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2-Pyridyl substituents enhance the activity of palladium–phospha-adamantane catalysts for the methoxycarbonylation of phenylacetylene†

Timothy A. Shuttleworth, Alexandra M. Miles-Hobbs, Paul G. Pringle* and Hazel A. Sparkes

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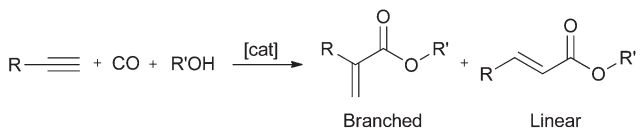
The synthesis of a series of CgPAr ligands is reported, where CgP is the 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamant-6-yl moiety and Ar = 2-pyridyl (**L_2**), 3-pyridyl (**L_3**), 2-pyrimidyl (**L_4**), 4-R-2-pyridyl [R = Me (**L_{5a}**), CF_3 (**L_{6a}**), $SiMe_3$ (**L_{7a}**)] or 6-R-2-pyridyl [R = Me (**L_{5b}**), CF_3 (**L_{6b}**), $SiMe_3$ (**L_{7b}**). Testing of these ligands in the Pd-catalysed methoxycarbonylation of phenylacetylene reveals that the activity and branched selectivity of the catalysts derived from these ligands varies as a function of the N-heterocycle, with the catalyst derived from **L_{5b}** being the most active of those tested. This, together with the poor performance of catalysts derived from **L_3** supports the hypothesis that the catalysis proceeds by a "proton shuttling" mechanism, an idea that previously had only been applied to arylphosphines. Reaction of $[PtCl_2(cod)]$ with L where L = **L_2** or **L_{4-7}** yields a *rac*/*meso* mixture of the *trans*-$[PtCl_2(L)_2]$ (**1a–h**) complexes, three of which are structurally characterised. ^{31}P NMR spectroscopy shows that reaction of **L_3** with $[PtCl_2(cod)]$ gives a mixture of mononuclear and binuclear metal complexes in solution. The complex *trans*-$[PdCl_2(\mathbf{L_2})_2]$ (**4**) reacts with $AgBF_4$ to give the $[PdCl(\kappa^1\text{-}\mathbf{L_2})(\kappa^2\text{-}\mathbf{L_2})]BF_4$ (**5**) with spectroscopic and structural characterisation confirming the presence of a P,N-chelate. ^1H and ^{31}P NMR evidence supports the assignment of a pyridyl-protonated species being formed upon treatment of **4** with $TsOH{\cdot}H_2O$ in CD_2Cl_2; both the protonated species and chelate **5** are observed when the reaction is carried out in MeOH.

Introduction

The palladium-catalysed methoxycarbonylation of alkynes (Scheme 1) is an atom-efficient way of producing branched or linear α,β-unsaturated esters from readily available feedstocks.[1,2]

The methoxycarbonylation of propyne (Scheme 1, R = Me) has been extensively studied owing to the industrial interest in the branched product, methyl methacrylate (MMA) which is a precursor to poly(methyl methacrylate).[3] The methoxycarbonylation of phenylacetylene (Scheme 1, R = Ph) produces methyl atropate (branched product), a precursor to ibuprofen[2] or methyl cinnamate (linear product), which has applications in the perfume and flavouring industries.[4]



Scheme 1

The activity, selectivity and stability of the palladium catalyst for methoxycarbonylation depend critically on the ligand. Drent *et al.* reported that changing the ligand from PPh_3 to $Ph_2P(2\text{-py})$ (**L_1**) led to an increase in rate of three orders of magnitude for propyne and an increase in branched selectivity from 89% to 99%.[3] It was postulated that a "non-classical" carbomethoxy mechanism involving P,N-chelates was in operation and the greater catalyst activity was a result of the $Ph_2P(2\text{-py})$ acting as a "proton messenger",[3] by bringing the proton into close proximity to the metal and thereby promoting the protonolysis of the proposed vinyl-palladium intermediate as shown in Scheme 2.

Recently, Bühl *et al.* reported a computational study of several possible pathways for methoxycarbonylation.[5] Drent's original mechanism was challenged, as it was found that the postulated, selectivity-determining transition state would

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK. E-mail: Paul.Pringle@bristol.ac.uk

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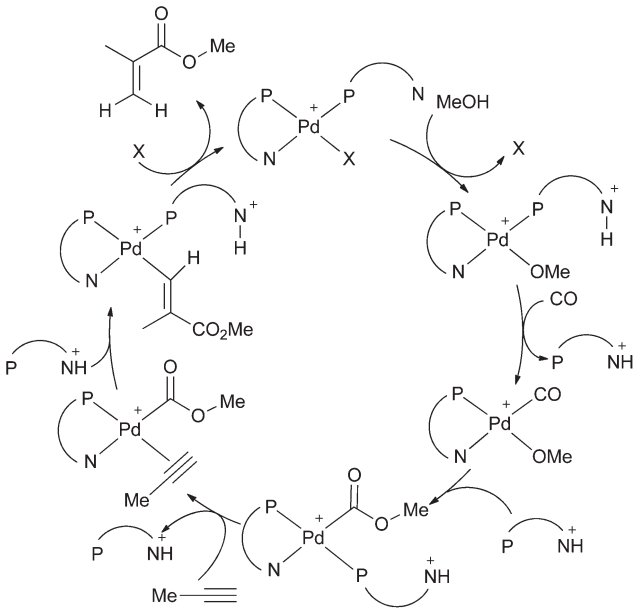
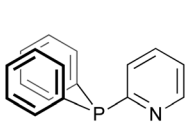


Scheme 2 Drent's non-classical carbomethoxy mechanism.[3]

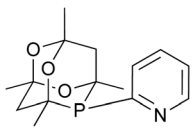
favour the formation of linear product (methyl crotonate) over the branched product (MMA). Instead, an alternative cycle involving labile P,N-chelates was proposed which proceeded by an *in situ* base mechanism (Scheme 3)[5] closely related to that described by Scrivanti *et al.*[6] This was suggested to be the most plausible mechanism due to it having surmountable barriers congruent with the high turnover and selectivity observed experimentally with $\mathbf{L_1}$. Common to the Drent and Bühl mechanisms (Schemes 2 and 3) is the chelation of the P,N ligand which acts to stabilise the catalyst. Catalysts derived from Ph_2P(2-py) have been shown to be excellent for phenylacetylene methoxycarbonylation (Scheme 1, R = Ph).[3,6]

It has also been observed that substituents on the 2-pyridyl ring have a pronounced effect upon the performance of the catalyst; moreover Ph_2P(3-py) and Ph_2P(4-py) give catalysts of much lower activity.[3] Palladium complexes of other monophosphines with the potential to form heterodonor P,L-chelates (*e.g.* pyrimidylphosphines,[7] iminophosphines,[8] phosphinoquinilines,[9] furylphosphines[10] and so called TROPPs[11]) have been shown to be efficient methoxycarbonylation catalysts. It is notable that in all of these ligands an Ar_2P moiety is present.[12]

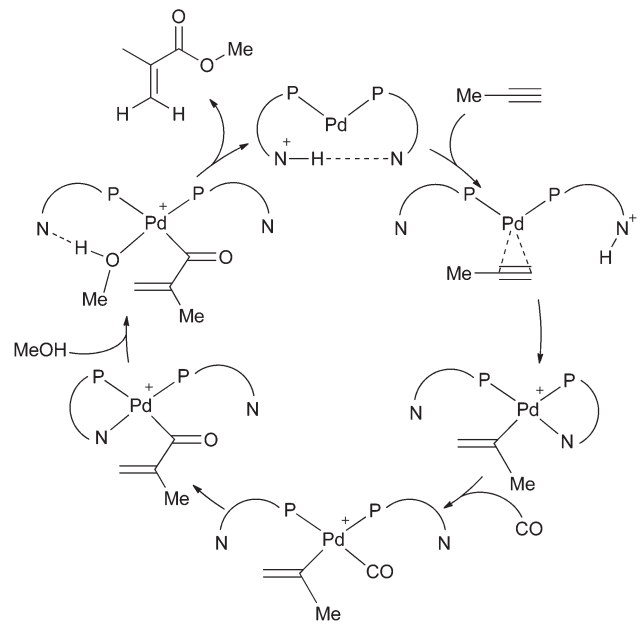
Ligands incorporating the 6-phospha-2,4,8-trioxa-1,3,5,7-tetramethyladamant-6-yl (CgP) moiety are effective for a range of Pd-catalysed carbonylation reactions.[13] CgPR and ^{t}Bu$_2$PR are comparable in terms of bulk but very different in σ/π-bonding characteristics: the donor properties of CgPR are comparable to a $(PhO)_2PR$.[14] It was therefore of interest to investigate CgP(2-py) ($\mathbf{L_2}$) and its derivatives as ligands for Pd-catalysed methoxycarbonylation of phenylacetylene. We show here that the Pd–$\mathbf{L_2}$ catalysts are active and that 4- and 6-substituents on the 2-pyridyl affect the performance of the catalyst. The platinum and palladium coordination chemistry of these ligands has been explored which has given some insight into the function of $\mathbf{L_2}$ and related ligands.



Ph_2P(2-py) ($\mathbf{L_1}$)



CgP(2-py) ($\mathbf{L_2}$)



Scheme 3 Bühl's *in situ* base mechanism.[5]

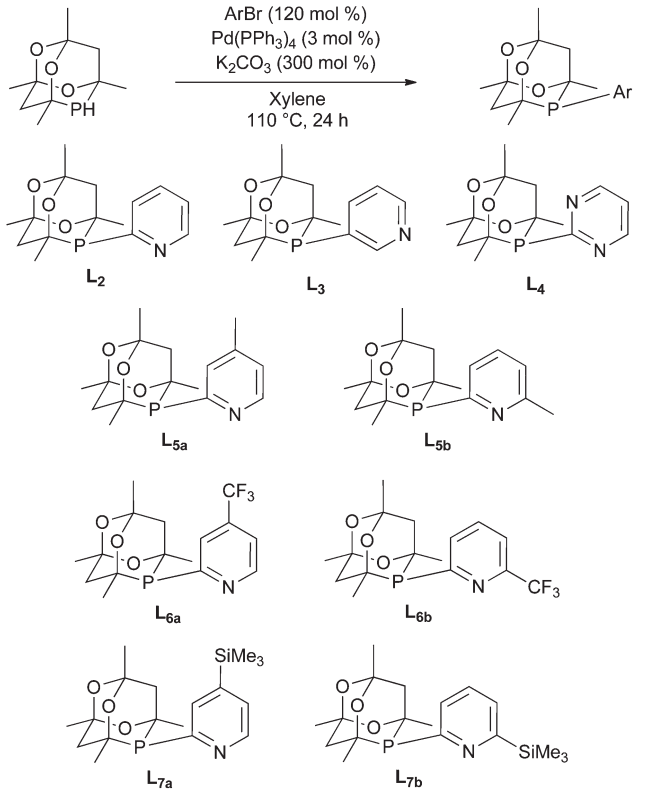
Results and discussion

Ligand synthesis

The synthesis of CgP(2-py) ($\mathbf{L_2}$) has previously been reported *via* a Pd-catalysed P-arylation of CgPH[15] and we have extended the route to the preparation of cage phosphines containing 3-pyridyl ($\mathbf{L_3}$), 2-pyrimidyl ($\mathbf{L_4}$), 4-substituted-2-pyridyl ($\mathbf{L_{5-7a}}$) and 6-substituted-2-pyridyl ($\mathbf{L_{5-7b}}$) (Scheme 4). These air-stable ligands were purified by column chromatography and have been fully characterised. Crystals of all of the ligands $\mathbf{L_{2-7}}$ suitable for X-ray crystallography have been obtained. The structures are very similar to each other and so only $\mathbf{L_2}$, as a representative structure, is shown in Fig. 1 along with its main metrical parameters; the structures of $\mathbf{L_{3-7}}$ are given in the ESI.†

Methoxycarbonylation catalysis

In order to draw comparisons in performance among the ligands, the methoxycarbonylation of phenylacetylene (eqn (1)) has been carried out in the presence of $\mathbf{L_{1-7}}$, PPh_3 and CgPPh under the same reaction conditions and the results are presented in Table 1.



