Dalton Transactions

PAPER



Cite this: DOI: 10.1039/c6dt03983a

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

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The synthesis of a series of CgPAr ligands is reported, where CgP is the 6-phospha-2,4,8-trioxa-1,3,5,7tetramethyladamant-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 L₃ 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 = L₂ or L₄₋₇ 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 L₃ with [PtCl₂(cod)] gives a mixture of mononuclear and binuclear metal complexes in solution. The complex trans-[PdCl₂(L_2)₂] (4) reacts with AgBF₄ to give the [PdCl(κ^{1} - L_2)(κ^{2} - L_2)]BF₄ (5) with spectroscopic and structural characterisation confirming the presence of a P,N-chelate. ¹H and ³¹P NMR evidence supports the assignment of a pyridyl-protonated species being formed upon treatment of $\mathbf{4}$ with TsOH·H₂O in CD_2Cl_2 ; both the protonated species and chelate 5 are observed when the reaction is carried out in MeOH

Received 17th October 2016, Accepted 30th November 2016 DOI: 10.1039/c6dt03983a www.rsc.org/dalton

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



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 \dagger Electronic supplementary information (ESI) available: Crystal structures of ligands $L_{2\text{-}7}$ and crystal structure and refinement details. CCDC 1497885–1497898. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt03983a

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 ibuprofen² or methyl cinnamate (linear product), which has applications in the perfume and flavouring industries.⁴

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 PPh₃ to Ph₂P(2-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 Ph₂P(2-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



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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 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



Scheme 3 Bühl's in situ base mechanism.⁵

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 Ph₂P(3-py) and Ph₂P(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 furylphosphines¹⁰ and so called TROPPs¹¹) have been shown to be efficient methoxycarbonylation catalysts. It is notable that in all of these ligands an Ar₂P moiety is present.¹²

Ligands incorporating the 6-phospha-2,4,8-trioxa-1,3,5,7tetramethyladamant-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) (L₂) and its derivatives as ligands for Pd-catalysed methoxycarbonylation of phenylacetylene. We show here that the Pd-L₂ 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 L₂ and related ligands.



Results and discussion

Ligand synthesis

The synthesis of CgP(2-py) (L_2) has previously been reported *via* a Pd-catalysed P-arylation of CgPH¹⁵ and we have extended the route to the preparation of cage phosphines containing 3-pyridyl (L_3), 2-pyrimidyl (L_4), 4-substituted-2-pyridyl (L_{5-7a}) and 6-substituted-2-pyridyl (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 L_{2-7} suitable for X-ray crystallography have been obtained. The structures are very similar to each other and so only L_2 , as a representative structure, is shown in Fig. 1 along with its main metrical parameters; the structures of 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 L_{1-7} , PPh₃ and CgPPh under the same reaction conditions and the results are presented in Table 1.





Fig. 1 Crystal structure of L₂. 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 PPh₃ catalyst produced low and inconsistent conversions (entry 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 L_1 (entry 3) contrasts sharply with that of the isosteric PPh₃ analogue (entry 1). The CgPPh is superior to PPh₃ 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

Entry	ligand	% Conversion ^b		
		4.5 h	1 h	% Branched ^c
1	PPh ₃	13	_	96
2	CgPPh	72	_	82
3	L	100	100	99
4	L_2	89	59	81
5	L ₅₉	63	34	91
6	L _{5b}	100	95	95
7	L _{6a}	92	64	84
8	L _{6b}	32	21	87
9	L_{7a}	89	55	73
10	L _{7b}	87	34	94
11	L_3	14	_	99
12	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 cm³ 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 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 L_3 (entry 11). The pyrimidyl group in ligand L_4 (entry 12) led to a catalyst with lower activity than L_2 .

The results for the catalysts derived from L_{5-7a} and L_{5-7b} show that substituents Me, CF3 and SiMe3 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 L_2 . However, there appears to be no consistent trends associated with the stereoelectronic effect of the substituents. Relative to L_2 : (1) the 4-Me ligand L_{5a} (entry 5) gives a significantly lower conversion while the 6-Me ligand L_{5b} (entry 6) gives a significantly higher conversion; (2) the 4-CF₃ and 4-SiMe₃ ligands, L_{6a} (entry 7) and L_{7a} (entry 9), perform similarly to L2 while the 6-CF3 and 6-SiMe3 ligands, L6b (entry 8) and L_{7b} (entry 10), produce catalysts of lower activity than L_2 . In terms of branched selectivity, there is some evidence that the 6-substituted 2-pyridyl ligands L_{5-7b} give more branchedselective catalysts than their 4-substituted isomers L5-7a (entries 5-10). Others have reported similar observations with 4- and 6-substituted pyridyl derivatives of L₁; 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 Pdcatalysis, the coordination chemistry of L_{2-7} with Pt and Pd has been investigated.

Coordination chemistry

Ligands L_{2-7} have been reacted with $[PtCl_2(cod)]$ (cod = 1,5cyclooctadiene) in CH₂Cl₂. With the exception of the reaction with L_3 (see below), products of the type *trans*- $[PtCl_2(L)_2]$ (1a–h) were obtained (Scheme 5) which have been fully characterised.



The ³¹P NMR spectra of the products in each case showed two closely spaced singlets with ¹⁹⁵Pt satellites (${}^{1}J_{P-Pt}$ values are typical of *trans*-[PtCl₂(PR₃)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 [PtCl₂(cod)] with the 3-pyridyl ligand L₃ gave different results from those for all of the 2-pyridyl ligands L₂, and L_{4–7}. The ³¹P NMR spectrum of the products of the reaction of [PtCl₂(cod)] with 2 equiv. of the 3-pyridyl ligand L₃ showed four signals with ¹⁹⁵Pt satellites, as well as free ligand ($\delta_{\rm P}$ –29.5 ppm). Two of the signals were assigned to *rac/meso*-[PtCl₂(L₃)₂] (1i) because of the similarity of their ³¹P NMR data ($\delta_{\rm P}$ –2.6 ppm, ¹*J*_{P,Pt} = 2703 Hz; $\delta_{\rm P}$ –2.8 ppm, ¹*J*_{P,Pt} = 2710 Hz) to those of the analogues 1a–h. The remaining two signals were assigned to binuclear complexes of the type [Pt₂Cl₂(L₃)₂(µ-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-***1***d*, 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–Cl1 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 ${}^{1}J_{P,Pt}$ values (δ_{P} 8.3 ppm, ${}^{1}J_{P,Pt} = 4592$ Hz; δ_{P} 7.9 ppm ${}^{1}J_{P,Pt} = 4608$ Hz). Two types of isomerism (*syn/anti* and *rac/meso*) would be expected for $[Pt_2Cl_2(L_3)_2(\mu-Cl)_2]$; 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. CgPPh¹⁴ 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-***1***g*, 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–Cl1 103.66(8), C4–P1–Cl1 111.82(9).



