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PAPER

A recyclable perfluoroalkylated PCP pincer palladium complex†‡

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A new fluorous PCP pincer ligand has been coordinated to Ni(II), Pd(II) and Pt(II). The air stable palladium complex, which promotes Heck reactions between methyl acrylate and either aryl bromides or iodides, can be recovered intact by fluorous solid-phase extraction and was reused four times in the Heck reaction between methyl acrylate and 4-bromoacetophenone without loss in catalytic activity.

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Introduction

Since Horváth and Rábai's seminal paper on fluorous biphase catalysis in 1994, fluorous chemistry has continued to evolve and offer new approaches for designing recyclable catalysts.[1,2] In fluorous biphase catalysis it is essential that the catalysts contain >60% fluorine by molecular weight in order to give good liquid/liquid separation between organic and perfluorocarbon solvents. On the other hand, "light fluorous" molecules normally require <50% fluorine by molecular weight and so, the cost of the fluorous catalyst can be reduced by minimising the number of fluorous ponytails attached to the catalyst. The other advantages of the "light fluorous" approach over fluorous biphase catalysis are that the "light fluorous" catalysts can be used in conventional organic solvents, thus avoiding the use of the expensive perfluorocarbon solvents, they can be recovered and recycled efficiently by solid-phase extraction on fluorous reverse phase silica gel, and similar, if not better, catalytic activity can be achieved with the perfluoroalkylated catalyst compared to the parent, non-fluorinated catalyst. In 2003 we reported the first example of a "light fluorous" catalyst, which promoted additions of 1,3-diketones to ethyl cyanoformate in dichloromethane and the perfluoroalkylated nickel catalyst was recovered by solid-phase extraction on fluorous reverse phase silica gel.[3] Although "light fluorous" catalysis has been applied successfully to a number of organic-based catalysts,[4] there have been relatively few reports on the recycling of metal-based catalysts by fluorous solid-phase extraction.[5]

Homogeneous palladium catalysts are one of the most versatile and useful tools in an organic chemist's armoury for the synthesis of carbon–carbon bonds offering a range of versatile reactions.[6] Tridentate palladium pincer complexes offer unique advantages over conventional palladium catalysts, [$Pd(OAc)_2/PPh_3$], because the metal–carbon σ-bond is responsible for the high stability of the pincer complex preventing, at least to a large extent, the metal dissociating from the ligand (leaching) and giving a high degree of thermal stability.[7] Since much of our early work on fluorous biphase catalysis had concentrated on the applications of perfluoroalkylated phosphines,[8] we were interested in synthesising a "light fluorous" pincer PCP ligand and evaluating fluorous solid-phase extraction as a separation technique for recycling the palladium complex.

There have been a few reports on the synthesis and applications of pincer complexes incorporating perfluoroalkyl groups (Fig. 1). In 1998 the first fluorous NCN nickel complexes **1** were tested in the Kharash addition between carbon tetrachloride and methyl methacrylate, but they were not sufficiently soluble in perfluorocarbon solvents for them to be investigated under fluorous biphasic conditions.[9a] In the same study, a ruthenium PCP pincer complex **2** was synthesised, but there have been no reports of catalysis with this metal complex.[9b] More recently, fluorous PCP complexes containing aliphatic perfluoroalkyl phosphines (**3** and **4**) were prepared, but again, there have been no reports about the catalytic applications of these complexes.[10] In contrast, Curran synthesised the fluorous SCS pincer palladium complex **5** which was used successfully to catalyse a number of Heck reactions between aromatic iodides or bromides with either methyl acrylate or styrene in dimethylacetamide under microwave conditions.[5c] The light fluorous catalyst was recycled three times by fluorous solid-phase extraction but only 75–83% of the catalyst was recovered after each cycle, probably as a result of handling such small amounts of catalyst (42 mg). Gladysz has also reported the straightforward syntheses of a family of fluorous SCS pincer palladium complexes **6** and demonstrated that they can be used as catalyst precursors for promoting the Heck reaction between iodobenzene and methyl acrylate.[10c] Unfortunately, it was not possible to recycle the fluorous palladium complexes and the active catalysts were believed to be palladium nanoparticles. In this paper we report the synthesis of a stable fluorous PCP palladium complex, which promotes Heck reactions and can be recycled efficiently by fluorous solid-phase extraction.[11]

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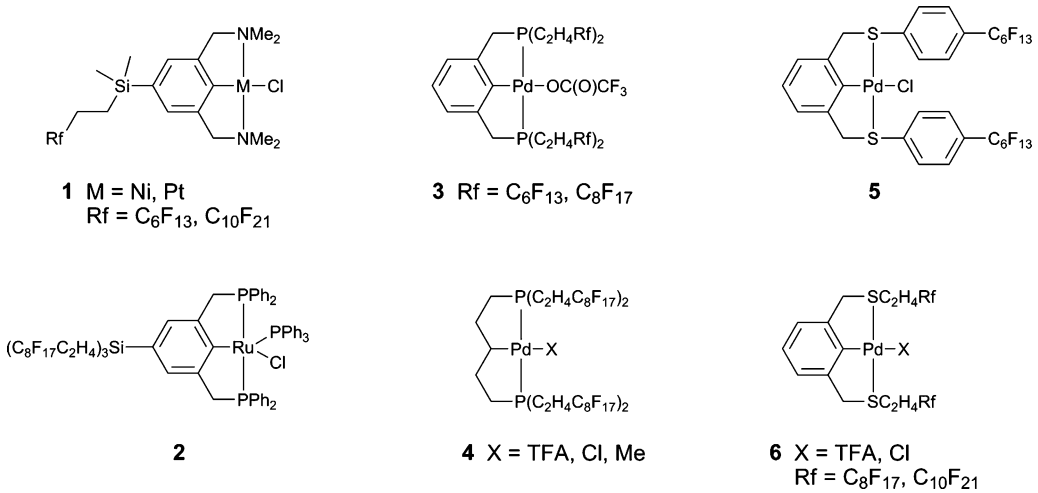


Fig. 1 Previously reported perfluoroalkylated pincer complexes.