Scheme 4

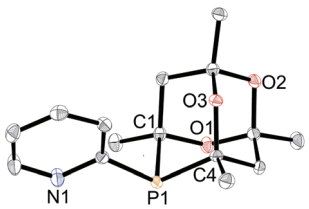
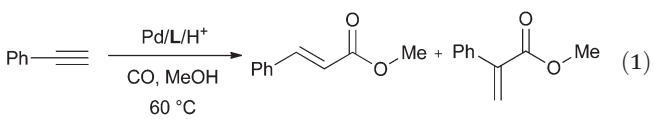


Fig. 1 Crystal structure of L_2. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1–C1 1.8857(12), P1–C4 1.8734(12), P1–C11 1.8395(12); C1–P1–C4 92.71(5), C1–P1–C11 101.83(5), C4–P1–C11 106.34(5).

Under the conditions we used for the catalysis, the PPh_3 catalyst produced low and inconsistent conversions (entry 1)



(1)

and at the end of the runs, copious amounts of black deposit, presumably metallic palladium, was observed indicating that the catalyst was not stable. As previously reported,[4] the very high activity of the catalyst derived from $\mathbf{L_1}$ (entry 3) contrasts sharply with that of the isosteric PPh_3 analogue (entry 1). The CgPPh is superior to PPh_3 in producing a moderately active catalyst (entry 2) that shows no evidence of decomposition to metallic Pd during the catalytic runs.

Table 1 Catalytic methoxycarbonylation of phenylacetylene[a]

		% Conversion[b]		
Entry	ligand	4.5 h	1 h	% Branched[c]
1	PPh_3	13	—	96
2	CgPPh	72	—	82
3	$\mathbf{L_1}$	100	100	99
4	$\mathbf{L_2}$	89	59	81
5	$\mathbf{L_{5a}}$	63	34	91
6	$\mathbf{L_{5b}}$	100	95	95
7	$\mathbf{L_{6a}}$	92	64	84
8	$\mathbf{L_{6b}}$	32	21	87
9	$\mathbf{L_{7a}}$	89	55	73
10	$\mathbf{L_{7b}}$	87	34	94
11	$\mathbf{L_3}$	14	—	99
12	$\mathbf{L_4}$	75	47	86
13	—	<2	—	—

[a] Reaction conditions: 5.5 mmol of phenylacetylene, 5.5×10^{-3} mmol of $Pd(OAc)_2$, 2.2 mmol of *p*-tolylsulfonic acid monohydrate, 1.1 mmol of ligand, 1.5 cm^3 of MeOH, 45 bar of CO, 60 °C. [b] Conversion and selectivity determined by ^1H NMR (see Experimental for details). Each result is an average of 2 or more runs. [c] The rest of the product was the linear isomer.

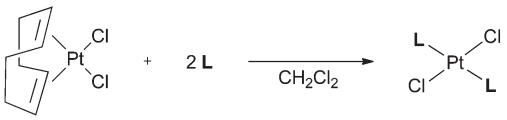
Ligand $\mathbf{L_2}$ (entry 4) produced a higher activity catalyst than CgPPh (entry 3) indicating that the 2-pyridyl group has a positive effect within the CgPAr series of ligands. This is reinforced by the low activity observed with the 3-pyridyl isomer $\mathbf{L_3}$ (entry 11). The pyrimidyl group in ligand $\mathbf{L_4}$ (entry 12) led to a catalyst with lower activity than $\mathbf{L_2}$.

The results for the catalysts derived from $\mathbf{L_{5–7a}}$ and $\mathbf{L_{5–7b}}$ show that substituents Me, CF_3 and $SiMe_3$ at the 4- and 6-positions in the 2-pyridyl ring can, in some cases, have a significant effect on the conversion compared to the unsubstituted $\mathbf{L_2}$. However, there appears to be no consistent trends associated with the stereoelectronic effect of the substituents. Relative to $\mathbf{L_2}$: (1) the 4-Me ligand $\mathbf{L_{5a}}$ (entry 5) gives a significantly lower conversion while the 6-Me ligand $\mathbf{L_{5b}}$ (entry 6) gives a significantly higher conversion; (2) the 4-CF_3 and 4-$SiMe_3$ ligands, $\mathbf{L_{6a}}$ (entry 7) and $\mathbf{L_{7a}}$ (entry 9), perform similarly to $\mathbf{L_2}$ while the 6-CF_3 and 6-$SiMe_3$ ligands, $\mathbf{L_{6b}}$ (entry 8) and $\mathbf{L_{7b}}$ (entry 10), produce catalysts of lower activity than $\mathbf{L_2}$. In terms of branched selectivity, there is some evidence that the 6-substituted 2-pyridyl ligands $\mathbf{L_{5–7b}}$ give more branched-selective catalysts than their 4-substituted isomers $\mathbf{L_{5–7a}}$ (entries 5–10). Others have reported similar observations with 4- and 6-substituted pyridyl derivatives of $\mathbf{L_1}$; that is, greater branched selectivity was obtained with 6-substituted than with 4-substituted pyridyl ligands.[4]

In order to elucidate the function of the 2-pyridyl in the Pd-catalysis, the coordination chemistry of $\mathbf{L_{2–7}}$ with Pt and Pd has been investigated.

Coordination chemistry

Ligands $\mathbf{L_{2–7}}$ have been reacted with $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) in CH_2Cl_2. With the exception of the reaction with $\mathbf{L_3}$ (see below), products of the type *trans*-$[PtCl_2(L)_2]$ (**1a–h**) were obtained (Scheme 5) which have been fully characterised.



L =	L_2	L_4	L_{5a}	L_{5b}	L_{6a}	L_{6b}	L_{7a}	L_{7b}
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**

Scheme 5

The ^{31}P NMR spectra of the products in each case showed two closely spaced singlets with ^{195}Pt satellites ($^1J_{P-Pt}$ values are typical of *trans*-[$PtCl_2(PR_3)_2$] complexes) consistent with the presence of *rac* and *meso* diastereomers resulting from the chirality of the cage ligands.[14]

Crystals suitable for X-ray crystallography of **1c**, **1d**, **1e** and **1g** (*meso* isomers in each case) were grown by slow diffusion of hexane into a CH_2Cl_2 solution of a *rac*/*meso* mixture of the corresponding complex. As shown in Fig. 2–5, in each case, the ligands adopt an *anti* conformation, with the C(pyridyl)–P–P–C(pyridyl) torsion angle of 180°.

The reaction of [$PtCl_2$(cod)] with the 3-pyridyl ligand $\mathbf{L_3}$ gave different results from those for all of the 2-pyridyl ligands $\mathbf{L_2}$, and $\mathbf{L_{4-7}}$. The ^{31}P NMR spectrum of the products of the reaction of [$PtCl_2$(cod)] with 2 equiv. of the 3-pyridyl ligand $\mathbf{L_3}$ showed four signals with ^{195}Pt satellites, as well as free ligand (δ_P −29.5 ppm). Two of the signals were assigned to *rac*/*meso*-[$PtCl_2(\mathbf{L_3})_2$] (**1i**) because of the similarity of their ^{31}P NMR data (δ_P −2.6 ppm, $^1J_{P,Pt}$ = 2703 Hz; δ_P −2.8 ppm, $^1J_{P,Pt}$ = 2710 Hz) to those of the analogues **1a–h**. The remaining two signals were assigned to binuclear complexes of the type [$Pt_2Cl_2(\mathbf{L_3})_2(\mu\text{-}Cl)_2$]

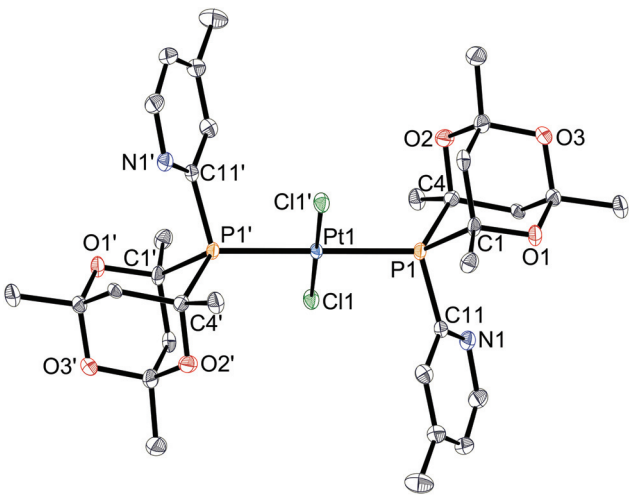


Fig. 2 Crystal structure of *meso*-**1c** showing the *anti*–*trans* conformation adopted by the ligands. Hydrogen atoms omitted for clarity. Atoms suffixed with a dash (′) are related by symmetry operation (–*x*, –*y*, –*z*). Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Pt1–Cl1 2.3125(7), Pt1–P1 2.3259(7), P1–C1 1.884(3), P1–C4 1.879(3), P1–C11 1.837(3); C1–P1–C4 94.10(13), C1–P1–C11 109.47(13), C4–P1–C11 105.41(13).

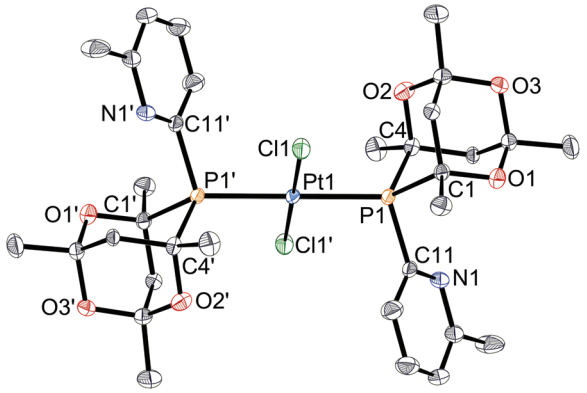


Fig. 3 Crystal structure of *meso*-**1d**, showing the *anti*–*trans* conformation adopted by the ligands. Hydrogen atoms omitted for clarity. Atoms suffixed with a dash (′) are related by symmetry operation (–*x*, 1–*y*, –*z*). Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Pt1–Cl1 2.3119(6), Pt1–P1 2.3198(6), P1–C1 1.883(3), P1–C4 1.878(3), P1–C11 1.845(3); C1–P1–C4 93.99(11), C1–P1–C11 103.98(12), C4–P1–C11 111.54(12).

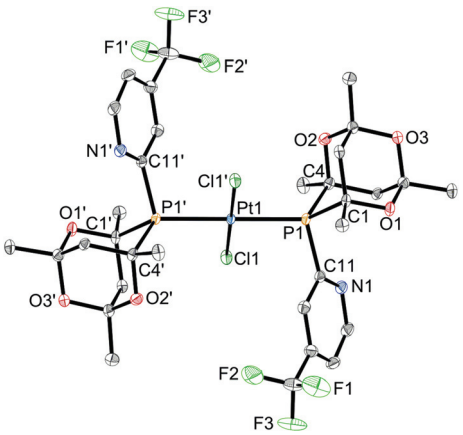


Fig. 4 Crystal structure of *meso*-**1e**, showing the *anti*–*trans* conformation adopted by the ligands. Hydrogen atoms omitted for clarity. Atoms suffixed with a dash (′) are related by symmetry operation (–*x*, 1–*y*, –*z*). Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Pt1–Cl1 2.3056(5), Pt1–P1 2.3227(5), P1–C1 1.877(2), P1–C4 1.886(3), P1–C11 1.842(2); C1–P1–C4 94.43(10), C1–P1–C11 105.04(13), C4–P1–C11 109.69(10).

on the basis of their large $^1J_{P,Pt}$ values (δ_P 8.3 ppm, $^1J_{P,Pt}$ = 4592 Hz; δ_P 7.9 ppm $^1J_{P,Pt}$ = 4608 Hz). Two types of isomerism (*syn*/*anti* and *rac*/*meso*) would be expected for [$Pt_2Cl_2(\mathbf{L_3})_2(\mu\text{-}Cl)_2$]; in view of the 0.4 ppm difference in their δ_P values, we tentatively assign the two observed ^{31}P NMR signals to *syn*- and *anti*-**2** (Scheme 6) with the signals expected for the *rac* and *meso* isomers unresolved. Mixtures of mononuclear and binuclear products were also reported in the reaction of [$PtCl_2$(cod)] with 2 equiv. CgPPh[14] and so the observation of exclusive formation of mononuclear complexes **1a–h** appears to be an effect of the 2-pyridyl group. It is tempting to associate this with weak Pt···N interactions stabilising the mononuclear complexes