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 L₂ could form 4-membered P,N-chelates. Treatment of the *trans* complex **1a** with 1 equiv. of AgBF₄ gave a precipitate of AgCl and a solution whose ³¹P{¹H} NMR spectrum was consistent with the formation of the monochelate **3**[BF₄] (Scheme 7). Two doublets were observed at -48.1 ppm (¹*J*_{P,Pt} = 2728 Hz) and +0.8 ppm (¹*J*_{P,Pt} = 3514 Hz) with a small ²*J*_{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



value of ${}^{1}J_{P,Pt}$ 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[BF₄] (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 L_2 yielded *trans*- $[PdCl_2(L_2)_2]$ (4) which has been fully characterised. Treatment of 4 with 1 equiv. of AgBF₄ gave a product assigned the structure 5[BF₄], the Pd analogue of 3[BF₄] (Scheme 8). Crystals of 5[BF₄] 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)



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-Cl1 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,Nchelate. The signals remain distinct but broaden as the temperature is raised (e.g. $w_{1/2} \sim 70$ Hz at 100 °C in CHCl₂CHCl₂) 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 $[PdCl{\kappa^{1}-Ph_{2}P}]$ (2-py){ κ^2 -Ph₂P(2-py)}]BF₄ (an analogue of 5[BF₄]) is fluxional but with a coalescence temperature for the ³¹P 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} -L₂ to coordinate. Energy barriers to M-P bond rotation in complexes containing *cis*-M(CgPH)₂ moieties have previously been shown¹⁸ 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·H₂O to a suspension of 4 in CD_2Cl_2 gave a homogenous yellow solution. The ³¹P 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 ³¹P NMR signals equivalent on the NMR timescale. In the ¹H 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 ³¹P 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 ³¹P{¹H} 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.

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 Ph₂P(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 ³¹P 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. CH₂Cl₂ and hexane were collected from a Grubbs type solvent purification system, and deoxygenated by bubbling with N₂ for 30 minutes. Xylene and CD₂Cl₂ 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 N₂ for 30 minutes. Other commercial reagents were used as supplied unless otherwise stated. [PtCl₂(cod)],¹⁹ [PdCl₂(cod)],²⁰ 1,3,5,7-tetramethyl-4,6,8-trioxa-2-phospha-adamantane (CgPH),²¹ CgPPh,¹⁴ Ph₂P(2-py)²² (L₁) 2-bromo-4-(trimethylsilyl)pyridine,²³ and 2-bromo-6-(trimethylsilyl)pyridine²⁴ were synthesised accord-

ing to literature procedures. ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P 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 ¹³C-observe (DCH) cryogenic probe. Chemical shifts δ are given in parts per million (ppm) and coupling constants J are in Hz. ¹H and ¹³C chemical shifts were referenced to residual solvent peaks. ¹¹B, ¹⁹F and ³¹P chemical shifts were referenced to BF₃·OEt₂, CFCl₃ and 85% H₃PO₄ 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 F254 (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 cm³). 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 Et₂O. Removal of the solvents *in vacuo* yielded the crude product.

CgP(2-py) (L₂). 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) (L₃). 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 CH₂Cl₂ solution of the product. ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 8.93–8.92 (m, 1H, ArH (H-2)), 8.61-8.59 (m, 1H, ArH (H-6)), 8.19-8.15 (m, 1H, ArH (H-4)), 7.31–7.26 (m, 1H, ArH (H-5)), 2.05 (dd, ${}^{2}J_{H,H}$ = 13.3 Hz, ${}^{3}J_{H,P}$ = 7.3 Hz, 1H, CgP CH₂), 1.94 (dd, ${}^{3}J_{H,P}$ = 25.1 Hz, ${}^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH₂), 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 CH₃), 1.41 (s, 6H, CgP CH₃), 1.25 (d, ${}^{3}J_{H,P}$ = 13.3 Hz, 3H, CgP CH₃). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃): $\delta_{\rm C}$ 155.6 (d, ${}^{2}J_{\rm C,P}$ = 26.4 Hz, ArC (C-2)), 150.5 (s, ArC (C-6)), 142.3 (d, ${}^{2}J_{C,P}$ = 14.5 Hz, ArC (C-4)), 130.6 (d, ${}^{1}J_{C,P}$ = 32.4 Hz, ArC (C-3)), 123.6 (d, ${}^{3}J_{C,P}$ = 4.4 Hz, ArC (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 CH_2), 36.4 (d, ${}^2J_{C,P}$ = 1.9 Hz, CgP CH_2), 28.1 (s, CgP *C*H₃), 27.9 (s, CgP *C*H₃), 27.5 (d, ${}^{2}J_{C,P}$ = 22.2 Hz, CgP *C*H₃), 26.9 (d, ${}^{2}J_{C,P}$ = 11.1 Hz, CgP CH₃). ${}^{31}P{}^{1}H$ NMR (162 MHz, CDCl₃): δ_P –29.5 (s, CgP). HRMS (EI): m/z calc. for C₁₅H₂₀NO₃P $[M]^+$ = 293.1184; obs. = 283.1174. Elem. Anal. found (calc. for C₁₅H₂₀NO₃P): C, 61.78 (61.43); H, 6.94 (6.87); N, 5.00 (4.78).

CgP(2-pyrm) (L₄). 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 CH₂Cl₂ solution of the product. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 8.69 (d, ³ $J_{\rm H,H}$ = 4.9 Hz, 2H, ArH (H-4 and H 6)), 7.13 (t, ${}^{3}J_{H,H}$ = 4.9 Hz, 1H, ArH (H-5)), 2.19 (d, ${}^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH₂), 2.14 (dd, ${}^{2}J_{H,H}$ = 13.1 Hz, ${}^{3}J_{H,P}$ = 6.7 Hz, 1H, CgP CH₂), 1.92 (dd, ${}^{3}J_{H,P}$ = 25.2 Hz, ${}^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH₂), 1.78 (d, ${}^{3}J_{H,P}$ = 12.0 Hz, 3H, CgP CH₃), 1.72 (d, ${}^{3}J_{H,P}$ = 12.7 Hz, 3H, CgP CH₃), 1.66 (dd, ${}^{2}J_{H,H}$ = 13.3 Hz, ${}^{3}J_{H,P}$ = 4.7 Hz, 1H, CgP CH₂), 1.42 (s, 3H, CgP CH₃), 1.27 (s, 3H, CgP CH_3). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ_C 174.8 (d, ¹ $J_{C,P}$ = 9.7 Hz, ArC (C-2)), 156.1 (d, ${}^{2}J_{C,P}$ = 5.0 Hz, ArC (C-4 and C-6)), 119.3 (s, ArC (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 CH₂), 38.5 (d, ${}^{2}J_{C,P}$ = 1.9 Hz, CgP CH₂), 28.7 (d, ${}^{2}J_{C,P}$ = 19.3 Hz, CgP CH₃), 28.1 (s, CgP CH_3), 27.9 (s, CgP CH_3), 27.6 (d, ${}^2J_{C,P}$ = 10.2 Hz, CgP CH_3). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, CDCl₃): δ_P –18.5 (s, CgP). HRMS (EI): m/z calc. for $C_{14}H_{19}N_2O_3P [M]^+ = 294.1133$; obs. = 294.1137. Elem. Anal. found (calc. for C₁₄H₁₉N₂O₃P): 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 CH₂Cl₂ solution of the product. ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 8.53 (d, ${}^{3}J_{H,H} = 5.0$ Hz, 1H, ArH (H-6)), 7.77 (s, 1H, ArH (H-3)), 7.02 (d, ${}^{3}J_{H,H} = 5.0$ Hz, 1H, ArH (H-5)), 2.34 (s, 3H, Ar–CH₃), 2.07 (dd, ${}^{2}J_{H,H}$ = 13.2 Hz, ${}^{3}J_{H,P}$ = 6.7 Hz, 1H, CgP CH₂), 1.91 (dd, ${}^{3}J_{H,P}$ = 23.4 Hz, ${}^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH₂), 1.83 (d, ${}^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH₂), 1.57 (d, ${}^{3}J_{H,P}$ = 12.4 Hz, 3H, CgP CH₃), 1.50 (dd, ${}^{2}J_{H,H}$ = 13.3 Hz, ${}^{3}J_{H,P}$ = 4.1 Hz, 1H, CgP CH₂), 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 CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃): $\delta_{\rm C}$ 160.4 (d, ¹J_{C,P} = 12.7 Hz, ArC (C-2)), 149.9 (d, ${}^{3}J_{C,P}$ = 14.2 Hz, ArC (C-6)), 146.5 (d, ${}^{3}J_{C,P}$ = 1.8 Hz, ArC (C-4)), 130.2 (d, ${}^{2}J_{C,P}$ = 10.5 Hz, ArC (C-3)), 124.0 (s, ArC (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 CH₂), 37.5 (d, ${}^{2}J_{C,P}$ = 2.1 Hz, CgP CH₂), 28.2 (s, CgP CH₃), 28.0 (s, CgP CH₃), 27.9 (d, ${}^{3}J_{C,P}$ = 20.6 Hz, CgP CH₃), 27.3 (d, ${}^{3}J_{C,P}$ = 11.7 Hz, CgP CH₃), 21.4 (s, Ar-CH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta_{\rm P}$ -24.5 (s, CgP). 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 CHCl₃ solution. ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 7.78 (d, ³ $J_{\rm H,H}$ = 7.7 Hz, 1H, ArH (H-3)), 7.51 (t, ³ $J_{\rm H,H}$ = 7.7 Hz, 1H, ArH (H-4)), 7.06 (d, ² $J_{\rm H,H}$ = 8.2 Hz, 1H, ArH (H-5)), 2.54 (s, 3H, Ar–CH₃), 2.07 (dd, ² $J_{\rm H,H}$ = 13.2 Hz, ³ $J_{\rm H,P}$ = 6.7 Hz, 1H, CgP CH₂), 1.89 (dd, ³ $J_{\rm H,P}$ = 23.1 Hz, ² $J_{\rm H,H}$ = 13.2 Hz, 1H, CgP CH₂), 1.82 (d, ² $J_{\rm H,H}$ = 13.3 Hz, 1H, CgP CH₂), 1.55 (dd, ² $J_{\rm H,H}$ = 13.3 Hz, ³ $J_{\rm H,P}$ = 4.1 Hz, 1H, CgP CH₂), 1.55

