Supporting Info for:

Intramolecular transcyclometallation: the exchange of an aryl-Pt bond for an alkyl-Pt bond via an agostic intermediate

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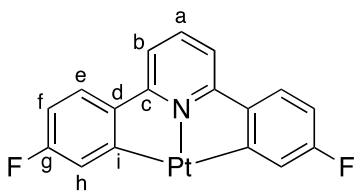
General

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, HMQC, HMBC and COSY pulse sequences. ^{1}H-^{19}F, ^{1}H-^{31}P and ^{1}H-^{195}Pt correlation spectra were recorded using a variant of the HMBC pulse sequence. ^{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) whereas the ^{195}Pt chemical shifts quoted are taken from the 2D HETCOR spectra (referenced to external Na_2PtCl_6). All elemental analyses were performed by Warwick Analytical Service. Starting platinum complex **1a** was prepared as previously reported (Cave, G. W. V.; Alcock, N. W.; Rourke, J. P., *Organometallics* **1999,** *18*, 1801; Cave, G. W. V.; Fanizzi, F. P.; Deeth, R. J.; Errington, W.; Rourke, J. P., *Organometallics* **2000,** *19*, 1355.).
Crystals of **1a** suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Fig S1 and Tables 1 and 2.

The following labelling scheme is used for all symmetrical C^N^C-Pt complexes:



Synthesis of complexes 1b, 1c

The following general method was used: to a solution of [(2,6-di(4-fluorophenyl)pyridine)Pt(DMSO)] **1a** in chloroform at room temperature was added a chloroform solution of 1 equivalent of the appropriate phosphine. The mixture was stirred for five minutes before solvent and liberated DMSO were removed under high vacuum. If necessary, column chromatography (chloroform on silica) was used to purify the products.

1b PMe_3

δ_H : 7.61 (1H, t, $^3J_{H-H}$ = 8Hz, H_a), 7.51 (2H, dd, $^3J_{H-H}$ = 8Hz, $^4J_{H-F}$ = 2Hz, H_e), 7.29 (2H, dd, $^3J_{H-F}$ = 8Hz, $^4J_{H-H}$ = 2Hz H_h), 7.25 (2H, dd, $^3J_{H-H}$ = 8Hz, $^4J_{H-P}$ = 1.5Hz, H_b), 6.76 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8Hz, $^4J_{H-H}$ = 2Hz, H_f), 1.91 (9H, dt, $^3J_{H-H}$ = $^3J_{H-F}$ = 10Hz, $^4J_{H-H}$ = 17 Hz, PMe_3).

δ_F : -110.43ppm ($^4J_{F-Pt}$ =28 Hz). δ_P : -27.42ppm ($^1J_{P-Pt}$ = 3655 Hz). δ_{Pt} : -4195 ppm (d, ~3670 Hz)

Anal. Found (expected for $C_{20}H_{18}F_2NPPt$): C 44.52 (44.78); H 3.72 (3.38); N 2.54 (2.61).

Crystals of **1b** suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Fig S2 and Tables 1 and 3.

1c PBu_3

δ_H : 7.62 (1H, t, $^3J_{H-H}$ = 8Hz, H_a), 7.52 (2H, dd, $^3J_{H-H}$ = 7Hz, $^4J_{H-F}$ = 2Hz, H_e), 7.27 (2H, dd, $^3J_{H-H}$ = 8Hz, $^3J_{H-F}$ = 3 Hz, H_h),7.22 (2H, d, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2Hz, H_b), 6.78 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 7Hz, $^4J_{H-H}$ = 2Hz, H_f), 2.10 (6H, m, $PCH_2CH_2CH_2CH_3$), 1.55 (6H, m, $PCH_2CH_2CH_2CH_3$), 1.45 (6H, m, $PCH_2CH_2CH_2CH_3$), 0.89 (9H, t, $^3J_{H-H}$ = 7Hz, $PCH_2CH_2CH_2CH_3$). GOESY: Irradiation of H_j enhances H_h.

δ_F : -111.59 ($^4J_{F-Pt}$ = 28 Hz). δ_P : 2.33 ($^1J_{P-Pt}$ = 3643 Hz). δ_{Pt} : -4215 (d, ≈3700 Hz).

Anal. Found (expected for $C_{29}H_{36}F_2NPPt$) : C 52.17 (52.56); H 5.50 (5.48); N 2.03 (2.11).

Oxidation of complexes 1b, 1c

In a typical procedure, 10mg of complex **1** was dissolved in chloroform and the solution cooled to -40°C. One equivalent of solid $PhICl_2$ was added directly into the solution, with agitation or stirring to ensure dissolution. After reaction, the solvent was removed and the solid product washed with hexane, before drying under vacuum.

Synthesis of complexes 2b(c) and 2b(t)

Clean formation of **2b(t)** at -40°C in chloroform, but within 20 minutes at room temperature, a mixture of **2b(c)** and **2b(t)** is seen. The proportion remains unchanged with time at around 85:15 **2b(t)**:**2b(c)**, and it proved impossible to separate them.

