Supporting Information for

Reversible C-C bond formation at a triply cyclometallated platinum(IV) centre

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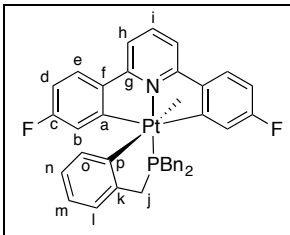
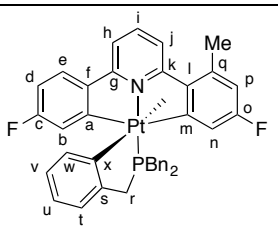
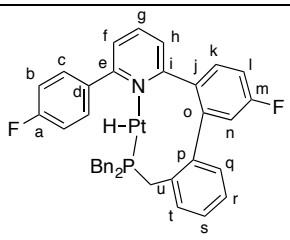
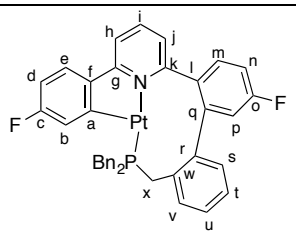
Contents:

Experimental

General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400, 500 or 600 MHz spectrometers and were recorded at room temperature, in chloroform, unless stated otherwise. ^{1}H and ^{13}C signals are referenced to external TMS, assignments being made with the use of decoupling, GOESY and COSY pulse sequences. ^{19}F and ^{31}P chemical shifts are quoted from the directly observed signals (referenced to external $CFCl_3$ and 85% H_3PO_4, respectively). ^{1}H-^{195}Pt correlation spectra were recorded using a variant of the HMBC pulse sequence and the ^{195}Pt chemical shifts reported are taken from these spectra (referenced to external Na_2PtCl_6). All elemental analyses were performed by Warwick Analytical Service. The initial [(2,6-di(4-fluorophenyl)pyridine)Pt(DMSO)] complex was prepared as previously reported (G. W. V. Cave, N. W. Alcock and J. P. Rourke, *Organometallics,* 1999**, 18**, 1801-1803. (b) G. W. V. Cave, F. P. Fanizzi, R. J. Deeth, W. Errington and J. P. Rourke, *Organometallics,* 2000**, 19**, 1355-1364.).

The following labelling schemes were used for symmetrical and unsymmetrical complexes, as appropriate:

			
1 **2(t) 2(c)**	**Me-1** **Me-2(t) Me-2(c)** **3 b-Me(3)** **4 b-Me-4**	**9**	**5 a-Me-5 b-Me-5** **6** **7 a-Me-7 b-Me-7** **8 10**

Synthesis of Complex 1

PBn_3 (64 mg, 0.21 mol, 1.1 eq) was added to a solution of [(2,6-di(4-fluorophenyl)pyridine) Pt(DMSO)] (100 mg, 0.19 mol) in $CHCl_3$ (10 ml). The solution was stirred (10 min at RT) before the solvent was removed under vacuum. The crude product was then purified by column chromatography on silica, loading and eluting with toluene to give pure 1 (151 mg, 0.18 mol, 95%).

δ_H = 7.67 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_i), 7.50 (2H, dd, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{H\text{-}F}$ = 5.5 Hz, H_e), 7.41 (6H, d, $^3J_{H\text{-}H}$ = 7.5, Bn-*o*), 7.29 (2H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_h), 7.23 (9H, m, Bn-*m*,*p*), 7.01 (2H, dd, $^3J_{H\text{-}H}$ = 11 Hz, $^4J_{H\text{-}J}$ = 3 Hz, $^3J_{H\text{-}Pt}$ = 25 Hz, H_b), 6.70 (2H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 9 Hz, $^4J_{H\text{-}H}$ = 3 Hz, H_d), 3.54 (6H, d, $^2J_{H\text{-}P}$ = 10 Hz, $^3J_{H\text{-}Pt}$ = 31 Hz, Bn-CH_2) ppm.

δ_C = 29.59 (d, $^1J_{C\text{-}P}$ = 32 Hz, $^2J_{C\text{-}Pt}$ = 32 Hz, Bn-CH_2), 109.36 (d, $^2J_{C\text{-}F}$ = 23.5 Hz, C_d), 113.57 (d, $^4J_{C\text{-}P}$ = 3 Hz, $^3J_{C\text{-}Pt}$ = 26.5 Hz, C_h), 123.26 (d, $^2J_{C\text{-}F}$ = 17 Hz, $^2J_{C\text{-}Pt}$ = 56 Hz, C_b), 124.86 (d, $^3J_{C\text{-}F}$ = 8 Hz, $^3J_{C\text{-}Pt}$ = 28 Hz, C_e), 125.8 (s, Bn-*p*), 127.47 (s, Bn-*m*), 129.336 (d, $^3J_{C\text{-}P}$ = 6 Hz, Bn-*o*), 132.66 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, $^3J_{C\text{-}Pt}$ = 17 Hz, Bn-*i*), 139.07 (s, C_i), 145.82 (t, $^3J_{C\text{-}P}$ = $^4J_{C\text{-}F}$ = 2 Hz, $^2J_{C\text{-}Pt}$ = 27.5 Hz, C_f), 163.20 (d, $^1J_{C\text{-}F}$ = 253 Hz, $^3J_{C\text{-}Pt}$ = 53 Hz, C_c), 164.13 (s, $^2J_{C\text{-}Pt}$ = 67 Hz, C_g), 168.53 (m, $^1J_{C\text{-}Pt}$ = 719 Hz, C_a) ppm.

δ_F = -110.54 ($^4J_{F\text{-}Pt}$ = 28 Hz) ppm. δ_P = -1.23 ($^1J_{P\text{-}Pt}$ = 3847 Hz) ppm. δ_{Pt} = -4151 (d, $^1J_{Pt\text{-}P}$ = ~3900 Hz) ppm.

HR-MS (ESI): found 764.1774, calculated 764.1784 = $C_{38}H_{30}F_2PN^{194}Pt = [M]^+$.

Elemental analysis found (calculated): C 59.43 (59.68), H 3.99 (3.95) N 1.72 (1.83).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 1 and Table S1; full details on page S19.

Synthesis of Me-1

Complex **1** (120 mg, $15.7x10^{-2}$ mmol) was dissolved in iodomethane (3 ml) and heated at reflux for two days, by which time an insoluble product had formed. The solvent was then removed, and the product washed with acetone. To the dry powder was added $AgBF_4$ (excess) and the mixture solubilized in acetone (10 ml); the resulting insoluble AgCl was removed by filtration. K_2CO_3 solution (2M, 1 ml) was then added, and the mixture stirred and heated to 50°C for 2 hours. The solvent was then removed, and the crude product was purified by column chromatography on silica, loading and eluting with toluene. (89 mg, $11.4x10^{-2}$ mmol, 73%).

Me-1 δ_H = 7.60 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.45 (1H, d, $^3J_{H-H}$ = 8 Hz, H_j), 7.38 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, H_e), 7.31 (6H, d, $^3J_{H-H}$ = 7 Hz, Bn-*o*), 7.21 (1H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.13 (9H, m, Bn-*m*,*p*), 6.80 (1H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-Pt}$ = ~30 Hz, H_n), 6.75 (1H, dd, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = ~25 Hz, H_b), 6.58 (1H, td, $^3J_{H-F}$ = $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 2 Hz, H_d), 6.42 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 1.5 Hz, H_p), 3.43 (6H, d, $^2J_{H-P}$ = 9 Hz, $^3J_{H-Pt}$ = 32 Hz, Bn*CH*$_2$), 2.52 (3H, s, Me) ppm.

δ_C = 19.21 (s, Me), 25.52 (d, $^1J_{C-P}$ = 30 Hz, $^2J_{C-Pt}$ = 30 Hz, Bn*CH*$_2$), 105.11 (d, $^2J_{C-F}$ = 20 Hz, C_d), 109.32 (m, $C_{h,p}$), 113.77 (d, $^4J_{H-P}$ = 3 Hz, $^3J_{H-Pt}$ = 27 Hz, H_j), 117.03 (d, $^2J_{C-F}$ = 18 Hz, $^2J_{C-Pt}$ = 47 Hz, C_n), 118.86 (d, $^2J_{C-F}$ = 18 Hz, $^2J_{C-Pt}$ = 56 Hz, C_b), 120.81 (d, $^3J_{C-F}$ = 10 Hz, $^3J_{C-Pt}$ = 30 Hz, C_e), 121.60 (d, $^5J_{C-P}$ = 2 Hz, Bn-*p*), 123.33 (s, Bn-*m*), 125.18 (d, $^3J_{C-P}$ = 5.5 Hz, Bn-*o*), 128.61 (d, $^2J_{C-P}$ = 5 Hz, $^3J_{C-Pt}$ = 16 Hz, Bn-*q*), 113.32 (d, $^3J_{C-F}$ = 8 Hz, C_q), 134.43 (s, C_i), 140.42 (m, C_l), 141.66 (m, C_f), 157.81 (d, $^1J_{C-F}$ = 253 Hz, $^3J_{C-Pt}$ = 56 Hz, C_o), 159.02 (d, $^1J_{C-F}$ = 252 Hz, $^3J_{C-Pt}$ = 46 Hz, C_c) 160.37 (s, $^2J_{C-Pt}$ = 61 Hz, $C_{g/k}$), 160.67 (s, $^2J_{C-Pt}$ = 61 Hz, $C_{g/k}$), 165.78 (m, $^1J_{C-Pt}$ = 700 Hz, C_a), 166.15 (m, $^1J_{C-Pt}$ = 702 Hz, C_m) ppm.

δ_F = -110.69 ($^4J_{F-Pt}$ = 26.5 Hz, F_c), -113.14 ($^4J_{F-Pt}$ = 29 Hz, F_o) ppm. δ_P = 1.18 ($^1J_{P-Pt}$ = 3893 Hz) ppm. δ_{Pt} = -4097 (d, $^1J_{Pt-P}$ = ~3900 Hz) ppm.

HR-MS (ESI): found 778.1918, calculated 778.1940 = $C_{39}H_{32}F_2NP^{194}Pt = [M]^+$.

Elemental analysis found (calculated): C 60.00 (60.15), H 4.07 (4.14) N 1.73 (1.80).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 6 and Table S1; full details on page S24.

Synthesis of Complex 2(t)

Complex **1** (80 mg, 10.4×10^{-2} mmol) was dissolved in acetone (40 ml), and water (10 ml) added. To this solution, an acetone solution of $PhICl_2$ (34 mg, 12.6×10^{-2} mmol, 1.2 eq) was added dropwise with stirring at room temperature, resulting in the yellow colour disappearing. The solvent was removed, the crude product washed with acetone and collected by filtration as a light cream solid (75 mg, 93.9×10^{-3} mmol, 90%).

2(t) δ_H = 7.95 (1H, t, $^3J_{H-H}$ = 8.5 Hz, H_i), 7.76 (2H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 6 Hz, H_e), 7.64 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^5J_{H-P}$ = 1.5 Hz, H_h), 6.37 (6H, m, Bn-*m,p*), 7.34 (2H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = 43 Hz, H_b), 7.21 (4H, d, $^3J_{H-H}$ = 7 Hz, Bn-*o*), 6.93 (1H, d, $^3J_{H-H}$ = 7 Hz, H_l), 6.83 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2 Hz, H_d), 6.91 (1H, t, $^3J_{H-H}$ = 7 Hz, H_m), 6.57 (1H, t, $^3J_{H-H}$ = 7 Hz, H_n), 6.19 (1H, d, $^3J_{H-H}$ = Hz, $^3J_{H-Pt}$ = 47 Hz, H_o), 4.20 (2H, dd, $^2J_{H-H}$ = 15 Hz, $^2J_{H-P}$ = 12 Hz, Bn*CH*$_2$), 4.06 (2H, dd, $^2J_{H-H}$ = 15 Hz, $^2J_{H-P}$ = 12 Hz, $^3J_{H-Pt}$ = 18 Hz, Bn*CH*$_2$), 3.61 (2H, d, $^2J_{H-P}$ = 11 Hz, $^3J_{H-Pt}$ = 16 Hz, H_j) ppm.

δ_C = 29.28 (d, $^1J_{C-P}$ = 30 Hz, $^2J_{C-Pt}$ = 25 Hz, Bn*CH*$_2$), 34.76 (d, $^1J_{C-P}$ = 40 Hz, $^2J_{C-Pt}$ = 62 Hz, C_j), 111.68 (d, $^2J_{C-F}$ = 25.5 Hz, C_d), 116.59 (s, C_h), 122.49 (d, $^2J_{C-F}$ = 19 Hz, $^2J_{C-Pt}$ = 32 Hz, C_b), 125.17 (s, C_m), 125.61 (d, $^3J_{C-P}$ = 18 Hz, C_l), 126.89 (s, $^3J_{C-Pt}$ = 45 Hz, C_n), 129.79 (s, Bn-*p*), 128.02 (d, $^3J_{C-F}$ = 8 Hz, $^3J_{C-Pt}$ = 16 Hz, C_e), 128.84(s, $^2J_{C-Pt}$ = 13.5 Hz, C_o), 129.21 (s, Bn-*m*), 130.39 (d, $^3J_{C-P}$ = Hz, Bn-*o*), 131.19 (s, $^1J_{C-Pt}$ = 449 Hz, C_p), 131.93 (d, $^2J_{C-P}$ = 8 Hz, $^3J_{C-Pt}$ = 16 Hz, Bn-*i*), 140.23 (s, C_i), 140.53 (d, $^2J_{C-P}$ = 9 Hz, C_k), 143.47 (m, C_f), 161.91 (s, $^2J_{C-Pt}$ = 33 Hz, C_g), 162.49 (m, $^1J_{C-Pt}$ = 468 Hz, C_a), 163.10 (d, $^1J_{C-Pt}$ = 256 Hz, $^3J_{C-F}$ = 40 Hz, C_c) ppm.

δ_F = -108.450 ($^4J_{F-Pt}$ = 20 Hz) ppm. δ_P = 19.37 ($^1J_{P-Pt}$ = 2649 Hz) ppm. δ_{Pt} = -2911 (d, $^1J_{Pt-P}$ = ~2700 Hz) ppm.

HR-MS (ESI): found 762.1628, calculated 762.1627 = $C_{38}H_{29}F_2NP^{194}Pt = [M\text{-}Cl]^+$.

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 2 and Table S1; full details on page S30.

Synthesis of Me-2(t)

Complex **Me-1** (50 mg, 64.3x10^{-3} mmol) was dissolved in acetone (40 ml), and water (10 ml) added. To this solution, an acetone solution of $PhICl_2$ (21 mg, 77.1x10^{-3} mmol, 1.2 eq) was added dropwise with stirring at room temperature, resulting in the yellow colour disappearing. The solvent was removed, and the crude product washed with acetone and collected by filtration as a light cream solid. (43 mg, 52.7x10^{-3} mmol, 82%).

δ_H = 7.93 (2H, m, $H_{i,j}$), 7.76 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, H_e), 7.65 (1H, d, $^3J_{H-H}$ = 7 Hz, H_h), 7.37 (7H, m, Bn), 7.31 (1H, d, $^3J_{H-F}$ = Hz, H_n), 7.24 (2H, d, $^3J_{H-H}$ = 6.5 Hz, Bn), 7.17 (2H, d, $^3J_{H-H}$ = 6.5 Hz, Bn), 6.91 (1H, d, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-Pt}$ = 12 Hz, H_t), 6.83 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.79 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_u), 6.65 (1H, dd, $^3J_{H-F}$ = Hz, $^4J_{H-H}$ = Hz, H_p), 6.58 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_v), 6.18 (1H, d, $^3J_{H-H}$ = 7.5 Hz, $^3J_{H-Pt}$ = 47 Hz, H_w), 4.21 (2H, m, BnCH_2), 4.06 (2H, m, BnCH_2), 3.60 (2H, d, $^2J_{H-P}$ = 11.5 Hz, $^3J_{H-Pt}$ = 15 Hz, H_r), 2.75 (3H, s, Me) ppm.

δ_C = 24.95 (s, Me), 28.90 (d, $^1J_{C-P}$ = 29 Hz, $^2J_{C-Pt}$ = 28 Hz, BnCH_2), 29.70 (d, $^1J_{C-Pt}$ = 29 Hz, $^2J_{C-P}$ = 22 Hz, BnCH_2), 34.77 (d, $^1J_{C-P}$ = 40 Hz, $^2J_{C-Pt}$ = 68 Hz, C_r), 111.65 (d, $^2J_{C-F}$ = 24 Hz, C_d), 115.96 (d, $^2J_{C-F}$ = 20 Hz, C_p), 116.45 (d, $^4J_{C-P}$ = 3.5 Hz, $^3J_{C-Pt}$ = 18 Hz, C_h), 120.43 (m, $C_{j,n}$), 122.35 (d, $^2J_{C-F}$ = 18 Hz, $^2J_{C-Pt}$ = 18 Hz, C_b), 125.11 (s, C_u), 125.62 (d, $^3J_{C-P}$ = 17.5 Hz, $^3J_{C-Pt}$ = 39 Hz, C_t), 126.86 (s, $^3J_{C-Pt}$ = 46 Hz, C_v), 127.76 (m, Bn), (d, $^3J_{C-F}$ = 8.5 Hz, $^3J_{C-Pt}$ = 23 Hz, C_e), 128.74 (s, $^2J_{C-Pt}$ = 14 Hz, C_w), 127.17 (m, Bn), 130.42 (m, Bn), 131.52 (s, C_s), 132.04 (m, Bn), 139.97 (s, C_i), 140.62 (d, $^3J_{C-F}$ = 7.5 Hz, C_q), 140.65 (d, $^2J_{C-P}$ = 10.5 Hz, $^1J_{C-Pt}$ = 53 Hz, C_x), 142.01 (t, $^3J_{C-P}$ = $^4J_{C-F}$ = 2.5 Hz, $^2J_{C-Pt}$ = 13.5 Hz, C_l), 143.65 (t, $^3J_{C-P}$ = $^4J_{C-F}$ = 2.5 Hz, $^2J_{C-Pt}$ = ~13 Hz, C_f), 161.84 (d, $^1J_{C-F}$ = 254 Hz, $^3J_{C-Pt}$ = 53 Hz, C_c), 162.40 (s, $^2J_{C-Pt}$ = 32 Hz, C_k), 162.91 (s, $^2J_{C-Pt}$ = 31 Hz, C_g), 163.07 (d, $^1J_{C-F}$ = 256 Hz, $^3J_{C-Pt}$ = 36 Hz, C_o), 163.38 (m, $^1J_{C-Pt}$ = 558 Hz, $C_{a/m}$), 163.97 (m, $^1J_{C-Pt}$ = 556 Hz, $C_{a/m}$) ppm.

δ_F = -108.61 ($^4J_{F-Pt}$ = 19 Hz, F_c), -111.30 ($^4J_{F-Pt}$ = 22 Hz, F_o) ppm. δ_P = 19.76 ($^1J_{P-Pt}$ = 2657 Hz) ppm. δ_{Pt} = -2885 (d, $^1J_{Pt-P}$ = ~2700 Hz) ppm.

HR-MS (ESI): found 776.1787, calculated 776.1784 = $C_{39}H_{31}F_2NP^{194}Pt$ = $[M\text{-}Cl]^+$.

Synthesis of Complexes 3 and 4

To a solution of **1** (20 mg, 26.2×10^{-3} mmol) in chloroform (10 ml), was added a solution of $PhICl_2$ (3.6 mg, 13.1×10^{-3} mmol, 0.5 eq in 2 ml chloroform) dropwise at room temperature. After addition of the final drop, solvent was removed, and the crude mixture washed with hexane. Acetone was used to dissolve the **4**, leaving behind **2(t)**. To a sample of the **4** (9 mg) in chloroform (0.6 ml) was added $PhICl_2$ (4 mg, excess) at room temperature. Full conversion to **3** was observed, though it was not isolated.

3 δ_H = 7.91 (1H, t, $^3J_{H-H}$ = 8 Hz, Hi), 7.83 (1H, d, $^3J_{H-H}$ = 8 Hz, $H_{h/j}$), 7.78 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-F}$ = 5 Hz, H_m), 7.33 (1H, d, $^3J_{H-H}$ = 8 Hz, $H_{h/j}$), 7.16 (6H, m, Bn-*p*), 7.10 (9H, m, $H_{b,n}$, Bn-*m*), 7.04 (1H, m, C_e), 6.93 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2 Hz, H_d), 6.41 (6H, d, $^3J_{H-H}$ = 7.5 Hz, Bn-*o*), 3.94 (6H, d, $^2J_{H-H}$ = 13 Hz, $^3J_{H-Pt}$ = 11 Hz, Bn*CH*$_2$) ppm.

δ_C = 31.63 (d, $^1J_{C-P}$ = 32 Hz, $^2J_{C-Pt}$ = 26 Hz, Bn*CH*$_2$), 113.62 (d, $^2J_{C-F}$ = 20 Hz, C_d), 114.9562 (d, $^2J_{C-F}$ = 23 Hz, C_n), 119.26, (s, $C_{h/j}$), 122.35 (d, $^2J_{C-F}$ = 21 Hz, $^2J_{C-Pt}$ = 35 Hz, C_b), 126.66 (d, $^4J_{C-P}$ = 5 Hz, $C_{h/j}$), 127.65 (d, $^5J_{C-P}$ = 4 Hz, Bn-*p*), 128.90 (d, $^4J_{C-P}$ = 3 Hz, Bn-*m*), 130.03 (d, $^3J_{C-F}$ = 5 Hz, C_e), 131.07 (d, $^3J_{C-P}$ = 6.5 Hz, Bn-*o*), 131.73 (d, $^2J_{C-P}$ = 9.5 Hz, Bn-*i*), 132.36 (d, $^3J_{C-F}$ = 8 Hz, C_m), 130.60 (s, $C_{f/l}$), 139.97 (s, C_i), 140.89 ($C_{f/l}$), 141.36 (d, $^3J_{C-F}$ = 6 Hz, C_a), 161.75 (d, $^1J_{C-F}$ = 255 Hz, C_c), 163.47 (s, C_k), 163.93 (d, $^1J_{C-F}$ = 248 Hz, C_o), 164.31 (d, $^3J_{C-P}$ = 4 Hz, C_g) ppm.

δ_F = -107.92 ($^4J_{F-Pt}$ = 29.5 Hz), -111.26 ppm. δ_P = 9.14 ($^1J_{P-Pt}$ = 2434 Hz) ppm. δ_{Pt} = -1719 (d, $^1J_{Pt-P}$ = ~2450 Hz) ppm.

4 δ_H = 7.94 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_i), 7.90 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-F}$ = 4.5 Hz, H_e), 7.72 (1H, d, $^3J_{H-H}$ = 7.5 Hz, H_h), 7.52 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-F}$ = 5.5 Hz, H_m), 7.47 (1H, d, $^3J_{H-H}$ = 7.5 Hz, H_j), 7.37 (1H, m, Bn-*o*), 7.25 (9H, m, Bn-*m,p*), 7.10 (2H, t, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, H_n), 6.73 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.66 (1H, dt, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = $^4J_{H-P}$ = 2 Hz, $^3J_{H-Pt}$ = ~55 Hz, H_b), 3.46 (6H, d, $^2J_{H-P}$ = 11 Hz, $^3J_{H-Pt}$ = 30 Hz, Bn*CH*$_2$) ppm.

δ_C = 29.53 (d, $^1J_{C-P}$ = 34.5 Hz, $^2J_{C-Pt}$ = 34.5 Hz, Bn*CH*$_2$), 110.23 (d, $^2J_{C-F}$ = 23.5 Hz, C_d), 114.90 (d, $^2J_{C-F}$ = 23.5 Hz, C_n), 115.96 (s, C_h), 121.66 (dd, $^2J_{C-F}$ = 20 Hz, $^3J_{C-P}$ = 2 Hz, C_b), 122.76 (d, $^4J_{C-P}$ = 2 Hz, C_j), 126.15 (d, $^3J_{C-F}$ = 9.5 Hz, $^3J_{C-Pt}$ = 44 Hz, C_e), 126.82 (s, Bn-*p*), 128.38 (s, Bn-*m*), 130.40 (d, $^3J_{C-P}$ = 5.5 Hz, Bn-*o*), 131.175 (d, $^3J_{C-F}$ = 8 Hz, C_m), 133.71 (d, $^2J_{C-P}$ = 5.5 Hz, Bn-*i*), 136.66 (s, C_l), 139.19 (s, C_i), 142.76 (s, C_f), 146.19 (t, $^2J_{C-P}$ = $^3J_{C-F}$ = 6 Hz, C_a), 160.71 (s, C_k), 162.09 (d, $^1J_{C-F}$ = 253 Hz, C_c), 163.83 (d, $^1J_{C-F}$ = 250 Hz, C_o), 164.51 (s, C_g) ppm.

δ_F = -110.84 ($^4J_{F-Pt}$ = 64 Hz), -111.36 ppm. δ_P = -1.76 ($^1J_{P-Pt}$ = 4272 Hz) ppm. δ_{Pt} = -3807 (d, $^1J_{Pt-P}$ = ~4300 Hz) ppm.

HR-MS (ESI): found 764.1779, calculated 764.1784 = $C_{38}H_{31}F_2NP^{194}Pt$ = $[M\text{-}Cl]^+$.

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 3 and Table S1; full details on page S36.

Synthesis of b-Me-3 and b-Me-4

To a chloroform solution of **Me-1** (10 mg, $12.9x10^{-3}$ mmol) was added $PhICl_2$ (1.8 mg, $6.43x10^{-3}$ mmol, 0.5eq) which gave a 50/50 mixture of **Me-2(t)** and **b-Me-4**. The complexes were not physically separated, but the spectroscopic data acquired on pure **Me-2(t)** allowed the identification of data from **b-Me-4**. The use of one equivalent of $PhICl_2$ gave an equivalent mixture of **Me-2(t)** and **b-Me-3**.

b-Me-3 (key data only) δ_H = 2.41 (3H, s, Me) ppm. δ_F = -107.90 ($^4J_{F\text{-}Pt}$ = 63 Hz), -112.52 ppm. δ_P = 7.50 ($^1J_{P\text{-}Pt}$ = 2432 Hz) ppm.

b-Me-4 δ_H = 7.89 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_i), 7.70 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, $H_{h/j}$), 7.53 (1H, dd, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{H\text{-}F}$ = 5.5 Hz, H_m), 7.48 (1H, dd, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}F}$ = 5 Hz, H_e), 7.32 (6H, d, $^3J_{H\text{-}H}$ = 7.5 Hz, Bn-*o*), 7.30 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, $H_{h/j}$), 7.22 (9H, m, Bn-*m,p*), 7.01 (1H, dd, $^3J_{H\text{-}F}$ = 10 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, H_p), 6.92 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8.5 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, H_n), 6.67 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2 Hz, H_d), 6.42 (1H, dt, $^3J_{H\text{-}F}$ = 8.5 Hz, $^4J_{H\text{-}H}$ = $^4J_{H\text{-}P}$ = 2 Hz, $^3J_{H\text{-}Pt}$ = 54 Hz, H_b), 3.43 (6H, m, BnCH_2), 2.61 (3H, s, Me) ppm.

δ_F = -110.96 ($^4J_{F\text{-}Pt}$ = 63 Hz), -112.78 ppm. δ_P = -1.96 ($^1J_{P\text{-}Pt}$ = 4253 Hz) ppm. δ_{Pt} = -3821 (d, $^1J_{Pt\text{-}P}$ = ~4300 Hz) ppm.

Synthesis of Complex 2(c) and 5

Solid complex **2(t)** (60 mg, 75.2x10^{-3} mmol) was added to the top of a silica column and chloroform run through. After 20 column volumes of chloroform, the solvent system was changed to 40:60 EtOAC:hexane which cleanly eluted first **5** (yield 47 mg, 58.7x10^{-3} mmol 78 %), followed by the **2(c)** (yield 12 mg, 15.0x10^{-3} mmol 20 %).

2(c) δ_H = 8.34 (1H, d, $^4J_{H\text{-}P}$ = 7.5 Hz, $^3J_{H\text{-}Pt}$ = 31 Hz, H_o), 7.84 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_i), 7.80 (2H, dd, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{H\text{-}F}$ = 5 Hz, H_e), 7.60 (2H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_h), 7.27 (1H, m, $H_{l/m}$), 7.24 (2H, m, $H_{l/m}$), 7.15 (2H, t, $^3J_{H\text{-}H}$ = 7.5 Hz, Bn-*p*), 7.07 (4H, t, $^3J_{H\text{-}H}$ = 7.5 Hz, Bn-*m*), 7.02 (2H, dd, $^3J_{H\text{-}F}$ = 10.5 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, $^3J_{H\text{-}Pt}$ = ~20 Hz, H_b), 6.90 (2H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8.5 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, H_d), 6.19 (4H, d, $^3J_{H\text{-}H}$ = 7.5 Hz, Bn-*o*), 2.97 (4H, m, BnCH_2), 2.65 (2H, m, H_j) ppm.

δ_C = 29.40 (d, $^1J_{C\text{-}P}$ = 29 Hz, $^2J_{C\text{-}Pt}$ = 34 Hz, BnCH_2), 34.42 (d, $^1J_{C\text{-}P}$ = 47 Hz, $^2J_{C\text{-}Pt}$ = 66 Hz, C_j), 112.16 (d, $^2J_{C\text{-}F}$ = 24 Hz, C_d), 116.72 (s, $^3J_{C\text{-}Pt}$ = 13 Hz, C_h), 121.66 (d, $^2J_{C\text{-}F}$ = 18 Hz, $^2J_{C\text{-}Pt}$ = 22 Hz, H_b), 125.37 (m, $C_{l/m,n}$), 127.59 (d, $^5J_{C\text{-}Pt}$ = 3 Hz, Bn-*p*), 128.26 (m, $C_{e,l/m}$), 128.23 (d, $^4J_{C\text{-}P}$ = 3 Hz, Bn-*m*), 129.43 (d, $^3J_{C\text{-}P}$ = 5 Hz, Bn-*o*), 131.16 (d, $^2J_{C\text{-}P}$ = 10 Hz, $^2J_{C\text{-}Pt}$ = 26 Hz, C_k), 136.00 (s, C_o), 138.09 (d, $^2J_{C\text{-}P}$ = 9 Hz, $^1J_{C\text{-}Pt}$ = 50 Hz, C_p), 140.07 (s, C_i), 140.57 (s, Bn-*i*), 143.73 (m, C_f), 161.45 (s, $^2J_{C\text{-}Pt}$ = 33 Hz, C_g), 161.68 (m, $^1J_{C\text{-}Pt}$ = 532 Hz, H_a), 164.13 (d, $^1J_{C\text{-}F}$ = 40 Hz, $^4J_{C\text{-}Pt}$ = 254 Hz, C_c) ppm.

δ_F = -108.14 ($^4J_{F\text{-}Pt}$ = 21 Hz) ppm. δ_P = 29.00 ($^1J_{P\text{-}Pt}$ = 2692 Hz) ppm. δ_{Pt} = -3114 (d, $^1J_{Pt\text{-}P}$ = ~2700 Hz) ppm.

HR-MS (ESI): found 762.1627, calculated 762.1594 = $C_{38}H_{29}F_2NP^{194}Pt$ = $[M\text{-}Cl]^+$; found 820.1213, calculated 820.1195 = $C_{38}H_{29}F_2ClNP^{194}PtNa$ = $[M+Na]^+$.

Elemental analysis found (calculated.EtOAc): C 54.32 (56.86), H 4.59 (4.20), N 1.40 (1.58).

5 δ_H = 7.85 (1H, t, $^3H_{H\text{-}H}$ = 8 Hz, H_i), 7.72 (1H, dd, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{H\text{-}F}$ = 5.5 Hz, H_m), 7.48 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_h), 7.46 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_j), 7.35 (6H, m, H_e, Bn), 7.23 (6H, m, H_v, Bn'), 7.07 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8 Hz, $^3J_{H\text{-}H}$ = 2.5 Hz, H_n), 6.94 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_u), 6.88 (1H, dd, $^3J_{H\text{-}F}$ = 9.5 Hz, $^4J_{H\text{-}H}$ = 2.5 Hz, H_p), 6.68 (1H, t, $^3J_{H\text{-}H}$ = 8 Hz, H_t), 6.61 (1H, td, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}F}$ = 8 Hz, $^3J_{H\text{-}H}$ = 2.5 Hz, H_d), 6.55 (1H, dt, $^3J_{H\text{-}F}$ = 10.5 Hz, $^4J_{H\text{-}H}$ = $^4J_{H\text{-}P}$ = 2.5 Hz, $^3J_{H\text{-}Pt}$ = ~60 Hz, H_b), 6.28 (1H, d, $^3J_{H\text{-}H}$ = 8 Hz, H_s), 4.12 (1H, dd, $^2J_{H\text{-}H}$ = 14 Hz, $^2J_{H\text{-}P}$ = 9 Hz, $H_{Bn'}$), 4.03 (1H, dd, $^2J_{H\text{-}H}$ = 13.5 Hz, $^2J_{H\text{-}P}$ = 11 Hz, H_x), 3.49 (1H, dd, $^2J_{H\text{-}H}$ = 15.5 Hz, $^2J_{H\text{-}P}$ = 8.5 Hz, H_{Bn}), 3.35 (2H, m, $H_{x,Bn}$), 3.09 (1H, t, $^2J_{H\text{-}P}$ = $^2J_{H\text{-}H}$ = 14 Hz, $H_{Bn'}$) ppm.

δ_C = 24.82 (d, $^1J_{C\text{-}P}$ = 20 Hz, C_{Bn}), 25.78 (d, $^1J_{C\text{-}P}$ = 30 Hz, $C_{Bn'}$), 33.33 (d, $^1J_{C\text{-}P}$ = 36 Hz, C_x), 110.12 (d, $^2J_{C\text{-}F}$ = 22.5 Hz, C_d), 113.60 (d, $^2J_{C\text{-}F}$ = 22.5 Hz, C_n), 116.59 (s, C_h), 118.00 (d, $^2J_{C\text{-}F}$ = 20 Hz, C_p), 121.78 (dd, $^2J_{C\text{-}F}$ = 19 Hz, $^3J_{C\text{-}P}$ = 5 Hz, C_b), 125.24 (m, $C_{j,e}$), 126.209 (d, $^5J_{C\text{-}P}$ = 4 Hz, C_t), 126.69 (d, $^5J_{C\text{-}P}$ = 3 Hz, Bn-*p*), 127.04 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, C_u), 127.48 (s, Bn'-*p*), 128.44

(s, Bn-*m*), 129.00 (s, Bn'-*m*), 130.00 (d, $^{3}J_{C\text{-}P}$ = 7.5 Hz, Bn'-*o*), 130.10 (d, $^{3}J_{C\text{-}P}$ = 5 Hz, C_v), 130.42 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, Bn-*o*), 131.47 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, C_s), 133.09 (d, $^{2}J_{C\text{-}P}$ = 10 Hz, C_{Bn}), 133.54 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, $C_{Bn'}$), 134.41 (d, $^{3}J_{C\text{-}F}$ = 9 Hz, C_m), 135.70 (m, C_l), 135.97 (d, $^{2}J_{C\text{-}P}$ = 3 Hz, C_w), 136.16 (s, C_i), 141.33 (d, $^{3}J_{C\text{-}P}$ = 5 Hz, C_r), 141.68 (s, C_f), 144.36 (d, $^{3}J_{C\text{-}F}$ = 8 Hz, C_q), 144.78 (dd, $^{3}J_{C\text{-}F}$ = 6 Hz, $^{2}J_{C\text{-}P}$ = 3.5 Hz, C_a), 159.72 (s, C_k), 162.50 (dd, $^{1}J_{C\text{-}F}$ = 253 Hz, $^{4}J_{C\text{-}P}$ = 3.5 Hz, H_c), 163.03 (d, $^{1}J_{C\text{-}F}$ = 249 Hz, C_o), 163.30 (d, $^{3}J_{C\text{-}P}$ = 3.5 Hz, C_g) ppm.