(d, ${}^{3}J_{H,P} = 12.3$ Hz, 3H, CgP CH₃), 1.41 (d, ${}^{3}J_{H,P} = 12.5$ Hz, 3H, CgP CH₃), 1.40 (s, 3H, CgP CH₃), 1.35 (s, 3H, CgP CH₃). ${}^{13}C\{{}^{1}H\}$ NMR (126 MHz, CDCl₃): δ_{C} 160.1 (d, ${}^{1}J_{C,P} = 10.7$ Hz, ArC (C-6)), 158.9 (d, ${}^{3}J_{C,P} = 14.4$ Hz, ArC (C-2)), 135.6 (d, ${}^{3}J_{C,P} = 1.2$ Hz, ArC (C-4)), 126.2 (d, ${}^{2}J_{C,P} = 8.4$ Hz, ArC (C 3)), 122.6 (s, ArC (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 CH₂), 37.6 (d, ${}^{2}J_{C,P} = 2.1$ Hz, CgP CH₂), 28.2 (s, CgP CH₃), 28.0 (s, CgP CH₃), 27.9 (d, ${}^{2}J_{C,P} = 20.4$ Hz, CgP CH₃), 27.3 (d, ${}^{2}J_{C,P} = 11.8$ Hz, CgP CH₃), 24.3 (s, Ar–CH₃). ${}^{31}P\{{}^{1}H\}$ NMR (162 MHz, CDCl₃): $\delta_{P} - 24.9$ (s, CgP). HRMS (ESI): m/z calc. for C₁₆H₂₃NO₃P [M + H]⁺ = 308.1410; obs. = 308.1404. Elem. Anal. found (calc. for C₁₆H₂₂NO₃P): 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 CH2Cl2 solution of the product. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 8.88 (d, ${}^{3}J_{H,H} = 5.0$ Hz, 1H, ArH (H-6)), 8.23 (s, 1H, ArH (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 CH₂), 1.94 (dd, ${}^{3}J_{H,P}$ = 23.6 Hz, ${}^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH₂), 1.69 (d, ${}^{2}J_{H,H}$ = 13.4 Hz, 1H, CgP CH₂), 1.59 (d, ${}^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH₃), 1.54 (dd, ${}^{2}J_{H,H}$ = 13.3 Hz, ${}^{3}J_{H,P}$ = 4.2 Hz, 1H, CgP CH₂), 1.43 (s, 3H, CgP CH₃), 1.42 (d, ${}^{3}J_{H,P}$ = 12.8 Hz, 3H, CgP CH₃), 1.36 (s, 3H, CgP CH₃). ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CDCl₃): $\delta_{\rm C}$ 163.5 (d, ${}^{1}J_{\rm C,P}$ = 18.1 Hz, ArC (C-2)), 150.9 (d, ${}^{3}J_{C,P}$ = 13.1 Hz, ArC (C-6)), 137.8 (q, ${}^{2}J_{C,F}$ = 33.9 Hz, ArC (C-4)), 124.8 (dq, ${}^{2}J_{C,P}$ = 10.0 Hz, ${}^{3}J_{C,F}$ = 3.5 Hz, ArC (C-3)), 122.9 (q, ${}^{1}J_{C,F}$ = 273.5 Hz, Ar–*C*F₃), 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 CH₂), 37.6 (d, ${}^{2}J_{C,P}$ = 2.0 Hz, CgP CH_2), 28.0 (s, CgP CH_3), 27.7 (s, CgP CH_3), 27.8 (d, ${}^2J_{C,P}$ = 20.6 Hz, CgP CH₃), 27.3 (d, ${}^{2}J_{C,P}$ = 11.4 Hz, CgP CH₃). 19 F NMR (377 MHz, CDCl₃): $\delta_{\rm F}$ -64.8 (s, Ar-CF₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ_P –24.2 (s, CgP). HRMS (EI): m/z calc. for $C_{16}H_{19}F_{3}NO_{3}P[M]^{+} = 361.1055$; obs. = 361.1057. Elem. Anal. found (calc. for C₁₆H₁₉F₃NO₃P): C, 53.01 (53.19); H, 5.37 (5.30); N, 3.96 (3.88).