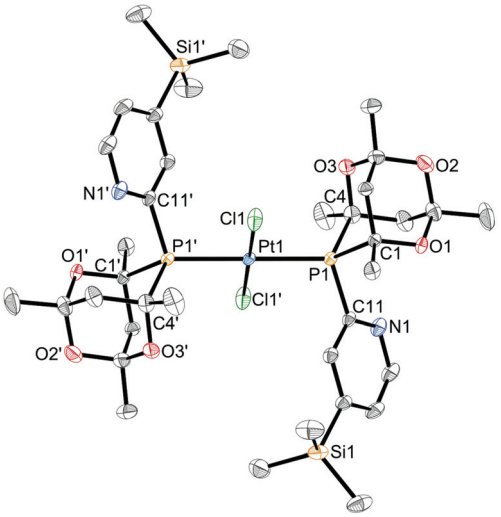
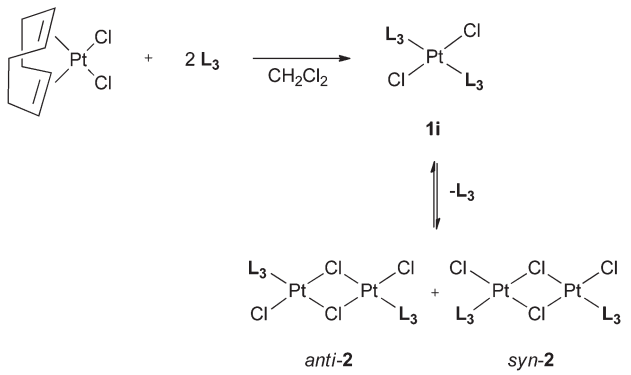


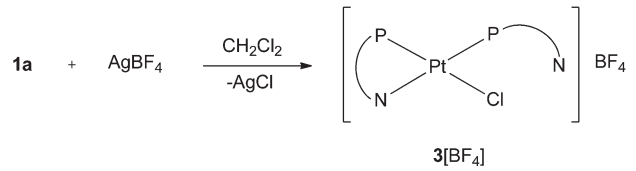
Fig. 5 Crystal structure of *meso*-**1g**, showing the *anti–trans* conformation adopted by the ligands. Disordered atoms in CgP moiety and hydrogen atoms omitted for clarity. Atoms suffixed with a dash (′) are related by symmetry operation (1–*x*, –*y*, –*z*). Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Pt1–Cl1 2.3022(5), Pt1–P1 2.3193(5), P1–C1 1.877(2), P1–C4 1.875(2), P1–C11 1.833(2); C1–P1–C4 94.23(9), C1–P1–C11 103.66(8), C4–P1–C11 111.82(9).



Scheme 6

although in the solid state at least, no such interactions were detected in complexes **1c–e** and **1g** (see Fig. 2–5).

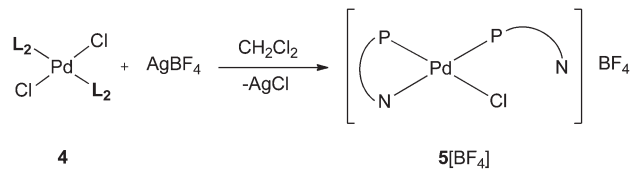
The ability of 2-pyridylphosphines to switch between P-monodentate and P,N-bidentate coordination has been invoked as part of the explanation for the high activity of Pd-complexes of 2-pyridylphosphines in methoxycarbonylation.[3,5,6] It was therefore of interest to investigate if 2-pyridylphosphine $\mathbf{L_2}$ could form 4-membered P,N-chelates. Treatment of the *trans* complex **1a** with 1 equiv. of $AgBF_4$ gave a precipitate of AgCl and a solution whose $^{31}P\{^1H\}$ NMR spectrum was consistent with the formation of the monochelate **3**[BF_4] (Scheme 7). Two doublets were observed at −48.1 ppm ($^1J_{P,Pt}$ = 2728 Hz) and +0.8 ppm ($^1J_{P,Pt}$ = 3514 Hz) with a small $^2J_{P,P}$ of 11 Hz typical of *cis* coordinated phosphines. The signal at −48.1 ppm is assigned to the P,N-chelate since its high field shift is characteristic of a 4-membered chelate.[16] The lower



Scheme 7

value of $^1J_{P,Pt}$ for the chelate-P is consistent with the ring strain being relieved by lengthened Pt–P bonds; the crystal structure of the Pd analogue **5**[BF_4] (see below) supports this inference.

In a similar manner to that described above for the Pt analogues, reaction of [$PdCl_2$(cod)] with 2 equiv. of $\mathbf{L_2}$ yielded *trans*-[$PdCl_2(\mathbf{L_2})_2$] (**4**) which has been fully characterised. Treatment of **4** with 1 equiv. of $AgBF_4$ gave a product assigned the structure **5**[BF_4], the Pd analogue of **3**[BF_4] (Scheme 8). Crystals of **5**[BF_4] suitable for X-ray crystallography were obtained and its crystal structure determined (Fig. 6) which confirmed the *cis* orientation of the two P-donors. The chelate ring strain is apparent from the acute P–Pd–N angle of 69.0°. The Pd–P length within the chelate is longer (by *ca.* 0.02 Å)



Scheme 8

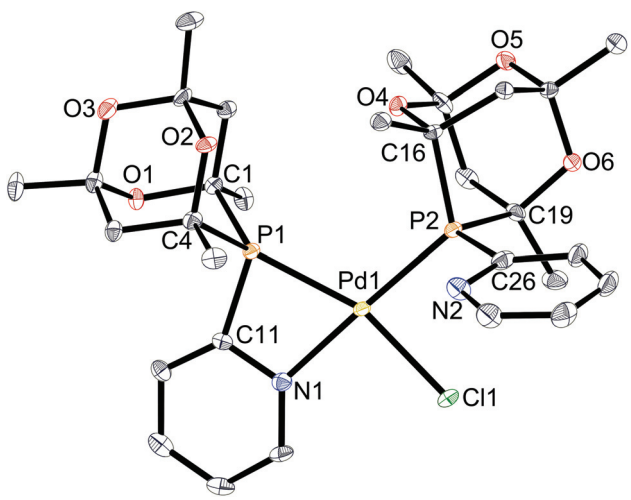


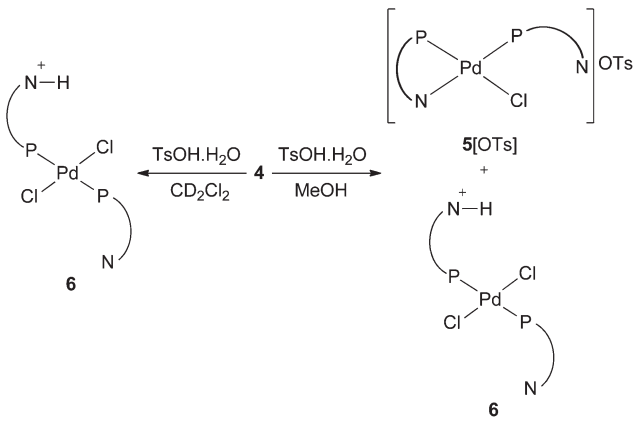
Fig. 6 Crystal structure of **5**[BF_4]. The $[BF_4]^-$ counterion, hydrogen atoms and CH_2Cl_2 solvent molecule are omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°): Pd1–Cl1 2.2989(10), Pd1–P1 2.3170(10), Pd1–P2 2.2779(10), Pd1–N1 2.073(3), P1–C11 1.829(4), P2–C26 1.819(4); P1–Pd1–P2 112.44(3), P1–Pd1–N1 68.95(9), P1–C11–N1 101.9(3), P2–Pd1–Cl1 86.17(4), P1–Pd1–Cl1 161.35(4), P2–Pd1–N1 176.87(9), C1–P1–C4 95.33(17), C16–P2–C19 94.48(16).

than that for the monodentate ligand perhaps reflecting the ring strain.

The $^{31}P\{^{1}H\}$ NMR spectrum of **5**[BF_4] in $CHCl_2CHCl_2$ showed a slightly broadened ($w_{1/2} \sim 8$ Hz) signal at 28.8 ppm, corresponding to the monodentate ligand, and a sharp doublet at −42.7 ppm ($^{2}J_{P,P}$ = 3.2 Hz), assigned to the P,N-chelate. The signals remain distinct but broaden as the temperature is raised (*e.g.* $w_{1/2} \sim 70$ Hz at 100 °C in $CHCl_2CHCl_2$) indicating that cation **5** is fluxional, which is associated with intramolecular interchange of chelating and non-chelating P,N ligands. Iggo *et al.* have shown that the complex [PdCl{κ^1-Ph_2P(2-py)}{κ^2-Ph_2P(2-py)}]BF_4 (an analogue of **5**[BF_4]) is fluxional but with a coalescence temperature for the ^{31}P NMR signals of −30 °C which is at least 150 °C lower than for cation **5**.[17] The high barrier to exchange in **5** can be rationalised in terms of steric hindrance to Pd–P bond rotation which may be required in order for the pyridyl-nitrogen in the κ^1-**L$_2$** to coordinate. Energy barriers to M–P bond rotation in complexes containing *cis*-M(CgPH)$_2$ moieties have previously been shown[18] to be of the order of 50 kJ mol^{-1}.

Complex **4** is only sparingly soluble in CD_2Cl_2 but addition of 1.1 equiv. of TsOH·H_2O to a suspension of **4** in CD_2Cl_2 gave a homogenous yellow solution. The ^{31}P NMR spectrum showed two broad peaks at 6.0 and 3.7 ppm ($w_{1/2} \sim 57$ Hz and 53 Hz respectively), which are tentatively assigned to diastereoisomers of protonated species such as **6** (Scheme 9) with rapid proton exchange rendering the ^{31}P NMR signals equivalent on the NMR timescale. In the ^{1}H NMR spectrum of **6** a broad signal centred at 6.55 ppm is assigned to the exchanging N–H. When a suspension of **4** in MeOH was treated with TsOH, the ^{31}P NMR spectrum of the resulting solution displayed two broad signals at 6.3 and 4.5 ppm (assigned to **6**) but in addition, two signals at 28.8 and −42.2 ppm are present, suggesting that the P,N-chelate **5**[OTs] is also generated (Scheme 9).

The Pd and Pt coordination chemistry of **L$_2$** has shown that the ligand can be monodentate (κ^1) or chelating (κ^2) and the pyridyl-N can be protonated by TsOH. These properties are essential for the catalyst to be able to function in a manner similar to **L$_1$** shown in Schemes 1 and 2. Tellingly, the $^{31}P\{^{1}H\}$ NMR spectrum of the mixture obtained after catalysis runs involving Pd and **L$_2$** showed, amongst other peaks, a prominent signal at −37.8 ppm, reminiscent of the peak observed at −42.1 ppm for the cation **5**, suggesting that a four-membered Pd chelate is present.



Scheme 9

Conclusions

A series of substituted pyridyl-functionalised phospha-adamantyl ligands **L$_{2–7}$** have been made and fully characterised. It was found that, in some cases, substituents on the pyridyl ring had a marked effect on the rate of Pd-catalysed methoxycarbonylation of phenylacetylene. The 6-methyl substituted ligand **L$_{5b}$** showed good activity and selectivity for the branched product albeit lower than that of the well-known Ph_2P(2-py) (**L$_1$**). The catalytic performance is a function of the substituents on the pyridine consistent with the idea that a mechanism involving P,N-chelation and "proton shuttling" may be operating.

The Pt and Pd coordination chemistry of **L$_{2–7}$** has been probed and the ability of the ligands to form P,N-chelates has been established in solution from the characteristic ^{31}P NMR spectra and in the solid state by the crystal structure of a palladium complex containing **L$_2$** ligands bound in a κ^1- and κ^2-mode. Moreover protonation of the pyridyl-N in a Pd-**L$_2$** complex has been observed in solution. In contrast to the CgP(2-py) ligands, the CgP(3-py) ligand **L$_3$** gives binuclear Pt complexes in a similar fashion to the CgPPh.

The methoxycarbonylation activity with catalysts derived from CgP(2-py) and its derivatives demonstrates that the 2-pyridyl effect is not restricted to Ph_2P(2-py) and its derivatives. The CgP and Ph_2P moieties has very different stereoelectronic effects and therefore the results presented hold out the prospect that other R_2P(2-py) ligands may be useful for alkyne methoxycarbonylation catalysis.