δ_F = -110.38 ($^{4}J_{F\text{-}Pt}$ = 57 Hz), -112.08 ppm. δ_P = -9.29 ($^{1}J_{P\text{-}Pt}$ = 4552 Hz) ppm. δ_{Pt} = -3985 (d, $^{1}J_{Pt\text{-}P}$ = ~4500 Hz) ppm.

HR-MS (ESI): found 762.1622, calculated 762.1627 = $C_{38}H_{29}F_2NP^{194}Pt$ = $[M\text{-}Cl]^+$.

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 4 and Table S1; full details on page S41.

Elemental analysis found (calculated.$CHCl_3$): C 52.10 (51.52), H 3.44 (3.46), N 1.51 (1.50).

Synthesis of Me-2(c) and a-Me-5 and b-Me-5

Me-2(t) (20 mg, $24.6x10^{-3}$ mmol) was dissolved in chloroform (5 ml) and heated to 50°C (5 days). The solvent was then removed, **a-Me-5** and **b-Me-5** extracted with acetone, leaving the less soluble **Me-2(c)**. **Me-2(c)** was purified by column chromatography on silica, loading with dichloromethane and eluting with EtOAc (yield 10 mg, $12.3x10^{-3}$ mmol, 50%). **a-Me-5** and **b-Me-5** could not be separated from each other, but it was possible to separate their spectroscopic data.

Me-2(c) δ_H = 8.27 (1H, d, $^3J_{H-H}$ = 8 Hz, $^3J_{H-Pt}$ = 31.5 Hz, H_s), 7.80 (1H, d, $^3J_{H-H}$ = 8 Hz, H_j), 7.76 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.73 (1H, dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-F}$ = 3 Hz, H_e), 7.56 (1H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.20 (1H, m, H_t), 7.14 (2H, m, $H_{u,v}$), 7.08 (2H, m, Bn-*p*), 7.00 (4H, m, Bn-*m*), 6.92 (1H, dd, $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 22 Hz, H_b), 6.87 (1H, dd, $^3J_{H-F}$ = 7 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 24 Hz, H_n), 6.82 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.65 (1H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2.5 Hz, H_p), 6.15 (2H, dd, $^3J_{H-H}$ = 7.5 Hz, Bn-*o*), 6.12 (2H, dd, $^3J_{H-H}$ = 7.5 Hz, Bn-*o*), 2.83 (4H, m, H_x, BnCH_2), 2.69 (3H, s, Me) 2.56 (2H, m, BnCH_2) ppm.

δ_C = 24.36 (s, Me), 29.27 (m, BnCH_2), 34.38 (d, $^1J_{C-P}$ = 47 Hz, $^2J_{C-Pt}$ = 64 Hz, C_x), 112.08 (d, $^2J_{C-F}$ = 23 Hz, C_d), 116.13 (d, $^2J_{C-F}$ = 25 Hz, C_p), 116.51 (s, $^3J_{C-Pt}$ = 15 Hz, C_h), 119.24 (d, $^2J_{C-F}$ = 17 Hz, $^2J_{C-Pt}$ = 22 Hz, C_n), 120.58 (s, $^3J_{C-Pt}$ = 14.5 Hz, C_j), 121.50 (d, $^2J_{C-F}$ = 18 Hz, $^2J_{C-Pt}$ = 26 Hz, C_b), 125.27 (m, $C_{u,v}$), 127.56 (s, Bn-*p*), 128.31 (m, $C_{e,t}$), 128.91 (s, Bn-*m*), 129.41 (m, Bn-*o*), 131.24 (m, Bn-*i*), 136.04 (s, C_s), 138.15 (d, $^2J_{C-P}$ = 8 Hz, $^1J_{C-Pt}$ = 25.5 Hz, C_r), 139.83 (s, C_i), 141.20 (d, $^2J_{C-P}$ = 7 Hz, $^2J_{C-Pt}$ = 23 Hz, C_w), 141.43 (s, C_q), 142.32 (m , C_l), 143.80 (m, C_f), 162.06 (s, $^2J_{C-Pt}$ = 30 Hz, C_k), 162.35 (s, $^2J_{C-Pt}$ = 29.5 Hz, C_g), 162.59 (m, $^1J_{C-Pt}$ = 528 Hz, $C_{b/m}$), 162.73 (d, $^1J_{C-F}$ = 259 Hz, $^3J_{C-Pt}$ = 35 Hz, C_o), 163.23 (m, $^1J_{C-Pt}$ = 530 Hz, $C_{b/m}$), 164.04 (d, $^1J_{C-F}$ = 259 Hz, $^3J_{C-Pt}$ = 36 Hz, C_c) ppm.

δ_F = -108.24 ($^4J_{F-Pt}$ = 20 Hz), -110.53 ($^4J_{F-Pt}$ = 23 Hz) ppm. δ_P = 29.06 ($^1J_{P-Pt}$ = 2723 Hz) ppm.

δ_{Pt} = -3120 (d, $^1J_{Pt-P}$ = ~3100 Hz) ppm.

HR-MS (ESI): found 776.1787, calculated 776.1784 = $C_{39}H_{31}F_2PN^{194}Pt$ = $[M-Cl]^+$.

Elemental analysis found (calculated.CH_2Cl_2): C 52.75 (53.49), H 3.77 (3.70), N 1.72 (1.56).

a-Me-5 δ_H = 7.85 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.68 (2H, m, $H_{h,m}$), 7.46 (1H, d, $^3J_{H-H}$ = 8 Hz, H_j), 7.34 (5H, m, Bn), 7.15 (6H, H_v, Bn), 7.07 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = Hz, H_n), 6.95 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_u), 6.87 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_p), 6.70 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_t), 6.44 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.39 (1H, dt, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = $^4J_{H-P}$ = 2.5 Hz, H_b), 6.29 (1H, d, $^3J_{H-H}$ = 7.5 Hz, H_s), 4.04 (2H, m, H_x, BnCH_2)*, 3.48 (1H, dd, $^2J_{H-H}$ = 15.5 Hz, $^2J_{H-P}$ = 8 Hz, BnCH_2), 3.30 (2H, m, H_x, BnCH_2), 3.16 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 14 Hz, BnCH_2)*, 2.53 (3H, s, Me) ppm. * Same carbon

δ_C = 23.87 (s, Me), 24.69 (d, $^1J_{C-P}$ = 21 Hz, Bn*CH*$_2$), 26.05 (d, $^1J_{C-P}$ = 28 Hz, Bn*CH*$_2$)*, 33.22 (d, $^1J_{C-P}$ = 37 Hz, C_x), 113.51 (d, $^2J_{C-F}$ = 23 Hz, C_d), 114.10 (d, $^2J_{C-F}$ = 22.5 Hz, C_n), 117.79 (d, $^2J_{C-F}$ = 22 Hz, C_p), 119.88(dd, $^2J_{C-F}$ = 19 Hz, $^3J_{C-P}$ = 6 Hz, C_b), 120.26 (s, C_h), 125.27 (s, C_j), 126.28 (d, $^5J_{C-P}$ = 4 Hz, C_t), 126.43 (d, $^5J_{C-P}$ = 2 Hz, Bn-*p*), 127.03 (d, $^4J_{C-P}$ = 3 Hz, C_u), 127.38 (m, Bn-*p*), 128.39 (s, Bn-*m*), 128.96 (s, Bn-*m*), 130.04 (m, Bn-*o*), 130.39 (m, C_v, Bn-*o*), 131.29 (d, $^4J_{C-P}$ = 3.5 Hz, C_s), 133.13 (d, $^3J_{C-F}$ = 9 Hz, C_m), 133.62 (m, Bn-*i*), 134.58 (d, $^3J_{C-F}$ = 8.5 Hz, C_m), 135.97 (m, $C_{l,w}$), 137.56 (s, C_i), 140.66 (s, C_r), 141.32 (m, C_f), 144.06 (d, $^3J_{C-F}$ = 8.5 Hz, C_q), 148.23 (m, C_a), 159.86 (s, C_k), 162.92 (d, $^1J_{C-F}$ = 249 Hz, C_o), 162.99 (d, $^1J_{C-F}$ = 246 Hz, $^4J_{C-P}$ = 5 Hz, C_c), 164.08 (s, C_g) ppm.

δ_F = -112.37, -113.51 ($^4J_{F-Pt}$ = 52 Hz) ppm. δ_P = -8.22 ($^1J_{P-Pt}$ = 4527 Hz) ppm. δ_{Pt} = -3439 (d, $^1J_{Pt-P}$ = ~4800 Hz) ppm.

b-Me-5 δ_H = 7.79 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.44 (1H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.34 (7H, m, $H_{e,j}$, Bn), 7.15 (6H, m, H_v, Bn), 6.93 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_n), 6.89 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_u), 6.69 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_p), 6.66 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_t), 6.61 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.51 (1H, dt, $^3J_{H-F}$ = 10.5 Hz, $^4J_{H-H}$ = $^4J_{H-P}$ = 2.5 Hz, $^3J_{H-Pt}$ = ~28 Hz, H_b), 6.32 (1H, d, $^3J_{H-H}$ = 7.5 Hz, H_s), 4.25 (1H, dd, $^2J_{H-H}$ = 15 Hz, $^2J_{H-P}$ = 10 Hz, Bn*CH*$_2$)*, 3.96 (1H, dd, $^2J_{H-H}$ = 13 Hz, $^2J_{H-P}$ = 10.5 Hz, H_x), 3.37 (3H, m, H_x, Bn*CH*$_2$), 2.89 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 15 Hz, Bn*CH*$_2$)*, 2.42 (3H, s, Me) ppm. * Shows same carbon

δ_C = 22.38 (s, Me), 24.76 (d, $^1J_{C-P}$ = 21 Hz, Bn*CH*$_2$), 25.69 (d, $^1J_{C-P}$ = 28.5 Hz, Bn*CH*$_2$)*, 33.17 (d, $^1J_{C-P}$ = 35 Hz, C_x), 110.05 (d, $^2J_{C-F}$ = 24 Hz, C_d), 115.22 (d, $^2J_{C-F}$ = 21 Hz, C_p), 115.80 (d, $^2J_{C-F}$ = 22 Hz, C_n), 117.00 (s, C_h), 121.91 (dd, $^2J_{C-F}$ = 19 Hz, $^3J_{C-P}$ = 5 Hz, C_b), 125.02 (d, $^3J_{C-F}$ = 10 Hz, C_e), 125.82 (d, $^5J_{C-P}$ = 4 Hz, C_t), 126.82 (m, C_u, Bn-*p*), 127.40 (m, C_j Bn-*p*), 128.42 (s, Bn-*m*), 129.03 (s, Bn-*m*), 130.04 (d, $^3J_{C-P}$ = 7 Hz, Bn-*p*), 130.39 (d, $^3J_{C-P}$ = 5 Hz, Bn-*p*), 130.94 (m, $C_{s,v}$), 133.21 (d, $^3J_{C-F}$ = 11 Hz, C_m), 133.49 (m, Bn-*i*), 135.42 (s, C_l), 135.94 (s, C_w), 136.78 (s, C_i), 141.29 (s, C_r), 141.81 (m, C_f), 143.81 (d, $^3J_{C-F}$ = 9.5 Hz, C_q), 145.36 (m, C_a), 157.98 (s, C_k), 162.32 (d, $^1J_{C-F}$ = 249.5 Hz, C_o), 162.69 (d, $^1J_{C-F}$ = 254.5 Hz, $^4J_{C-P}$ = 5 Hz, C_c), 164.11 (s, C_g) ppm.

δ_F = -110.49 ($^4J_{F-Pt}$ = 53 Hz), -113.73 ppm. δ_P = -6.91 ($^1J_{P-Pt}$ = 4622 Hz) ppm. δ_{Pt} = -3466 (d, $^1J_{Pt-P}$ = ~4750 Hz) ppm.

HR-MS (ESI mixture): found 776.1781, calculated 776.1784 = $C_{39}H_{31}F_2PN^{194}Pt$ = $[M-Cl]^+$.

Synthesis of Complex 6

Complex 5 (10 mg, $12.5x10^{-3}$ mmol) was dissolved in chloroform (1 ml) and treated with $PhICl_2$ (4 mg, $15.0x10^{-3}$ mmol, 1.2 eq) at room temperature. The solvent was removed under vacuum, and the crude product washed with hexane (10.8 mg, $12.4x10^{-3}$ mmol, 99%).

6 δ_H = 8.11 (1H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 5.5 Hz, H_m), 7.89 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 23 Hz, H_b), 7.70 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_i), 7.40 (6H, m, $H_{e,h/j,n}$, Bn), 7.23 (2H, d, $^3J_{H-H}$ = Hz, Bn-*o*), 7.10 (4H, $H_{h/j}$, Bn), 6.96 (4H, m, $H_{d,t,u,v}$), 6.73 (1H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2.5 Hz, H_q), 6.55 (1H, d, $^3J_{H-H}$ = 7 Hz, H_s), 6.34 (2H, d, $^3J_{H-H}$ = 8 Hz, Bn-*o*), 4.76 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 15 Hz, BnCH_2)*, 3.86 (1H, dd, $^2J_{H-H}$ = 16 Hz, $^2J_{H-P}$ = 9.5 Hz, BnCH_2)*, 3.75 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 14 Hz, H_x), 3.54 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 15 Hz, BnCH_2)**, 3.15 (1H, dd, $^2J_{H-H}$ = 15 Hz, $^2J_{H-P}$ = 11 Hz, BnCH_2)**, 2.66 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 14 Hz, H_x) ppm.

*,** protons attached to the same carbon.

δ_C = 26.69 (d, $^1J_{C-P}$ = 30 Hz, C_x), 30.04 (d, $^1J_{C-P}$ = 27 Hz, BnCH_2), 31.62 (d, $^1J_{C-P}$ = 36 Hz, BnCH_2), 114.25 (m, $C_{d,p}$), 115.24 (d, $^2J_{C-F}$ = 22.5 Hz, C_n), 118.33 (d, $^2J_{C-F}$ = 24.5 Hz, $^2J_{C-Pt}$ = 24.5 Hz, C_n), 126.87 (d, $^3J_{C-F}$ = 9.5 Hz, C_e), 127.07 (d, $^5J_{C-P}$ = 3 Hz, Bn-*p*), 127.30 (d, $^4J_{C-P}$ = 3 Hz, C_u), 127.93 (d, $^5J_{C-P}$ = 2.5 Hz, Bn-*p*), 128.35 (d, $^3J_{C-P}$ = 2.5 Hz, C_v), 128.47 (d, $^4J_{C-P}$ = 3.5 Hz, Bn-*m*), 129.27 (s, $^3J_{C-Pt}$ = 18 Hz, $C_{h/j}$), 129.69 (d, $^4J_{C-P}$ = 3.5 Hz, Bn-*m*), 130.26 (s, C_s), 130.62 (m, Bn-*o*), 130.94 (d, $^2J_{C-P}$ = 9.5 Hz, Bn-*i*), 131.60 (s, $C_{h/j}$), 131.90 (d, $^2J_{C-P}$ = 9.5 Hz, Bn-*i*), 133.48 (d, $^3J_{C-F}$ = 10 Hz, C_m), 135.82 (d, $^4J_{C-F}$ = 3.5 Hz, C_l), 138.68 (d, $^4J_{C-F}$ = 1.5 Hz, C_l), 139.00 (s, C_i), 140.51 (d, $^3J_{C-F}$ = 8 Hz, C_q), 140.74 (d, $^3J_{C-P}$ = 6 Hz, C_r), 141.44 (d, $^2J_{C-P}$ = 6.5 Hz, C_w), 162.42 (s, $C_{g/k}$), 162.47 (d, $^1J_{C-F}$ = 275.5 Hz, C_c), 163.07 (d, $^1J_{C-F}$ = 249.5 Hz, C_o), 165.05 (s, $C_{g/k}$) ppm.

δ_F = -103.68 ($^4J_{F-Pt}$ = 28.5 Hz), -111.13 ppm. δ_P = -0.41 ($^1J_{P-Pt}$ = 2271 Hz) ppm. δ_{Pt} (213K) = -1902 (d, $^1J_{Pt-P}$ = ~2300 Hz) ppm.

Elemental analysis found (calculated): C 49.94 (52.46), H 3.12 (3.36), N 1.42 (1.61).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 5 and Table S1; full details on page S47.

Synthesis of Complex 7

$AgBF_4$ (4.8 mg, 25.00x10^{-3} mmol, 2eq) was added to a slurry of the complex **2(t)** (10 mg, 12.53x10^{-3} mmol, 1eq) in acetone (0.6 ml). AgCl was removed by filtration, giving a clear, deep yellow solution of **7**.

7 δ_H (Acetone-d_6) = 8.30 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 8.01 (1H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.88 (1H, d, $^3J_{H-H}$ = 8 Hz, H_j), 7.76 (1H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 5.5 Hz, H_m), 7.73 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, H_e), 7.60 (1H, d, $^3J_{H-H}$ = 7 Hz, H_v)*, 7.52 (2H, d, $^3J_{H-H}$ = 7 Hz, H_{Bn}), 7.39 (7H, m, $H_{u,n,Bn,Bn'}$), 7.23 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_p), 7.22 (3H, m, $H_{Bn'}$), 7.17 (1H, t, $^3J_{H-H}$ = 8 Hz, H_t), 7.08 (1H, d, $^3J_{H-H}$ = 8 Hz, H_s), 6.87 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.46 (1H, dt, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = $^4J_{H-P}$ = 2.5 Hz, $^3J_{H-Pt}$ = ~90 Hz, H_b)**, 4.32 (1H, dd, $^2J_{H-H}$ = 15 Hz, $^2J_{H-P}$ = 9.5 Hz, H_x), 3.98 (3H, m, $H_{x,Bn}$), 3.49 (2H, d, $^2J_{H-H}$ = 12.5 Hz, $H_{Bn'}$) ppm.

*At 298 K, irradiating this proton strongly affects Bn_{alkyl} protons, and weakly affects Bn'_{alkyl}, with no effect on H_x.

**At 298 K, irradiating this proton affects one H_x proton, and both Bn_{alkyl}, but no effect on Bn'_{alkyl} protons.

δ_C (Acetone-d_6) = 27.03 (d, $^1J_{C-P}$ = 25 Hz, C_{Bn}), 27.99 (d, $^1J_{C-P}$ = 27 Hz, $C_{Bn'}$), 28.90 (m, C_x), 112.56 (d, $^2J_{C-F}$ = 25 Hz, C_d), 116.60 (d, $^2J_{C-F}$ = 25 Hz, C_n), 118.37 (m, $C_{h,p}$), 123.00 (dd, $^2J_{C-F}$ = 21 Hz, $^3J_{C-P}$ = 6 Hz, H_b), 125.15 (s, C_j), 126.05 (m, C_a), 126.49 (d, $^3J_{C-F}$ = 9 Hz, C_e), 127.30 (d, $^5J_{C-P}$ = 3 Hz, $C_{Bn'}$), 127.77 (d, $^5J_{C-P}$ = 3 Hz, C_{Bn}), 128.37 (s, C_l), 128.63 (d, $^1J_{C-P}$ = 1.5 Hz, $C_{Bn'}$), 129.11 (d, $^1J_{C-P}$ = 1.5 Hz, C_{Bn}), 129.76 (d, $^3J_{C-P}$ = 7 Hz, $C_{Bn'}$), 129.96 (m, C_{Bn}), 130.57 (d, $^3J_{C-P}$ = 5 Hz, C_{Bn}), 130.89 (s, C_u), 131.80 (d, $^3J_{C-F}$ = 8 Hz, C_q), 132.18 (d, $^3J_{C-P}$ = 5 Hz, C_v), 132.83 (m, $C_{l,Bn}$), 134.63 (d, $^3J_{C-F}$ = 9.5 Hz, C_m), 135.31 (d, $^2J_{C-P}$ = 3.5 Hz, C_w), 136.53 (s, C_s), 139.27 (br s, C_r), 140.90 (s, C_f), 142.49 (s, C_i)158.66 (s, C_k), 160.71 (d, $^3J_{C-P}$ = 3 Hz, C_g), 161.56 (dd, $^1J_{C-F}$ = 255 Hz, $^4J_{C-P}$ = 5 Hz, C_c), 163.08 (d, $^1J_{C-F}$ = 250 Hz, C_o) ppm.

δ_F (Acetone-d_6) = -108.51 ($^4J_{F-Pt}$ = 65 Hz), -110.60 ppm. δ_P (Acetone-d_6) = -9.49 ($^1J_{P-Pt}$ = 4119 Hz) ppm. δ_{Pt} (Acetone-d_6) = -3612 (d, $^1J_{Pt-P}$ = ~4200 Hz) ppm.

HR-MS (ESI): found 762.1637, calculated 762.1627 = $C_{38}H_{29}F_2NP^{194}Pt = [M]^+$.

Synthesis of Complexes a-Me-7 and b-Me-7

To a slurry of **Me-2(t)** (10 mg, $12.3x10^{-3}$ mmol) in acetone (0.6 ml) was added $AgBF_4$ (3 mg, $14.8\ x10^{-3}$ mmol, 1.2 eq). AgCl was removed by filtration, leaving a clear solution of the two isomeric products.

a-Me-7 δ_H (Acetone-d_6) = 8.22 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.97 (1H, d, $^3J_{H-H}$ = 8 Hz, $H_{h/j}$), 7.77 (1H, d, $^3J_{H-H}$ = 8 Hz, $H_{h/j}$), 7.51 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, H_m), 7.27 (H_n), 6.63 (1H, dd, $^3J_{H-F}$ = 9.5 Hz, $^4J_{H-H}$ = 3 Hz, H_d), 6.19 (1H, m, $^3J_{H-Pt}$ = 110 Hz, H_b), 2.53 (3H, s, Me) ppm.

δ_F (Acetone-d_6) = -109.64, -110.18 ($^4J_{F-Pt}$ = 72 Hz) ppm. δ_P (Acetone-d_6) = -7.73 ($^1J_{P-Pt}$ = 4043 Hz) ppm. δ_{Pt} (Acetone-d_6) = -3632 (d, $^1J_{Pt-P}$ = ~4050 Hz) ppm.

b-Me-7 δ_H (Acetone-d_6) = 8.15 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.91 (1H, d, $^3J_{H-H}$ = 8 Hz, $H_{h/j}$), 7.76 (1H, d, $^3J_{H-H}$ = 8 Hz, $H_{h/j}$), 7.51 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, H_m), 7.47 (1H, d, $^3J_{H-H}$ = 8 Hz, H_v), 7.27 (H_n), 6.84 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_t), 6.76 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.58 (2H, m, $H_{b,s}$) 2.32 (3H, s, Me) ppm.

δ_F (Acetone-d_6) = -109.95 ($^4J_{F-Pt}$ = 63 Hz), -112.68 ppm. δ_P (Acetone-d_6) = -0.55 ($^1J_{P-Pt}$ = 4463 Hz) ppm. δ_{Pt} (Acetone-d_6) = -3478 (d, $^1J_{Pt-P}$ = ~4450 Hz) ppm.

HR-MS (ESI mixture): found 776.1788, calculated 776.1784 = $C_{39}H_{31}F_2PN^{194}Pt = [M]^+$.

Synthesis of Complex 8

Complex **7** was dissolved in acetone (0.6 ml) in an NMR tube with J Young valve. The solvent was then frozen by immersion in liquid nitrogen, and the ir atmosphere then removed by vacuum. The atmosphere was replaced with CO gas, the tube sealed, and then the solvent was allowed to thaw. The yellow solution became almost colourless within one minute indicating the reaction was complete.

8 δ_H (Acetone-d_6) = 8.00 (2H, m, $H_{e,h}$), 7.96 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.71 (1H, d, $^3J_{H-H}$ = 7.5 Hz, H_s), 7.50 (1H, dd, $^3J_{H-H}$ = 5.5 Hz, $^4J_{H-F}$ = 8.5 Hz, H_m), 7.39 (1H, t, $^3J_{H-H}$ = 7 Hz, H_t), 7.26 (7H, m, $H_{j,n,u,v}$, Bn-*m,p*), 7.19 (1H,dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2.5 Hz, H_p), 7.14 (1H, td, $^3J_{H-F}$ = $^4J_{H-P}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, H_b), 7.08 (5H, m, H_d, Bn-*o*), 7.02 (1H, t, $^3J_{H-H}$ = 7.5 Hz, Bn-*p*), 6.91 (2H, t, $^3J_{H-H}$ = 7.5 Hz, Bn-*m*), 3.66 (d, $^2J_{H-P}$ = 10 Hz, $^3J_{H-Pt}$ = 15 Hz, BnCH_2), 3.53 (1H, dd, $^2J_{H-H}$ = 14 Hz, $^2J_{H-P}$ = 6.5 Hz, BnCH_2)*, 3.41 (1H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 14.5 Hz, H_x)**, 3.36 (1H, dd, $^2J_{H-H}$ = 14 Hz, $^2J_{H-P}$ = 12 Hz, BnCH_2)*, 3.04 (1H, dd, $^2J_{H-H}$ = 14.5 Hz, $^2J_{H-P}$ = 11 Hz, H_x)** ppm.

*,** Coupled protons.

δ_C (Acetone-d_6) = 33.55 (d, $^1J_{C-P}$ = 18 Hz, C_x), 34.47 (d, $^1J_{C-P}$ = 23.5 Hz, Bn-CH_2), 36.29 (d, $^1J_{C-P}$ = 25.5 Hz, Bn-CH_2), 114.10 (d, $^2J_{C-F}$ = 21 Hz, C_d), 116.06 (d, $^2J_{C-F}$ = 21 Hz, C_n), 117.40 (d, $^2J_{C-F}$ = 24.5 Hz, C_p), 119.37 (s, $^3J_{H-Pt}$ = 35 Hz, C_h), 122.43 (d, $^2J_{C-F}$ = 21 Hz, $^2J_{C-Pt}$ = 98 Hz, C_n), 126.91 (s, $^3J_{H-Pt}$ = 24.5 Hz, C_j), 127.72 (m, C_t, Bn-*p*), 128.21 (dd, $^3J_{C-F}$ = 8.5 Hz, $^4J_{C-P}$ = 6 Hz, C_e), 128.83 (s, Bn-*m*), 129.18 (s, C_u), 129.38 (s, Bn-*m*), 129.84 (d, $^3J_{C-P}$ = 6.5 Hz, Bn-*o*), 130.27 (s, C_s), 130.49 (d, $^3J_{C-P}$ = 4.5 Hz, Bn-*o*), 131.61 (d, $^2J_{C-P}$ = 6 Hz, Bn-*i*), 132.09 (d, $^3J_{C-P}$ = 6 Hz, C_v), 132.20 (d, $^3J_{C-P}$ = 6 Hz, C_r), 133.11 (d, $^2J_{C-P}$ = 4 Hz, Bn-*i*), 135.26 (d, $^3J_{C-F}$ = 9 Hz, C_m), 135.53 (s, C_l), 138.81 (s, C_w), 140.63 (d, $^3J_{C-F}$ = 9 Hz, C_q), 140.94 (s, C_f), 141.88 (s, C_i), 158.37 (dd, $^2J_{C-P}$ = 95 Hz, $^3J_{C-F}$ = 5 Hz, C_a), 161.35 (d, $^3J_{C-P}$ = 5 Hz, C_g), 162.84 (d, $^1J_{C-F}$ = 255 Hz, $^4J_{C-P}$ = 10.5 Hz, C_c), 163.60 (d, $^2J_{C-P}$ = 9 Hz, CO), 163.78 (d, $^1J_{C-F}$ = 254 Hz, C_o), 165.73 (d, $^3J_{C-P}$ = 4 Hz, C_k) ppm.

δ_F (Acetone-d_6) = -105.85, -109.55 ($^4J_{F-Pt}$ = 36 Hz, $^5J_{F-P}$ = 5.5 Hz) ppm. δ_P (Acetone-d_6) = 11.50 ($^1J_{P-Pt}$ = 1694 Hz) ppm. δ_{Pt} (Acetone-d_6) = -3976 (d, $^1J_{Pt-P}$ = ~1700 Hz) ppm.

HR-MS (ESI): found 762.1606, calculated 762.1627 = $C_{38}H_{29}F_2PN^{194}Pt$ = $[M\text{-}CO]^+$; found 790.1560, calculated 790.1576 = $C_{39}H_{29}F_2PNO^{194}Pt$ = $[M]^+$.

IR (solid): 2097 cm^{-1}.

Synthesis of Complex 9

Complex **7** was dissolved in acetone (0.6 ml) in an NMR tube with J Young valve. The solvent was then frozen by immersion in liquid nitrogen, and the atmosphere removed with vacuum. The atmosphere was replaced with H_2 gas, the tube sealed, and then the solvent allowed to thaw. The yellow solution became almost colourless within one minute indicating the reaction was complete.

9 δ_H (Acetone-d_6) = 8.02 (1H, t, $^3J_{H-H}$ = 8.5 Hz, H_g), 7.58 (3H, m, $H_{h,k,t}$), 7.36 (1H, d, $^3J_{H-H}$ = 8.5 Hz, H_f), 7.29 (1H, t, $^3J_{H-H}$ = 8.5 Hz, H_s), 7.20 (2H, t, $^3J_{H-H}$ = $^3J_{H-F}$ = 9 Hz, H_b), 7.06 (8H, m, $H_{c,l}$, Bn-*m*,*p*), 6.96 (1H, t, $^3J_{H-H}$ = 7 Hz, H_r), 6.90 (2H, t, $^3J_{H-H}$ = 7 Hz, Bn-*o*), 6.84 (1H, m, H_n), 6.78 (2H, t, $^3J_{H-H}$ = 6 Hz, Bn-*o*), 6.49 (1H, t, $^3J_{H-H}$ = 8 Hz, H_n), 3.74 (1H, m, H_v), 3.35 (3H, m, H_v, BnCH_2), 2.40 (1H, dd, $^2J_{H-P}$ = 13 Hz, $^2J_{H-H}$ = 11 Hz, BnCH_2), -24.34 (1H, m, $^1J_{H-Pt}$ = 1230 Hz, PtH) ppm.

δ_C (Acetone-d_6) = 29.04 (m, C_v), 35.01 (d, $^1J_{C-P}$ = Hz, BnCH_2), 37.88 (m, BnCH_2), 115.18 (d, $^2J_{C-F}$ = 19.5 Hz, C_l), 115.77 (d, $^2J_{C-F}$ = 24 Hz, C_b), 116.70 (d, $^2J_{C-F}$ = 26 Hz, C_n), 125.46 (m, C_f), 126.62 (m, C_h), 126.80 (d, $^5J_{C-P}$ = 2 Hz, Bn-*p*), 126.87 (d, $^5J_{C-P}$ = 3 Hz, Bn-*p*), 127.13 (m, C_r), 128.13 (d, $^4J_{C-P}$ = 2 Hz, Bn-*m*), 128.31 (m, C_s, Bn-*m*), 129.82 (d, $^3J_{C-P}$ = 5 Hz, Bn-*o*), 130.26 (d, $^4J_{C-P}$ = 3 Hz, C_q), 130.51 (d, $^3J_{C-P}$ = 6 Hz, Bn-*o*), 130.76 (d, $^3J_{C-P}$ = 4.5 Hz, C_t), 131.01 (d, $^3J_{C-F}$ = 9.5 Hz, C_k), 131.31 (d, $^3J_{C-F}$ = 9 Hz, C_c), 132.60 (m, C_j), 132.78 (d, $^2J_{C-P}$ = 6.5 Hz, Bn-*i*), 133.23 (d, $^2J_{C-P}$ = 6 Hz, Bn-*i*), 136.08 (m, C_d), 136.38 (d, $^3J_{C-P}$ = 3.5 Hz, C_p), 131.71 (m, C_u), 139.85 (s, C_g), 141.37 (d, $^3J_{C-F}$ = 8.5 Hz, C_o), 160.27 (s, C_i), 160.82 (s, C_e), 162.42 (d, $^1J_{C-F}$ = 248 Hz, H_m), 163.41 (d, $^1J_{C-F}$ = 247 Hz, H_a) ppm.

δ_F (Acetone-d_6) = -110.40, -112.62 ppm. δ_P (Acetone-d_6) = 1.31 ($^1J_{P-Pt}$ = 5015 Hz) ppm. δ_{Pt} (Acetone-d_6) = -4419 (d, $^1J_{Pt-P}$ = ~5000 Hz), (d, $^1J_{Pt-H}$ = ~1500 Hz) ppm.

HR-MS (ESI): found 764.1772, calculated 764.1784 = $C_{38}H_{31}F_2PN^{194}Pt = [M]^+$.

Synthesis of Complex 10

A solution of **a-Me-7** and **b-Me-7** in chloroform was left to stand for 4 weeks, after which crystals suitable for Xray analysis formed, Figure 8 and Table S1; full details on page S53.

δ_H = 7.74 (1H, t, $^3J_{H-H}$ = 7 Hz, H_i), 6.99 (4H, d, $^3J_{H-H}$ = 7.5 Hz, Bn-*o*), 6.67 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2 Hz, H_d), 1.95 (3H, s, Me) ppm.

δ_F = -108.83 ($^4J_{F-Pt}$ = 49 Hz), -112.66 ppm. δ_P = 59.78 ppm.