CgP(6-CF₃-2-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 CH₂Cl₂ solution of the product. ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 8.06 (d, ³ $J_{\rm H,H}$ = 7.9 Hz, 1H, ArH (H-3)), 7.81 (t, ${}^{3}J_{H,H}$ = 8.2 Hz, 1H, ArH (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 CH₂), 1.95 (dd, ${}^{3}J_{H,P}$ = 23.9 Hz, ${}^{2}J_{H,H}$ = 13.3 Hz, 1H, CgP CH₂), 1.94 (d, ${}^{2}J_{H,H}$ = 13.4 Hz, 1H, CgP CH₂), 1.57 (d, ${}^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH₃), 1.58-1.54 (m, 1H CgP CH₂), 1.48 (d, ${}^{3}J_{H,P}$ = 12.8 Hz, 3H, CgP CH₃), 1.42 (s, 3H, CgP CH₃), 1.34 (s, 3H, CgP CH₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): $\delta_{\rm C}$ 162.4 (d, ${}^{1}J_{C,P}$ = 21.0 Hz, ArC (C-2)), 148.6 (qd, ${}^{2}J_{C,F}$ = 34.6 Hz, ${}^{3}J_{C,P}$ = 10.8 Hz, ArC (C-6)), 136.6 (d, ${}^{3}J_{C,P}$ = 2.4 Hz, ArC (C-4)), 131.9 (d, ${}^{2}J_{C,P}$ = 13.7 Hz, ArC (C-3)), 121.5 (q, ${}^{1}J_{C,F}$ = 274.5 Hz, Ar–CF₃), 119.4 (q, ${}^{3}J_{C,F}$ = 2.7 Hz, ArC (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*H₂), 37.7 (d, ${}^{2}J_{C,P} = 2.0$ Hz, CgP *C*H₂), 28.0 (s, CgP *C*H₃), 27.9 (s, CgP *C*H₃), 27.8 (d, ${}^{2}J_{C,P} = 20.0$ Hz, CgP *C*H₃), 27.4 (d, ${}^{2}J_{C,P} = 11.4$ Hz, CgP *C*H₃). ¹⁹F NMR (377 MHz, CDCl₃): $\delta_{F} -68.1$ (s, Ar–CF₃). ³¹P {¹H} NMR (162 MHz, CDCl₃): $\delta_{P} -23.6$ (s, CgP). HRMS (EI): *m/z* calc. for C₁₆H₁₉F₃NO₃P [M]⁺ = 361.1055; obs. = 361.1058. Elem. Anal. found (calc. for C₁₆H₁₉F₃NO₃P): C, 53.32 (53.19); H, 5.38 (5.30); N, 3.75 (3.88).

CgP(4-SiMe₃-2-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 CH₂Cl₂ solution of the product. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 8.64 (d, ³ $J_{\rm H,H}$ = 4.7 Hz, 1H, ArH (H-3)), 8.11 (br s, 1H, ArH (H-6)), 7.30 (d, ${}^{3}J_{H,H} = 4.7$ Hz, 1H, ArH (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 CH₂), 1.57 (d, ${}^{3}J_{H,P}$ = 12.4 Hz, 3H, CgP CH₃), 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 CH₃), 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 $(CH_3)_3$). ¹³C $\{^{1}H\}$ NMR (126 MHz, CDCl₃): $\delta_{\rm C}$ 159.6 (d, ${}^{1}J_{\rm C,P}$ = 13.5 Hz, ArC (C-2)), 149.8 (s, ArC (C-4)), 149.1 (d, ${}^{2}J_{C,P}$ = 13.4 Hz, ArC (C-3)), 133.9 (d, ${}^{3}J_{C,P} = 9.1$ Hz, ArC (C-6)), 127.3 (s, ArC (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 CH_2), 37.5 (d, ${}^2J_{C,P}$ = 2.1 Hz, CgP CH_2), 28.2–27.8 (m, CgP CH_3), 27.3 (d, ${}^{2}J_{C,P}$ = 11.6 Hz, CgP CH_3), 1.6 (s, Si(CH_3)₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta_{\rm P}$ –26.9 (s, CgP). HRMS (ESI): m/z calc. for C₁₈H₂₉NO₃PSi $[M + H]^+$ = 366.1649; obs. = 366.1662. Elem. Anal. found (calc. for C₁₈H₂₈NO₃PSi): C, 59.55 (59.15); H, 7.89 (7.72); N, 4.02 (3.83).

CgP(6-SiMe₃-2-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 CH₂Cl₂ solution of the product. ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 7.71 (d, ³ $J_{\rm H,H}$ = 7.9 Hz, 1H, ArH (H-3)), 7.50 (t, ${}^{3}J_{H,H}$ = 7.7 Hz, 1H, ArH (H-4)), 7.38 (d, ${}^{3}J_{H,H}$ = 7.5 Hz, 1H, ArH (H-5)), 2.15 (d, ${}^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH₂), 2.10 (dd, ${}^{2}J_{H,H}$ = 13.2 Hz, ${}^{3}J_{H,P}$ = 6.5 Hz, 1H, CgP CH₂), 1.91 (dd, ${}^{3}J_{H,P}$ = 23.5 Hz, ${}^{2}J_{H,H}$ = 13.2 Hz, 1H, CgP CH₂), 1.57–1.51 (m, 3H, CgP CH₃ and 1H CgP CH₂), 1.47 (d, ${}^{3}J_{H,P}$ = 12.5 Hz, 3H, CgP CH₃), 1.42 (s, 3H, CgP CH₃), 1.33 (s, 3H, CgP CH₃), 0.30 (s, 9H, Si(CH₃)₃). ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃): $\delta_{\rm C}$ 167.0 (d, ${}^{3}J_{\rm C,P}$ = 10.0 Hz, Ar*C* (C-6)), 160.5 (d, ${}^{1}J_{\rm C,P}$ = 13.4 Hz, ArC (C-2)), 133.0 (d, ${}^{3}J_{C,P}$ = 3.2 Hz, ArC (C-4)), 128.4 (d, ${}^{2}J_{C,P}$ = 17.2 Hz, ArC (C-3)), 127.4 (s, ArC (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 CH_2), 37.7 (d, ${}^{2}J_{C,P}$ = 2.0 Hz, CgP CH_2), 28.1 (s, CgP CH_3), 28.0 (s, CgP *C*H₃), 27.9 (d, ${}^{2}J_{C,P}$ = 19.9 Hz, CgP *C*H₃), 27.4 (d, ${}^{2}J_{C,P}$ = 11.6 Hz, CgP CH₃), 1.6 (s, Si(CH₃)₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ_P –26.9 (s, CgP). HRMS (ESI): m/z calc. for $C_{18}H_{29}NO_3PSi [M + H]^+ = 366.1649; obs. = 366.1651. Elem.$ Anal. found (calc. for C₁₈H₂₈NO₃PSi): 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 cm³) with TsOH·H₂O (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 L₂ (0.157 g, 0.537 mmol) in CH₂Cl₂ (2 cm³) was added to a solution of [PtCl₂(cod)] (0.100 g, 0.267 mmol) in CH_2Cl_2 (2 cm³) and stirred for 24 hours. In air, the product was then precipitated in hexane $(ca. 25 \text{ cm}^3)$. 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. ¹H NMR (500 MHz, CD_2Cl_2): δ_H 8.76 (d, ${}^{3}J_{H,H}$ = 4.9 Hz) and 8.76 (d, ${}^{3}J_{H,H}$ = 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, ArH (H-4)), 7.32-7.26 (m, 2H, ArH (H-5)), 3.04 (dt, ${}^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) and 2.95 (dt, ${}^{2}J_{H,H}$ = 13.6 Hz, $J_{\rm H,P}$ = 2.3 Hz) (total 2H, CgP CH₂), 1.98–1.86 (m, 3H, CgP CH₂), 1.85 (vir t, $J_{H,P}$ = 6.2 Hz) and 1.80 (vir t, $J_{H,P}$ = 6.2 Hz) (total 6H, CgP CH₃), 1.74 (vir t, $J_{H,P}$ = 6.7 Hz) and 1.69 (vir t, $J_{\rm H,P}$ = 6.7 Hz) (total 6H, CgP CH₃), 1.66–1.59 (m, 1H, CgP CH₂), 1.39 (s) and 1.34 (s) (total 6H, CgP CH₃), 1.27 (s) and 1.26 (s) (total 6H, CgP CH₃). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): $\delta_{\rm C}$ 154.2 (vir t, $J_{C,P}$ = 154.1 Hz, ArC (C-2)), 149.6 (app q, $J_{C,P}$ = 8.4 Hz, ArC (C-6)), 134.7 (app q, J_{C,P} = 3.3 Hz, ArC (C-4)), 130.7 (app q, $J_{C,P}$ = 8.3 Hz, ArC (C-3)), 123.9 (s, ArC (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 CH₂), 41.9-41.8 (m, CgP CH₂), 27.9 (s, CgP CH₃), 27.7 (s, CgP CH₃), 27.6 (br s) and 27.2 (br s) (CgP CH₃), 26.0 (vir t, $J_{C,P}$ = 2.0 Hz) and 25.8 (vir t, $J_{C,P}$ = 2.5 Hz) (CgP CH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): $\delta_{\rm P}$ -0.6 (s, ${}^{1}J_{P,Pt}$ = 2740 Hz) and -1.1 (s, ${}^{1}J_{P,Pt}$ = 2727 Hz) (CgP). 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 C₃₀H₄₀Cl₂N₂O₆P₂Pt): C, 42.64 (42.26); H, 5.13 (4.73); N, 3.44 (3.29).