Results and discussion

Synthesis and coordination chemistry of the fluorous pincer ligand 9

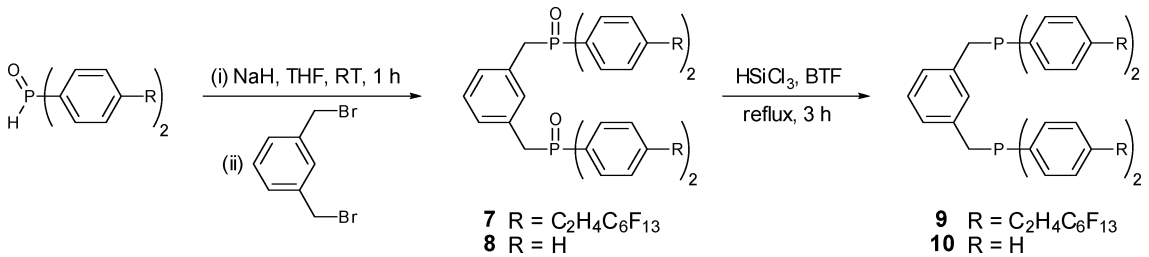
The syntheses of the fluorous and non-fluorous pincer phosphine ligands **9** and **10** are shown in Scheme 1. After reacting *bis*(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenyl)phosphine oxide[12] with sodium hydride for 1 h, 1,3-*bis*(bromomethyl)benzene was added and the reaction mixture was stirred at room temperature overnight to afford the perfluoroalkylated pincer phosphine oxide **7** in 82% yield. In the second step **7** was reduced by refluxing with an excess of trichlorosilane in benzotrifluoride for 3 h.[13] After removing the excess of trichlorosilane, a basic work-up was used to isolate the perfluoroalkylated pincer phosphine **9**. The non-fluorinated PCP pincer ligand **10** was also prepared by the same protocol (overall yield 88%) for direct comparison with the fluorous ligand **9**.

The PCP ligands **9** and **10** were coordinated to nickel, palladium and platinum by refluxing with either $[NiCl_2.6H_2O]$, $[PdCl_2(CH_3CN)_2]$ or $[PtCl_2(COD)]$ in 2-methoxyethanol (Scheme 2).[14] All of the complexes were fully characterised by ^1H, ^{31}P and ^{19}F NMR spectroscopy, elemental analysis, mass spectrometry and infrared spectroscopy. In the ^1H NMR spectra of all of the complexes, the benzylic protons appeared as a virtual triplet at approximately 3.8 ppm, which collapsed to a singlet in the $^1H\{^{31}P\}$ NMR spectra and is characteristic of the benzylic protons coupling with 2 phosphorus atoms held in a *trans*-arrangement. $^{31}P\{^1H\}$ NMR data for the fluorous and non-fluorous metal complexes show only very small differences in Δ_P, which is the difference in the chemical shift between the metal complex and the free ligand, between the fluorous and non-fluorous complexes indicating that there are negligible differences in the binding properties of the complexes and that the phosphorus donor atoms are insulated effectively from the electron-withdrawing effects of the perfluoroalkyl groups.

Crystals of the non-fluorinated nickel complex **12**, suitable for X-ray crystallography, were grown by slow diffusion of hexane into a dichloromethane solution of **12** and the molecular structure is shown in Fig. 2. The coordination geometry around the nickel centre is distorted square planar since the three donor atoms of the ligand, C(1), P(1) and P(2), are held in two fused five-membered chelate rings. In fact, the two chelating rings are quite strained with a small C(1)–Ni(1)–P angle (average 82.5°) which distorts the P(1)–Ni(1)–P(2) angle to 164.81° (see ESI†).

Catalysis and recycling studies of the fluorous palladium pincer complex 13

Since there are no reports of the non-fluorinated palladium pincer complex catalysing a Heck reaction, a Design of Experiment software package was used to optimise the reaction conditions for the Heck reaction between bromobenzene and methyl acrylate, and a range of solvents, organic and inorganic bases were screened (see ESI†). With a 1 mole % catalyst loading the optimum conditions were *N*-methyl-2-pyrrolidone (NMP) in combination with potassium hydrogen carbonate (1 equivalent)



Scheme 1 Syntheses of PCP pincer ligands **9** and **10**.

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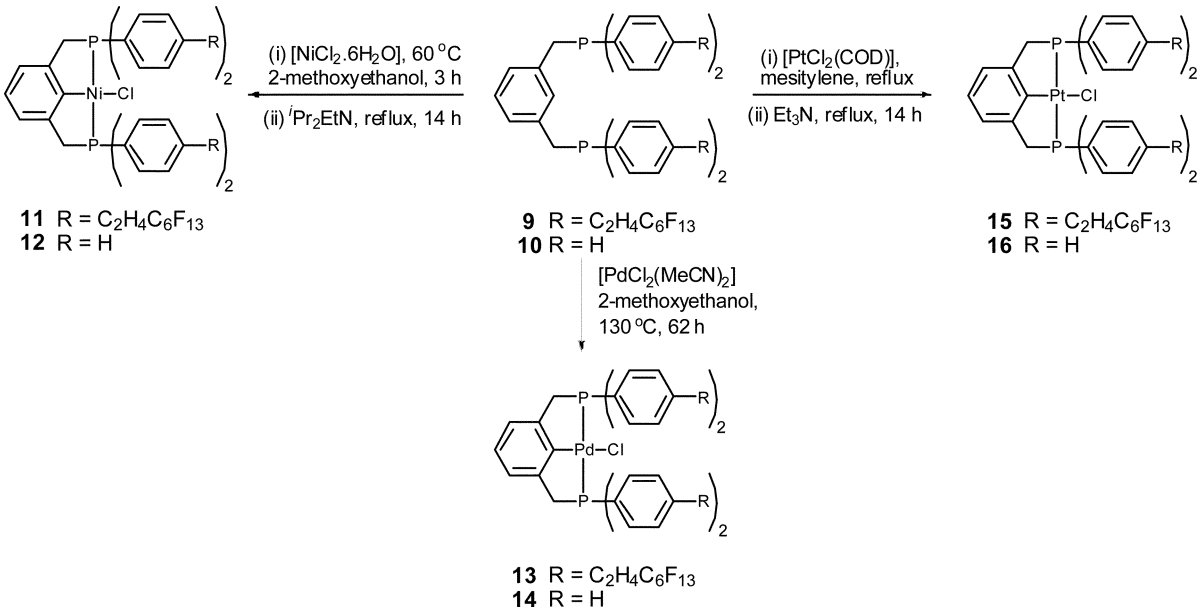

Scheme 2 Coordination chemistry of the PCP pincer ligands **9** and **10**.

