Supporting Information for

Long-lived Five-Coordinate Platinum(IV) Intermediates: Regiospecific C-C Coupling

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Contents:

2t-Pr
ps20

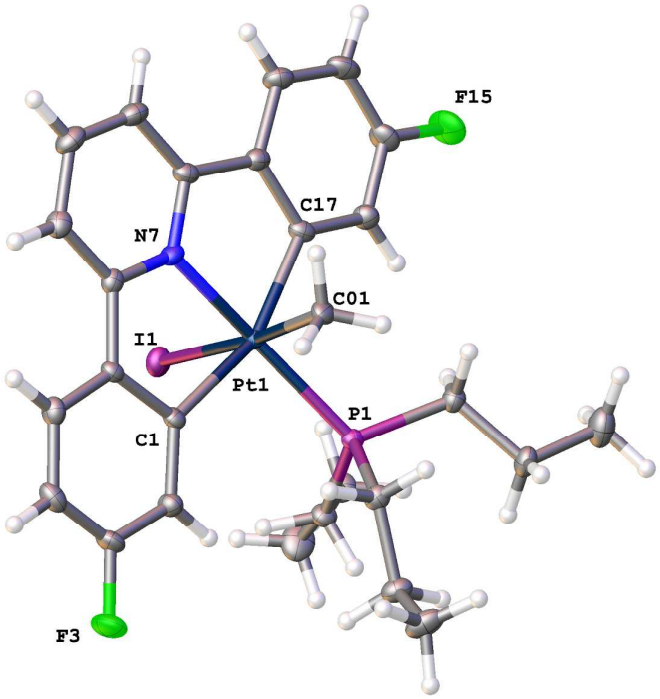

Figure SI1 *Solid state structure of ps20 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level.*

Crystal structure determination of [ps20]
The asymmetric unit contains the double C-metallated Pt complex containing tripropylphosphine with trans addition of methyl iodide.
Four times all this in the unit cell.

Possible pi-pi interaction from the very edge of symmetry related complexes.
Interaction defined by atoms used to define mean planes through interacting systems and closest atomic contact.

The interacting complexes are related by an inversion centre so they are parallel.
Closest atomic contact C4 - C9_$1 3.3085 (0.0056) Angstroms

Further pi stacking information from Olex2
For plane C1-C6-C5-C4-C3-C2
N7-C11-C10-C9-C8-C7@3_665 (1-X,1-Y,-Z)
angle: 1.650, centroid-centroid distance: 3.885, shift distance 2.031
For plane C17-C16-C15-C14-C13-C12
No interactions found
For plane N7-C11-C10-C9-C8-C7
No interactions found

The ligand angles in the complex are characterized by two mean planes orthogonal to each other and the deviation of atoms out of these defined planes

* -0.0727 (0.0017) C1
* 0.1159 (0.0018) N7
* -0.0658 (0.0016) C17
* 0.0804 (0.0011) P1
* -0.0578 (0.0012) Pt1

Rms deviation of fitted atoms = 0.0811

And

* 0.1833 (0.0019) C1
* 0.1857 (0.0019) C17
* -0.0800 (0.0015) I1
* -0.0997 (0.0019) C01
* -0.1893 (0.0014) Pt1

Rms deviation of fitted atoms = 0.1551

Symmetry operator used to define symmetry equivalent atoms discussed in above discussion was
$1 1-X,1-Y,-Z

Experimental

Single crystals of $C_{27}H_{33}F_2INPPt$ **[ps20]** were grown from deuterated 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. 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. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{27}H_{33}F_2INPPt$ (M =762.50 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 12.70561(18) Å, b = 14.9295(3) Å, c = 13.7143(2) Å, β = 93.1156(13)°, V = 2597.58(7) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 6.682 mm^{-1}, *Dcalc* = 1.950 g/cm^3, 19825 reflections measured (5.056° ≤ 2Θ ≤ 65.242°), 8654 unique (R_{int} = 0.0297, R_{sigma} = 0.0414) which were used in all calculations. The final R_1 was 0.0271 (I > 2σ(I)) and wR_2 was 0.0867 (all data).

Table S1 Crystal data and structure refinement for ps20.

Identification code	ps20
Empirical formula	$C_{27}H_{33}F_2INPPt$
Formula weight	762.50
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.70561(18)
b/Å	14.9295(3)
c/Å	13.7143(2)
α/°	90
β/°	93.1156(13)
γ/°	90
Volume/Å^3	2597.58(7)
Z	4
ρ_{calc}g/cm^3	1.950
μ/mm^{-1}	6.682
F(000)	1464.0
Crystal size/mm^3	0.3 × 0.12 × 0.1 colourless block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.056 to 65.242
Index ranges	-18 ≤ h ≤ 19, -12 ≤ k ≤ 22, -19 ≤ l ≤ 20
Reflections collected	19825
Independent reflections	8654 [R_{int} = 0.0297, R_{sigma} = 0.0414]
Data/restraints/parameters	8654/0/302
Goodness-of-fit on F^2	1.149
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0672
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0867
Largest diff. peak/hole / e Å^{-3}	1.07/-1.99

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps20. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	3725(3)	4308(3)	1693(2)	14.0(7)
P1	3838.6(7)	3066.0(7)	3648.8(6)	13.19(17)
C01	4247(3)	5073(3)	3694(3)	19.3(8)
I1	5784.9(2)	2815.1(2)	1649.7(2)	19.66(6)
Pt1	4857.5(2)	4045.6(2)	2823.4(2)	11.73(5)
C2	2795(3)	3865(3)	1401(3)	17.7(7)
C3	2170(3)	4193(3)	619(3)	20.1(8)
F3	1270(2)	3743(2)	361.4(18)	31.2(6)
C4	2414(3)	4946(3)	99(3)	21.4(8)
C5	3354(3)	5375(3)	352(3)	19.1(7)
C6	4011(3)	5060(3)	1128(2)	14.3(7)
C7	5036(3)	5480(3)	1388(2)	15.6(7)
N7	5579(2)	5067(2)	2136(2)	14.8(6)
C8	5481(3)	6217(3)	948(3)	19.9(8)
C9	6454(3)	6522(3)	1318(3)	22.9(8)
C10	6968(3)	6112(3)	2102(3)	21.6(8)
C11	6517(3)	5369(3)	2526(3)	16.6(7)
C12	6920(3)	4841(3)	3371(3)	17.0(7)
C13	7906(3)	5030(3)	3838(3)	21.5(8)
C14	8287(3)	4504(3)	4604(3)	24.5(9)
C15	7686(3)	3786(3)	4867(3)	22.6(8)
F15	8064(2)	3251(2)	5602.8(18)	35.6(7)

C16	6718(3)	3582(3)	4430(3)	18.1(7)
C17	6285(3)	4118(3)	3668(3)	16.4(7)
C18	4299(3)	2841(3)	4910(2)	17.7(7)
C19	3515(3)	2379(3)	5549(3)	21.6(8)
C20	4052(4)	2058(4)	6504(3)	33.3(11)
C21	2518(3)	3552(3)	3772(3)	16.7(7)
C22	1563(3)	2924(3)	3728(3)	21.4(8)
C23	572(3)	3444(3)	3959(3)	27.8(9)
C24	3665(3)	1962(3)	3096(3)	17.4(7)
C25	4551(3)	1298(3)	3372(3)	20.2(8)
C26	4511(4)	478(3)	2705(3)	32.8(10)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps20. 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}
C1	15.9(16)	12.5(17)	13.5(15)	-2.7(13)	-0.8(12)	0.2(13)
P1	13.3(4)	11.9(4)	14.5(4)	-1.4(3)	1.0(3)	-0.2(3)
C01	22.2(18)	20(2)	15.3(16)	-5.4(15)	1.8(13)	-4.5(15)
I1	22.07(12)	18.34(13)	19.04(12)	0.69(9)	5.53(9)	4.23(10)
Pt1	11.35(7)	10.87(7)	12.90(7)	-0.30(5)	0.16(4)	-0.11(5)
C2	17.4(17)	17.5(19)	17.9(17)	1.3(14)	-1.1(13)	-0.8(14)
C3	16.1(17)	23(2)	20.9(18)	-2.2(15)	-5.8(14)	-0.9(15)
F3	23.7(13)	35.6(16)	33.0(13)	3.2(12)	-12.6(10)	-8.8(11)
C4	24.8(19)	21(2)	17.5(17)	-3.3(15)	-5.0(14)	5.3(16)
C5	23.7(18)	16.5(19)	16.9(16)	2.5(14)	0.8(14)	3.0(15)
C6	14.4(15)	14.5(18)	13.8(15)	-3.1(13)	-1.3(12)	0.2(13)
C7	18.4(17)	13.2(18)	15.5(15)	-0.3(13)	3.6(13)	1.6(14)
N7	16.0(14)	10.7(15)	17.8(14)	-0.3(11)	3.0(11)	-2.3(11)
C8	24.9(19)	14.3(18)	20.8(17)	0.7(15)	2.6(14)	0.9(15)
C9	23.5(19)	16(2)	30(2)	2.1(16)	8.0(16)	-2.5(16)
C10	17.9(18)	20(2)	26.9(19)	-1.2(16)	3.9(15)	-4.8(15)
C11	15.0(16)	15.7(18)	18.9(16)	-3.7(14)	-0.3(13)	-1.2(14)
C12	15.5(16)	17.2(19)	18.5(16)	-2.9(14)	1.8(13)	-1.6(14)
C13	14.8(17)	21(2)	28(2)	-1.6(16)	1.6(14)	-1.1(15)
C14	14.2(17)	30(2)	29(2)	-8.1(18)	-3.8(14)	0.9(16)
C15	16.4(18)	27(2)	23.5(19)	0.0(17)	-6.0(14)	4.9(16)
F15	30.7(14)	39.0(18)	35.2(13)	11.3(12)	-16.1(11)	2.1(12)
C16	15.2(16)	19(2)	20.2(17)	1.7(15)	-1.3(13)	1.5(14)
C17	14.0(16)	16.1(19)	18.9(17)	-4.1(14)	-1.2(13)	0.5(13)
C18	18.9(17)	17.1(19)	17.0(16)	0.7(14)	2.4(13)	0.3(14)
C19	23.3(19)	24(2)	18.0(17)	5.0(16)	4.5(14)	1.6(16)
C20	37(3)	39(3)	25(2)	9(2)	7.2(18)	8(2)
C21	16.0(16)	14.0(18)	20.1(16)	0.8(14)	2.0(13)	2.3(14)
C22	17.9(18)	17(2)	29(2)	1.1(16)	2.4(15)	-1.5(15)
C23	16.5(18)	21(2)	47(2)	6(2)	6.8(17)	1.4(16)
C24	19.9(17)	14.5(18)	17.8(16)	-3.8(14)	0.7(13)	-1.4(14)
C25	26(2)	10.8(18)	23.5(18)	0.4(15)	2.0(15)	3.6(15)
C26	49(3)	17(2)	34(2)	-4.8(19)	9(2)	3(2)

Table S4 Bond Lengths for ps20.

Atom	Atom	Length/Å
C1	Pt1	2.094(3)
C1	C2	1.394(5)
C1	C6	1.422(5)
P1	Pt1	2.2925(9)
P1	C18	1.827(4)
P1	C21	1.844(4)
P1	C24	1.823(4)
C01	Pt1	2.117(4)
I1	Pt1	2.7497(3)
Pt1	N7	2.037(3)
Pt1	C17	2.101(4)
C2	C3	1.388(5)
C3	F3	1.356(5)
C3	C4	1.376(6)
C4	C5	1.383(6)
C5	C6	1.399(5)
C6	C7	1.472(5)
C7	N7	1.354(5)
C7	C8	1.389(5)
N7	C11	1.356(5)
C8	C9	1.388(6)
C9	C10	1.372(6)
C10	C11	1.390(5)
C11	C12	1.471(5)
C12	C13	1.405(5)
C12	C17	1.419(5)
C13	C14	1.378(6)
C14	C15	1.376(6)
C15	F15	1.355(5)
C15	C16	1.372(5)
C16	C17	1.404(5)
C18	C19	1.527(5)
C19	C20	1.521(6)
C21	C22	1.532(5)
C22	C23	1.526(5)
C24	C25	1.533(5)
C25	C26	1.527(6)

Table S5 Bond Angles for ps20.

Atom	Atom	Atom	Angle/°
C2	C1	Pt1	131.4(3)
C2	C1	C6	117.1(3)
C5	C6	C7	121.7(3)
N7	C7	C6	113.4(3)

C6	C1	Pt1	111.4(2)
C18	P1	Pt1	115.11(13)
C18	P1	C21	103.42(17)
C21	P1	Pt1	109.59(13)
C24	P1	Pt1	115.50(12)
C24	P1	C18	104.66(18)
C24	P1	C21	107.65(18)
C1	Pt1	P1	95.81(10)
C1	Pt1	C01	91.40(14)
C1	Pt1	I1	89.44(10)
C1	Pt1	C17	159.43(15)
P1	Pt1	I1	97.72(2)
C01	Pt1	P1	87.11(11)
C01	Pt1	I1	175.00(11)
N7	Pt1	C1	79.96(13)
N7	Pt1	P1	170.60(9)
N7	Pt1	C01	84.63(14)
N7	Pt1	I1	90.67(9)
N7	Pt1	C17	79.61(14)
C17	Pt1	P1	104.75(11)
C17	Pt1	C01	89.05(14)
C17	Pt1	I1	88.43(10)
C3	C2	C1	119.7(4)
F3	C3	C2	117.7(4)
F3	C3	C4	118.7(3)
C4	C3	C2	123.6(4)
C3	C4	C5	117.6(3)
C4	C5	C6	120.5(4)
C1	C6	C7	117.0(3)
C5	C6	C1	121.4(3)
N7	C7	C8	119.2(3)
C8	C7	C6	127.4(3)
C7	N7	Pt1	117.9(2)
C7	N7	C11	123.3(3)
C11	N7	Pt1	118.3(2)
C9	C8	C7	118.5(4)
C10	C9	C8	121.1(4)
C9	C10	C11	119.6(4)
N7	C11	C10	118.3(3)
N7	C11	C12	113.2(3)
C10	C11	C12	128.5(3)
C13	C12	C11	121.0(3)
C13	C12	C17	121.9(4)
C17	C12	C11	117.0(3)
C14	C13	C12	120.0(4)
C15	C14	C13	117.8(4)
F15	C15	C14	118.3(3)
F15	C15	C16	117.9(4)
C16	C15	C14	123.7(4)
C15	C16	C17	120.2(4)
C12	C17	Pt1	111.6(3)
C16	C17	Pt1	132.2(3)
C16	C17	C12	116.2(3)
C19	C18	P1	116.2(3)
C20	C19	C18	111.1(3)
C22	C21	P1	118.6(3)
C23	C22	C21	110.0(3)
C25	C24	P1	114.3(3)
C26	C25	C24	111.7(4)

Table S6 Torsion Angles for ps20.