 $[PtCl_2(L_4)_2]$ (1b). A solution of L₄ (0.033 g, 0.110 mmol) in CH₂Cl₂ (1 cm³) was added to a solution of [PtCl₂(cod)] (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm³) 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. ¹H NMR (500 MHz, CD₂Cl₂): $\delta_{\rm H}$ 8.76 (d, ${}^{3}J_{\rm H,H}$ = 4.9 Hz) and 8.75 (d, ${}^{3}J_{H,H}$ = 4.9 Hz) (total 4H, Ar*H* (H-4 and H-6)), 7.25–7.22 (m, 2H, ArH (H-5)), 3.16 (d of vir t, ${}^{2}J_{H,H}$ = 13.7 Hz, $J_{H,P}$ = 1.8 Hz) and 3.13 (d of vir t, ${}^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH₂), 2.29 (d, ${}^{3}J_{H,H}$ = 13.8 Hz) and 2.21 (d, ${}^{3}J_{H,H}$ = 13.8 Hz) (total 2H, CgP CH₂), 1.92-1.83 (m, 12H, CgP CH₃), 1.82-1.70 (m, 4H, CgP CH₃), 1.37 (s) and 1.35 (s) (total 6H, CgP CH₃), 1.20 (s, 6H, CgP CH₃). ${}^{13}C{}^{1}H$ NMR (126 MHz, CD₂Cl₂): $\delta_{\rm C}$ 168.0 (vir t, $J_{\rm C,P}$ = 46.1 Hz, ArC (C-2)), 156.2 (vir t, $J_{\rm C,P}$ = 5.6 Hz) and 156.1 (vir t, $J_{C,P}$ = 5.6 Hz) (ArC (C-4 and C-6)), 121.3 (s, ArC (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 CH₂), 42.6-42.4 (m, CgP CH₂), 27.9 (s, CgP CH₃), 27.7

(s) and 27.6 (s) (CgP *C*H₃), 27.4 (vir t, $J_{C,P} = 2.4$ Hz) and 27.3 (vir t, $J_{C,P} = 2.4$ Hz) (CgP *C*H₃), 26.7 (br s) and 26.6 (br s) (CgP *C*H₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): $\delta_P - 0.8$ (s, ¹ $J_{P,Pt} = 2707$ Hz) and -0.9 (s, ¹ $J_{P,Pt} = 2706$ Hz) (Cg*P*). HRMS (ESI): *m*/z calc. for C₂₈H₃₈ClN₄O₆P₂Pt [M - Cl]⁺ = 818.1600; obs. = 818.1606. Elem. Anal. found (calc. for C₂₈H₃₈Cl₂N₄O₆P₂Pt): C, 39.66 (39.35); H, 4.57 (4.48); N, 6.34 (6.56).

 $[PtCl_2(L_{5a})_2]$ (1c). A solution of L_{5a} (0.018 g, 0.058 mmol) in CH_2Cl_2 (1 cm³) 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 cm³). 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 CH₂Cl₂ solution of the product. rac: meso compounds observed in 3:2 ratio. ¹H NMR (500 MHz, CD₂Cl₂): $\delta_{\rm H}$ 8.60 (d, ³ $J_{\rm H,H}$ = 5.0 Hz) and 8.58 (d, ${}^{3}J_{H,H} = 5.0$ Hz) (total 2H, ArH (H-6)), 7.89 (br s) and 7.86 (br s) (total 2H, ArH (H-3)), 7.14 (d, ${}^{3}J_{H,H}$ = 4.7 Hz) and 7.10 (d, ${}^{3}J_{H,H}$ = 5.0 Hz) (total 2H, ArH (H-5)), 3.05 (d of vir t, ${}^{2}J_{\rm H,H}$ = 13.6 Hz, $J_{\rm H,P}$ = 2.1 Hz) and 2.95 (d of vir t, ${}^{2}J_{\rm H,H}$ = 13.6 Hz, $J_{H,P} = 2.1$ Hz) (total 2H, CgP CH₂), 2.38 (s) and 2.35 (s) (total 6H, Ar-CH₃), 2.05-2.02 (m, 1H, CgP CH₂), 1.98-1.88 (m, 2H, CgP CH₂), 1.84 (vir t, $J_{H,P}$ = 6.2 Hz) and 1.80 (vir t, $J_{H,P}$ = 6.2 Hz) (total 6H, CgP CH₃), 1.73 (vir t, $J_{H,P}$ = 6.6 Hz) and 1.68 (vir t, $J_{H,P}$ = 6.6 Hz) (total 6H, CgP CH₃), 1.65–1.56 (m, 3H, CgP CH₂), 1.39 (s) and 1.34 (s) (total 6H, CgP CH₃), 1.27 (s) and 1.26 (s) (total 6H, CgP CH₃). ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CD₂Cl₂): $\delta_{\rm C}$ 159.3 (vir t, $J_{{\rm C},{\rm P}}$ = 34.6 Hz, ArC (C-2)), 149.8 (vir t, $J_{{\rm C},{\rm P}}$ = 8.7 Hz) and 149.6 (vir t, J_{C,P} = 8.7 Hz) (ArC (C-6)), 146.9-146.7 (br s, ArC (C-4)), 132.2 (vir t, $J_{C,P}$ = 8.7 Hz) and 132.0 (vir t, $J_{C,P}$ = 8.7 Hz) (ArC (C-3)), 125.6 (s, ArC (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 CH₂), 42.4 (s) and 42.3 (s) (CgP CH₂), 27.8 (s, CgP CH₃), 27.64 (s) and 27.56 (s) (CgP CH₃), 27.5 (br s) and 27.4 (br s) (CgP CH₃), 26.1 (vir t, $J_{C,P}$ = 2.2 Hz) and 25.9 (vir t, $J_{C,P} = 2.4 \text{ Hz}$ (CgP CH₃), 21.7 (s) and 21.6 (s) (Ar–CH₃). ³¹P{¹H} NMR (162 MHz, CD_2Cl_2): $\delta_P - 0.6$ (s, ${}^{1}J_{P,Pt} = 2738$ Hz) and -1.0(s, ${}^{1}J_{P,Pt}$ = 2729 Hz) (CgP). 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 C₃₂H₄₄Cl₂N₂O₆P₂Pt): C, 43.47 (43.64); H, 5.07 (5.04); N, 3.19 (3.18).

