Electronic Supplementary Information

Synthesis and Antiproliferative Activity of a Series of New Platinum and Palladium Diphosphane Complexes

Contents:

A Supplementary Tables

Table S1 Synthesis of $[M(dppe)R_2]$ and $[M(cod)R_2]$.

precursor complex	reagent	product	yield (%) [a]
$[Pt(dppe)Cl_2]$	LiC_6F_4H-2	$[Pt(dppe)(C_6F_4H\text{-}2)_2]$ (**1**)	22
$[Pt(dppe)Cl_2]$	LiC_6F_4H-3	$[Pt(dppe)(C_6F_4H\text{-}3)_2]$ (**2**)	27
$[Pt(dppe)Cl_2]$	LiC_6F_4H-4	$[Pt(dppe)(C_6F_4H\text{-}4)_2]$ (**3**)	19
$[Pt(dppe)Cl_2]$	$Mg(C_6F_4(C_5H_{10}N))$ Br	$[Pt(dppe)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ (**4**)	4
$[Pd(dppe)Cl_2]$	LiC_6F_4H-2	$[Pd(dppe)(C_6F_4H\text{-}2)_2]$ (**5**)	21
$[Pd(dppe)Cl_2]$	LiC_6F_4H-3	$[Pd(dppe)(C_6F_4H\text{-}3)_2]$ (**6**)	31
$[Pd(dppe)Cl_2]$	LiC_6F_4H-4	$[Pd(dppe)(C_6F_4H\text{-}4)_2]$ (**7**)	27
$[Pd(dppe)Cl_2]$	$Mg(C_6F_4(C_5H_{10}N))Br$	$[Pd(dppe)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ (**8**)	5
$[Pt(hex)(C_6F_4H\text{-}3)_2]$	dppe	**2**	80
$[Pt(hex)(C_6F_4H\text{-}4)_2]$	dppe	**3**	64
$[Pt(hex)(C_6F_3H_2\text{-}3,5)_2]$	dppe	$[Pt(dppe)(C_6F_3H_2\text{-}3,5)_2]$ (**9**)	73
$[Pt(hex)(C_6F_4(OMe)\text{-}4)_2]$	dppe	$[Pt(dppe)(C_6F_4(OMe)\text{-}4)_2]$ (**10**)	71
$[Pt(cod)Cl_2]$	$Li(C_6F_3H_2\text{-}5,6)$	$[Pt(cod)(C_6F_3H_2\text{-}5,6)_2]$ (**11**)	40
$[Pt(cod)Cl_2]$	$Li(C_6F_3H_2\text{-}3,6)$	$[Pt(cod)(C_6F_3H_2\text{-}3,6)_2]$ (**12**)	53
$[Pt(cod)Cl_2]$	$Mg(C_6F_4(C_5H_{10}N))Br$	$[Pt(cod)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ (**13**)	47
$[Pd(cod)Cl_2]$	$Mg(C_6F_4(C_5H_{10}N))Br$	$[Pd(cod)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ (**14**)	26
$[Pt(cod)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ (**13**)	dppe	**4**	83
$[Pd(cod)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ (**14**)	dppe	**8**	79
$[Pt(hex)(C_6F_3H_2\text{-}3,6)_2]$	dppe	$[Pt(dppe)(C_6F_3H_2\text{-}3,6)_2]$ (**15**)	77
$[Pt(dppm)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(dppm)Cl(C_6F_5)]$ [b]	93
$[Pt(dppe)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(dppe)Cl(C_6F_5)]$ [b]	94
$[Pt(dppp)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(dppp)Cl(C_6F_5)]$ [b]	99
$[Pt(dppm)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(dppb)Cl(C_6F_5)]$ [b]	87
$[Pt(dppe)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(dppp)Cl(C_6F_4(OMe)\text{-}4)]$ (**16**)	86
$[Pt(dppe)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(dppp)Cl(C_6F_4(OEt)\text{-}4)]$ (**17**)	97
$[Pt(depp)Cl_2]$	$TlO_2CC_6F_5$	$[Pt(depp)Cl(C_6F_5)]$ (**18**)	91
$[Pd(dppp)Cl_2]$	$TlO_2CC_6F_5$	$[Pd(dppp)Cl(C_6F_5)]$ (**19**)	90

[a] Yield based on precursor complex; further details in the Experimental Section. [b] From reference 1. Note that the numbering refer to the positions of the non-F substituents in the polyfluoroaryl ligands.

Table S2 Reagents and transfer agent used for **1**, **6-8** and **11-14**.

complex	transfer agent (mmol)	polyfluorobenzene (mmol)	platinum/ palladium precursor (mmol)
1	*n*-BuLi (1.6)	$(C_6F_4H\text{-}2)Br$ (1.6)	$[Pt(dppe)Cl_2]$ (0.75)
2	*n*-BuLi (1.6)	$(C_6F_4H\text{-}3)Br$ (1.6)	$[Pt(dppe)Cl_2]$ (0.75)
3	*n*-BuLi (1.6)	$(C_6F_4H\text{-}4)Br$ (1.6)	$[Pt(dppe)Cl_2]$ (0.75)
4	Mg (1.6)	$(C_6F_4(C_5H_{10}N))Br$ (1.6)	$[Pt(dppe)Cl_2]$ (0.75)
5	*n*-BuLi (2.6)	$(C_6F_4H\text{-}2)Br$ (2.6)	$[Pd(dppe)Cl_2]$ (1.25)
6	*n*-BuLi (1.8)	$(C_6F_4H\text{-}3)Br$ (1.8)	$[Pd(dppe)Cl_2]$ (0.85)
7	*n*-BuLi (1.8)	$(C_6F_4H\text{-}4)Br$ (1.8)	$[Pd(dppe)Cl_2]$ (0.87)
8	Mg (1.6)	$(C_6F_4(C_5H_{10}N))Br$ (1.6)	$[Pd(dppe)Cl_2]$ (0.75)
11	*n*-BuLi (1.3)	$(C_6F_3H_2\text{-}5,6)Br$ (1.3)	$[Pt(cod)Cl_2]$ (0.67)
12	*n*-BuLi (1.9)	$(C_6F_3H_2\text{-}3,6)Br$ (1.9)	$[Pt(cod)Cl_2]$ (0.93)
13	Mg (1.6)	$(C_6F_4(C_5H_{10}N))Br$ (1.6)	$[Pt(cod)Cl_2]$ (0.78)
14	Mg (3.5)	$(C_6F_4(C_5H_{10}N))Br$ (3.5)	$[Pd(cod)Cl_2]$ (1.7)

Table S3 Reagents and transfer agent used for **1**, **6-8** and **11-14**.

complex	$[M(diene)R_2]$ (mmol)	dppe (mmol)
2	$[Pt(hex)(C_6F_4H\text{-}3)_2]$ (0.31)	(0.31)
3	$[Pt(hex)(C_6F_4H\text{-}4)_2]$ (0.21)	(0.21)
4	$[Pt(cod)(C_6F_4(C_5H_{10}N))_2]$ (0.24)	(0.24)
8	$[Pd(cod)(C_6F_4(C_5H_{10}N))_2]$ (0.21)	(0.21)
9	$[Pt(cod)(C_6F_3H_2\text{-}3,5)_2]$ (0.50)	(0.50)
10	$[Pt(hex)(C_6F_4(OMe)\text{-}4)_2]$ (0.25)	(0.25)
15	$[Pt(cod)(C_6F_3H_2\text{-}3,6)_2]$ (0.50)	(0.50)

