M_r = 658.1978 $(M - Cl)^+$ (calcd for $C_{30}H_{37}P_2Pt$ 658.1964).

Preparation of [PtCl(CH_3)(L_{3e})] (1e/2e)

A solution of $\mathbf{L_{3e}}$ (62 mg, 0.13 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 30 s to a stirred solution of [PtCl(CH_3)(cod)] (45 mg, 0.13 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred overnight. The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording a white solid (71 mg, 75%). The product was obtained as a mixture of two isomers in a 1 : 1 ratio (**3e** : **4e**) at room temperature. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −40 °C): For **3e**: δ 48.0 (P^tBu_2, d, *J*(PPt) = 1853 Hz, *J*(PP) = 21 Hz), 7.7 (PAr_2, d, *J*(PPt) = 4469 Hz, *J*(PP) = 21 Hz). For **4e**: δ 48.7 (P^tBu_2, d, *J*(PPt) = 4251 Hz, *J*(PP) = 21 Hz), 10.9 (PAr_2, d, *J*(PPt) = 1768 Hz, *J*(PP) = 21 Hz). ^1H NMR (400 MHz, CD_2Cl_2): For **3e** or **4e**: δ 8.79 (1 H, br s), 7.52–6.79 (7 H, m), 3.68–2.23 (OCH_3 + CH_2, 7 H, br m), 1.46 ($C(CH_3)_3$, 9 H, d, *J*(HP) = 12.5 Hz), 1.39 ($C(CH_3)_3$, 9 H, d, *J*(HP) = 12.5 Hz), 0.98–0.83 (CH_3-Pt, 3 H, m). For **3e** or **4e**: δ 8.79 (1 H, br s), 7.52–6.79 (7 H, m), 3.68–2.23 (OCH_3 + CH_2, 7 H, br m), 1.19 ($C(CH_3)_3$, 9 H, d, *J*(HP) = 12.7 Hz), 1.18 ($C(CH_3)_3$, 9 H, d, *J*(HP) = 12.7 Hz), −0.04 (CH_3-Pt, 3 H, br s, *J*(HPt) = 52.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 162.5 (s), 161.4 (br s), 143.6 (br s), 140.8 (br s), 135.4–134.1 (br signals), 132.9 (br s), 132.2 (br s), 131.6 (br s), 130.5 (br s), 129.9 (br s), 129.1 (s),

128.2 (br s), 127.7 (br s), 126.7 (br s), 126.2 (br s), 120.9 (d, J(CP) = 14.0 Hz), 120.8 (d, J(CP) = 14.8 Hz), 120.5 (br s), 120.3 (br s), 115.6 (s), 114.0 (s), 112.2 (br d, J(CP) = 27.3 Hz), 56.1 (br s), 55.8 (br s), 55.2 (br s), 37.6 (br d, J(CP) = 10.9 Hz), 37.4 (br d, J(CP) = 15.6 Hz), 32.4 (s), 31.1 (br s), 31.0 (br s), 30.2 (br s), 30.1 (br d, J(CP) = 3.9 Hz), 28.5 (s), 27.6 (br s), 25.9 (br s), 22.9 (s), 14.4 (dd, J(CP*trans*) = 94.2 Hz), J(CP*cis*) = 28.0 Hz), 12.1 (dd, J(CP*trans*) = 65.4 Hz, J(CP*cis*) = 33.5 Hz). Accurate mass spectrum: M_r = 690.2241 $(M - Cl)^+$ (calcd for $C_{30}H_{41}O_2P_2Pt$ 690.2224). Elemental analysis (calcd for $C_{30}H_{41}ClO_2P_2Pt$): C: 49.99 (49.62), H: 5.91 (5.69).