[PtCl₂(L_{5b})₂] (1d). A solution of L_{5b} (0.017 g, 0.055 mmol) in CH₂Cl₂ (1 cm³) was added to a solution of [PtCl₂(cod)] (0.010 g, 0.027 mmol) in CH₂Cl₂ (1 cm³) and stirred for 24 hours. In air, the product was then precipitated in hexane (*ca.* 25 cm³). 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 CH₂Cl₂ solution of the product. *rac* : *meso* compounds observed in 3 : 2 ratio. ¹H NMR (500 MHz, CD₂Cl₂): $\delta_{\rm H}$ 7.87–7.84 (m, 2H, Ar*H* (H-3)),

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7.58-7.53 (m, 2H, ArH (H-4)), 7.16-7.12 (m, 2H, ArH (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 CH₂), 2.62 (s) and 2.57 (s) (total 6H, Ar–CH₃), 2.17 (d, ${}^{2}J_{H,H}$ = 13.7 Hz, 1H, CgP CH₂), 1.90-1.87 (m, 2H, CgP CH₂) 1.85 1.70 (m, 12H, CgP CH₃), 1.64–1.60 (m, 3H, CgP CH₂), 1.37 (s) and 1.34 (s) (total 6H, CgP CH₃), 1.25 (s, 6H, CgP CH₃). ¹³C{¹H} 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) (ArC (C-6)), 153.7 (vir t, $J_{C,P}$ = 34.8 Hz) and 153.6 (vir t, $J_{C,P}$ = 35.6 Hz) (ArC (C-2)), 135.4-135.3 (m, ArC (C-4)), 128.7 (vir t, $J_{\rm C,P}$ = 9.3 Hz) and 128.5 (vir t, $J_{\rm C,P}$ = 8.2 Hz) (ArC (C-3)), 124.2 (s) and 124.1 (s) (ArC (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 CH₂), 42.5 (s) and 42.4 (s) (CgP CH₂), 27.9 (s, CgP CH₃), 27.8 (s) and 27.6 (s) (CgP CH₃), 27.7 (br s) and 27.4 (br s) (CgP CH₃), 26.4 (vir t, $J_{C,P}$ = 2.4 Hz) and 26.0 (vir t, $J_{C,P}$ = 2.4 Hz) (CgP CH₃), 24.8 (s) and 24.7 (s) (Ar-CH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): $\delta_{\rm P}$ -1.2 (s, ${}^{1}J_{P,Pt}$ = 2731 Hz) and -1.5 (s, ${}^{1}J_{P,Pt}$ = 2723 Hz) (CgP). 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 C₃₂H₄₄Cl₂N₂O₆P₂Pt): 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 cm³) was added to a solution of [PtCl₂(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 cm³). 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 CH₂Cl₂ solution of the product. rac: meso compounds observed in 3:1 ratio. ¹H NMR (500 MHz, CD₂Cl₂): $\delta_{\rm H}$ 8.96 (d, ${}^{3}J_{\rm H,H}$ = 5.0 Hz) and 8.93 (d, ${}^{3}J_{H,H} = 5.0 \text{ Hz}$) (total 2H, ArH (H-6)), 8.29 (br s) and 8.26 (br s) (total 2H, ArH (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, ArH (H-5)), 3.02 (d of vir t, ${}^{2}J_{H,H}$ = 13.7 Hz, $J_{\rm H,P}$ = 2.3 Hz) and 2.93 (d of vir t, ${}^{2}J_{\rm H,H}$ = 13.7 Hz, $J_{\rm H,P}$ = 2.4 Hz) (total 2H, CgP CH₂), 1.98-1.86 (m, 4H, CgP CH₂), 1.84-1.71 (m, 12H, CgP CH₃), 1.69-1.67 (m, 2H, CgP CH₂), 1.41 (s) and 1.36 (s) (total 6H, CgP CH₃), 1.28 (s, 6H, CgP CH₃). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): $\delta_{\rm C}$ 156.9 (vir t, $J_{\rm C,P}$ = 33.7 Hz, ArC (C-2)), 151.0 (vir t, $J_{C,P}$ = 8.2 Hz, ArC (C-6)), 137.3 (q of vir t, ${}^{2}J_{C,F}$ = 33.9 Hz, $J_{C,P}$ = 3.6 Hz, ArC (C-4)), 126.8–126.6 (m, ArC (C-3)), 123.2 (q, ${}^{1}J_{C,F}$ = 273.5 Hz, Ar-CF₃), 118.4 (q, ${}^{3}J_{C,F}$ = 3.5 Hz, ArC (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 CH_2), 42.5 (s, CgP CH_2), 27.9 (s, CgP CH₃), 27.7 (s) and 27.6 (s) (CgP CH₃), 27.5 (br s) and 27.4 (br s) (CgP CH₃), 26.0 (vir t, $J_{C,P}$ = 2.5 Hz) and 25.9 (vir t, $J_{C,P}$ = 2.5 Hz) (CgP CH₃). ¹⁹F NMR (377 MHz, CD₂Cl₂): $\delta_{\rm F}$ -65.13 (s) and -65.16 (s) (Ar-CF₃). ³¹P{¹H} NMR (162 MHz, CD_2Cl_2 : δ_P 1.2 (s, ${}^1J_{P,Pt}$ = 2759 Hz) and 0.7 (s, ${}^1J_{P,Pt}$ = 2750 Hz) (CgP). 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 cm³) was added to a solution of [PtCl₂(cod)] (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm³) and stirred for 24 hours. In air, the product was then precipitated in hexane (ca. 25 cm³). 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. ¹H NMR (500 MHz, CD_2Cl_2): δ_H 8.30 (d, ${}^{3}J_{H,H}$ = 8.0 Hz) and 8.25 (d, ${}^{3}J_{H,H} = 8.0 \text{ Hz}$) (total 2H, ArH (H-3)), 7.90 (t, ${}^{3}J_{H,H} = 8.0 \text{ Hz}$) and 7.85 (d, ${}^{3}J_{H,H}$ = 8.0 Hz) (total 2H, ArH (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, ArH (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 CH₂), 2.16 (d, ${}^{2}J_{H,H}$ = 13.8 Hz) and 2.14 (d, ${}^{2}J_{H,H}$ = 13.8 Hz) (total 2H, CgP CH₂), 1.95-1.84 (m, 2H, CgP CH₂), 1.78-1.68 (m, 14H, CgP CH₃ and CH₂), 1.41 (s) and 1.36 (s) (6H, CgP CH₃), 1.27 (br s, 6H, CgP CH₃). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): $\delta_{\rm C}$ 156.1 (vir t, $J_{\rm C,P}$ = 32.0 Hz) and 156.0 (vir t, J_{C,P} = 32.5 Hz) (ArC (C-2)), 148.1 (vir t, $J_{\rm C,P}$ = 7.3 Hz) and 147.8 (vir t, $J_{\rm C,P}$ = 7.8 Hz) (ArC (C-6)), 136.7 (vir t, $J_{C,P}$ = 5.6 Hz, ArC (C-4)), 134.2 (vir t, $J_{C,P}$ = 9.5 Hz, ArC (C-3)), 121.9 (q, ${}^{1}J_{C,F} = 274.0$ Hz) and 121.8 (q, ${}^{1}J_{C,F} = 274.4$ Hz) (Ar-CF₃), 121.2 (br s) and 121.1 (br s) (ArC (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 CH₂), 42.4 (s) and 42.3 (s) (CgP CH_2), 27.8 (s, CgP CH_3), 27.7 (s) and 27.6 (s) (CgP CH₃), 27.2 (s) and 27.71 (s) (CgP CH₃), 26.2 (br s, CgP CH₃). ¹⁹F NMR (470 MHz, CD₂Cl₂): $\delta_{\rm F}$ –68.4 (s) and –68.5 (s) (Ar–CF₃). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): $\delta_{\rm P}$ 0.2 (s, ¹J_{P,Pt} = CgP). HRMS (ESI): m/zcalc. 2756 for Hz, $C_{32}H_{38}Cl_2F_6N_2NaO_6P_2Pt [M + Na]^+ = 1010.1029; obs. =$ 1010.1027. Elem. Anal. found (calc. for C₃₂H₃₈Cl₂F₆N₂O₆P₂Pt): 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 cm³) was added to a solution of $[PtCl_2(cod)]$ (0.020 g, 0.053 mmol) in CH_2Cl_2 (1 cm³) and stirred for 24 hours. In air, the product was then precipitated in hexane (ca. 25 cm³). 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 CH2Cl2 solution of the product. rac: meso compounds observed in 1:1 ratio. ¹H 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, ArH (H-3)), 8.19–8.17 (m) and 8.15–8.13 (m) (total 2H, ArH (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, ArH (H-5)), 3.07 (d of vir t, ${}^{2}J_{\rm H,H}$ = 13.6 Hz, $J_{\rm H,P}$ = 2.3 Hz) and 2.97 (d of vir t, ${}^{2}J_{\rm H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH₂), 2.04 (d, ² $J_{H,H}$ = 13.7 Hz) and 1.93 (d, ${}^{2}J_{H,H}$ = 13.5 Hz, 2H, CgP CH₂), 1.92–1.85 (m, 2H, CgP CH₂), 1.82 (vir t, $J_{H,P}$ = 6.2 Hz) and (vir t, $J_{H,P}$ = 6.1 Hz) (total 6H, CgP CH₃), 1.72 (vir t, $J_{H,P}$ = 6.6 Hz) and 1.68