Experimental

General procedures

All reactions were carried out under an atmosphere of dry nitrogen, unless otherwise stated, using standard Schlenk line techniques and oven dried (200 °C) glassware. CH_2Cl_2 and hexane were collected from a Grubbs type solvent purification system, and deoxygenated by bubbling with N_2 for 30 minutes. Xylene and CD_2Cl_2 were dried over activated 4 Å molecular sieves for 72 hours and deoxygenated by successive freeze–pump–thaw cycles. MeOH was purchased as anhydrous, stored over 3 Å molecular sieves and deoxygenated by bubbling with N_2 for 30 minutes. Other commercial reagents were used as supplied unless otherwise stated. [$PtCl_2$(cod)],[19] [$PdCl_2$(cod)],[20] 1,3,5,7-tetramethyl-4,6,8-trioxa-2-phospha-adamantane (CgPH),[21] CgPPh,[14] Ph_2P(2-py)[22] (**L$_1$**) 2-bromo-4-(trimethylsilyl)pyridine,[23] and 2-bromo-6-(trimethylsilyl)pyridine[24] were synthesised accord-

ing to literature procedures. ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded at ambient temperature unless otherwise stated, on Jeol ECP (Eclipse) 300, Jeol ECS 300, Jeol ECS 400, Varian 400-MR, Varian VNMRS 500 spectrometers and a Bruker Avance III HD 500 spectrometer equipped with a ^{13}C-observe (DCH) cryogenic probe. Chemical shifts δ are given in parts per million (ppm) and coupling constants J are in Hz. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent peaks. ^{11}B, ^{19}F and ^{31}P chemical shifts were referenced to $BF_3{\cdot}OEt_2$, $CFCl_3$ and 85% H_3PO_4 respectively. Mass Spectra were recorded by the University of Bristol Mass Spectrometry Service on VG Analytical Autospec (EI) or VG Analytical Quattro (ESI) spectrometers. Elemental Analysis was carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol. X-ray crystallography was performed by the University of Bristol X-ray Analytical Service using Bruker AXS Microstar or Bruker Kappa Apex II diffractometers. Thin Layer Chromatography (TLC) was performed using Merck Kieselgel 60 F_{254} (Merck) aluminium backed plates (0.25 mm layer of silica). Flash column chromatography was performed using a Biotage Isolera Spektra One Chromatographic Isolation system.

General procedure for the synthesis of pyridyl-functionalised phospha-adamantyl ligands. A Schlenk flask was charged with a suspension of CgPH (1 equiv.), K_2CO_3 (3 equiv.) and $[Pd(PPh_3)_4]$ (3 mol%) in xylene (6 cm^3). The desired ArBr (1.2 equiv.) was added and the mixture heated to 110 °C and stirred for 24 h. The mixture was then allowed to cool and, in air, passed through silica, eluting with Et_2O. Removal of the solvents *in vacuo* yielded the crude product.

CgP(2-py) (L_2). Prepared according to a literature procedure.[14] Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. Spectroscopic data the same as those reported.

CgP(3-py) (L_3). Purification by flash column chromatography (20% EtOAc/hexane) yielded the product as a white solid (0.432 g, 71%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.93–8.92 (m, 1H, Ar*H* (H-2)), 8.61–8.59 (m, 1H, Ar*H* (H-6)), 8.19–8.15 (m, 1H, Ar*H* (H-4)), 7.31–7.26 (m, 1H, Ar*H* (H-5)), 2.05 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 7.3 Hz, 1H, CgP CH_2), 1.94 (dd, $^{3}J_{H,P}$ = 25.1 Hz, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.66 (d, $^{2}J_{H,H}$ = 13.5 Hz, 1H, CgP CH_2), 1.51 (dd, $^{2}J_{H,H}$ = 13.4 Hz, $^{3}J_{H,P}$ = 4.3 Hz, 1H, CgP CH_2), 1.49 (d, $^{3}J_{H,P}$ = 12.8 Hz, 3H, CgP CH_3), 1.41 (s, 6H, CgP CH_3), 1.25 (d, $^{3}J_{H,P}$ = 13.3 Hz, 3H, CgP CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ_C 155.6 (d, $^{2}J_{C,P}$ = 26.4 Hz, Ar*C* (C-2)), 150.5 (s, Ar*C* (C-6)), 142.3 (d, $^{2}J_{C,P}$ = 14.5 Hz, Ar*C* (C-4)), 130.6 (d, $^{1}J_{C,P}$ = 32.4 Hz, Ar*C* (C-3)), 123.6 (d, $^{3}J_{C,P}$ = 4.4 Hz, Ar*C* (C-5)), 97.0 (s, CgP quat. C), 96.2 (s, CgP quat. C), 73.3 (d, $^{1}J_{C,P}$ = 21.6 Hz, CgP quat. C), 73.2 (d, $^{1}J_{C,P}$ = 7.3 Hz, CgP quat. C), 45.3 (d, $^{2}J_{C,P}$ = 17.7 Hz, CgP *C*H$_2$), 36.4 (d, $^{2}J_{C,P}$ = 1.9 Hz, CgP *C*H$_2$), 28.1 (s, CgP *C*H$_3$), 27.9 (s, CgP *C*H$_3$), 27.5 (d, $^{2}J_{C,P}$ = 22.2 Hz, CgP *C*H$_3$), 26.9 (d, $^{2}J_{C,P}$ = 11.1 Hz, CgP *C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ_P −29.5 (s, Cg*P*). HRMS (EI): *m*/*z* calc. for $C_{15}H_{20}NO_3P$ $[M]^+$ = 293.1184; obs. = 283.1174. Elem. Anal. found (calc. for $C_{15}H_{20}NO_3P$): C, 61.78 (61.43); H, 6.94 (6.87); N, 5.00 (4.78).

CgP(2-pyrm) (L_4). Purification by flash column chromatography (20% EtOAc/hexane) yielded the product as a white solid (0.679 g, 80%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of the product. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.69 (d, $^{3}J_{H,H}$ = 4.9 Hz, 2H, Ar*H* (H-4 and H 6)), 7.13 (t, $^{3}J_{H,H}$ = 4.9 Hz, 1H, Ar*H* (H-5)), 2.19 (d, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 2.14 (dd, $^{2}J_{H,H}$ = 13.1 Hz, $^{3}J_{H,P}$ = 6.7 Hz, 1H, CgP CH_2), 1.92 (dd, $^{3}J_{H,P}$ = 25.2 Hz, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.78 (d, $^{3}J_{H,P}$ = 12.0 Hz, 3H, CgP CH_3), 1.72 (d, $^{3}J_{H,P}$ = 12.7 Hz, 3H, CgP CH_3), 1.66 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 4.7 Hz, 1H, CgP CH_2), 1.42 (s, 3H, CgP CH_3), 1.27 (s, 3H, CgP CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ_C 174.8 (d, $^{1}J_{C,P}$ = 9.7 Hz, Ar*C* (C-2)), 156.1 (d, $^{2}J_{C,P}$ = 5.0 Hz, Ar*C* (C-4 and C-6)), 119.3 (s, Ar*C* (C-5)), 96.6 (s, CgP quat. C), 96.4 (s, CgP quat. C), 74.4 (d, $^{1}J_{C,P}$ = 24.8 Hz, CgP quat. C), 73.9 (d, $^{1}J_{C,P}$ = 6.9 Hz, CgP quat. C), 45.6 (d, $^{2}J_{C,P}$ = 17.1 Hz, CgP *C*H$_2$), 38.5 (d, $^{2}J_{C,P}$ = 1.9 Hz, CgP *C*H$_2$), 28.7 (d, $^{2}J_{C,P}$ = 19.3 Hz, CgP *C*H$_3$), 28.1 (s, CgP *C*H$_3$), 27.9 (s, CgP *C*H$_3$), 27.6 (d, $^{2}J_{C,P}$ = 10.2 Hz, CgP *C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ_P −18.5 (s, Cg*P*). HRMS (EI): *m*/*z* calc. for $C_{14}H_{19}N_2O_3P$ $[M]^+$ = 294.1133; obs. = 294.1137. Elem. Anal. found (calc. for $C_{14}H_{19}N_2O_3P$): C, 57.10 (57.14); H, 6.53 (6.51); N, 9.33 (9.52).

CgP(4-Me-2-py) (L_{5a}). Purification by flash column chromatography (40% diethyl ether/hexane) yielded the product as a white solid (0.343 g, 74%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.53 (d, $^{3}J_{H,H}$ = 5.0 Hz, 1H, Ar*H* (H-6)), 7.77 (s, 1H, Ar*H* (H-3)), 7.02 (d, $^{3}J_{H,H}$ = 5.0 Hz, 1H, Ar*H* (H-5)), 2.34 (s, 3H, Ar–CH_3), 2.07 (dd, $^{2}J_{H,H}$ = 13.2 Hz, $^{3}J_{H,P}$ = 6.7 Hz, 1H, CgP CH_2), 1.91 (dd, $^{3}J_{H,P}$ = 23.4 Hz, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.83 (d, $^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH_2), 1.57 (d, $^{3}J_{H,P}$ = 12.4 Hz, 3H, CgP CH_3), 1.50 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 4.1 Hz, 1H, CgP CH_2), 1.41 (s, 3H, CgP CH_3), 1.40 (d, $^{3}J_{H,P}$ = 12.4 Hz, 3H, CgP CH_3), 1.37 (s, 3H, CgP CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ_C 160.4 (d, $^{1}J_{C,P}$ = 12.7 Hz, Ar*C* (C-2)), 149.9 (d, $^{3}J_{C,P}$ = 14.2 Hz, Ar*C* (C-6)), 146.5 (d, $^{3}J_{C,P}$ = 1.8 Hz, Ar*C* (C-4)), 130.2 (d, $^{2}J_{C,P}$ = 10.5 Hz, Ar*C* (C-3)), 124.0 (s, Ar*C* (C-5)), 96.9 (s, CgP quat. C), 96.3 (s, CgP quat. C), 73.5 (d, $^{1}J_{C,P}$ = 9.9 Hz, CgP quat. C), 73.1 (d, $^{1}J_{C,P}$ = 22.9 Hz, CgP quat. C), 45.2 (d, $^{2}J_{C,P}$ = 16.7 Hz, CgP *C*H$_2$), 37.5 (d, $^{2}J_{C,P}$ = 2.1 Hz, CgP *C*H$_2$), 28.2 (s, CgP *C*H$_3$), 28.0 (s, CgP *C*H$_3$), 27.9 (d, $^{3}J_{C,P}$ = 20.6 Hz, CgP *C*H$_3$), 27.3 (d, $^{3}J_{C,P}$ = 11.7 Hz, CgP *C*H$_3$), 21.4 (s, Ar–*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ_P −24.5 (s, Cg*P*). HRMS (EI): *m*/*z* calc. for $C_{16}H_{22}NO_3P$ $[M]^+$ = 307.1337; obs. = 307.1331. Elem. Anal. found (calc. for $C_{16}H_{22}NO_3P$): C, 62.32 (62.53); H, 7.25 (7.22); N, 4.54 (4.56).

CgP(6-Me-2-py) (L_{5b}). Purification by flash column chromatography (5% EtOAc/hexane) yielded the product as a white solid (0.578 g, 82%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a $CHCl_3$ solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.78 (d, $^{3}J_{H,H}$ = 7.7 Hz, 1H, Ar*H* (H-3)), 7.51 (t, $^{3}J_{H,H}$ = 7.7 Hz, 1H, Ar*H* (H-4)), 7.06 (d, $^{2}J_{H,H}$ = 8.2 Hz, 1H, Ar*H* (H-5)), 2.54 (s, 3H, Ar–CH_3), 2.07 (dd, $^{2}J_{H,H}$ = 13.2 Hz, $^{3}J_{H,P}$ = 6.7 Hz, 1H, CgP CH_2), 1.89 (dd, $^{3}J_{H,P}$ = 23.1 Hz, $^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH_2), 1.82 (d, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.48 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 4.1 Hz, 1H, CgP CH_2), 1.55

(d, $^{3}J_{H,P}$ = 12.3 Hz, 3H, CgP CH_3), 1.41 (d, $^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH_3), 1.40 (s, 3H, CgP CH_3), 1.35 (s, 3H, CgP CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ_C 160.1 (d, $^{1}J_{C,P}$ = 10.7 Hz, Ar*C* (C-6)), 158.9 (d, $^{3}J_{C,P}$ = 14.4 Hz, Ar*C* (C-2)), 135.6 (d, $^{3}J_{C,P}$ = 1.2 Hz, Ar*C* (C-4)), 126.2 (d, $^{2}J_{C,P}$ = 8.4 Hz, Ar*C* (C 3)), 122.6 (s, Ar*C* (C-5)), 96.9 (s, CgP quat. C), 96.3 (s, CgP quat. C), 73.6 (d, $^{1}J_{C,P}$ = 9.9 Hz, CgP quat. C), 73.1 (d, $^{1}J_{C,P}$ = 22.9 Hz, CgP quat. C), 45.2 (d, $^{2}J_{C,P}$ = 16.7 Hz, CgP *C*H_2), 37.6 (d, $^{2}J_{C,P}$ = 2.1 Hz, CgP *C*H_2), 28.2 (s, CgP *C*H_3), 28.0 (s, CgP *C*H_3), 27.9 (d, $^{2}J_{C,P}$ = 20.4 Hz, CgP *C*H_3), 27.3 (d, $^{2}J_{C,P}$ = 11.8 Hz, CgP *C*H_3), 24.3 (s, Ar–*C*H_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ_P −24.9 (s, Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{16}H_{23}NO_3P$ $[M + H]^+$ = 308.1410; obs. = 308.1404. Elem. Anal. found (calc. for $C_{16}H_{22}NO_3P$): C, 62.44 (62.53); H, 7.27 (7.22); N, 4.57 (4.56).