Table S4 Experimental and calculated ^{19}F NMR chemical shifts (ppm) for *cis*-$[Pt(dppe)(R)_2]$[a] compared to experimental values reported for related complexes.

complex	F(2)	F(3)	F(4)	F(5)	F(6)
$[Pt(dppe)(C_6F_4H\text{-}6)_2]$ (**1**)	–120.3 (–118.1)	–160.1 (–154.1)	–166.4 (–166.0)	–144.1 (–141.0)	- -
$[Pt(dppe)(C_6F_4H\text{-}5)_2]$ (**2**)	–112.0 (–109.9)	–169.3 (–164.5)	–143.1 (–138.7)	- -	–93.1 (–94.6)
$[Pt(dppe)(C_6F_4H\text{-}4)_2]$ (**3**)	–119.6 (–118.1)	–142.7 (–137.0)	- -	–142.7 (–137.0)	–119.6 (–118.1)
$[Pd(dppe)(C_6F_4H\text{-}6)_2]$ (**5**)	–117.9 (–115.6)	–159.9 (–156.3)	–166.0 (–162.4)	–143.6 (–140.3)	- -
$[Pd(dppe)(C_6F_4H\text{-}5)_2]$ (**6**)	–109.8 (–107.2)	–163.5 (–163.8)	–139.7 (–138.9)	- -	–86.4 (–91.9)
$[Pd(dppe)(C_6F_4H\text{-}4)_2]$ (**7**)	–113.9 (–115.4)	–136.7 (–137.7)	- -	–136.7 (–137.7)	–113.9 (–115.4)
$[Pt(dppe)(C_6F_3H_2\text{-}3,5)_2]$ (**9**)	–86.9 (–86.2)	–120.1 (–115.7)	- -	- -	–86.9 (–86.2)
$[Pt(dppe)(C_6F_4(OMe)\text{-}4)_2]$ (**10**)	–119.3 (–120.2)	–159.6 (–160.7)	- -	–159.6 (–160.7)	119.3 – (–120.2)
$[Pt(dppe)(C_6F_5)_2]$ [b]	–118.3	–164.7	–162.9	–164.7	–118.3

[Pt(dppe)(C_6F_5)Cl] [b]	–119.3	–164.4	–162.4	–164.4	–119.3
[Pt(dppe)(SC_6F_4H-4)$_2$] [c]	–133.4	–143.7	-	–143.7	–133.4
[a] Experimental data from measurements in $CDCl_3$, calculated shifts are in (brackets). Shifts were calculated as reported in ref. 2. [b] From ref. 3. [c] From ref. 4.					

B Supplementary Figures

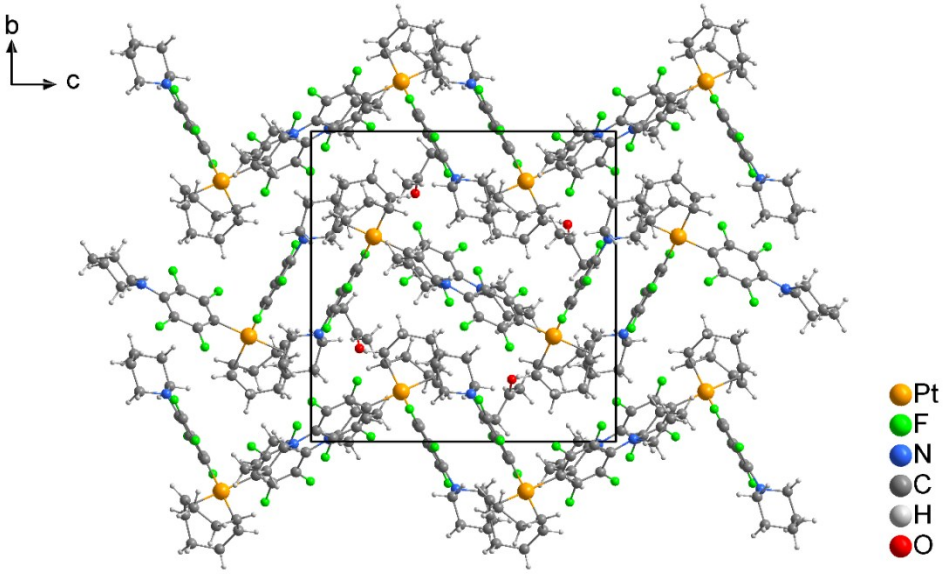
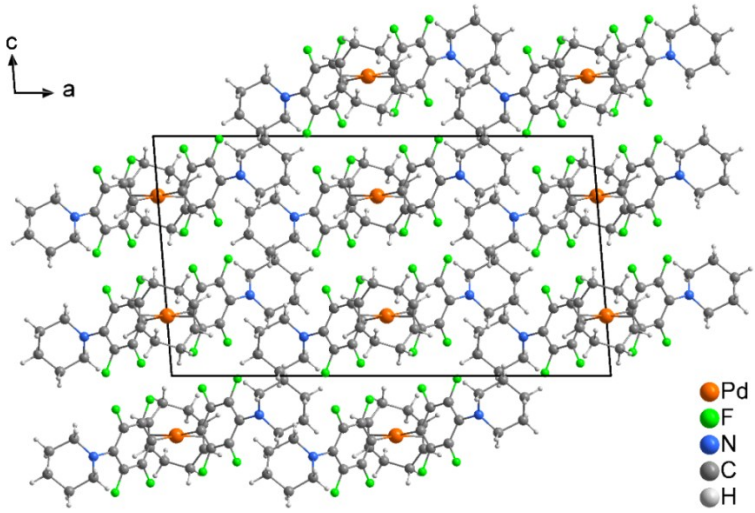


Fig. S1. Crystal structure of [Pt(cod)($C_6F_4(C_5H_{10}N$-4)$_2$]•acetone (**13•acetone**) viewed along the crystallographic *a* axis.



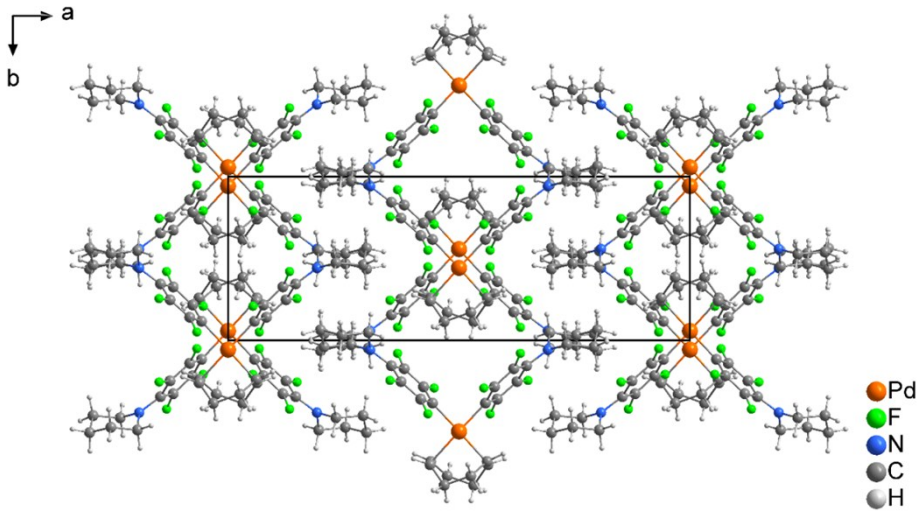


Fig. S2. Crystal structure of [Pd(cod)($C_6F_4(C_5H_{10}N)$-4)$_2$] (**14**) viewed along the crystallographic axes *b* (top) and *c* (bottom).