2b(t) δ_H : δ = 7.83 (1H, t, $^3J_{H-H}$ = 8Hz, H_a), 7.79 (2H, dd, $^3J_{H-H}$ = 8Hz, $^4J_{H-F}$ = 3Hz, H_e), 7.53 (2H, dd, $^3J_{H-H}$ = 8Hz, $^5J_{H-P}$ = 2Hz, H_b), 7.28 (2H, dd, $^4J_{H-H}$ = 3Hz, $^3J_{H-F}$ = 9Hz, H_h), 6.87 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8Hz, $^4J_{H-H}$ = 3Hz, H_f), 2.14 (9H, d, $^2J_{H-P}$ = 11Hz, $^3J_{H-Pt}$ = 16Hz, PMe_3).
δ_F : -107.64 ($^4J_{F-Pt}$ = 16 Hz). δ_F : -29.25 ppm ($^1J_{P-Pt}$ = 2360 Hz). δ_{Pt} : -2368ppm (d, ≈ 2360 Hz)
2b(c) δ_H : 7.85 (1H, t, $^3J_{H-H}$ = 8Hz, H_a), 7.80 (2H, dd, $^4J_{H-H}$ = 2Hz, $^3J_{H-F}$ = 9Hz, H_h), 7.72 (2H, dd, $^3J_{H-H}$ = 8Hz, $^4J_{H-F}$ = 3Hz, H_e), 7.41 (2H, d, $^3J_{H-H}$ = 8Hz, H_b), 6.95 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8Hz, $^4J_{H-H}$ = 3Hz, H_f), 1.97 (9H, d, $^2J_{H-P}$ = 12Hz, $^3J_{H-Pt}$ = 24Hz, PMe_3).
δ_F : -105.15 ($^4J_{F-Pt}$ = 15 Hz). δ_P : -12.19 ($^1J_{P-Pt}$ = 2390 Hz). δ_{Pt} : -1885ppm (d, ≈ 2400 Hz).
HR-MS (ESI): found *m/z* 606.0214, 570.0449, calc for $C_{20}H_{19}F_2Cl_2NP^{194}Pt$ = 606.0227 (MH^+); calc for $C_{20}H_{18}F_2ClNP^{194}Pt$ = 570.0460 $[M\text{-}Cl]^+$)

Synthesis of complexes 2c(c) and 2c(t)

The oxidation of **1c** was performed following the general procedure, but in acetone. Initially, **2c(t)** was formed and could be isolated, but leaving a chloroform solution at room temperature to stand (typically 5 days) resulted in complete isomerisation to **2c(c)**.

2c(t) δ_H : 7.86 (1H, t, J = 8Hz, H_a), 7.77 (2H, dd, J = 8.5, 5.5 Hz, H_e), 7.55 (2H, dd, J = 8, J_{PH} = 2 Hz, H_b), 7.27 (2H, dd, J = 2.5, J_{HF} = 6.5 Hz, $^3J_{H\text{-}Pt}$ = 23 Hz, H_h) 6.88 (2H, td, J = J_{HF} = 8.5, J = 2.5 Hz, H_f), 2.50 (6H, m, $PCH_2CH_2CH_2CH_3$), 1.75 (6H, m, $PCH_2CH_2CH_2CH_3$), 1.54 (6H, m, $PCH_2CH_2CH_2CH_3$), 0.98 (9H, t, J = 7.5 Hz, $PCH_2CH_2CH_2CH_3$).

Significant enhancement of H_h when PBu protons irradiated (64 scans GOESY).

δ_F : -108.77 ($^4J_{F\text{-}Pt}$ = 15 Hz). δ_P : -13.75 ($^1J_{P\text{-}Pt}$ = 2306 Hz). δ_{Pt} : -2276 (d, ~2400 Hz).

732.1648, calc for $C_{29}H_{37}F_2Cl_2NP^{194}Pt$ = 732.1630 (MH^+).

Crystals suitable for Xray analysis were grown by the evaporation of solvent from a chloroform solution, Fig S3 and Tables 1, 4 and 5.

2c(c) δ_H : 7.75 (2H, t, ^{3}J = 8 Hz, H_a), 7.68 (2H, dd, ^{3}J = 8.5, $^4J_{HF}$ = 5.5 Hz, H_e), 7.50 (2H, d, ^{3}J = 8 Hz, H_b), 7.30 (1H, dd, ^{4}J = 2.5, $^3J_{HF}$ = 7.5 Hz, $^3J_{H\text{-}Pt}$ = 22 Hz, H_h), 6.88 (2H, td, ^{3}J = $^3J_{HF}$ = 8.5, ^{4}J = 2.5 Hz, H_f), 1.72 (6H, m, $PCH_2CH_2CH_2CH_3$), 1.14 (6H, m, $PCH_2CH_2CH_2CH_3$), 0.98 (6H, m, $PCH_2CH_2CH_2CH_3$), 0.75 (9H, t, J = 7.5 Hz, $PCH_2CH_2CH_2CH_3$).