Table S1 Xray data for the structures reported

Complex	**1**	**2(t)**	**4**	**5**	**6**	**Me-1**	**10**
Empirical formula	$C_{38}H_{30}F_2NPPt$	$C_{38}H_{29}ClF_2NPPt$	$C_{38}H_{31}ClF_2NPPt$	$C_{39}H_{30}Cl_4F_2NPPt$	$C_{39}H_{30}Cl_6F_2NPPt$	$C_{40.4}H_{33.2}Cl_{4.2}F_2NPPt$	$C_{42}H_{34}Cl_{10}F_2NOPP$
Formula weight	764.69	799.13	801.15	918.50	989.40	945.63	1187.26
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	100(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P-1	P-1	P-1	$P2_1/n$	I2/a	I2/a
a/Å	12.1213(8)	11.3911(3)	8.51403(11)	10.06885(9)	11.49295(19)	14.61871(18)	23.6952(4)
b/Å	12.1909(7)	11.7933(4)	10.31938(18)	10.97968(11)	22.2749(4)	17.9381(3)	14.2502(3)
c/Å	12.2729(8)	12.8630(3)	18.7511(3)	17.46056(18)	14.2990(2)	28.6293(4)	27.6824(5)
α/°	68.816(6)	100.845(2)	83.1662(13)	107.6381(9)	90	90	90
β/°	69.917(6)	97.595(2)	79.6553(12)	97.2289(9)	91.1028(14)	98.6391(12)	103.1991(19)
γ/°	64.636(6)	117.163(3)	76.3618(13)	105.2604(8)	90	90	90
Volume/Å^3	1489.22(19)	1462.18(7)	1569.92(4)	1729.76(3)	3659.93(10)	7422.36(19)	9100.3(3)
Z	2	2	2	2	4	8	8
ϱ_{calc}g/cm^3	1.705	1.815	1.695	1.763	1.796	1.692	1.733
μ/mm^{-1}	9.654	10.686	4.646	11.208	4.357	4.167	3.749
F(000)	752.0	784.0	788.0	900.0	1936.0	3720.0	4656.0
Crystal size/mm^3	0.18 × 0.14 × 0.06 yellow block	0.185 × 0.095 × 0.03 colourless block	0.24 × 0.2 × 0.06 yellow block	0.18 × 0.08 × 0.04 yellow block	0.2 × 0.1 × 0.06 colourless block	0.57 × 0.11 × 0.05 yellow block	0.423 × 0.22 × 0.09 colourless block
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.7107
2Θ range /°	7.928 to 147.8	7.226 to 156.402	4.792 to 67.348	8.664 to 147.208	4.504 to 63.73	4.878 to 64.756	5.036 to 61.916
Index ranges	-15 ≤ h ≤ 15 -15 ≤ k ≤ 15 -15 ≤ l ≤ 15	-14 ≤ h ≤ 14 -14 ≤ k ≤ 14 -16 ≤ l ≤ 16	-12 ≤ h ≤ 13 -15 ≤ k ≤ 16 -29 ≤ l ≤ 29	-12 ≤ h ≤ 12 -13 ≤ k ≤ 13 -21 ≤ l ≤ 20	-17 ≤ h ≤ 16 -32 ≤ k ≤ 31 -20 ≤ l ≤ 20	-22 ≤ h ≤ 21 -26 ≤ k ≤ 26 -42 ≤ l ≤ 40	-34 ≤ h ≤ 31 -20 ≤ k ≤ 18 -38 ≤ l ≤ 39
Reflections collected	27666	27557	54759	59546	104681	113385	41772
Independent reflections	5891 [R_{int} = 0.0565, R_{sigma} = 0.0336]	6188 [R_{int} = 0.0564, R_{sigma} = 0.0440]	11737 [R_{int} = 0.0370, R_{sigma} = 0.0305]	6645 [R_{int} = 0.0543, R_{sigma} = 0.0224]	11956 [R_{int} = 0.0546, R_{sigma} = 0.0334]	12768 [R_{int} = 0.0573 R_{sigma} = 0.0396]	12881 [R_{int} = 0.029 R_{sigma} = 0.0351]
Data/restraints/parameters	5891/90/388	6188/0/397	11737/0/397	6645/0/433	11956/0/451	12768/22/503	12881/72/557
Goodness-of-fit on F^2	1.032	1.019	1.017	1.041	1.049	1.041	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0762	R_1 = 0.0257, wR_2 = 0.0600	R_1 = 0.0210, wR_2 = 0.0422	R_1 = 0.0198, wR_2 = 0.0488	R_1 = 0.0255, wR_2 = 0.0490	R_1 = 0.0393, wR_2 = 0.0870	R_1 = 0.0404, wR_2 =
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0772	R_1 = 0.0301, wR_2 = 0.0619	R_1 = 0.0250, wR_2 = 0.0435	R_1 = 0.0200, wR_2 = 0.0489	R_1 = 0.0352, wR_2 = 0.0519	R_1 = 0.0646, wR_2 = 0.0958	R_1 = 0.0513, wR_2 =
Largest diff peak/hole /eÅ^{-3}	1.48/-1.24	0.95/-0.58	0.87/-0.95	0.70/-1.03	1.46/-0.92	1.70/-1.27	2.09/-1.60

ps33 Complex 1

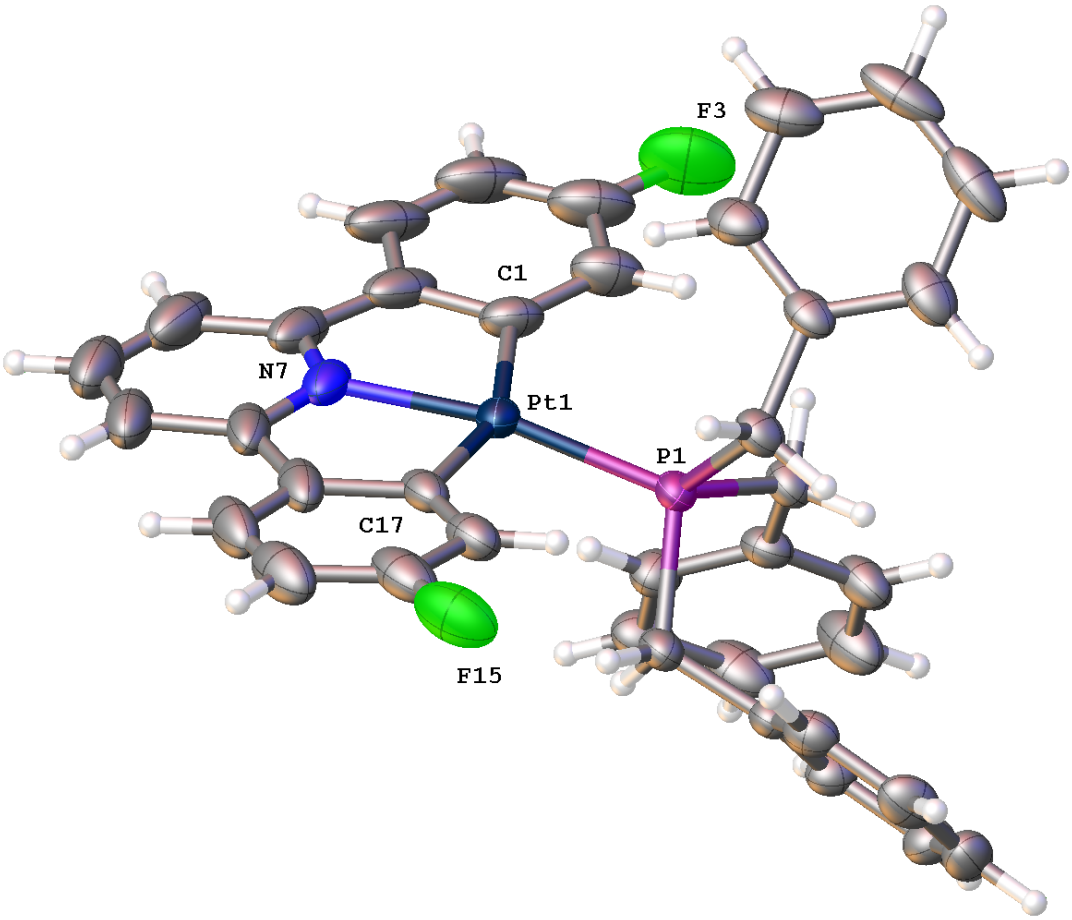


Figure SI1 *solid state structure of ps33 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level*

Crystal structure determination of [ps33]
The asymmetric unit contains the complex, there are two of these in the unit cell. The thermal ellipsoids at the back edge of the pyridine ligand are particularly large and elongated. These atoms were restrained with a SIMU restraint to give them more reasonable thermal parameters. The Pt-P bond is rather bent compared to the rest of the Pt bonds. As a measure of this, the distance the phosphorus P1 lies out of a mean plane through the other atoms (C1, N7, C13 and Pt1) is shown below
Least-squares planes (x,y,z in crystal coordinates) and deviations from them

(* indicates atom used to define plane)

10.6987 (0.0103) x - 0.3413 (0.0226) y + 3.9482 (0.0165) z = 10.8593 (0.0183)

* -0.0659 (0.0018) Pt1
* 0.0401 (0.0011) C1
* -0.0142 (0.0004) N7
* 0.0400 (0.0011) C17
-0.5329 (0.0053) P1

Rms deviation of fitted atoms = 0.0440

Additionally, the bond angle to the trans N ligand is shown below
N7 - Pt1 - P1 168.72 (0.10) degrees

Experimental
Single crystals of $C_{38}H_{30}F_2NPPt$ **[ps33]** were grown from chloroform solution. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on a Rigaku Oxford Diffraction SuperNova diffractometer with a dual source (Cu at zero) with an AtlasS2 CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.
1 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{38}H_{30}F_2NPPt$ (M =764.69 g/mol): triclinic, space group P-1 (no. 2), a = 12.1213(8) Å, b = 12.1909(7) Å, c = 12.2729(8) Å, α = 68.816(6)°, β = 69.917(6)°, γ = 64.636(6)°, V = 1489.22(19) Å^3, Z = 2, T = 150(2) K, μ(CuKα) = 9.654 mm^{-1}, *Dcalc* =

1.705 g/cm^3, 27666 reflections measured (7.928° ≤ 2Θ ≤ 147.8°), 5891 unique (R_{int} = 0.0565, R_{sigma} = 0.0336) which were used in all calculations. The final R_1 was 0.0294 (I > 2σ(I)) and wR_2 was 0.0772 (all data).

Table 1 Crystal data and structure refinement for ps33.

Identification code	ps33
Empirical formula	$C_{38}H_{30}F_2NPPt$
Formula weight	764.69
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.1213(8)
b/Å	12.1909(7)
c/Å	12.2729(8)
α/°	68.816(6)
β/°	69.917(6)
γ/°	64.636(6)
Volume/Å^3	1489.22(19)
Z	2
ϱ_{calc}g/cm^3	1.705
μ/mm^{-1}	9.654
F(000)	752.0
Crystal size/mm^3	0.18 × 0.14 × 0.06 yellow block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.928 to 147.8
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	27666
Independent reflections	5891 [R_{int} = 0.0565, R_{sigma} = 0.0336]
Data/restraints/parameters	5891/90/388
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0762
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0772
Largest diff. peak/hole / e Å^{-3}	1.48/-1.24

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps33. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	7659.8(2)	1673.4(2)	6726.0(2)	33.96(7)
P1	7354.1(7)	3656.3(7)	6542.9(7)	29.01(16)
F15	10049(3)	3019(3)	1949(2)	71.7(8)
F3	6320(4)	1175(4)	11626(3)	90.9(11)
N7	7651(3)	6(3)	6736(4)	48.0(8)
C26	6229(3)	6044(3)	5012(3)	29.6(6)
C19	9376(3)	3593(3)	7192(3)	35.5(7)
C32	6450(3)	4448(3)	7765(3)	36.1(7)
C25	6498(3)	4650(3)	5347(3)	35.5(7)
C1	7063(4)	978(4)	8553(4)	46.4(9)
C17	8426(3)	1693(3)	4919(3)	39.4(7)
C20	9726(3)	2343(4)	7825(4)	45.5(8)
C37	3259(4)	4102(4)	8498(4)	45.0(8)
C18	8790(3)	4028(3)	6140(3)	35.8(7)
C27	5104(3)	6854(3)	5533(3)	33.9(7)
C28	4846(3)	8136(3)	5183(3)	39.1(7)
C38	4545(3)	3865(3)	8095(3)	39.1(7)
C29	5697(4)	8638(3)	4305(3)	43.6(8)
C31	7085(3)	6562(3)	4131(3)	36.4(7)
C33	5070(3)	4624(3)	8209(3)	34.3(7)
C12	8457(4)	637(4)	4648(5)	55.0(9)
C2	6871(4)	1398(5)	9544(4)	56.7(10)
C21	10288(4)	1952(5)	8776(4)	56.9(11)
C16	8974(3)	2483(4)	3960(3)	42.9(8)
C15	9497(4)	2251(5)	2828(4)	58.8(10)
C34	4291(4)	5615(4)	8740(4)	47.6(9)
C30	6823(4)	7843(4)	3780(3)	44.3(8)
C24	9567(3)	4447(4)	7558(4)	47.3(9)
C6	6876(4)	-171(4)	8813(5)	62.5(10)
C11	7975(4)	-254(4)	5659(5)	58.3(9)
C36	2502(4)	5083(5)	9030(4)	55.1(11)
C7	7155(4)	-665(4)	7780(5)	61.8(10)
C22	10499(4)	2797(6)	9106(4)	63.7(14)
C35	3022(4)	5841(5)	9149(4)	62.3(12)
C23	10133(4)	4035(6)	8506(4)	58.5(13)
C13	8941(4)	447(5)	3507(5)	62.9(10)
C3	6490(5)	726(6)	10698(5)	70.5(12)
C10	7824(5)	-1323(4)	5631(6)	70.9(11)
C5	6477(5)	-810(5)	9971(5)	71.3(12)
C9	7322(6)	-2021(4)	6653(7)	78.1(12)

C8	6984(5)	-1729(4)	7744(7)	76.7(12)
C14	9471(4)	1245(5)	2574(5)	66.3(11)
C4	6273(5)	-378(5)	10916(5)	75.1(13)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps33. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	32.39(9)	26.46(9)	47.2(1)	-8.76(6)	-20.33(6)	-5.60(6)
P1	27.8(4)	28.2(3)	35.7(4)	-10.1(3)	-13.8(3)	-7.1(3)
F15	52.4(15)	113(2)	48.8(13)	-33.1(14)	-10.0(11)	-18.5(15)
F3	99(2)	114(3)	44.0(14)	3.3(15)	-21.3(14)	-38(2)
N7	42.0(17)	27.8(13)	82(2)	-10.7(14)	-36.5(16)	-4.3(12)
C26	28.7(14)	30.0(14)	34.0(14)	-9.4(11)	-14.6(11)	-6.7(12)
C19	22.5(14)	49.4(18)	39.8(16)	-19.8(14)	-7.4(12)	-9.9(13)
C32	32.3(16)	40.3(16)	42.5(17)	-15.6(14)	-12.4(13)	-11.4(13)
C25	34.9(16)	35.1(16)	43.2(17)	-14.1(13)	-19.7(13)	-6.3(13)
C1	44(2)	42.3(19)	46.2(19)	4.8(15)	-23.8(15)	-11.9(16)
C17	33.3(16)	41.0(17)	49.7(19)	-23.0(15)	-22.4(14)	1.4(13)
C20	33.0(17)	53(2)	48(2)	-18.0(16)	-15.3(14)	-3.1(15)
C37	34.2(18)	53(2)	48.1(19)	-6.6(16)	-13.6(14)	-16.8(16)
C18	31.1(15)	43.4(17)	39.0(16)	-12.7(13)	-11.1(12)	-14.1(13)
C27	27.8(15)	34.2(15)	37.3(16)	-6.7(12)	-10.2(12)	-8.4(12)
C28	37.1(17)	33.3(16)	43.6(18)	-10.1(13)	-14.0(14)	-5.1(13)
C38	31.9(16)	38.2(16)	48.2(18)	-9.4(14)	-13.3(14)	-10.9(13)
C29	57(2)	35.9(17)	42.9(18)	-2.2(14)	-20.6(16)	-20.0(16)
C31	32.0(16)	45.4(17)	29.4(14)	-9.9(13)	-7.0(12)	-11.0(13)
C33	29.0(15)	40.8(17)	33.4(15)	-10.2(13)	-12.5(12)	-7.5(13)
C12	42.8(17)	44.2(17)	94(2)	-38.9(16)	-38.3(17)	5.9(14)
C2	55(2)	64(2)	45.8(19)	4.9(17)	-23.4(16)	-23.0(18)
C21	35.8(19)	80(3)	45(2)	-9(2)	-15.1(16)	-12(2)
C16	37.4(18)	51(2)	44.6(19)	-20.9(16)	-18.0(14)	-5.2(15)
C15	38.0(18)	80(2)	65(2)	-39.7(19)	-22.5(16)	-1.2(17)
C34	37.4(19)	62(2)	52(2)	-30.2(18)	-16.2(15)	-7.7(17)
C30	49(2)	54(2)	30.9(15)	0.9(14)	-9.2(14)	-28.3(17)
C24	32.6(17)	69(2)	54(2)	-29.9(19)	-3.2(15)	-22.7(17)
C6	51.5(19)	46.4(18)	88(2)	18.5(17)	-47.7(18)	-20.2(15)
C11	48.6(18)	36.0(15)	110(3)	-32.2(17)	-49.4(18)	3.3(14)
C36	28.4(17)	86(3)	54(2)	-31(2)	-10.2(15)	-11.7(18)
C7	54.7(19)	33.6(15)	106(3)	6.5(17)	-52.6(19)	-16.6(14)
C22	33.8(19)	127(5)	39(2)	-30(3)	-8.7(15)	-28(2)
C35	40(2)	88(3)	67(3)	-50(3)	-13.8(18)	-3(2)
C23	37.7(19)	110(4)	53(2)	-49(3)	3.6(17)	-36(2)
C13	48.8(19)	64(2)	93(2)	-54.4(18)	-32.4(17)	5.9(16)
C3	62(2)	81(2)	54(2)	11.9(18)	-31.0(17)	-22.6(19)
C10	65(2)	40.3(17)	130(3)	-32.6(18)	-57(2)	-2.6(16)
C5	62(2)	62(2)	82(2)	26.8(19)	-48.1(19)	-26.2(17)
C9	74(2)	38.4(17)	142(3)	-19(2)	-61(2)	-12.1(17)
C8	67(2)	37.1(17)	131(3)	2.0(19)	-55(2)	-16.6(16)
C14	48.4(19)	82(2)	77(2)	-51.9(19)	-23.7(17)	2.8(17)
C4	64(2)	76(2)	69(2)	28(2)	-38.8(19)	-29.6(19)

Table 4 Bond Lengths for ps33.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	P1	2.2200(8)	C27	C28	1.383(5)
Pt1	N7	2.033(3)	C28	C29	1.378(5)
Pt1	C1	2.075(4)	C38	C33	1.392(5)
Pt1	C17	2.085(4)	C29	C30	1.391(6)
P1	C32	1.842(3)	C31	C30	1.381(5)
P1	C25	1.839(3)	C33	C34	1.395(5)
P1	C18	1.844(3)	C12	C11	1.460(8)
F15	C15	1.341(6)	C12	C13	1.383(7)
F3	C3	1.353(7)	C2	C3	1.388(6)
N7	C11	1.357(7)	C21	C22	1.375(8)
N7	C7	1.345(6)	C16	C15	1.391(6)
C26	C25	1.508(4)	C15	C14	1.385(7)
C26	C27	1.395(4)	C34	C35	1.379(6)
C26	C31	1.393(4)	C24	C23	1.381(7)
C19	C20	1.386(6)	C6	C7	1.473(8)
C19	C18	1.505(5)	C6	C5	1.382(7)
C19	C24	1.399(5)	C11	C10	1.405(6)
C32	C33	1.513(5)	C36	C35	1.390(7)
C1	C2	1.396(7)	C7	C8	1.416(7)
C1	C6	1.419(6)	C22	C23	1.365(8)
C17	C12	1.424(5)	C13	C14	1.377(8)
C17	C16	1.395(6)	C3	C4	1.395(9)
C20	C21	1.386(6)	C10	C9	1.348(9)
C37	C38	1.395(5)	C5	C4	1.348(9)
C37	C36	1.382(6)	C9	C8	1.390(10)

Table 5 Bond Angles for ps33.

Atom	Atom	Atom	Angle/°
N7	Pt1	P1	168.72(10)
N7	Pt1	C1	80.05(17)
N7	Pt1	C17	79.84(16)
C1	Pt1	P1	103.82(12)
C1	Pt1	C17	159.19(17)
C17	Pt1	P1	96.93(11)
C32	P1	Pt1	123.20(12)
C32	P1	C18	99.32(16)
C25	P1	Pt1	108.02(11)
C25	P1	C32	102.44(16)
C25	P1	C18	106.92(16)
C18	P1	Pt1	115.32(12)
C11	N7	Pt1	117.2(3)
C7	N7	Pt1	117.5(3)
C7	N7	C11	124.6(4)
C27	C26	C25	121.4(3)
C31	C26	C25	120.4(3)
C31	C26	C27	118.2(3)
C20	C19	C18	120.9(3)
C20	C19	C24	118.6(4)
C24	C19	C18	120.5(3)
C33	C32	P1	117.9(2)
C26	C25	P1	118.1(2)
C2	C1	Pt1	132.3(3)
C2	C1	C6	115.8(4)
C6	C1	Pt1	111.8(4)
C12	C17	Pt1	112.2(3)
C16	C17	Pt1	132.8(3)
C16	C17	C12	114.8(4)
C21	C20	C19	120.2(4)
C36	C37	C38	120.0(4)
C19	C18	P1	112.3(2)
C28	C27	C26	120.9(3)
C29	C28	C27	120.4(3)
C33	C38	C37	120.4(4)
C28	C29	C30	119.4(3)
C30	C31	C26	120.8(3)
C38	C33	C32	123.5(3)
C38	C33	C34	118.9(3)
C34	C33	C32	117.6(3)
C17	C12	C11	115.8(4)
C13	C12	C17	122.3(5)
C13	C12	C11	121.8(4)
C3	C2	C1	120.6(5)
C22	C21	C20	120.5(5)
C15	C16	C17	122.0(4)
F15	C15	C16	119.5(4)
F15	C15	C14	118.4(4)
C14	C15	C16	122.1(5)
C35	C34	C33	120.7(4)
C31	C30	C29	120.3(3)
C23	C24	C19	120.2(4)
C1	C6	C7	116.3(4)
C5	C6	C1	122.3(6)
C5	C6	C7	121.4(5)
N7	C11	C12	114.4(3)
N7	C11	C10	118.1(5)
C10	C11	C12	127.5(5)
C37	C36	C35	119.9(4)
N7	C7	C6	113.5(4)
N7	C7	C8	117.1(6)
C8	C7	C6	129.3(5)
C23	C22	C21	119.8(4)
C34	C35	C36	120.2(4)
C22	C23	C24	120.7(4)
C14	C13	C12	121.6(4)
F3	C3	C2	118.1(5)
F3	C3	C4	120.0(5)
C2	C3	C4	121.9(6)
C9	C10	C11	119.5(6)
C4	C5	C6	121.1(5)
C10	C9	C8	121.5(5)
C9	C8	C7	119.2(6)
C13	C14	C15	117.0(4)
C5	C4	C3	118.3(5)

Table 6 Torsion Angles for ps33.

A	B	C	D	Angle/°
Pt1	P1	C32	C33	-63.9(3)
Pt1	P1	C25	C26	-177.2(2)
Pt1	P1	C18	C19	-77.4(2)
Pt1	N7	C11	C12	8.3(4)
Pt1	N7	C11	C10	-172.1(3)
Pt1	N7	C7	C6	-9.6(5)
Pt1	N7	C7	C8	171.0(3)
Pt1	C1	C2	C3	-178.3(4)
Pt1	C1	C6	C7	1.2(5)
Pt1	C1	C6	C5	-179.9(4)
Pt1	C17	C12	C11	-0.7(4)
Pt1	C17	C12	C13	-179.2(3)
Pt1	C17	C16	C15	175.9(3)
P1	C32	C33	C38	24.6(5)
P1	C32	C33	C34	-154.4(3)
F15	C15	C14	C13	177.5(4)
F3	C3	C4	C5	-178.6(5)
N7	C11	C10	C9	2.7(7)
N7	C7	C8	C9	-0.5(7)
C26	C27	C28	C29	0.3(6)
C26	C31	C30	C29	0.2(6)
C19	C20	C21	C22	0.4(6)
C19	C24	C23	C22	-0.8(5)
C32	P1	C25	C26	51.4(3)
C32	P1	C18	C19	56.3(3)
C32	C33	C34	C35	179.1(4)
C25	P1	C32	C33	57.6(3)
C25	P1	C18	C19	162.5(2)
C25	C26	C27	C28	-177.3(3)
C25	C26	C31	C30	177.1(3)
C1	C2	C3	F3	179.9(4)
C1	C2	C3	C4	-0.6(8)
C1	C6	C7	N7	5.3(6)
C1	C6	C7	C8	-175.4(4)
C37	C38	C33	C34	0.6(6)
C37	C36	C35	C34	-0.2(8)
C18	P1	C32	C33	167.4(3)
C18	P1	C25	C26	-52.5(3)
C18	C19	C20	C21	178.6(3)
C18	C19	C24	C23	-178.4(3)
C27	C26	C25	P1	-93.4(4)
C27	C26	C31	C30	-0.3(5)
C27	C28	C29	C30	-0.5(6)
C28	C29	C30	C31	0.2(6)
C38	C37	C36	C35	0.8(7)
C38	C33	C34	C35	0.1(6)
C31	C26	C25	P1	89.3(4)
C31	C26	C27	C28	0.1(5)
C33	C34	C35	C36	-0.2(7)
C12	C17	C16	C15	0.6(5)
C12	C11	C10	C9	-177.8(4)
C12	C13	C14	C15	-0.1(7)
C2	C1	C6	C7	-176.2(4)
C2	C1	C6	C5	2.7(6)
C2	C3	C4	C5	1.9(8)
C21	C22	C23	C24	-0.8(6)
C16	C17	C12	C11	175.5(3)
C16	C17	C12	C13	-2.9(6)
C16	C15	C14	C13	-2.3(7)
C24	C19	C20	C21	-2.0(5)
C24	C19	C18	P1	-122.1(3)
C6	C1	C2	C3	-1.6(7)
C6	C7	C8	C9	-179.8(5)
C6	C5	C4	C3	-0.8(8)
C11	N7	C7	C6	-179.3(4)
C11	N7	C7	C8	1.3(6)
C11	C12	C13	C14	-175.6(4)
C11	C10	C9	C8	-2.0(8)

C1	C6	C5	C4	-1.5(7)	C36	C37	C38	C33	-1.0(6)
C17	C12	C11	N7	-4.8(5)	C7	N7	C11	C12	178.0(4)
C17	C12	C11	C10	175.7(4)	C7	N7	C11	C10	-2.4(6)
C17	C12	C13	C14	2.7(7)	C7	C6	C5	C4	177.3(5)
C17	C16	C15	F15	-177.8(4)	C13	C12	C11	N7	173.7(4)
C17	C16	C15	C14	2.0(7)	C13	C12	C11	C10	-5.9(7)
C20	C19	C18	P1	57.3(4)	C10	C9	C8	C7	0.9(8)
C20	C19	C24	C23	2.2(5)	C5	C6	C7	N7	-173.6(4)
C20	C21	C22	C23	1.0(6)	C5	C6	C7	C8	5.7(7)
C37	C38	C33	C32	-178.4(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps33.

Atom	*x*	*y*	*z*	U(eq)
H32A	6851	3966	8457	43
H32B	6528	5286	7496	43
H25A	6980	4344	4617	43
H25B	5687	4518	5589	43
H20	9580	1753	7606	55
H37	2904	3589	8407	54
H18A	9403	3623	5498	43
H18B	8585	4946	5820	43
H27	4508	6521	6136	41
H28	4077	8674	5550	47
H38	5066	3182	7742	47
H29	5515	9519	4061	52
H31	7859	6027	3768	44
H2	7003	2150	9428	68
H21	10531	1093	9202	68
H16	8992	3200	4083	51
H34	4638	6140	8822	57
H30	7416	8182	3176	53
H24	9307	5312	7154	57
H36	1627	5238	9315	66
H22	10897	2521	9751	76
H35	2501	6517	9512	75
H23	10270	4619	8742	70
H13	8908	-253	3364	75
H10	8075	-1552	4897	85
H5	6345	-1566	10103	86
H9	7197	-2728	6626	94
H8	6643	-2238	8459	92
H14	9804	1112	1791	80
H4	5988	-813	11710	90