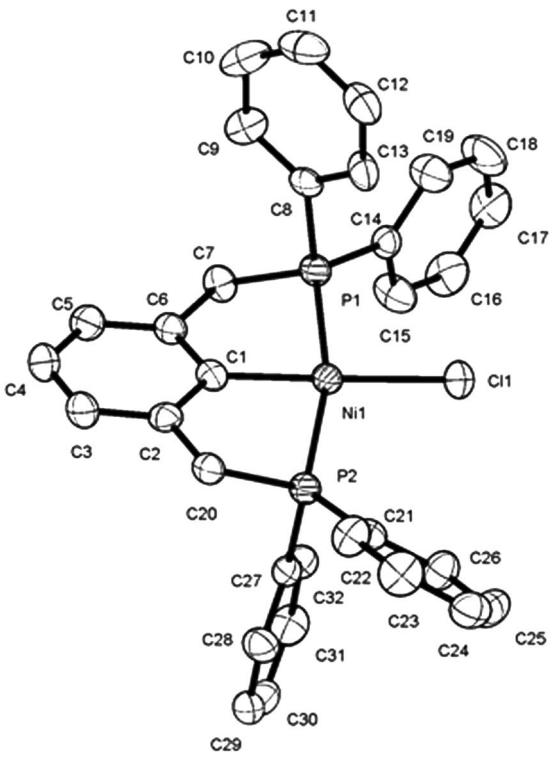

Fig. 2 The molecular structure of [NiCl(PCP)] **12** showing 50% displacement ellipsoids. The hydrogen atoms have been omitted for clarity.

and tetra-*n*-butylammonium bromide (TBAB, 0.2 equivalents) at 120 °C. Under these optimum conditions the fluorous and non-fluorous palladium pincer complexes, **13** and **14**, were tested in a range of Heck reactions to evaluate their versatility towards different substrates (Table 1). Initially, a series of aryl iodides and aryl bromides were all reacted successfully. Marginally better yields were obtained with the fluorous catalyst **13** for the benzene and acetophenone substrates, but the non-fluorous catalyst **14** was much superior for the anisoles.

The Heck reaction between 4-bromoacetophenone and methyl acrylate was investigated in more detail and the catalytic activities of the two palladium complexes were compared directly by monitoring the reaction by GC over a 6 h timeframe (Fig. 3). Under these reaction conditions the perfluoroalkylated palladium pincer complex **13** was slightly more active with the reaction complete after 4 h compared to 6 h for the non-fluorinated palladium complex **14**. Unfortunately, neither of the palladium complexes were able to promote the Heck reaction between 4-chloroacetophenone and methyl acrylate under the reaction conditions used.

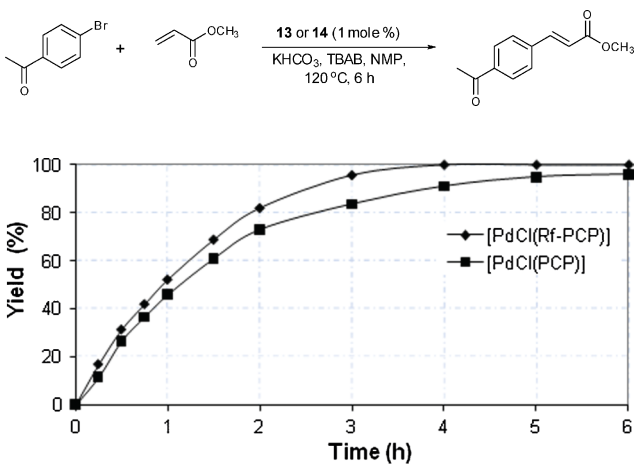

Fig. 3 Rate of formation of Heck product.

Only the perfluoroalkylated palladium complex **13** could be recycled using fluorous solid-phase extraction. After removing the solvent by Kugelröhr distillation, the resulting solid was dissolved in acetonitrile and loaded onto a short column of fluorous reverse phase silica gel which had been preconditioned

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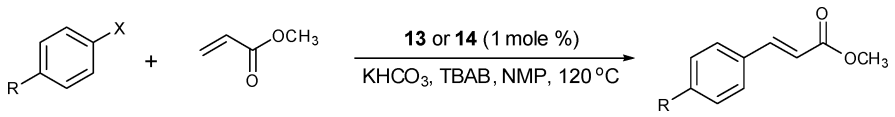
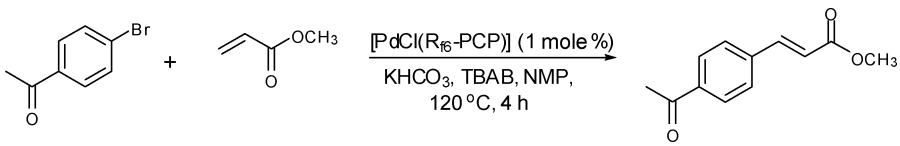
Table 1 Optimised Heck reaction conditions applied to a range of substrates



Substrate				
R	X	Catalyst	Time (h)	Yield (%)[a]
CH_3CO	I	**13** [PdCl(R_{f6}-PCP)]	5	>98
CH_3CO	I	**14** [PdCl(PCP)]	5	87
H	I	**13** [PdCl(R_{f6}-PCP)]	5	91
H	I	**14** [PdCl(PCP)]	5	81
CH_3O	I	**13** [PdCl(R_{f6}-PCP)]	5	66
CH_3O	I	**14** [PdCl(PCP)]	5	>98
CH_3CO	Br	**13** [PdCl(R_{f6}-PCP)]	5	>98
CH_3CO	Br	**14** [PdCl(PCP)]	5	>98
H	Br	**13** [PdCl(R_{f6}-PCP)]	24	82
H	Br	**14** [PdCl(PCP)]	24	79
CH_3O	Br	**13** [PdCl(R_{f6}-PCP)]	24	57
CH_3O	Br	**14** [PdCl(PCP)]	24	>98

[a] Determined by GC.

Table 2 Recycling results of **13** in the Heck reaction



Run	Catalyst used (mg)	Recovered catalyst (mg)[a]	Yield[b] (%)	Accumulative TON[c]	Pd leaching (%)[d]
1	50.0	48.2 (96%)	>99	99	0.19
2[e]	48.2	45.0 (93%)	>99	198[f]	0.06
3[e]	45.0	40.5 (90%)	>99	297[f]	0.05
4[e]	40.5	36.4 (90%)	>99	396[f]	0.05

[a] Weight percent is shown in parenthesis. [b] Determined by GC using tolyl ether as the internal standard. [c] TON = mmol of product/mmol of catalyst. [d] Determined by ICP-OES. [e] Catalysis using **13** from the previous run. [f] Accumulative TON = TON from reaction + TON from previous reaction(s).

with acetonitrile. The column was eluted with acetonitrile to give the clean organic product, and 96% of the fluorous palladium complex was recovered by elution with ethyl acetate. The column was then washed with water in order to remove the TBAB and inorganics, before preconditioning with acetonitrile to prepare the column for the next cycle.