Preparation of [PtCl(CH$_3$)(L$_{3f}$)] (3f/4f)

A solution of **L$_{3f}$** (46 mg, 0.090 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 30 s to a stirred solution of [PtCl(CH_3)-(cod)] (31 mg, 0.090 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred overnight. The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording a pale yellow solid (59 mg, 85%). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 11.3 (PCH_2Cg, d, J(PPt) = 4328 Hz, J(PP) = 13 Hz), −6.1 (PCg, d, J(PPt) = 1403 Hz, J(PP) = 13 Hz). The ^{31}P NMR spectrum of the product showed the presence of only one isomer (**4f**) and from the signal to noise ratio, it was therefore deduced that the ratio **4f** : **3f** was at least 30 : 1. Accurate mass spectrum: M_r = 730.2030 $(M - Cl)^+$ (calcd for $C_{28}H_{41}O_6P_2Pt$ 730.2021).

Preparation of [PdCl(CH$_3$)(L$_{3b}$)] (5b/6b)

A solution of **L$_{3b}$** (70 mg, 0.16 mmol) in CH_2Cl_2 (2 mL) was added dropwise over 30 s to a stirred solution of [PdCl(CH_3)-(cod)] (43 mg, 0.16 mmol) in CH_2Cl_2 (2 mL). The solution was stirred overnight and then filtered through Celite® to remove Pd(0). The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording an orange solid (49 mg, 50%). The product was obtained as a mixture of two isomers in a 1 : 37 ratio (**5b** : **6b**) at room temperature. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): For **5b**: δ 60.5 (P^tBu_2, d, J(PP) = 9 Hz), −39.4 (PCg, d, J(PP) = 9 Hz). For **6b**: δ 70.3 (P^tBu_2, d, J(PP) = 34 Hz), −16.7 (PCg, d, J(PP) = 34 Hz). ^1H NMR (400 MHz, CD_2Cl_2): For **5b**: δ 7.55–7.09 (4 H, m), 4.65 (CH_2, 2 H, dd, J(HH) = 13.9 Hz, J(HP) = 3.9 Hz), 3.30–3.19 (CH_2P, 2 H, m), 1.94–0.89 (37 H, m). For **6b**: δ 8.77–8.73 (1 H, m), 8.63–8.59 (1 H, m), 8.18 (1 H, d, J(HH) = 8.0 Hz), 7.94–7.90 (1 H, m), 4.87 (CH_2, 2 H, dd, J(HH) = 13.9 Hz, J(HP) = 2.5 Hz), 3.66–3.54 (CH_2P, 2 H, m), 1.94–0.89 (37 H, m). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 142.1 (d, J(CP) = 10.1 Hz), 139.0 (s), 135.0 (s), 134.3–134.2 (m), 130.8 (d, J(CP) = 1.5 Hz), 128.6–128.5 (m), 97.6 (CO_2CH_3, s), 96.7 (CO_2CH_3, s), 77.4 ($COCH_3$, s), 75.3 ($COCH_3$, d, J(CP) = 11.7 Hz), 43.6 (CH_2, d, J(CP) = 7.8 Hz), 39.2 (CH_2, s), 32.2 ($C(CH_3)_3$, d, J(CP) = 1.6 Hz), 31.9 ($C(CH_3)_3$, d, J(CP) = 2.3 Hz), 31.6 ($C(CH_3)_3$, d, J(CP) = 3.1 Hz), 30.5 ($C(CH_3)_3$, d, J(CP) = 3.1 Hz), 29.7 (CH_2P, d, J(CP) = 12.5 Hz), 28.0 (CH_3, s), 27.6 (CH_3, s), 27.2 (CH_3, s), 26.2 (CH_3, d, J(CP) = 7.0 Hz), 4.7 (CH_3-Pd, dd, J(CP*trans*) = 88.0 Hz, J(CP*cis*) = 5.5 Hz). ESI mass spectrum: m/z 457.1 $(M - Cl)^+$.

Preparation of [PdCl(CH$_3$)(L$_{3c}$)] (5c/6c)