Refinement model description

Number of restraints - 90, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2. Uiso/Uaniso restraints and constraints
C2 ≈ C3 ≈ F3 ≈ C4 ≈ C5 ≈ C6 ≈ C7 ≈ C8 ≈ C9
≈ C10 ≈ C11 ≈ C12 ≈ C13 ≈ C14 ≈ C15 ≈ F15: within
1.7A with sigma of 0.004 and sigma for terminal atoms of 0.008
3.a Secondary CH2 refined with riding coordinates:
 C32(H32A,H32B), C25(H25A,H25B), C18(H18A,H18B)
3.b Aromatic/amide H refined with riding coordinates:
 C20(H20), C37(H37), C27(H27), C28(H28), C38(H38), C29(H29), C31(H31), C2(H2),
 C21(H21), C16(H16), C34(H34), C30(H30), C24(H24), C36(H36), C22(H22), C35(H35),
  C23(H23), C13(H13), C10(H10), C5(H5), C9(H9), C8(H8), C14(H14), C4(H4)
```

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Me-1 ps32

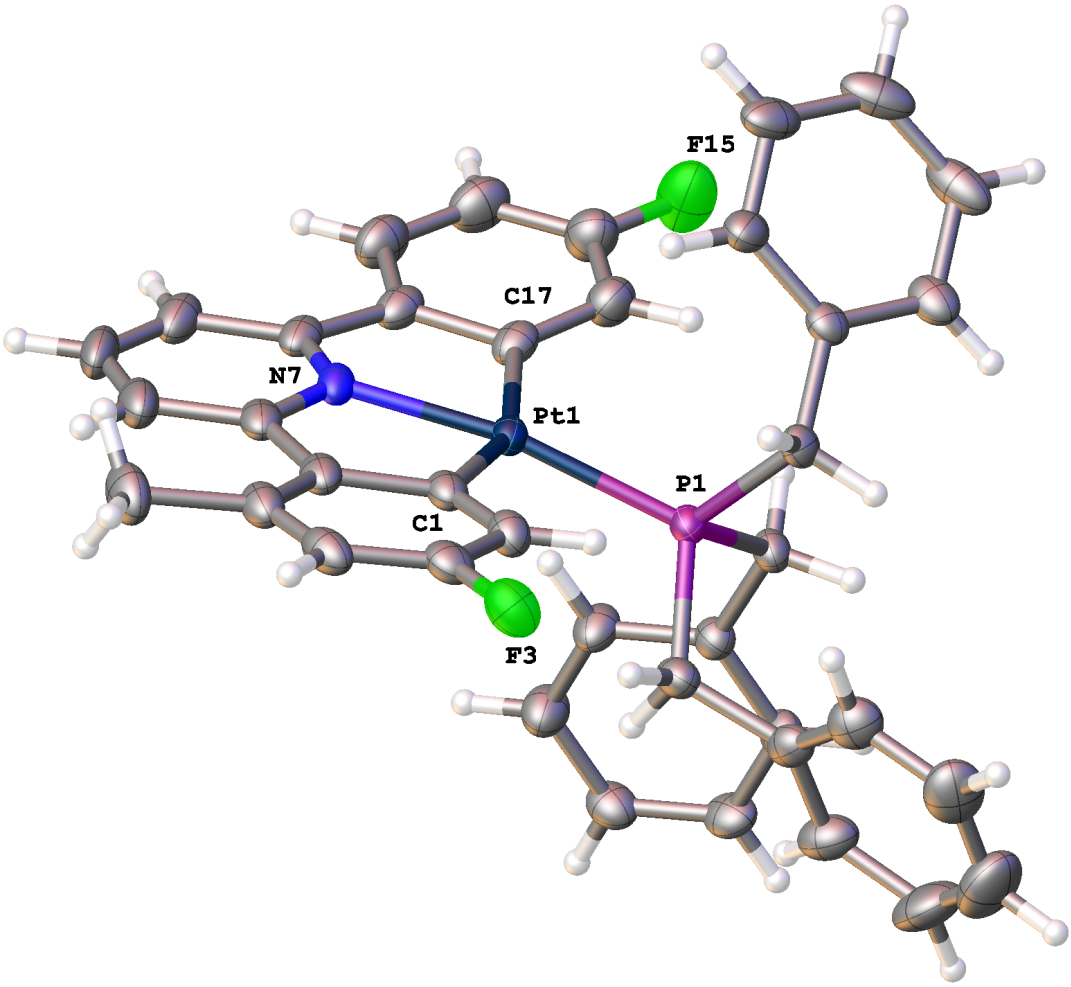


Figure SI2 *solid state structure of the complex in ps32 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level*

Crystal structure determination of [ps32]
The asymmetric unit contains the complex and a lot of surrounding diffuse electron density. This was modeled as very disordered chloroform solvent. In one position, a molecule of chloroform was modeled over three very closely related positions. The occupancy was originally linked to free variables but the occupancy of the components was fixed at 80:10:10 based on thermal parameters. Only the major component was refined anisotropically.
The other electron density was also modeled a chloroform disordered over two closely related positions behind a PART -1 and PART -2 instruction as it straddled the 2 fold axis. Both these components were refined isotropically at 40% occupancy.
Many DFIX, SIMU and DELU restraints were used to give these disordered components reasonable bond lengths angles and thermal parameters.
The methyl substituent on the pyridine ligand was also disordered over two positions (as the ligand is symmetrical, it could end up on either of the 4-fluorophenyl rings). The occupancy of the two positions was linked to a free variable which refined to 77:23. The minor component was refined isotropically.

The Pt-P bond is rather bent compared to the rest of the Pt bonds. As a measure of this, the distance the phosphorus P1 lies out of a mean plane through the other atoms (C1, N7, C13 and Pt1) is shown below
Least-squares planes (x,y,z in crystal coordinates) and deviations from them

(* indicates atom used to define plane)
14.2403 (0.0053) x + 0.7582 (0.0203) y + 2.0960 (0.0462) z = 10.2214 (0.0262)
* 0.0825 (0.0016) Pt1
* -0.0502 (0.0010) C1
* 0.0176 (0.0004) N7
* -0.0499 (0.0010) C17
0.5416 (0.0047) P1

Rms deviation of fitted atoms = 0.0550

Additionally, the bond angle to the trans N ligand is shown below
N7 - Pt1 - P1 169.79 (0.08) degrees

Experimental
Single crystals of $C_{40.4}H_{33.2}Cl_{4.2}F_2NPPt$ **[ps32]** were grown from chloroform. A suitable crystal was selected and mounted on a glass fibre

with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

4 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
5 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
6 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{40.4}H_{33.2}Cl_{4.2}F_2NPPt$ (M =945.63 g/mol): monoclinic, space group I2/a (no. 15), a = 14.61871(18) Å, b = 17.9381(3) Å, c = 28.6293(4) Å, β = 98.6391(12)°, V = 7422.36(19) Å^3, Z = 8, T = 150(2) K, μ(MoKα) = 4.167 mm^{-1}, *Dcalc* = 1.692 g/cm^3, 113385 reflections measured (4.878° ≤ 2Θ ≤ 64.756°), 12768 unique (R_{int} = 0.0573, R_{sigma} = 0.0396) which were used in all calculations. The final R_1 was 0.0393 (I > 2σ(I)) and wR_2 was 0.0958 (all data).

Table 1 Crystal data and structure refinement for ps32.

Identification code	ps32
Empirical formula	$C_{40.4}H_{33.2}Cl_{4.2}F_2NPPt$
Formula weight	945.63
Temperature/K	150(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	14.61871(18)
b/Å	17.9381(3)
c/Å	28.6293(4)
α/°	90
β/°	98.6391(12)
γ/°	90
Volume/Å^3	7422.36(19)
Z	8
ϱ_{calc}g/cm^3	1.692
μ/mm^{-1}	4.167
F(000)	3720.0
Crystal size/mm^3	0.567 × 0.107 × 0.05 yellow block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.878 to 64.756
Index ranges	-22 ≤ h ≤ 21, -26 ≤ k ≤ 26, -42 ≤ l ≤ 40
Reflections collected	113385
Independent reflections	12768 [R_{int} = 0.0573, R_{sigma} = 0.0396]
Data/restraints/parameters	12768/22/503
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.0870
Final R indexes [all data]	R_1 = 0.0646, wR_2 = 0.0958
Largest diff. peak/hole / e Å^{-3}	1.70/-1.27

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps32. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	6047.6(2)	5582.2(2)	6052.3(2)	23.90(4)
P1	6256.7(6)	5525.3(5)	6843.1(3)	22.83(17)
C1	6035(2)	4455(2)	5910.1(13)	28.0(7)
C2	5878(2)	3846(2)	6195.7(13)	29.9(8)
C3	5879(2)	3136(2)	6021.8(14)	32.8(8)
F3	5754.9(17)	2553.3(14)	6316.1(9)	41.8(6)
C4	6018(2)	2964(2)	5568.2(15)	36.0(9)
C5	6141(2)	3547(2)	5266.4(14)	34.2(9)
C5A	6281(4)	3321(4)	4767(2)	45.8(17)
C6	6146(2)	4289(2)	5430.8(13)	30.8(8)
N7	6104.6(19)	5601.4(18)	5348.6(10)	27.4(6)
C7	6231(2)	4947(2)	5133.2(13)	31.7(8)
C8	6440(3)	4976(3)	4671.0(14)	44.1(11)
C9	6509(3)	5652(3)	4455.9(14)	45.6(12)
C10	6386(3)	6311(3)	4687.4(14)	40.1(10)
C11	6185(2)	6278(2)	5149.9(12)	30.9(8)
C12	6037(2)	6906(2)	5458.0(13)	32.1(8)
C13	5959(3)	7634(3)	5291.5(15)	41(1)
C13A	6127(16)	7963(9)	4822(9)	72(8)
C14	5715(3)	8205(3)	5579.5(16)	45.3(10)
F15	5296(2)	8567.5(15)	6304.8(10)	58.7(8)
C15	5558(3)	8018(3)	6027.5(15)	41.1(9)
C16	5646(3)	7300(2)	6201.9(14)	36.6(9)
C17	5913(2)	6717(2)	5928.2(13)	29.6(7)
C18	7133(2)	4823(2)	7068.6(13)	29.5(7)
C19	7267(3)	4621(2)	7585.2(13)	29.8(7)
C20	6649(3)	4147(2)	7764.9(15)	37.9(9)
C21	6811(4)	3917(3)	8230.1(18)	51.3(12)
C22	7593(5)	4150(4)	8526(2)	66.5(16)
C23	8199(4)	4631(3)	8356.3(19)	59.7(14)

C24	8040(3)	4867(3)	7886.6(16)	40.6(9)
C25	6692(2)	6336(2)	7200.3(12)	26.6(7)
C26	7675(2)	6560(2)	7160.1(12)	25.4(7)
C27	8317(2)	6658(2)	7567.6(13)	29.7(7)
C28	9223(3)	6850(2)	7537.5(14)	34.4(8)
C29	9511(3)	6953(2)	7102.6(14)	34.2(8)
C30	8877(3)	6863(3)	6696.0(14)	37.9(9)
C31	7968(3)	6673(2)	6725.0(13)	34.3(8)
C32	5204(2)	5304(2)	7093.6(12)	26.1(7)
C33	4473(2)	5898(2)	6982.1(13)	25.1(7)
C34	4273(2)	6391(2)	7327.1(15)	34.6(8)
C35	3584(3)	6928(2)	7219.0(19)	46.1(11)
C36	3096(3)	6977(2)	6771.0(19)	45.4(11)
C37	3296(3)	6491(3)	6424.1(17)	40.8(10)
C38	3978(2)	5962(2)	6530.2(14)	32.5(8)
C1E	7596(10)	4501(9)	10167(6)	99(5)
Cl1A	5944(2)	5560.2(18)	8496.9(10)	110.2(10)
C1F	7093(12)	3800(15)	10051(8)	114(6)
C1D	6500(20)	5628(19)	8781(12)	23(6)
Cl1B	5602(9)	6122(9)	8474(5)	58(3)
Cl1D	7852(8)	5096(6)	9743(4)	102(3)
C1B	5787(7)	6265(5)	8855(4)	91(3)
Cl1E	6882(8)	3245(7)	9567(4)	105(3)
C1C	6281(9)	5845(13)	8978(7)	49(11)
Cl1C	6050(15)	6415(12)	8505(8)	89(5)
Cl2A	6920.3(17)	6618.1(17)	9134.1(10)	101.6(8)
Cl2E	6285(10)	4416(8)	10185(5)	124(5)
Cl2B	7422(8)	6049(8)	9002(5)	57(3)
Cl2C	7375(16)	5765(13)	9240(9)	99(6)
Cl2D	8343(10)	3768(10)	10255(7)	138(7)
Cl3D	6498(10)	4163(10)	10041(7)	135(5)
Cl3B	5993(14)	5030(10)	9220(8)	100(6)
Cl3E	8229(13)	3994(18)	10236(12)	246(17)
Cl3C	5739(16)	5177(13)	8966(9)	97(6)
Cl3A	5218.9(17)	5945.2(18)	9333.5(8)	96.6(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps32. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	18.05(6)	34.31(8)	19.45(6)	-2.63(6)	3.17(4)	-1.68(5)
P1	19.3(4)	28.9(5)	20.4(4)	-2.4(3)	3.7(3)	0.2(3)
C1	17.6(14)	40(2)	26.0(15)	-7.0(15)	2.0(12)	0.4(14)
C2	24.4(16)	37(2)	29.2(17)	-8.0(15)	5.8(13)	-2.1(14)
C3	19.9(15)	40(2)	39(2)	-4.3(17)	4.9(14)	-0.2(14)
F3	40.3(13)	35.9(13)	51.4(15)	-5.1(11)	14.2(11)	-2(1)
C4	24.5(16)	41(2)	42(2)	-17.4(18)	3.2(15)	0.0(15)
C5	22.8(16)	50(2)	29.0(18)	-12.6(17)	1.7(14)	-0.9(16)
C5A	41(3)	62(4)	36(3)	-22(3)	10(2)	-5(3)
C6	18.3(14)	47(2)	25.6(17)	-9.8(15)	0.2(12)	-0.7(14)
N7	17.0(12)	45.2(18)	20.1(13)	-3.8(13)	3.4(10)	-3.5(12)
C7	17.2(14)	52(2)	25.1(17)	-6.7(16)	0.8(12)	-0.8(15)
C8	31.0(19)	76(3)	25.4(19)	-11(2)	3.8(15)	5(2)
C9	33(2)	84(4)	20.1(17)	1(2)	6.3(15)	1(2)
C10	26.8(18)	69(3)	24.8(18)	3.9(19)	3.1(14)	-7.4(19)
C11	17.1(14)	51(2)	23.5(16)	2.9(16)	0.0(12)	-5.1(15)
C12	24.0(16)	44(2)	26.5(17)	4.3(16)	-1.2(13)	-6.8(15)
C13	39(2)	49(3)	34(2)	10.5(19)	4.2(17)	-5.7(19)
C14	47(2)	44(3)	42(2)	11(2)	0.7(19)	-4(2)
F15	90(2)	38.4(15)	47.9(16)	0.8(12)	11.0(15)	11.8(15)
C15	46(2)	39(2)	37(2)	-0.3(18)	3.6(18)	5.5(19)
C16	37(2)	42(2)	30.4(19)	2.7(17)	2.7(16)	0.0(17)
C17	25.2(16)	38(2)	24.6(16)	0.8(15)	-1.6(13)	-7.3(15)
C18	23.9(16)	34(2)	29.6(18)	-5.6(15)	2.4(13)	4.7(14)
C19	31.8(18)	26.4(18)	30.1(18)	-4.6(14)	0.7(14)	6.9(14)
C20	41(2)	30(2)	42(2)	-1.3(17)	3.4(18)	1.5(17)
C21	67(3)	37(2)	51(3)	12(2)	14(2)	9(2)
C22	96(5)	61(3)	40(3)	14(3)	0(3)	17(3)
C23	60(3)	66(3)	44(3)	-1(3)	-22(2)	13(3)
C24	36(2)	39(2)	43(2)	-3.8(18)	-7.5(17)	3.2(17)
C25	22.6(15)	34.3(19)	23.7(16)	-5.6(14)	5.4(12)	-0.7(14)
C26	24.2(15)	27.4(18)	24.4(16)	-4.5(13)	3.5(12)	-1.1(13)
C27	31.5(17)	31.4(19)	25.6(17)	-8.7(15)	2.5(14)	0.3(15)
C28	28.1(17)	38(2)	33.8(19)	-9.8(16)	-5.1(14)	-2.3(15)
C29	24.7(16)	37(2)	40(2)	-9.1(16)	2.9(15)	-4.2(15)
C30	29.6(18)	53(3)	31.2(19)	-1.6(18)	4.4(15)	-7.8(17)
C31	26.7(17)	49(2)	25.8(17)	-2.3(17)	-0.4(13)	-8.8(16)
C32	22.7(15)	32.6(18)	24.1(16)	1.5(14)	7.4(12)	-0.6(13)
C33	18.9(14)	27.6(17)	29.8(17)	-1.2(14)	6.7(12)	-3.2(13)

C34	23.4(16)	38(2)	42(2)	-12.0(17)	5.5(15)	-4.9(15)
C35	28.2(19)	37(2)	74(3)	-25(2)	11(2)	-3.3(16)
C36	23.5(17)	31(2)	82(3)	4(2)	8(2)	0.6(15)
C37	20.8(16)	52(3)	49(2)	14(2)	6.3(16)	2.0(16)
C38	22.1(16)	46(2)	29.9(18)	2.3(17)	5.2(14)	1.9(15)
Cl1A	105(2)	140(3)	81.7(16)	-50.2(16)	4.4(14)	22.0(17)
C1B	109(7)	69(6)	102(7)	-7(5)	40(6)	29(5)
Cl2A	78.3(14)	115(2)	108.6(19)	-27.3(16)	6.2(13)	-15.4(14)
Cl3A	85.4(15)	141(2)	62.7(12)	-38.3(14)	8.1(11)	-15.8(15)

Table 4 Bond Lengths for ps32.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	P1	2.2409(9)	C20	C21	1.380(6)
Pt1	C1	2.062(4)	C21	C22	1.381(8)
Pt1	N7	2.029(3)	C22	C23	1.376(9)
Pt1	C17	2.071(4)	C23	C24	1.396(7)
P1	C18	1.842(4)	C25	C26	1.514(5)
P1	C25	1.835(4)	C26	C27	1.394(5)
P1	C32	1.837(3)	C26	C31	1.391(5)
C1	C2	1.405(6)	C27	C28	1.384(5)
C1	C6	1.437(5)	C28	C29	1.386(6)
C2	C3	1.367(6)	C29	C30	1.384(5)
C3	F3	1.372(5)	C30	C31	1.386(5)
C3	C4	1.379(5)	C32	C33	1.508(5)
C4	C5	1.385(6)	C33	C34	1.389(5)
C5	C5A	1.529(6)	C33	C38	1.389(5)
C5	C6	1.411(6)	C34	C35	1.395(6)
C6	C7	1.472(6)	C35	C36	1.373(7)
N7	C7	1.351(5)	C36	C37	1.384(7)
N7	C11	1.353(5)	C37	C38	1.377(6)
C7	C8	1.404(5)	C1E	Cl1D	1.699(4)
C8	C9	1.370(7)	C1E	Cl2D	1.702(4)
C9	C10	1.381(7)	C1E	Cl3D	1.703(4)
C10	C11	1.400(5)	Cl1A	C1B	1.666(9)
C11	C12	1.466(6)	C1F	Cl1E	1.698(4)
C12	C13	1.390(6)	C1F	Cl2E	1.702(4)
C12	C17	1.426(5)	C1F	Cl3E	1.701(4)
C13	C13A	1.52(3)	C1D	Cl1C	1.70(4)
C13	C14	1.395(7)	C1D	Cl2C	1.71(4)
C14	C15	1.378(6)	C1D	Cl3C	1.53(4)
F15	C15	1.357(5)	Cl1B	C1C	1.699(4)
C15	C16	1.379(6)	C1B	Cl2A	1.840(11)
C16	C17	1.397(6)	C1B	Cl3A	1.799(10)
C18	C19	1.506(5)	C1C	Cl2B	1.699(4)
C19	C20	1.394(6)	C1C	Cl3B	1.696(4)
C19	C24	1.387(6)			

Table 5 Bond Angles for ps32.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Pt1	P1	98.67(11)	F15	C15	C16	119.1(4)
C1	Pt1	C17	158.79(15)	C15	C16	C17	120.9(4)
N7	Pt1	P1	169.79(8)	C12	C17	Pt1	111.9(3)
N7	Pt1	C1	79.69(14)	C16	C17	Pt1	131.9(3)
N7	Pt1	C17	80.22(14)	C16	C17	C12	116.0(4)
C17	Pt1	P1	102.30(10)	C19	C18	P1	119.3(3)
C18	P1	Pt1	111.55(12)	C20	C19	C18	120.9(4)
C25	P1	Pt1	120.67(12)	C24	C19	C18	120.5(4)
C25	P1	C18	100.49(17)	C24	C19	C20	118.5(4)
C25	P1	C32	101.19(16)	C21	C20	C19	120.8(4)
C32	P1	Pt1	114.16(12)	C20	C21	C22	120.4(5)
C32	P1	C18	107.14(17)	C23	C22	C21	119.5(5)
C2	C1	Pt1	130.2(3)	C22	C23	C24	120.4(5)
C2	C1	C6	116.5(3)	C19	C24	C23	120.4(5)
C6	C1	Pt1	113.2(3)	C26	C25	P1	114.9(2)
C3	C2	C1	120.2(4)	C27	C26	C25	119.8(3)
C2	C3	F3	118.6(3)	C31	C26	C25	122.0(3)
C2	C3	C4	124.0(4)	C31	C26	C27	118.2(3)
F3	C3	C4	117.3(4)	C28	C27	C26	120.6(3)
C3	C4	C5	118.0(4)	C27	C28	C29	120.8(3)
C4	C5	C5A	115.6(4)	C30	C29	C28	119.0(4)
C4	C5	C6	119.9(3)	C29	C30	C31	120.3(4)
C6	C5	C5A	124.5(4)	C30	C31	C26	121.1(3)
C1	C6	C7	114.7(3)	C33	C32	P1	111.9(2)
C5	C6	C1	121.2(4)	C34	C33	C32	121.1(3)
C5	C6	C7	124.1(3)	C34	C33	C38	118.3(4)
C7	N7	Pt1	117.8(3)	C38	C33	C32	120.6(3)
C7	N7	C11	124.1(3)	C33	C34	C35	120.3(4)
C11	N7	Pt1	116.9(2)	C36	C35	C34	120.5(4)

N7	C7	C6	113.8(3)	C35	C36	C37	119.6(4)
N7	C7	C8	117.5(4)	C38	C37	C36	120.0(4)
C8	C7	C6	128.7(4)	C37	C38	C33	121.4(4)
C9	C8	C7	119.9(4)	Cl1D	C1E	Cl2D	112.7(10)
C8	C9	C10	121.2(4)	Cl1D	C1E	Cl3D	111.9(9)
C9	C10	C11	118.6(4)	Cl2D	C1E	Cl3D	108.7(9)
N7	C11	C10	118.7(4)	Cl1E	C1F	Cl2E	121.1(10)
N7	C11	C12	113.9(3)	Cl1E	C1F	Cl3E	115.0(11)
C10	C11	C12	127.4(4)	Cl3E	C1F	Cl2E	118.4(11)
C13	C12	C11	121.8(4)	Cl1C	C1D	Cl2C	115(2)
C13	C12	C17	122.1(4)	Cl3C	C1D	Cl1C	111(2)
C17	C12	C11	115.9(4)	Cl3C	C1D	Cl2C	108(2)
C12	C13	C13A	130.6(7)	Cl1A	C1B	Cl2A	109.3(5)
C12	C13	C14	120.2(4)	Cl1A	C1B	Cl3A	110.4(6)
C14	C13	C13A	109.1(7)	Cl3A	C1B	Cl2A	105.6(6)
C15	C14	C13	117.6(4)	Cl1B	C1C	Cl2B	114.6(9)
C14	C15	C16	123.0(4)	Cl3B	C1C	Cl1B	116.7(11)
F15	C15	C14	117.9(4)	Cl3B	C1C	Cl2B	118.2(10)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps32.

Atom	*x*	*y*	*z*	U(eq)
H2	5770	3927	6511	36
H4	6029	2461	5466	43
H5	6222	3447	4949	41
H5AA	5817	3569	4536	69
H5AB	6215	2779	4732	69
H5AC	6902	3470	4713	69
H8	6534	4528	4508	53
H9	6645	5667	4142	55
H10	6436	6778	4536	48
H13	6072	7743	4980	49
H13A	6007	8500	4820	108
H13B	6771	7874	4779	108
H13C	5712	7725	4564	108
H14	5659	8706	5471	54
H16	5523	7201	6512	44
H18A	6980	4359	6886	35
H18B	7736	4999	6994	35
H20	6110	3980	7565	45
H21	6381	3596	8348	62
H22	7711	3980	8843	80
H23	8730	4803	8561	72
H24	8464	5197	7773	49
H25A	6280	6765	7105	32
H25B	6654	6226	7536	32
H27	8131	6592	7869	36
H28	9652	6913	7819	41
H29	10135	7083	7084	41
H30	9065	6933	6396	45
H31	7538	6619	6443	41
H32A	4953	4821	6965	31
H32B	5361	5252	7441	31
H34	4607	6362	7638	41
H35	3450	7263	7457	55
H36	2625	7341	6699	54
H37	2964	6524	6113	49
H38	4112	5633	6289	39
H1E	7644	4785	10470	119
H1D	6745	5315	8540	28
H1B	5420	6672	8676	109
H1C	6098	6212	9209	59

Table 7 Atomic Occupancy for ps32.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H5	0.231(11)	C5A	0.769(11)	H5AA	0.769(11)
H5AB	0.769(11)	H5AC	0.769(11)	H13	0.769(11)
C13A	0.231(11)	H13A	0.231(11)	H13B	0.231(11)
H13C	0.231(11)	C1E	0.2	H1E	0.2
Cl1A	0.8	C1F	0.2	C1D	0.1
H1D	0.1	Cl1B	0.1	Cl1D	0.2
C1B	0.8	H1B	0.8	Cl1E	0.2
C1C	0.1	H1C	0.1	Cl1C	0.1
Cl2A	0.8	Cl2E	0.2	Cl2B	0.1
Cl2C	0.1	Cl2D	0.2	Cl3D	0.2
Cl3B	0.1	Cl3E	0.2	Cl3C	0.1
Cl3A	0.8				

Refinement model description

Number of restraints - 22, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 C1C-Cl1B = C1C-Cl2B = C1C-Cl3B
 1.7 with sigma of 0.004
 Cl1B-Cl2B = Cl2B-Cl3B = Cl3B-Cl1B
 2.9 with sigma of 0.02
 C1E-Cl1D = C1E-Cl2D = C1E-Cl3D
 1.7 with sigma of 0.004
 Cl1D-Cl2D = Cl2D-Cl3D = Cl3D-Cl1D
 2.9 with sigma of 0.02
 C1F-Cl1E = C1F-Cl2E = C1F-Cl3E
 1.7 with sigma of 0.004
 Cl1E-Cl2E = Cl2E-Cl3E = Cl3E-Cl1E
 2.9 with sigma of 0.02
 H10-H13B
 2.1 with sigma of 0.02
 H10-H13C
 2.1 with sigma of 0.02
3. Rigid bond restraints
 C1F, Cl1E, Cl2E, Cl3E
 with sigma for 1-2 distances of 0.002 and sigma for 1-3 distances of 0.002
4. Uiso/Uaniso restraints and constraints
C1E ≈ Cl1D ≈ Cl2D ≈ Cl3D: within 1.7A with sigma of 0.002 and sigma
for terminal atoms of 0.004
C1F ≈ Cl1E ≈ Cl2E ≈ Cl3E: within 1.7A with sigma of 0.003 and sigma
for terminal atoms of 0.006
5. Others
 Sof(H5)=Sof(C13A)=Sof(H13A)=Sof(H13B)=Sof(H13C)=1-FVAR(1)
 Sof(C5A)=Sof(H5AA)=Sof(H5AB)=Sof(H5AC)=Sof(H13)=FVAR(1)
 Fixed Sof: C1E(0.2) H1E(0.2) Cl1A(0.8) C1F(0.2) C1D(0.1) H1D(0.1) Cl1B(0.1)
 Cl1D(0.2) C1B(0.8) H1B(0.8) Cl1E(0.2) C1C(0.1) H1C(0.1) Cl1C(0.1) Cl2A(0.8)
 Cl2E(0.2) Cl2B(0.1) Cl2C(0.1) Cl2D(0.2) Cl3D(0.2) Cl3B(0.1) Cl3E(0.2)
 Cl3C(0.1) Cl3A(0.8)
6.a Ternary CH refined with riding coordinates:
 C1E(H1E), C1D(H1D), C1B(H1B), C1C(H1C)
6.b Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C25(H25A,H25B), C32(H32A,H32B)
6.c Me refined with riding coordinates:
 C13A(H13A,H13B,H13C)
6.d Aromatic/amide H refined with riding coordinates:
 C2(H2), C4(H4), C5(H5), C8(H8), C9(H9), C10(H10), C13(H13), C14(H14),
 C16(H16), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24), C27(H27), C28(H28),
  C29(H29), C30(H30), C31(H31), C34(H34), C35(H35), C36(H36), C37(H37), C38(H38)
6.e Idealised Me refined as rotating group:
 C5A(H5AA,H5AB,H5AC)
```

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

ps29new Complex 2(t)

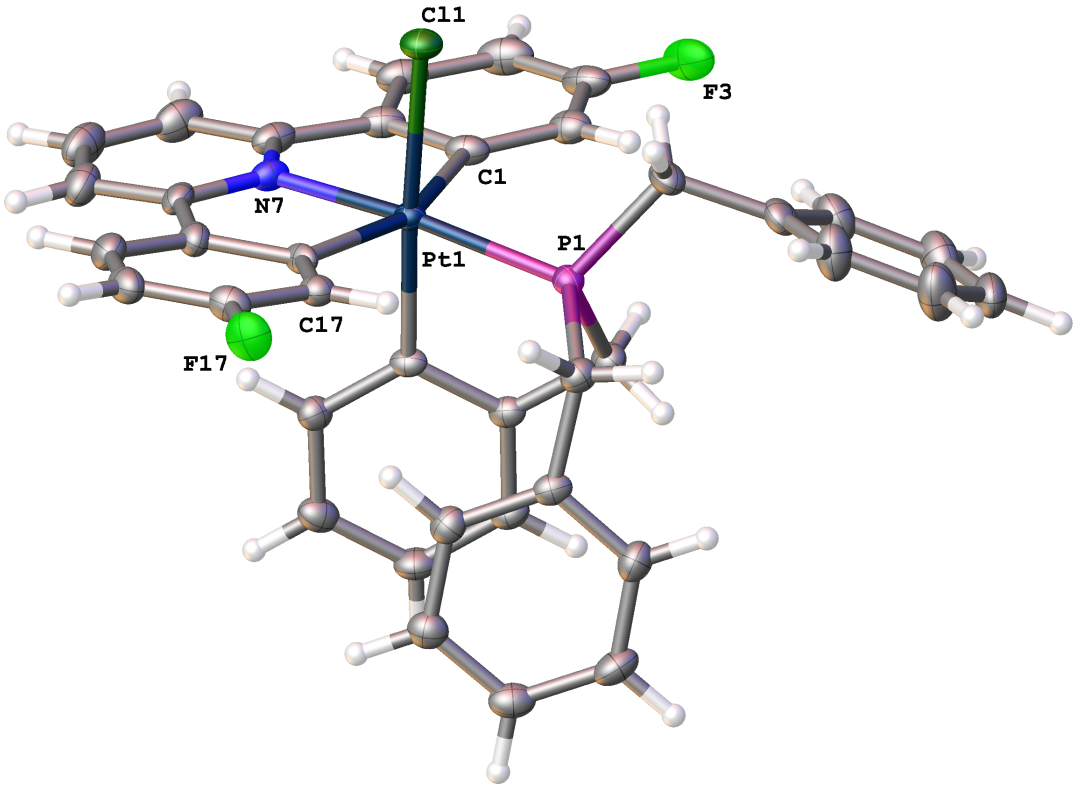


Figure SI3 *solid state structure of the complex in ps29new with thermal ellipsoids drawn at 50% probability level and only key atoms labeled.*

Crystal structure determination of [ps29new]
The asymmetric unit contains the complex, there are two in the unit cell.

Shortest contacts are tabulated below
Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.95	2.95	3.780(4)	147.1	C29-H29...Cl1_$5
0.99	2.94	3.651(4)	129.4	C25-H25B...Cl1_$4
0.95	2.56	3.266(4)	131.4	C36-H36...F3_$6

Lots of possible pi stacking characterized as atoms used to define mean planes through interacting pi systems, angle between interacting rings and closest atomic contact.

Pi stacking between the two non coordinated benzyl groups of the tribenzyl phosphine
C19 C20 C21 C22 C23 C24 to C26 C27 C28 C29 C30 C31 Angle between mean planes 10.207 (0.105) degrees
Closest atomic contact C19 - C26 3.1536 (0.0046) Angstroms

Pi stacking between one fluorophenyl ring and a symmetry related fluorophenyl ring across inversion centre
C1 C2 C3 F3 C4 C5 C6 to C1_$1 C2_$1 C3_$1 F3_$1 C4_$1 C5_$1 C6_$1
Angle between mean plane zero degrees (across inversion centre)
Closest atomic contact C2 - C4_$1 3.3412 (0.0052) Angstroms

Pi stacking between the fluorophenyl ring and a symmetry related fluorophenyl ring across an inversion centre
C12 C13 C14 C15 C16 C17 to C12_$2 C13_$2 C14_$2 C15_$2 C16_$2 C17_$2
Angle between mean plane zero degrees (across inversion centre)
Closest atomic contact C13 - C15_$2 3.3731 (0.0050) Angstroms

One of the uncoordinated benzyls and a symmetry related benzyl group of another tris benzylphosphine
C26 C27 C28 C29 C30 C31 to C26_$3 C27_$3 C28_$3 C29_$3 C30_$3 C31_$3
Angle between mean plane zero degrees (across inversion centre)
Closest atomic contact C26 - C30_$3 3.3699 (0.0050) Angstroms

To get some info of the coordinated benzyl, the angle between mean planes through di –fluorophenyl pyridine and the coordinated benzyl of tribenzyl phosphine
C1 F3 C4 C6 N7 C9 C12 C14 F17 C17 to C19 C20 C21 C22 C23 C24 is 85.440 (0.092) degrees

Symmetry operators used to generate symmetry equivalent atoms discussed above were $1 2-X,1-Y,-Z
$2 1-X,1-Y,1-Z
$3 1-X,-Y,1-Z

$4 2-X,1-Y,1-Z
$5 -1+X,-1+Y,+Z
$6 2-X,-Y,-Z

Experimental

Single crystals of $C_{38}H_{29}ClF_2NPPt$ **[ps29new]** were grown from acetone in an nmr tube. A suitable crystal was selected and mounted on a Mitegen head with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

7 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
8 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
9 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{38}H_{29}ClF_2NPPt$ (M =799.13 g/mol): triclinic, space group P-1 (no. 2), a = 11.3911(3) Å, b = 11.7933(4) Å, c = 12.8630(3) Å, α = 100.845(2)°, β = 97.595(2)°, γ = 117.163(3)°, V = 1462.18(7) Å^3, Z = 2, T = 150(2) K, μ(CuKα) = 10.686 mm^{-1}, *Dcalc* = 1.815 g/cm^3, 27557 reflections measured (7.226° ≤ 2Θ ≤ 156.402°), 6188 unique (R_{int} = 0.0564, R_{sigma} = 0.0440) which were used in all calculations. The final R_1 was 0.0257 (I > 2σ(I)) and wR_2 was 0.0619 (all data).

Table 1 Crystal data and structure refinement for ps29new.

Identification code	ps29new
Empirical formula	$C_{38}H_{29}ClF_2NPPt$
Formula weight	799.13
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.3911(3)
b/Å	11.7933(4)
c/Å	12.8630(3)
α/°	100.845(2)
β/°	97.595(2)
γ/°	117.163(3)
Volume/Å^3	1462.18(7)
Z	2
ϱ_{calc}g/cm^3	1.815
μ/mm^{-1}	10.686
F(000)	784.0
Crystal size/mm^3	0.185 × 0.095 × 0.03 colourless block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.226 to 156.402
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	27557
Independent reflections	6188 [R_{int} = 0.0564, R_{sigma} = 0.0440]
Data/restraints/parameters	6188/0/397
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0257, wR_2 = 0.0600
Final R indexes [all data]	R_1 = 0.0301, wR_2 = 0.0619
Largest diff. peak/hole / e Å^{-3}	0.95/-0.58

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps29new. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	7562.0(2)	4188.0(2)	2610.0(2)	15.94(5)
Cl1	9907.6(8)	5955.2(8)	3462.1(7)	23.95(16)
P1	7848.1(8)	2515.5(8)	2974.8(6)	17.23(16)
C1	7970(3)	3984(4)	1056(3)	22.3(7)
C2	8571(4)	3318(4)	552(3)	25.3(7)
C3	8732(4)	3349(4)	-499(3)	29.9(8)
F3	9342(3)	2689(2)	-944(2)	37.9(6)
C4	8335(4)	4031(4)	-1084(3)	33.7(9)
C5	7764(4)	4725(4)	-590(3)	29.4(8)
C6	7586(3)	4721(4)	472(3)	23.1(7)
C7	7053(4)	5510(4)	1038(3)	24.6(7)
N7	7052(3)	5466(3)	2079(2)	20.0(5)
C8	6569(4)	6271(4)	621(3)	32.5(8)
C9	6061(4)	6908(4)	1272(4)	34.6(9)
C10	6046(4)	6825(4)	2332(3)	30.9(8)
C11	6575(3)	6093(3)	2744(3)	21.6(7)
C12	6659(3)	5872(3)	3828(3)	22.2(7)
C13	6407(4)	6605(4)	4670(3)	26.1(7)
C14	6557(4)	6429(4)	5710(3)	26.9(8)
C15	6962(4)	5534(4)	5861(3)	24.1(7)
C16	7248(3)	4808(3)	5058(3)	20.8(7)
C17	7082(3)	4948(3)	3999(3)	18.6(6)
F17	7125(3)	5355(2)	6884.1(18)	32.8(5)
C18	6679(3)	1153(3)	1770(3)	20.3(6)

C19	5456(3)	1344(3)	1556(3)	18.3(6)
C20	5622(3)	2628(3)	1890(2)	17.1(6)
C21	4489(3)	2794(3)	1745(3)	20.5(6)
C22	3184(4)	1689(4)	1291(3)	25.1(7)
C23	3020(4)	426(4)	965(3)	25.0(7)
C24	4149(4)	255(3)	1092(3)	22.2(7)
C25	7311(4)	1839(3)	4115(3)	22.5(7)
C26	5799(3)	892(3)	3892(3)	19.6(6)
C27	4851(4)	1325(3)	3914(3)	22.1(7)
C28	3460(4)	415(4)	3669(3)	24.9(7)
C29	3016(4)	-937(4)	3407(3)	26.6(7)
C30	3947(4)	-1385(4)	3402(3)	28.5(8)
C31	5333(4)	-465(4)	3644(3)	25.0(7)
C32	9595(3)	2800(4)	3143(3)	25.0(7)
C33	9670(3)	1536(4)	2908(3)	25.3(7)
C34	9902(5)	1027(5)	3748(4)	37.0(9)
C35	9928(6)	-160(6)	3533(4)	44.3(11)
C36	9736(4)	-860(4)	2479(4)	36.0(9)
C37	9536(4)	-347(5)	1638(4)	37.3(10)
C38	9517(4)	842(5)	1850(3)	32.5(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps29new. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	15.23(7)	14.85(7)	14.58(7)	2.63(5)	3.43(4)	5.53(5)
Cl1	18.0(3)	21.2(4)	23.3(4)	3.5(3)	3.3(3)	3.7(3)
P1	15.1(3)	16.6(3)	17.2(4)	2.3(3)	2.9(3)	6.7(3)
C1	19.4(15)	22.3(16)	15.6(14)	3.2(12)	5.2(12)	3.3(13)
C2	24.0(16)	20.5(16)	22.1(16)	0.7(13)	6.4(13)	5.4(13)
C3	26.5(17)	24.1(17)	26.8(18)	1.6(14)	12.9(14)	2.9(14)
F3	40.9(13)	32.3(12)	32.2(12)	0.3(10)	22.4(10)	11.4(10)
C4	33.4(19)	32(2)	18.2(16)	2.2(15)	9.1(14)	3.5(16)
C5	27.4(18)	28.7(18)	20.6(17)	9.4(14)	3.1(14)	4.4(15)
C6	20.1(15)	23.0(16)	15.2(15)	4.1(13)	1.7(12)	3.0(13)
C7	22.3(16)	20.2(16)	23.3(17)	8.8(13)	0.1(13)	4.6(13)
N7	19.3(13)	18.3(13)	18.1(13)	7.1(11)	2.2(10)	5.9(11)
C8	36(2)	28.4(19)	26.8(18)	11.5(15)	0.9(15)	11.5(17)
C9	35(2)	26.8(19)	39(2)	12.9(17)	-1.2(17)	14.3(16)
C10	32.2(19)	21.8(17)	36(2)	4.7(15)	1.8(16)	14.2(15)
C11	20.1(15)	13.1(14)	28.0(17)	4.3(13)	3.0(13)	6.9(12)
C12	20.3(15)	18.4(15)	26.6(17)	2.8(13)	5.3(13)	9.9(13)
C13	26.4(17)	19.0(16)	31.4(19)	4.9(14)	7.3(14)	11.0(14)
C14	23.5(16)	22.9(17)	30.5(18)	0.6(14)	8.8(14)	10.4(14)
C15	22.3(15)	28.2(17)	16.3(15)	2.8(13)	4.8(12)	9.2(14)
C16	18.3(14)	18.8(15)	21.9(16)	4.1(13)	5.2(12)	6.9(13)
C17	17.3(14)	15.9(14)	17.0(14)	-2.7(12)	6.7(11)	5.9(12)
F17	40.9(12)	40.8(13)	19.6(10)	6.6(9)	11.9(9)	22.1(11)
C18	19.9(15)	18.1(15)	18.7(15)	1.1(12)	3.0(12)	7.9(12)
C19	19.0(15)	17.4(15)	13.4(13)	1.8(11)	4.2(11)	5.8(12)
C20	16.2(14)	16.2(14)	11.5(13)	0.4(11)	2.1(11)	3.7(12)
C21	20.3(15)	20.7(16)	19.8(15)	6.3(13)	3.3(12)	9.9(13)
C22	20.0(16)	29.1(18)	24.8(17)	10.5(14)	4.4(13)	10.3(14)
C23	19.2(15)	21.3(16)	24.0(17)	3.7(13)	2.0(13)	3.6(13)
C24	22.6(16)	18.2(15)	18.7(15)	2.2(12)	3.8(12)	5.9(13)
C25	22.7(16)	20.2(15)	22.2(16)	5.1(13)	4.0(13)	9.2(13)
C26	21.3(15)	18.5(15)	13.7(14)	4.3(12)	3.2(11)	5.9(13)
C27	25.8(16)	20.4(15)	17.7(15)	2.8(12)	4.0(12)	10.9(14)
C28	24.3(17)	27.0(17)	21.2(16)	6.2(14)	6.7(13)	10.9(14)
C29	22.4(16)	26.3(18)	21.5(16)	6.2(14)	1.9(13)	5.4(14)
C30	31.5(19)	17.3(16)	27.7(18)	6.2(14)	2.8(14)	5.9(14)
C31	30.5(18)	21.5(16)	24.4(17)	6.1(13)	5.2(14)	14.6(15)
C32	15.4(14)	24.5(17)	30.2(18)	2.4(14)	3.5(13)	8.4(13)
C33	16.5(15)	27.8(18)	30.8(18)	4.8(15)	3.9(13)	12.1(14)
C34	47(2)	46(2)	32(2)	9.6(18)	8.5(18)	35(2)
C35	59(3)	54(3)	47(3)	25(2)	24(2)	43(3)
C36	31.7(19)	28.1(19)	52(3)	5.2(18)	12.5(18)	20.0(17)
C37	35(2)	43(2)	33(2)	-3.7(18)	3.8(16)	24.8(19)
C38	31.0(19)	42(2)	29.8(19)	6.2(17)	7.8(15)	23.9(17)

Table 4 Bond Lengths for ps29new.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	Cl1	2.4425(8)	C13	C14	1.393(6)
Pt1	P1	2.2609(9)	C14	C15	1.364(6)
Pt1	C1	2.106(3)	C15	C16	1.384(5)
Pt1	N7	2.039(3)	C15	F17	1.374(4)
Pt1	C17	2.097(3)	C16	C17	1.402(5)
Pt1	C20	2.057(3)	C18	C19	1.508(5)
P1	C18	1.823(3)	C19	C20	1.409(5)

P1	C25	1.842(4)	C19	C24	1.398(5)
P1	C32	1.836(3)	C20	C21	1.385(5)
C1	C2	1.387(5)	C21	C22	1.402(5)
C1	C6	1.419(6)	C22	C23	1.384(5)
C2	C3	1.393(5)	C23	C24	1.384(5)
C3	F3	1.359(5)	C25	C26	1.513(5)
C3	C4	1.374(7)	C26	C27	1.391(5)
C4	C5	1.378(6)	C26	C31	1.391(5)
C5	C6	1.408(5)	C27	C28	1.396(5)
C6	C7	1.465(5)	C28	C29	1.388(6)
C7	N7	1.350(5)	C29	C30	1.385(6)
C7	C8	1.396(6)	C30	C31	1.394(5)
N7	C11	1.351(5)	C32	C33	1.508(5)
C8	C9	1.374(7)	C33	C34	1.382(6)
C9	C10	1.387(6)	C33	C38	1.393(5)
C10	C11	1.398(6)	C34	C35	1.389(7)
C11	C12	1.464(5)	C35	C36	1.379(7)
C12	C13	1.399(5)	C36	C37	1.376(7)
C12	C17	1.418(5)	C37	C38	1.389(6)