The recovered palladium complex was reused in the next run using the same reaction conditions, except the amount of substrate was lowered in order to keep the catalyst loading at 1 mole % throughout the recycling experiments. The recycling results are summarised in Table 2, whilst Fig. 4 shows the kinetic data for each of the recycles and demonstrates clearly that there was no loss in catalytic activity over the 4 runs. An accumulative turnover number (TON) of 396 was achieved and recovery of the fluorous complex was extremely good, ranging from 90–96% of the palladium complex. ICP-OES analysis of palladium leaching in to the organic product gave a combined total of 0.35% of the total palladium for the four runs. The organic fractions were also analysed by ^1H and $^{19}F\{^1H\}$ NMR spectroscopy which revealed that there was no catalyst, ligand or oxidised ligand in the organic

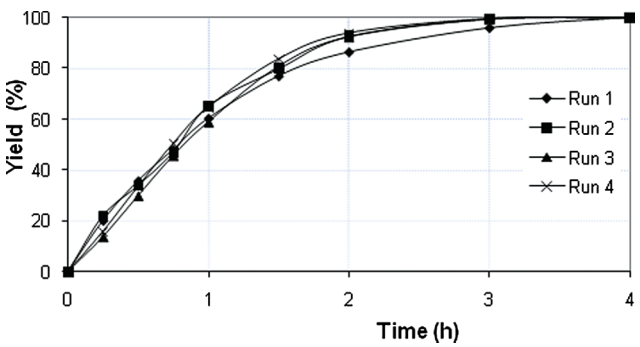


Fig. 4 Recycling results of **13** in the Heck reaction.

product. Finally, ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy of the recovered fluorous palladium complex confirmed that there was no sign of decomposition.

There is considerable evidence that palladacycles and pincer palladium complexes function as precatalysts that release highly active forms of metallic palladium which then promote the Heck

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reaction.[15,16] Kinetic studies of these systems normally show an induction period and sigmoidal kinetics.[17,18] In contrast, our kinetic studies on the palladium pincer complexes **13** and **14** in Fig. 3 and 4, have revealed that the Heck reaction occurred without an induction period. Despite this observation, however, the function of the fluorinated and non-fluorinated palladium pincer complexes in these Heck reactions is not known, but they are probably acting as precursors of ultra-low levels of soluble ligandless palladium metal. From the reaction optimisation studies with the palladium complex **14** (see ESI†), it was obvious that the incorporation of TBAB was essential for high yields in the Heck reaction with bromobenzene. Although TBAB was used initially as a phase transfer catalyst to transfer the inorganic salt into the organic solvent, it may actually be performing a secondary role since it is well established that tetraalkylammonium halides stabilise nano-sized transition metal colloids and palladium clusters stabilised by quaternary ammonium salts have been shown to be active catalysts in the Heck reaction with aryl bromides.[19] In this work, if the small amount of palladium detected in the product phase represents the actual catalyst that was released from palladium complex **13**, then these Heck reactions were promoted by about 0.003 mole % palladium. Regardless of its function, however, the perfluoroalkylated PCP pincer palladium complex **13** is an easy-to-handle, air stable complex that promotes the Heck reaction, can be recovered intact by fluorous solid-phase extraction and reused without loss in catalytic activity.

Conclusions

The novel fluorous PCP pincer ligand **9** was synthesised in two steps from *bis*(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenyl)phosphine oxide and it was straightforward to coordinate **9** to nickel, palladium and platinum. Both the fluorous and non-fluorinated palladium complexes, **13** and **14**, promoted a range of Heck reactions between methyl acrylate and either aryl iodides or bromides. Recycling was only possible with the perfluoroalkylated pincer palladium complex **13**, which was recovered and reused four times in the Heck reaction between methyl acrylate and 4-bromoacetophenone without loss in catalytic activity.

Experimental

Proton, ^{19}F and ^{13}C NMR spectroscopies were carried out on a Bruker ARX 300 spectrometer at 300.14, 282.41 and 75.5 MHz respectively. All chemical shifts are quoted in ppm using the high frequency positive convention; ^{1}H NMR spectra were referenced to external $SiMe_4$; ^{19}F NMR spectra to external $CFCl_3$ and ^{13}C NMR spectra to external $SiMe_4$. The highly coupled ^{13}C signals of the fluorinated carbons are not listed below. Elemental analyses were performed by the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. GC analyses were performed using a Perkin Elmer Clarus 500 GC using a Perkin Elmer-Elite Series PE-5 column (30 m × 0.25 mm, 5% diphenyl, 95% dimethyl polysiloxane). *Bis*(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenyl)phosphine oxide was prepared by the literature method.[12] Fluoroflash® silica gel (40 μm) was purchased from Fluorous Technologies.

Preparation of 1,3-*bis*[methyl*bis*(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenyl) phosphine oxide] benzene 7

A 250 mL, three-necked round-bottomed flask was charged with *bis*(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenyl)phosphine oxide (3.86 g, 4.31 mmol), sodium hydride (60% on oil, 0.17 g, 4.31 mmol) and dry THF (40 mL). After stirring the reaction mixture for 1 h under nitrogen, a solution of 1,3-*bis*(bromomethyl)benzene (0.55 g, 2.10 mmol) in dry THF (15 mL) was added slowly and the reaction mixture was then allowed to stir overnight at room temperature. The reaction was quenched slowly with water (1 mL) and stirred for 10 min. The organic layer was extracted with $CHCl_3$ (3 × 50 mL), dried ($MgSO_4$) and concentrated to give the crude product as a brown oil which was washed with hot petroleum ether (40–60 °C) to give **7** as a white powder (3.27 g, 82%). mp 162–164 °C (from petroleum ether). (Found C, 40.6; H, 2.1. Calc. for $C_{64}H_{40}F_{52}O_2P_2$: C, 40.65; H, 2.1); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.50 (8 H, dd, $^{3}J_{HP}$ = 11.0 Hz, $^{3}J_{HH}$ = 8.0 Hz, ArH), 7.14 (8 H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HP}$ = 1.6 Hz, ArH), 7.11 (1 H, br s, ArH-2), 6.91–6.81 (3 H, m, ArH-5 and ArH-4), 3.46 (4 H, d, $^{2}J_{HP}$ = 13.5 Hz, $PhCH_2$), 2.86–2.81 (8 H, m, CH_2), 2.34–2.17 (8 H, m, CH_2); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.50 (8 H, d, $^{3}J_{HH}$ = 8.0 Hz, ArH), 7.14 (8 H, d, $^{3}J_{HH}$ = 8.0 Hz, ArH), 7.11 (1 H, s, ArH-2), 6.91–6.81 (3 H, m, ArH-5 and ArH-4), 3.46 (4 H, s, $PhCH_2$), 2.86–2.81 (8 H, m, CH_2), 2.34–2.17 (8 H, m, CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ_F −81.13 (12 F, t, $^{4}J_{FF}$ = 9.9 Hz, CF_3), −114.82 (8 F, t, $^{4}J_{FF}$ = 13.8 Hz, α-CF_2), −122.12 (8 F, m, CF_2), −123.12 (8 F, m, CF_2), −123.78 (8 F, m, CF_2), −126.43 (8 F, m, CF_2); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 29.4 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 143.3 (C), 132.3 (t, $J_{CP} = J_{CP'}$ = 4.8 Hz, CH), 132.0 (d, J_{CP} = 10.3 Hz, CH), 131.6 (d, J_{CP} = 9.6 Hz, CH), 130.6 (d, $^{1}J_{CP}$ = 100.7 Hz, C), 128.6 (d, J_{CP} = 12.2 Hz, CH), 37.9 (d, $^{1}J_{CP}$ = 66.6 Hz, CH_2), 32.4 (t, $^{2}J_{CF}$ = 22.1 Hz, CH_2), 26.4 (CH_2); despite several attempts using different deuterated solvents and high field NMR spectroscopy, two peaks are missing in the ^{13}C NMR spectrum for the middle aromatic ring, maybe due to overlapping of the aryl peaks. *m*/*z* (FAB) 1891 (MH^+); ν_{max}/cm^{-1} (solid) 1604 (w), 1181 (br, s), 1140 (s), 1073 (s).