A	B	C	D	Angle/°
C1	C2	C3	F3	−179.8(3)
C1	C2	C3	C4	0.1(6)
C1	C6	C7	N7	1.1(5)
C1	C6	C7	C8	−179.8(4)
P1	C18	C19	C20	168.4(3)
P1	C21	C22	C23	173.6(3)
P1	C24	C25	C26	−165.8(3)
Pt1	C1	C2	C3	179.1(3)
Pt1	C1	C6	C5	−177.9(3)
Pt1	C1	C6	C7	3.1(4)
Pt1	P1	C18	C19	165.9(3)
Pt1	P1	C21	C22	145.0(3)
Pt1	P1	C24	C25	85.2(3)
Pt1	N7	C11	C10	−175.0(3)
Pt1	N7	C11	C12	4.8(4)
C2	C1	C6	C5	4.0(5)
C2	C1	C6	C7	−175.0(3)
C2	C3	C4	C5	2.4(6)
C3	C4	C5	C6	−1.6(6)
F3	C3	C4	C5	−177.7(3)
C4	C5	C6	C1	−1.5(6)
C4	C5	C6	C7	177.4(3)
C5	C6	C7	N7	−177.9(3)
C5	C6	C7	C8	1.2(6)
C6	C1	C2	C3	−3.2(5)
C6	C7	N7	Pt1	−5.1(4)
C6	C7	N7	C11	−176.6(3)
C6	C7	C8	C9	178.8(4)
C7	N7	C11	C10	−3.4(5)
C7	N7	C11	C12	176.4(3)
C7	C8	C9	C10	−0.4(6)
N7	C7	C8	C9	−2.1(5)
N7	C11	C12	C13	176.9(3)
N7	C11	C12	C17	−1.0(5)
C8	C7	N7	Pt1	175.7(3)
C8	C7	N7	C11	4.2(5)
C8	C9	C10	C11	1.2(6)
C9	C10	C11	N7	0.7(6)
C9	C10	C11	C12	−179.1(4)
C10	C11	C12	C13	−3.3(6)
C10	C11	C12	C17	178.8(4)
C11	C12	C13	C14	−177.4(4)
C11	C12	C17	Pt1	−2.9(4)
C11	C12	C17	C16	175.5(3)
C12	C13	C14	C15	1.8(6)
C13	C12	C17	Pt1	179.2(3)
C13	C12	C17	C16	−2.4(5)
C13	C14	C15	F15	178.4(4)
C13	C14	C15	C16	−2.0(6)
C14	C15	C16	C17	−0.1(6)
C15	C16	C17	Pt1	−179.8(3)
C15	C16	C17	C12	2.2(5)
F15	C15	C16	C17	179.5(3)
C17	C12	C13	C14	0.4(6)
C18	P1	C21	C22	−91.7(3)
C18	P1	C24	C25	−42.5(3)
C21	P1	C18	C19	46.4(3)
C21	P1	C24	C25	−152.0(3)
C24	P1	C18	C19	−66.2(3)
C24	P1	C21	C22	18.7(3)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps20.

Atom	*x*	*y*	*z*	U(eq)
H01A	4773	5550	3789	29
H01B	4080	4827	4330	29
H01C	3605	5318	3367	29
H2	2591	3341	1735	21
H4	1953	5164	−417	26
H5	3554	5888	−4	23
H8	5126	6506	408	24
H9	6771	7022	1022	27
H10	7629	6334	2355	26

H13	8311	5521	3626	26
H14	8944	4633	4939	29
H16	6339	3076	4643	22
H18A	4940	2464	4900	21
H18B	4508	3417	5221	21
H19A	2943	2802	5689	26
H19B	3196	1860	5192	26
H20A	4615	1636	6366	50
H20B	3533	1761	6897	50
H20C	4353	2573	6865	50
H21A	2528	3874	4403	20
H21B	2402	4005	3250	20
H22A	1470	2657	3068	26
H22B	1680	2433	4206	26
H23A	503	3971	3534	42
H23B	624	3636	4643	42
H23C	-47	3058	3847	42
H24A	2989	1708	3294	21
H24B	3614	2031	2377	21
H25A	5240	1600	3329	24
H25B	4489	1102	4057	24
H26A	4593	668	2029	49
H26B	3831	175	2750	49
H26C	5082	66	2907	49

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
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C19(H19A,H19B), C21(H21A,H21B), C22(H22A,H22B), C24(H24A,
 H24B), C25(H25A,H25B)
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)
2.c Idealised Me refined as rotating group:
 C01(H01A,H01B,H01C), C20(H20A,H20B,H20C), C23(H23A,H23B,H23C), C26(H26A,H26B,
 H26C)
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This report has been created with Olex2, compiled on 2015.01.26 svn.r3151 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

2c-Bu
ps4

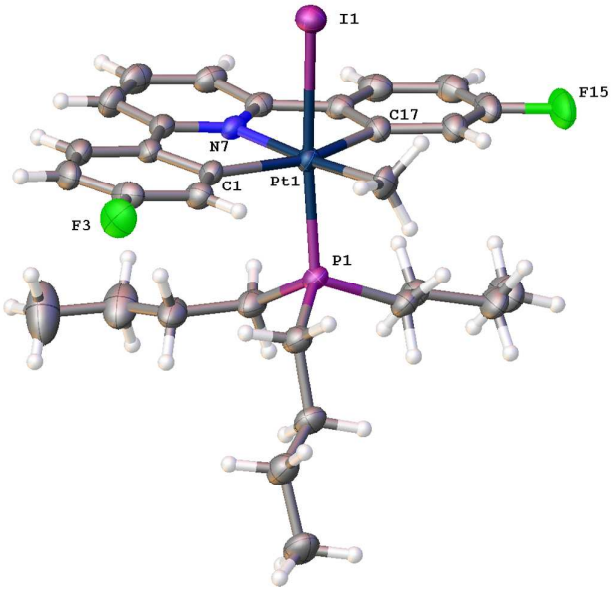

Figure SI2 Solid state structure of the major component in ps4 (the methyl-iodo)

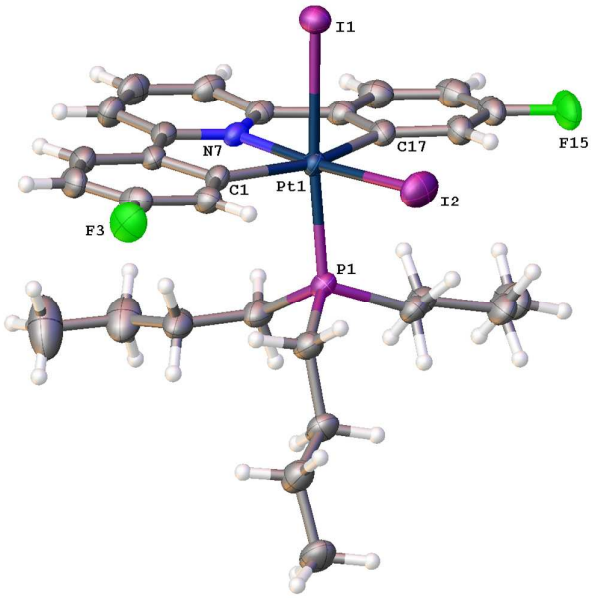

Figure SI3 Solid state structure of the minor component in ps4 (the di-iodide)

The asymmetric unit contains a Pt complex with a double C alkylated bis 4-fluorophenyl pyridine, a triButylphosphine and iodide and a position that is occupied by either another iodide or a methyl.
The methyl/iodo disorder was linked to a free variable and refined to an occupancy of 87:13 (methyl:iodo)
Both substituents were refined isotropically
There is 4 times all this in the unit cell

There is possibly a very off set pi stacking interaction between two complexes related by an inversion center. The interacting pi systems are parallel (as related by an inversion centre) with the closest atomic contact 3.2981 (0.0061) Angstroms C13 - C9_$1
Symmetry operator used to generate equivalent atoms $1 1-X,-Y,1-Z
But really there is virtually no overlap of the atoms (check with Mercury)

Experimental

Single crystals of $C_{29.87}H_{38.6}F_2I_{1.13}NPPt$ **[ps4]** were grown from chloroform. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil on an Oxford Diffraction 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 XS [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. (2008). Acta Cryst. A64, 112-122.
6 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
7

Crystal structure determination of [ps4]

Crystal Data for $C_{29.86638}H_{38.59914}F_2I_{1.13362}NPPt$ (M =819.53 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.2244(3) Å, b = 17.8517(5) Å, c = 16.3216(4) Å, β = 94.312(3)°, V = 2970.62(13) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 5.987 mm^{-1}, *Dcalc* = 1.832 g/cm^3, 34214 reflections measured (7.018° ≤ 2Θ ≤ 63.212°), 9116 unique (R_{int} = 0.0420, R_{sigma} = 0.0351) which were used in all calculations. The final R_1 was 0.0342 (I > 2σ(I)) and wR_2 was 0.0856 (all data).