CgP(4-CF_3-2-py) (L_{6a}). Purification by flash column chromatography (20% diethyl ether/hexane) yielded the product as a white solid (0.673 g, 80%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.88 (d, $^{3}J_{H,H}$ = 5.0 Hz, 1H, Ar*H* (H-6)), 8.23 (s, 1H, Ar*H* (H-3)), 7.43 (d, $^{3}J_{H,H}$ = 5.0 Hz, 1H, Ar*H* (H-5)), 2.08 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 6.9 Hz, 1H, CgP CH_2), 1.94 (dd, $^{3}J_{H,P}$ = 23.6 Hz, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.69 (d, $^{2}J_{H,H}$ = 13.4 Hz, 1H, CgP CH_2), 1.59 (d, $^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH_3), 1.54 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 4.2 Hz, 1H, CgP CH_2), 1.43 (s, 3H, CgP CH_3), 1.42 (d, $^{3}J_{H,P}$ = 12.8 Hz, 3H, CgP CH_3), 1.36 (s, 3H, CgP CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ_C 163.5 (d, $^{1}J_{C,P}$ = 18.1 Hz, Ar*C* (C-2)), 150.9 (d, $^{3}J_{C,P}$ = 13.1 Hz, Ar*C* (C-6)), 137.8 (q, $^{2}J_{C,F}$ = 33.9 Hz, Ar*C* (C-4)), 124.8 (dq, $^{2}J_{C,P}$ = 10.0 Hz, $^{3}J_{C,F}$ = 3.5 Hz, Ar*C* (C-3)), 122.9 (q, $^{1}J_{C,F}$ = 273.5 Hz, Ar–*C*F_3), 118.4 (q, $^{3}J_{C,F}$ = 3.5 Hz, Ar*C* (C-5)), 97.0 (s, CgP quat. C), 96.3 (s, CgP quat. C), 73.6 (d, $^{1}J_{C,P}$ = 9.7 Hz, CgP quat. C), 72.0 (d, $^{1}J_{C,P}$ = 22.8 Hz, CgP quat. C), 44.9 (d, $^{2}J_{C,P}$ = 16.5 Hz, CgP *C*H_2), 37.6 (d, $^{2}J_{C,P}$ = 2.0 Hz, CgP *C*H_2), 28.0 (s, CgP *C*H_3), 27.7 (s, CgP *C*H_3), 27.8 (d, $^{2}J_{C,P}$ = 20.6 Hz, CgP *C*H_3), 27.3 (d, $^{2}J_{C,P}$ = 11.4 Hz, CgP *C*H_3). ^{19}F NMR (377 MHz, $CDCl_3$): δ_F −64.8 (s, Ar–CF_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ_P −24.2 (s, Cg*P*). HRMS (EI): *m*/*z* calc. for $C_{16}H_{19}F_3NO_3P$ $[M]^+$ = 361.1055; obs. = 361.1057. Elem. Anal. found (calc. for $C_{16}H_{19}F_3NO_3P$): C, 53.01 (53.19); H, 5.37 (5.30); N, 3.96 (3.88).

CgP(6-CF_3-2-py) (L_{6b}). Purification by flash column chromatography (10% EtOAc/hexane) yielded the product as a white solid (0.633 g, 76%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.06 (d, $^{3}J_{H,H}$ = 7.9 Hz, 1H, Ar*H* (H-3)), 7.81 (t, $^{3}J_{H,H}$ = 8.2 Hz, 1H, Ar*H* (H-4)), 7.58 (d, $^{3}J_{H,H}$ = 7.8 Hz, 1H, Ar*H* (H-5)), 2.09 (dd, $^{2}J_{H,H}$ = 13.1 Hz, $^{3}J_{H,P}$ = 6.8 Hz, 1H, CgP CH_2), 1.95 (dd, $^{3}J_{H,P}$ = 23.9 Hz, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.94 (d, $^{2}J_{H,H}$ = 13.4 Hz, 1H, CgP CH_2), 1.57 (d, $^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH_3), 1.58–1.54 (m, 1H CgP CH_2), 1.48 (d, $^{3}J_{H,P}$ = 12.8 Hz, 3H, CgP CH_3), 1.42 (s, 3H, CgP CH_3), 1.34 (s, 3H, CgP CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ_C 162.4 (d, $^{1}J_{C,P}$ = 21.0 Hz, Ar*C* (C-2)), 148.6 (qd, $^{2}J_{C,F}$ = 34.6 Hz, $^{3}J_{C,P}$ = 10.8 Hz, Ar*C* (C-6)), 136.6 (d, $^{3}J_{C,P}$ = 2.4 Hz, Ar*C* (C-4)), 131.9 (d, $^{2}J_{C,P}$ = 13.7 Hz, Ar*C* (C-3)), 121.5 (q, $^{1}J_{C,F}$ = 274.5 Hz, Ar–*C*F_3), 119.4 (q, $^{3}J_{C,F}$ = 2.7 Hz, Ar*C* (C-5)), 96.6 (s, CgP quat. C), 96.4 (s, CgP quat. C), 73.8 (d, $^{1}J_{C,P}$ = 9.0 Hz, CgP quat. C), 73.1 (d, $^{1}J_{C,P}$ = 23.3 Hz, CgP quat. C), 45.1 (d, $^{2}J_{C,P}$ = 16.9 Hz, CgP *C*H_2), 37.7 (d, $^{2}J_{C,P}$ = 2.0 Hz, CgP *C*H_2), 28.0 (s, CgP *C*H_3), 27.9 (s, CgP *C*H_3), 27.8 (d, $^{2}J_{C,P}$ = 20.0 Hz, CgP *C*H_3), 27.4 (d, $^{2}J_{C,P}$ = 11.4 Hz, CgP *C*H_3). ^{19}F NMR (377 MHz, $CDCl_3$): δ_F −68.1 (s, Ar–CF_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ_P −23.6 (s, Cg*P*). HRMS (EI): *m*/*z* calc. for $C_{16}H_{19}F_3NO_3P$ $[M]^+$ = 361.1055; obs. = 361.1058. Elem. Anal. found (calc. for $C_{16}H_{19}F_3NO_3P$): C, 53.32 (53.19); H, 5.38 (5.30); N, 3.75 (3.88).

CgP(4-$SiMe_3$-2-py) (L_{7a}). Purification by flash column chromatography (10% EtOAc/hexane) yielded the product as a white solid (0.390 g, 56%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of the product. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.64 (d, $^{3}J_{H,H}$ = 4.7 Hz, 1H, Ar*H* (H-3)), 8.11 (br s, 1H, Ar*H* (H-6)), 7.30 (d, $^{3}J_{H,H}$ = 4.7 Hz, 1H, Ar*H* (H-5)), 2.10 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 6.6 Hz, 1H, CgP CH_2), 1.92 (dd, $^{3}J_{H,P}$ = 23.4 Hz, $^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH_2), 1.80 (d, $^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH_2), 1.57 (d, $^{3}J_{H,P}$ = 12.4 Hz, 3H, CgP CH_3), 1.51 (dd, $^{2}J_{H,H}$ = 13.3 Hz, $^{3}J_{H,P}$ = 4.1 Hz, 1H, CgP CH_2), 1.42 (s, 3H, CgP CH_3), 1.41 (d, $^{3}J_{H,P}$ = 12.6 Hz, 3H, CgP CH_3), 1.37 (s, 3H, CgP CH_3), 0.32 (s, 9H, Si(CH_3)$_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ_C 159.6 (d, $^{1}J_{C,P}$ = 13.5 Hz, Ar*C* (C-2)), 149.8 (s, Ar*C* (C-4)), 149.1 (d, $^{2}J_{C,P}$ = 13.4 Hz, Ar*C* (C-3)), 133.9 (d, $^{3}J_{C,P}$ = 9.1 Hz, Ar*C* (C-6)), 127.3 (s, Ar*C* (C-5)), 96.9 (s, CgP quat. C), 96.3 (s, CgP quat. C), 73.5 (d, $^{1}J_{C,P}$ = 9.7 Hz, CgP quat. C), 73.1 (d, $^{1}J_{C,P}$ = 22.7 Hz, CgP quat. C), 45.2 (d, $^{2}J_{C,P}$ = 16.7 Hz, CgP *C*H_2), 37.5 (d, $^{2}J_{C,P}$ = 2.1 Hz, CgP *C*H_2), 28.2–27.8 (m, CgP *C*H_3), 27.3 (d, $^{2}J_{C,P}$ = 11.6 Hz, CgP *C*H_3), 1.6 (s, Si(*C*H_3)$_3$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ_P −26.9 (s, Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{18}H_{29}NO_3PSi$ $[M + H]^+$ = 366.1649; obs. = 366.1662. Elem. Anal. found (calc. for $C_{18}H_{28}NO_3PSi$): C, 59.55 (59.15); H, 7.89 (7.72); N, 4.02 (3.83).

CgP(6-$SiMe_3$-2-py) (L_{7b}). Purification by flash column chromatography (10% EtOAc/hexane) yielded the product as a white solid (0.424 g, 42%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (d, $^{3}J_{H,H}$ = 7.9 Hz, 1H, Ar*H* (H-3)), 7.50 (t, $^{3}J_{H,H}$ = 7.7 Hz, 1H, Ar*H* (H-4)), 7.38 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H, Ar*H* (H-5)), 2.15 (d, $^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH_2), 2.10 (dd, $^{2}J_{H,H}$ = 13.2 Hz, $^{3}J_{H,P}$ = 6.5 Hz, 1H, CgP CH_2), 1.91 (dd, $^{3}J_{H,P}$ = 23.5 Hz, $^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH_2), 1.57–1.51 (m, 3H, CgP CH_3 and 1H CgP CH_2), 1.47 (d, $^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH_3), 1.42 (s, 3H, CgP CH_3), 1.33 (s, 3H, CgP CH_3), 0.30 (s, 9H, Si(CH_3)$_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ_C 167.0 (d, $^{3}J_{C,P}$ = 10.0 Hz, Ar*C* (C-6)), 160.5 (d, $^{1}J_{C,P}$ = 13.4 Hz, Ar*C* (C-2)), 133.0 (d, $^{3}J_{C,P}$ = 3.2 Hz, Ar*C* (C-4)), 128.4 (d, $^{2}J_{C,P}$ = 17.2 Hz, Ar*C* (C-3)), 127.4 (s, Ar*C* (C-5)), 96.9 (s, CgP quat. C), 96.4 (s, CgP quat. C), 73.7 (d, $^{1}J_{C,P}$ = 8.7 Hz, CgP quat. C), 73.2 (d, $^{1}J_{C,P}$ = 23.4 Hz, CgP quat. C), 45.3 (d, $^{2}J_{C,P}$ = 16.8 Hz, CgP *C*H_2), 37.7 (d, $^{2}J_{C,P}$ = 2.0 Hz, CgP *C*H_2), 28.1 (s, CgP *C*H_3), 28.0 (s, CgP *C*H_3), 27.9 (d, $^{2}J_{C,P}$ = 19.9 Hz, CgP *C*H_3), 27.4 (d, $^{2}J_{C,P}$ = 11.6 Hz, CgP *C*H_3), 1.6 (s, Si(*C*H_3)$_3$). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ_P −26.9 (s, Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{18}H_{29}NO_3PSi$ $[M + H]^+$ = 366.1649; obs. = 366.1651. Elem. Anal. found (calc. for $C_{18}H_{28}NO_3PSi$): C, 59.29 (59.15); H, 7.79 (7.72); N, 3.87 (3.83). (The stability of this ligand was tested by

heating in MeOH (*ca.* 0.5 cm^3) with $TsOH{\cdot}H_2O$ (2 equiv.) and $Pd(OAc)_2$ (0.1 equiv.) for 24 h and no decomposition was observed.)