(vir t, $J_{H,P}$ = 6.6 Hz) (total 6H, CgP CH₃), 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 CH₃), 1.26 (s) and 1.25 (s) (total 6H, CgP CH₃), 0.30 (s) and 0.28 (s) (total 18H, Si(CH₃)₃). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2): δ_C 153.5 (vir t, $J_{C,P}$ = 33.7 Hz, ArC (C-2)), 149.8–149.7 (m, ArC (C-4)), 149.0-148.8 (m, ArC (C-3)), 135.7-135.5 (m, ArC (C-6)), 128.9 (br s, ArC (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 CH₂), 42.4 (m, CgP CH₂), 28.0 (s, CgP CH₃), 27.8 (s) and 27.7 (s) (CgP CH₃), 27.6 (br s) and 27.5 (br s) (CgP CH₃), 26.1 (br s) and 25.9 (br s) (CgP CH_3), -1.59 (s) and -1.62 (s) (Si(CH_3)₃). ³¹P{¹H} NMR (162 MHz, CD_2Cl_2): $\delta_P - 0.8$ (s, ${}^1J_{P,Pt} = 2728$ Hz) and -1.3(s, ${}^{1}J_{P,Pt} = 2647$ Hz) (CgP). 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 C₃₆H₅₆Cl₂N₂O₆P₂PtSi₂): C, 43.61 (43.37); H, 5.80 (5.66); N, 2.95 (2.81).

[PtCl₂(L_{7b})₂] (1h). A solution of L_{7b} (0.040 g, 0.110 mmol) in CH_2Cl_2 (1 cm³) was added to a solution of [PtCl₂(cod)] (0.020 g, 0.053 mmol) in CH₂Cl₂ (1 cm³) and stirred for 24 hours. In air, the product was then precipitated in hexane $(ca. 25 \text{ cm}^3)$. 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. ¹H NMR (500 MHz, CD_2Cl_2): δ_H 7.96 (d, ³ $J_{H,H}$ = 8.0 Hz) and 7.88 (d, ${}^{3}J_{H,H}$ = 8.0 Hz) (total 2H, ArH (H-3)), 7.60–7.52 (m, 2H, ArH (H-4)), 7.48 (d, ${}^{3}J_{H,H}$ = 7.4 Hz) and 7.44 (d, ${}^{3}J_{H,H}$ = 7.4 Hz) (total 2H, ArH (H-5)), 3.10–3.04 (m, 2H, CgP CH₂), 2.29 (d, ${}^{2}J_{H,H}$ = 13.6 Hz) and 2.18 (d, ${}^{2}J_{H,H}$ = 13.6 Hz) (total 2H, CgP CH₂), 1.87-1.58 (m, 16H, CgP CH₃ CH₂), 1.36 (s) and 1.33 (s) (total 6H, CgP CH₃), 1.26 (s) and 1.25 (s) (total 6H, CgP CH₃), 0.33 (s) and 0.32 (s) (total 18H, Si(CH₃)₃). ${}^{13}C_1^{(1)}H_1^{(1)}$ NMR (126 MHz, CD_2Cl_2): δ_C 169.0 (br s) and 168.8 (br s) (ArC (C-6)), 155.1 (s) and 155.0 (s) (ArC (C-2)), 133.0-132.8 (m, ArC (C-4)), 130.4 (vir t, $J_{C,P}$ = 10.2 Hz) and 130.2 (vir t $J_{C,P}$ = 9.7 Hz) (ArC (C-3)), 128.9 (s) and 128.8 (s) (ArC (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 CH₂), 42.4 (s) and 42.3 (s) (CgP CH₂), 28.0 (s, CgP CH₃), 27.8 (s) and 27.7 (s) (CgP CH₃), 27.4 (br s) and 27.3 (br s) (CgP CH₃), 26.4 (br s) and 26.3 (br s) (CgP CH₃), -1.56 (s) and -1.57 (s) (Si(CH₃)₃). ${}^{31}P{}^{1}H{}$ NMR (202 MHz, CD_2Cl_2): $\delta_P - 1.6$ (s, ${}^{1}J_{P,Pt} = 2722$ Hz) and -1.9(s, ${}^{1}J_{P,Pt}$ = 2724 Hz) (CgP). 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 C₃₆H₅₆Cl₂N₂O₆P₂PtSi₂): 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 CH₂Cl₂ (1 cm³) and the mixture stirred. The reaction was monitored over 24 hours by ³¹P NMR spectroscopy (see text for details).