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
 At 1.5 times of:
  All C(H,H,H) groups
2. Others
 Sof(I2)=1-FVAR(1)
 Sof(C100)=Sof(H10A)=Sof(H10B)=Sof(H10C)=FVAR(1)
3.a Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C19(H19A,H19B), C20(H20A,H20B), C22(H22A,H22B), C23(H23A,
 H23B), C24(H24A,H24B), C26(H26A,H26B), C27(H27A,H27B), C28(H28A,H28B)
3.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)
3.c Idealised Me refined as rotating group:
 C100(H10A,H10B,H10C), C21(H21A,H21B,H21C), C25(H25A,H25B,H25C), C29(H29A,H29B,
 H29C)
```

This report has been created with Olex2, compiled on 2014.07.22 svn.r2960 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Table S8 Crystal data and structure refinement for ps4.

Identification code	ps4
Empirical formula	$C_{29.87}H_{38.6}F_2I_{1.13}NPPt$
Formula weight	819.53
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2244(3)
b/Å	17.8517(5)
c/Å	16.3216(4)
α/°	90
β/°	94.312(3)
γ/°	90
Volume/Å^3	2970.62(13)
Z	4
ρ_{calc}g/cm^3	1.832
μ/mm^{-1}	5.987
F(000)	1584.0
Crystal size/mm^3	0.45 × 0.45 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.018 to 63.212
Index ranges	-13 ≤ h ≤ 14, -25 ≤ k ≤ 23, -24 ≤ l ≤ 22
Reflections collected	34214
Independent reflections	9116 [R_{int} = 0.0420, R_{sigma} = 0.0351]
Data/restraints/parameters	9116/0/339
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0804
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.0856
Largest diff. peak/hole / e Å^{-3}	1.70/-1.50

Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps4. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	3552.3(2)	2219.4(2)	5436.3(2)	22.29(5)
I1	6101.5(3)	2180.0(2)	5086.4(2)	31.18(7)
C100	3990(6)	3194(4)	6081(4)	33.6(12)
I2	4138(3)	3484.5(17)	6279(2)	46.4(10)

C1	3109(4)	2638(2)	4251(2)	25.2(7)
C2	3038(4)	3372(2)	3959(2)	30.9(8)
C3	2796(4)	3495(2)	3118(3)	34.4(9)
F3	2735(3)	4219.0(15)	2854.5(17)	47.1(7)
C4	2608(4)	2940(3)	2549(3)	36.2(9)
C5	2672(4)	2208(2)	2827(3)	31.7(9)
C6	2923(4)	2056(2)	3665(2)	25.9(7)
C7	2994(4)	1281(2)	3975(2)	26.6(7)
N7	3262(3)	1242.7(17)	4799.4(19)	23.9(6)
C8	2850(4)	614(2)	3541(3)	35.0(9)
C9	3010(4)	-63(2)	3957(3)	37.8(10)
C10	3314(4)	-79(2)	4798(3)	33.9(9)
C11	3433(4)	596(2)	5225(2)	26.6(7)
C12	3803(4)	704(2)	6104(2)	28.8(8)
C13	3982(4)	101(3)	6643(3)	35.7(9)
C14	4367(4)	224(3)	7465(3)	39.9(10)
C15	4570(4)	950(3)	7713(3)	38.5(10)
F15	4947(3)	1071(2)	8521.0(15)	53.2(8)
C16	4400(4)	1562(3)	7206(2)	32.4(8)
C17	3986(4)	1455(2)	6375(2)	27.8(8)
P1	1463.4(10)	2348.8(6)	5819.3(6)	27.2(2)
C18	327(4)	1651(3)	5386(3)	34.9(9)
C19	-130(4)	1757(3)	4481(3)	40.5(10)
C20	-635(6)	1014(4)	4097(3)	61.0(16)
C21	-1055(8)	1097(5)	3214(4)	90(3)
C22	760(4)	3255(2)	5515(3)	33.2(9)
C23	-561(4)	3441(2)	5837(3)	34.1(9)
C24	-1180(5)	4142(3)	5449(3)	41.5(10)
C25	-2429(5)	4362(3)	5816(3)	47.3(12)
C26	1335(4)	2259(2)	6932(3)	32.4(9)
C27	1138(4)	1467(3)	7255(2)	34.6(9)
C28	1290(5)	1448(3)	8189(3)	41.1(10)
C29	1085(6)	670(3)	8531(3)	55.6(14)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps4. 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	22.92(8)	25.42(7)	18.81(7)	-1.57(5)	3.35(5)	-1.
I1	26.72(13)	32.66(13)	34.52(14)	3.41(10)	4.7(1)	-1.6
C100	42(3)	30(3)	29(3)	-10(2)	3(2)	
I2	51.0(17)	34.5(16)	54.7(19)	-12.5(12)	10.3(13)	-6.
C1	25.2(18)	30.9(18)	20.2(16)	-1.0(14)	4.9(14)	-0.
C2	30.3(19)	35(2)	28.0(19)	3.4(16)	5.4(15)	2.
C3	33(2)	37(2)	34(2)	12.3(18)	7.8(17)	4.
F3	60.4(18)	39.4(14)	41.5(15)	15.3(12)	4.7(13)	5.
C4	34(2)	52(3)	22.6(18)	5.5(18)	3.1(16)	3.
C5	27.9(19)	44(2)	24.0(18)	-1.9(16)	5.5(15)	1.
C6	21.2(17)	34.7(19)	22.3(17)	-1.2(15)	4.4(14)	0.
C7	21.3(17)	33.8(19)	24.9(17)	-3.9(15)	4.3(14)	-0.
N7	21.9(14)	25.9(14)	24.6(15)	-4.7(12)	6.1(12)	-1.
C8	38(2)	36(2)	31(2)	-9.3(17)	4.0(17)	0.
C9	39(2)	33(2)	43(2)	-12.3(19)	6.9(19)	-2.
C10	33(2)	28.0(18)	42(2)	-4.1(17)	10.5(18)	0.
C11	22.0(17)	28.0(17)	30.5(18)	-1.3(15)	7.4(14)	-3.
C12	24.1(18)	34.9(19)	28.3(18)	4.9(16)	8.6(15)	1.
C13	31(2)	37(2)	40(2)	7.4(19)	7.6(18)	1.
C14	31(2)	53(3)	37(2)	16(2)	7.1(18)	
C15	27(2)	65(3)	23.9(18)	9(2)	2.8(16)	
F15	49.0(17)	86(2)	23.4(12)	12.7(14)	-2.5(11)	-3.
C16	28.7(19)	43(2)	25.4(18)	2.2(17)	2.7(15)	-2.
C17	23.3(18)	37(2)	23.1(17)	2.3(15)	4.3(14)	-1.
P1	27.3(5)	31.7(5)	23.4(4)	-2.1(4)	6.6(4)	2
C18	27.5(19)	42(2)	35(2)	-6.9(19)	8.2(16)	-4.
C19	29(2)	57(3)	37(2)	-10(2)	6.6(17)	
C20	58(3)	83(4)	44(3)	-4(3)	14(3)	-1
C21	112(6)	109(6)	47(3)	-2(4)	-5(4)	-1
C22	33(2)	37(2)	31(2)	1.4(17)	7.4(16)	5.
C23	35(2)	31.0(19)	37(2)	-3.1(17)	7.9(17)	5.
C24	48(3)	43(2)	34(2)	2.0(19)	9(2)	
C25	52(3)	45(3)	45(3)	-3(2)	8(2)	
C26	33(2)	39(2)	26.3(19)	-2.5(16)	8.3(16)	3.
C27	31(2)	47(2)	27.3(19)	2.4(18)	8.3(16)	0.
C28	38(2)	60(3)	26(2)	5(2)	9.3(18)	
C29	51(3)	76(4)	41(3)	17(3)	10(2)	

Table S11 Bond Lengths for ps4.

Atom	Atom	Length/Å
Pt1	I1	2.7108(3)
Pt1	C100	2.065(7)
Pt1	I2	2.688(3)
Pt1	C1	2.091(4)
Pt1	N7	2.040(3)
Pt1	C17	2.074(4)
Pt1	P1	2.2818(11)
C1	C2	1.394(5)
C1	C6	1.416(5)
C2	C3	1.394(6)
C3	F3	1.363(5)
C3	C4	1.360(6)
C4	C5	1.384(6)
C5	C6	1.398(5)
C6	C7	1.474(6)
C7	N7	1.354(5)
C7	C8	1.388(5)
N7	C11	1.352(5)
C8	C9	1.388(6)
C9	C10	1.386(6)
C10	C11	1.391(5)
C11	C12	1.469(5)
C12	C13	1.393(6)
C12	C17	1.420(6)
C13	C14	1.386(6)
C14	C15	1.368(7)
C15	F15	1.363(5)
C15	C16	1.374(6)
C16	C17	1.404(5)
P1	C18	1.810(4)
P1	C22	1.824(4)
P1	C26	1.838(4)
C18	C19	1.527(6)
C19	C20	1.541(7)
C20	C21	1.480(8)
C22	C23	1.522(6)
C23	C24	1.519(6)
C24	C25	1.503(7)
C26	C27	1.528(6)
C27	C28	1.521(6)
C28	C29	1.517(7)

Table S12 Bond Angles for ps4.

Atom	Atom	Atom	Angle/°
C100	Pt1	I1	87.38(18)
C100	Pt1	C1	101.19(19)
C100	Pt1	C17	98.7(2)
C100	Pt1	P1	86.93(18)
I2	Pt1	I1	87.08(7)
C1	Pt1	I1	87.67(11)
C1	Pt1	I2	101.38(12)
C1	Pt1	P1	94.30(11)
N7	Pt1	I1	88.61(9)
N7	Pt1	C100	175.85(19)
N7	Pt1	I2	175.51(11)
N7	Pt1	C1	79.71(14)
N7	Pt1	C17	80.15(14)
N7	Pt1	P1	97.05(9)
C17	Pt1	I1	89.01(11)
C17	Pt1	I2	98.49(13)
C17	Pt1	C1	159.65(15)
C17	Pt1	P1	90.97(11)
P1	Pt1	I1	174.25(3)
P1	Pt1	I2	87.23(7)
C2	C1	Pt1	130.9(3)
C2	C1	C6	117.2(3)
C6	C1	Pt1	111.8(3)
C3	C2	C1	119.0(4)
F3	C3	C2	117.4(4)
C4	C3	C2	124.3(4)
C4	C3	F3	118.3(4)
C3	C4	C5	117.5(4)
C4	C5	C6	120.3(4)
C1	C6	C7	117.2(3)
C5	C6	C1	121.6(4)
C5	C6	C7	121.2(4)
N7	C7	C6	112.9(3)
N7	C7	C8	118.0(4)
C8	C7	C6	129.0(4)
C7	N7	Pt1	118.3(3)
C11	N7	Pt1	117.4(2)
C11	N7	C7	124.2(3)
C7	C8	C9	119.5(4)
C10	C9	C8	120.8(4)
C9	C10	C11	118.9(4)
N7	C11	C10	118.6(4)
N7	C11	C12	113.8(3)
C10	C11	C12	127.5(4)
C13	C12	C11	121.8(4)
C13	C12	C17	121.7(4)
C17	C12	C11	116.5(3)
C14	C13	C12	120.2(4)
C15	C14	C13	117.5(4)
C14	C15	C16	124.4(4)
F15	C15	C14	117.5(4)
F15	C15	C16	118.1(4)
C15	C16	C17	119.3(4)
C12	C17	Pt1	112.1(3)
C16	C17	Pt1	131.1(3)
C16	C17	C12	116.9(4)
C18	P1	Pt1	114.18(14)
C18	P1	C22	106.0(2)
C18	P1	C26	103.6(2)
C22	P1	Pt1	111.91(14)
C22	P1	C26	106.88(19)
C26	P1	Pt1	113.56(15)
C19	C18	P1	115.6(3)
C18	C19	C20	110.9(4)
C21	C20	C19	112.0(5)
C23	C22	P1	116.2(3)
C24	C23	C22	112.9(4)
C25	C24	C23	113.0(4)
C27	C26	P1	116.2(3)
C28	C27	C26	111.1(4)
C29	C28	C27	112.5(4)

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps4.

Atom	*x*	*y*	*z*	U(eq)
H10A	4842	3141	6393	50
H10B	3311	3290	6461	50
H10C	4025	3613	5696	50
H2	3152	3783	4328	37

H4	2439	3052	1982	43
H5	2545	1807	2448	38
H8	2645	620	2963	42
H9	2909	-520	3661	45
H10	3440	-542	5079	41
H13	3839	-395	6447	43
H14	4485	-180	7841	48
H16	4560	2052	7416	39
H18A	748	1153	5452	42
H18B	-454	1648	5709	42
H19A	608	1945	4180	49
H19B	-839	2135	4432	49
H20A	70	633	4162	73
H20B	-1384	833	4393	73
H21A	-314	1271	2917	135
H21B	-1771	1462	3148	135
H21C	-1359	612	2991	135
H22A	1392	3650	5703	40
H22B	663	3275	4907	40
H23A	-1164	3013	5726	41
H23B	-444	3510	6439	41
H24A	-546	4560	5519	50
H24B	-1366	4056	4853	50
H25A	-2814	4797	5520	71
H25B	-2239	4491	6396	71
H25C	-3049	3943	5770	71
H26A	2143	2468	7217	39
H26B	592	2572	7085	39
H27A	252	1287	7062	42
H27B	1790	1127	7033	42
H28A	2179	1626	8378	49
H28B	646	1796	8407	49
H29A	228	479	8317	83
H29B	1117	694	9132	83
H29C	1777	336	8364	83

Table S14 Atomic Occupancy for ps4.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C100	0.867(2)	H10A	0.867(2)	H10B	0.867(2)
H10C	0.867(2)	I2	0.133(2)		

Me-6-Pr
ps25

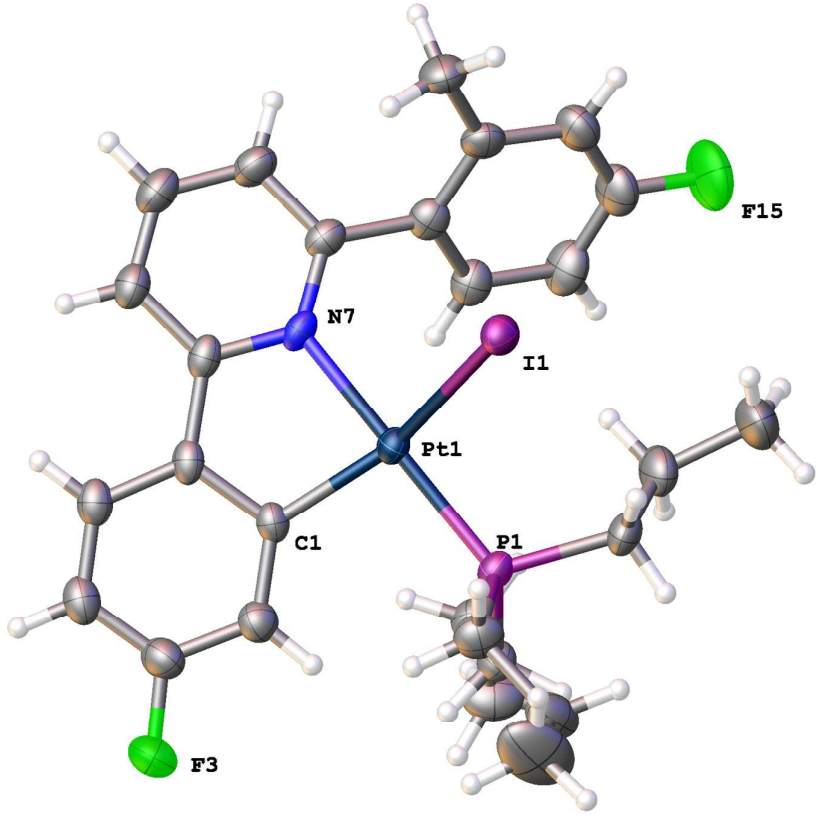

Figure SI4 *solid state structure of ps25 with thermal ellipsoids drawn at 50% probability level and only key atoms labeled.*

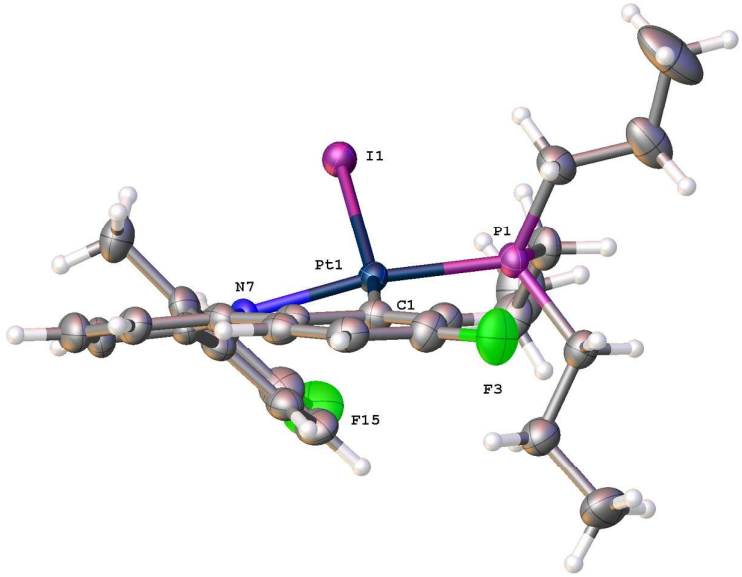

Figure SI5 *Different view of ps25 looking along the chelated phenyl ring trying to highlight the jaunty angle of the iodide*

Crystal structure determination of [ps25]
The asymmetric unit contains the complex, four times all this in the unit cell.
Angle between mean planes through various pi system described by angle used to define plane and angle between them.

Plane C1 C2 C3 C4 C5 C6 to N7 C7 C8 C9 C10 C11 angle 11.321 (0.306) degrees
Plane N7 C7 C8 C9 C10 C11 to C12 C13 C14 C15 C16 C17 angle 50.161 (0.188) degrees

Trying to get some measure of iodide out of plane of the other chelated atoms by describing a mean plane through C1 N7 P1 Pt1

and the distance I1 is out of this plane (* indicates atoms used to define plane)
* -0.0012 (0.0001) C1
* 0.0573 (0.0007) N7
* 0.0540 (0.0006) P1
* -0.1101 (0.0013) Pt1
-1.4933 (0.0061) I1

There is pi stacking between symmetry related chelated phenyl pyridine portion of the molecule (see Mercury).
Angle between mean planes through interacting systems is zero degrees as they are parallel as interaction occurs across an inversion centre. Closest atomic contact is C5 - C7_$1 3.3103 (0.0066)
Symmetry operator used to generate atom in above discussion was $1 1-X,1-Y,1-Z

Experimental
Single crystals of $C_{27}H_{33}F_2INPPt$ **[ps25]** were **????**. 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.
8 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
9 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
10 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.
Crystal Data for $C_{27}H_{33}F_2INPPt$ (M =762.50 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 17.1855(2) Å, b = 12.17889(16) Å, c = 13.62801(18) Å, β = 106.9357(13)°, V = 2728.64(6) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 19.291 mm^{-1}, *Dcalc* = 1.856 g/cm^3, 26064 reflections measured (9.036° ≤ 2Θ ≤ 156.396°), 5784 unique (R_{int} = 0.0576, R_{sigma} = 0.0366) which were used in all calculations. The final R_1 was 0.0364 (I > 2σ(I)) and wR_2 was 0.1012 (all data).

Table S15 Crystal data and structure refinement for ps25.

Identification code	ps25
Empirical formula	$C_{27}H_{33}F_2INPPt$
Formula weight	762.50
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.1855(2)
b/Å	12.17889(16)
c/Å	13.62801(18)
α/°	90
β/°	106.9357(13)
γ/°	90
Volume/Å^3	2728.64(6)
Z	4
ρ_{calc}g/cm^3	1.856
μ/mm^{-1}	19.291
F(000)	1464.0
Crystal size/mm^3	0.406 × 0.303 × 0.16 yellow block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.036 to 156.396
Index ranges	-21 ≤ h ≤ 21, -15 ≤ k ≤ 14, -16 ≤ l ≤ 17
Reflections collected	26064
Independent reflections	5784 [R_{int} = 0.0576, R_{sigma} = 0.0366]
Data/restraints/parameters	5784/0/302
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0380, wR_2 = 0.1012
Largest diff. peak/hole / e Å^{-3}	1.86/-2.05

Table S16 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps25. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	7045.5(2)	4750.4(2)	6039.3(2)	25.52(8)
I1	7233.0(2)	4371.5(3)	8053.3(2)	32.75(10)
P1	7865.0(6)	3344(1)	5977.0(9)	30.0(2)
C1	6373(3)	4740(4)	4556(4)	28.2(9)
C2	6380(3)	4006(5)	3779(4)	35.7(10)
C3	5742(3)	4021(5)	2861(4)	40.6(11)
F3	5781(2)	3293(4)	2125(3)	57.2(10)
C4	5087(3)	4714(5)	2694(4)	38.6(11)
C5	5065(3)	5433(4)	3457(4)	33.8(10)
C6	5692(2)	5470(4)	4380(4)	29.4(9)
C7	5710(2)	6272(4)	5183(4)	29.2(9)

N7	6388(2)	6223(3)	5997(3)	27.0(7)
C8	5127(3)	7086(4)	5132(4)	36.3(10)
C9	5263(3)	7863(5)	5882(5)	42.6(12)
C10	5994(3)	7883(4)	6658(5)	39.3(11)
C11	6556(3)	7046(4)	6697(4)	30.8(9)
C12	7396(3)	7106(4)	7419(4)	33.3(9)
C13	8037(3)	7015(4)	6980(4)	36.5(10)
C14	8843(3)	7110(5)	7589(5)	46.1(13)
C15	8983(3)	7291(5)	8618(5)	48.0(13)
F15	9759(2)	7369(5)	9219(4)	75.2(14)
C16	8363(3)	7354(5)	9070(5)	45.7(12)
C17	7562(3)	7285(4)	8477(4)	37.1(10)
C18	6899(3)	7331(6)	8989(5)	47.0(13)
C19	8753(3)	3238(5)	7122(4)	39.5(11)
C20	9250(3)	4281(6)	7411(5)	49.2(14)
C21	9835(5)	4207(8)	8503(7)	76(3)
C22	8347(3)	3379(5)	4940(4)	36.4(10)
C23	8530(4)	4526(5)	4626(5)	43.7(12)
C24	9047(5)	4501(7)	3889(6)	60.0(17)
C25	7384(4)	2006(5)	5909(5)	44.5(12)
C26	7916(5)	997(6)	5982(5)	58.0(17)
C27	7441(9)	-40(7)	6077(9)	100(4)

Table S17 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps25. 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	20.86(11)	26.69(13)	29.19(12)	1.05(6)	7.55(8)	0.93(5)
I1	33.47(16)	34.30(18)	30.62(16)	2.82(11)	9.54(11)	3.63(10)
P1	26.7(5)	28.0(5)	34.8(6)	1.3(4)	8.4(4)	4.5(4)
C1	24.1(19)	30(2)	27(2)	3.6(16)	3.2(16)	-1.9(15)
C2	35(2)	39(3)	33(2)	1(2)	8.9(18)	0.4(19)
C3	37(2)	46(3)	38(3)	-9(2)	9(2)	-3(2)
F3	57.6(19)	66(2)	41.6(18)	-20.3(17)	3.8(15)	6.7(18)
C4	31(2)	47(3)	35(3)	6(2)	4.4(19)	-2.9(19)
C5	26(2)	38(2)	36(2)	9(2)	6.4(18)	-2.3(17)
C6	19.5(18)	36(2)	31(2)	6.9(19)	5.1(16)	-1.4(16)
C7	21.4(17)	30(2)	36(2)	8.0(18)	8.1(16)	1.1(16)
N7	22.6(15)	23.2(17)	36.8(19)	6.6(15)	11.3(14)	5.2(13)
C8	26.9(19)	40(3)	41(2)	6(2)	8.6(17)	5.1(18)
C9	36(2)	40(3)	54(3)	5(2)	16(2)	10(2)
C10	38(2)	31(2)	50(3)	-3(2)	14(2)	5.6(19)
C11	31(2)	26(2)	38(2)	1.9(18)	14.8(17)	2.0(16)
C12	32(2)	26(2)	42(2)	0.7(19)	10.9(18)	-3.2(16)
C13	33(2)	33(2)	44(3)	5(2)	11.4(19)	-2.8(18)
C14	29(2)	47(3)	64(4)	7(3)	15(2)	-6(2)
C15	33(2)	49(3)	56(3)	-4(3)	3(2)	-11(2)
F15	34.4(17)	98(4)	80(3)	-3(3)	-3.9(17)	-19(2)
C16	42(3)	44(3)	45(3)	-9(2)	3(2)	-6(2)
C17	42(2)	27(2)	42(3)	-8(2)	12(2)	1.8(18)
C18	45(3)	53(3)	45(3)	-10(3)	17(2)	9(2)
C19	30(2)	45(3)	40(3)	3(2)	5.2(18)	13(2)
C20	29(2)	66(4)	48(3)	-7(3)	3(2)	2(2)
C21	53(4)	92(6)	63(5)	-27(4)	-15(3)	12(4)
C22	31(2)	43(3)	36(2)	-2(2)	9.7(17)	3.6(19)
C23	42(3)	43(3)	49(3)	-2(3)	18(2)	-3(2)
C24	76(4)	60(4)	56(4)	0(3)	38(3)	-5(4)
C25	51(3)	33(3)	51(3)	0(2)	17(2)	-2(2)
C26	85(5)	39(3)	40(3)	-1(3)	4(3)	7(3)
C27	157(11)	33(4)	93(7)	-2(4)	11(7)	-14(6)

Table S18 Bond Lengths for ps25.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	I1	2.7083(3)	C8	C9	1.363(8)
Pt1	P1	2.2347(11)	C9	C10	1.387(8)
Pt1	C1	2.015(5)	C10	C11	1.394(7)
Pt1	N7	2.112(4)	C11	C12	1.492(6)
P1	C19	1.842(5)	C12	C13	1.402(7)
P1	C22	1.836(5)	C12	C17	1.403(7)
P1	C25	1.818(6)	C13	C14	1.397(7)
C1	C2	1.389(7)	C14	C15	1.369(9)
C1	C6	1.432(6)	C15	F15	1.350(6)
C2	C3	1.402(7)	C15	C16	1.380(9)
C3	F3	1.356(7)	C16	C17	1.380(8)
C3	C4	1.372(8)	C17	C18	1.501(8)
C4	C5	1.367(8)	C19	C20	1.517(9)

C5	C6	1.398(7)	C20	C21	1.536(9)
C6	C7	1.460(7)	C22	C23	1.520(8)
C7	N7	1.356(6)	C23	C24	1.524(9)
C7	C8	1.397(7)	C25	C26	1.518(9)
N7	C11	1.355(6)	C26	C27	1.530(12)

Table S19 Bond Angles for ps25.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pt1	I1	91.01(3)	C7	N7	Pt1	112.6(3)
C1	Pt1	I1	151.59(13)	C11	N7	Pt1	127.3(3)
C1	Pt1	P1	98.11(14)	C11	N7	C7	120.0(4)
C1	Pt1	N7	80.32(17)	C9	C8	C7	119.5(5)
N7	Pt1	I1	94.41(11)	C8	C9	C10	120.2(5)
N7	Pt1	P1	171.18(10)	C9	C10	C11	118.7(5)
C19	P1	Pt1	113.42(18)	N7	C11	C10	120.7(4)
C22	P1	Pt1	116.26(18)	N7	C11	C12	117.8(4)
C22	P1	C19	101.8(2)	C10	C11	C12	121.0(5)
C25	P1	Pt1	114.0(2)	C13	C12	C11	116.4(5)
C25	P1	C19	103.5(3)	C13	C12	C17	120.0(5)
C25	P1	C22	106.4(3)	C17	C12	C11	123.6(4)
C2	C1	Pt1	129.7(4)	C14	C13	C12	120.4(5)
C2	C1	C6	117.4(4)	C15	C14	C13	118.0(5)
C6	C1	Pt1	111.5(3)	C14	C15	C16	122.5(5)
C1	C2	C3	119.6(5)	F15	C15	C14	118.8(6)
F3	C3	C2	117.2(5)	F15	C15	C16	118.7(6)
F3	C3	C4	119.7(5)	C15	C16	C17	120.2(5)
C4	C3	C2	123.1(5)	C12	C17	C18	121.9(5)
C5	C4	C3	118.0(5)	C16	C17	C12	118.8(5)
C4	C5	C6	121.4(5)	C16	C17	C18	119.2(5)
C1	C6	C7	116.9(4)	C20	C19	P1	115.2(4)
C5	C6	C1	120.5(5)	C19	C20	C21	111.3(6)
C5	C6	C7	122.6(4)	C23	C22	P1	114.5(4)
N7	C7	C6	114.2(4)	C22	C23	C24	112.0(5)
N7	C7	C8	120.3(5)	C26	C25	P1	117.8(5)
C8	C7	C6	125.4(4)	C25	C26	C27	110.3(8)

Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps25.

Atom	*x*	*y*	*z*	U(eq)
H2	6814	3497	3868	43
H4	4661	4696	2067	46
H5	4616	5917	3358	41
H8	4639	7098	4579	44
H9	4856	8393	5874	51
H10	6110	8455	7153	47
H13	7922	6887	6264	44
H14	9281	7051	7298	55
H16	8487	7445	9791	55
H18A	6416	6952	8562	70
H18B	6764	8099	9079	70
H18C	7085	6972	9661	70
H19A	8562	3012	7710	47
H19B	9114	2650	7005	47
H20A	8879	4913	7368	59
H20B	9565	4407	6919	59
H21A	10170	3544	8564	114
H21B	9522	4173	8998	114
H21C	10188	4856	8642	114
H22A	8862	2960	5160	44
H22B	7986	3004	4332	44
H23A	8820	4947	5247	52
H23B	8012	4909	4295	52
H24A	8795	4013	3313	90
H24B	9593	4231	4249	90
H24C	9087	5244	3631	90
H25A	7124	1964	6468	53
H25B	6944	1966	5253	53
H26A	8401	1061	6587	70
H26B	8104	946	5362	70
H27A	6991	−140	5449	149
H27B	7224	33	6664	149
H27C	7804	−678	6179	149

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
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C19(H19A,H19B), C20(H20A,H20B), C22(H22A,H22B), C23(H23A,H23B), C25(H25A,
 H25B), C26(H26A,H26B)
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)
2.c Idealised Me refined as rotating group:
 C18(H18A,H18B,H18C), C21(H21A,H21B,H21C), C24(H24A,H24B,H24C), C27(H27A,H27B,
 H27C)
```