Table 5 Bond Angles for ps29new.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pt1	Cl1	96.45(3)	N7	C11	C12	113.5(3)
C1	Pt1	Cl1	91.42(9)	C10	C11	C12	128.2(3)
C1	Pt1	P1	96.30(11)	C13	C12	C11	120.9(3)
N7	Pt1	Cl1	91.88(8)	C13	C12	C17	121.9(4)
N7	Pt1	P1	170.83(8)	C17	C12	C11	117.1(3)
N7	Pt1	C1	79.61(14)	C14	C13	C12	120.1(4)
N7	Pt1	C17	79.78(13)	C15	C14	C13	117.3(3)
N7	Pt1	C20	90.93(13)	C14	C15	C16	124.6(4)
C17	Pt1	Cl1	86.02(9)	C14	C15	F17	118.1(3)
C17	Pt1	P1	104.57(10)	F17	C15	C16	117.3(3)
C17	Pt1	C1	159.13(15)	C15	C16	C17	119.4(3)
C20	Pt1	Cl1	176.97(10)	C12	C17	Pt1	111.4(2)
C20	Pt1	P1	80.68(10)	C16	C17	Pt1	131.4(3)
C20	Pt1	C1	87.96(12)	C16	C17	C12	116.7(3)
C20	Pt1	C17	95.61(12)	C19	C18	P1	104.4(2)
C18	P1	Pt1	100.67(12)	C20	C19	C18	119.6(3)
C18	P1	C25	103.21(16)	C24	C19	C18	120.9(3)
C18	P1	C32	111.99(16)	C24	C19	C20	119.4(3)
C25	P1	Pt1	122.20(12)	C19	C20	Pt1	117.8(2)
C32	P1	Pt1	114.93(13)	C21	C20	Pt1	122.6(2)
C32	P1	C25	103.29(17)	C21	C20	C19	119.6(3)
C2	C1	Pt1	131.6(3)	C20	C21	C22	120.2(3)
C2	C1	C6	117.1(3)	C23	C22	C21	120.3(3)
C6	C1	Pt1	111.2(2)	C24	C23	C22	119.8(3)
C1	C2	C3	120.2(4)	C23	C24	C19	120.7(3)
F3	C3	C2	117.4(4)	C26	C25	P1	114.6(2)
F3	C3	C4	119.2(3)	C27	C26	C25	122.6(3)
C4	C3	C2	123.3(4)	C31	C26	C25	119.0(3)
C3	C4	C5	117.5(3)	C31	C26	C27	118.5(3)
C4	C5	C6	120.8(4)	C26	C27	C28	120.7(3)
C1	C6	C7	117.1(3)	C29	C28	C27	119.8(3)
C5	C6	C1	121.0(4)	C30	C29	C28	120.2(3)
C5	C6	C7	121.9(4)	C29	C30	C31	119.3(4)
N7	C7	C6	113.7(3)	C26	C31	C30	121.4(3)
N7	C7	C8	118.9(4)	C33	C32	P1	113.5(2)
C8	C7	C6	127.4(4)	C34	C33	C32	120.6(4)
C7	N7	Pt1	117.9(3)	C34	C33	C38	117.6(4)
C7	N7	C11	123.8(3)	C38	C33	C32	121.8(4)
C11	N7	Pt1	117.8(2)	C33	C34	C35	120.8(4)
C9	C8	C7	118.8(4)	C36	C35	C34	121.2(5)
C8	C9	C10	121.2(4)	C37	C36	C35	118.5(4)
C9	C10	C11	119.0(4)	C36	C37	C38	120.5(4)
N7	C11	C10	118.2(4)	C37	C38	C33	121.3(4)

Table 6 Hydrogen Bonds for ps29new.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C25	H25B	Cl1[1]	0.99	2.94	3.651(4)	129.4
C29	H29	Cl1[2]	0.95	2.95	3.780(4)	147.1
C36	H36	F3[3]	0.95	2.56	3.266(4)	131.4

[1]2-X,1-Y,1-Z; [2]-1+X,-1+Y,+Z; [3]2-X,-Y,-Z

Table 7 Torsion Angles for ps29new.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Pt1	P1	C18	C19	-39.7(2)	C11	C12	C13	C14	-176.8(3)
Pt1	P1	C25	C26	78.5(3)	C11	C12	C17	Pt1	2.4(4)
Pt1	P1	C32	C33	-155.5(2)	C11	C12	C17	C16	175.8(3)

Pt1	C1	C2	C3	-179.5(3)
Pt1	C1	C6	C5	-179.8(3)
Pt1	C1	C6	C7	2.6(4)
Pt1	N7	C11	C10	-171.3(3)
Pt1	N7	C11	C12	7.3(4)
Pt1	C20	C21	C22	-177.3(3)
P1	C18	C19	C20	27.4(4)
P1	C18	C19	C24	-148.6(3)
P1	C25	C26	C27	-76.6(4)
P1	C25	C26	C31	102.7(3)
P1	C32	C33	C34	-96.2(4)
P1	C32	C33	C38	84.2(4)
C1	C2	C3	F3	179.3(3)
C1	C2	C3	C4	0.7(6)
C1	C6	C7	N7	2.5(4)
C1	C6	C7	C8	-177.5(3)
C2	C1	C6	C5	2.4(5)
C2	C1	C6	C7	-175.2(3)
C2	C3	C4	C5	0.7(6)
C3	C4	C5	C6	-0.6(6)
F3	C3	C4	C5	-177.8(3)
C4	C5	C6	C1	-1.0(5)
C4	C5	C6	C7	176.5(3)
C5	C6	C7	N7	-175.1(3)
C5	C6	C7	C8	4.9(6)
C6	C1	C2	C3	-2.2(5)
C6	C7	N7	Pt1	-6.8(4)
C6	C7	N7	C11	-178.3(3)
C6	C7	C8	C9	177.7(4)
C7	N7	C11	C10	0.3(5)
C7	N7	C11	C12	178.8(3)
C7	C8	C9	C10	1.2(6)
N7	C7	C8	C9	-2.4(5)
N7	C11	C12	C13	170.1(3)
N7	C11	C12	C17	-6.3(4)
C8	C7	N7	Pt1	173.3(3)
C8	C7	N7	C11	1.7(5)
C8	C9	C10	C11	0.8(6)
C9	C10	C11	N7	-1.5(5)
C9	C10	C11	C12	-179.9(4)
C10	C11	C12	C13	-11.5(6)
C10	C11	C12	C17	172.1(3)
C12	C13	C14	C15	0.5(5)
C13	C12	C17	Pt1	-173.9(3)
C13	C12	C17	C16	-0.5(5)
C13	C14	C15	C16	0.8(5)
C13	C14	C15	F17	179.5(3)
C14	C15	C16	C17	-2.0(5)
C15	C16	C17	Pt1	173.6(3)
C15	C16	C17	C12	1.7(5)
C17	C12	C13	C14	-0.6(5)
F17	C15	C16	C17	179.3(3)
C18	P1	C25	C26	-33.4(3)
C18	P1	C32	C33	-41.4(3)
C18	C19	C20	Pt1	2.1(4)
C18	C19	C20	C21	-176.7(3)
C18	C19	C24	C23	175.6(3)
C19	C20	C21	C22	1.4(5)
C20	C19	C24	C23	-0.4(5)
C20	C21	C22	C23	-1.3(5)
C21	C22	C23	C24	0.3(6)
C22	C23	C24	C19	0.5(5)
C24	C19	C20	Pt1	178.2(2)
C24	C19	C20	C21	-0.6(5)
C25	P1	C18	C19	87.2(2)
C25	P1	C32	C33	69.0(3)
C25	C26	C27	C28	177.9(3)
C25	C26	C31	C30	-178.2(3)
C26	C27	C28	C29	0.5(5)
C27	C26	C31	C30	1.1(5)
C27	C28	C29	C30	0.9(6)
C28	C29	C30	C31	-1.2(6)
C29	C30	C31	C26	0.2(6)
C31	C26	C27	C28	-1.4(5)
C32	P1	C18	C19	-162.3(2)
C32	P1	C25	C26	-150.2(3)
C32	C33	C34	C35	177.9(4)
C32	C33	C38	C37	-177.5(4)
C33	C34	C35	C36	0.6(8)
C34	C33	C38	C37	2.8(6)
C34	C35	C36	C37	1.0(7)
C35	C36	C37	C38	-0.6(7)
C36	C37	C38	C33	-1.3(6)
C38	C33	C34	C35	-2.4(6)

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps29new.

Atom	*x*	*y*	*z*	U(eq)
H2	8873	2839	924	30
H4	8450	4023	-1803	40
H5	7487	5214	-971	35
H8	6591	6346	-99	39
H9	5715	7414	990	42
H10	5682	7261	2771	37
H13	6133	7223	4531	31
H14	6383	6911	6291	32
H16	7554	4221	5224	25
H18A	7095	1201	1139	24
H18B	6422	284	1912	24
H21	4597	3659	1953	25
H22	2409	1806	1207	30
H23	2134	-320	654	30
H24	4034	-611	862	27
H25A	7809	1371	4295	27
H25B	7580	2588	4765	27
H27	5152	2249	4099	26
H28	2820	720	3681	30
H29	2069	-1557	3229	32
H30	3646	-2309	3236	34
H31	5971	-773	3639	30
H32A	10029	3319	2648	30
H32B	10121	3337	3902	30
H34	10046	1495	4482	44
H35	10081	-495	4122	53
H36	9741	-1678	2337	43
H37	9411	-810	908	45
H38	9397	1190	1261	39

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C25(H25A,H25B), C32(H32A,H32B)
2.b Aromatic/amide H refined with riding coordinates:
 C2(H2), C4(H4), C5(H5), C8(H8), C9(H9), C10(H10), C13(H13), C14(H14),
 C16(H16), C21(H21), C22(H22), C23(H23), C24(H24), C27(H27), C28(H28), C29(H29),
  C30(H30), C31(H31), C34(H34), C35(H35), C36(H36), C37(H37), C38(H38)
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This report has been created with Olex2, compiled on 2016.02.16 svn.r3265 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

PS34 4

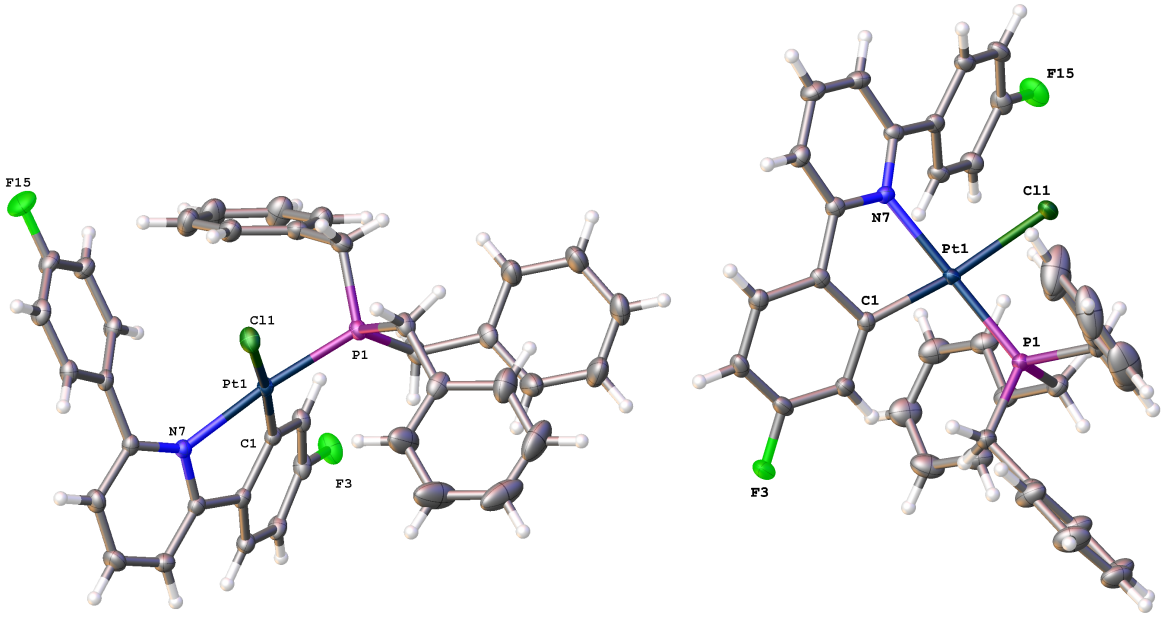

Figure SI4 *Two views of pss34 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level*

Crystal structure determination of [ps34]
The asymmetric unit contains the complex, twice this in the unit cell.
The chelated pyridine and fluorophenyl ring are at a rather jaunty angle to the plane of the atoms chelated to the Pt.
This is described as the angle between mean planes between either the aromatic ring of interest or the atoms chelated to Pt.

Angles in the bis fluorophenylpyridine ligand
Angle between coordinated phenyl C1 C2 C3 C4 C5 C6 to pyridine N7 C7 C8 C9 C10 C11 is 28.885 (0.079) degrees

Angle between pyridine N7 C7 C8 C9 C10 C11 and non coordinated fluorophenyl C12 C13 C14 C15 C16 C17 is 32.453 (0.077) degrees

Angles between the plane of the atoms coordinated to Pt and the chelated aromatics
Angle between pyridine ring N7 C7 C8 C9 C10 C11 and a plane described by atoms coordinated to Pt1, Pt1 C1 N7 Cl1 P1 is 38.080 (0.055) degrees

Angle between a plane described by atoms coordinated to Pt1, Pt1 C1 N7 Cl1 P1 and coordinated fluorphenyl ring C1 C2 C3 C4 C5 C6 is 29.756 (0.047) degrees

There is possible pi stacking between the bis fluorophenylpyridine and a symmetry related ligand (see Mercury)
Angle between mean planes through interacting pi systems is zero because its across an inversion centre.
Closest atomic contact C8 - C17_$1 3.2996 (0.0025) Angstroms

Symmetry operator used to generate symmetry related atom in above contact $1 1-X,1-Y,1-Z

More info on pi stacking from Olex2

Plane #2 C12 C17 C16 C15 C14 C13
Plane #6 N7 C11 C10 C9 C8 C7

Considering plane #6 plane #6 has interaction with plane #2
#6@2_666 (1-X,1-Y,1-Z)

angle: 0.000, centroid-centroid distance: 3.820 Angstroms, off set shift distance of the two centroids 0.535 Angstroms

Experimental
Single crystals of $C_{38}H_{31}ClF_2NPPt$ **[ps34]** were grown from chloroform. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.
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11 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
12 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{38}H_{31}ClF_2NPPt$ (M =801.15 g/mol): triclinic, space group P-1 (no. 2), a = 8.51403(11) Å, b = 10.31938(18) Å, c = 18.7511(3) Å, α = 83.1662(13)°, β = 79.6553(12)°, γ = 76.3618(13)°, V = 1569.92(4) Å^3, Z = 2, T = 150(2) K, μ(MoKα) = 4.646 mm^{-1}, *Dcalc* = 1.695 g/cm^3, 54759 reflections measured (4.792° ≤ 2Θ ≤ 67.348°), 11737 unique (R_{int} = 0.0370, R_{sigma} = 0.0305) which were used in all calculations. The final R_1 was 0.0210 (I > 2σ(I)) and wR_2 was 0.0435 (all data).

Table 1 Crystal data and structure refinement for ps34.

Identification code	ps34
Empirical formula	$C_{38}H_{31}ClF_2NPPt$
Formula weight	801.15
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.51403(11)
b/Å	10.31938(18)
c/Å	18.7511(3)
α/°	83.1662(13)
β/°	79.6553(12)
γ/°	76.3618(13)
Volume/Å^3	1569.92(4)
Z	2
ϱ_{calc}g/cm^3	1.695
μ/mm^{-1}	4.646
F(000)	788.0
Crystal size/mm^3	0.24 × 0.2 × 0.06 yellow block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.792 to 67.348
Index ranges	-12 ≤ h ≤ 13, -15 ≤ k ≤ 16, -29 ≤ l ≤ 29
Reflections collected	54759
Independent reflections	11737 [R_{int} = 0.0370, R_{sigma} = 0.0305]
Data/restraints/parameters	11737/0/397
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0210, wR_2 = 0.0422
Final R indexes [all data]	R_1 = 0.0250, wR_2 = 0.0435
Largest diff. peak/hole / e Å^{-3}	0.87/-0.95

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps34. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	3031.1(2)	6894.2(2)	6862.5(2)	14.37(2)
Cl1	3581.5(6)	9084.7(4)	6686.6(2)	22.87(8)
C1	2481.8(19)	5114.3(16)	6879.8(9)	16.3(3)
P1	2209.2(5)	7285.4(4)	8034.8(2)	16.92(8)
C2	2476(2)	4055.6(17)	7417.3(9)	19.8(3)
C3	1960(2)	2942.7(17)	7294.6(10)	22.0(3)
F3	1975.5(15)	1929.6(11)	7833.9(6)	30.0(3)
C4	1423(2)	2787.2(18)	6667.8(10)	22.4(3)
C5	1498(2)	3799.8(18)	6110.6(10)	20.3(3)
C6	2052.4(19)	4927.7(17)	6206.1(9)	17.1(3)
C7	2534.5(19)	5845.5(17)	5587.9(9)	17.8(3)
N7	3559.6(16)	6579.3(14)	5735.6(7)	15.5(3)
C8	2161(2)	5905.5(18)	4892.6(10)	21.4(3)
C9	2924(2)	6661(2)	4333.9(10)	25.6(4)
C10	4108(2)	7263.0(19)	4471.3(10)	23.0(3)
C11	4432.8(19)	7199.5(17)	5181.3(9)	17.4(3)
C12	5858(2)	7658.8(17)	5323.0(9)	17.5(3)
C13	6418(2)	8692.6(17)	4879.3(9)	20.4(3)
C14	7833(2)	9056.1(18)	4972.5(10)	23.6(4)
C15	8677(2)	8351.8(19)	5505.8(11)	23.7(4)
F15	10068.6(14)	8691.2(13)	5601.9(7)	33.9(3)
C16	8187(2)	7313.0(18)	5953.6(10)	22.2(3)
C17	6758(2)	6969.3(17)	5861.0(9)	19.5(3)
C18	1044(2)	8979.6(17)	8228.3(10)	21.8(3)
C19	-662(2)	9421.1(18)	8039.4(12)	27.0(4)
C20	-1971(3)	9837(2)	8585.6(15)	42.5(6)
C21	-3557(3)	10263(3)	8420(2)	58.8(8)
C22	-3834(3)	10307(3)	7728(2)	62.2(9)
C23	-2545(3)	9921(3)	7175.0(19)	63.7(10)
C24	-957(3)	9470(3)	7336.0(14)	44.1(6)
C25	1051(2)	6130.4(19)	8602.7(10)	24.5(4)
C26	-80(2)	6621.2(18)	9285.2(10)	23.5(4)
C27	498(3)	6778(2)	9906.2(11)	32.1(5)
C28	-570(3)	7227(2)	10522.6(11)	36.9(5)
C29	-2237(3)	7511(2)	10531.2(11)	35.5(5)
C30	-2826(3)	7316(3)	9923.6(13)	40.8(6)
C31	-1751(3)	6882(2)	9306.3(11)	34.9(5)
C32	3969(2)	7234.6(19)	8487.6(10)	23.2(4)
C33	5276(2)	5977(2)	8372.8(10)	23.3(4)
C34	6493(2)	5932(2)	7763.9(11)	27.3(4)
C35	7660(2)	4761(2)	7628.0(12)	34.1(5)
C36	7619(3)	3621(2)	8093.4(13)	38.1(5)

C37	6438(3)	3662(2)	8706.6(13)	37.5(5)
C38	5277(2)	4836(2)	8848.3(11)	30.5(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps34. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	15.25(3)	13.47(3)	13.85(3)	-0.04(2)	-0.45(2)	-3.97(2)
Cl1	30.3(2)	16.55(18)	21.06(19)	-0.51(15)	2.97(16)	-9.62(15)
C1	14.0(7)	16.6(7)	18.0(7)	-3.6(6)	-0.2(6)	-3.5(5)
P1	20.11(19)	15.19(19)	14.92(18)	-1.02(15)	-0.44(15)	-4.66(15)
C2	22.8(8)	17.3(8)	17.7(8)	-2.3(6)	1.0(6)	-3.9(6)
C3	25.0(8)	14.3(7)	22.7(8)	0.1(6)	5.5(7)	-4.3(6)
F3	46.3(7)	17.6(5)	23.8(6)	2.0(4)	2.5(5)	-10.2(5)
C4	21.7(8)	18.8(8)	26.8(9)	-5.0(7)	4.0(7)	-9.2(6)
C5	18.2(7)	21.5(8)	21.6(8)	-5.1(7)	0.6(6)	-6.3(6)
C6	13.3(7)	17.0(7)	19.7(7)	-1.8(6)	0.3(6)	-2.8(6)
C7	14.6(7)	18.1(7)	19.5(8)	-2.6(6)	-1.0(6)	-2.1(6)
N7	15.7(6)	16.2(6)	14.3(6)	-0.9(5)	-1.3(5)	-4.2(5)
C8	20.2(8)	24.5(9)	21.1(8)	-3.5(7)	-4.8(6)	-5.9(6)
C9	28.9(9)	30.4(10)	17.4(8)	0.1(7)	-6.5(7)	-5.3(8)
C10	24.7(8)	26.1(9)	16.1(8)	2.0(7)	-0.9(6)	-5.3(7)
C11	16.1(7)	17.2(7)	16.5(7)	-0.2(6)	0.1(6)	-1.8(6)
C12	16.2(7)	17.7(7)	17.2(7)	-2.1(6)	1.7(6)	-4.1(6)
C13	21.7(8)	18.1(8)	18.7(8)	-0.1(6)	1.6(6)	-3.2(6)
C14	25.1(8)	18.4(8)	25.5(9)	1.5(7)	3.6(7)	-8.6(7)
C15	18.0(8)	23.3(9)	30.6(9)	-4.2(7)	0.8(7)	-8.6(6)
F15	25.2(6)	34.8(7)	46.1(7)	2.1(6)	-5.9(5)	-17.7(5)
C16	18.6(8)	23.8(9)	24.2(8)	0.1(7)	-2.6(6)	-6.2(6)
C17	18.8(7)	19.6(8)	19.0(8)	1.4(6)	1.0(6)	-6.2(6)
C18	26.8(8)	16.7(8)	20.9(8)	-3.9(6)	1.2(7)	-5.3(6)
C19	23.4(8)	16.6(8)	39.0(11)	-4.8(8)	0.9(8)	-3.7(7)
C20	32.6(11)	38.7(13)	49.4(14)	-9.2(11)	8.6(10)	-2.8(9)
C21	27.7(12)	46.0(15)	94(2)	-19.7(16)	11.5(14)	-0.8(11)
C22	29.1(12)	39.3(14)	123(3)	-31.6(17)	-24.0(15)	4.9(10)
C23	48.8(15)	57.0(18)	88(2)	-36.3(17)	-38.1(16)	19.2(13)
C24	36.2(12)	45.3(14)	48.5(14)	-20.8(12)	-15(1)	10.4(10)
C25	34.5(10)	20.4(8)	18.2(8)	-2.0(7)	1.2(7)	-8.9(7)
C26	29.3(9)	21.3(8)	18.9(8)	2.5(7)	1.0(7)	-9.4(7)
C27	27.3(9)	44.9(12)	19.8(9)	-0.3(8)	-0.6(7)	-3.1(9)
C28	37.0(11)	51.4(14)	19.3(9)	-5.0(9)	-2.1(8)	-4.5(10)
C29	34.3(11)	41.2(12)	23.3(9)	0.0(9)	5.7(8)	-1.8(9)
C30	25.4(10)	60.8(16)	32.1(11)	3.3(11)	2.4(8)	-9.9(10)
C31	32.2(10)	53.1(14)	23.3(9)	-3.4(9)	-1.6(8)	-19.1(10)
C32	25.9(8)	25.1(9)	20.3(8)	-3.5(7)	-5.1(7)	-7.1(7)
C33	21.3(8)	29.8(9)	20.3(8)	-1.1(7)	-6.8(6)	-6.4(7)
C34	23.4(9)	35.5(11)	22.5(9)	1.9(8)	-4.8(7)	-7.1(8)
C35	24.0(9)	43.2(12)	30.1(10)	-0.6(9)	-1.2(8)	-0.8(8)
C36	27.6(10)	38.8(12)	40.5(12)	1(1)	-4.9(9)	4.6(9)
C37	32.4(10)	35.0(11)	38.6(12)	10.9(9)	-4.6(9)	-2.2(9)
C38	25.9(9)	37.4(11)	25.7(9)	3.5(8)	-3.5(7)	-5.3(8)

Table 4 Bond Lengths for ps34.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	Cl1	2.3884(4)	C14	C15	1.372(3)
Pt1	C1	1.9947(17)	C15	F15	1.359(2)
Pt1	P1	2.2384(4)	C15	C16	1.378(3)
Pt1	N7	2.1274(13)	C16	C17	1.390(2)
C1	C2	1.396(2)	C18	C19	1.509(3)
C1	C6	1.423(2)	C19	C20	1.394(3)
P1	C18	1.8374(17)	C19	C24	1.379(3)
P1	C25	1.844(2)	C20	C21	1.397(4)
P1	C32	1.8382(19)	C21	C22	1.353(5)
C2	C3	1.379(3)	C22	C23	1.386(4)
C3	F3	1.365(2)	C23	C24	1.397(3)
C3	C4	1.374(3)	C25	C26	1.517(2)
C4	C5	1.391(3)	C26	C27	1.383(3)
C5	C6	1.396(2)	C26	C31	1.379(3)
C6	C7	1.470(2)	C27	C28	1.389(3)
C7	N7	1.364(2)	C28	C29	1.377(3)
C7	C8	1.388(2)	C29	C30	1.378(3)
N7	C11	1.353(2)	C30	C31	1.388(3)
C8	C9	1.388(3)	C32	C33	1.506(3)
C9	C10	1.377(3)	C33	C34	1.394(3)
C10	C11	1.399(2)	C33	C38	1.389(3)
C11	C12	1.478(2)	C34	C35	1.389(3)
C12	C13	1.394(2)	C35	C36	1.382(3)
C12	C17	1.400(2)	C36	C37	1.383(3)
C13	C14	1.388(3)	C37	C38	1.391(3)

Table 5 Bond Angles for ps34.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Pt1	Cl1	172.43(5)	C13	C12	C17	119.10(16)
C1	Pt1	P1	99.70(5)	C17	C12	C11	119.96(15)
C1	Pt1	N7	79.14(6)	C14	C13	C12	120.93(17)
P1	Pt1	Cl1	86.424(16)	C15	C14	C13	117.95(17)
N7	Pt1	Cl1	94.32(4)	C14	C15	C16	123.47(17)
N7	Pt1	P1	174.23(4)	F15	C15	C14	118.68(17)
C2	C1	Pt1	131.79(13)	F15	C15	C16	117.84(17)
C2	C1	C6	116.64(16)	C15	C16	C17	118.04(17)
C6	C1	Pt1	111.56(12)	C16	C17	C12	120.49(16)
C18	P1	Pt1	116.76(6)	C19	C18	P1	118.39(13)
C18	P1	C25	105.94(8)	C20	C19	C18	119.2(2)
C18	P1	C32	98.86(9)	C24	C19	C18	121.80(18)
C25	P1	Pt1	116.91(6)	C24	C19	C20	119.0(2)
C32	P1	Pt1	110.78(6)	C19	C20	C21	120.0(3)
C32	P1	C25	105.59(9)	C22	C21	C20	120.6(3)
C3	C2	C1	119.66(17)	C21	C22	C23	120.3(2)
F3	C3	C2	117.77(17)	C22	C23	C24	119.7(3)
F3	C3	C4	117.77(16)	C19	C24	C23	120.4(2)
C4	C3	C2	124.46(17)	C26	C25	P1	118.44(13)
C3	C4	C5	116.81(17)	C27	C26	C25	122.50(18)
C4	C5	C6	120.45(17)	C31	C26	C25	119.66(18)
C1	C6	C7	115.45(15)	C31	C26	C27	117.80(18)
C5	C6	C1	121.67(16)	C26	C27	C28	121.1(2)
C5	C6	C7	121.81(16)	C29	C28	C27	120.5(2)
N7	C7	C6	113.15(15)	C28	C29	C30	118.86(19)
N7	C7	C8	120.89(16)	C29	C30	C31	120.3(2)
C8	C7	C6	125.65(17)	C26	C31	C30	121.4(2)
C7	N7	Pt1	108.80(10)	C33	C32	P1	112.57(13)
C11	N7	Pt1	129.91(12)	C34	C33	C32	119.64(18)
C11	N7	C7	119.60(14)	C38	C33	C32	121.64(17)
C7	C8	C9	119.13(17)	C38	C33	C34	118.69(18)
C10	C9	C8	119.34(17)	C35	C34	C33	120.6(2)
C9	C10	C11	119.78(17)	C36	C35	C34	120.2(2)
N7	C11	C10	120.27(16)	C35	C36	C37	119.7(2)
N7	C11	C12	118.88(15)	C36	C37	C38	120.3(2)
C10	C11	C12	120.43(16)	C33	C38	C37	120.56(19)
C13	C12	C11	120.64(16)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps34.

Atom	*x*	*y*	*z*	U(eq)
H2	2825	4101	7865	24
H4	1021	2025	6617	27
H5	1170	3723	5662	24
H8	1393	5436	4800	26
H9	2631	6761	3861	31
H10	4702	7720	4085	28
H13	5823	9155	4508	25
H14	8206	9770	4676	28
H16	8809	6846	6315	27
H17	6389	6261	6165	23
H18A	966	9062	8755	26
H18B	1691	9621	7966	26
H20	-1784	9832	9071	51
H21	-4448	10524	8796	71
H22	-4916	10604	7621	75
H23	-2741	9963	6689	76
H24	-75	9194	6958	53
H25A	386	5847	8293	29
H25B	1851	5322	8749	29
H27	1644	6575	9911	38
H28	-148	7338	10942	44
H29	-2968	7836	10949	43
H30	-3973	7479	9927	49
H31	-2176	6763	8889	42
H32A	4445	8019	8298	28
H32B	3588	7298	9016	28
H34	6524	6710	7439	33
H35	8490	4743	7214	41
H36	8399	2813	7992	46
H37	6419	2885	9032	45
H38	4477	4859	9274	37

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C25(H25A,H25B), C32(H32A,H32B)
2.b Aromatic/amide H refined with riding coordinates:
 C2(H2), C4(H4), C5(H5), C8(H8), C9(H9), C10(H10), C13(H13), C14(H14),
 C16(H16), C17(H17), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24), C27(H27),
  C28(H28), C29(H29), C30(H30), C31(H31), C34(H34), C35(H35), C36(H36),
 C37(H37), C38(H38)
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This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

ps38 complex 5

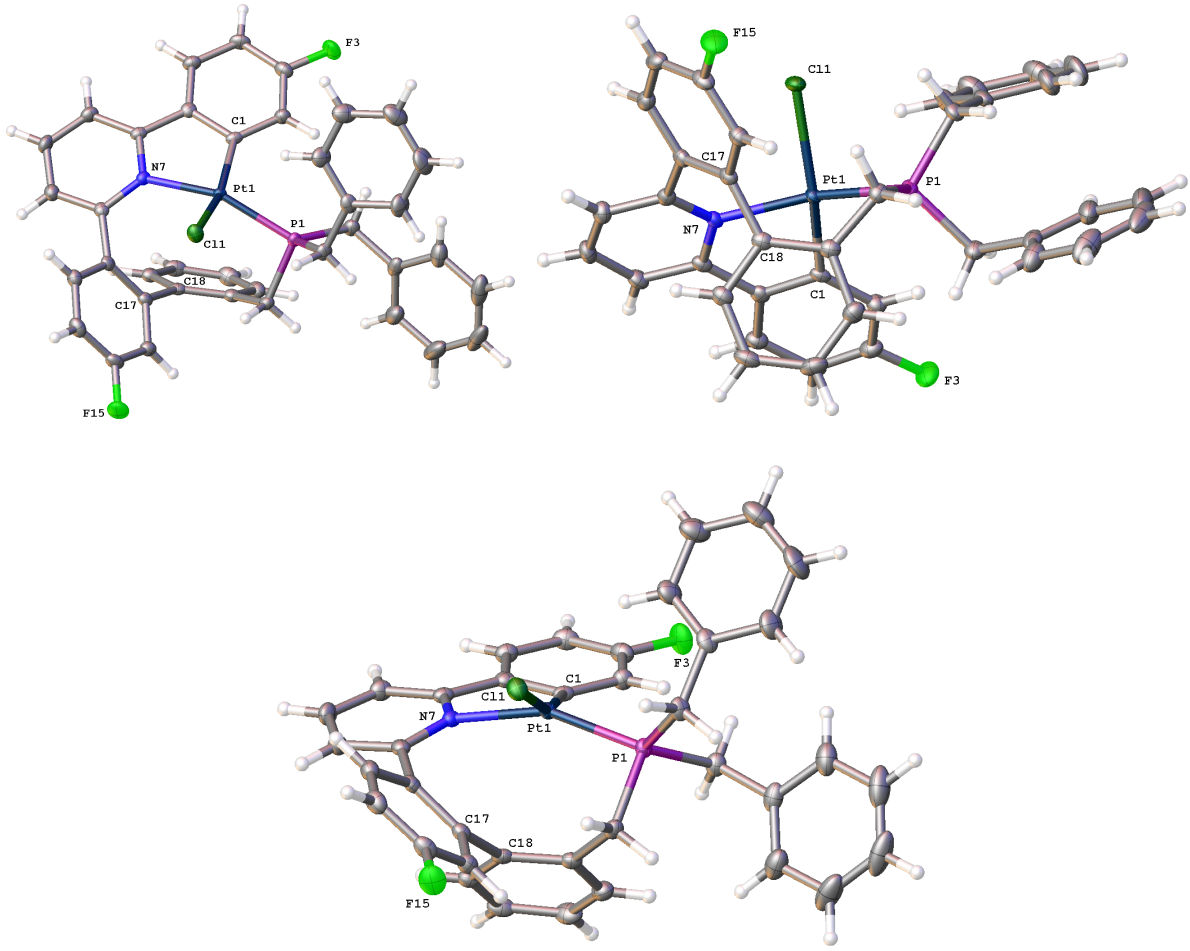

Figure SI5 *three different views of ps38 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level*

Crystal structure determination of [ps38]
The asymmetric unit contains the complex, there are two in the unit cell. Coordination at Pt is substantially distorted away from square planar, but is not tetrahedral.

As an example, see the mean plane through the coordinated atoms C1 N7 Cl1 P1 Pt1
Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

0.7440 (0.0056) x + 10.3496 (0.0021) y - 6.0824 (0.0080) z = 0.5798 (0.0057)

* 0.4432 (0.0009) C1
* -0.4646 (0.0009) N7
* 0.3526 (0.0009) Cl1
* -0.3666 (0.0009) P1
* 0.0354 (0.0006) Pt1
The coordinated atoms are far out of a mean plane

Some steric parameters describing the angle between pi systems defined by atoms used to define a mean plane and angle between this mean plane.