Preparation of 1,3-*bis*[methyldiphenylphosphine oxide]benzene 8

The title compound was prepared similarly to **7** using diphenylphosphine oxide (1.19 g, 5.87 mmol), sodium hydride (60% on oil, 0.24 g, 5.87 mmol) and 1,3-*bis*(bromomethyl)benzene (0.191 M solution in THF, 15.4 mL, 2.93 mmol). After quenching the reaction slowly with water (1 mL), the THF was removed and the residue was extracted with $CHCl_3$ (3 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated to give a white solid which was washed with hot petroleum ether (40–60 °C) to give **8** as a white solid (1.51 g, 98%). mp 91–93 °C (from petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.56 (8 H, dd, $^{3}J_{HP}$ = 8.1 Hz, $^{3}J_{HH}$ = 7.3 Hz, ArH), 7.40–7.36 (4 H, m, ArH), 7.31 (8 H, td, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HP}$ = 2.4 Hz, ArH), 6.98 (1 H, s, ArH-2), 6.88–6.83 (1 H, m, ArH-5), 6.79 (2 H, d, $^{3}J_{HH}$ = 6.8 Hz, ArH-4), 3.46 (4 H, d, $^{2}J_{HP}$ = 13.7 Hz, $PhCH_2$); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.56 (8 H, d, $^{3}J_{HH}$ = 7.3 Hz, ArH), 7.40–7.36 (4 H, m, ArH), 7.31 (8 H, t, $^{3}J_{HH}$ = 7.3 Hz, ArH), 6.98 (1 H, s, ArH-2), 6.88–6.83 (1 H, m, ArH-5), 6.79 (2 H, d, $^{3}J_{HH}$ = 6.8 Hz, ArH-4), 3.46 (4 H, s, $PhCH_2$); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 30.0 (s);^{13}C NMR (75 MHz,

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d^6-DMSO) δ_C 133.42 (d, $^1J_{CP}$ = 96.9 Hz, C), 132.26 (t, $J_{CP} = J_{CP'}$ = 4.8 Hz, CH), 131.94 (d, J_{CP} = 9.8 Hz, C), 131.51 (CH), 130.69 (d, J_{CP} = 9.4 Hz, CH), 128.48 (d, J_{CP} = 11.6 Hz, CH), 128.11 (CH), 127.54 (CH), 36.04 (d, $^1J_{CP}$ = 66.2 Hz, CH_2); *m/z* (FAB) 507.16425 (MH^+. $C_{32}H_{29}O_2P_2$ requires 507.16428); ν_{max}/cm^{-1} (solid) 3436 (br, w), 1680 (m), 1487 (s), 1160 (s), 1118 (s), 695 (s).

Preparation of 1,3-*bis*[methyl*bis*(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenyl) phosphine]benzene 9

A flame-dried 200 mL Schlenk flask was charged with **7** (4.35 g, 2.30 mmol) and BTF (20 mL). The reaction mixture was heated to reflux before trichlorosilane (2.18 g, 1.63 mL, 16.10 mmol) was added. The reaction mixture was refluxed for 3 h, cooled and the excess trichlorosilane was removed under vacuum. A solution of sodium hydroxide (3.22 g, 80.50 mmol) in water (20 mL) was added and the reaction mixture was stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to give **9** as an orange solid (1.77 g, 41%). mp 80–82 °C (from hexane). (Found C, 41.25; H, 2.2. Calc. for $C_{64}H_{40}F_{52}P_2$: C, 41.35; H, 2.2); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.19 (8 H, t, $^3J_{HH} = {}^3J_{HP}$ = 7.7 Hz, ArH), 7.04 (8 H, d, $^3J_{HH}$ = 7.7 Hz, ArH), 6.87 (1 H, t, $^3J_{HH}$ = 7.5 Hz, ArH-5), 6.78 (1 H, s, ArH-2), 6.68 (2 H, d, $^3J_{HH}$ = 7.5 Hz, ArH-4), 3.18 (4 H, s, $PhCH_2$), 2.82–2.76 (8 H, m, CH_2), 2.33–2.16 (8 H, m, CH_2); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.19 (8 H, d, $^3J_{HH}$ = 7.7 Hz, ArH), 7.04 (8 H, d, $^3J_{HH}$ = 7.7 Hz, ArH), 6.87 (1 H, t, $^3J_{HH}$ = 7.5 Hz, ArH-5), 6.78 (1 H, s, ArH-2), 6.68 (2 H, d, $^3J_{HH}$ = 7.5 Hz, ArH-4), 3.18 (4 H, s, $PhCH_2$), 2.82–2.76 (8 H, m, CH_2), 2.33–2.16 (8 H, m, CH_2); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P –11.5 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ_F –81.13 (12 F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), –114.76 (8 F, t, $^4J_{FF}$ = 13.9 Hz, α-CF_2), –122.04 (8 F, m, CF_2), –123.03 (8 F, m, CF_2), –123.62 (8 F, m, CF_2), –126.35 (8 F, m, CF_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 139.79 (C), 137.27 (d, $^2J_{CP}$ = 7.5 Hz, C), 136.56 (d, $^1J_{CP}$ = 15.4 Hz, C), 133.28 (d, J_{CP} = 18.5 Hz, CH), 131.65 (t, $J_{CP} = J_{CP'}$ = 8.5 Hz, CH), 130.48 (t, $J_{CP} = J_{CP'}$ = 6.8 Hz, CH), 128.34 (d, J_{CP} = 6.5 Hz, CH), 127.06 (d, J_{CP} = 4.0 Hz, CH), 35.98 (d, $^1J_{CP}$ = 15.7 Hz, CH_2), 32.72 (t, $^2J_{CF}$ = 22.0 Hz, CH_2), 26.21 (CH_2); *m/z* (FAB) 1858 (M^+); ν_{max}/cm^{-1} (solid) 1605 (w), 1194 (br, s), 1146 (s), 1120 (m).