This report has been created with Olex2, compiled on 2015.09.30 svn.r3233 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Me-6-Bu
ps35

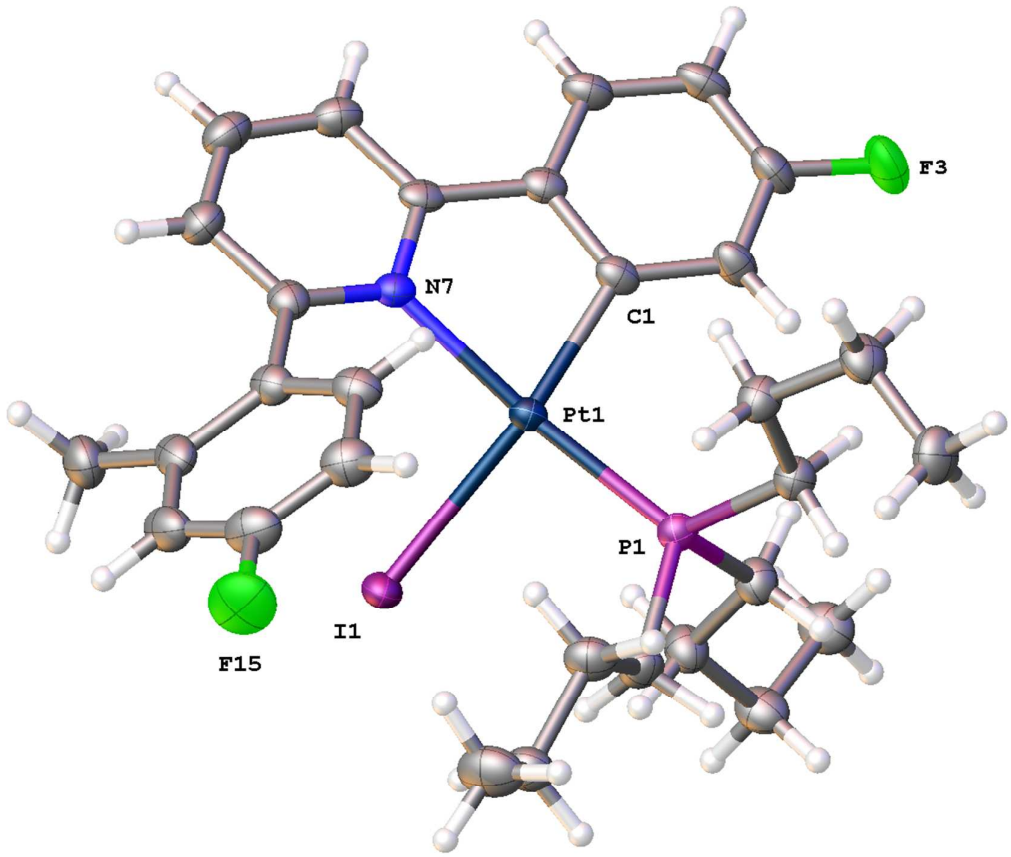

Figure SI6 *solid state structure of ps35 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level*

Crystal structure determination of [ps35]
The asymmetric unit contains the complex, there are four complexes in the unit cell.

The angle between mean planes through the chelated phenyl and pyridine is
Ring C1 C2 C3 C4 C5 C6 to ring N7 C7 C8 C9 C10 C11 is 7.193 (0.187) degrees

The angle between mean planes through the chelated pyridine ring and the free fluorophenyl ring is
Ring N7 C7 C8 C9 C10 C11 to ring C12 C13 C14 C15 C16 C17 is 46.170 (0.106) degrees

There is a possible pi stacking interaction between the chelated phenyl pyridine and a symmetry related chelated phenyl pyridine. This is described as atoms used to define a mean plane through interacting pi systems, angle between these mean planes and closest atomic contact.
C1 C3 C5 N7 C8 C10 to C1_$1 C3_$1 C5_$1 N7_$1 C8_$1 C10_$1 is zero degrees between planes as there is an inversion centre relating the two interacting rings so they are parallel.
Closest atomic contact is C5 - C7_$1 3.3184 (0.0039) Angstroms

Symmetry operator used to define symmetry related atoms discussed above was $1 2-X,1-Y,1-Z

Experimental
Single crystals of $C_{30}H_{39}F_2INPPt$ **[ps35]** 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 Dual 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.
11 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
12 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
13 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{30}H_{39}F_2INPPt$ (M =804.58 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 17.9485(2) Å, b = 12.31107(18) Å, c = 13.88543(18) Å, β = 110.0913(15)°, V = 2881.48(7) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 6.029 mm^{-1}, *Dcalc* = 1.855 g/cm^3, 56183 reflections measured (6.454° ≤ 2Θ ≤ 69.214°), 11614 unique (R_{int} = 0.0429, R_{sigma} = 0.0369) which were used in all calculations. The final R_1 was 0.0295 (I > 2σ(I)) and wR_2 was 0.0652 (all data).

Table S21 Crystal data and structure refinement for ps35.