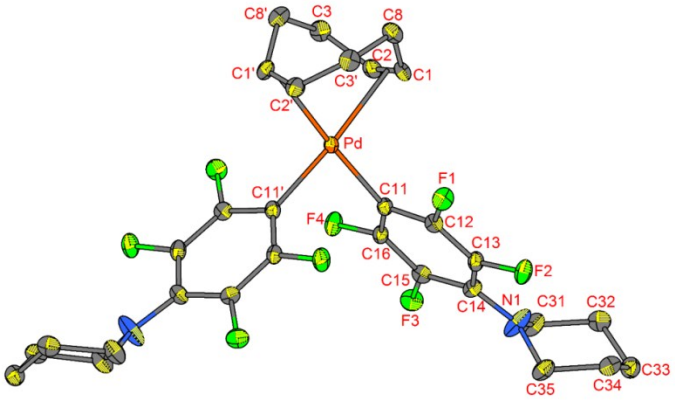


Fig. S3. Molecular structure of [Pd(cod)($C_6F_4(C_5H_{10}N)$-4)$_2$] (**14**) showing 50% thermal ellipsoids, with hydrogen atoms omitted for clarity.

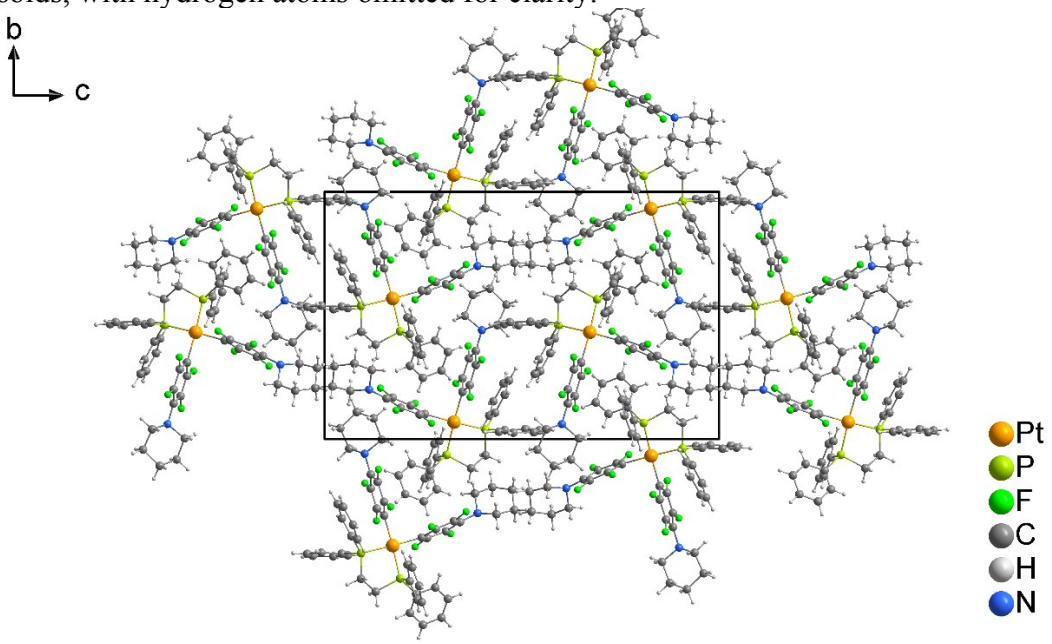


Fig. S4. Crystal structure of [Pt(dppe)($C_6F_4(C_5H_{10}N)$-4)$_2$] (**4**) viewed along the crystallographic *a* axis.

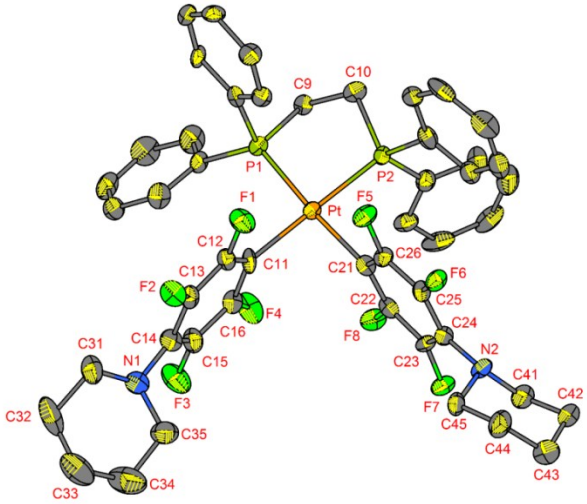


Fig. S5. Molecular structure of [Pt(dppe)($C_6F_4(C_5H_{10}N)$-4)$_2$] (**4**) showing 50% thermal ellipsoids, with hydrogen atoms and lattice acetone molecules omitted for clarity.

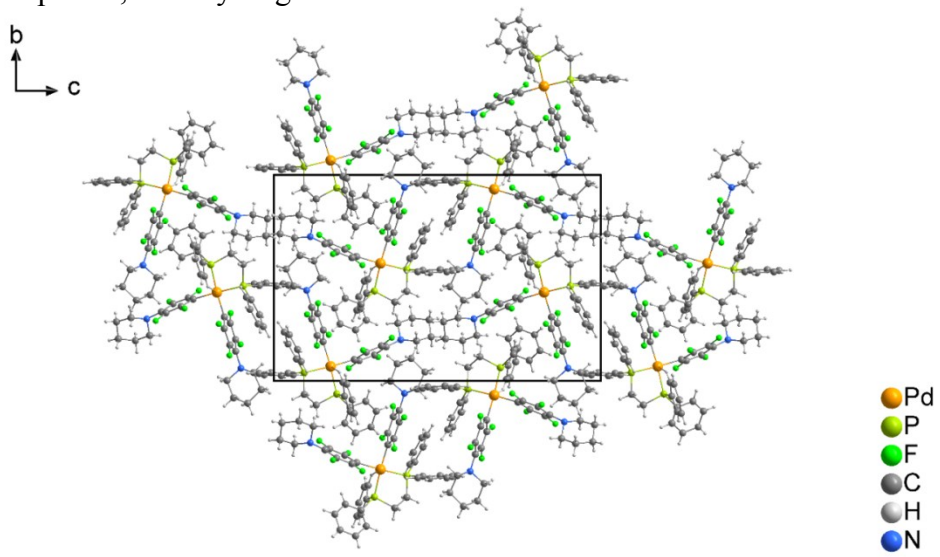


Fig. S6. Crystal structure of [Pd(dppe)($C_6F_4(C_5H_{10}N)$-4)$_2$] viewed along the crystallographic *a* axis.