 $[PtCl(\kappa^{1}-L_{2})(\kappa^{2}-L_{2})]BF_{4}$ (3 $[BF_{4}]$). AgBF₄ (0.003 g, 0.015 mmol) was added to a CH₂Cl₂ solution (2 cm³) 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%). ¹H NMR (400 MHz, CD₂Cl₂): $\delta_{\rm H}$ 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 C*H*₃ and CgP C*H*₂). ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂): $\delta_{\rm B}$ –2.1 (s, *BF*₄). ¹⁹F NMR (377 MHz, CD₂Cl₂): $\delta_{\rm F}$ –152.8 (s, *BF*₄). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): $\delta_{\rm P}$ 0.8 (d, ²*J*_{P,P} = 11.8 Hz, ¹*J*_{P,Pt} = 3514 Hz, monodentate Cg*P*). -48.1 (d, ²*J*_{P,P} = 11.6 Hz, ¹*J*_{P,Pt} = 2947 Hz, chelate Cg*P*). HRMS (ESI): *m*/z calc. for C₃₀H₄₀ClN₂O₆P₂Pt [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 cm³) was added to a solution of $[PdCl_2(cod)]$ (0.050 g, 0.175 mmol) in CH_2Cl_2 (2 cm³) and stirred for 24 hours. In air, the product was then precipitated in hexane (ca. 25 cm³). 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. ¹H NMR (500 MHz, CD_2Cl_2): δ_H 8.73 (d, ${}^{3}J_{H,H}$ = 4.3 Hz) and 8.71 (d, ${}^{3}J_{H,H}$ = 4.4 Hz) (total 2H, Ar*H* (H-6)), 8.01 (d, ${}^{3}J_{H,H}$ = 4.4 Hz, 2H, ArH (H-3)), 7.70–7.66 (m, 2H, ArH (H-4)), 7.29 (appq, ${}^{3}J_{H,H} = 4.4$ Hz, 2H, ArH (H-5)), 3.04 (d of vir t, ${}^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) and 2.96 (d of vir t, ${}^{2}J_{H,H}$ = 13.6 Hz, $J_{H,P}$ = 2.3 Hz) (total 2H, CgP CH₂), 2.24 (s) and 2.35 (s) (total 1H, CgP CH₂), 1.99-1.89 (m, 3H, CgP CH₂), 1.84 (vir t, $J_{H,P}$ = 6.3 Hz) and 1.80 (vir t, $J_{\rm H,P}$ = 6.3 Hz) (total 6H, CgP CH₃), 1.73 (vir t, $J_{\rm H,P}$ = 6.8 Hz) and 1.70 (vir t, J_{H,P} = 6.6 Hz) (total 6H, CgP CH₃), 1.59–1.54 (m, 2H, CgP CH₂), 1.38 (s) and 1.35 (s) (total 6H, CgP CH₃), 1.27 (s, 6H, CgP CH₃). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): $\delta_{\rm C}$ 155.6 (vir t, $J_{\rm C,P}$ = 30.4 Hz) and 156.0 (vir t, $J_{C,P}$ = 29.7 Hz) (ArC (C-2)), 150.1 (app q, $J_{C,P}$ = 8.0 Hz, ArC (C-6)), 135.4 (br s, ArC (C-4)), 131.1 (vir t, $J_{C,P}$ = 8.7 Hz) and 130.1 (vir t, $J_{C,P}$ = 8.2 Hz) (ArC (C 3)), 124.5 (s, ArC (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 CH₂), 42.5-42.4 (m, CgP CH₂), 28.2 (br s) and 28.1 (br s) (CgP CH₃), 27.8 (s, CgP CH₃), 27.73 (s) and 27.68 (s) (CgP CH₃), 26.8 (vir t, $J_{C,P}$ = 2.5 Hz) and 26.6 (vir t, $J_{C.P}$ = 2.7 Hz) (CgP CH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): $\delta_{\rm P}$ 4.4 (s) and 4.3 (s) (CgP). HRMS (ESI): m/z calc. for $C_{30}H_{40}ClN_2O_6P_2Pd$ [M - Cl]⁺ = 727.1088; obs. = 727.1103. Elem. Anal. found (calc. for C₃₀H₄₀Cl₂N₂O₆P₂Pd): C, 47.16 (47.17); H, 5.29 (5.28); N, 3.85 (3.67).

 $[PdCl(\kappa^{1}-L_{2})(\kappa^{2}-L_{2})]BF_{4}$ (5 $[BF_{4}]$). AgBF₄ (0.008 g, 0.039 mmol) was added to a CH₂Cl₂ solution (3 cm³) 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

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CH₂Cl₂ solution of the product. ¹H NMR (500 MHz, CD₂Cl₂): δ_H 8.92-8.89 (m, 1H, ArH), 8.79-8.78 (m, 1H, ArH), 8.41-8.36 (m, 1H, ArH), 8.06-8.02 (m, 2H, ArH), 7.87-7.79 (m, 2H, ArH), 7.79-7.47 (m, 1H, ArH), 2.43-1.27 (m, 32H, CgP CH₃ and CgP CH₂). ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂): $\delta_{\rm B}$ -2.2 (s, BF₄). $^{19}\mathrm{F}$ NMR (377 MHz, CD₂Cl₂): δ_{F} –152.8 (s, BF₄). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121 MHz, CD_2Cl_2): δ_P 28.8 (br s, monodentate CgP), -42.1 (d, ${}^{2}J_{P,P}$ = 3.2 Hz, chelate CgP). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD₂Cl₂, -90 °C): $\delta_{\rm P}$ 28.8 (d, ${}^{2}J_{\rm P,P}$ = 3.2 Hz, monodentate CgP), -42.0 (br s, chelate CgP). 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 C₃₀H₄₀BClF₄N₂O₆P₂Pd·CH₂Cl₂): C, 41.79 (41.36); H, 4.86 (4.70); N, 3.20 (3.11) (the presence of CH₂Cl₂ was confirmed by ¹H NMR spectroscopy and was observed in the crystal structure).

Protonation studies

TsOH·H₂O (0.003 g, 0.015 mmol) was added to a suspension of **4** (0.010 g, 0.013 mmol) in CD₂Cl₂ (0.7 cm³), upon which the solution became homogeneous, yielding species assigned to the protonated species **6**. ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ_P 6.0 (br s, CgP) and 3.7 (br s, CgP). An analogous procedure in MeOH (0.7 cm³) also gave a homogenous solution, assigned to be a mixture of **6** and a P,N-chelate species related to 5[OTs]. ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ_P 28.8 (br s, monodentate CgP), 6.3 (br s, CgP) and 4.5 (br s, CgP), -42.2 (br s, chelate CgP).

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 N2. Solutions of Pd(OAc)2 (0.0055 mmol) in MeOH (0.5 $\text{cm}^3)$ and TsOH·H2O (0.22 mmol) in MeOH (0.5 cm³) 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 CDCl₃ and analysed by ¹H NMR spectroscopy. Conversion and selectivity was determined by integration of the phenylacetylene alkynyl proton ($\delta_{\rm H}$ 3.10 ppm) and the methyl atropate ($\delta_{\rm H}$ 6.38 and 5.90 ppm) and methyl cinnamate ($\delta_{\rm H}$ 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-K α radiation ($\lambda = 0.71073$ 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.

Acknowledgements

The Bristol Chemical Synthesis Centre for Doctoral Training (BCS CDT) funded by the Engineering and Physical Sciences Research Council (EPSRC) (EP/G036764/1) and the University of Bristol are thanked for a PhD studentship (to T. A. S.).

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