Identification code	ps35
Empirical formula	$C_{30}H_{39}F_2INPPt$
Formula weight	804.58
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.9485(2)
b/Å	12.31107(18)
c/Å	13.88543(18)
α/°	90
β/°	110.0913(15)
γ/°	90
Volume/Å^3	2881.48(7)
Z	4
ρ_{calc}g/cm^3	1.855
μ/mm^{-1}	6.029
F(000)	1560.0
Crystal size/mm^3	0.2 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.454 to 69.214
Index ranges	-28 ≤ h ≤ 27, -18 ≤ k ≤ 16, -22 ≤ l ≤ 21
Reflections collected	56183
Independent reflections	11614 [R_{int} = 0.0429, R_{sigma} = 0.0369]
Data/restraints/parameters	11614/0/329
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0571
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.0652
Largest diff. peak/hole / e Å^{-3}	2.00/-1.34

Table S22 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps35.
U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	8694.7(15)	4860(2)	5428(2)	23.6(5)
I1	7624.1(2)	4329.8(2)	1955.2(2)	26.70(4)
P1	7207.8(4)	3406.6(6)	4164.3(6)	22.66(14)
Pt1	7962.1(2)	4776.0(2)	3966.2(2)	19.71(3)
C2	8765.5(16)	4174(3)	6261(2)	28.8(6)
C3	9434.9(17)	4213(3)	7122(2)	30.3(6)
C5	10004.8(16)	5597(3)	6438(2)	28.7(6)
C6	9339.4(16)	5583(2)	5542(2)	23.7(5)
F3	9488.7(11)	3500.7(19)	7894.3(15)	43.4(5)
C4	10060.7(17)	4904(3)	7242(2)	31.5(7)
C7	9274.8(15)	6310(2)	4686(2)	23.1(5)
N7	8578.4(13)	6226.2(19)	3890.1(17)	21.8(4)
C8	9842.0(17)	7070(3)	4654(3)	30.0(6)
C9	9680.2(19)	7755(3)	3830(3)	34.0(7)
C10	8935.6(18)	7744(3)	3076(3)	31.5(6)
C11	8380.9(17)	6979(2)	3128(2)	25.4(6)
C12	7539.4(17)	7045(2)	2442(2)	26.5(6)
C13	7310.2(19)	7183(2)	1379(2)	30.5(6)
C13A	7887(2)	7173(3)	809(3)	40.6(8)
C14	6505(2)	7267(3)	819(3)	37.3(8)
C15	5962.1(19)	7214(3)	1308(3)	38.6(8)
F15	5176.0(12)	7310(2)	734.8(19)	57.8(7)
C16	6163.9(19)	7084(3)	2339(3)	35.9(7)
C17	6968.2(17)	6998(3)	2914(2)	29.8(6)
C18	6316.4(16)	3160(3)	3049(2)	28.7(6)
C19	5731.0(17)	4097(3)	2713(3)	32.6(7)
C20	5161.7(18)	3957(3)	1614(3)	35.7(7)
C21	4487(2)	4784(3)	1288(3)	49.8(10)
C22	6796.7(17)	3557(2)	5196(2)	26.8(6)
C23	6601.2(18)	4711(3)	5418(3)	29.9(6)
C24	6252(2)	4761(3)	6287(3)	35.6(7)
C25	5532(2)	4047(3)	6119(3)	38.7(8)
C26	7645.0(18)	2054(3)	4430(2)	29.5(6)
C27	7933.6(19)	1587(3)	3611(3)	32.1(7)
C28	8121(2)	368(3)	3761(3)	36.3(7)
C29	8806(2)	118(3)	4725(3)	39.5(8)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	19.8(11)	29.9(15)	20.6(12)	-3.9(11)	6.1(9)	2.7(10)
I1	34.13(9)	25.16(10)	20.03(8)	-3.75(7)	8.31(7)	-4.62(7)
P1	20.2(3)	22.9(4)	23.8(3)	-0.2(3)	6.2(3)	0.7(2)
Pt1	18.46(4)	21.38(6)	18.17(5)	-1.93(4)	4.84(3)	-0.08(3)
C2	21.0(12)	42.5(19)	20.9(13)	2.3(12)	4.5(10)	3.2(11)
C3	28.5(14)	44(2)	17.7(12)	1.3(12)	7.6(10)	5.8(12)
C5	22.2(12)	34.5(17)	25.8(14)	-7.1(12)	3.6(10)	0.9(11)
C6	22.5(12)	25.7(15)	22.1(12)	-6.5(10)	6.7(10)	2(1)
F3	38.5(10)	63.0(15)	25.0(9)	13.5(9)	6.2(8)	1.4(9)
C4	24.3(13)	45(2)	21.0(13)	-7.4(12)	1.6(10)	5.3(12)
C7	22.3(12)	24.9(15)	22.3(12)	-10.4(10)	8.1(10)	-0.4(10)
N7	22.1(10)	21.0(12)	21.2(10)	-4.7(9)	6.0(8)	-0.6(8)
C8	24.3(13)	30.2(17)	33.8(15)	-7.5(12)	7.9(11)	-2.7(11)
C9	33.4(15)	28.3(18)	41.8(18)	-4.9(14)	14.8(13)	-7.9(12)
C10	35.3(15)	25.2(17)	33.8(16)	-0.9(12)	11.7(13)	-4.6(12)
C11	30.4(13)	21.7(15)	24.3(13)	-2.9(11)	9.8(11)	1.4(10)
C12	29.8(13)	19.7(14)	25.9(13)	1.1(11)	4.4(11)	3.1(10)
C13	42.2(16)	18.8(15)	27.3(14)	2.2(11)	8.0(12)	0.8(12)
C13A	51(2)	40(2)	29.4(16)	7.1(14)	12.3(15)	-1.0(15)
C14	44.5(18)	28.2(18)	29.5(16)	6.1(13)	0.1(13)	0.8(13)
C15	31.1(15)	31.4(19)	42.9(19)	3.3(14)	-0.7(14)	6.0(13)
F15	33.9(11)	65.6(16)	56.7(15)	11.1(12)	-6.4(10)	8.5(10)
C16	30.7(15)	32.3(18)	41.6(19)	-1.1(14)	8.5(13)	5.2(12)
C17	30.7(14)	25.5(16)	29.8(15)	-3.5(12)	6.1(12)	5.0(11)
C18	23.3(12)	28.9(17)	30.4(15)	-0.1(12)	4.8(11)	-4.7(11)
C19	25.1(13)	34.7(19)	33.0(16)	-3.1(13)	3.4(12)	2.3(11)
C20	30.5(15)	40(2)	30.9(16)	-0.4(14)	2.7(12)	-0.6(13)
C21	40.7(19)	48(2)	46(2)	-1.6(18)	-4.8(16)	7.5(16)
C22	25.5(13)	26.7(16)	28.7(14)	1.3(11)	10.1(11)	1.8(10)
C23	31.6(14)	26.2(16)	34.4(16)	0.0(12)	14.7(12)	2.2(11)
C24	44.1(18)	33.9(19)	33.0(16)	-2.2(14)	18.8(14)	4.4(14)
C25	36.9(17)	43(2)	43.3(19)	6.8(15)	22.3(15)	4.0(14)
C26	33.0(14)	27.3(16)	29.4(15)	2.0(12)	12.2(12)	4.2(12)
C27	40.0(16)	29.0(17)	29.1(15)	0.2(12)	14.3(13)	4.3(13)
C28	41.9(17)	30.3(19)	34.1(17)	-3.8(13)	9.6(14)	8.3(13)
C29	41.3(18)	34.2(19)	40.6(19)	-1.1(15)	10.9(15)	11.1(14)

Table S23 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps35. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+\ldots]$.

Table S24 Bond Lengths for ps35.

Atom	Atom	Length/Å
C1	Pt1	2.007(3)
C1	C2	1.402(4)
C1	C6	1.425(4)
I1	Pt1	2.7024(2)
P1	Pt1	2.2374(8)
P1	C18	1.830(3)
P1	C22	1.833(3)
P1	C26	1.823(3)
Pt1	N7	2.122(2)
C2	C3	1.374(4)
C3	F3	1.363(4)
C3	C4	1.373(5)
C5	C6	1.397(4)
C5	C4	1.381(5)
C6	C7	1.461(4)
C7	N7	1.358(3)
C7	C8	1.395(4)
N7	C11	1.359(4)
C8	C9	1.370(5)
C9	C10	1.386(4)
C10	C11	1.390(4)
C11	C12	1.486(4)
C12	C13	1.400(4)
C12	C17	1.395(4)
C13	C13A	1.504(5)
C13	C14	1.390(4)
C14	C15	1.367(5)
C15	F15	1.366(4)
C15	C16	1.360(5)
C16	C17	1.393(4)
C18	C19	1.521(4)
C19	C20	1.527(4)
C20	C21	1.526(5)
C22	C23	1.519(4)
C23	C24	1.539(4)
C24	C25	1.514(5)
C26	C27	1.516(4)
C27	C28	1.536(5)
C28	C29	1.506(5)

Table S25 Bond Angles for ps35.

Atom	Atom	Atom	Angle/°
C2	C1	Pt1	130.2(2)
C2	C1	C6	116.4(2)
C6	C1	Pt1	111.7(2)
C18	P1	Pt1	114.26(11)
C18	P1	C22	102.05(14)
C22	P1	Pt1	116.29(10)
C26	P1	Pt1	118.45(10)
C26	P1	C18	102.15(15)
C26	P1	C22	101.24(14)
C1	Pt1	I1	153.15(8)
C1	Pt1	P1	97.38(9)
C1	Pt1	N7	80.52(11)
P1	Pt1	I1	92.48(2)
N7	Pt1	I1	93.17(6)
N7	Pt1	P1	171.06(6)
C3	C2	C1	120.1(3)
F3	C3	C2	117.8(3)
C11	N7	Pt1	127.71(18)
C9	C8	C7	119.5(3)
C8	C9	C10	119.8(3)
C9	C10	C11	119.3(3)
N7	C11	C10	120.2(3)
N7	C11	C12	118.2(3)
C10	C11	C12	121.2(3)
C13	C12	C11	123.3(3)
C17	C12	C11	116.5(3)
C17	C12	C13	120.2(3)
C12	C13	C13A	123.2(3)
C14	C13	C12	118.1(3)
C14	C13	C13A	118.5(3)
C15	C14	C13	120.0(3)
F15	C15	C14	118.5(3)
C16	C15	C14	123.4(3)
C16	C15	F15	118.1(3)

F3	C3	C4	118.0(3)	C15	C16	C17	117.5(3)
C4	C3	C2	124.2(3)	C16	C17	C12	120.8(3)
C4	C5	C6	120.9(3)	C19	C18	P1	116.4(2)
C1	C6	C7	117.2(2)	C18	C19	C20	112.1(3)
C5	C6	C1	121.3(3)	C21	C20	C19	114.3(3)
C5	C6	C7	121.4(3)	C23	C22	P1	115.9(2)
C3	C4	C5	117.1(3)	C22	C23	C24	112.4(3)
N7	C7	C6	114.2(2)	C25	C24	C23	114.3(3)
N7	C7	C8	120.2(3)	C27	C26	P1	115.4(2)
C8	C7	C6	125.6(3)	C26	C27	C28	112.6(3)
C7	N7	Pt1	111.91(19)	C29	C28	C27	113.2(3)
C7	N7	C11	120.2(2)				

Table S26 Torsion Angles for ps35.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	F3	-177.5(3)	N7	C11	C12	C13	-138.1(3)
C1	C2	C3	C4	0.7(5)	N7	C11	C12	C17	44.0(4)
C1	C6	C7	N7	2.4(4)	C8	C7	N7	Pt1	165.7(2)
C1	C6	C7	C8	-179.9(3)	C8	C7	N7	C11	-9.4(4)
P1	C18	C19	C20	161.7(2)	C8	C9	C10	C11	-4.8(5)
P1	C22	C23	C24	179.5(2)	C9	C10	C11	N7	-2.4(5)
P1	C26	C27	C28	-167.2(2)	C9	C10	C11	C12	169.9(3)
Pt1	C1	C2	C3	162.9(2)	C10	C11	C12	C13	49.4(4)
Pt1	C1	C6	C5	-166.4(2)	C10	C11	C12	C17	-128.5(3)
Pt1	C1	C6	C7	13.8(3)	C11	C12	C13	C13A	6.0(5)
Pt1	P1	C18	C19	-60.0(3)	C11	C12	C13	C14	-178.0(3)
Pt1	P1	C22	C23	32.4(2)	C11	C12	C17	C16	178.1(3)
Pt1	P1	C26	C27	-60.8(3)	C12	C13	C14	C15	0.0(5)
Pt1	N7	C11	C10	-164.8(2)	C13	C12	C17	C16	0.2(5)
Pt1	N7	C11	C12	22.6(4)	C13	C14	C15	F15	179.4(3)
C2	C1	C6	C5	0.3(4)	C13	C14	C15	C16	0.3(5)
C2	C1	C6	C7	-179.6(3)	C13A	C13	C14	C15	176.1(3)
C2	C3	C4	C5	-0.1(5)	C14	C15	C16	C17	-0.3(5)
C5	C6	C7	N7	-177.5(3)	C15	C16	C17	C12	0.0(5)
C5	C6	C7	C8	0.2(4)	F15	C15	C16	C17	-179.4(3)
C6	C1	C2	C3	-0.8(4)	C17	C12	C13	C13A	-176.2(3)
C6	C5	C4	C3	-0.4(4)	C17	C12	C13	C14	-0.2(4)
C6	C7	N7	Pt1	-16.4(3)	C18	P1	C22	C23	-92.6(2)
C6	C7	N7	C11	168.4(2)	C18	P1	C26	C27	65.7(3)
C6	C7	C8	C9	-175.4(3)	C18	C19	C20	C21	171.6(3)
F3	C3	C4	C5	178.1(3)	C22	P1	C18	C19	66.4(3)
C4	C5	C6	C1	0.3(4)	C22	P1	C26	C27	170.8(2)
C4	C5	C6	C7	-179.8(3)	C22	C23	C24	C25	-54.7(4)
C7	N7	C11	C10	9.6(4)	C26	P1	C18	C19	170.8(2)
C7	N7	C11	C12	-163.0(3)	C26	P1	C22	C23	162.2(2)
C7	C8	C9	C10	4.9(5)	C26	C27	C28	C29	-65.2(4)
N7	C7	C8	C9	2.2(4)					

Table S27 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps35.

Atom	*x*	*y*	*z*	U(eq)
H2	8350	3681	6230	35
H5	10425	6091	6495	34
H4	10512	4906	7852	38
H8	10337	7113	5200	36
H9	10077	8237	3776	41
H10	8806	8253	2529	38
H13A	8022	7921	691	61
H13B	7646	6805	149	61
H13C	8370	6786	1215	61
H14	6332	7362	97	45
H16	5771	7054	2655	43
H17	7130	6906	3636	36
H18A	6484	2958	2464	34
H18B	6035	2528	3201	34
H19A	6028	4785	2766	39
H19B	5422	4145	3180	39
H20A	5467	4013	1143	43
H20B	4930	3219	1539	43
H21A	4183	4692	557	75
H21B	4708	5520	1408	75
H21C	4139	4672	1689	75
H22A	6307	3117	5020	32
H22B	7181	3251	5832	32
H23A	6215	5026	4787	36
H23B	7090	5156	5610	36

H24A	6669	4545	6936	43
H24B	6105	5523	6364	43
H25A	5132	4213	5452	58
H25B	5311	4182	6663	58
H25C	5688	3282	6136	58
H26A	8098	2081	5084	35
H26B	7246	1552	4528	35
H27A	8417	1981	3622	39
H27B	7522	1703	2930	39
H28A	7644	-20	3783	44
H28B	8245	92	3164	44
H29A	9280	501	4711	59
H29B	8906	-667	4769	59
H29C	8677	356	5323	59