Mean plane C1 C2 C3 C4 C5 C6 (coordinated fluorophenyl ring) to mean plane N7 C7 C8 C9 C10 C11 (coordinated pyridine) is 8.229 (0.078) degrees

Mean plane N7 C7 C8 C9 C10 C11 (coordinated pyridine) to mean plane C12 C13 C14 C15 C16 C17 (non coordinated fluorophenyl ring) is 47.642 (0.072) degrees

Mean plane C12 C13 C14 C15 C16 C17 (non coordinated fluorophenyl ring) to mean plane C18 C19 C20 C21 C22 C23 (bonded C17-C18 to benzyl of phosphine) is 55.812 (0.072) dgrees

There is probably pi stacking between the coordinated pyridine and fluorophenyl rings related by an inversion centre

Mean plane C1 C3 C5 N7 C8 C10 to mean plane C1_$1 C3_$1 C5_$1 N7_$1 C8_$1 C10_$1 is zero degrees (as related by an inversion centre) Closest atomic contact C5 - C7_$1 3.3005 (0.0032) Agstroms

H bond between chloroform and chloride ligand
Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
1.00	2.44	3.412(3)	164.4	C39-H39...Cl1

Experimental

Single crystals of $C_{39}H_{30}Cl_4F_2NPPt$ **[ps38]** were grown from chloroform/petrol. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on a Rigaku Oxford Diffraction SuperNova diffractometer with a Duel source (Cu at zero) equipped with an AtlasS2 CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

13 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
14 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
15 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{39}H_{30}Cl_4F_2NPPt$ (M =918.50 g/mol): triclinic, space group P-1 (no. 2), a = 10.06885(9) Å, b = 10.97968(11) Å, c = 17.46056(18) Å, α = 107.6381(9)°, β = 97.2289(9)°, γ = 105.2604(8)°, V = 1729.76(3) Å^3, Z = 2, T = 150(2) K, μ(CuKα) = 11.208 mm^{-1}, *Dcalc* = 1.763 g/cm^3, 59546 reflections measured (8.664° ≤ 2Θ ≤ 147.208°), 6645 unique (R_{int} = 0.0543, R_{sigma} = 0.0224) which were used in all calculations. The final R_1 was 0.0198 (I > 2σ(I)) and wR_2 was 0.0489 (all data).

ps38

Table 1 Crystal data and structure refinement for ps38.

Identification code	ps38
Empirical formula	$C_{39}H_{30}Cl_4F_2NPPt$
Formula weight	918.50
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.06885(9)
b/Å	10.97968(11)
c/Å	17.46056(18)
α/°	107.6381(9)
β/°	97.2289(9)
γ/°	105.2604(8)
Volume/Å^3	1729.76(3)
Z	2
ϱ_{calc}g/cm^3	1.763
μ/mm^{-1}	11.208
F(000)	900.0
Crystal size/mm^3	0.18 × 0.08 × 0.04 yellow block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.664 to 147.208
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -21 ≤ l ≤ 20
Reflections collected	59546
Independent reflections	6645 [R_{int} = 0.0543, R_{sigma} = 0.0224]
Data/restraints/parameters	6645/0/433
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0198, wR_2 = 0.0488
Final R indexes [all data]	R_1 = 0.0200, wR_2 = 0.0489
Largest diff. peak/hole / e Å^{-3}	0.70/-1.03

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps38. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	5978(2)	4120(2)	6060.2(15)	14.5(5)
Cl1	2606.5(6)	4948.3(6)	7205.6(4)	19.05(12)
P1	5448.8(6)	4490.5(6)	7956.6(4)	14.61(12)
Pt1	4444.5(2)	4194.3(2)	6669.1(2)	12.23(4)
C2	7438(3)	4679(2)	6369.8(17)	18.3(5)
C3	8321(3)	4814(3)	5837.9(18)	21.1(5)
F3	9732.3(15)	5387.8(17)	6172.4(11)	29.8(4)
C4	7867(3)	4422(3)	4995.0(18)	21.3(5)
C5	6418(3)	3859(2)	4676.9(17)	19.1(5)
C6	5486(2)	3715(2)	5192.9(16)	16.1(5)
C7	3958(2)	3124(2)	4878.8(16)	15.3(5)
N7	3220(2)	3095.5(19)	5471.5(13)	13.7(4)
C8	3261(3)	2565(2)	4047.9(17)	19.8(5)
C9	1825(3)	1906(3)	3839.6(17)	21.7(5)
C10	1120(3)	1751(3)	4450.7(17)	20.6(5)
C11	1836(2)	2346(2)	5274.6(16)	15.8(5)
C12	1093(2)	2109(2)	5924.9(16)	15.8(5)
C13	-227(3)	2304(2)	5902.6(17)	19.6(5)
C14	-1003(3)	2105(3)	6480.3(18)	22.5(5)
C15	-436(3)	1703(3)	7080.8(17)	21.0(5)
F15	-1184.4(16)	1488.0(17)	7652.4(11)	30.1(4)
C16	851(3)	1474(2)	7124.2(16)	18.5(5)

C17	1639(2)	1672(2)	6542.6(16)	15.4(5)
C18	2946(2)	1260(2)	6545.1(16)	16.0(5)
C19	2977(3)	279(2)	5822.3(17)	18.6(5)
C20	4080(3)	-257(3)	5771.5(18)	23.6(6)
C21	5163(3)	176(3)	6460(2)	26.5(6)
C22	5152(3)	1150(3)	7177.6(18)	22.2(5)
C23	4071(2)	1738(2)	7239.9(16)	17.0(5)
C24	4247(2)	2932(2)	8014.9(16)	17.2(5)
C25	7266(3)	4477(3)	8276.9(17)	20.3(5)
C26	7680(3)	4530(3)	9154.3(18)	23.7(6)
C27	7308(3)	3399(4)	9378(2)	33.7(7)
C28	7686(3)	3488(5)	10192(2)	46.1(9)
C29	8455(3)	4716(5)	10795(2)	48.3(10)
C30	8859(4)	5837(4)	10576(2)	45.2(9)
C31	8486(3)	5750(3)	9763(2)	33.4(7)
C32	5300(3)	5877(3)	8810.6(16)	20.1(5)
C33	6211(3)	7255(3)	8863.1(17)	20.9(5)
C34	7123(3)	8155(3)	9603(2)	32.1(7)
C35	7966(4)	9415(3)	9654(2)	41.1(8)
C36	7904(3)	9807(3)	8972(2)	37.7(7)
C37	6989(3)	8933(3)	8240(2)	33.8(7)
C38	6149(3)	7673(3)	8186.4(19)	27.5(6)
C39	1940(4)	7945(3)	7837(2)	36.6(7)
Cl2	2012.5(9)	8342.5(8)	6942.3(5)	43.49(19)
Cl3	3366(1)	9076.1(16)	8636.5(7)	73.4(4)
Cl4	328.5(9)	7956.2(10)	8129.2(6)	48.1(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps38. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	21.3(11)	12.3(10)	13.7(13)	5.4(9)	8.9(10)	8.3(9)
Cl1	17.2(2)	19.2(3)	19.4(3)	1.7(2)	6.4(2)	8.6(2)
P1	14.8(3)	16.9(3)	11.1(3)	3.4(2)	3.6(2)	4.8(2)
Pt1	13.31(6)	12.24(6)	10.89(6)	2.94(4)	4.56(4)	4.13(4)
C2	18.7(11)	20.4(12)	16.5(14)	6.4(10)	6.6(10)	6.2(9)
C3	17.2(11)	19.7(12)	28.0(16)	9.0(11)	8.6(11)	6.2(10)
F3	14.4(7)	41.3(9)	29.6(10)	9.9(8)	8.2(7)	3.7(6)
C4	23.9(12)	20.9(12)	24.3(15)	8.5(11)	15.7(11)	10.2(10)
C5	23.6(12)	19.6(12)	17.7(14)	7.7(10)	9.4(10)	9.1(10)
C6	19.7(11)	11.3(10)	17.4(13)	4.4(9)	4.3(10)	6.2(9)
C7	21.8(12)	12.5(10)	14.5(13)	5.7(9)	7.3(10)	7.4(9)
N7	17.2(9)	11.4(9)	12.0(11)	3.0(8)	3.4(8)	4.8(7)
C8	25.8(12)	19.8(12)	14.8(13)	5.5(10)	7.6(10)	8.5(10)
C9	26.4(13)	22.1(12)	12.4(13)	3.3(10)	0(1)	6.1(10)
C10	19.8(12)	19.0(12)	19.6(14)	6.1(10)	1.3(10)	3(1)
C11	17.0(11)	12(1)	18.4(13)	5.1(9)	3.1(10)	5.2(9)
C12	16.3(11)	11.8(10)	14.6(13)	1.1(9)	3.0(9)	1.1(9)
C13	17.7(11)	17.8(11)	20.1(14)	4.1(10)	1.2(10)	4.8(9)
C14	15.6(11)	21.1(12)	27.2(16)	3.3(11)	5.1(11)	6(1)
C15	20.0(12)	19.7(12)	20.0(14)	3.4(10)	10.5(10)	2.1(10)
F15	24.2(8)	40.6(9)	27.4(10)	12.0(8)	16.1(7)	8.5(7)
C16	20.1(11)	16.9(11)	16.7(13)	4.6(10)	6(1)	3.9(9)
C17	15.9(11)	12.7(10)	15.1(13)	2.7(9)	4.5(9)	2.5(9)
C18	19.2(11)	12.9(10)	18.5(13)	7.9(10)	7.9(10)	5.1(9)
C19	22.3(12)	14.3(11)	19.6(14)	6.4(10)	7.2(10)	4.6(9)
C20	32.0(14)	16.5(12)	25.7(16)	6.3(11)	15.8(12)	10.2(10)
C21	23.8(13)	22.9(13)	39.1(18)	12.4(12)	12.2(12)	13.2(11)
C22	21.0(12)	21.0(12)	27.2(15)	11.3(11)	4.9(11)	7.8(10)
C23	18.9(11)	14.4(11)	19.7(14)	8(1)	7.5(10)	5.0(9)
C24	17.6(11)	20.2(12)	15.6(13)	8.5(10)	5.3(10)	5.8(9)
C25	17.6(11)	26.0(13)	18.2(14)	7.1(11)	6.7(10)	7.7(10)
C26	16.1(11)	39.6(15)	17.5(15)	9.1(12)	6.3(10)	12.4(11)
C27	24.5(14)	50.7(19)	29.4(18)	20.2(15)	5.2(12)	10.7(13)
C28	32.2(16)	85(3)	39(2)	42(2)	13.2(15)	21.0(18)
C29	31.8(16)	103(3)	21.8(18)	27(2)	11.4(14)	31.3(19)
C30	32.7(16)	70(2)	21.8(18)	-2.2(16)	-0.6(14)	23.2(17)
C31	25.5(14)	44.5(17)	24.3(17)	3.2(13)	1.3(12)	13.9(13)
C32	22.1(12)	22.6(12)	13.3(13)	2(1)	5.9(10)	7.3(10)
C33	20.7(12)	20.1(12)	17.3(14)	-1.3(10)	6(1)	7.6(10)
C34	36.3(15)	30.1(15)	19.0(16)	-2.0(12)	1.9(13)	7.5(12)
C35	38.3(17)	29.3(16)	32.2(19)	-8.7(14)	0.9(15)	-1.2(13)
C36	38.4(17)	22.8(14)	41(2)	1.5(13)	14.6(15)	1.1(12)
C37	45.8(17)	22.6(14)	30.7(18)	5.9(12)	15.2(14)	8.0(13)
C38	34.5(15)	20.8(13)	20.2(15)	0.5(11)	5.1(12)	5.8(11)
C39	57(2)	34.6(16)	35.3(19)	17.6(14)	24.5(16)	28.9(15)
Cl2	58.5(5)	35.7(4)	31.9(4)	17.3(3)	11.6(4)	1.0(3)
Cl3	42.4(5)	141.4(11)	39.8(6)	30.2(7)	9.4(4)	36.7(6)

Cl4	45.6(4)	57.7(5)	32.2(5)	5.9(4)	15.0(4)	10.7(4)

Table 4 Bond Lengths for ps38.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Pt1	1.987(2)	C15	C16	1.381(4)
C1	C2	1.398(3)	C16	C17	1.398(4)
C1	C6	1.423(4)	C17	C18	1.499(3)
Cl1	Pt1	2.4001(6)	C18	C19	1.400(4)
P1	Pt1	2.2346(6)	C18	C23	1.410(4)
P1	C24	1.857(2)	C19	C20	1.387(4)
P1	C25	1.850(2)	C20	C21	1.383(4)
P1	C32	1.834(3)	C21	C22	1.383(4)
Pt1	N7	2.095(2)	C22	C23	1.403(3)
C2	C3	1.377(4)	C23	C24	1.524(4)
C3	F3	1.362(3)	C25	C26	1.516(4)
C3	C4	1.380(4)	C26	C27	1.386(4)
C4	C5	1.390(4)	C26	C31	1.389(4)
C5	C6	1.392(4)	C27	C28	1.391(4)
C6	C7	1.462(3)	C28	C29	1.382(6)
C7	N7	1.351(3)	C29	C30	1.373(6)
C7	C8	1.397(4)	C30	C31	1.390(5)
N7	C11	1.357(3)	C32	C33	1.517(4)
C8	C9	1.380(4)	C33	C34	1.392(4)
C9	C10	1.381(4)	C33	C38	1.391(4)
C10	C11	1.392(4)	C34	C35	1.390(5)
C11	C12	1.485(4)	C35	C36	1.384(5)
C12	C13	1.398(3)	C36	C37	1.377(5)
C12	C17	1.413(3)	C37	C38	1.386(4)
C13	C14	1.385(4)	C39	Cl2	1.750(3)
C14	C15	1.372(4)	C39	Cl3	1.749(4)
C15	F15	1.363(3)	C39	Cl4	1.763(3)

Table 5 Bond Angles for ps38.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	Pt1	128.52(19)	C15	C14	C13	117.7(2)
C2	C1	C6	116.9(2)	C14	C15	C16	123.0(3)
C6	C1	Pt1	112.89(17)	F15	C15	C14	118.9(2)
C24	P1	Pt1	96.81(8)	F15	C15	C16	118.0(2)
C25	P1	Pt1	124.07(9)	C15	C16	C17	119.5(2)
C25	P1	C24	106.25(11)	C12	C17	C18	122.8(2)
C32	P1	Pt1	118.76(9)	C16	C17	C12	118.8(2)
C32	P1	C24	105.32(12)	C16	C17	C18	118.1(2)
C32	P1	C25	103.28(12)	C19	C18	C17	116.5(2)
C1	Pt1	Cl1	158.48(6)	C19	C18	C23	119.5(2)
C1	Pt1	P1	104.44(7)	C23	C18	C17	123.8(2)
C1	Pt1	N7	80.56(9)	C20	C19	C18	121.8(2)
P1	Pt1	Cl1	87.97(2)	C21	C20	C19	118.9(3)
N7	Pt1	Cl1	95.35(6)	C22	C21	C20	120.0(2)
N7	Pt1	P1	155.83(5)	C21	C22	C23	122.4(3)
C3	C2	C1	119.7(2)	C18	C23	C24	123.9(2)
C2	C3	C4	124.3(2)	C22	C23	C18	117.3(2)
F3	C3	C2	117.4(2)	C22	C23	C24	118.5(2)
F3	C3	C4	118.2(2)	C23	C24	P1	109.74(17)
C3	C4	C5	116.7(2)	C26	C25	P1	115.50(18)
C4	C5	C6	120.9(2)	C27	C26	C25	122.7(3)
C1	C6	C7	116.2(2)	C27	C26	C31	118.0(3)
C5	C6	C1	121.5(2)	C31	C26	C25	119.3(3)
C5	C6	C7	122.4(2)	C26	C27	C28	121.2(3)
N7	C7	C6	114.0(2)	C29	C28	C27	120.1(3)
N7	C7	C8	120.3(2)	C30	C29	C28	119.2(3)
C8	C7	C6	125.6(2)	C29	C30	C31	120.8(4)
C7	N7	Pt1	113.59(15)	C26	C31	C30	120.7(3)
C7	N7	C11	120.7(2)	C33	C32	P1	113.25(19)
C11	N7	Pt1	125.57(17)	C34	C33	C32	120.5(3)
C9	C8	C7	119.1(2)	C38	C33	C32	121.7(2)
C8	C9	C10	119.5(2)	C38	C33	C34	117.8(3)
C9	C10	C11	120.0(2)	C35	C34	C33	120.8(3)
N7	C11	C10	119.5(2)	C36	C35	C34	120.5(3)
N7	C11	C12	120.8(2)	C37	C36	C35	119.1(3)
C10	C11	C12	119.7(2)	C36	C37	C38	120.5(3)
C13	C12	C11	117.3(2)	C37	C38	C33	121.2(3)
C13	C12	C17	119.3(2)	Cl2	C39	Cl4	111.07(18)
C17	C12	C11	123.3(2)	Cl3	C39	Cl2	110.05(19)
C14	C13	C12	121.7(2)	Cl3	C39	Cl4	110.55(19)

Table 6 Hydrogen Bonds for ps38.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C39	H39	Cl1	1.00	2.44	3.412(3)	164.4

Table 7 Torsion Angles for ps38.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	F3	178.8(2)	C12	C17	C18	C23	131.0(3)
C1	C2	C3	C4	-0.3(4)	C13	C12	C17	C16	-1.2(4)
C1	C6	C7	N7	2.5(3)	C13	C12	C17	C18	171.5(2)
C1	C6	C7	C8	-174.7(2)	C13	C14	C15	F15	-179.4(2)
P1	C25	C26	C27	81.2(3)	C13	C14	C15	C16	-0.9(4)
P1	C25	C26	C31	-100.0(3)	C14	C15	C16	C17	0.9(4)
P1	C32	C33	C34	-128.7(2)	C15	C16	C17	C12	0.2(4)
P1	C32	C33	C38	52.6(3)	C15	C16	C17	C18	-172.9(2)
Pt1	C1	C2	C3	-163.91(19)	F15	C15	C16	C17	179.4(2)
Pt1	C1	C6	C5	166.94(18)	C16	C17	C18	C19	119.7(3)
Pt1	C1	C6	C7	-14.0(2)	C16	C17	C18	C23	-56.2(3)
Pt1	P1	C24	C23	47.00(16)	C17	C12	C13	C14	1.2(4)
Pt1	P1	C25	C26	-172.99(16)	C17	C18	C19	C20	-175.1(2)
Pt1	P1	C32	C33	-72.74(19)	C17	C18	C23	C22	173.0(2)
Pt1	N7	C11	C10	174.94(16)	C17	C18	C23	C24	-12.9(4)
Pt1	N7	C11	C12	-7.4(3)	C18	C19	C20	C21	1.2(4)
C2	C1	C6	C5	0.5(3)	C18	C23	C24	P1	-95.4(2)
C2	C1	C6	C7	179.6(2)	C19	C18	C23	C22	-2.7(3)
C2	C3	C4	C5	0.1(4)	C19	C18	C23	C24	171.4(2)
C3	C4	C5	C6	0.5(4)	C19	C20	C21	C22	-1.5(4)
F3	C3	C4	C5	-179.0(2)	C20	C21	C22	C23	-0.3(4)
C4	C5	C6	C1	-0.8(4)	C21	C22	C23	C18	2.4(4)
C4	C5	C6	C7	-179.8(2)	C21	C22	C23	C24	-172.0(2)
C5	C6	C7	N7	-178.5(2)	C22	C23	C24	P1	78.6(2)
C5	C6	C7	C8	4.3(4)	C23	C18	C19	C20	1.0(4)
C6	C1	C2	C3	0.0(3)	C24	P1	C25	C26	-62.7(2)
C6	C7	N7	Pt1	9.8(2)	C24	P1	C32	C33	-179.64(18)
C6	C7	N7	C11	-166.77(19)	C25	P1	C24	C23	-81.50(18)
C6	C7	C8	C9	172.7(2)	C25	P1	C32	C33	69.1(2)
C7	N7	C11	C10	-9.0(3)	C25	C26	C27	C28	-179.0(3)
C7	N7	C11	C12	168.7(2)	C25	C26	C31	C30	178.7(3)
C7	C8	C9	C10	-3.3(4)	C26	C27	C28	C29	-0.4(5)
N7	C7	C8	C9	-4.3(3)	C27	C26	C31	C30	-2.4(4)
N7	C11	C12	C13	132.7(2)	C27	C28	C29	C30	-1.1(5)
N7	C11	C12	C17	-48.8(3)	C28	C29	C30	C31	0.9(5)
C8	C7	N7	Pt1	-172.95(17)	C29	C30	C31	C26	0.9(5)
C8	C7	N7	C11	10.5(3)	C31	C26	C27	C28	2.2(4)
C8	C9	C10	C11	4.8(4)	C32	P1	C24	C23	169.35(16)
C9	C10	C11	N7	1.2(4)	C32	P1	C25	C26	47.9(2)
C9	C10	C11	C12	-176.4(2)	C32	C33	C34	C35	179.6(3)
C10	C11	C12	C13	-49.7(3)	C32	C33	C38	C37	-179.8(3)
C10	C11	C12	C17	128.8(3)	C33	C34	C35	C36	0.8(5)
C11	C12	C13	C14	179.8(2)	C34	C33	C38	C37	1.4(4)
C11	C12	C17	C16	-179.7(2)	C34	C35	C36	C37	0.3(5)
C11	C12	C17	C18	-6.9(4)	C35	C36	C37	C38	-0.4(5)
C12	C13	C14	C15	-0.2(4)	C36	C37	C38	C33	-0.4(5)
C12	C17	C18	C19	-53.1(3)	C38	C33	C34	C35	-1.6(4)

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps38.

Atom	*x*	*y*	*z*	U(eq)
H2	7820	4965	6945	22
H4	8512	4532	4649	26
H5	6059	3569	4099	23
H8	3769	2637	3632	24
H9	1325	1560	3280	26
H10	146	1240	4309	25
H13	-600	2581	5481	24
H14	-1898	2243	6461	27
H16	1199	1183	7546	22
H19	2222	-28	5353	22
H20	4091	-910	5272	28
H21	5915	-197	6441	32
H22	5903	1432	7645	27
H24A	4641	2763	8507	21
H24B	3314	3044	8067	21
H25A	7375	3650	7899	24
H25B	7935	5258	8209	24
H27	6785	2549	8969	40
H28	7416	2702	10335	55
H29	8701	4784	11353	58
H30	9399	6682	10985	54
H31	8786	6533	9621	40
H32A	4302	5853	8743	24
H32B	5576	5741	9335	24
H34	7169	7904	10078	39

H35	8591	10013	10162	49
H36	8484	10667	9007	45
H37	6934	9194	7769	41
H38	5519	7085	7678	33
H39	2011	7018	7722	44

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2.a Ternary CH refined with riding coordinates:
 C39(H39)
2.b Secondary CH2 refined with riding coordinates:
 C24(H24A,H24B), C25(H25A,H25B), C32(H32A,H32B)
2.c Aromatic/amide H refined with riding coordinates:
 C2(H2), C4(H4), C5(H5), C8(H8), C9(H9), C10(H10), C13(H13), C14(H14),
 C16(H16), C19(H19), C20(H20), C21(H21), C22(H22), C27(H27), C28(H28), C29(H29),
  C30(H30), C31(H31), C34(H34), C35(H35), C36(H36), C37(H37), C38(H38)
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This report has been created with Olex2, compiled on 2016.02.16 svn.r3265 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

ps39 Complex 6

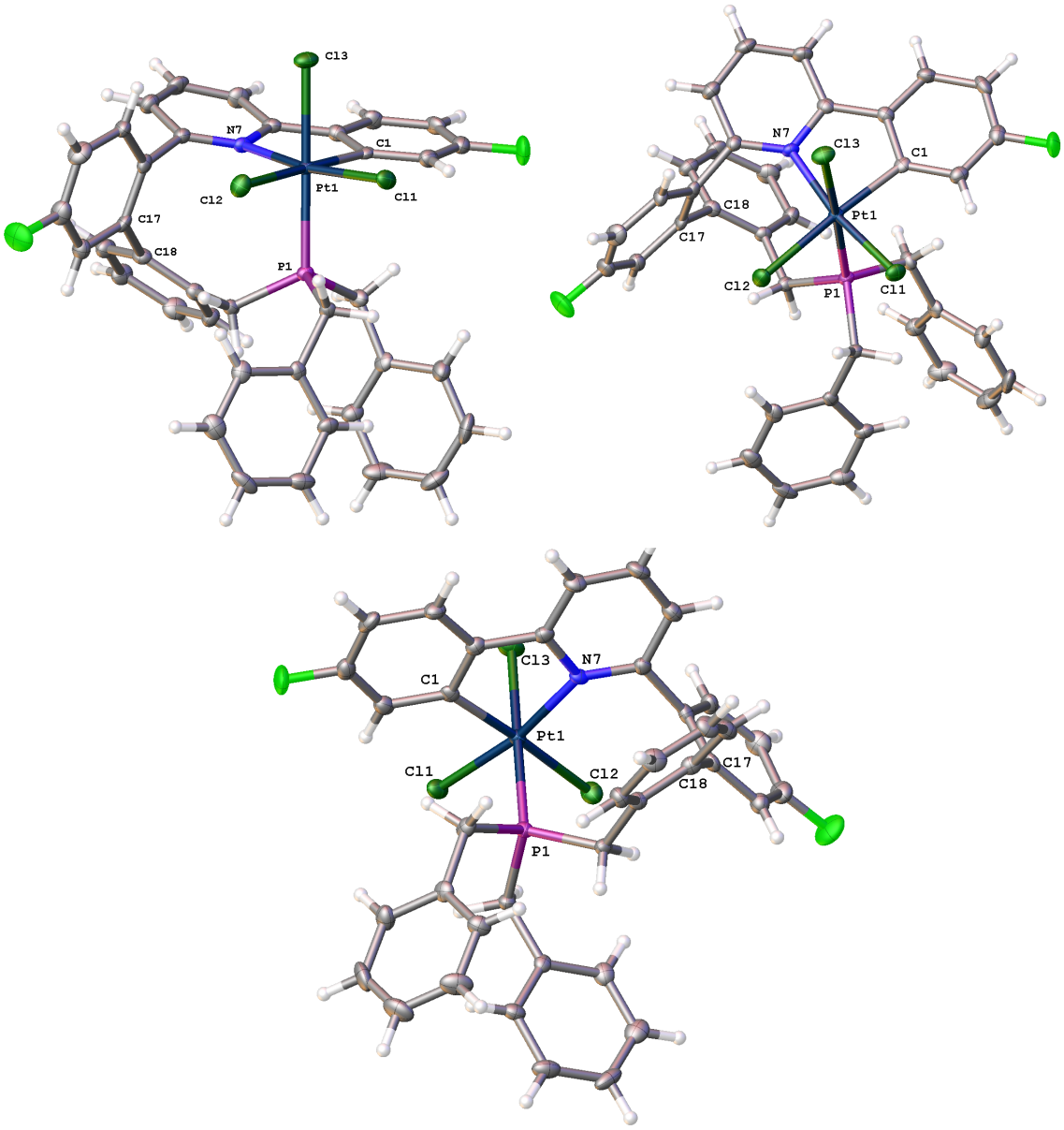

Figure SI6 *Three different views of ps39 with only selected atoms labeled and thermal ellipsoids drawn at 50% probability level*

Crystal structure determination of [ps39]

The asymmetric unit contains the complex and a molecule of chloroform, there are four times this in the unit cell.
No intra or inter molecular pi stacking. The CH of the chloroform has some reasonably short contacts with the chloro ligands of the complex tabulated below.

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
1.00	2.94	3.729(3)	136.5	C39-H39...Cl1
1.00	3.04	3.800(3)	133.8	C39-H39...Cl2
1.00	2.69	3.544(3)	143.2	C39-H39...Cl3

Interesting things

The coordination environment
Mean plane through the Pt bound atoms Cl1 Cl2 Pt1 C1 N7
* -0.0666 (0.0007) Cl1
* 0.0357 (0.0007) Cl2
* 0.0493 (0.0006) Pt1
* 0.0528 (0.0009) C1
* -0.0712 (0.0007) N7
Rms deviation of fitted atoms = 0.0566

The RMS deviation is much larger than for one of the flat aromatic rings so most atoms a bit out of mean plane?

Not sure how this compares the atoms in a Pt chelated plane that don't have all these steric clashes?

Angle between the mean plane of the coordinated atoms Cl1 Cl2 Pt1 C1 N7 to a mean plane through the pyridine ring C7 N7 C8 C9 C10 C11 is 16.530 (0.074) degrees as measure of the tilt of the coordinated pyridine to the chelate plane.

Angles in the ligand
Angle between mean plane through the coordinated fluorophenyl ring C1 C2 C3 C4 C5 C6 to the coordinated pyridine ring C7 N7 C8 C9 C10 C11 is 10.769 (0.097) degrees

Angle between coordinated pyridine C7 N7 C8 C9 C10 C11 and free fluorophenyl ring C12 C13 C14 C15 C16 C17 is 84.126 (0.069) degrees

Angle between free fluorophenyl ring C12 C13 C14 C15 C16 C17 and benzyl aromatic C18 C19 C20 C21 C22 C23 of tribenzylphosphine joined by C17- C18 bond is 88.849 (0.059) degrees

Experimental
Single crystals of $C_{39}H_{30}Cl_6F_2NPPt$ **[ps39]** were grown from chloroform. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on a Rigaku Oxford Diffraction SuperNova diffractometer with a duel source (Cu at zero) equipped with an AtlasS2 CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.
16 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
17 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
18 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{39}H_{30}Cl_6F_2NPPt$ (M =989.40 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.49295(19) Å, b = 22.2749(4) Å, c = 14.2990(2) Å, β = 91.1028(14)°, V = 3659.93(10) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 4.357 mm^{-1}, $Dcalc$ = 1.796 g/cm^3, 104681 reflections measured (4.504° ≤ 2Θ ≤ 63.73°), 11956 unique (R_{int} = 0.0546, R_{sigma} = 0.0334) which were used in all calculations. The final R_1 was 0.0255 (I > 2σ(I)) and wR_2 was 0.0519 (all data).

Table 1 Crystal data and structure refinement for ps39.

Identification code	ps39
Empirical formula	$C_{39}H_{30}Cl_6F_2NPPt$
Formula weight	989.40
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.49295(19)
b/Å	22.2749(4)
c/Å	14.2990(2)
α/°	90
β/°	91.1028(14)
γ/°	90
Volume/Å^3	3659.93(10)
Z	4
ϱ_{calc}g/cm^3	1.796
μ/mm^{-1}	4.357
F(000)	1936.0
Crystal size/mm^3	0.2 × 0.1 × 0.06 colourless block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.504 to 63.73
Index ranges	-17 ≤ h ≤ 16, -32 ≤ k ≤ 31, -20 ≤ l ≤ 20
Reflections collected	104681
Independent reflections	11956 [R_{int} = 0.0546, R_{sigma} = 0.0334]
Data/restraints/parameters	11956/0/451
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0255, wR_2 = 0.0490
Final R indexes [all data]	R_1 = 0.0352, wR_2 = 0.0519
Largest diff. peak/hole / e Å^{-3}	1.46/-0.92

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps39. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	7372.0(2)	7713.3(2)	8952.2(2)	13.39(2)
Cl1	6044.5(5)	7196.5(2)	9834.2(4)	21.06(11)
P1	7304.1(5)	8466.6(2)	10066.4(4)	13.5(1)
Cl3	7475.5(5)	6884.6(2)	7898.8(4)	24.27(11)
Cl2	8826.6(5)	7272.4(3)	9984.9(4)	22.41(11)
Cl4	6892.0(7)	5641.3(3)	10692.4(5)	40.55(16)
Cl5	6795.5(8)	5285.5(4)	8749.6(6)	51.1(2)
Cl6	9003.0(6)	5501.7(4)	9662.0(6)	49.8(2)
N7	8386.0(15)	8147.8(8)	7943.7(11)	14.9(3)
F15	13037.9(14)	7755.8(7)	10556.4(11)	38.3(4)
F3	2973.2(12)	8196.8(7)	7745.1(10)	33.5(3)
C1	6070.0(18)	8054.5(9)	8132.5(13)	14.8(4)
C7	7719.7(19)	8370.7(10)	7222.5(14)	16.3(4)
C6	6463.7(19)	8352.9(10)	7340.7(14)	17.1(4)
C11	9559.0(18)	8117.5(10)	7846.6(14)	17.0(4)

C2	4882.4(19)	7994.6(10)	8267.7(15)	19.5(4)
C8	8224(2)	8575.4(10)	6402.5(15)	21.0(4)
C25	7058.5(19)	8146.9(10)	11241.3(13)	16.9(4)
C32	6117.6(19)	8994.3(10)	9805.4(15)	19.7(4)
C24	8641.4(18)	8896.7(10)	10231.2(14)	16.3(4)
C12	10379.4(18)	7985.2(10)	8638.4(14)	16.9(4)
C39	7538(2)	5720.2(12)	9588.4(17)	29.0(5)
C17	10714.6(18)	8462.2(10)	9214.6(15)	17.7(4)
C28	9299(2)	8597.1(11)	13103.4(16)	27.2(5)
C13	10952(2)	7433.9(11)	8708.0(16)	21.7(5)
C26	7627.2(19)	8462.6(10)	12067.8(14)	17.3(4)
C3	4135.5(19)	8246.2(11)	7612.9(16)	21.8(5)
C22	8704(2)	9816.6(10)	9188.9(15)	19.5(4)
C31	7008(2)	8857.6(10)	12627.0(14)	20.1(4)
C23	9164.6(18)	9259.2(9)	9448.2(14)	15.3(4)
C5	5671(2)	8597.4(11)	6695.0(15)	22.0(5)
C30	7527(2)	9121.6(11)	13411.7(15)	26.1(5)
C18	10197.7(18)	9068.5(9)	9036.8(14)	16.2(4)
C29	8674(2)	8993.7(11)	13646.5(16)	28.1(5)
C27	8777(2)	8331.5(10)	12322.5(15)	21.2(5)
C4	4488(2)	8545.6(11)	6833.2(16)	23.7(5)
C10	10063(2)	8280.9(11)	7010.1(15)	21.2(5)
C21	9248(2)	10177.4(10)	8538.0(16)	22.8(5)
C34	6135(2)	9850.1(10)	10979.1(15)	21.9(5)
C15	12140(2)	7826.4(12)	9934.1(17)	25.6(5)
C33	5626.9(19)	9328.1(10)	10622.2(15)	18.5(4)
C14	11845(2)	7354.6(11)	9361.2(17)	25.5(5)
C16	11603(2)	8379.7(11)	9886.4(16)	22.4(5)
C35	5650(2)	10147.1(11)	11726.2(17)	30.2(6)
C9	9396(2)	8515.4(11)	6285.4(15)	23.7(5)
C20	10281(2)	9992.1(11)	8146.9(16)	23.8(5)
C19	10747(2)	9443.2(10)	8395.4(15)	21.3(5)
C38	4618(2)	9115.4(11)	11035.0(17)	25.5(5)
C36	4646(2)	9930.0(12)	12130.9(18)	33.3(6)
C37	4131(2)	9414.9(13)	11787.1(19)	33.2(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps39. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	15.45(4)	11.92(4)	12.86(4)	0.15(3)	1.52(3)	-0.51(3)
Cl1	24.8(3)	20.1(3)	18.4(2)	1.15(19)	3.5(2)	-7.5(2)
P1	15.1(2)	12.6(2)	12.8(2)	0.53(18)	1.20(18)	0.1(2)
Cl3	35.3(3)	16.5(2)	21.1(2)	-4.4(2)	5.4(2)	-1.0(2)
Cl2	22.2(3)	23.3(3)	21.8(2)	6.9(2)	1.0(2)	5.3(2)
Cl4	43.7(4)	37.3(4)	41.0(4)	6.0(3)	9.9(3)	6.4(3)
Cl5	54.4(5)	49.9(5)	48.1(4)	-7.1(4)	-17.9(4)	-5.2(4)
Cl6	31.8(4)	66.5(5)	51.0(4)	-16.6(4)	-2.2(3)	16.9(4)
N7	17.0(8)	13.0(8)	14.8(8)	-0.8(6)	3.2(6)	-0.9(7)
F15	34.5(9)	38.2(10)	41.4(9)	3.2(7)	-18.4(7)	11.4(7)
F3	14.5(7)	47.6(10)	38.2(8)	2.1(7)	-2.7(6)	0.0(7)
C1	17.3(10)	13.5(10)	13.6(9)	-1.8(7)	-0.2(7)	-0.9(8)
C7	18.7(10)	15.7(10)	14.4(9)	-1.6(8)	0.3(8)	-0.5(8)
C6	19.4(10)	15.7(10)	16.1(9)	-1.4(8)	-0.4(8)	0.9(8)
C11	17.5(10)	15.3(10)	18.1(9)	-3.4(8)	1.3(8)	0.3(8)
C2	18.1(10)	19.7(11)	20.9(10)	-2.7(8)	0.9(8)	-2.5(9)
C8	26.9(12)	21.0(11)	15.2(9)	2.7(8)	1.4(8)	0.8(9)
C25	20.4(10)	17.4(10)	13.0(9)	1.1(8)	1.4(8)	-0.9(8)
C32	20.1(11)	18.9(11)	19.9(10)	-2.4(8)	-3.0(8)	3.6(9)
C24	18.1(10)	15.3(10)	15.7(9)	0.0(8)	0.5(8)	-2.8(8)
C12	13.3(9)	18.5(11)	19.1(10)	1.2(8)	4.1(8)	0.6(8)
C39	29.3(13)	28.0(13)	29.6(12)	1.3(10)	-3.1(10)	4.9(11)
C17	15.4(10)	19.1(11)	18.6(10)	1.0(8)	3.0(8)	1.7(8)
C28	27.3(12)	28.5(13)	25.5(11)	13(1)	-6.5(10)	-4.6(10)
C13	19.8(11)	19.5(11)	25.8(11)	-2.1(9)	4.0(9)	3.5(9)
C26	21.1(11)	16.3(10)	14.6(9)	5.0(8)	0.6(8)	-1.2(8)
C3	14.9(10)	24.9(12)	25.5(11)	-7.9(9)	-1.7(8)	-1.8(9)
C22	21.7(11)	17.4(11)	19.4(10)	-0.3(8)	2.3(8)	0.8(9)
C31	25.4(11)	18.1(11)	16.9(10)	2.0(8)	3.1(8)	-0.6(9)
C23	17(1)	13.4(10)	15.4(9)	0.6(7)	-1.6(7)	-3.0(8)
C5	24.0(11)	26.3(12)	15.8(10)	-0.2(9)	-1.5(8)	2.4(9)
C30	40.6(14)	20.0(12)	17.8(10)	-1.2(9)	3.4(10)	-3.4(10)
C18	17.9(10)	14.6(10)	15.9(9)	0.1(8)	-1.4(8)	-0.6(8)
C29	40.4(15)	26.6(13)	17(1)	4.6(9)	-9(1)	-11.6(11)
C27	23.3(11)	19.4(11)	20.8(10)	7.4(8)	0.7(9)	1.7(9)
C4	21.7(11)	26.2(12)	23.0(11)	-5.2(9)	-6.9(9)	4.3(10)
C10	18(1)	26.0(12)	19.8(10)	-2.0(9)	4.7(8)	0.7(9)
C21	28.9(12)	15.7(11)	23.7(11)	4.8(9)	-0.1(9)	-0.3(9)