A solution of **L$_{3c}$** (95 mg, 0.22 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 30 s to a stirred solution of [PdCl(CH_3)(cod)] (40 mg, 0.22 mmol) in CH_2Cl_2 (1 mL). The solution was stirred overnight and then filtered through Celite® to remove Pd(0). The volatiles were removed under reduced pressure and the residue was washed with pentane and dried under reduced pressure affording a pale brown solid (91 mg, 72%). The product was obtained as a mixture of two isomers in a 25 : 1 ratio (**5c** : **6c**) at room temperature. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): For **5c**: δ 47.3 (P^tBu_2, d, J(PP) = 45 Hz), 34.5 (PPh_2, d, J(PP) = 45 Hz). For **6c**: 75.2 (P^tBu_2, d, J(PP) = 41 Hz), 9.0 (PPh_2, d, J(PP) = 41 Hz). ^1H NMR (400 MHz, CD_2Cl_2): For **5c**: δ 7.58–7.18 (13 H, m), 6.76–6.72 (1 H, m), 2.90 (CH_2, br d, J(HP) = 5.4 Hz), 1.29 ($C(CH_3)_3$, 18 H, d, J(HP) = 12.7 Hz), 0.54 (CH_3-Pd, dd, J(HP*trans*) = 7.3 Hz, J(HP*cis*) = 3.7 Hz). For **6c**: δ 7.58–6.72 (obscured by **5c**), 3.01 (CH_2, 2 H, br m), 1.09 ($C(CH_3)_3$, 18 H, d, J(HP) = 11.0 Hz), 1.04 (CH_3-Pd, 3 H, dd, J(HP*trans*) = 7.8 Hz, J(HP*cis*) = 2.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 142.7 (d, J(CP) = 12.5 Hz), 134.8 (br s), 134.7 (br s), 134.5 (d, J(CP) = 13.2 Hz), 134.3 (d, J(CP) = 13.6 Hz), 133.3 (dd, J(CP) = 8.2 Hz, J(CP) = 4.3 Hz), 131.8 (d, J(CP) = 2.3 Hz), 131.5 (d, J(CP) = 2.3 Hz), 129.2 (d, J(CP) = 11.3 Hz), 127.8 (dd, J(CP) = 7.8 Hz, J(CP) = 2.3 Hz), 36.9 ($C(CH_3)_3$, d, J(CP) = 4.7 Hz), 30.2 ($C(CH_3)_3$, d, J(CP) = 4.7 Hz), 27.0 (CH_2, dd, J(CP) = 11.7 Hz, J(CP) = 8.2 Hz), 17.7 (CH_3-Pd, dd, J(CP*trans*) = 100.0 Hz, J(CP*cis*) = 1.6 Hz). Accurate mass spectrum (ESI): M_r = 541.1414 $(M - Cl)^+$ (calcd for $C_{28}H_{37}P_2Pd$ 541.1400). Elemental analysis (calcd for $C_{28}H_{37}ClP_2Pt$): C: 59.68 (58.24), H: 6.72 (6.46).

Generation of [PdCl(^{13}COCH$_3$)(L$_{3b}$)] (7b/8b)

A three-necked flask provided with a stirring bar was connected to a ^{13}CO gas cylinder and a Schlenk line *via* a T-shape connector with an oil bubbler. When the system was under ^{13}CO atmosphere, a solution of [PdCl(CH_3)(**L$_{3b}$**)] (**5b**/**6b**) (60 mg, 0.10 mmol) in CD_2Cl_2 (0.7 mL) was placed and the mixture was stirred for 20 min. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): Data only discernible for major isomer **8b**: δ 59.4 (P^tBu_2, br d, J(PP) = 48 Hz, J(^{13}CP*cis*) not resolved), −21.4 (PCg, dd, J(^{13}CP*trans*) = 101 Hz, J(PP) = 48 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 228.4 ({^{13}C(O)(CH_3)}-Pd, dd, J(^{13}CP*trans*) = 101.0 Hz, J(^{13}CP*cis*) = 14.5 Hz). IR (cm^{-1}): ν_{CO} 1638.