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
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C19(H19A,H19B), C20(H20A,H20B), C22(H22A,H22B), C23(H23A,
 H23B), C24(H24A,H24B), C26(H26A,H26B), C27(H27A,H27B), C28(H28A,H28B)
2.b Aromatic/amide H refined with riding coordinates:
 C2(H2), C5(H5), C4(H4), C8(H8), C9(H9), C10(H10), C14(H14), C16(H16), C17(H17)
2.c Idealised Me refined as rotating group:
 C13A(H13A,H13B,H13C), C21(H21A,H21B,H21C), C25(H25A,H25B,H25C), C29(H29A,H29B,
 H29C)
```

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-Pr
ps19

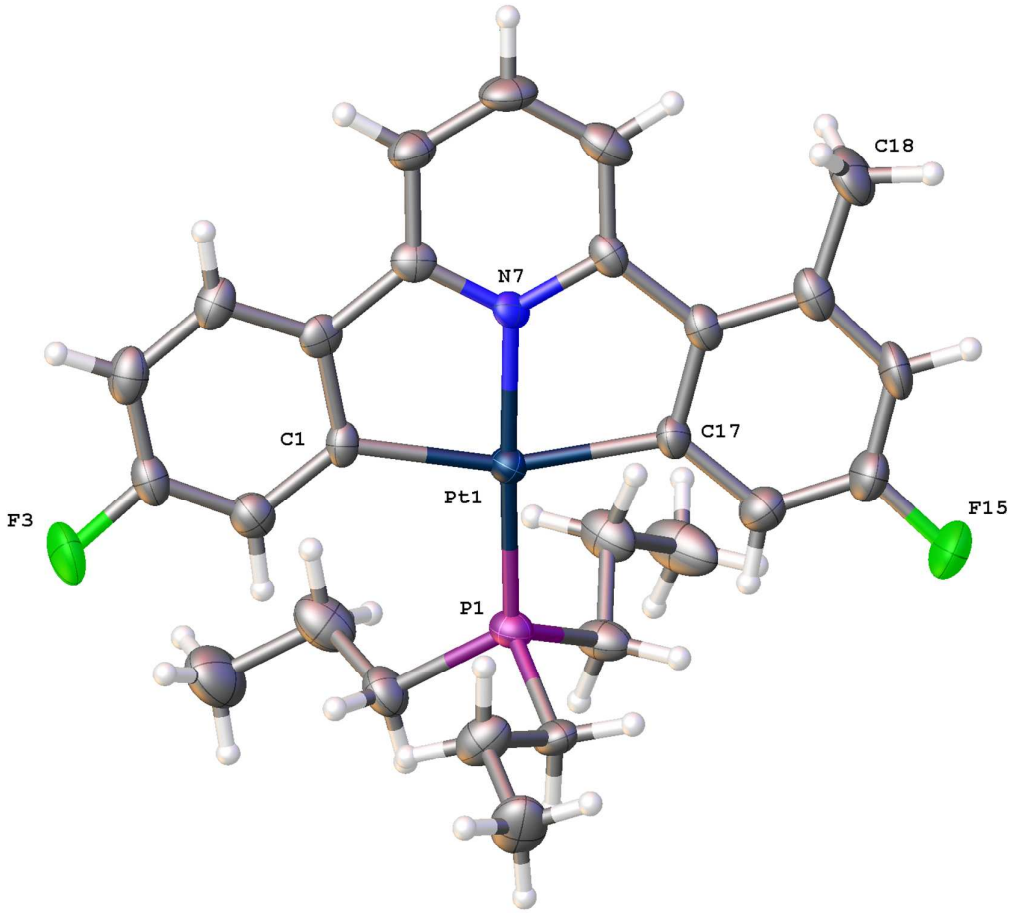

Figure SI7 *Solid state structure of ps19 with only key atoms labeled. Thermal ellipsoids drawn at 50% probability level*

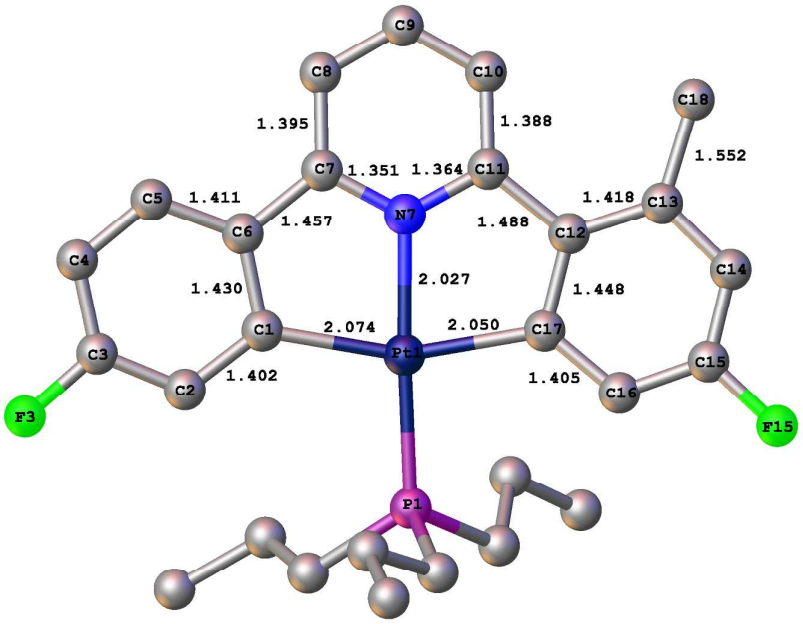

Figure SI8 **Bond lengths in the structure of Me-1-Pr**

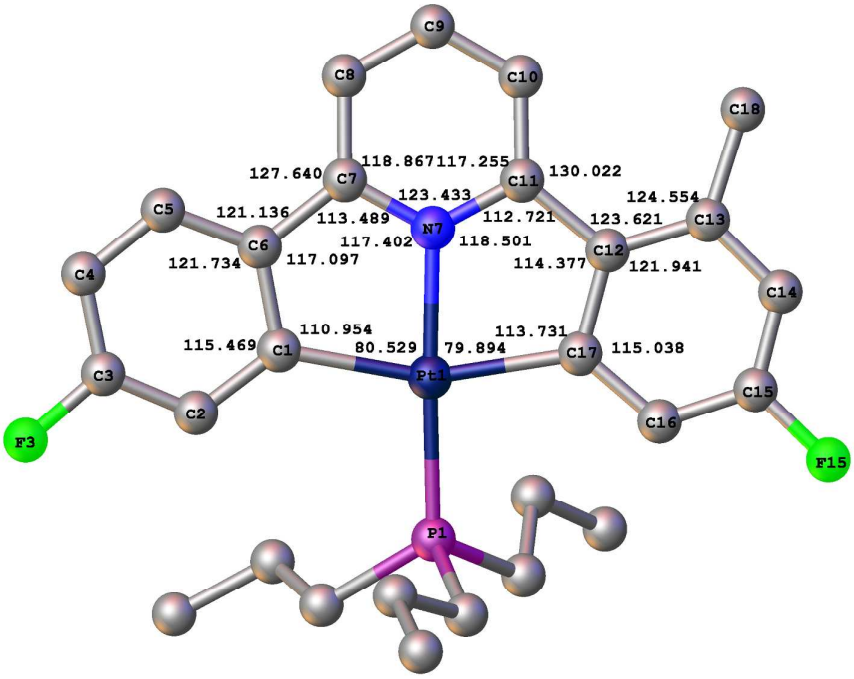

Figure SI9 **Bond angles in the structure of Me-1-Pr**

Crystal structure determination of [ps19]
The asymmetric unit contains the Pt complex, there are four in the unit cell.
The ligand has a slight bevel. Difficult to find a way of defining this.

Plan A
Define mean planes through the three aromatic systems and the angles between them.
This is detailed below by atoms used to define mean plane and the angle between them and the next defined mean plane

C1 C2 C3 C4 C5 C6 to C7 N7 C8 C9 C10 C11 angle 6.784 (0.365) degrees

C7 N7 C8 C9 C10 C11 to C12 C13 C14 C15 C16 C17 angle 8.229 (0.375) degrees

Plan B
Define mean plane through chelated atoms on Pt1 (with associated distances of relevant atoms out of this mean plane) then define the angle between this mean plan and mean planes through the aromatic rings

Mean plane of Pt1 and atoms attached to Pt1 and deviations of those atoms from mean plane

* 0.0778 (0.0027) C1
* -0.1027 (0.0029) N7
* 0.0822 (0.0028) C17
* -0.0678 (0.0018) P1
* 0.0105 (0.0019) Pt1

Rms deviation of fitted atoms = 0.0749

Angle between mean planes through the aromatic rings and the above mean plane are -
C1 C2 C3 C4 C5 C6 to C1 N7 C17 P1 Pt1 angle 8.577 (0.325) degrees
C7 N7 C8 C9 C10 C11 to C1 N7 C17 P1 Pt1 angle 11.522 (0.316) degrees
C12 C13 C14 C15 C16 C17 to C1 N7 C17 P1 Pt1 angle 11.130 (0.329) degrees

There is some possible pi stacking described by angle between mean planes through the aromatic systems involved and closest atomic contact. The interaction is quite off-set

Several types of possible pi stacking
One between the concave surfaces of the ligand (reasonable) and one a bit longer between the convex surfaces of the ligand with little overlap (view via Mercury). There is also an overlap between ring C1-C6 and a symmetry related C1-C6 ring between just the ends of symmetry related complexes.

Concave pi stacking
Angle between mean planes through interacting Pi systems is zero as interaction occurs across an inversion centre.
Closest atomic contact C5 - C3_$2 3.3539 (0.0093)

Convex pi stacking
Angle between mean planes through interacting Pi systems is zero as interaction occurs across an inversion centre.
Closest atomic contact C12 - C10_$1 3.5293 (0.0091)

C1-C6 ring interaction
Angle between mean planes through interacting Pi systems is zero as interaction occurs across an inversion centre.
Closest atomic contact C5 - C11_$3 3.3911 (0.0087)

Further information on pi stacking from Olex2 (it has only considered the concave interaction and the end ring interaction)
For plane C2-C3-C4-C5-C6-C1
C2-C3-C4-C5-C6-C1@3_556 (-X,-Y,1-Z)
angle: 0.000, centroid-centroid distance: 3.716, shift distance 1.619 (the end ring interaction)
N7-C11-C10-C9-C8-C7@3_566 (-X,1-Y,1-Z)
angle: 6.840, centroid-centroid distance: 3.672, shift distance 0.946 (the concave interaction)
For plane C17-C16-C15-C14-C13-C12
No interactions found
For plane N7-C11-C10-C9-C8-C7
No interactions found

Additionally, there could be some sort of interaction between the C18 methyl hydrogens and the Pt of a symmetry related complex tabulated below
Pt1 - H18A_$1 3.1775
Pt1 - C18_$14.0701 (0.0092)

It's a bit long and offset but for consideration. Care here as the hydrogens are placed at calculated positions (a bit close to the Pt to try finding them and doing a free refinement)

Symmetry operators used to define symmetry related atoms in above discussions were
$1 1-X,1-Y,1-Z
$2 -X,-Y,1-Z

$3 -X,1-Y,1-Z

Experimental
Single crystals of $C_{27}H_{32}F_2NPPt$ **[ps19]** were grown from deuterated chloroform. A suitable crystal was selected and mounted on a Mitegen loop 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 XL [3] refinement package using Least Squares minimisation.
14 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
15 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
16 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{27}H_{32}F_2NPPt$ (M =634.59 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.9623(3) Å, b = 9.2215(3) Å, c = 27.2996(8) Å, β = 100.217(3)°, V = 2468.17(14) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 5.780 mm^{-1}, *Dcalc* = 1.708 g/cm^3, 24451 reflections measured (4.688° ≤ 2Θ ≤ 65.326°), 8370 unique (R_{int} = 0.0602, R_{sigma} = 0.0681) which were used in all calculations. The final R_1 was 0.0535 (I > 2σ(I)) and wR_2 was 0.1525 (all data).

Table S28 Crystal data and structure refinement for ps19.

Identification code	ps19
Empirical formula	$C_{27}H_{32}F_2NPPt$
Formula weight	634.59
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9623(3)
b/Å	9.2215(3)
c/Å	27.2996(8)
α/°	90
β/°	100.217(3)
γ/°	90
Volume/Å^3	2468.17(14)
Z	4
ρ_{calc}g/cm^3	1.708
μ/mm^{-1}	5.780
F(000)	1248.0
Crystal size/mm^3	0.4 × 0.08 × 0.03 yellow block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.688 to 65.326
Index ranges	-15 ≤ h ≤ 13, -13 ≤ k ≤ 13, -41 ≤ l ≤ 39
Reflections collected	24451
Independent reflections	8370 [R_{int} = 0.0602, R_{sigma} = 0.0681]
Data/restraints/parameters	8370/0/293
Goodness-of-fit on F^2	1.155
Final R indexes [I>=2σ (I)]	R_1 = 0.0535, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.0811, wR_2 = 0.1525
Largest diff. peak/hole / e Å^{-3}	1.72/-3.42

Table S29 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps19. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	2409.3(2)	3746.1(2)	5890.3(2)	23.50(8)
C1	769(6)	2449(6)	5589(2)	24.3(12)
P1	2917.7(18)	2918.9(19)	6668.7(6)	28.0(3)
C2	-79(7)	1503(7)	5796(3)	33.4(15)
C3	-1144(7)	814(7)	5503(3)	33.2(15)
F3	-1888(4)	-138(5)	5735.1(19)	52.2(12)
C4	-1505(8)	1017(7)	4997(3)	36.4(16)
C5	-738(6)	1980(7)	4778(3)	31.5(14)
C6	395(6)	2682(6)	5064(2)	26.5(13)
C7	1207(7)	3719(6)	4839(2)	26.3(12)
N7	2137(5)	4431(5)	5174.0(18)	21.6(10)
C8	1132(8)	4020(7)	4334(3)	34.3(15)
C9	2009(9)	5018(8)	4194(3)	40.8(17)
C10	2946(8)	5715(8)	4542(3)	36.6(16)
C11	3022(6)	5432(7)	5045(2)	27.0(12)
C12	3932(7)	6064(6)	5485(3)	28.6(13)
C13	4802(7)	7267(7)	5457(3)	34.0(15)
C14	5544(7)	7804(8)	5893(3)	39.5(17)
F15	6114(5)	7806(6)	6765.9(18)	61.7(14)
C15	5401(8)	7225(8)	6339(3)	40.6(17)
C16	4589(8)	6047(8)	6377(3)	37.6(16)
C17	3814(6)	5391(6)	5955(2)	26.6(12)
C18	5038(9)	7983(8)	4965(3)	48(2)
C19	2303(9)	1124(7)	6844(3)	40.0(17)
C20	2652(9)	-142(9)	6545(4)	51(2)

C21	1948(12)	−1534(10)	6681(4)	67(3)
C22	2260(7)	4103(8)	7111(2)	34.1(15)
C23	713(8)	4325(9)	6961(3)	42.1(17)
C24	112(9)	5351(10)	7295(3)	53(2)
C25	4770(7)	2728(8)	6917(3)	37.5(16)
C26	5579(7)	2248(9)	6523(3)	43.9(18)
C27	7088(8)	2056(12)	6738(4)	62(3)

Table S30 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps19. 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	23.56(13)	24.94(14)	22.15(12)	1.30(8)	4.49(9)	−1.35(9)
C1	21(3)	19(3)	33(3)	−3(2)	3(2)	−1(2)
P1	27.2(8)	32.7(8)	24.1(8)	5.0(6)	4.8(6)	0.7(7)
C2	34(4)	31(3)	36(4)	−1(3)	9(3)	1(3)
C3	27(3)	25(3)	47(4)	3(3)	8(3)	−4(3)
F3	38(2)	52(3)	68(3)	0(2)	14(2)	−24(2)
C4	26(3)	30(4)	51(4)	−7(3)	1(3)	1(3)
C5	26(3)	26(3)	39(4)	−6(3)	−3(3)	4(3)
C6	32(3)	17(3)	31(3)	−3(2)	6(3)	7(2)
C7	28(3)	23(3)	28(3)	3(2)	5(2)	9(2)
N7	28(3)	13(2)	24(2)	3.2(17)	6(2)	1.5(19)
C8	43(4)	33(3)	25(3)	1(2)	3(3)	1(3)
C9	59(5)	43(4)	21(3)	7(3)	8(3)	6(4)
C10	40(4)	36(4)	37(4)	13(3)	15(3)	4(3)
C11	22(3)	25(3)	34(3)	4(2)	8(3)	0(2)
C12	26(3)	23(3)	38(3)	2(2)	8(3)	−1(2)
C13	28(3)	27(3)	49(4)	4(3)	11(3)	−2(3)
C14	29(4)	34(4)	56(5)	3(3)	8(3)	−14(3)
F15	66(3)	70(3)	45(3)	−15(2)	−2(2)	−34(3)
C15	35(4)	44(4)	40(4)	−6(3)	0(3)	−11(3)
C16	38(4)	43(4)	32(4)	−1(3)	3(3)	−3(3)
C17	29(3)	20(3)	30(3)	−1(2)	6(3)	−5(2)
C18	53(5)	33(4)	60(5)	13(4)	13(4)	−11(4)
C19	43(4)	33(4)	44(4)	9(3)	9(3)	−6(3)
C20	53(5)	43(4)	61(6)	17(4)	19(4)	10(4)
C21	90(8)	45(5)	72(7)	10(4)	27(6)	−9(5)
C22	36(4)	47(4)	19(3)	−3(2)	4(3)	−6(3)
C23	35(4)	50(4)	39(4)	−10(3)	3(3)	10(3)
C24	45(5)	59(5)	60(6)	−18(4)	22(4)	2(4)
C25	33(4)	51(4)	29(3)	10(3)	7(3)	6(3)
C26	27(4)	58(5)	46(5)	15(4)	6(3)	5(3)
C27	29(4)	100(8)	56(6)	31(5)	10(4)	14(5)

Table S31 Bond Lengths for ps19.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	C1	2.074(6)	C8	C9	1.369(11)
Pt1	P1	2.2298(16)	C9	C10	1.369(11)
Pt1	N7	2.027(5)	C10	C11	1.388(9)
Pt1	C17	2.050(6)	C11	C12	1.488(9)
C1	C2	1.402(9)	C12	C13	1.418(9)
C1	C6	1.430(9)	C12	C17	1.448(9)
P1	C19	1.857(7)	C13	C14	1.378(10)
P1	C22	1.833(7)	C13	C18	1.553(11)
P1	C25	1.858(7)	C14	C15	1.360(11)
C2	C3	1.368(10)	F15	C15	1.362(8)
C3	F3	1.373(8)	C15	C16	1.369(10)
C3	C4	1.377(11)	C16	C17	1.405(9)
C4	C5	1.377(10)	C19	C20	1.501(11)
C5	C6	1.411(9)	C20	C21	1.539(12)
C6	C7	1.457(9)	C22	C23	1.536(10)
C7	N7	1.351(8)	C23	C24	1.509(10)
C7	C8	1.395(9)	C25	C26	1.521(10)
N7	C11	1.364(8)	C26	C27	1.524(10)

Table S32 Bond Angles for ps19.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Pt1	P1	102.18(18)	C7	N7	C11	123.4(5)
N7	Pt1	C1	80.5(2)	C11	N7	Pt1	118.5(4)
N7	Pt1	P1	174.21(15)	C9	C8	C7	119.0(7)
N7	Pt1	C17	79.9(2)	C10	C9	C8	120.8(7)
C17	Pt1	C1	159.8(3)	C9	C10	C11	120.7(7)
C17	Pt1	P1	97.78(18)	N7	C11	C10	117.3(6)
C2	C1	Pt1	133.4(5)	N7	C11	C12	112.7(5)
C2	C1	C6	115.5(6)	C10	C11	C12	130.0(6)

C6	C1	Pt1	111.0(4)	C13	C12	C11	123.6(6)
C19	P1	Pt1	121.4(3)	C13	C12	C17	121.9(6)
C19	P1	C25	99.9(4)	C17	C12	C11	114.4(5)
C22	P1	Pt1	112.1(2)	C12	C13	C18	124.6(7)
C22	P1	C19	100.9(4)	C14	C13	C12	118.3(7)
C22	P1	C25	105.3(3)	C14	C13	C18	117.1(6)
C25	P1	Pt1	115.1(2)	C15	C14	C13	120.5(6)
C3	C2	C1	120.9(7)	C14	C15	F15	119.3(7)
C2	C3	F3	116.9(7)	C14	C15	C16	122.4(7)
C2	C3	C4	124.2(7)	F15	C15	C16	118.3(7)
F3	C3	C4	118.9(6)	C15	C16	C17	121.7(7)
C5	C4	C3	117.2(6)	C12	C17	Pt1	113.7(4)
C4	C5	C6	120.5(7)	C16	C17	Pt1	131.0(5)
C1	C6	C7	117.1(5)	C16	C17	C12	115.0(6)
C5	C6	C1	121.7(6)	C20	C19	P1	115.7(6)
C5	C6	C7	121.1(6)	C19	C20	C21	111.0(8)
N7	C7	C6	113.5(5)	C23	C22	P1	111.3(5)
N7	C7	C8	118.9(6)	C24	C23	C22	114.2(7)
C8	C7	C6	127.6(6)	C26	C25	P1	112.7(5)
C7	N7	Pt1	117.4(4)	C25	C26	C27	111.8(7)

Table S33 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps19.

Atom	*x*	*y*	*z*	U(eq)
H2	88	1340	6145	40
H4	-2254	513	4807	44
H5	-972	2173	4431	38
H8	482	3539	4091	41
H9	1966	5229	3851	49
H10	3550	6400	4438	44
H14	6160	8585	5883	47
H16	4549	5662	6697	45
H18A	5419	7266	4763	72
H18B	5675	8795	5041	72
H18C	4167	8341	4780	72
H19A	2687	943	7199	48
H19B	1299	1169	6813	48
H20A	3653	-287	6609	61
H20B	2360	65	6186	61
H21A	963	-1458	6562	101
H21B	2126	-1660	7043	101
H21C	2307	-2370	6524	101
H22A	2464	3669	7447	41
H22B	2724	5055	7123	41
H23A	515	4701	6616	50
H23B	256	3372	6963	50
H24A	-883	5355	7200	80
H24B	464	6331	7260	80
H24C	366	5033	7642	80
H25A	5131	3669	7057	45
H25B	4899	2010	7191	45
H26A	5477	2980	6254	53
H26B	5206	1319	6376	53
H27A	7575	1749	6473	92
H27B	7195	1317	7000	92
H27C	7465	2978	6878	92

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
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C19(H19A,H19B), C20(H20A,H20B), C22(H22A,H22B), C23(H23A,H23B), C25(H25A,
 H25B), C26(H26A,H26B)
2.b Aromatic/amide H refined with riding coordinates:
 C2(H2), C4(H4), C5(H5), C8(H8), C9(H9), C10(H10), C14(H14), C16(H16)
2.c Idealised Me refined as rotating group:
 C18(H18A,H18B,H18C), C21(H21A,H21B,H21C), C24(H24A,H24B,H24C), C27(H27A,H27B,
 H27C)
```