Preparation of 1,3-*bis*[methyldiphenylphosphine]benzene 10

The title compound was prepared similarly to **9** using **8** (1.48 g, 2.82 mmol), trichlorosilane (2.68 g, 2.00 mL, 19.67 mmol) and BTF (20 mL) to give **10** as a colourless oil (1.21 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.65–7.58 (8 H, m, ArH), 7.50–7.48 (12 H, m, ArH), 7.22 (1 H, s, ArH-2), 7.19 (1 H, m, ArH-5), 7.06 (2 H, d, $^3J_{HH}$ = 7.8 Hz, ArH-4), 3.56 (4 H, s, $PhCH_2$); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.65–7.58 (8 H, m, ArH), 7.50–7.48 (12 H, m, ArH), 7.22 (1 H, s, ArH-2), 7.19 (1 H, m, ArH-5), 7.06 (2 H, d, $^3J_{HH}$ = 7.8 Hz, ArH-4), 3.56 (4 H, s, $PhCH_2$); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P –9.9 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 138.47 (d, $^1J_{CP}$ = 15.4 Hz, C), 137.47 (d, $^2J_{CP}$ = 7.7 Hz, C), 133.02 (d, J_{CP} = 18.4 Hz, CH), 131.90 (CH), 131.32 (d, J_{CP} = 9.0 Hz, CH), 130.61 (t, $J_{CP} = J_{CP'}$ = 6.8 Hz, CH), 128.78 (CH), 128.48 (d, J_{CP} = 6.5 Hz, CH), 36.03 (d, $^1J_{CP}$ = 15.8 Hz, CH_2); *m/z* (FAB) 475.17441 (M^+. $C_{32}H_{29}P_2$ requires 475.17445); ν_{max}/cm^{-1} (solid) 1673 (m), 1489 (s), 1163 (s), 1101 (s), 892 (m).

Preparation of {2,6-*bis*[methyl(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenylphosphino)]phenyl}nickel chloride 11

A 50 mL Schlenk flask was charged with **9** (0.753 g, 0.41 mmol), $NiCl_2.6H_2O$ (0.052 g, 0.41 mmol) and 2-methoxyethanol (20 mL). The colour changed instantly from green to purple. The reaction mixture was heated to 60 °C for 3 h before di*iso*propylethylamine (0.063 g, 0.49 mmol) was added carefully and the reaction mixture was refluxed overnight. Within 5 min the colour had changed from purple to golden yellow. The solvent was removed and the product was recrystallised from ethanol to isolate **11** as lime green crystals (0.55 g, 69%). mp 113–115 °C (from EtOH). (Found C, 39.4; H, 2.15. Calc. for $C_{64}H_{39}F_{52}ClP_2Ni$: C, 39.4; H, 2.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.73 (8 H, dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HP}$ = 5.1 Hz, ArH), 7.16 (8 H, d, $^3J_{HH}$ = 8.2 Hz, ArH), 7.07 (2 H, d, $^3J_{HH}$ = 6.7 Hz, ArH-4), 6.89–6.80 (1 H, m, ArH-5), 3.77 (4 H, vt, J_{HP} = 4.7 Hz, $PhCH_2$), 2.90–2.81 (8 H, m, CH_2), 2.40–2.19 (8 H, m, CH_2); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.73 (8 H, d, $^3J_{HH}$ = 8.2 Hz, ArH), 7.16 (8 H, d, $^3J_{HH}$ = 8.2 Hz, ArH), 7.07 (2 H, d, $^3J_{HH}$ = 6.7 Hz, ArH-4), 6.89–6.80 (1 H, m, ArH-5), 3.77 (4 H, s, $PhCH_2$), 2.90–2.81 (8 H, m, CH_2), 2.40–2.19 (8 H, m, CH_2); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 33.9 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ_F –80.81 (12 F, t, $^4J_{FF}$ = 9.4 Hz, CF_3), –114.60 (8 F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), –121.88 (8 F, m, CF_2), –122.87 (8 F, m, CF_2), –123.46 (8 F, m, CF_2), –126.15 (8 F, m, CF_2); *m/z* (FAB) 1915 ($M–Cl)^+$; ν_{max}/cm^{-1} (solid) 1204 (br, s), 1187 (s), 1141 (s), 1119 (s), 697 (m).

Preparation of {2,6-*bis*[methyl(diphenylphosphino)]phenyl}nickel chloride 12

The title compound was prepared similarly to **11**, using **10** (0.890 g, 1.88 mmol), $NiCl_2.6H_2O$ (0.428 g, 1.80 mmol), di*iso*propylethylamine (0.291 g, 2.25 mmol) and 2-methoxyethanol (20 mL). Recrystallisation from ethanol isolated **12** as a dark yellow powder (0.76 g, 75%). Crystals suitable for X-ray crystallography were grown by slow diffusion of hexane into a solution of DCM containing **12**. mp 280–282 °C (from ethanol). (Found C, 67.6; H, 4.7. Calc. for $C_{32}H_{27}ClP_2Ni$: C, 67.7; H, 4.8); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.87–7.73 (8 H, m, ArH), 7.42–7.25 (12 H, m, ArH), 6.89 (3 H, s, ArH), 3.78 (4 H, vt, J_{HP} = 3.8 Hz, $PhCH_2$); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.78 (8 H, d, $^3J_{HH}$ = 6.6 Hz, ArH), 7.40–7.25 (12 H, m, ArH), 6.89 (3 H, s, ArH), 3.78 (4 H, s, $PhCH_2$); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 34.8 (s); *m/z* (FAB) 566.06305 (M^+. $C_{32}H_{27}ClP_2Ni$ requires 566.06296), 531 ($M–Cl)^+$; ν_{max}/cm^{-1} (solid) 2929 (w), 1463 (m), 1171 (m), 741 (m).