$[PtCl_2(L_2)_2]$ (1a). A solution of $\mathbf{L_2}$ (0.157 g, 0.537 mmol) in CH_2Cl_2 (2 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.100 g, 0.267 mmol) in CH_2Cl_2 (2 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.184 g, 81%). *rac* : *meso* compounds observed in 3 : 2 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.76 (d, $^3J_{H,H}$ = 4.9 Hz) and 8.76 (d, $^3J_{H,H}$ = 4.9 Hz) (total 2H, Ar*H* (H-6)), 8.04–8.01 (m, 2H, Ar*H* (H-3)), 7.70–7.64 (m, 2H, Ar*H* (H-4)), 7.32–7.26 (m, 2H, Ar*H* (H-5)), 3.04 (dt, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) and 2.95 (dt, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH_2), 1.98–1.86 (m, 3H, CgP CH_2), 1.85 (vir t, $J_{H,P}$ = 6.2 Hz) and 1.80 (vir t, $J_{H,P}$ = 6.2 Hz) (total 6H, CgP CH_3), 1.74 (vir t, $J_{H,P}$ = 6.7 Hz) and 1.69 (vir t, $J_{H,P}$ = 6.7 Hz) (total 6H, CgP CH_3), 1.66–1.59 (m, 1H, CgP CH_2), 1.39 (s) and 1.34 (s) (total 6H, CgP CH_3), 1.27 (s) and 1.26 (s) (total 6H, CgP CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ_C 154.2 (vir t, $J_{C,P}$ = 154.1 Hz, Ar*C* (C-2)), 149.6 (app q, $J_{C,P}$ = 8.4 Hz, Ar*C* (C-6)), 134.7 (app q, $J_{C,P}$ = 3.3 Hz, Ar*C* (C-4)), 130.7 (app q, $J_{C,P}$ = 8.3 Hz, Ar*C* (C-3)), 123.9 (s, Ar*C* (C-5)), 96.4–96.2 (m, CgP quat. C), 74.9 (vir t, $J_{C,P}$ = 14.1 Hz) and 74.7 (vir t, $J_{C,P}$ = 14.1 Hz) (CgP quat. C), 73.8 (vir t, $J_{C,P}$ = 11.1 Hz) and 73.7 (vir t, $J_{C,P}$ = 11.1 Hz) (CgP quat. C), 42.2 (vir t, $J_{C,P}$ = 3.8 Hz) and 42.1 (vir t, $J_{C,P}$ = 3.8 Hz) (CgP *C*H_2), 41.9–41.8 (m, CgP *C*H_2), 27.9 (s, CgP *C*H_3), 27.7 (s, CgP *C*H_3), 27.6 (br s) and 27.2 (br s) (CgP *C*H_3), 26.0 (vir t, $J_{C,P}$ = 2.0 Hz) and 25.8 (vir t, $J_{C,P}$ = 2.5 Hz) (CgP *C*H_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ_P −0.6 (s, $^1J_{P,Pt}$ = 2740 Hz) and −1.1 (s, $^1J_{P,Pt}$ = 2727 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{30}H_{40}ClN_2O_6P_2Pt$ $[M - Cl]^+$ = 816.1695; obs. = 816.1690. Elem. Anal. found (calc. for $C_{30}H_{40}Cl_2N_2O_6P_2Pt$): C, 42.64 (42.26); H, 5.13 (4.73); N, 3.44 (3.29).

$[PtCl_2(L_4)_2]$ (1b). A solution of $\mathbf{L_4}$ (0.033 g, 0.110 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.043 g, 95%). *rac* : *meso* compounds observed in 1 : 1 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.76 (d, $^3J_{H,H}$ = 4.9 Hz) and 8.75 (d, $^3J_{H,H}$ = 4.9 Hz) (total 4H, Ar*H* (H-4 and H-6)), 7.25–7.22 (m, 2H, Ar*H* (H-5)), 3.16 (d of vir t, $^2J_{H,H}$ = 13.7 Hz, $J_{H,P}$ = 1.8 Hz) and 3.13 (d of vir t, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH_2), 2.29 (d, $^3J_{H,H}$ = 13.8 Hz) and 2.21 (d, $^3J_{H,H}$ = 13.8 Hz) (total 2H, CgP CH_2), 1.92–1.83 (m, 12H, CgP CH_3), 1.82–1.70 (m, 4H, CgP CH_3), 1.37 (s) and 1.35 (s) (total 6H, CgP CH_3), 1.20 (s, 6H, CgP CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ_C 168.0 (vir t, $J_{C,P}$ = 46.1 Hz, Ar*C* (C-2)), 156.2 (vir t, $J_{C,P}$ = 5.6 Hz) and 156.1 (vir t, $J_{C,P}$ = 5.6 Hz) (Ar*C* (C-4 and C-6)), 121.3 (s, Ar*C* (C-3)), 97.0 (s) and 96.96 (s) (CgP quat. C), 96.94 (s) and 96.92 (s) (CgP quat. C), 75.8–75.5 (m, CgP quat. C), 42.9–42.8 (m, CgP *C*H_2), 42.6–42.4 (m, CgP *C*H_2), 27.9 (s, CgP *C*H_3), 27.7 (s) and 27.6 (s) (CgP *C*H_3), 27.4 (vir t, $J_{C,P}$ = 2.4 Hz) and 27.3 (vir t, $J_{C,P}$ = 2.4 Hz) (CgP *C*H_3), 26.7 (br s) and 26.6 (br s) (CgP CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ_P −0.8 (s, $^1J_{P,Pt}$ = 2707 Hz) and −0.9 (s, $^1J_{P,Pt}$ = 2706 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{28}H_{38}ClN_4O_6P_2Pt$ $[M - Cl]^+$ = 818.1600; obs. = 818.1606. Elem. Anal. found (calc. for $C_{28}H_{38}Cl_2N_4O_6P_2Pt$): C, 39.66 (39.35); H, 4.57 (4.48); N, 6.34 (6.56).

$[PtCl_2(L_{5a})_2]$ (1c). A solution of $\mathbf{L_{5a}}$ (0.018 g, 0.058 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.010 g, 0.027 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.022 g, 86%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. *rac* : *meso* compounds observed in 3 : 2 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.60 (d, $^3J_{H,H}$ = 5.0 Hz) and 8.58 (d, $^3J_{H,H}$ = 5.0 Hz) (total 2H, Ar*H* (H-6)), 7.89 (br s) and 7.86 (br s) (total 2H, Ar*H* (H-3)), 7.14 (d, $^3J_{H,H}$ = 4.7 Hz) and 7.10 (d, $^3J_{H,H}$ = 5.0 Hz) (total 2H, Ar*H* (H-5)), 3.05 (d of vir t, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.1 Hz) and 2.95 (d of vir t, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.1 Hz) (total 2H, CgP CH_2), 2.38 (s) and 2.35 (s) (total 6H, Ar–CH_3), 2.05–2.02 (m, 1H, CgP CH_2), 1.98–1.88 (m, 2H, CgP CH_2), 1.84 (vir t, $J_{H,P}$ = 6.2 Hz) and 1.80 (vir t, $J_{H,P}$ = 6.2 Hz) (total 6H, CgP CH_3), 1.73 (vir t, $J_{H,P}$ = 6.6 Hz) and 1.68 (vir t, $J_{H,P}$ = 6.6 Hz) (total 6H, CgP CH_3), 1.65–1.56 (m, 3H, CgP CH_2), 1.39 (s) and 1.34 (s) (total 6H, CgP CH_3), 1.27 (s) and 1.26 (s) (total 6H, CgP CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ_C 159.3 (vir t, $J_{C,P}$ = 34.6 Hz, Ar*C* (C-2)), 149.8 (vir t, $J_{C,P}$ = 8.7 Hz) and 149.6 (vir t, $J_{C,P}$ = 8.7 Hz) (Ar*C* (C-6)), 146.9–146.7 (br s, Ar*C* (C-4)), 132.2 (vir t, $J_{C,P}$ = 8.7 Hz) and 132.0 (vir t, $J_{C,P}$ = 8.7 Hz) (Ar*C* (C-3)), 125.6 (s, Ar*C* (C-5)), 96.9 (s, CgP quat. C), 96.8 (s) and 96.7 (s) (CgP quat. C), 75.5 (vir t, $J_{C,P}$ = 14.0 Hz) and 75.3 (vir t, $J_{C,P}$ = 14.0 Hz) (CgP quat. C), 74.4 (vir t, $J_{C,P}$ = 11.1 Hz) and 74.3 (vir t, $J_{C,P}$ = 11.1 Hz) (CgP quat. C), 42.9 (app q, $J_{C,P}$ = 4.1 Hz, CgP *C*H_2), 42.4 (s) and 42.3 (s) (CgP *C*H_2), 27.8 (s, CgP *C*H_3), 27.64 (s) and 27.56 (s) (CgP *C*H_3), 27.5 (br s) and 27.4 (br s) (CgP *C*H_3), 26.1 (vir t, $J_{C,P}$ = 2.2 Hz) and 25.9 (vir t, $J_{C,P}$ = 2.4 Hz) (CgP *C*H_3), 21.7 (s) and 21.6 (s) (Ar–*C*H_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ_P −0.6 (s, $^1J_{P,Pt}$ = 2738 Hz) and −1.0 (s, $^1J_{P,Pt}$ = 2729 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{32}H_{44}ClN_2O_6P_2Pt$ $[M - Cl]^+$ = 844.2009; obs. = 844.1993. Elem. Anal. found (calc. for $C_{32}H_{44}Cl_2N_2O_6P_2Pt$): C, 43.47 (43.64); H, 5.07 (5.04); N, 3.19 (3.18).

$[PtCl_2(L_{5b})_2]$ (1d). A solution of $\mathbf{L_{5b}}$ (0.017 g, 0.055 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.010 g, 0.027 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.020 g, 78%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. *rac* : *meso* compounds observed in 3 : 2 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 7.87–7.84 (m, 2H, Ar*H* (H-3)),

7.58–7.53 (m, 2H, Ar*H* (H-4)), 7.16–7.12 (m, 2H, Ar*H* (H-5)), 3.09 (d of vir t, $^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.1 Hz) and 2.99 (d of vir t, $^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.1 Hz) (total 2H, CgP CH_2), 2.62 (s) and 2.57 (s) (total 6H, Ar–CH_3), 2.17 (d, $^{2}J_{H,H}$ = 13.7 Hz, 1H, CgP CH_2), 1.90–1.87 (m, 2H, CgP CH_2) 1.85 1.70 (m, 12H, CgP CH_3), 1.64–1.60 (m, 3H, CgP CH_2), 1.37 (s) and 1.34 (s) (total 6H, CgP CH_3), 1.25 (s, 6H, CgP CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ_C 159.3 (vir t, $J_{C,P}$ = 8.6 Hz) and 159.0 (vir t, $J_{C,P}$ = 8.6 Hz) (Ar*C* (C-6)), 153.7 (vir t, $J_{C,P}$ = 34.8 Hz) and 153.6 (vir t, $J_{C,P}$ = 35.6 Hz) (Ar*C* (C-2)), 135.4–135.3 (m, Ar*C* (C-4)), 128.7 (vir t, $J_{C,P}$ = 9.3 Hz) and 128.5 (vir t, $J_{C,P}$ = 8.2 Hz) (Ar*C* (C-3)), 124.2 (s) and 124.1 (s) (Ar*C* (C-5)), 97.0 (s) and 96.9 (s) (CgP quat. C), 96.8 (s) and 96.7 (s) (CgP quat. C), 75.6 (vir t, $J_{C,P}$ = 14.0 Hz) and 75.4 (vir t, $J_{C,P}$ = 14.0 Hz) (CgP quat. C), 74.5 (vir t, $J_{C,P}$ = 11.1 Hz) and 74.2 (vir t, $J_{C,P}$ = 11.1 Hz) (CgP quat. C), 42.9 (vir t, $J_{C,P}$ = 3.8 Hz) and 42.7 (vir t, $J_{C,P}$ = 3.8 Hz) (CgP *C*H_2), 42.5 (s) and 42.4 (s) (CgP *C*H_2), 27.9 (s, CgP *C*H_3), 27.8 (s) and 27.6 (s) (CgP *C*H_3), 27.7 (br s) and 27.4 (br s) (CgP *C*H_3), 26.4 (vir t, $J_{C,P}$ = 2.4 Hz) and 26.0 (vir t, $J_{C,P}$ = 2.4 Hz) (CgP *C*H_3), 24.8 (s) and 24.7 (s) (Ar–*C*H_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ_P −1.2 (s, $^{1}J_{P,Pt}$ = 2731 Hz) and −1.5 (s, $^{1}J_{P,Pt}$ = 2723 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{32}H_{44}ClN_2O_6P_2Pt$ $[M - Cl]^+$ = 844.2009; obs. = 844.2012. Elem. Anal. found (calc. for $C_{32}H_{44}Cl_2N_2O_6P_2Pt$): C, 43.73 (43.64); H, 5.12 (5.04); N, 3.24 (3.18).