This report has been created with Olex2, compiled on 2015.01.26 svn.r3150 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Me_2-6-Pr
ps37

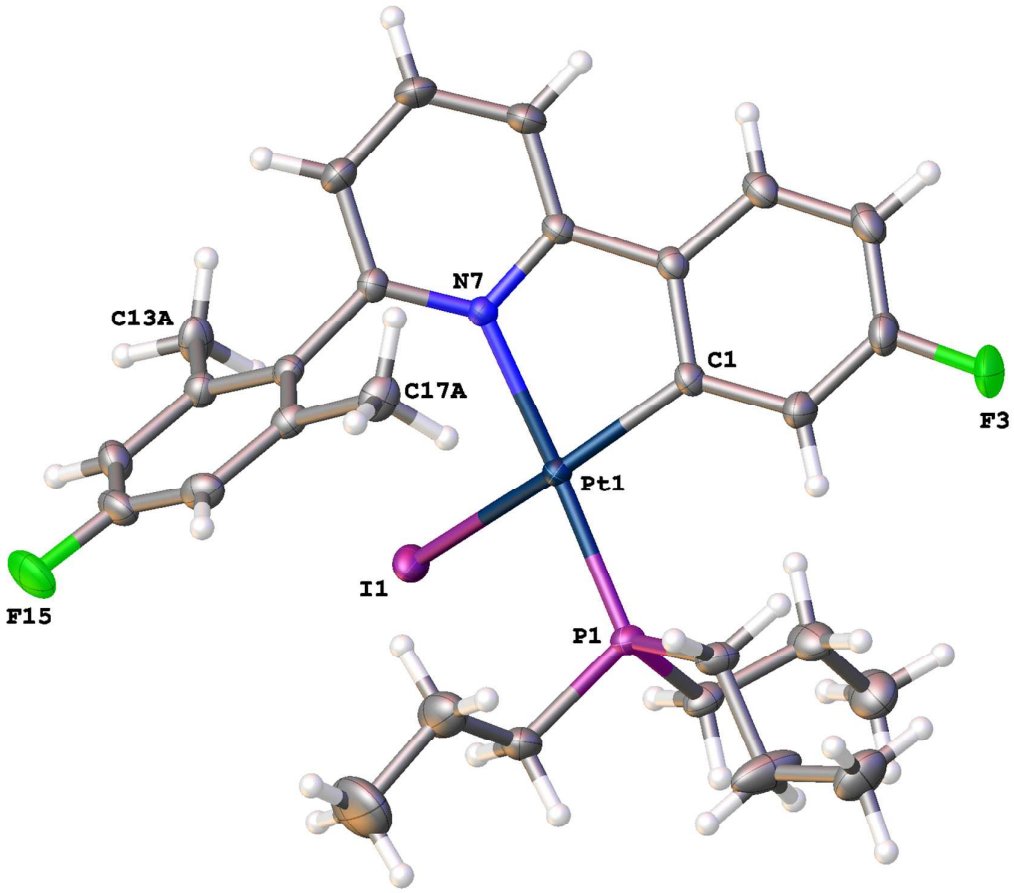

Figure SI10 *solid state structure of ps37 with only key atoms labeled and thermal ellipsoids at 50% probability level*

Crystal structure determination of [ps37]
The asymmetric unit contains the complex, there are 4 in the unit cell.

Angle between mean planes through various pi systems to characterize some of the bond angles in the bis fluorophenylpyridine system
In the chelated fluorphenylpyridine
Plane C1 C2 C3 C4 C5 C6 to plane N7 C11 C10 C9 C8 C7 is 9.770 (0.117) degrees

Between pyridine ring to dimethylated fluorophenyl ring
Plane N7 C11 C10 C9 C8 C7 to plane C12 C13 C14 C15 C16 C17 is 64.907 (0.076) degrees

The chelate flurophenylpyridine ring is a little twisted (see above) and the Pt lies slightly outside this plane
As a measure of this see the mean plane data below and how far the Pt lies outside this mean plane
Mean plane through chelate fluorophenylpyridine ligand C1 C3 C5 N7 C8 C10 and how far Pt1 lies out of the plane

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

7.2721 (0.0027) x + 8.8397 (0.0125) y + 1.5906 (0.0120) z = 6.9680 (0.0054)

* 0.0173 (0.0015) C1
* 0.0978 (0.0016) C3
* -0.0756 (0.0017) C5
* -0.1499 (0.0015) N7
* -0.0330 (0.0017) C8
* 0.1436 (0.0016) C10
-0.4505 (0.0025) Pt1
Rms deviation of fitted atoms = 0.0998

Similarly as a measure of how far the iodide is out of the plane formed by the other chelated atoms and Pt1

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)
7.1038 (0.0040) x + 7.7981 (0.0062) y + 4.5290 (0.0199) z = 8.0890 (0.0119)
* 0.0007 (0.0001) C1
* 0.0663 (0.0003) N7
* -0.1300 (0.0006) Pt1
* 0.0630 (0.0003) P1
-1.4930 (0.0029) I1
Rms deviation of fitted atoms = 0.0795

Probable pi stacking interaction between a chelated fluorophenylpyridine and a symmetry related chelated fluorophenylpyridine defined by atoms used to define the interacting systems, angles between these mean planes and closest atomic contact are
Mean plane C1 C3 C5 N7 C8 C10 to mean plane C1_$2 C3_$2 C5_$2 N7_$2 C8_$2 C10_$2
Angle between mean planes is zero because they are parallel related by another inversion centre
Closest atomic contact is C5 - C7_$2 3.3272 (0.0031)

There is also a possible interaction (but longer) on the other face of the fluorophenylpyridine ligand
Plane C1 C2 C3 C4 C5 C6 to plane C1_$1 C2_$1 C3_$1 C4_$1 C5_$1 C6_$1
Angle between mean planes is zero because they are parallel related by an inversion centre
Closest atomic contact is C1 - C3_$1 3.6712 (0.0033) Angstroms

Symmetry operators used to generate equivalent atoms in above contacts were
$1 1-X,1-Y,1-Z
$2 -X,1-Y,1-Z

Some important bits
There is an A alert in the cif checker for a close contact between a hydrogen of a CH2 on the tris-propylphosphine to an H on the chelated fluorophenylpyridine ring

Alert level A
PLAT410_ALERT_2_A Short Intra H...H Contact H2 .. H21A .. 1.78 Ang.

I can see the electron density associated with these hydrogens in a difference density map and placing them at calculated positions puts them in the correct orientation relative to the observed electron density so I am happy the hydrogens are there and occupying the correct orientations.
I believe that this steric interaction comes about because the tri-propylphosphine has to adopt the best (?) angle in relation to the Pt1-I1 and Pt1-C1 bonds to stop the steric clash with the bonds between the P-C bonds to the propyl chains (P1-C18, P1-21 and P1-C24). I have tried to show this below but it ends up being cluttered.

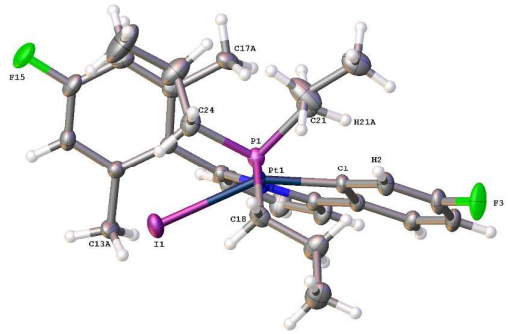

Figure SI11 *Picture looking very roughly down the P1-Pt1 bond trying to highlight how the P-C bonds of the tris-propylphophine don't overlap with the Pt1-I1 and Pt1-C1 bonds. The clashing atoms H2 and H21A are labeled*

I guess this must be the lowest energy orientation with respect to crystal packing forces?

Experimental
Single crystals of $C_{28}H_{35}F_2INPPt$ **[ps37]** were grown from chloroform (?). A suitable crystal was selected and mounted on a Rigaku Oxford Diffraction Xcalibur Gemini diffractometer with a 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.
17 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
18 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
19 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{28}H_{35}F_2INPPt$ (M =776.53 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 8.56227(7) Å, b = 17.96588(15) Å, c = 18.24470(15) Å, β = 96.9421(8)°, V = 2785.98(4) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 6.232 mm^{-1}, *Dcalc* = 1.851 g/cm^3, 85124 reflections measured (4.792° ≤ 2Θ ≤ 64.83°), 9618 unique (R_{int} = 0.0428, R_{sigma} = 0.0258) which were used in all calculations. The final R_1 was 0.0223 (I > 2σ(I)) and wR_2 was 0.0437 (all data).

Table S34 Crystal data and structure refinement for ps37.