C34	26.2(12)	17.7(11)	21.9(10)	2.4(9)	3.4(9)	1.8(9)
C15	19.9(11)	32.0(14)	24.6(11)	3.4(10)	-4.4(9)	6.5(10)
C33	17.6(10)	18.0(11)	19.7(10)	0.5(8)	-2.3(8)	6.2(8)
C14	24.2(12)	21.3(12)	30.9(12)	3.6(9)	1.2(10)	8.7(9)
C16	22.4(11)	23.4(12)	21.3(10)	-0.2(9)	-2.0(9)	1.3(9)
C35	47.0(16)	17.8(12)	25.7(12)	-3.6(9)	2.3(11)	4.5(11)
C9	27.3(12)	27.7(12)	16.4(10)	0.2(9)	8.4(9)	-0.9(10)
C20	30.0(13)	21.3(12)	20.3(10)	3.9(9)	4.0(9)	-7.1(10)
C19	20.9(11)	22.7(12)	20.4(10)	-0.5(9)	4.5(8)	-3.3(9)
C38	18.5(11)	24.5(12)	33.6(13)	-0.9(10)	0.8(9)	2.4(9)
C36	42.8(16)	31.2(14)	26.4(12)	0.7(10)	11.7(11)	17.9(12)
C37	24.8(13)	37.6(15)	37.7(14)	6.5(12)	11.1(11)	7.9(11)

Table 4 Bond Lengths for ps39.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	Cl1	2.3060(5)	C12	C17	1.394(3)
Pt1	P1	2.3162(5)	C12	C13	1.396(3)
Pt1	Cl3	2.3870(5)	C17	C18	1.495(3)
Pt1	Cl2	2.4175(5)	C17	C16	1.401(3)
Pt1	N7	2.1070(16)	C28	C29	1.386(4)
Pt1	C1	2.031(2)	C28	C27	1.390(3)
P1	C25	1.851(2)	C13	C14	1.385(3)
P1	C32	1.833(2)	C26	C31	1.394(3)
P1	C24	1.823(2)	C26	C27	1.395(3)
Cl4	C39	1.766(3)	C3	C4	1.367(3)
Cl5	C39	1.751(3)	C22	C23	1.397(3)
Cl6	C39	1.753(3)	C22	C21	1.388(3)
N7	C7	1.366(3)	C31	C30	1.391(3)
N7	C11	1.360(3)	C23	C18	1.401(3)
F15	C15	1.358(3)	C5	C4	1.383(3)
F3	C3	1.357(3)	C30	C29	1.384(4)
C1	C6	1.396(3)	C18	C19	1.400(3)
C1	C2	1.389(3)	C10	C9	1.379(3)
C7	C6	1.457(3)	C21	C20	1.386(3)
C7	C8	1.395(3)	C34	C33	1.393(3)
C6	C5	1.395(3)	C34	C35	1.383(3)
C11	C12	1.489(3)	C15	C14	1.371(4)
C11	C10	1.388(3)	C15	C16	1.379(3)
C2	C3	1.377(3)	C33	C38	1.394(3)
C8	C9	1.367(3)	C35	C36	1.388(4)
C25	C26	1.513(3)	C20	C19	1.378(3)
C32	C33	1.503(3)	C38	C37	1.392(3)
C24	C23	1.514(3)	C36	C37	1.377(4)

Table 5 Bond Angles for ps39.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Pt1	P1	87.370(19)	Cl5	C39	Cl6	110.03(14)
Cl1	Pt1	Cl3	90.032(19)	Cl6	C39	Cl4	109.78(14)
Cl1	Pt1	Cl2	85.42(2)	C12	C17	C18	118.92(19)
P1	Pt1	Cl3	175.622(19)	C12	C17	C16	119.7(2)
P1	Pt1	Cl2	84.619(19)	C16	C17	C18	121.1(2)
Cl3	Pt1	Cl2	91.66(2)	C29	C28	C27	120.1(2)
N7	Pt1	Cl1	169.78(5)	C14	C13	C12	120.2(2)
N7	Pt1	P1	99.46(5)	C31	C26	C25	121.6(2)
N7	Pt1	Cl3	83.59(5)	C31	C26	C27	118.3(2)
N7	Pt1	Cl2	102.69(5)	C27	C26	C25	120.0(2)
C1	Pt1	Cl1	90.83(6)	F3	C3	C2	118.3(2)
C1	Pt1	P1	95.26(6)	F3	C3	C4	117.5(2)
C1	Pt1	Cl3	88.30(6)	C4	C3	C2	124.2(2)
C1	Pt1	Cl2	176.26(6)	C21	C22	C23	121.3(2)
C1	Pt1	N7	81.03(7)	C30	C31	C26	120.9(2)
C25	P1	Pt1	110.69(7)	C22	C23	C24	121.07(19)
C32	P1	Pt1	111.06(7)	C22	C23	C18	118.56(19)
C32	P1	C25	107.79(10)	C18	C23	C24	120.03(19)
C24	P1	Pt1	115.49(7)	C4	C5	C6	120.3(2)
C24	P1	C25	103.16(10)	C29	C30	C31	120.0(2)
C24	P1	C32	108.14(10)	C23	C18	C17	122.66(18)
C7	N7	Pt1	111.98(13)	C19	C18	C17	117.85(19)
C11	N7	Pt1	127.57(14)	C19	C18	C23	119.4(2)
C11	N7	C7	118.92(17)	C30	C29	C28	119.8(2)
C6	C1	Pt1	113.56(15)	C28	C27	C26	120.9(2)
C2	C1	Pt1	126.81(16)	C3	C4	C5	117.7(2)
C2	C1	C6	119.6(2)	C9	C10	C11	120.8(2)
N7	C7	C6	116.41(18)	C20	C21	C22	119.9(2)
N7	C7	C8	121.1(2)	C35	C34	C33	120.7(2)
C8	C7	C6	122.4(2)	F15	C15	C14	118.6(2)
C1	C6	C7	116.38(19)	F15	C15	C16	118.0(2)
C5	C6	C1	120.3(2)	C14	C15	C16	123.3(2)

C5	C6	C7	123.24(19)	C34	C33	C32	122.4(2)
N7	C11	C12	123.15(18)	C34	C33	C38	118.3(2)
N7	C11	C10	120.4(2)	C38	C33	C32	119.2(2)
C10	C11	C12	116.02(19)	C15	C14	C13	118.5(2)
C3	C2	C1	117.9(2)	C15	C16	C17	118.1(2)
C9	C8	C7	119.9(2)	C34	C35	C36	120.4(2)
C26	C25	P1	117.32(15)	C8	C9	C10	118.6(2)
C33	C32	P1	116.59(15)	C19	C20	C21	119.5(2)
C23	C24	P1	122.04(15)	C20	C19	C18	121.3(2)
C17	C12	C11	117.54(19)	C37	C38	C33	120.9(2)
C17	C12	C13	120.2(2)	C37	C36	C35	119.8(2)
C13	C12	C11	121.3(2)	C36	C37	C38	119.9(2)
Cl5	C39	Cl4	110.45(15)				

Table 6 Hydrogen Bonds for ps39.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C39	H39	Cl1	1.00	2.94	3.729(3)	136.5
C39	H39	Cl3	1.00	2.69	3.544(3)	143.2
C39	H39	Cl2	1.00	3.04	3.800(3)	133.8

Table 7 Torsion Angles for ps39.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Pt1	P1	C25	C26	146.38(15)	C25	P1	C24	C23	-178.00(17)
Pt1	P1	C32	C33	153.97(15)	C25	C26	C31	C30	176.8(2)
Pt1	P1	C24	C23	61.12(19)	C25	C26	C27	C28	-177.2(2)
Pt1	N7	C7	C6	8.9(2)	C32	P1	C25	C26	-91.98(18)
Pt1	N7	C7	C8	-168.04(17)	C32	P1	C24	C23	-63.99(19)
Pt1	N7	C11	C12	-26.4(3)	C32	C33	C38	C37	-179.4(2)
Pt1	N7	C11	C10	161.29(16)	C24	P1	C25	C26	22.28(19)
Pt1	C1	C6	C7	0.3(2)	C24	P1	C32	C33	-78.34(19)
Pt1	C1	C6	C5	178.20(17)	C24	C23	C18	C17	11.1(3)
Pt1	C1	C2	C3	-178.10(16)	C24	C23	C18	C19	-172.28(19)
P1	C25	C26	C31	99.6(2)	C12	C11	C10	C9	-168.3(2)
P1	C25	C26	C27	-84.6(2)	C12	C17	C18	C23	89.3(3)
P1	C32	C33	C34	83.6(2)	C12	C17	C18	C19	-87.4(3)
P1	C32	C33	C38	-97.3(2)	C12	C17	C16	C15	1.8(3)
P1	C24	C23	C22	77.6(2)	C12	C13	C14	C15	0.4(3)
P1	C24	C23	C18	-109.1(2)	C17	C12	C13	C14	1.1(3)
N7	C7	C6	C1	-6.4(3)	C17	C18	C19	C20	175.6(2)
N7	C7	C6	C5	175.8(2)	C13	C12	C17	C18	171.78(19)
N7	C7	C8	C9	4.6(3)	C13	C12	C17	C16	-2.2(3)
N7	C11	C12	C17	-83.2(3)	C26	C31	C30	C29	0.0(3)
N7	C11	C12	C13	107.9(2)	C22	C23	C18	C17	-175.5(2)
N7	C11	C10	C9	4.5(3)	C22	C23	C18	C19	1.2(3)
F15	C15	C14	C13	-178.1(2)	C22	C21	C20	C19	1.4(4)
F15	C15	C16	C17	177.0(2)	C31	C26	C27	C28	-1.3(3)
F3	C3	C4	C5	180.0(2)	C31	C30	C29	C28	-0.7(3)
C1	C6	C5	C4	-0.1(3)	C23	C22	C21	C20	-1.4(4)
C1	C2	C3	F3	-179.16(19)	C23	C18	C19	C20	-1.2(3)
C1	C2	C3	C4	0.7(3)	C18	C17	C16	C15	-172.0(2)
C7	N7	C11	C12	168.9(2)	C29	C28	C27	C26	0.6(3)
C7	N7	C11	C10	-3.4(3)	C27	C28	C29	C30	0.4(3)
C7	C6	C5	C4	177.6(2)	C27	C26	C31	C30	0.9(3)
C7	C8	C9	C10	-3.5(3)	C10	C11	C12	C17	89.4(2)
C6	C1	C2	C3	-1.2(3)	C10	C11	C12	C13	-79.5(3)
C6	C7	C8	C9	-172.1(2)	C21	C22	C23	C24	173.5(2)
C6	C5	C4	C3	-0.4(3)	C21	C22	C23	C18	0.1(3)
C11	N7	C7	C6	175.81(18)	C21	C20	C19	C18	-0.1(4)
C11	N7	C7	C8	-1.1(3)	C34	C33	C38	C37	-0.3(3)
C11	C12	C17	C18	2.7(3)	C34	C35	C36	C37	0.1(4)
C11	C12	C17	C16	-171.21(19)	C33	C34	C35	C36	-0.2(4)
C11	C12	C13	C14	169.7(2)	C33	C38	C37	C36	0.2(4)
C11	C10	C9	C8	-1.0(4)	C14	C15	C16	C17	-0.3(4)
C2	C1	C6	C7	-176.93(19)	C16	C17	C18	C23	-96.8(3)
C2	C1	C6	C5	0.9(3)	C16	C17	C18	C19	86.5(3)
C2	C3	C4	C5	0.1(4)	C16	C15	C14	C13	-0.8(4)
C8	C7	C6	C1	170.5(2)	C35	C34	C33	C32	179.4(2)
C8	C7	C6	C5	-7.3(3)	C35	C34	C33	C38	0.2(3)
C25	P1	C32	C33	32.6(2)	C35	C36	C37	C38	-0.2(4)

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps39.

Atom	*x*	*y*	*z*	U(eq)
H2	4594	7787	8795	23
H8	7755	8756	5926	25
H25A	6209	8137	11342	20
H25B	7334	7726	11240	20
H32A	6401	9293	9351	24
H32B	5476	8769	9495	24

H24A	8509	9178	10754	20
H24B	9248	8611	10450	20
H39	7497	6151	9396	35
H28	10085	8507	13265	33
H13	10729	7112	8307	26
H22	8004	9951	9464	23
H31	6220	8948	12470	24
H5	5946	8800	6158	26
H30	7094	9390	13787	31
H29	9032	9177	14178	34
H27	9209	8057	11957	25
H4	3939	8712	6401	28
H10	10877	8231	6936	25
H21	8912	10551	8361	27
H34	6821	10004	10707	26
H14	12243	6982	9411	31
H16	11829	8696	10297	27
H35	6006	10502	11964	36
H9	9745	8633	5717	28
H20	10666	10241	7711	29
H19	11455	9317	8126	26
H38	4257	8761	10800	31
H36	4315	10136	12643	40
H37	3445	9264	12063	40

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2.a Ternary CH refined with riding coordinates:
 C39(H39)
2.b Secondary CH2 refined with riding coordinates:
 C25(H25A,H25B), C32(H32A,H32B), C24(H24A,H24B)
2.c Aromatic/amide H refined with riding coordinates:
 C2(H2), C8(H8), C28(H28), C13(H13), C22(H22), C31(H31), C5(H5), C30(H30),
 C29(H29), C27(H27), C4(H4), C10(H10), C21(H21), C34(H34), C14(H14), C16(H16),
 C35(H35), C9(H9), C20(H20), C19(H19), C38(H38), C36(H36), C37(H37)
```

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

ps40 Complex 10

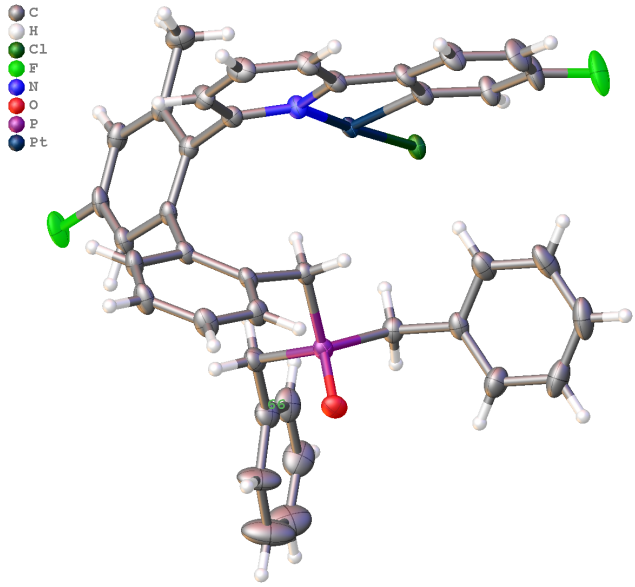

Figure SI7 Solid state structure of the asymmetric unit of ps40. The complex sits on an inversion centre between the platinum chloro dimer shown below in Figure SI8

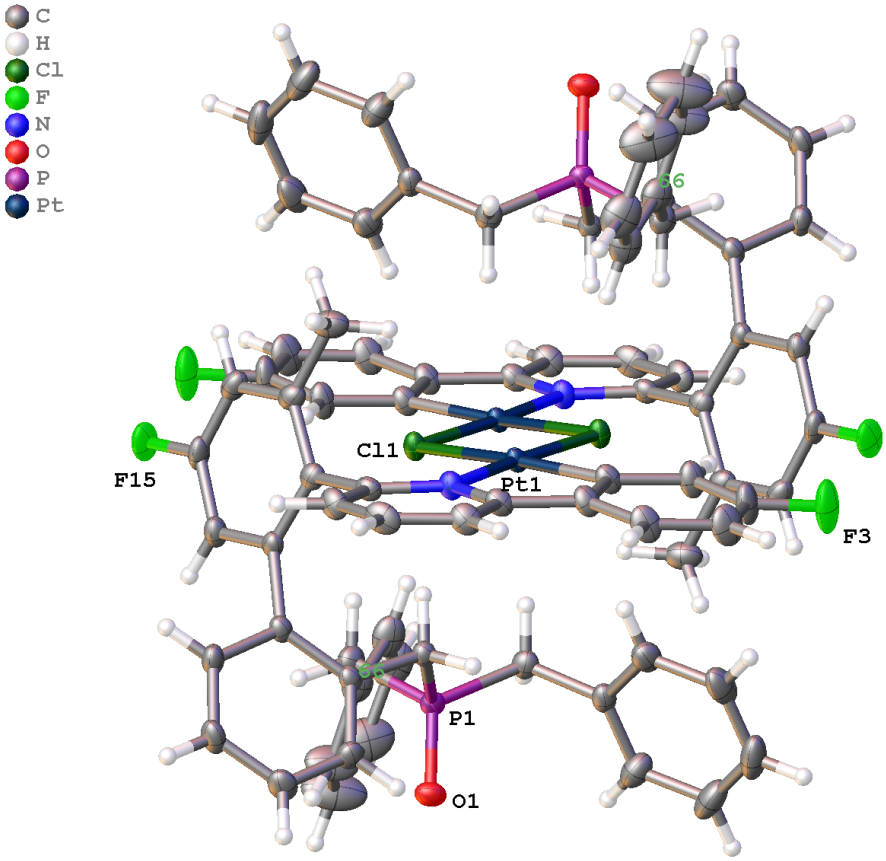

Figure SI8 Solid state structure of ps40.

Crystal structure determination of [ps40]

The crystals were optically almost perfect (could have easily proposed to Liz Taylor with one) but were incredibly sensitive to solvent loss. The data was recorded at 100K and enough reflections were recorded before decompositions.

The asymmetric unit contains a Pt, a chloride and a biphenylpyridine ligand which has formed a C-C bond to one of the benzyls of the tribenzyl phosphine, and oxidized to the P=O oxide
There are also three molecules of chloroform.

One of the benzene rings of a benzyl of the phosphine was modeled as disordered over two positions. The occupancy was linked to a free variable which refined to 77:23. The minor component was refined isotropically. Both rings were refined with an AFIX 66 restraint. Two of

the chloroforms were modeled as disordered about the carbon. The occupancy of the disordered components were fixed at 75:25. The minor components were refined isotropically. Several SIMU and DFIX restraints were used in the refinement of the disordered solvent.

Experimental

Single crystals of $C_{42}H_{34}Cl_{10}F_2NOPPt$ **[ps40]** were grown from chloroform. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on a Rigaku Oxford Diffraction SuperNova diffractometer with a duel source (Cu at zero) equipped with an AtlasS2 CCD area detector.. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

19 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
20 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
21 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{42}H_{34}Cl_{10}F_2NOPPt$ (M =1187.26 g/mol): monoclinic, space group I2/a (no. 15), a = 23.6952(4) Å, b = 14.2502(3) Å, c = 27.6824(5) Å, β = 103.1991(19)°, V = 9100.3(3) Å^3, Z = 8, T = 100(2) K, μ(MoKα) = 3.749 mm^{-1}, $Dcalc$ = 1.733 g/cm^3, 41772 reflections measured (5.036° ≤ 2Θ ≤ 61.916°), 12881 unique (R_{int} = 0.0299, R_{sigma} = 0.0351) which were used in all calculations. The final R_1 was 0.0404 (I > 2σ(I)) and wR_2 was 0.1033 (all data).

Table 1 Crystal data and structure refinement for ps40.

Identification code	ps40
Empirical formula	$C_{42}H_{34}Cl_{10}F_2NOPPt$
Formula weight	1187.26
Temperature/K	100(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	23.6952(4)
b/Å	14.2502(3)
c/Å	27.6824(5)
α/°	90
β/°	103.1991(19)
γ/°	90
Volume/Å^3	9100.3(3)
Z	8
ϱ_{calc}g/cm^3	1.733
μ/mm^{-1}	3.749
F(000)	4656.0
Crystal size/mm^3	0.423 × 0.22 × 0.094 colourless block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.036 to 61.916
Index ranges	-34 ≤ h ≤ 31, -20 ≤ k ≤ 18, -38 ≤ l ≤ 39
Reflections collected	41772
Independent reflections	12881 [R_{int} = 0.0299, R_{sigma} = 0.0351]
Data/restraints/parameters	12881/72/557
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.0951
Final R indexes [all data]	R_1 = 0.0513, wR_2 = 0.1033
Largest diff. peak/hole / e Å^{-3}	2.09/-1.60

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps40. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C40	6178(4)	5840(8)	5095(3)	95(3)
Cl5	5569.9(14)	6651(2)	4859.1(11)	79.9(9)
Cl6	5879.8(14)	4708(2)	4915.4(11)	93.2(11)
Cl7	6768.3(16)	6097(4)	4930.7(16)	126.5(16)
Cl5A	6596(12)	6936(15)	5028(10)	214(8)
Cl6A	6649(4)	5171(7)	4693(4)	87(3)
Cl7A	5591(5)	6078(10)	4683(5)	110(3)
Cl0A	3906(3)	147(4)	5629(2)	45.9(12)
C1	6185.5(17)	1647(3)	6782.3(15)	21.5(8)
O1	6053.6(13)	5458(2)	8131.2(11)	25.2(6)
Pt1	6800.9(2)	1886.7(2)	7379.3(2)	15.12(5)
P1	6469.1(4)	4701.4(8)	8077.5(4)	18.91(19)
C2	6181.9(19)	1929(3)	6294.8(16)	27.4(9)
C19	5886.9(18)	2542(3)	9246.2(15)	23.8(8)
C26	6321.4(17)	5003(3)	7048.7(15)	23.3(8)
Cl3	3488.8(15)	3041.2(18)	7231.6(8)	110.0(11)
F3	5682.3(13)	2107(3)	5467.6(10)	48.7(9)
Cl2	3934.1(8)	3067.4(10)	6353.0(6)	53.4(4)
C18	6154.0(16)	2685(3)	8850.4(14)	19.4(7)
Cl1	7401.5(4)	2586.0(7)	6940.7(3)	18.78(17)
C4	5192(2)	1385(4)	6011.4(18)	36.0(11)
Cl4	4707.3(12)	2814.3(14)	7313.0(11)	115.8(12)
C24	6157.8(17)	3533(3)	8036.7(14)	19.9(7)
C5	5189.0(18)	1093(4)	6486.3(17)	29.2(10)

C3	5686(2)	1798(4)	5932.6(16)	34.4(11)
C33A	7467.3(19)	5520(3)	8623.2(17)	29.8(9)
C34	7965(5)	5329(13)	8455(7)	34(10)
C35	8349(6)	6050(20)	8419(8)	34(7)
C36	8237(10)	6958(17)	8551(8)	37(7)
C37	7739(13)	7149(6)	8719(10)	42(8)
C38	7354(8)	6430(6)	8755(8)	51(14)
C38A	7286(4)	6324(7)	8830(6)	50(3)
C37A	7597(5)	7156(7)	8883(7)	69(4)
C36A	8098(5)	7195(8)	8712(6)	64(4)
C35A	8289(3)	6435(11)	8495(4)	45(3)
C34A	7974(3)	5592(11)	8453(3)	36.2(19)
C6	5684.6(18)	1224(3)	6869.8(15)	22.8(8)
C7	5709.2(17)	982(3)	7385.2(15)	21.0(8)
N7	6213.5(14)	1249(2)	7714.3(12)	18.8(6)
C8	5268.0(18)	520(3)	7545.3(17)	25.4(9)
Cl8	3527(2)	1007(5)	5327(2)	187(3)
C20	5359.7(19)	2963(4)	9256.4(16)	28.4(10)
Cl8A	4127(7)	608(13)	4664(7)	122(7)
C21	5087.7(18)	3528(4)	8867.5(16)	28.5(9)
C9	5328.7(19)	309(3)	8037.7(18)	28.1(9)
C22	5351.9(17)	3681(3)	8473.9(16)	24.7(8)
Cl9	3298.1(10)	-714.1(17)	4757.1(9)	58.4(5)
C23	5886.7(17)	3280(3)	8460.8(14)	19.0(7)
C25	6760.3(17)	4835(3)	7530.6(15)	23.3(8)
Cl9A	2984(3)	-154(6)	4857(3)	64.4(17)
C10	5825.5(18)	601(3)	8368.8(16)	24.8(8)
C27	6131(2)	5906(4)	6909.1(18)	33.5(10)
Cl10	4289.7(12)	415(2)	4739.2(9)	48.1(5)
C28	5749(2)	6069(4)	6455(2)	41.6(13)
C29	5551(2)	5336(5)	6139.5(18)	44.1(14)
C11	6257.5(16)	1080(3)	8206.4(15)	19.3(7)
C30	5732(2)	4431(5)	6278.1(18)	41.1(13)
C31	6113.5(19)	4267(4)	6732.8(17)	31(1)
C12	6767.5(17)	1395(3)	8584.8(14)	19.8(7)
C32	7104.6(18)	4652(3)	8589.0(16)	25.3(8)
C13	7273.6(17)	848(3)	8687.3(15)	22.1(8)
C13A	7317(2)	-24(3)	8392.8(19)	31.8(10)
C14	7738.0(18)	1110(3)	9071.1(16)	25.9(9)
C15	7683.9(18)	1898(3)	9339.6(15)	26.2(9)
F15	8142.8(11)	2164(2)	9704(1)	36.7(7)
C39	4014(3)	2581(4)	6946(2)	48.4(14)
C16	7188.4(17)	2436(3)	9261.9(15)	23.8(8)
C41	3612(4)	306(9)	4868(4)	140(6)
C17	6717.6(16)	2183(3)	8881.9(14)	19.0(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for ps40. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C40	91(6)	135(8)	58(5)	25(5)	12(4)	28(6)
Cl5	89(2)	85.8(19)	70.2(16)	25.7(15)	29.3(15)	44.2(16)
Cl6	91(2)	95(2)	69.6(16)	-38.8(15)	-30.8(15)	46.0(17)
Cl7	77(2)	199(5)	110(3)	45(3)	35(2)	26(3)
C1	15.4(17)	30(2)	18.9(18)	-6.4(16)	2.8(14)	-4.4(15)
O1	19.8(14)	27.2(15)	28.6(15)	-3.6(12)	5.7(12)	5.1(12)
Pt1	10.39(7)	21.69(8)	13.39(7)	-2.32(5)	2.93(5)	-2.09(5)
P1	14.5(4)	23.3(5)	18.2(4)	-0.7(4)	2.3(4)	2.8(4)
C2	18.7(19)	44(3)	17.9(18)	-3.0(18)	1.1(15)	-8.1(18)
C19	19.7(18)	36(2)	15.1(17)	2.3(16)	2.1(14)	2.1(17)
C26	15.7(17)	37(2)	17.5(17)	0.7(17)	3.7(14)	2.9(16)
Cl3	179(3)	105.3(18)	60.8(12)	38.0(12)	58.4(16)	91.0(19)
F3	31.6(15)	94(3)	15.8(13)	3.4(15)	-4.0(11)	-14.5(16)
Cl2	70.1(11)	39.1(7)	50.8(8)	3.1(6)	13.7(8)	-8.1(7)
C18	14.6(16)	28(2)	15.4(16)	-2.8(15)	2.5(13)	-0.3(15)
Cl1	12.3(4)	29.6(5)	14.4(4)	-0.1(3)	2.9(3)	-2.9(3)
C4	23(2)	54(3)	26(2)	-10(2)	-4.5(17)	-11(2)
Cl4	111.8(19)	40.6(9)	143(2)	-16.9(12)	-77.9(17)	6.3(11)
C24	16.9(17)	26(2)	16.2(17)	-1.4(15)	2.8(14)	2.0(15)
C5	18.5(19)	41(3)	26(2)	-9.0(19)	2.2(16)	-13.0(18)
C3	25(2)	61(3)	14.3(18)	-2(2)	0.2(16)	-7(2)
C33A	20.6(19)	37(2)	28(2)	-0.3(19)	-2.2(17)	-3.3(18)
C38A	33(4)	34(4)	78(6)	-26(4)	3(4)	-10(3)
C37A	41(5)	47(5)	117(10)	-38(5)	13(6)	-12(4)
C36A	38(5)	48(5)	97(9)	-11(6)	-5(5)	-15(4)
C35A	26(3)	54(7)	51(5)	6(5)	-2(3)	-13(4)
C34A	20(3)	53(6)	33(4)	5(3)	-1(2)	-7(3)
C6	19.8(18)	29(2)	19.5(18)	-7.0(16)	3.3(15)	-6.7(16)
C7	16.2(17)	25.0(19)	21.8(18)	-5.8(16)	4.3(14)	-4.0(15)

N7	14.3(14)	24.7(17)	18.3(15)	-0.1(13)	5.5(12)	-5.0(13)
C8	20.0(19)	28(2)	29(2)	-4.7(17)	6.5(16)	-7.9(16)
Cl8	137(4)	275(7)	188(5)	-178(5)	118(4)	-106(4)
C20	20.2(19)	48(3)	18.2(18)	-0.4(18)	7.3(15)	1.4(19)
C21	16.1(18)	44(3)	25(2)	-3.1(19)	5.3(16)	3.2(18)
C9	21.8(19)	30(2)	37(2)	-3.7(19)	15.9(18)	-9.0(17)
C22	16.7(17)	34(2)	21.9(19)	1.2(17)	1.7(15)	5.0(17)
Cl9	51.3(11)	61.8(13)	59.7(13)	14.7(11)	7.6(10)	-16(1)
C23	15.4(17)	26(2)	14.7(16)	-3.6(15)	2.1(13)	-0.5(15)
C25	17.8(18)	30(2)	22.4(19)	2.6(17)	5.6(15)	0.9(16)
C10	26(2)	28(2)	23.8(19)	0.6(17)	11.7(16)	-5.5(17)
C27	28(2)	38(3)	32(2)	10(2)	1.1(19)	3(2)
Cl10	40.9(11)	68.1(15)	37.6(10)	-1.8(10)	13.5(9)	-12.7(11)
C28	30(2)	55(3)	38(3)	24(3)	5(2)	7(2)
C29	27(2)	82(4)	22(2)	12(3)	1.9(18)	5(3)
C11	16.1(17)	22.9(19)	20.8(18)	-0.8(15)	7.9(14)	0.7(15)
C30	27(2)	69(4)	25(2)	-15(2)	-0.6(18)	6(2)
C31	22(2)	44(3)	25(2)	-4(2)	2.0(17)	7.2(19)
C12	16.6(17)	24(2)	19.4(17)	3.2(15)	5.9(14)	-0.4(15)
C32	22.5(19)	30(2)	20.4(19)	-2.6(17)	-1.4(15)	0.2(17)
C13	17.9(17)	26(2)	24.0(19)	5.1(16)	7.9(15)	2.9(15)
C13A	26(2)	29(2)	42(3)	-1(2)	11.9(19)	3.3(18)
C14	17.2(18)	37(2)	24(2)	9.0(18)	4.7(15)	5.0(17)
C15	17.4(18)	45(3)	14.3(17)	3.9(17)	-0.6(14)	1.5(18)
F15	20.5(12)	66(2)	18.1(12)	-2.6(13)	-6.6(10)	4.8(13)
C39	60(4)	38(3)	38(3)	-1(2)	-7(3)	8(3)
C16	18.8(18)	37(2)	15.2(17)	-0.7(16)	2.1(14)	0.8(17)
C41	60(5)	233(14)	143(9)	-146(10)	60(6)	-84(7)
C17	15.7(16)	27.3(19)	14.5(16)	2.4(15)	4.6(13)	2.4(15)

Table 4 Bond Lengths for ps40.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C40	Cl5	1.846(9)	C33A	C32	1.496(6)
C40	Cl6	1.785(12)	C34	C35	1.3900
C40	Cl7	1.610(10)	C35	C36	1.3900
C40	Cl5A	1.883(17)	C36	C37	1.3900
C40	Cl6A	1.991(12)	C37	C38	1.3900
C40	Cl7A	1.619(13)	C38A	C37A	1.385(13)
Cl0A	C41	2.075(12)	C37A	C36A	1.377(14)
C1	Pt1	1.968(4)	C36A	C35A	1.365(14)
C1	C2	1.406(6)	C35A	C34A	1.406(14)
C1	C6	1.401(5)	C6	C7	1.456(6)
O1	P1	1.490(3)	C7	N7	1.381(5)
Pt1	Cl1[1]	2.4607(9)	C7	C8	1.391(5)
Pt1	Cl1	2.2982(9)	N7	C11	1.364(5)
Pt1	N7	2.052(3)	C8	C9	1.371(6)
P1	C24	1.814(4)	Cl8	C41	1.665(9)
P1	C25	1.811(4)	C20	C21	1.381(7)
P1	C32	1.818(4)	Cl8A	C41	1.520(14)
C2	C3	1.372(6)	C21	C22	1.392(6)
C19	C18	1.400(5)	C9	C10	1.381(6)
C19	C20	1.392(6)	C22	C23	1.398(5)
C26	C25	1.512(6)	Cl9	C41	1.630(10)
C26	C27	1.389(7)	Cl9A	C41	1.620(9)
C26	C31	1.382(7)	C10	C11	1.388(5)
Cl3	C39	1.748(7)	C27	C28	1.391(7)
F3	C3	1.358(5)	Cl10	C41	1.730(8)
Cl2	C39	1.752(6)	C28	C29	1.374(9)
C18	C23	1.404(6)	C29	C30	1.385(9)
C18	C17	1.500(5)	C11	C12	1.477(6)
Cl1	Pt1[1]	2.4606(9)	C30	C31	1.391(6)
C4	C5	1.380(7)	C12	C13	1.404(5)
C4	C3	1.373(7)	C12	C17	1.412(6)
Cl4	C39	1.755(7)	C13	C13A	1.502(6)
C24	C23	1.505(5)	C13	C14	1.395(6)
C5	C6	1.404(6)	C14	C15	1.369(7)
C33A	C34	1.3900	C15	F15	1.357(5)
C33A	C38	1.3900	C15	C16	1.377(6)
C33A	C38A	1.391(9)	C16	C17	1.395(6)
C33A	C34A	1.389(8)			

[1]3/2-X,1/2-Y,3/2-Z

Table 5 Bond Angles for ps40.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl6	C40	Cl5	103.9(5)	C1	C6	C5	121.5(4)
Cl7	C40	Cl5	114.5(6)	C1	C6	C7	115.2(4)
Cl7	C40	Cl6	116.1(6)	C5	C6	C7	123.3(4)
Cl5A	C40	Cl6A	88.1(10)	N7	C7	C6	114.6(3)

Cl7A	C40	Cl5A	98.2(11)
Cl7A	C40	Cl6A	102.0(7)
C2	C1	Pt1	126.7(3)
C6	C1	Pt1	115.1(3)
C6	C1	C2	118.0(4)
C1	Pt1	Cl1	93.50(12)
C1	Pt1	Cl1[1]	171.00(13)
C1	Pt1	N7	81.59(15)
Cl1	Pt1	Cl1[1]	79.15(3)
N7	Pt1	Cl1[1]	105.73(9)
N7	Pt1	Cl1	175.09(9)
O1	P1	C24	113.70(18)
O1	P1	C25	113.17(19)
O1	P1	C32	113.50(19)
C24	P1	C32	105.4(2)
C25	P1	C24	105.8(2)
C25	P1	C32	104.4(2)
C3	C2	C1	118.6(4)
C20	C19	C18	121.4(4)
C27	C26	C25	120.4(4)
C31	C26	C25	120.9(4)
C31	C26	C27	118.7(4)
C19	C18	C23	119.0(4)
C19	C18	C17	116.1(4)
C23	C18	C17	124.9(3)
Pt1	Cl1	Pt1[1]	100.85(3)
C3	C4	C5	118.1(4)
C23	C24	P1	114.3(3)
C4	C5	C6	119.7(4)
C2	C3	C4	124.2(4)
F3	C3	C2	117.9(4)
F3	C3	C4	117.9(4)
C34	C33A	C38	120.0
C34	C33A	C32	109.6(8)
C38	C33A	C32	130.2(8)
C38A	C33A	C32	118.7(7)
C34A	C33A	C38A	116.7(9)
C34A	C33A	C32	124.6(8)
C33A	C34	C35	120.0
C36	C35	C34	120.0
C35	C36	C37	120.0
C38	C37	C36	120.0
C37	C38	C33A	120.0
C37A	C38A	C33A	122.9(11)
C36A	C37A	C38A	118.5(10)
C35A	C36A	C37A	121.2(8)
C36A	C35A	C34A	119.4(8)
C33A	C34A	C35A	121.3(10)

[1]3/2-X,1/2-Y,3/2-Z

N7	C7	C8	121.4(4)
C8	C7	C6	124.0(4)
C7	N7	Pt1	113.5(3)
C11	N7	Pt1	128.6(3)
C11	N7	C7	117.9(3)
C9	C8	C7	120.3(4)
C21	C20	C19	119.8(4)
C20	C21	C22	119.2(4)
C8	C9	C10	118.3(4)
C21	C22	C23	121.9(4)
C18	C23	C24	123.1(3)
C22	C23	C18	118.6(4)
C22	C23	C24	118.2(4)
C26	C25	P1	116.0(3)
C9	C10	C11	120.9(4)
C26	C27	C28	120.6(5)
C29	C28	C27	120.3(5)
C28	C29	C30	119.5(5)
N7	C11	C10	121.1(4)
N7	C11	C12	121.2(3)
C10	C11	C12	117.7(4)
C29	C30	C31	120.2(5)
C26	C31	C30	120.6(5)
C13	C12	C11	119.8(4)
C13	C12	C17	120.3(4)
C17	C12	C11	119.4(3)
C33A	C32	P1	112.3(3)
C12	C13	C13A	120.7(4)
C14	C13	C12	119.6(4)
C14	C13	C13A	119.7(4)
C15	C14	C13	118.6(4)
C14	C15	C16	123.7(4)
F15	C15	C14	118.3(4)
F15	C15	C16	118.0(4)
Cl3	C39	Cl2	109.9(3)
Cl3	C39	Cl4	109.6(4)
Cl2	C39	Cl4	110.7(4)
C15	C16	C17	118.7(4)
Cl8	C41	Cl10	112.5(4)
Cl8A	C41	Cl0A	107.2(9)
Cl8A	C41	Cl9A	157.0(10)
Cl9	C41	Cl8	123.4(6)
Cl9	C41	Cl10	116.5(6)
Cl9A	C41	Cl0A	93.9(6)
C12	C17	C18	122.5(3)
C16	C17	C18	117.9(4)
C16	C17	C12	119.1(4)

Table 6 Torsion Angles for ps40.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	F3	177.5(5)	C7	C8	C9	C10	2.7(7)
C1	C2	C3	C4	-1.7(8)	N7	C7	C8	C9	-0.8(7)
C1	C6	C7	N7	3.0(6)	N7	C11	C12	C13	-83.0(5)
C1	C6	C7	C8	-177.0(4)	N7	C11	C12	C17	104.7(4)
O1	P1	C24	C23	-55.0(3)	C8	C7	N7	Pt1	178.5(3)
O1	P1	C25	C26	-49.6(4)	C8	C7	N7	C11	-2.6(6)
O1	P1	C32	C33A	-64.0(4)	C8	C9	C10	C11	-1.3(7)
Pt1	C1	C2	C3	-172.3(4)	C20	C19	C18	C23	1.1(6)
Pt1	C1	C6	C5	173.8(4)	C20	C19	C18	C17	-179.3(4)
Pt1	C1	C6	C7	-3.1(5)	C20	C21	C22	C23	-0.1(7)
Pt1	N7	C11	C10	-177.2(3)	C21	C22	C23	C18	1.8(7)
Pt1	N7	C11	C12	2.4(6)	C21	C22	C23	C24	-176.2(4)
P1	C24	C23	C18	-103.3(4)	C9	C10	C11	N7	-2.2(7)
P1	C24	C23	C22	74.6(4)	C9	C10	C11	C12	178.1(4)
C2	C1	C6	C5	-0.8(7)	C23	C18	C17	C12	-73.8(6)
C2	C1	C6	C7	-177.7(4)	C23	C18	C17	C16	114.3(5)
C19	C18	C23	C24	175.6(4)	C25	P1	C24	C23	-179.8(3)
C19	C18	C23	C22	-2.3(6)	C25	P1	C32	C33A	59.7(4)
C19	C18	C17	C12	106.6(5)	C25	C26	C27	C28	176.9(4)
C19	C18	C17	C16	-65.3(5)	C25	C26	C31	C30	-176.7(4)
C19	C20	C21	C22	-1.1(7)	C10	C11	C12	C13	96.6(5)
C26	C27	C28	C29	0.4(8)	C10	C11	C12	C17	-75.6(5)
C18	C19	C20	C21	0.6(7)	C27	C26	C25	P1	86.1(5)
C4	C5	C6	C1	0.0(7)	C27	C26	C31	C30	1.6(7)
C4	C5	C6	C7	176.7(5)	C27	C28	C29	C30	0.5(8)
C24	P1	C25	C26	75.5(4)	C28	C29	C30	C31	-0.3(8)

C24	P1	C32	C33A	171.0(3)	C29	C30	C31	C26	-0.8(7)
C5	C4	C3	C2	0.9(9)	C11	C12	C13	C13A	4.1(6)
C5	C4	C3	F3	-178.3(5)	C11	C12	C13	C14	-175.1(4)
C5	C6	C7	N7	-173.8(4)	C11	C12	C17	C18	3.7(6)
C5	C6	C7	C8	6.1(7)	C11	C12	C17	C16	175.5(4)
C3	C4	C5	C6	0.0(8)	C31	C26	C25	P1	-95.6(4)
C33A	C34	C35	C36	0.0	C31	C26	C27	C28	-1.4(7)
C33A	C38A	C37A	C36A	1.9(18)	C12	C13	C14	C15	0.3(6)
C34	C33A	C38	C37	0.0	C32	P1	C24	C23	70.0(3)
C34	C33A	C32	P1	-105.6(9)	C32	P1	C25	C26	-173.6(3)
C34	C35	C36	C37	0.0	C32	C33A	C34	C35	175.4(6)
C35	C36	C37	C38	0.0	C32	C33A	C38	C37	-174.4(8)
C36	C37	C38	C33A	0.0	C32	C33A	C38A	C37A	179.1(9)
C38	C33A	C34	C35	0.0	C32	C33A	C34A	C35A	179.4(6)
C38	C33A	C32	P1	69.2(12)	C13	C12	C17	C18	-168.5(4)
C38A	C33A	C34A	C35A	0.7(10)	C13	C12	C17	C16	3.3(6)
C38A	C33A	C32	P1	77.8(8)	C13	C14	C15	F15	-178.3(4)
C38A	C37A	C36A	C35A	-0.1(17)	C13	C14	C15	C16	1.9(7)
C37A	C36A	C35A	C34A	-1.3(14)	C13A	C13	C14	C15	-178.8(4)
C36A	C35A	C34A	C33A	0.9(11)	C14	C15	C16	C17	-1.5(7)
C34A	C33A	C38A	C37A	-2.1(14)	C15	C16	C17	C18	171.0(4)
C34A	C33A	C32	P1	-100.9(6)	C15	C16	C17	C12	-1.1(6)
C6	C1	C2	C3	1.6(7)	F15	C15	C16	C17	178.7(4)
C6	C7	N7	Pt1	-1.6(5)	C17	C18	C23	C24	-3.9(6)
C6	C7	N7	C11	177.4(4)	C17	C18	C23	C22	178.2(4)
C6	C7	C8	C9	179.2(4)	C17	C12	C13	C13A	176.3(4)
C7	N7	C11	C10	4.0(6)	C17	C12	C13	C14	-2.9(6)
C7	N7	C11	C12	-176.3(4)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps40.

Atom	*x*	*y*	*z*	U(eq)
H40	6261	5867	5458	114
H40A	6158	5608	5424	114
H2	6509	2199	6220	33
H19	6066	2157	9508	29
H4	4868	1304	5752	43
H24A	5865	3484	7729	24
H24B	6459	3080	8023	24
H5	4861	810	6552	35
H34	8040	4720	8366	40
H35	8682	5920	8306	41
H36	8494	7439	8527	44
H37	7663	7758	8808	51
H38	7022	6558	8868	61
H38A	6942	6302	8936	60
H37A	7470	7676	9032	83
H36A	8311	7749	8745	77
H35A	8624	6475	8375	54
H34A	8107	5071	8309	43
H8	4930	354	7317	31
H20	5191	2864	9524	34
H21	4732	3803	8868	34
H9	5043	-23	8146	34
H22	5167	4061	8212	30
H25A	7031	5357	7585	28
H25B	6978	4274	7494	28
H10	5871	475	8705	30
H27	6261	6406	7121	40
H28	5626	6677	6365	50
H29	5298	5446	5835	53
H30	5599	3931	6067	49
H31	6230	3657	6825	37
H32A	6981	4570	8897	30
H32B	7338	4113	8546	30
H13A	7046	-483	8456	48
H13B	7703	-272	8489	48
H13C	7229	126	8046	48
H14	8077	757	9143	31
H39	3961	1900	6914	58
H16	7168	2959	9459	29
H41	3383	658	4586	168
H41A	3477	950	4894	168

Table 8 Atomic Occupancy for ps40.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H40	0.75	H40A	0.25	Cl5	0.75
Cl6	0.75	Cl7	0.75	Cl5A	0.25
Cl6A	0.25	Cl7A	0.25	Cl0A	0.25

C34	0.23(3)	H34	0.23(3)	C35	0.23(3)
H35	0.23(3)	C36	0.23(3)	H36	0.23(3)
C37	0.23(3)	H37	0.23(3)	C38	0.23(3)
H38	0.23(3)	C38A	0.77(3)	H38A	0.77(3)
C37A	0.77(3)	H37A	0.77(3)	C36A	0.77(3)
H36A	0.77(3)	C35A	0.77(3)	H35A	0.77(3)
C34A	0.77(3)	H34A	0.77(3)	Cl8	0.75
Cl8A	0.25	Cl9	0.75	Cl9A	0.25
Cl10	0.75	H41	0.75	H41A	0.25

Refinement model description

Number of restraints - 72, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 C40-Cl5A
 1.75 with sigma of 0.02
 C40-Cl6A
 1.75 with sigma of 0.02
 C40-Cl7A
 1.75 with sigma of 0.02
 C41-Cl0A
 1.75 with sigma of 0.02
 C41-Cl8A
 1.75 with sigma of 0.02
 C41-Cl9A
 1.75 with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
Cl5 ≈ Cl5A ≈ Cl7 ≈ Cl6A ≈ Cl6 ≈ Cl7A ≈ C40: within 1.7A
with sigma of 0.01 and sigma for terminal atoms of 0.02
C33A ≈ C38A ≈ C37A ≈ C36A ≈ C35A ≈ C34A: within 1.7A with
sigma of 0.04 and sigma for terminal atoms of 0.08
4. Others
 Sof(C38A)=Sof(H38A)=Sof(C37A)=Sof(H37A)=Sof(C36A)=Sof(H36A)=Sof(C35A)=
 Sof(H35A)=Sof(C34A)=Sof(H34A)=1-FVAR(1)
 Sof(C34)=Sof(H34)=Sof(C35)=Sof(H35)=Sof(C36)=Sof(H36)=Sof(C37)=Sof(H37)=
 Sof(C38)=Sof(H38)=FVAR(1)
 Fixed Sof: H40(0.75) H40A(0.25) Cl5(0.75) Cl6(0.75) Cl7(0.75) Cl5A(0.25)
 Cl6A(0.25) Cl7A(0.25) Cl0A(0.25) Cl8(0.75) Cl8A(0.25) Cl9(0.75) Cl9A(0.25)
 Cl10(0.75) H41(0.75) H41A(0.25)
5.a Ternary CH refined with riding coordinates:
 C40(H40), C40(H40A), C39(H39), C41(H41), C41(H41A)
5.b Secondary CH2 refined with riding coordinates:
 C24(H24A,H24B), C25(H25A,H25B), C32(H32A,H32B)
5.c Aromatic/amide H refined with riding coordinates:
 C2(H2), C19(H19), C4(H4), C5(H5), C34(H34), C35(H35), C36(H36), C37(H37),
 C38(H38), C38A(H38A), C37A(H37A), C36A(H36A), C35A(H35A), C34A(H34A), C8(H8),
 C20(H20), C21(H21), C9(H9), C22(H22), C10(H10), C27(H27), C28(H28), C29(H29),
 C30(H30), C31(H31), C14(H14), C16(H16)
5.d Fitted hexagon refined as free rotating group:
 C33A(C34,C35,C36,C37,C38)
5.e Idealised Me refined as rotating group:
 C13A(H13A,H13B,H13C)
```