Generation of [PdCl(^{13}COCH$_3$)(L$_{3c}$)] (7c/8c)

A three-necked flask provided with a stirring bar was connected to a ^{13}CO gas cylinder and a Schlenk line *via* a T-shape connector with an oil bubbler. When the system was under ^{13}CO atmosphere, a solution of [PdCl(CH_3)(**L$_{3c}$**)] (**5c**/**6c**) (50 mg, 0.09 mmol) in CD_2Cl_2 (0.7 mL) was placed and the mixture was stirred for 30 min. The product was obtained as a mixture of two isomers in a 9 : 1 ratio (**7c** : **8c**) at room temperature. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): For **7c**: δ 39.2 (P^tBu_2, dd, J(^{13}CP*trans*) = 120 Hz, J(PP) = 71 Hz), 14.6 (PPh_2, dd, J(PP) = 71 Hz, J(^{13}CP*cis*) = 16 Hz). For **8c**: δ 63.9 (P^tBu_2, dd, J(PP) = 68 Hz, J(^{13}CP*cis*) = 16 Hz), 5.6 (PPh_2, dd, J(^{13}CP*trans*) =

Table 2 Crystallographic data

Compound	**1a**·CH_2Cl_2	**2a**·CH_2Cl_2	**2b**·CH_2Cl_2	**3c**/**4c**
Colour, habit	Colourless plate	Colourless plate	Yellow block	Colourless rhomboid
Size/mm	0.4 × 0.4 × 0.05	0.2 × 0.1 × 0.05	0.15 × 0.15 × 0.05	0.49 × 0.47 × 0.15
Empirical formula	$C_{25}H_{45}Cl_5P_2Pt$	$C_{24}H_{44}Cl_4P_2Pt$	$C_{26}H_{42}Cl_4O_3P_2Pt$	$C_{27\cdot87}H_{36\cdot61}Cl_{1\cdot13}P_2Pt$
M	779.89	731.42	801.43	668.70
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	7.4494(2)	9.4152(5)	12.461(3)	11.4182(1)
b/Å	22.2352(7)	21.846(1)	15.187(3)	15.7441(1)
c/Å	18.5251(6)	15.4768(7)	17.334(4)	15.0578(1)
a/°	90.00	90.00	85.45(3)	90.00
b/°	95.723(2)	115.504(3)	79.62(3)	103.5301(8)
g/°	90.00	90.00	77.63(3)	90.00
V/Å^3	3053.18(16)	2873.1(2)	3148.8(12)	2631.80(3)
Z	4	4	4	4
m/mm^{-1}	5.152	5.379	4.923	5.582
T/K	120	293	173	100
$q_{min,max}$	2.39, 32.43	1.73, 27.54	1.20, 27.48	2.24, 30.10
Completeness	0.962 to *q* = 32.43°	0.997 to *q* = 27.54°	0.994 to *q* = 27.48°	0.999 to *q* = 30.10°
Reflections: total/independent	10 671/10 671	48 854/6613	36 228/14 356	142 333/7730
R_{int}	0.0000[a]	0.0225	0.0564	0.0458
Final R_1 and wR_2	0.0837, 0.1808	0.0216, 0.0566	0.0426, 0.0881	0.0254, 0.0592
Largest peak, hole/eÅ^{-3}	5.077, −4.063	1.171, −1.801	3.402, −2.557	3.368, −1.200
r_{calc}/g cm^{-3}	1.697	1.691	1.691	1.688

Compound	**3d**/**4d**	**4a**	**4b**	**4f**·CH_2Cl_2
Colour, habit	0.12 × 0.10 × 0.08	Colourless block	Colourless block	Colourless block
Size/mm	$C_{30}H_{41}ClP_2Pt$	0.12 × 0.12 × 0.07	0.27 × 0.21 × 0.19	0.33 × 0.26 × 0.08
Empirical Formula	694.10	$C_{48}H_{90}Cl_2P_4Pt_2$	$C_{26}H_{43}ClO_3P_2Pt$	$C_{29}H_{43}Cl_3O_6P_2Pt$
M	Monoclinic	1252.16	696.07	851.01
Crystal system	$P2_1/c$	Monoclinic	Monoclinic	Monoclinic
Space group	10.9460(5)	$P2_1/c$	$P2_1/c$	$P2_1$
a/Å	15.7116(6)	15.9715(7)	11.0658(1)	10.588(4)
b/Å	18.9402(7)	20.0553(8)	14.8858(1)	14.583(5)
c/Å	90.00	18.7186(8)	17.0888(2)	11.873(4)
a/°	120.965(3)	90.00	90.00	90.00
b/°	90.00	118.759(3)	102.379(1)	116.01(2)
g/°	2793.1(2)	90.00	90.00	90.00
V/Å^3	4	5256.2(4)	2749.48(4)	1647.6(10)
Z	5.251	4	4	2
m/mm^{-1}	100	5.571	5.342	4.638
T/K	2.51, 27.58	100	173	100
$q_{min,max}$	0.994 to *q* = 27.58°	1.45, 27.52	2.43, 30.11	2.57, 30.52
Completeness	81 357/6438	0.996 to *q* = 27.52°	0.997 to *q* = 30.11°	0.997 to *q* = 30.52°
Reflections: total/independent	0.0610	54 476/12 047	140 525/8071	24 888/9839
R_{int}	0.0393, 0.0871	0.0814	0.0468	0.0262
Final R_1 and wR_2	1.600, −2.065	0.0405, 0.0954	0.0243, 0.0637	0.0197, 0.0402
Largest peak, hole/eÅ^{-3}	1.651	1.792, −1.340	3.137, −0.947	1.666, −0.920
r_{calc}/g cm^{-3}		1.582	1.682	1.715
Flack parameter				0.006(3)