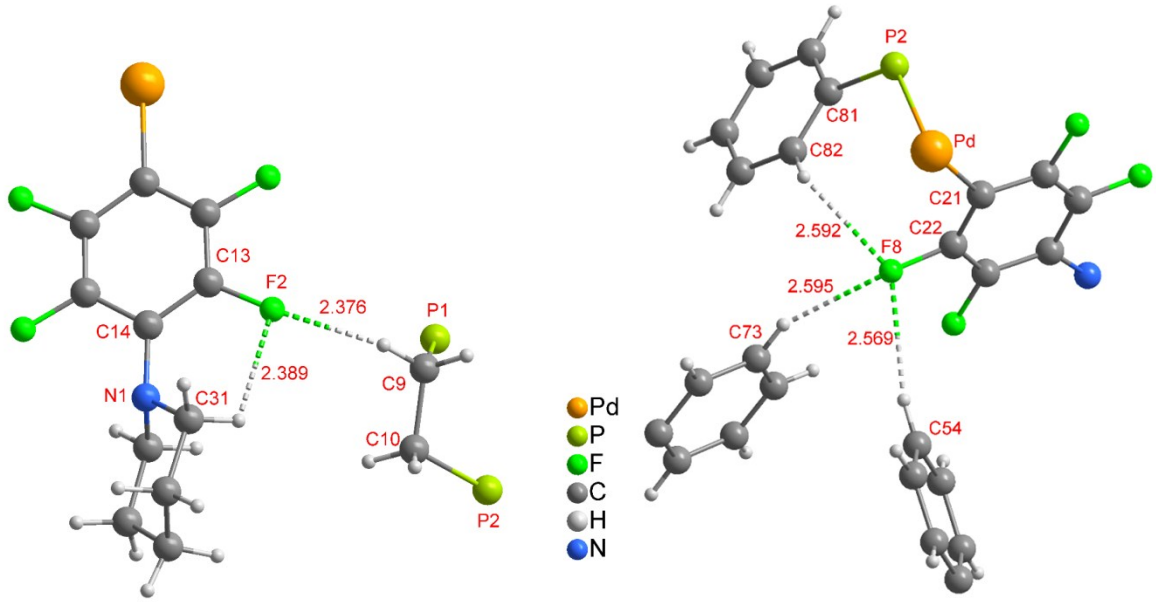


Fig. S7. Fluorine-hydrogen bonds in [Pd(dppe)($C_6F_4(C_5H_{10}N$-4)$_2$]. **Left**: F2 interactions. **Right**: F8 interactions.

C Experimental Section – Syntheses

General synthesis of complexes 1, 5-7 and 11-12:

In a typical reaction, 1.8 mmol *n*-BuLi was added dropwise to a solution of the desired bromo-polyfluorobenzene (1.5 mmol) in about 100 mL of dry diethyl ether under a nitrogen atmosphere at –78 °C and the mixture was allowed to stir for 1 h. After this time, the solution was transferred to a Schlenk flask containing 0.75 mmol of [M(dppe)Cl_2] with M = Pt (500 mg) or Pd (432 mg) or [Pt(cod)Cl_2] (281 mg) suspended in 50 mL of diethyl ether and stirred for 4 h at –78 °C. The reaction mixture was allowed to warm up to room temperature and was then hydrolysed using a solution of aqueous NH_4Cl (5% w/v in H_2O). The suspension was extracted with diethyl ether (3 × 30 mL) and the resulting ether layers were combined, dried with anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The symmetric complexes [M(dppe)$(R)_2$] and [Pt(cod)$(R)_2$] were separated from the unsymmetric derivatives [M(dppe)(R)Cl] and [Pt(cod)(R)Cl] through careful crystallisation from acetone or CH_2Cl_2 solutions at about –20 °C. Exact amounts of starting materials for each product are given in Table S2.

1: [Pt(dppe)(C_6F_4H-6)$_2$] Yield: 22% (0.15 g) colourless solid, mp. 238-240 ˚C. Anal. calcd. (%) for $C_{38}H_{26}F_8P_2Pt$ (891.63): C 51.19; H 2.94; F 17.04; found: C 50.74; H 2.92; F 16.66. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43-7.68 (m, 20H, Ph), 6.48 (m, ^{195}Pt satellites $^3J_{(Pt\text{-}H)}$ =

74 Hz, 2H, H(2)), 2.33 (d, $^{3}J_{(P-H)}$= 18 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –120.45 (m, ^{195}Pt satellites $^{3}J_{(Pt-F)}$ = 333 Hz, 2F, F(2)), –144.10 (m, 2F, F(5)), –160.13 (m, 2F, F(3)), –166.43 (m, 2F, F(4)). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 41.6 (m, ^{195}Pt satellites $^{1}J_{(Pt-P)}$ = 2070 Hz). MS (ESI pos.): m/z: 914 (40%, $[M+Na]^+$). IR (ATR): 3062 (w), 2092 (w), 1613 (m), 1584 (s), 1560 (w), 1522 (m), 1496 (m), 1484 (m), 1434 (s), 1401 (m), 1299 (m), 1278 (m), 1239 (w), 1187 (m), 1153 (m), 1102 (s), 1063 (s), 1020 (w), 987 (s), 978 (s), 879 (m), 856 (m), 848 (m), 840 (m), 821 (s), 796 (s), 781 (s), 742 (s), 689 (s) cm^{-1}.

5: [Pd(dppe)(C_6F_4H-6)$_2$] Yield: 20% (0.21 g) brown solid, mp. 210-213 ˚C. Anal. calcd, (%) for $C_{38}H_{26}F_8P_2Pd$ (802.98): C 56.84; H 3.26; found: C 56.72; H 3.18. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.30-7.51 (m, 20H, Ph), 6.60 (m, 2H, H(2)), 2.35 (d $^{3}J_{(P-H)}$ = 18 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –168.3 (m, 2F, F(4)), –161.7 (m, 2F, F(3)), –145.1 (m, 2F, F(5)), –117.2 (m, 2F, F(2)). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 43.8. MS (ESI neg.): m/z: 837 (30%, $[M+Cl^-]$). MS (ESI pos.): m/z: 857 (5%, $[M+Na+MeOH]^+$); 825 (10%, $[M+Na]^+$). IR (ATR): 3050 (w), 2913 (w), 2077 (w), 1612 (w), 1580 (w), 1482 (sh), 1493 (s), 1427 (s), 1294 (m), 1189 (m), 1097 (s), 1060 (s), 974 (s), 920 (w), 856 (m), 810 (m), 781 (s), 739 (s), 688 (s) cm^{-1}.

6: [Pd(dppe)(C_6F_4H-5)$_2$] Yield: 28% (0.21 g) colourless solid, mp. 208-210 ˚C. Anal. calcd. (%) for $C_{38}H_{26}F_8P_2Pd$ (802.98): C 56.84; H 3.26; found: C 56.93; H 3.22. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.29-7.48 (m, 20H, Ph), 6.14 (m, 2H, H(3)), 2.24 (d, $^{3}J_{(P-H)}$ = 19 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –86.35 (m, 2F, F(6)), –109.75 (m, 2F, F(2)), –133.68 (m, 2F, F(4)), –163.48 (m, 2F, F(3)). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 45.8. MS (ESI pos.): m/z: 825 (40%, $[M+Na]^+$). IR (ATR): 3060 (w), 2908 (w), 2106 (w), 1609 (s), 1582 (s), 1471 (s), 1435 (s), 1399 (s), 1323 (m), 1277 (m), 1198 (m), 1152(w), 1110 (m), 1099 (s), 1029 (s), 991 (s), 980 (w), 878 (m), 817 (s), 742 (s), 685 (s) cm^{-1}.