Crystal data for 12†

$C_{32}H_{27}ClNiP_2$, M = 567.64, monoclinic, space group $P2_1/n$, a = 10.146(4) Å, b = 15.988(7) Å, c = 16.899(7) Å, α = 90°, β = 105.768(8)°, γ = 90°, U = 2638.0(18) Å^3 (by least-squares refinement), T = 150(2) K, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, Z = 4, D_c = 1.429 mg m^{-3}, $F(000)$ = 1176, dimensions 0.20 mm × 0.16 mm × 0.08 mm, μ(Mo-Kα) = 0.978 mm^{-1}, empirical absorption correction, maximum and minimum transmission factors of 0.928 and 0.604 respectively,

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Bruker APEX 2000 CCD diffractometer, data collection range $1.79 < \theta < 26.00°$, $-12 \le h \le 12$, $-19 \le k \le 19$, $-20 \le l \le 20$, no crystal decay was detected; 20 425 reflections were measured and 5182 were unique ($R_{int} = 0.0789$), final $R_1 = 0.0591$, w$R_2 = 0.1210$ (0.0865 and 0.1308 respectively for all the data). The final residual Fourier map showed peaks of 0.881 and −0.548 e Å^{-3}.

Structure solution and refinement

Structure solution by direct methods and structure refinement on F^2 employed SHELXTL version 6.10.[20] Hydrogen atoms were included in calculated positions (C–H = 0.95–099 Å) riding on the bonded atom with isotropic displacement parameters set to 1.2 Ueq(C) for all H atoms. All non-H atoms were refined with anisotropic displacement parameters. The data were corrected for Lorentz and polarization effects.

Preparation of {2,6-*bis*[methyl(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenylphosphino)]phenyl}palladium chloride 13

A 50 mL Schlenk flask was charged with **9** (1.77 g, 0.95 mmol), [$PdCl_2(MeCN)_2$] (0.25 g, 0.95 mmol) and 2-methoxyethanol (20 mL). The reaction mixture was heated to 130 °C for 62 h. After cooling the reaction mixture to room temperature, the solvent was removed. The crude material was dissolved in $CHCl_3$, filtered to remove any palladium metal and the solvent was removed to give an orange solid which was washed with hexane (3 × 10 mL). The product **13** was obtained as a yellow/orange powder (1.01 g, 53%). mp 140–142 °C (from $CHCl_3$). (Found C, 38.4; H, 2.0. Calc. for $C_{64}H_{39}F_{52}ClP_2Pd$: C, 38.4; H, 2.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.74 (8 H, dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HP}$ = 5.7 Hz, ArH), 7.18 (8 H, d, $^3J_{HH}$ = 7.7 Hz, ArH), 7.05 (2 H, d, $^3J_{HH}$ = 7.5 Hz, ArH-4), 6.98–6.93 (1 H, m, ArH-5), 3.88 (4 H, vt, J_{HP} = 4.7 Hz, $PhCH_2$), 2.87–2.80 (8 H, m, CH_2), 2.36–2.18 (8 H, m, CH_2); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.74 (8 H, d, $^3J_{HH}$ = 8.0 Hz, ArH), 7.18 (8 H, d, $^3J_{HH}$ = 7.7 Hz, ArH), 7.05 (2 H, d, $^3J_{HH}$ = 7.5 Hz, ArH-4), 6.98–6.93 (1 H, m, ArH-5), 3.88 (4 H, s, $PhCH_2$), 2.87–2.80 (8 H, m, CH_2), 2.36–2.18 (8 H, m, CH_2); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 32.7 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ_F −81.00 (12 F, t, $^4J_{FF}$ = 11.3 Hz, CF_3), −114.67 (8 F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), −121.94 (8 F, m, CF_2), −122.95 (8 F, m, CF_2), −123.57 (8 F, m, CF_2), −126.29 (8 F, m, CF_2); *m*/*z* (FAB) 1963 (M–Cl)$^+$; ν_{max}/cm^{-1} (solid) 1191 (br, s), 1142 (s), 1086 (m), 1073 (m).

Preparation of {2,6-*bis*[methyl(diphenylphosphino)]phenyl}palladium chloride 14

The title compound was prepared similarly to **13**, using **10** (0.620 g, 1.31 mmol), [$PdCl_2(MeCN)_2$] (0.300 g, 1.16 mmol) and 2-methoxyethanol (20 mL). The product **14** was obtained as a yellow powder (0.65 g, 91%). mp 250 °C (dec.) (from hexane). (Found C, 62.3; H, 4.5. Calc. for $C_{32}H_{27}ClP_2Pd$: C, 62.5; H, 4.4); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.83–7.70 (8 H, m, ArH), 7.35–7.29 (12 H, m, ArH), 7.04 (2 H, d, $^3J_{HH}$ = 7.3 Hz, ArH-4), 6.95 (1 H, m, ArH-5), 3.89 (4 H, vt, J_{HP} = 4.7 Hz, $PhCH_2$); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.83–7.70 (8 H, m, ArH), 7.35–7.29 (12 H, m, ArH), 7.04 (2 H, d, $^3J_{HH}$ = 7.3 Hz, ArH-4), 6.95 (1 H, m, ArH-5), 3.89 (4 H, s, $PhCH_2$); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 33.5 (s); *m*/*z* (FAB) 577.06248 ((M–Cl)$^+$. $C_{32}H_{27}P_2Pd$ requires 577.06240); ν_{max}/cm^{-1} (solid) 1484 (s), 1435 (m), 1102 (m), 1025 (m), 958 (m), 846 (m), 741 (m), 691 (s).