[a] Non-merohedral twin.

128 Hz, *J*(PP) = 68 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): For **7c**: *δ* 7.71–7.01 (13 H, m), 6.72–6.67 (1 H, m), 2.81 (CH_2, 2 H, br d, *J*(HP) = 6.3 Hz), 2.04 ($CH_3{}^{13}C$(O), 3 H, br dd, *J*($H^{13}C$) = 5.6 Hz, *J*(HP*trans*) = 1.2 Hz), 1.25 ($C(CH_3)_3$, 18 H, d, *J*(HP) = 12.6 Hz). For **8c**: *δ* 8.37–8.29 (1 H, m), 7.71–7.01 (13 H, m), 3.48 (CH_2, 2 H, br d, *J*(HP) = 11.1 Hz), 2.66 ($CH_3{}^{13}C$(O), 3 H, br dd, *J*($H^{13}C$) = 5.5 Hz, *J*(HP*trans*) = 1.0 Hz), 1.39 ($C(CH_3)_3$, 18 H, d, *J*(HP) = 14.8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): For **7c**: *δ* 242.0 ({^{13}C(O)(CH_3)}-Pd, dd, *J*(^{13}CP*trans*) = 120.4 Hz, *J*(^{13}CP*cis*) = 16.4 Hz), 142.6 (d, *J*(CP) = 13.4 Hz), 135.5–134.6 (br), 134.3–134.2 (br), 133.8–133.5 (br), 133.1–132.8 (br), 132.5–131.6 (br), 130.6 (br s), 129.9–128.8 (br), 127.9–127.7 (br), 40.5 (br s), 40.3 (br s), 36.3–36.2 (br), 30.7 (br s), 30.1 (s), 30.0 (s), 27.0 (s). For **8c**: *δ* 241.4 ({^{13}C(O)(CH_3)}-Pd, dd, *J*(^{13}CP*trans*) = 126.4 Hz, *J*(^{13}CP*cis*) = 13.2 Hz).

Crystal structure determinations

All X-ray diffraction experiments were carried out using Mo-K_a radiation (*λ* = 0.71073 Å). Diffraction data for **2b** were collected on a Bruker SMART diffractometer at 173 K. Collections for **1a**, **2a**, **3d**/**4d**, **4a** and **4f** were carried out at 100 K on a Bruker APEX II diffractometer. Collections for **3c**/**4c** and **4b** were carried out using an Oxford Diffraction Gemini diffractometer,

also at 100 K. Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[23,24] from several series of exposures measuring 1° (**3c**/**4c**, **4b**) or 0.5° (all others) in ω or ϕ. Absorption corrections were based on equivalent reflections using CrysAlis RED[24] (**3c**/**4c**, **4b**), TWINABS (**1**) or SADABS.[25] The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXL.[26] Crystal structure and refinement data are given in Table 2. The crystal of **1a** was a non-merohedral twin with two domains. These were indexed independently and integrated simultaneously using the APEX II software. Refinement proceeded smoothly to give the structure shown and a ratio of 0.53 : 0.47 for the different domains.

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