7: [Pd(dppe)(C_6F_4H-4)$_2$] Yield: 27% (0.19 g) colourless solid, mp. 208-210 ˚C. Anal. calcd. (%) for $C_{38}H_{26}F_8P_2Pd$ (802.98): C 56.84; H 3.26; found: C 57.00; H 3.28. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.33-7.60 (m, 20H, Ph), 6.46 (m, 2H, H(4)), 2.33 (d, $^{3}J_{(P-H)}$ = 19 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –113.87 (m, 4F, F(2,6)), –136.67 (m, 4F, F(3,5)). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 44.8. MS (ESI pos.): m/z: 825 (10%, $[M+Na]^+$), 653 (60%, $[Pd(dppe)(HC_6F_4)]^+$. IR (ATR): 3055 (w), 2924 (w), 2117 (w), 1710 (w), 1620 (m), 1590 (m), 1491 (m), 1449 (s), 1410 (m), 1329 (m), 1261 (w), 1205 (w), 1180 (w), 1156 (s), 1098 (s), 1040 (w), 1025 (m), 960 (w), 937 (m), 882 (s), 820 (s), 745 (s), 690 (s) cm^{-1}.

11: [Pt(cod)($C_6F_3H_2$-5,6)$_2$] Yield: 40% (0.15 g) colourless solid, mp. 246-248 ˚C. Anal. calcd. (%) for $C_{20}H_{16}F_6Pt$ (565.42): C 42.47; H 2.85; found: C 42.40; H 2.89. ^{1}H NMR

($CDCl_3$): δ/ppm = 6.88 (m, ^{195}Pt satellites $^3J_{(Pt-H)}$ = 72 Hz, 2H, H(6)), 6.73 (m, 2H, H(5)), 5.23 (m, ^{195}Pt satellites $^3J_{(Pt-H)}$ = 38 Hz, 4H, CH), 2.55 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –119.85 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 302 Hz, 2F, F(2)), –144.18 (m, 2F, F(4)), –163.10 (m, 2F, F(3)). MS (ESI neg.): m/z: 564 (30%, $[M-H]^-$). IR (ATR): 3393 (w), 2960 (w), 2928 (sh), 2113 (w), 1872 (w), 1772 (m), 1674 (w), 1610 (sh), 1595 (m), 1551 (w), 1485 (s), 1431 (s), 1345 (m), 1316 (m), 1280 (s), 1261 (s), 1211 (m), 1170 (w), 1103 (w), 1084 (s), 1004 (s), 862 (s), 800 (s), 766 (m), 690 (s) cm^{-1}.

12: [Pt(cod)($C_6F_3H_2$-3,6)$_2$] Yield: 53% (0.28 g) yellow solid, mp. 230-234 ˚C. Anal. calcd. (%) for $C_{20}H_{16}F_6Pt$ (565.42): C 42.47; H 2.85; found: C 42.47; H 2.85. ^{1}H NMR ($CDCl_3$): δ/ppm = 6.99 (m, ^{195}Pt satellites $^3J_{(Pt-H)}$ = 86 Hz], 2H, H(6)), 6.65 (m, 2H, H(3)), 5.22 (m, [^{195}Pt satellites $^3J_{(Pt-H)}$ = 40 Hz], 4H, CH), 2.56 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –99.94 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 311 Hz, 2F, F(2)), –142.61 (m, 2F, F(5)), –145.98 (m, 2F, F(4)). MS (ESI neg.): m/z: 564 (80%, $[M-H]^-$). IR (ATR): 1604 (m), 1576 (w), 1540 (w), 1490 (sh), 1467 (s), 1374 (s), 1340 (m), 1271 (s), 1220 (sh), 1171 (s), 1140 (w), 1120 (s), 1021 (w), 990 (m), 960 (sh), 920 (w), 879 (s), 838 (s), 786 (s), 716 (s), 660 (m) cm^{-1}.

General synthesis of complexes 2-4, 8-10 and 15:

In a typical reaction, 100 mg (0.25 mmol) dppe was added to a solution of 0.25 mmol [Pt(diene)($R)_2$)] (R = C_6F_4H-5, C_6F_4H-4, C_6F_4(OMe)-4, $C_6F_3H_2$-3,5, $C_6F_3H_2$-3,6, and $C_6F_4(C_5H_{10}N)$-4; diene = 1,5-hexadiene, 1,5-cyclooctadiene) in THF. This mixture was then allowed to stir for 15 min. at ambient temperature. The THF was evaporated, and the complex was then recrystallised from acetone at –20 °C. Exact amounts of starting materials for each product are given in Table S3.

2: [Pt(dppe)(C_6F_4H-5)$_2$] Yield: 80% (0.22 g) colourless solid, mp. 230-235 ˚C. Anal. calcd. (%) for $C_{38}H_{26}F_8P_2Pt$ (891.64): C 51.19; H 2.94; found: C 51.20; H 2.96. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.40-7.54 (m, 20H, Ph), 6.24 (m, 2H, H(3)), 2.28 (d, $^3J_{(P-H)}$ = 18 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –93.14 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 297 Hz, 2F, F(6)), –112.04 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 298 Hz, 2F, F(2)), –169.25 (m, 2F, F3), –143.06 (m, 2F, F(4)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = 40.6 (s, ^{195}Pt satellites $^1J_{(Pt-P)}$ = 2251 Hz). MS (ESI pos.): m/z: 914 (100%, $[M+Na]^+$). IR (ATR): 3060 (w), 2910 (w), 2340 (w), 1617 (m), 1590 (m), 1468 (s), 1434 (s), 1406 (s), 1329 (m), 1278 (m), 1204 (m), 1180 (w), 1162 (w), 1129 (s), 1100 (s), 1035 (s), 1010 (s), 971 (w), 920 (sh), 881 (s), 820 (s), 742 (s), 687 (s) cm^{-1}.

3: [Pt(dppe)(C_6F_4H-4)$_2$] Yield: 64% (0.12 g) colourless solid, mp. 244-245 ˚C. Anal. calcd. (%) for $C_{38}H_{26}F_8P_2Pt$ (891.64): C 51.19; H 2.94; found: C 51.22; H 3.03. ^{1}H NMR

($CDCl_3$): δ/ppm = 7.31-7.50 (m, 20H, Ph), 6.43 (m, 2H, H(4)), 2.33 (d, $^3J_{(P-H)}$ = 18 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –119.56 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 314 Hz, 4F, F(2,6)), –142.65 (m, 4F, F(3,5)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 40.6 (s, ^{195}Pt satellites $^1J_{(Pt-P)}$ = 2272 Hz). MS (ESI pos.): m/z: 914 (100%, $[M+Na]^+$); 742 (30%, $[Pt(dppe)(p\text{-}HC_6F_4)]^+$). IR (ATR): 3075 (w), 2896 (m), 2830 (w), 1620 (m), 1588 (m), 1453 (m), 1440 (sh), 1336 (m), 1255 (w), 1200 (m), 1167 (s), 1096 (s), 1010 (w), 995 (m), 888 (s), 821 (s), 745 (s), 691 (s) cm^{-1}.