Preparation of {2,6-*bis*[methyl(4-1*H*,1*H*,2*H*,2*H*-perfluorooctylphenylphosphino)]phenyl} platinum chloride 15

A 50 mL Schlenk flask was charged with **9** (0.700 g, 0.38 mmol), [$PtCl_2$(COD)] (0.141 g, 0.38 mmol) and mesitylene (250 mL). The reaction mixture was refluxed before triethylamine (0.046 g, 0.45 mmol) was added carefully. After refluxing the reaction mixture overnight, it was cooled to room temperature and filtered through Celite. The solvent was removed and the residue was purified by recrystallisation from DCM–hexane to give pure **15** as colourless crystals (0.31 g, 40%). mp 128–130 °C (from hexane). (Found C, 36.7; H, 2.0. Calc. for $C_{64}H_{39}F_{52}ClP_2Pt$: C, 36.8; H, 1.9); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.77 (8 H, m, ArH), 7.20 (8 H, d, $^3J_{HH}$ = 8.0 Hz, ArH), 7.03 (2 H, d, $^3J_{HH}$ = 7.0 Hz, ArH-4), 6.98–6.92 (1 H, m, ArH-5), 3.81 (4 H, vt, J_{HP} = 4.7 Hz, $PhCH_2$), 2.90–2.79 (8 H, m, CH_2), 2.37–2.18 (8 H, m, CH_2); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.77 (8 H, d, $^3J_{HH}$ = 8.0 Hz, ArH), 7.20 (8 H, d, $^3J_{HH}$ = 8.0 Hz, ArH), 7.03 (2 H, d, $^3J_{HH}$ = 7.0 Hz, ArH-4), 6.98–6.92 (1 H, m, ArH-5), 3.81 (4 H, br s, $PhCH_2$), 2.90–2.79 (8 H, m, CH_2), 2.37–2.18 (8 H, m, CH_2); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 32.3 (s, $^1J_{PPt}$ = 2971 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ_F −81.00 (12 F, t, $^4J_{FF}$ = 9.8 Hz, CF_3), −114.67 (8 F, t, $^4J_{FF}$ = 13.6 Hz, α-CF_2), −121.95 (8 F, m, CF_2), −122.96 (8 F, m, CF_2), −123.59 (8 F, m, CF_2), −126.26 (8 F, m, CF_2); *m*/*z* (FAB) 2087 (M$^+$), 2052 (M–Cl)$^+$; ν_{max}/cm^{-1} (solid) 1187 (br, s), 1141 (s), 1119 (s), 8111 (m), 698 (m).

Preparation of {2,6-*bis*[methyl(diphenylphosphino)]phenyl}platinum chloride 16

The title compound was prepared similarly to **15**, using **10** (0.880 g, 1.85 mmol), [$PtCl_2$(COD)] (0.674 g, 1.80 mmol), triethylamine (0.225 g, 2.22 mmol) and mesitylene (250 mL). After washing with ethanol (3 × 20 mL), **16** was obtained as a white powder (0.863 g, 68%). mp 281–283 °C (from ethanol). (Found C, 54.5; H, 3.8. Calc. for $C_{32}H_{27}ClP_2Pt$: C, 54.6; H, 3.9); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.89–7.79 (8 H, m, ArH), 7.43–7.30 (12 H, m, ArH), 7.03 (2 H, d, $^3J_{HH}$ = 7.0 Hz, ArH-4), 6.96–6.92 (1 H, m, ArH-5), 3.89 (4 H, t, $^3J_{HPt}$ = 25.0 Hz, J_{HP} = 4.7 Hz, $PhCH_2$); ^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$) δ_H 7.89–7.79 (8 H, m, ArH), 7.43–7.30 (12 H, m, ArH), 7.03 (2 H, d, $^3J_{HH}$ = 7.0 Hz, ArH-4), 6.96–6.92 (1 H, m, ArH-5), 3.89 (4 H, s, $^3J_{HPt}$ = 25.0 Hz, $PhCH_2$); ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) δ_P 33.1 (s, $^1J_{PPt}$ = 2969 Hz); *m*/*z* (FAB) 702.09054 (M$^+$, $C_{32}H_{27}ClP_2Pt$ requires 702.09046), 668 (M–Cl)$^+$; ν_{max}/cm^{-1} (solid) 3017 (br, w), 1435 (s), 1217 (s), 1103 (m), 690 (s).

General procedure for the Heck reaction between aryl halides and methyl acrylate

Solid aryl halides (0.48 mmol), $KHCO_3$ (0.0505 g, 0.504 mmol), TBAB (0.0309 g, 0.096 mmol) and [PdCl(Rf-PCP)] **13** or [PdCl(PCP)] **14** (1 mole %, 0.0048 mmol) were added to a Radley's Carousel reaction tube. The tube was evacuated and refilled with argon (×3), before liquid aryl halides (0.48 mmol), methyl acrylate (0.0620 g, 0.0650 mL, 0.72 mmol) and NMP (2.00 mL) were added. The tube was placed into a preheated oil bath (120 °C) for the reaction time. After cooling to room temperature, the reaction mixture was poured into a volumetric flask (25 mL) and

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methanol was added. Samples were taken and analysed by GC. (200 °C for 5 min. Injector: 250 °C, detector: 240 °C. R_t 2.5 min (4-iodoacetophenone), 2.2 min (4-bromoacetophenone), 2.0 min (4-chloroacetophenone), 4.5 min (*trans*-methyl 4-acetylcinnamate). R_t 2.1 min (4-iodoanisole), 2.0 min (4-bromoanisole), 3.5 min (*trans*-methyl 4-methoxycinnamate).

General recycling procedure for the Heck reaction between 4-bromoacetophenone and methyl acrylate

4-Bromoacetophenone (0.4976 g, 2.500 mmol), $KHCO_3$ (0.2628 g, 2.630 mmol), TBAB (0.1612 g, 0.500 mmol), tolyl ether (0.4957 g, 2.500 mmol) and [PdCl(Rf-PCP)] **13** (50 mg, 1 mole%, 0.025 mmol) were added to a Radley's Carousel reaction tube. The tube was evacuated and refilled with argon (×3), before methyl acrylate (0.3228 g, 0.338 mL, 3.750 mmol) and NMP (5.00 mL) were added. The tube was placed into a preheated oil bath (120 °C), samples (0.01 mL) were taken over 4 h and analysed by GC. The reaction mixture was allowed to cool to room temperature under argon before the solvent and the remaining volatiles were removed by Kugelröhr distillation (0.1 mbar, 40 °C). The resulting solid was dissolved in acetonitrile (8 mL) and loaded onto a column of FRPSG (4 g) which had been preconditioned with acetonitrile. The flask was washed with dichloromethane (0.5 mL × 2) and finally with acetonitrile (2 mL). The column was eluted with acetonitrile (28 mL) to give the organic products and then ethyl acetate (90 mL) to give the fluorous palladium complex. Both fractions were concentrated and analysed by ^{1}H, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$NMR spectroscopy. The organic compound was also analysed by ICP-OES for any palladium leaching. The FRPSG column was washed with water (20 mL) to remove any inorganic salts and was regenerated with acetonitrile. The organic phase was analysed by gas chromatography to determine the conversion to product using tolyl ether as the internal standard (200 °C for 5 min. Injector: 250 °C, detector: 240 °C. R_t 2.2 min (4-bromoacetophenone), 3.2 min (tolyl ether), 4.5 min (*trans*-methyl 4-acetylcinnamate).

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