$[PtCl_2(L_{6a})_2]$ (1e). A solution of L_{6a} (0.020 g, 0.055 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.010 g, 0.027 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.019 g, 72%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. *rac* : *meso* compounds observed in 3 : 1 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.96 (d, $^{3}J_{H,H}$ = 5.0 Hz) and 8.93 (d, $^{3}J_{H,H}$ = 5.0 Hz) (total 2H, Ar*H* (H-6)), 8.29 (br s) and 8.26 (br s) (total 2H, Ar*H* (H-3)), 7.53 (d, $^{3}J_{H,H}$ = 4.4 Hz) and 7.50 (d, $^{3}J_{H,H}$ = 4.7 Hz) (total 2H, Ar*H* (H-5)), 3.02 (d of vir t, $^{2}J_{H,H}$ = 13.7 Hz, $J_{H,P}$ = 2.3 Hz) and 2.93 (d of vir t, $^{2}J_{H,H}$ = 13.7 Hz, $J_{H,P}$ = 2.4 Hz) (total 2H, CgP CH_2), 1.98–1.86 (m, 4H, CgP CH_2), 1.84–1.71 (m, 12H, CgP CH_3), 1.69–1.67 (m, 2H, CgP CH_2), 1.41 (s) and 1.36 (s) (total 6H, CgP CH_3), 1.28 (s, 6H, CgP CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ_C 156.9 (vir t, $J_{C,P}$ = 33.7 Hz, Ar*C* (C-2)), 151.0 (vir t, $J_{C,P}$ = 8.2 Hz, Ar*C* (C-6)), 137.3 (q of vir t, $^{2}J_{C,F}$ = 33.9 Hz, $J_{C,P}$ = 3.6 Hz, Ar*C* (C-4)), 126.8–126.6 (m, Ar*C* (C-3)), 123.2 (q, $^{1}J_{C,F}$ = 273.5 Hz, Ar–*C*F_3), 118.4 (q, $^{3}J_{C,F}$ = 3.5 Hz, Ar*C* (C-5)), 97.0–96.9 (m, CgP quat. C), 75.7 (vir t, $J_{C,P}$ = 14.0 Hz, CgP quat. C), 74.5 (vir t, $J_{C,P}$ = 11.0 Hz, CgP quat. C), 42.6 (vir t, $J_{C,P}$ = 4.0 Hz, CgP *C*H_2), 42.5 (s, CgP *C*H_2), 27.9 (s, CgP *C*H_3), 27.7 (s) and 27.6 (s) (CgP *C*H_3), 27.5 (br s) and 27.4 (br s) (CgP *C*H_3), 26.0 (vir t, $J_{C,P}$ = 2.5 Hz) and 25.9 (vir t, $J_{C,P}$ = 2.5 Hz) (CgP *C*H_3). ^{19}F NMR (377 MHz, CD_2Cl_2): δ_F −65.13 (s) and −65.16 (s) (Ar–CF_3). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ_P 1.2 (s, $^{1}J_{P,Pt}$ = 2759 Hz) and 0.7 (s, $^{1}J_{P,Pt}$ = 2750 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{32}H_{38}ClF_6N_2O_6P_2Pt$ $[M - Cl]^+$ = 952.1443; obs. = 952.1479. Elem. Anal. found (calc. for $C_{32}H_{38}Cl_2F_6N_2O_6P_2Pt$): C, 38.66 (38.88); H, 3.89 (3.87); N, 2.85 (2.83).

$[PtCl_2(L_{6b})_2]$ (1f). A solution of L_{6b} (0.040 g, 0.110 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as an off-white solid (0.044 g, 84%). *rac* : *meso* compounds observed in 2 : 1 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.30 (d, $^{3}J_{H,H}$ = 8.0 Hz) and 8.25 (d, $^{3}J_{H,H}$ = 8.0 Hz) (total 2H, Ar*H* (H-3)), 7.90 (t, $^{3}J_{H,H}$ = 8.0 Hz) and 7.85 (d, $^{3}J_{H,H}$ = 8.0 Hz) (total 2H, Ar*H* (H-4)), 7.68 (d, $^{3}J_{H,H}$ = 7.9 Hz) and 7.63 (d, $^{3}J_{H,H}$ = 7.9 Hz) (total 2H, Ar*H* (H-5)), 3.08 (d of vir t, $^{2}J_{H,H}$ = 13.7 Hz, $J_{H,P}$ = 2.2 Hz) and 3.01 (d of vir t, $^{2}J_{H,H}$ = 13.8 Hz, $J_{H,P}$ = 2.2 Hz) (total 2H, CgP CH_2), 2.16 (d, $^{2}J_{H,H}$ = 13.8 Hz) and 2.14 (d, $^{2}J_{H,H}$ = 13.8 Hz) (total 2H, CgP CH_2), 1.95–1.84 (m, 2H, CgP CH_2), 1.78–1.68 (m, 14H, CgP CH_3 and CH_2), 1.41 (s) and 1.36 (s) (6H, CgP CH_3), 1.27 (br s, 6H, CgP CH_3). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ_C 156.1 (vir t, $J_{C,P}$ = 32.0 Hz) and 156.0 (vir t, $J_{C,P}$ = 32.5 Hz) (Ar*C* (C-2)), 148.1 (vir t, $J_{C,P}$ = 7.3 Hz) and 147.8 (vir t, $J_{C,P}$ = 7.8 Hz) (Ar*C* (C-6)), 136.7 (vir t, $J_{C,P}$ = 5.6 Hz, Ar*C* (C-4)), 134.2 (vir t, $J_{C,P}$ = 9.5 Hz, Ar*C* (C-3)), 121.9 (q, $^{1}J_{C,F}$ = 274.0 Hz) and 121.8 (q, $^{1}J_{C,F}$ = 274.4 Hz) (Ar–*C*F_3), 121.2 (br s) and 121.1 (br s) (Ar*C* (C-5)), 97.1 (s) and 97.05 (s) (CgP quat. C), 97.03 (s) and 96.9 (s) (CgP quat. C), 75.7 (vir t, $J_{C,P}$ = 14.4 Hz) and 75.6 (vir t, $J_{C,P}$ = 14.4 Hz) (CgP quat. C), 74.8–74.5 (m, CgP quat. C), 42.7–42.6 (m, CgP *C*H_2), 42.4 (s) and 42.3 (s) (CgP *C*H_2), 27.8 (s, CgP *C*H_3), 27.7 (s) and 27.6 (s) (CgP *C*H_3), 27.2 (s) and 27.71 (s) (CgP *C*H_3), 26.2 (br s, CgP *C*H_3). ^{19}F NMR (470 MHz, CD_2Cl_2): δ_F −68.4 (s) and −68.5 (s) (Ar–CF_3). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2): δ_P 0.2 (s, $^{1}J_{P,Pt}$ = 2756 Hz, Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{32}H_{38}Cl_2F_6N_2NaO_6P_2Pt$ $[M + Na]^+$ = 1010.1029; obs. = 1010.1027. Elem. Anal. found (calc. for $C_{32}H_{38}Cl_2F_6N_2O_6P_2Pt$): C, 38.92 (38.88); H, 4.08 (3.87); N, 2.75 (2.83).

$[PtCl_2(L_{7a})_2]$ (1g). A solution of L_{7a} (0.040 g, 0.110 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of $[PtCl_2(cod)]$ (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.035 g, 66%). Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product. *rac* : *meso* compounds observed in 1 : 1 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.69 (d, $^{3}J_{H,H}$ = 4.7 Hz) and 8.66 (d, $^{3}J_{H,H}$ = 4.7 Hz) (total 2H, Ar*H* (H-3)), 8.19–8.17 (m) and 8.15–8.13 (m) (total 2H, Ar*H* (H-6)), 7.40 (d, $^{3}J_{H,H}$ = 4.6 Hz) and 7.36 (d, $^{3}J_{H,H}$ = 4.7 Hz) (total 2H, Ar*H* (H-5)), 3.07 (d of vir t, $^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) and 2.97 (d of vir t, $^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH_2), 2.04 (d, $^{2}J_{H,H}$ = 13.7 Hz) and 1.93 (d, $^{2}J_{H,H}$ = 13.5 Hz, 2H, CgP CH_2), 1.92–1.85 (m, 2H, CgP CH_2), 1.82 (vir t, $J_{H,P}$ = 6.2 Hz) and (vir t, $J_{H,P}$ = 6.1 Hz) (total 6H, CgP CH_3), 1.72 (vir t, $J_{H,P}$ = 6.6 Hz) and 1.68

(vir t, $J_{H,P}$ = 6.6 Hz) (total 6H, CgP CH_3), 1.74–1.67 (m, 6H, CgP CH_3), 1.64–1.58 (m, 2H, CgP CH_2), 1.40 (s) and 1.34 (s) (total 6H, CgP CH_3), 1.26 (s) and 1.25 (s) (total 6H, CgP CH_3), 0.30 (s) and 0.28 (s) (total 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ_C 153.5 (vir t, $J_{C,P}$ = 33.7 Hz, Ar*C* (C-2)), 149.8–149.7 (m, Ar*C* (C-4)), 149.0–148.8 (m, Ar*C* (C-3)), 135.7–135.5 (m, Ar*C* (C-6)), 128.9 (br s, Ar*C* (C-5)), 96.9–96.7 (m, CgP quat. C), 75.5 (vir t, $J_{C,P}$ = 13.9 Hz) and 75.3 (vir t, $J_{C,P}$ = 13.9 Hz) (CgP quat. C), 74.5–74.2 (m, CgP quat. C), 42.9 (m, CgP *C*H$_2$), 42.4 (m, CgP *C*H$_2$), 28.0 (s, CgP *C*H$_3$), 27.8 (s) and 27.7 (s) (CgP *C*H$_3$), 27.6 (br s) and 27.5 (br s) (CgP *C*H$_3$), 26.1 (br s) and 25.9 (br s) (CgP *C*H$_3$), −1.59 (s) and −1.62 (s) (Si(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ_P −0.8 (s, $^1J_{P,Pt}$ = 2728 Hz) and −1.3 (s, $^1J_{P,Pt}$ = 2647 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{36}H_{56}ClN_2O_6P_2PtSi_2$ $[M - Cl]^+$ = 960.2484; obs. = 960.2490. Elem. Anal. found (calc. for $C_{36}H_{56}Cl_2N_2O_6P_2PtSi_2$): C, 43.61 (43.37); H, 5.80 (5.66); N, 2.95 (2.81).