4: $[Pt(dppe)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ Yield: 83% (0.21 g) colourless solid, mp. 282-283 ˚C. Anal. calcd (%) for $C_{48}H_{44}F_8N_2P_2Pt$ (1057.91): C 54.48; H 4.19; N 2.65; found: C 54.32; H 4.24; N 2.64. ^1H NMR ($CDCl_3$): δ/ppm = 7.34-7.62 (m, 20H, Ph), 2.99 (s, 8H, CH_2), 2.33 (d, $^3J_{(P-H)}$ = 17 Hz, 4H, CH_2), 1.60 (m, 12H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –120.18 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 313 Hz, 4F, F(2,6)), –151.93 (m, 4F, F(3,5)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 41.7 (s, ^{195}Pt satellites $^1J_{(Pt-P)}$ = 2263 Hz). MS (ESI pos.): m/z: 1080 (30%, $[M+Na]^+$), 1058 (100%, $[M+H]^+$). IR (ATR): 3058 (w), 2919 (m), 2831 (w), 2100 (w), 1620(w), 1433 (s), 1390 (m), 1299 (w), 1260 (w), 1221 (m), 1150 (m), 1097 (s), 1045 (sh), 996 (m), 944 (s), 891 (m), 860 (m), 815 (s), 750 (s), 690 (s) cm^{-1}.

8: $[Pd(dppe)(C_6F_4(C_5H_{10}N)\text{-}4)_2]$ Yield: 79% (0.16 g) colourless solid, mp. 220˚C. Anal. calcd. (%) for $C_{48}H_{44}F_8N_2P_2Pd$ (969.25): C 59.49; H 4.58; N 2.89 ; found: C 59.87; H 5.03; N 3.17. ^1H NMR ($CDCl_3$): δ/ppm = 7.31-7.56 (m, 20H, Ph), 3.00 (s, 8H, CH_2), 2.30 (d, $^3J_{(P-H)}$ = 20 Hz, 4H, CH_2), 1.55 (s, 12H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –117.62 (s, 4F, F(2,6)), –151.26 (s, 4F, F(3,5)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 44.1. MS (ESI pos.): m/z: 991 (30%, $[M+Na]^+$), 969 (100%, $[M+H]^+$). IR (ATR): 3059 (w), 2923 (m), 2850 (w), 2098 (w), 1695 (m), 1621(m), 1460 (sh), 1432 (s), 1383 (m), 1342 (m), 1309 (m), 1272 (m), 1220 (m), 1190 (w), 1150 (m), 1095 (s), 1063 (s), 994 (s), 976 (w), 942 (s), 904 (m), 862 (w), 816 (s), 743 (s), 684 (s) cm^{-1}.

9: $[Pt(dppe)(C_6F_3H_2\text{-}3,5)_2]$ Yield: 73% (0.31 g) colourless solid. mp: 291-292˚C. Anal. calcd (%) for $C_{38}H_{28}F_6P_2Pt$ (855.66): C 53.33; H 3.30; found: C 53.15; H 3.28. ^1H NMR ($CDCl_3$): δ/ppm = 7.34-7.56 (m, 20H, Ph), 6.16 (s, 4H, H(3,5), 2.29 (d, $^3J_{(P-H)}$ = 17 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –86.92 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 302 Hz, 4F, F(2,6)), –120.07 (s, 2F, F(4)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 40.1 (s, ^{195}Pt satellites $^1J_{(Pt-P)}$ = 2219 Hz). MS (ESI pos.): m/z: 878 (30%, $[M+Na]^+$), 724 (20%, $[Pt(dppe)(C_6F_3H_2)]^+$). IR (ATR): 3062 (w), 2094 (w), 1679 (w), 1612 (m), 1584 (s), 1485 (m), 1435 (s), 1402 (s), 1308 (m), 1300 (m), 1279 (m), 1130 (w), 1152 (m), 1100 (s), 1062 (sh), 995 (s), 930 (sh), 883 (m), 840 (s), 820 (s), 745 (s), 690 (s) cm^{-1}.

10: [Pt(dppe)(C_6F_4(OMe)4-)$_2$] Yield: 71% (0.17 g) colourless solid, mp. 289-290˚C. Anal. calcd. (%) for $C_{40}H_{30}F_8O_2P_2Pt$ (951.70): C 50.48; H 3.18; found: C 50.47; H 3.16. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.32-7.58 (m, 20H, Ph), 3.85 (s, 6H, OCH_3), 2.33 (d, $^3J_{(P-H)}$ = 17 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –119.31 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 315 Hz, 4F, F(2,6)), –159.59 (m, 4F, F(3,5)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = 40.5 (s, ^{195}Pt satellites $^1J_{(Pt-P)}$ = 2278 Hz). MS (ESI pos.): m/z: 974 (100%, $[M+Na]^+$); 772 (30%, $[Pt(dppe)(C_6F_4OMe)]^+$). IR (ATR): 2934 (w), 2110 (w), 1580 (m), 1500 (s), 1432 (s), 1350 (s), 1330 (m), 1270 (m), 1183 (m), 1081 (s), 1070 (w), 1000 (w), 946 (s), 876 (s), 822 (s), 799 (s), 750 (s), 691 (s) cm^{-1}.

15: [Pt(dppe)($C_6F_3H_2$-3,6)$_2$] Yield: 77% (0.33 g) colourless solid. mp: 274-276 ˚C. Anal. calcd. (%) for $C_{38}H_{28}F_6P_2Pt$ (855.66): C 53.33; H 3.30; found: C 53.46; H 3.43. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.40-7.58 (m, 20H, Ph), 6.72 (m, [^{195}Pt satellites $^3J_{(Pt-H)}$ = 70 Hz], 2H, H(6)), 6.37 (m, 2H, H(3)), 2.30 (d, $^3J_{(P-H)}$= 21 Hz, 4H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –96.35 (m, ^{195}Pt satellites $^3J_{(Pt-F)}$ = 297 Hz, 2F, F(2)) –145.43 (m, 2F, F(4)), –148.21 (m, 2F, F5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = 41.2 (s, ^{195}Pt satellites $^1J_{(Pt-P)}$ = 2025 Hz). MS (ESI pos.): m/z: 878 [15%, $[M+Na]^+$), 724 (100%, $[Pt(dppe)(C_6F_3H_2)]^+$). IR (ATR): 3054 (w), 2067 (w), 1603 (m), 1468 (s), 1430 (s), 1410 (w), 1372 (s), 1350 (w), 1272 (s), 1170 (s), 1110 (s), 1100 (w), 989 (m), 873 (s), 850 (w), 770 (s), 786 (s), 645 (s), 688 (s) cm^{-1}.

General synthesis of complexes 13 and 14:

A catalytic amount of dibromoethane was added to a Schlenk flask containing magnesium turnings suspended in dry diethyl ether (30 mL). Once the magnesium metal was activated (bubbling in the solution), 1-bromo-4-piperidinotetrafluorobenzene in anhydrous diethyl ether was added dropwise to the reaction mixture which was stirred and heated to reflux for 4 h under a nitrogen atmosphere. After this time, the solution was transferred to a Schlenk flask containing [M(cod)Cl_2] (M = Pd, Pt), and the reaction mixture was placed in a sonic bath for 90 min. at ambient temperature. The solution was hydrolysed using NH_4Cl (5% w/v in H_2O), and the organic layer was then extracted three times with diethyl ether. Anhydrous magnesium sulphate was added to the ether fractions. The solution was then filtered, and the was solvent evaporated to dryness, and the residue was recrystallised from acetone and hexane.