This report has been created with Olex2, compiled on 2016.09.09 svn.r3337 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Variable temperature ^{1}H NMR spectra of **7** (600 MHz)

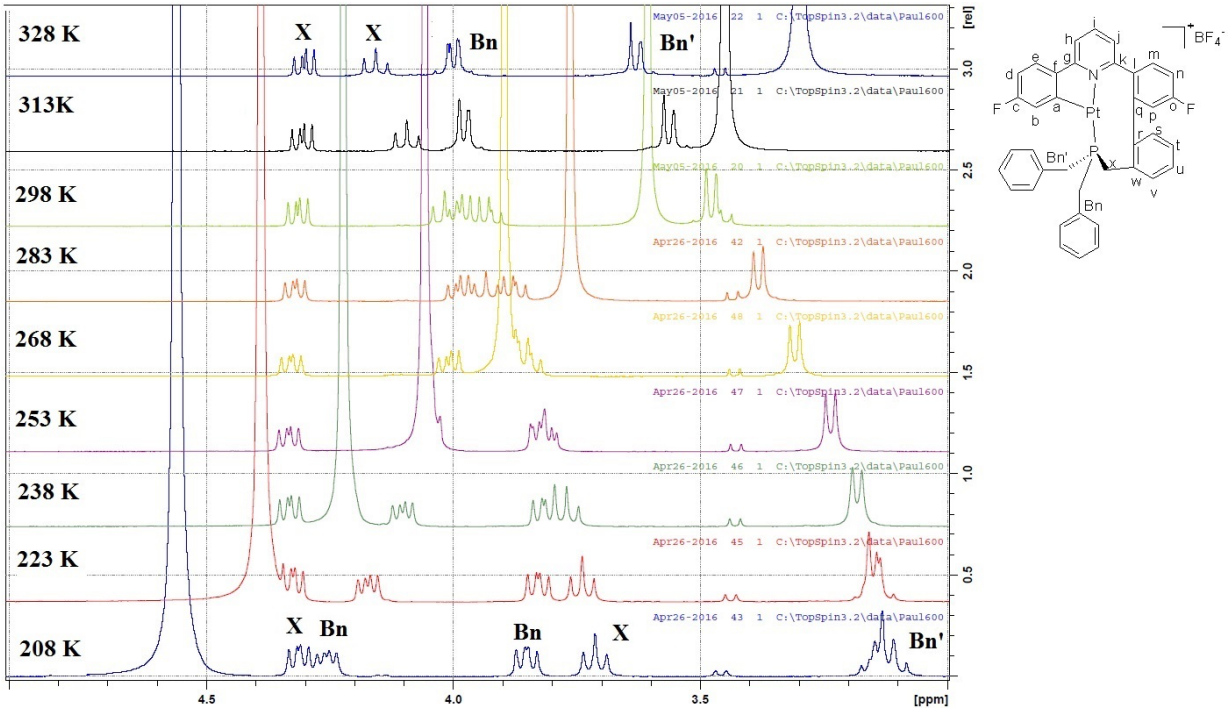

Fig SI9 *The benzyl region of the 1H NMR spectrum of 7 (600 MHz)*

At 208K five resonances are seen, though the one at 3.1ppm has relative integral 2 and appears to be a composite of two signals. At 328K the relative integrals are 1:1:2:2 for the signals labeled X, X, Bn, Bn'. We can extrapolate and suggest that the two X signals will have coalesced at about 358K.

Taking the two "X" peaks as being about 370 Hz apart at 208K, with a coalescence temperature at about 358K, we can calculate a barrier to coalescence to be 68 kJmol^{-1}.

Taking the two "Bn" peaks as being about 240 Hz apart at 208K, with a coalescence temperature at about 310K, we can calculate a barrier to coalescence to be 57 kJmol^{-1}.

Given the uncertainties associated with finding the low temperature limits, the coalescence temperatures, and that the two values above are for the same process, we suggest that a realistic value is 62±8 kJmol^{-1}.

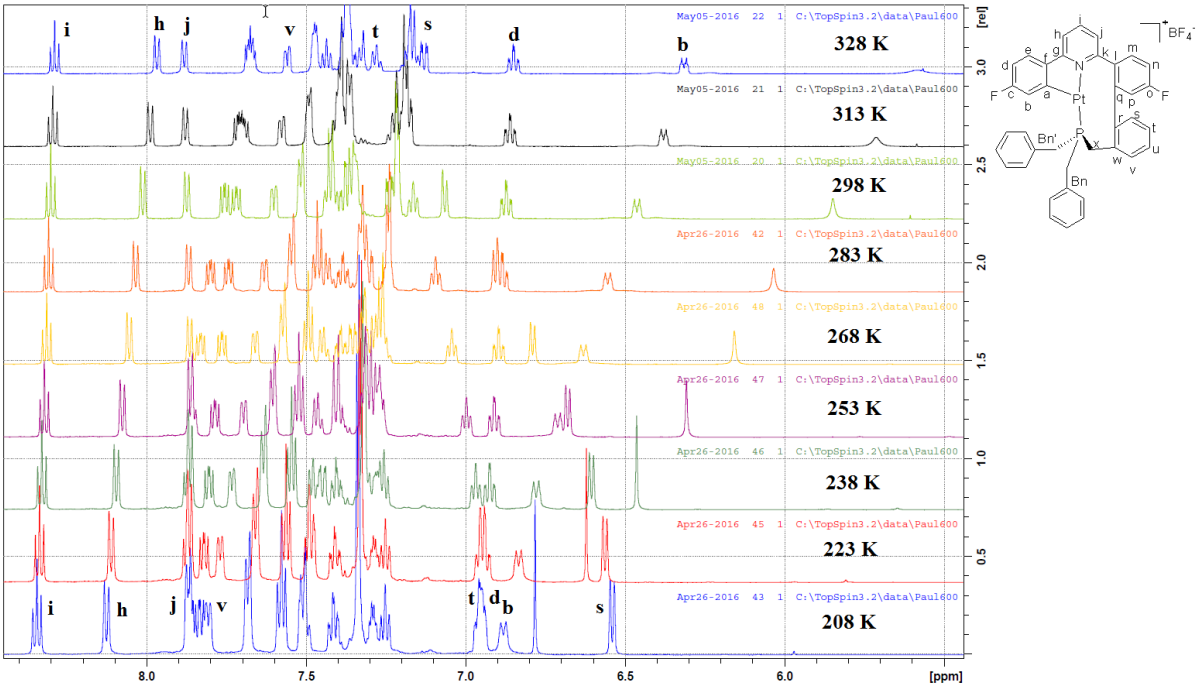

Fig SI10 *The aromatic region of the 1H NMR spectrum of 7 (600 MHz)*

Some of the resonances move quite dramatically, but they are all individual, and cannot coalesce.

A comparison of the NMR spectra of **5** with that of **7**

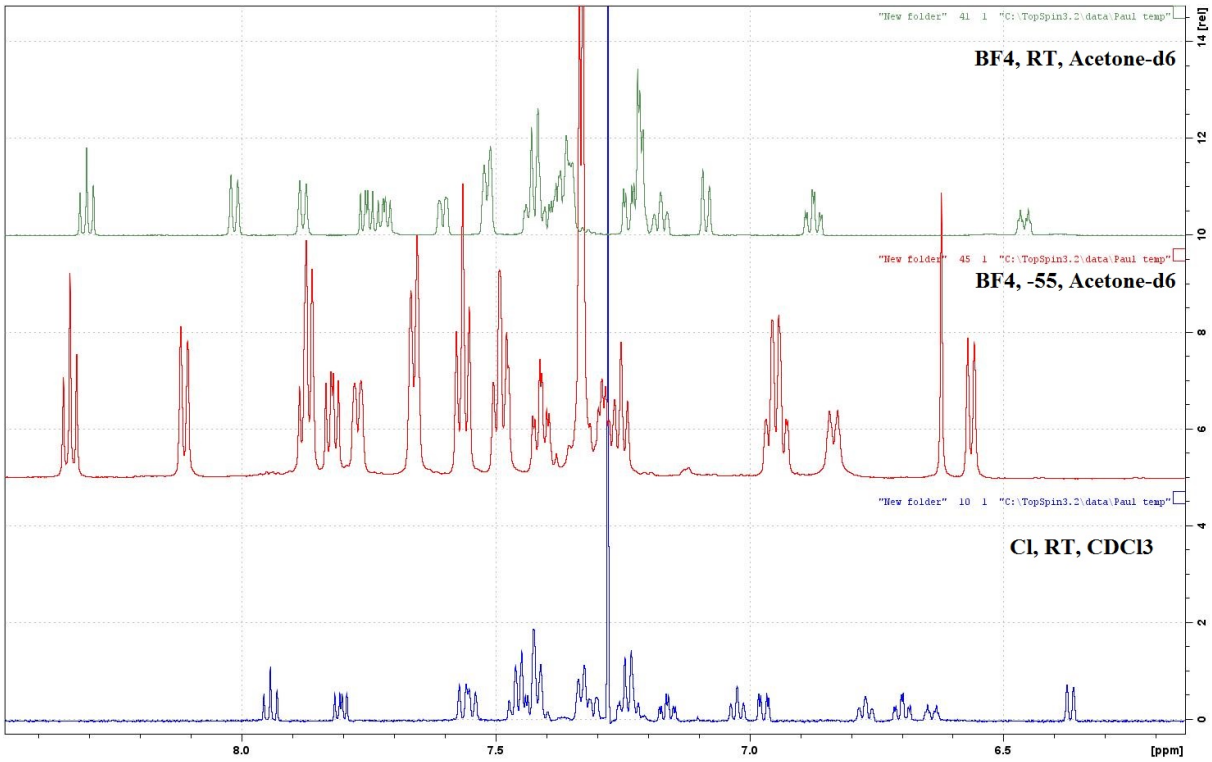

Fig SI1 *The aromatic region of the 1H NMR spectrum of 7(top two traces) and* ***5*** *(bottom trace) (600 MHz)*

The NMR spectrum of the aromatic region on the non-fluxional **5** (bottom) more closely resembles that of the fluxional **7** (upper traces) at the lower temperature (-55°C, middle) rather than the higher temperature (25°C), in keeping with the idea that, when the motion in **7** is frozen out, its structure resembles that of **5**.

Kinetic analysis of the isomerization of **a-Me7** to **b-Me7**

A sample of a mixture of **a-Me7** to **b-Me7**was generated in acetone from **Me-2(t)**, filtered and then sealed into an NMR tube. NMR spectra were recorded at hourly intervals for the first 24 hours, then less frequently, as recorded in the table below, for a total of 170 hours.
The normalized integrals for the methyl group resonances of **a-Me7** to **b-Me7** in the ^{1}H NMR are given columns 2 and 3 in the table below. Fig S112 plots these values versus time (hours).

The final column was generated by applying a linear adjustment to the amount of **a-Me7**, in order to give the best fit to values (i.e. such that the value at t = ∞ is zero), see Fig SI13. In practice the value subtracted was 0.12, which gave a 99.6% fit to a first order decay. This means an equilibrium concentration of 12% **a-Me7**, 88% **b-Me7** would be the end result, i.e. K = 7.33. The rate constant, taken from the graph fit line is 0.01653 h^{-1}; but this is actually the composite of k_1 and k_{-1}. (J W Moore and R G Pearson, "Kinetics and Mechanism" Third Ed, John Wiley and Sons, p 304)
Using K = k_1/k_{-1} = 7.33 and ($k_1 + k_{-1}$) = 0.01653, we can establish that k_1 = 0.01454
this in turn gives a half-life of 47.7 hours.

hours	a-Me-7	b-Me-7	Amount of a-Me7 adjusted for a zero end point
0	0.781	0.219	0.661
1	0.775	0.225	0.655
2	0.765	0.235	0.645
3	0.752	0.248	0.632
4	0.738	0.262	0.618
5	0.732	0.268	0.612
6	0.717	0.283	0.597
7	0.703	0.297	0.583
8	0.701	0.299	0.581
9	0.690	0.310	0.570
10	0.685	0.315	0.565
11	0.670	0.330	0.550
12	0.662	0.338	0.542
13	0.656	0.344	0.536
14	0.644	0.356	0.524
15	0.641	0.359	0.521
16	0.622	0.378	0.502
17	0.618	0.382	0.498
18	0.623	0.377	0.503
19	0.609	0.391	0.489
20	0.595	0.405	0.475

21	0.583	0.417	0.463
22	0.584	0.416	0.464
23	0.575	0.425	0.455
24	0.565	0.435	0.445
26	0.558	0.442	0.438
28	0.552	0.448	0.432
30	0.532	0.468	0.412
32	0.516	0.484	0.396
34	0.504	0.496	0.384
36	0.491	0.509	0.371
38	0.469	0.531	0.349
40	0.459	0.541	0.339
42	0.453	0.547	0.333
44	0.435	0.565	0.315
46	0.426	0.574	0.306
48	0.415	0.585	0.295
50	0.407	0.593	0.287
52	0.405	0.595	0.285
54	0.386	0.614	0.266
56	0.382	0.618	0.262
58	0.370	0.630	0.250
60	0.366	0.634	0.246
62	0.363	0.637	0.243
64	0.350	0.650	0.230
75	0.323	0.677	0.203
77	0.311	0.689	0.191
79	0.307	0.693	0.187
81	0.305	0.695	0.185
83	0.296	0.704	0.176
85	0.286	0.714	0.166
87	0.283	0.717	0.163
88	0.282	0.718	0.162
93	0.259	0.741	0.139
95	0.257	0.743	0.137
97	0.245	0.755	0.125
99	0.243	0.757	0.123
101	0.240	0.760	0.120
103	0.236	0.764	0.116
105	0.227	0.773	0.107
107	0.230	0.770	0.110
110	0.223	0.777	0.103
116	0.212	0.788	0.092
133	0.200	0.800	0.080
159	0.162	0.838	0.042
170	0.168	0.832	0.048

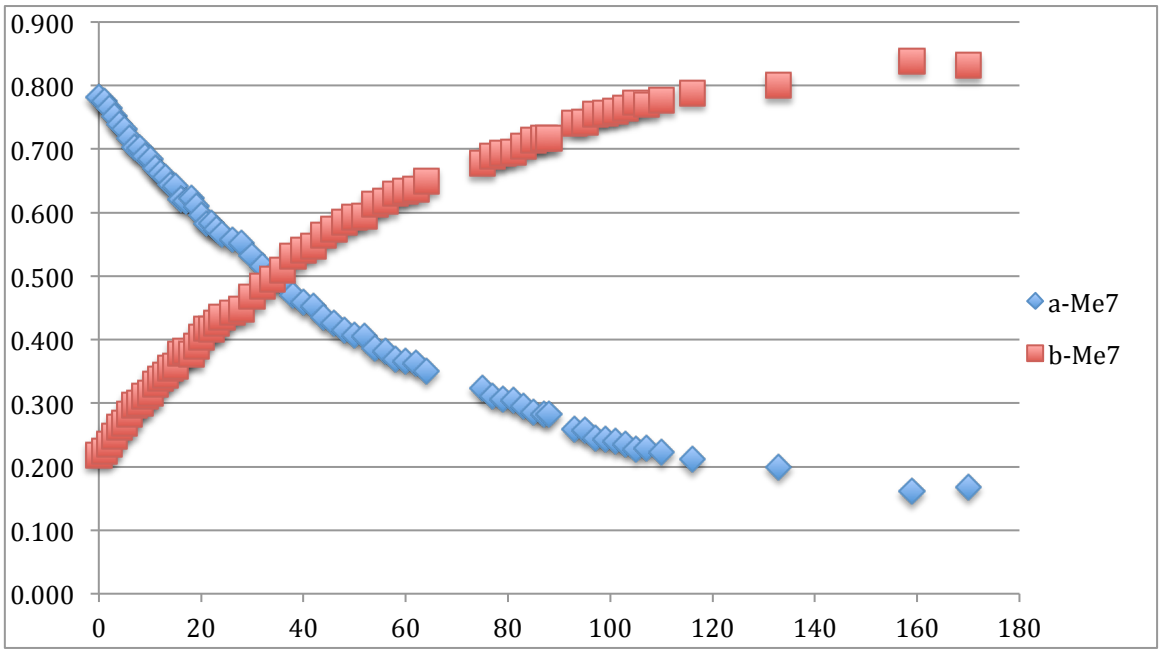

Fig SI8 *The normalized quantities of **a-Me7** and **b-Me7** as a function of time*

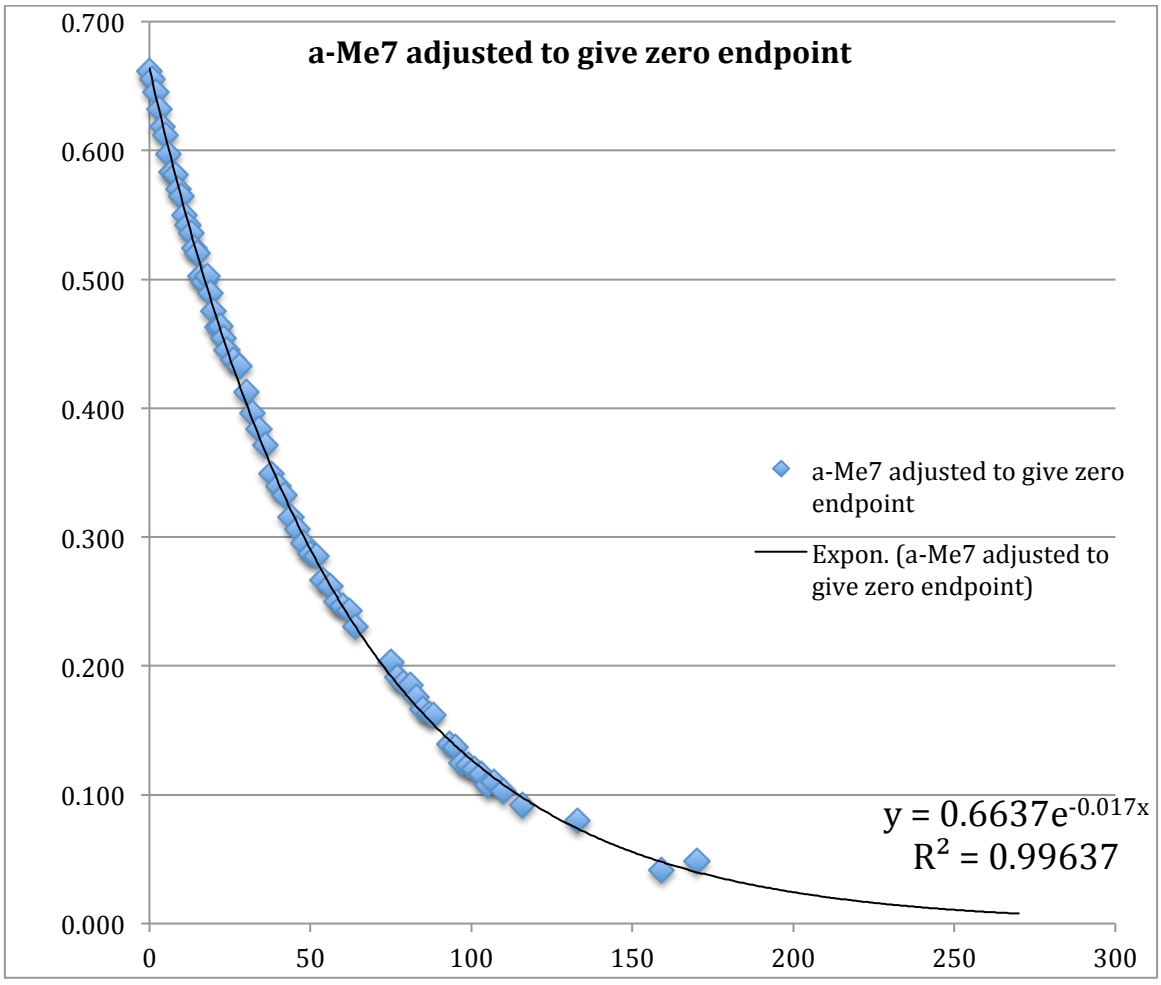

Fig SI8 *The quantity of **a-Me7** as a function of time*