[PtCl$_2$(L$_{7b}$)$_2$] (1h). A solution of **L$_{7b}$** (0.040 g, 0.110 mmol) in CH_2Cl_2 (1 cm^3) was added to a solution of [PtCl$_2$(cod)] (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a pale yellow solid (0.044 g, 83%). *rac* : *meso* compounds observed in 1 : 1 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 7.96 (d, $^3J_{H,H}$ = 8.0 Hz) and 7.88 (d, $^3J_{H,H}$ = 8.0 Hz) (total 2H, Ar*H* (H-3)), 7.60–7.52 (m, 2H, Ar*H* (H-4)), 7.48 (d, $^3J_{H,H}$ = 7.4 Hz) and 7.44 (d, $^3J_{H,H}$ = 7.4 Hz) (total 2H, Ar*H* (H-5)), 3.10–3.04 (m, 2H, CgP CH_2), 2.29 (d, $^2J_{H,H}$ = 13.6 Hz) and 2.18 (d, $^2J_{H,H}$ = 13.6 Hz) (total 2H, CgP CH_2), 1.87–1.58 (m, 16H, CgP CH_3 CH_2), 1.36 (s) and 1.33 (s) (total 6H, CgP CH_3), 1.26 (s) and 1.25 (s) (total 6H, CgP CH_3), 0.33 (s) and 0.32 (s) (total 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ_C 169.0 (br s) and 168.8 (br s) (Ar*C* (C-6)), 155.1 (s) and 155.0 (s) (Ar*C* (C-2)), 133.0–132.8 (m, Ar*C* (C-4)), 130.4 (vir t, $J_{C,P}$ = 10.2 Hz) and 130.2 (vir t $J_{C,P}$ = 9.7 Hz) (Ar*C* (C-3)), 128.9 (s) and 128.8 (s) (Ar*C* (C-5)), 96.9–96.8 (m, CgP quat. C), 75.6–75.3 (m) and 74.7–74.3 (m) (CgP quat. C), 42.9 (vir t, $J_{C,P}$ = 3.8 Hz) and 42.8 (vir t, $J_{C,P}$ = 3.9 Hz) (CgP *C*H$_2$), 42.4 (s) and 42.3 (s) (CgP *C*H$_2$), 28.0 (s, CgP *C*H$_3$), 27.8 (s) and 27.7 (s) (CgP *C*H$_3$), 27.4 (br s) and 27.3 (br s) (CgP *C*H$_3$), 26.4 (br s) and 26.3 (br s) (CgP *C*H$_3$), −1.56 (s) and −1.57 (s) (Si(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ_P −1.6 (s, $^1J_{P,Pt}$ = 2722 Hz) and −1.9 (s, $^1J_{P,Pt}$ = 2724 Hz) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{36}H_{57}Cl_2N_2O_6P_2PtSi_2$ $[M + H]^+$ = 996.2251; obs. = 996.2247. Elem. Anal. found (calc. for $C_{36}H_{56}Cl_2N_2O_6P_2PtSi_2$): C, 43.54 (43.37); H, 5.77 (5.66); N, 3.18 (2.81).

[PtCl$_2$(L$_3$)$_2$] (1i). The solution of **L$_3$** (0.020 g, 0.068 mmol) was added to a solution of [PtCl$_2$(cod)] (0.012 g, 0.034) in CH_2Cl_2 (1 cm^3) and the mixture stirred. The reaction was monitored over 24 hours by ^{31}P NMR spectroscopy (see text for details).

[PtCl(κ^1-L$_2$)(κ^2-L$_2$)]BF$_4$ (3[BF$_4$]). $AgBF_4$ (0.003 g, 0.015 mmol) was added to a CH_2Cl_2 solution (2 cm^3) of **1a** (0.013 g, 0.015 mmol) and stirred overnight. The cloudy mixture was then filtered through Celite to give a colourless solution, which was added to hexane to precipitate the product. After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as an off-white solid (0.010 g, 74%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ_H 9.26–9.06 (m, 1H, Ar*H*), 8.84–8.78 (m, 1H, Ar*H*), 8.53–8.48 (m, 1H, Ar*H*), 8.18–8.08 (m, 1H, Ar*H*), 7.97–7.91 (m, 2H, Ar*H*), 7.84 7.78 (m, 1H, Ar*H*), 7.45–7.41 (m, 1H, Ar*H*), 2.47–1.27 (m, 32H, CgP CH_3 and CgP CH_2). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ_B −2.1 (s, *B*F$_4$). ^{19}F NMR (377 MHz, CD_2Cl_2): δ_F −152.8 (s, B*F*$_4$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ_P 0.8 (d, $^2J_{P,P}$ = 11.8 Hz, $^1J_{P,Pt}$ = 3514 Hz, monodentate Cg*P*), −48.1 (d, $^2J_{P,P}$ = 11.6 Hz, $^1J_{P,Pt}$ = 2947 Hz, chelate Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{30}H_{40}ClN_2O_6P_2Pt$ $[M]^+$ = 816.1695; obs. = 816.1691.

[PdCl$_2$(L$_2$)$_2$] (4). A solution of **L$_2$** (0.103 g, 0.350 mmol) in CH_2Cl_2 (2 cm^3) was added to a solution of [PdCl$_2$(cod)] (0.050 g, 0.175 mmol) in CH_2Cl_2 (2 cm^3) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm^3). After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a yellow solid (0.129 g, 96%). *rac* : *meso* compounds observed in 1 : 1 ratio. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.73 (d, $^3J_{H,H}$ = 4.3 Hz) and 8.71 (d, $^3J_{H,H}$ = 4.4 Hz) (total 2H, Ar*H* (H-6)), 8.01 (d, $^3J_{H,H}$ = 4.4 Hz, 2H, Ar*H* (H-3)), 7.70–7.66 (m, 2H, Ar*H* (H-4)), 7.29 (appq, $^3J_{H,H}$ = 4.4 Hz, 2H, Ar*H* (H-5)), 3.04 (d of vir t, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) and 2.96 (d of vir t, $^2J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH_2), 2.24 (s) and 2.35 (s) (total 1H, CgP CH_2), 1.99–1.89 (m, 3H, CgP CH_2), 1.84 (vir t, $J_{H,P}$ = 6.3 Hz) and 1.80 (vir t, $J_{H,P}$ = 6.3 Hz) (total 6H, CgP CH_3), 1.73 (vir t, $J_{H,P}$ = 6.8 Hz) and 1.70 (vir t, $J_{H,P}$ = 6.6 Hz) (total 6H, CgP CH_3), 1.59–1.54 (m, 2H, CgP CH_2), 1.38 (s) and 1.35 (s) (total 6H, CgP CH_3), 1.27 (s, 6H, CgP CH_3). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ_C 155.6 (vir t, $J_{C,P}$ = 30.4 Hz) and 156.0 (vir t, $J_{C,P}$ = 29.7 Hz) (Ar*C* (C-2)), 150.1 (app q, $J_{C,P}$ = 8.0 Hz, Ar*C* (C-6)), 135.4 (br s, Ar*C* (C-4)), 131.1 (vir t, $J_{C,P}$ = 8.7 Hz) and 130.1 (vir t, $J_{C,P}$ = 8.2 Hz) (Ar*C* (C 3)), 124.5 (s, Ar*C* (C-5)), 97.0–96.8 (m, CgP quat. C), 76.3 (vir t, $J_{C,P}$ = 10.9 Hz) and 76.2 (vir t, $J_{C,P}$ = 10.8 Hz) (CgP quat. C), 75.0 (vir t, $J_{C,P}$ = 7.1 Hz) and 74.8 (vir t, $J_{C,P}$ = 7.0 Hz) (CgP quat. C), 43.2–43.1 (m, CgP *C*H$_2$), 42.5–42.4 (m, CgP *C*H$_2$), 28.2 (br s) and 28.1 (br s) (CgP *C*H$_3$), 27.8 (s, CgP *C*H$_3$), 27.73 (s) and 27.68 (s) (CgP *C*H$_3$), 26.8 (vir t, $J_{C,P}$ = 2.5 Hz) and 26.6 (vir t, $J_{C,P}$ = 2.7 Hz) (CgP *C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ_P 4.4 (s) and 4.3 (s) (Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{30}H_{40}Cl_2N_2O_6P_2Pd$ $[M - Cl]^+$ = 727.1088; obs. = 727.1103. Elem. Anal. found (calc. for $C_{30}H_{40}Cl_2N_2O_6P_2Pd$): C, 47.16 (47.17); H, 5.29 (5.28); N, 3.85 (3.67).

[PdCl(κ^1-L$_2$)(κ^2-L$_2$)]BF$_4$ (5[BF$_4$]). $AgBF_4$ (0.008 g, 0.039 mmol) was added to a CH_2Cl_2 solution (3 cm^3) of **4** (0.030 g, 0.039 mmol) and stirred overnight. The cloudy mixture was then filtered through Celite to give a yellow solution, which was added to hexane to precipitate the product. After the mixture was allowed to settle, the supernatant was removed using a pipette and the residual solvent removed *in vacuo* to give the product as a yellow solid (0.024 g, 76%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a

CH_2Cl_2 solution of the product. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 8.92–8.89 (m, 1H, Ar*H*), 8.79–8.78 (m, 1H, Ar*H*), 8.41–8.36 (m, 1H, Ar*H*), 8.06–8.02 (m, 2H, Ar*H*), 7.87–7.79 (m, 2H, Ar*H*), 7.79–7.47 (m, 1H, Ar*H*), 2.43–1.27 (m, 32H, CgP CH_3 and CgP CH_2). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ_B −2.2 (s, BF_4). ^{19}F NMR (377 MHz, CD_2Cl_2): δ_F −152.8 (s, BF_4). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ_P 28.8 (br s, monodentate Cg*P*), −42.1 (d, $^2J_{P,P}$ = 3.2 Hz, chelate Cg*P*). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −90 °C): δ_P 28.8 (d, $^2J_{P,P}$ = 3.2 Hz, monodentate Cg*P*), −42.0 (br s, chelate Cg*P*). HRMS (ESI): *m*/*z* calc. for $C_{30}H_{40}ClN_2O_6P_2Pd$ $[M]^+$ = 727.1088; obs. = 727.1118. Elem. Anal. found (calc. for $C_{30}H_{40}BClF_4N_2O_6P_2Pd{\cdot}CH_2Cl_2$): C, 41.79 (41.36); H, 4.86 (4.70); N, 3.20 (3.11) (the presence of CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy and was observed in the crystal structure).

Protonation studies

TsOH·H_2O (0.003 g, 0.015 mmol) was added to a suspension of **4** (0.010 g, 0.013 mmol) in CD_2Cl_2 (0.7 cm^3), upon which the solution became homogeneous, yielding species assigned to the protonated species **6**. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ_P 6.0 (br s, Cg*P*) and 3.7 (br s, Cg*P*). An analogous procedure in MeOH (0.7 cm^3) also gave a homogenous solution, assigned to be a mixture of **6** and a P,N-chelate species related to **5**[OTs]. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ_P 28.8 (br s, monodentate Cg*P*), 6.3 (br s, Cg*P*) and 4.5 (br s, Cg*P*), −42.2 (br s, chelate Cg*P*).

Phenylacetylene methoxycarbonylation

Adapted from previously reported procedure.[9] Catalysis was performed using a Baskerville Multi-Cell autoclave. The ligand (0.11 mmol) was added to the autoclave and the system put under an atmosphere of N_2. Solutions of $Pd(OAc)_2$ (0.0055 mmol) in MeOH (0.5 cm^3) and TsOH·H_2O (0.22 mmol) in MeOH (0.5 cm^3) were then added, followed by phenylacetylene (5.5 mmol). This was then washed in using MeOH (0.5 cm^3) and the autoclave flushed with three cycles of CO (*ca.* 10 bar). The autoclave was then pressurised to 45 bar and heated to 60 °C. After 1 hour or 4.5 hours, the autoclave was transferred to an ice bath and once cooled, the system was vented. A small amount of each sample was dissolved in $CDCl_3$ and analysed by ^{1}H NMR spectroscopy. Conversion and selectivity was determined by integration of the phenylacetylene alkynyl proton (δ_H 3.10 ppm) and the methyl atropate (δ_H 6.38 and 5.90 ppm) and methyl cinnamate (δ_H 7.71 and 6.42 ppm) alkenyl protons.

X-ray crystallography

All of the X-ray diffraction data were collected at 100 K on a Bruker Apex II diffractometer with CCD area detector using Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were carried out using SADABS.[25] All of the structures were solved using Superflip[26,27] and refined by full matrix least squares on F^2 using ShelXL[28,29] within Olex2.[30] The structure of *meso*-**1g** displayed disorder in the cage, the occupancies of the disordered atoms were refined with the sum of the occupancies set to 1 before being fixed at the refined values. Restraints were applied to the bond lengths and the thermal parameters of pairs of disordered atoms on almost the same site were constrained to be equal. The structure of **5** was twinned and refined as a 2-component twin. In addition, the BF_4^- counterion displayed disorder in the fluorine positions, the sum of the occupancies were set to equal 1 and refined before being fixed at the refined values. Restraints were applied to maintain sensible thermal parameters and B–F distances. Crystal structure and refinement details are given in Tables S1–S3 in ESI.† Crystallographic data for the compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC 1497885–1497898.

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