13: [Pt(cod)(C_6F_4(C_5H_{10}N)-4)$_2$]•acetone Yield: 47% (0.30 g) light-brown solid, mp. 218-219 ˚C. Anal. calcd. (%) for $C_{33}H_{38}F_8N_2OPt$ (acetone solvate) (825.75): C 47.99; H 4.64, N 3.39; found: C 48.01; H 4.60; N 3.39. ^{1}H NMR ($CDCl_3$): δ/ppm = 5.30 (s, ^{195}Pt satellites

$^{3}J_{(Pt-H)}$ = 45 Hz, 4H, CH), 3.07 (s, 8H, CH_2), 2.52 (s, 8H, CH_2), 2.14 (s, 6H, CH_3 (acetone)), 1.56 (m, 12H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –123.04 (m, ^{195}Pt satellites $^{3}J_{(Pt-F)}$ = 353 Hz, 4F, F(2,6)), –151.65 (m, 4F, F(3,5). MS (ESI pos.): m/z: 768 (100% $[M+H]^+$). IR (ATR): 2934 (m), 2843 (m), 1708 (s), 1629 (m), 1462 (s), 1442 (vs), 1384 (s), 1359 (s), 1318 (w), 1272 (m), 1220 (s), 1153 (m), 1097 (s), 1070 (sh), 1031 (w), 999 (m), 948 (vs), 902 (s), 867 (m), 822 (m), 780 (w), 766 (s), 730 (w), 696 (w) cm^{-1}.

14: [Pd(cod)($C_6F_4(C_5H_{10}N$-4)$_2$] Yield: 26% (0.30 g) light-brown solid, mp.: 242-245 ˚C. Anal. calcd. (%) for $C_{30}H_{32}F_8N_2Pd$ (679.01): C 53.06; H 4.75, N 4.13; found: C 53.29; H 4.96, N 4.09. ^{1}H NMR ($CDCl_3$): δ/ppm = 5.81 (s, 4H, CH), 3.07 (s, 8H, CH_2), 2.72 (s, 8H, CH_2), 1.56 (m, 12H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –119.93 (m, 4F, F(2,6)), –150.65 (m, 4F, F(3,5)). MS (ESI pos.): m/z: 679 (18% $[M+H]^+$), 465 (100%, $[C_5H_{10}NC_6F_4–C_6F_4NC_5H_{10}+H]^+$). IR (ATR): 3337 (w), 3175 (w), 2936 (m), 2849 (m), 1693 (m), 1619 (m), 1432 (s), 1384 (m), 1360 (m), 1270 (w), 1219 (s), 1152 (m), 1093 (s), 995 (m), 942 (s), 894 (m), 861 (m), 816 (w), 762 (m), 745 (m), 666 (m) cm^{-1}.

General synthesis of complexes 16, 17, and 18:

In a typical reaction, 0.35 mmol of *cis*-[M(dppp)Cl_2] and 0.36 mmol thallium pentafluorobenzoate were mixed in 10 mL of dry pyridine and heated to 50°C (for M = Pd) or 100°C (for M = Pt). The reaction was carried out under a slow nitrogen stream which was passed through a saturated barium hydroxide solution to monitor the decarboxylation reaction. After 2 h the reaction was complete, and the pyridine was removed under vacuum. The resultant residue was washed with 3×10 mL of *n*-hexane, and the residue was extracted using boiling acetone (100 mL), including careful filtration to remove KCl or insoluble impurities. The filtrate was evaporated to dryness to yield the desired material.

16: [Pt(dppp)Cl(C_6F_4(OMe)-4)] Yield 86% (0.25 g) of the colourless complex, mp.: 228-232 ˚C. Anal. calcd. (%) for $C_{34}H_{29}ClF_4OP_2Pt$ (822.07): C 49.68; H 3.56, Cl 4.31; found: C 49.66; H 3.54, Cl 4.33. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.84-7.09 (m, 20H, Ph) 3.78 (s, 3H, OCH_3), 2.94-2.56 (m, 2H, CH_2), 2.53-2.25 (m, 2H, CH_2), 2.14-1.85 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –120.9 (m, 2F, ^{195}Pt satellites $^{3}J_{(Pt-F)}$ = 272 Hz, F(2,6)), –159.4 (s, 2F, F(3,5)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = –3.48 (d, $^{2}J_{(P-P)}$ = 28 Hz, ^{195}Pt satellites $^{1}J_{(Pt-P)}$ = 3636 Hz, *trans* to Cl), –3.80 (d, ^{195}Pt satellites $^{1}J_{(Pt-P)}$ = 2037 Hz, *trans* to R),. MS (ESI pos.): m/z: 1607 (14%, $[2M-Cl]^+$), 844 (10% $[M+Na]^+$, 818 (100%, $[M-Cl+MeOH]^+$), 786 (40%, $[M-Cl]^+$). IR (ATR): 3051 (w), 3007 (w), 2943 (w), 2910 (m) 1633 (m), 1478 (vs), 1450 (vs),

1435 (vs) 1400 (m), 1354 (m), 1103 (vs), 1086 (vs), 957 (s), 943 (vs), 743 (s) 696 (vs,br), 669 (s), 519 (vs), 505 (vs), 480 (s), 465 (m), 423 (w) cm^{-1}.

17: [Pt(dppp)Cl(C_6F_4(OEt)-4)] Yield 97% (0.28 g) of the colourless complex, mp.: 232 ˚C. Anal. calcd. (%) for $C_{35}H_{31}ClF_4OP_2Pt$ (836.11): C 50.28; H 3.74, Cl 4.24; found: C 50.22; H 3.71, Cl 4.23. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.83-7.08 (m, 20H, Ph) 3.93 (q, 2H, OCH_2), 2.92-2.59 (m, 2H, CH_2), 2.53-2.25 (m, 2H, CH_2), 2.12-1.88 (m, 2H, CH_2), 1.25 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$): δ/ppm = –121.0 (m, 2F, ^{195}Pt satellites $^3J_{(Pt\text{-}F)}$ = 274 Hz, F(2,6)), –158.8 (m, 2F, F(3,5)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = –3.35 (d, 1P, $^2J_{(P\text{-}P)}$ = 28 Hz, ^{195}Pt satellites $^1J_{(Pt\text{-}P)}$ = 3642 Hz, *trans* to Cl), –3.77 (d, 1P, ^{195}Pt satellites $^1J_{(Pt\text{-}P)}$ = 2050 Hz, *trans* to R). MS (ESI pos.): m/z: 1636 (8%, $[2M\text{-}Cl]^+$), 859 (11% $[M+Na]^+$, 832 (100%, $[M\text{-}Cl+MeOH]^+$), 800 (40%, $[M\text{-}Cl]^+$). IR (ATR): 3063 (m), 2976 (m), 1630 (m), 1587 (m), 1572 /m) 1483 (vs), 1475 (vs), 1435 (vs), 1400 (s) 1387 (s) 1354 (s) 1310 (m) 1273 (m), 1184 (m), 1099 (vs) 1074 (vs), 1015 (m) 999 (m) 949 (vs) 928 (m) 752 (s), 743 (s) 698 (vs,br) 681 (s) 517 (vs) 501 (m) 490 (s), 453 (s), 430 (w) cm^{-1}.