Identification code	ps37
Empirical formula	$C_{28}H_{35}F_2INPPt$
Formula weight	776.53
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.56227(7)
b/Å	17.96588(15)
c/Å	18.24470(15)
α/°	90
β/°	96.9421(8)
γ/°	90
Volume/Å^3	2785.98(4)
Z	4
ρ_{calc}g/cm^3	1.851
μ/mm^{-1}	6.232
F(000)	1496.0
Crystal size/mm^3	0.3 × 0.3 × 0.2 orange block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.792 to 64.83
Index ranges	$-12 \le h \le 12$, $-27 \le k \le 26$, $-27 \le l \le 27$
Reflections collected	85124
Independent reflections	9618 [R_{int} = 0.0428, R_{sigma} = 0.0258]
Data/restraints/parameters	9618/0/312
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0223, wR_2 = 0.0413
Final R indexes [all data]	R_1 = 0.0306, wR_2 = 0.0437
Largest diff. peak/hole / e Å^{-3}	0.72/-0.84

Table S35 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ps37.
U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	2424.1(2)	4203.0(2)	6534.5(2)	15.68(2)
I1	510.6(2)	3647.6(2)	7482.6(2)	25.62(4)
P1	3798.6(7)	3136.1(3)	6641.8(3)	19.52(11)
C1	2892(2)	4527.9(12)	5529.4(11)	18.5(4)
C2	3602(3)	4137.7(13)	4994.8(12)	25.4(5)
C3	3458(3)	4379.7(14)	4274.7(13)	28.4(5)
C4	2636(3)	4998.5(14)	4027.7(12)	27.7(5)
C5	1924(3)	5398.0(13)	4537.5(11)	23.0(4)
F3	4154(2)	3958.5(10)	3783.8(8)	47.0(4)
C6	2041(2)	5178.5(12)	5279.1(11)	18.5(4)
C7	1338(3)	5609.7(12)	5827.5(11)	18.9(4)
N7	1500.4(19)	5305.9(9)	6517.6(9)	15.9(3)
C8	631(3)	6301.7(13)	5694.4(13)	28.5(5)
C9	153(3)	6703.3(14)	6267.8(13)	31.2(5)
C10	447(3)	6421.9(13)	6975.6(12)	25.1(5)
C11	1124(2)	5725.9(12)	7093.9(11)	18.0(4)
C12	1582(2)	5485.3(11)	7871.4(11)	17.3(4)
C13	434(2)	5393.2(12)	8350.8(11)	20.2(4)
C13A	-1307(3)	5407.6(15)	8092.7(12)	26.8(5)
C14	901(3)	5253.9(13)	9095.7(12)	24.8(5)
C15	2476(3)	5228.9(13)	9342.0(12)	27.3(5)
F15	2910.0(19)	5117.9(9)	10080.3(7)	40.7(4)
C16	3626(3)	5314.9(13)	8891.0(12)	26.0(5)
C17	3187(2)	5451.7(12)	8142.0(12)	19.8(4)
C17A	4446(3)	5584.7(14)	7648.1(14)	27.5(5)
C18	2762(3)	2324.6(12)	6221.1(13)	24.0(4)
C19	2447(3)	2343.5(14)	5381.0(14)	34.8(6)
C20	1620(4)	1654.5(16)	5053.9(16)	41.5(7)
C21	5745(3)	3122.6(13)	6318.8(13)	26.1(5)
C22	6601(4)	2386.3(16)	6377(2)	51.7(9)
C23	7986(3)	2361.8(16)	5934.3(17)	40.3(6)
C24	4310(3)	2845.5(14)	7601.6(12)	29.0(5)
C25	5182(4)	3430.6(17)	8097.6(15)	43.8(7)
C26	5647(6)	3134(2)	8875.4(18)	78.2(13)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	19.27(4)	13.93(4)	14.41(4)	1.25(3)	4.36(3)	1.32(3)
I1	32.57(8)	20.57(7)	26.30(7)	2.20(5)	14.13(6)	-1.88(6)
P1	23.3(3)	15.2(2)	20.7(3)	1.8(2)	5.2(2)	2.5(2)
C1	21(1)	19.4(10)	15.8(9)	1.9(8)	5.6(7)	-0.8(8)
C2	31.4(12)	23.0(11)	23.3(11)	0.7(9)	10.0(9)	3.2(9)
C3	38.7(13)	27.5(12)	21.7(11)	-3.4(9)	14.3(10)	-1.3(10)
C4	37.7(13)	28.9(12)	17(1)	2.3(9)	5.9(9)	-5.7(10)
C5	28.4(11)	22.0(11)	18.5(10)	2.6(8)	2.3(8)	-3.7(9)
F3	76.3(12)	44.2(10)	25.8(8)	-1.1(7)	28.0(8)	14.1(9)
C6	20.6(10)	18.5(10)	16.6(9)	1.3(8)	3.6(7)	-2.3(8)
C7	21.9(10)	17.9(10)	17.2(9)	2.5(8)	3.4(8)	-0.2(8)
N7	17.3(8)	15.5(8)	15.1(7)	1.0(6)	2.7(6)	0.7(6)
C8	40.1(14)	23.4(11)	22.1(11)	7.6(9)	4.5(10)	8.5(10)
C9	41.5(14)	22.9(12)	29.2(12)	5.1(9)	4.6(10)	14.6(10)
C10	31.2(12)	20.5(11)	24.3(11)	-0.9(9)	5.5(9)	7.8(9)
C11	18.2(9)	18.8(10)	17.6(9)	-0.5(7)	3.8(7)	0.9(8)
C12	19.3(9)	14.9(9)	17.6(9)	-1.9(7)	1.7(7)	1.7(7)
C13	20.9(10)	20.9(10)	18.9(9)	-1.7(8)	2.6(8)	1.3(8)
C13A	18.5(10)	38.8(14)	23.8(11)	-4(1)	5.7(8)	3.1(9)
C14	30.1(11)	27.1(12)	18.1(10)	1.1(9)	6.5(8)	-1.3(9)
C15	38.4(13)	24.3(12)	17.4(10)	3.5(9)	-3.9(9)	0.3(10)
F15	52.5(10)	48.2(10)	18.4(7)	6.5(6)	-8.2(6)	-2.6(8)
C16	23.4(11)	24.9(11)	27.3(11)	-1.3(9)	-5.9(9)	1.7(9)
C17	19.0(9)	16.1(10)	24.2(10)	-2.9(8)	1.8(8)	-0.5(8)
C17A	18.5(10)	30.9(12)	33.4(12)	-5.7(10)	5.1(9)	-2.0(9)
C18	26.0(11)	15(1)	32.0(12)	0.2(9)	7.3(9)	-0.3(8)
C19	48.1(16)	21.4(12)	33.5(13)	-0.4(10)	-0.8(11)	-3.6(11)
C20	54.5(18)	30.1(14)	39.4(15)	-4.5(12)	3.6(13)	-5.6(13)
C21	25.6(11)	20.4(11)	32.9(12)	4.1(9)	6.1(9)	4.0(9)
C22	35.8(15)	26.5(14)	98(3)	12.4(15)	30.5(16)	10.4(12)
C23	30.7(13)	34.6(15)	56.7(18)	-6.9(13)	9.4(12)	6.2(11)
C24	37.4(13)	24.6(12)	25.2(11)	5.0(9)	4.4(10)	8.6(10)
C25	56.4(19)	38.4(16)	32.8(14)	-2.9(12)	-9.7(13)	10.2(14)
C26	115(4)	80(3)	32.6(17)	3.1(18)	-19(2)	14(3)

Table S36 Anisotropic Displacement Parameters ($Å^2×10^3$) for ps37. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+\ldots]$.

Table 4 Bond Lengths for ps37.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	I1	2.71245(16)	C9	C10	1.381(3)
Pt1	P1	2.2454(6)	C10	C11	1.384(3)
Pt1	C1	2.010(2)	C11	C12	1.489(3)
Pt1	N7	2.1324(17)	C12	C13	1.402(3)
P1	C18	1.827(2)	C12	C17	1.405(3)
P1	C21	1.834(2)	C13	C13A	1.508(3)
P1	C24	1.829(2)	C13	C14	1.392(3)
C1	C2	1.398(3)	C14	C15	1.370(3)
C1	C6	1.423(3)	C15	F15	1.368(2)
C2	C3	1.375(3)	C15	C16	1.366(3)
C3	C4	1.363(4)	C16	C17	1.395(3)
C3	F3	1.364(3)	C17	C17A	1.505(3)
C4	C5	1.375(3)	C18	C19	1.524(3)
C5	C6	1.401(3)	C19	C20	1.513(4)
C6	C7	1.453(3)	C21	C22	1.509(3)
C7	N7	1.364(3)	C22	C23	1.514(4)
C7	C8	1.391(3)	C24	C25	1.523(4)
N7	C11	1.364(3)	C25	C26	1.523(4)
C8	C9	1.373(3)			

Table S37 Bond Angles for ps37.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Pt1	I1	88.912(15)	C7	N7	C11	118.88(18)
C1	Pt1	I1	152.99(6)	C11	N7	Pt1	128.65(13)
C1	Pt1	P1	99.62(6)	C9	C8	C7	120.0(2)
C1	Pt1	N7	80.30(7)	C8	C9	C10	118.9(2)
N7	Pt1	I1	95.71(4)	C9	C10	C11	120.1(2)
N7	Pt1	P1	169.77(5)	N7	C11	C10	120.86(19)
C18	P1	Pt1	114.93(8)	N7	C11	C12	120.95(18)
C18	P1	C21	105.60(11)	C10	C11	C12	117.88(19)
C18	P1	C24	102.85(11)	C13	C12	C11	120.32(18)
C21	P1	Pt1	118.06(8)	C13	C12	C17	120.38(19)
C24	P1	Pt1	112.91(8)	C17	C12	C11	118.73(19)
C24	P1	C21	100.50(11)	C12	C13	C13A	122.96(19)
C2	C1	Pt1	129.95(16)	C14	C13	C12	119.3(2)
C2	C1	C6	115.89(19)	C14	C13	C13A	117.7(2)
C6	C1	Pt1	112.36(14)	C15	C14	C13	118.8(2)
C3	C2	C1	120.8(2)	F15	C15	C14	117.8(2)
C4	C3	C2	123.8(2)	C16	C15	C14	123.5(2)
C4	C3	F3	119.0(2)	C16	C15	F15	118.7(2)
F3	C3	C2	117.1(2)	C15	C16	C17	118.8(2)
C3	C4	C5	117.1(2)	C12	C17	C17A	121.60(19)

C4	C5	C6	121.4(2)	C16	C17	C12	119.2(2)
C1	C6	C7	117.12(18)	C16	C17	C17A	119.1(2)
C5	C6	C1	121.0(2)	C19	C18	P1	114.99(16)
C5	C6	C7	121.84(19)	C20	C19	C18	113.3(2)
N7	C7	C6	114.70(18)	C22	C21	P1	116.17(18)
N7	C7	C8	120.84(19)	C21	C22	C23	113.1(2)
C8	C7	C6	124.35(19)	C25	C24	P1	114.54(18)
C7	N7	Pt1	112.43(13)	C26	C25	C24	111.5(3)

Table S38 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ps37.

Atom	*x*	*y*	*z*	U(eq)
H2	4190	3700	5131	30
H4	2560	5147	3525	33
H5	1340	5832	4384	28
H8	479	6496	5207	34
H9	-371	7167	6179	37
H10	184	6707	7382	30
H13A	-1568	5863	7808	40
H13B	-1894	5397	8522	40
H13C	-1590	4972	7781	40
H14	142	5177	9427	30
H16	4706	5282	9084	31
H17A	4544	5145	7339	41
H17B	5451	5679	7951	41
H17C	4162	6017	7332	41
H18A	3387	1874	6370	29
H18B	1743	2278	6422	29
H19A	1795	2785	5229	42
H19B	3460	2399	5177	42
H20A	1482	1692	4514	62
H20B	588	1611	5231	62
H20C	2254	1214	5204	62
H21A	5625	3281	5795	31
H21B	6415	3497	6604	31
H22A	5853	1986	6202	62
H22B	6979	2287	6902	62
H23A	7612	2428	5409	60
H23B	8518	1880	6009	60
H23C	8724	2762	6099	60
H24A	3331	2711	7809	35
H24B	4971	2393	7610	35
H25A	6139	3587	7883	53
H25B	4502	3874	8120	53
H26A	6349	2706	8856	117
H26B	4701	2981	9089	117
H26C	6192	3526	9182	117

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
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C18(H18A,H18B), C19(H19A,H19B), C21(H21A,H21B), C22(H22A,H22B), C24(H24A,
 H24B), C25(H25A,H25B)
2.b Aromatic/amide H refined with riding coordinates:
 C2(H2), C4(H4), C5(H5), C8(H8), C9(H9), C10(H10), C14(H14), C16(H16)
2.c Idealised Me refined as rotating group:
 C13A(H13A,H13B,H13C), C17A(H17A,H17B,H17C), C20(H20A,H20B,H20C), C23(H23A,
 H23B,H23C), C26(H26A,H26B,H26C)
```

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.

Comparison of structures of Me-6-Pr and Me_2-6-Pr

It is possible to overlay the structures of **Me-6-Pr** ps25 with **Me_2-6-Pr** ps37.

The steric clash is avoided in ps25(green) as the relevant propyl chain with H22B adopts a downward trajectory/direction/orientation thus getting a bit further away from H2(b)
The same propyl chain in ps37 is rotated by roughly 180 degrees about P1-C21 bond which forces H21A close to H2(a) (the red molecule).
The propyl chain in ps37 is forced into this orientation because of the clash with the (second) methyl group C17A

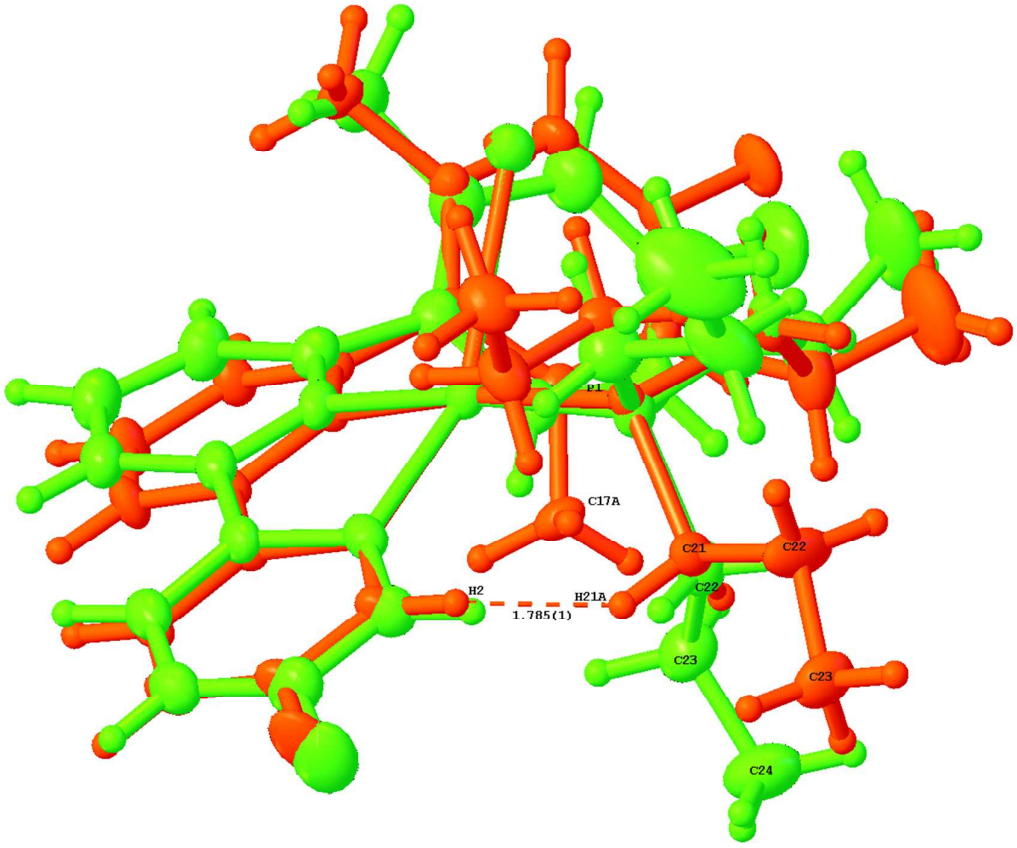

Figure SI12 **An overlay of the structures of Me-6-Pr with Me_2-6-Pr**