18: [Pd(dppp)Cl(C_6F_5)] Yield 90% (0.23 g) of the colourless complex, mp.: 216-220 ˚C. Anal. calcd. (%) for $C_{33}H_{26}ClF_5P_2Pd$ (721.38): C 54.95; H 3.63, Cl 4.91; found: C 55.01; H 3.69, Cl 4.93. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.85-7.10 (m, 20H, Ph) 2.73-2.55 (m, 2H, CH_2), 2.38-2.21 (m, 2H, CH_2), 2.15-1.86 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$): δ/ppm = –117.9 (m, 2F, F(2,6)), –162.3 (m, 1F, F(4), $^3J_{(F\text{-}F)}$ = 20 Hz), –163.3 (m, 2F, F(3,5)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ/ppm = 16.97 (d, 1P, $^2J_{(P\text{-}P)}$ = 42 Hz, *trans* to Cl), –3.75 (m, *trans* to R). MS (ESI pos.): m/z: 1407 (18%, $[2M\text{-}Cl]^+$), 743 (19% $[M+Na]^+$, 717 (70%, $[M\text{-}Cl+MeOH]^+$), 685 (100%, $[M\text{-}Cl]^+$). IR (ATR): 3054 (w), 1608 (w) 1495 (s), 1485 (m), 1456 (vs), 1437 (vs) 1414 (m), 1356 (m), 1350 (m), 1153 (m), 1101 (s), 1057 (s), 953 (vs), 789 (m), 744 (s), 696 (s), 663 (m), 511 (vs), 496 (m) 482 (m), 436 (w) cm^{-1}.

Attempted Reactions - Nucleophilic Substitution:

(i): [Pd(dppe)(C_6F_4($C_5H_{10}N$)-4)$_2$]

Piperidine (5 mL) was added to a round bottom flask containing [Pd(dppe)(C_6F_5)$_2$] (0.30 g, 0.36 mmol) and then heated to reflux for various amounts of time. The reaction mixture was monitored by ^{19}F NMR spectroscopy.

After 3 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –162.08 (m, 2F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –152.06 (m, 0.16F, F(3,5) product), –117.2 (m, 0.24F, F(2,6) product), –115.70 (m, 2F, F(2,6), [Pd(dppe)(C_6F_5)$_2$]).
After 6 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –161.08 (m, 2F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –151.95 (m, 0.20F, F(3,5) product), –116.92 (m, 0.24F, F(2,6) product), –115.70 (m, 2F, F(2,6), [Pd(dppe)(C_6F_5)$_2$].
After 14.5 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –162.08 (m, 2F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –153.45 (m, 0.90F, F(3,5) product), –117.12 (m, 1F, F(2,6) product), –115.70 (m, 4F, F(2,6), [Pd(dppe)(C_6F_5)$_2$].
After 36 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –162.08 (m, 2F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –153.45 (m, 1.5F, F(3,5) product), –118.12 (m, 1.6F, F(2,6) product), –115.70 (m, 4F, F(2,6), [Pd(dppe)(C_6F_5)$_2$].
After 1 week: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –162.08 (m, 2F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –153.50 (m, 2F, F(3,5) product), –118.03 (m, 2F, F(2,6) product), –115.70 (m, 4F, F(2,6), [Pd(dppe)(C_6F_5)$_2$].

(ii): [Pd(dppe)($C_6F_4(C_5H_{10}N)$-4)$_2$]

Piperidine (3 mL) was added to a microwave reactor tube containing [Pd(dppe)(C_6F_5)$_2$] (0.19 g, 0.23 mmol) and then run at the temperature 150°C, pressure 290 PSI at various amounts of time. The reaction mixture was monitored by ^{19}F NMR spectroscopy.
After 30 min: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –161.08 (m, 2F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –153.45 (m, 0.08F, F(3,5) product), –118.12 (m, 0.06F, F(2,6) product), –115.70 (m, 4F, F(2,6), [Pd(dppe)(C_6F_5)$_2$]).
After 1 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(4) [Pd(dppe)(C_6F_5)$_2$]), –161.08 (m, 2F, F(3,5) [Pd(dppe)(C_6F_5)$_2$]), –153.45 (m, 0.50F, F(3,5) product), –118.12 (m, 0.42F, F(2,6) product), –115.70 (m, 4F, F(2,6), [Pd(dppe)(C_6F_5)$_2$]).
After 3.5 h: Black/orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = no signals for starting material or product.

(iii): [Pt(dppe)($C_6F_4(C_5H_{10}N)$-4)$_2$]

Piperidine (3mL) was added to a microwave reactor tube containing [Pt(dppe)(C_6F_5)$_2$] (0.07 g, 0.0084 mmol) and then run at the temperature 150°C, pressure 290 PSI at various amounts of time. The reaction mixture was monitored by ^{19}F NMR spectroscopy.

After 4 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –165.87 (m, 4F, F(3,5) [Pt(dppe)(C_6F_5)$_2$]), –164.50 (m, 2F, F(4) [Pt(dppe)(C_6F_5)$_2$]), –151.50 (m, 1.6F, F(3,5) product), –120.12 (m [^{195}Pt satellites $^3J_{(Pt–F)}$ = 313 Hz], 1.5F, F(2,6) product), –118.30 (m, [^{195}Pt satellites $^3J_{(Pt-F)}$ = 312 Hz] 4F, F(2,6), [Pt(dppe)(C_6F_5)$_2$]).

After 6 hours: Black/orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = No signs of product or starting material.

(iv) [Pd(dppe)(C_6F_4(OCH(CH_3)$_2$)-4)]

A solution of Na(OCH(CH_3)$_2$ (0.48 g, 5.6 mmol) in anhydrous *iso*propanol was transferred to a round bottom flask containing [Pd(dppe)(C_6F_5)$_2$] (0.19 g, 0.23 mmol) under a nitrogen atmosphere. This solution was heated at refluxed at various times. The reaction mixture was monitored by ^{19}F NMR spectroscopy. No change in the ^{19}F NMR spectrum was observed after 30 h.

After 30 h: Appearance: colourless solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –164.50 (m, 4F, F(3,5), [Pd(dppe)(C_6F_5)$_2$]), –161.08 (m, 2F, F(4), [Pd(dppe)(C_6F_5)$_2$]), –115.70 (m, 4F, F(2,6), [Pd(dppe)(C_6F_5)$_2$]).

(v) [Pt(bpy)(C_6F_4($C_5H_{10}N$)-4)$_2$]:

Piperidine (3 mL) was added to a microwave reactor tube containing [Pt(bpy)(C_6F_5)$_2$] (0.09 g, 0.013 mmol) and then run at the temperature 150°C, pressure 290 PSI at various amounts of time. The reaction mixture was monitored by ^{19}F NMR spectroscopy.

After 4 h: Orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = –163.66 (m, 4F, F(3,5) [Pt(bpy)(C_6F_5)$_2$]), –161.22 (m, 2F, F(4) [Pt(bpy)(C_6F_5)$_2$]), –153.80 (m, 0.22F, F(3,5) product), –122.12 (m, 0.20F, F(2,6) product), –118.30 (m, [^{195}Pt satellites $^3J_{(Pt–F)}$ = 451 Hz] 4F, F(2,6), [Pt(bpy)(C_6F_5)$_2$]).

After 6 h: Appearance: black/orange solution. ^{19}F NMR ($CDCl_3$): δ/ppm = No signs of product or starting material.

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