No enhancement of H_h when PBu protons irradiated (64 scans GOESY).

δ_F : -106.38 ($^4J_{F\text{-}Pt}$ = 14 Hz). δ_P : -0.68 ($^1J_{P\text{-}Pt}$ = 2330 Hz). δ_{Pt} : -2639 (d, ~2300 Hz).

HR-MS (ESI): found *m/z* 696.1868, calc for $C_{29}H_{36}F_2ClNP^{194}Pt$ = 696.1863 $[M\text{-}Cl]^+$)

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Fig S4 and Tables 1, 6 and 7.

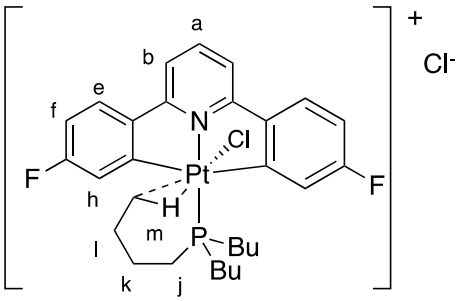
Synthesis of complexes 3, 4 and 5 (no silver)

The oxidation of **1c** was performed at -60°C in chloroform, typically yielding a mixture of 25% **3** and 75% **2c(t)**. When the reaction was allowed to warm up to -40°C, all the **3** transformed into **4**. These components remained unchanged on further warming to room temperature. Separation by column chromatography (chloroform/toluene on silica) gave pure **2c(t)** and **5**.

Synthesis of complexes 3, 4 and 5 (with silver)

1c was dissolved chloroform and cooled to -60°C in a Schlenk tube. 2 equivalents of $AgBF_4$ were added and the mixture stirred vigorously before 1 equivalent of $PhICl_2$ was added. The mixture was allowed to warm to -40°C before 4 equivalents of solid NaCl were added. After stirring for a further 5 minutes, the mixture was allowed to warm to room temperature whereupon it was filtered. The solvent was removed from the filtrate and the product further purified (if necessary) by column chromatography (chloroform/toluene on silica) giving pure **5**.

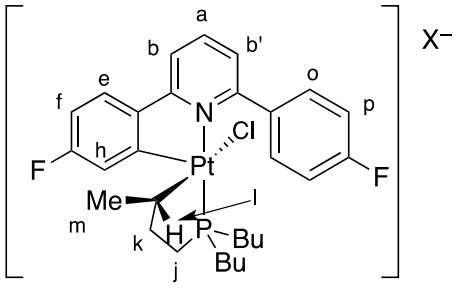
Agostic complex 3



δ_H (600MHz, 213K, $CDCl_3$): 8.01 (2H, d, $^3J_{H\text{-}H}$ = 8Hz, H_b), 7.33 (1H, t, $^3J_{H\text{-}H}$ = 7Hz, H_a), 6.68 (1H, d, $^3J_{H\text{-}H}$ = 9Hz, $^3J_{H\text{-}Pt}$ = 60 Hz, H_h), 2.78 (m, PBu), 2.49 (m, PBu), 2.19 (m, PBu), 1.92 (m, PBu), 1.78 (m, PBu), 1.43 (m, PBu), 2.49 (2H, m, H_k), 2.18 (2H, m, H_l), 0.75 (3H, t, ^{3}J = 6 Hz, $J_{H\text{-}Pt}$ ~20 Hz, H_m).

δ_P (213K, $CDCl_3$): 49.55 ($^1J_{P\text{-}Pt}$ = 3064 Hz). δ_F (213K, $CDCl_3$): -108.7 ($^4J_{F\text{-}Pt}$ = 15 Hz). δ_{Pt} (213K, $CDCl_3$): -2341 (d, ~3100 Hz)

Agostic complex 4



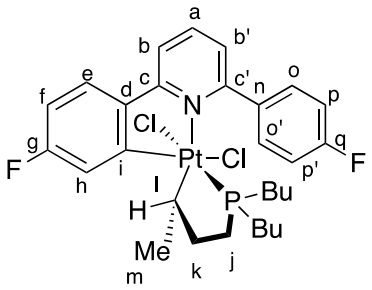
δ_H (500MHz, 263K, $CDCl_3$): 7.80 (2H, dd, $^3J_{H-F}$ = 4 Hz, $^3J_{H-H}$ = 8 Hz, H_o) 7.26 (1H, m, H_a), 7.04 (1H, dt, $^3J_{H-F}$ = 10Hz, $^4J_{H-H}$ = $^4J_{P-H}$ = 2.5 Hz, $^3J_{H-Pt}$ ~ 40 Hz, H_h), 2.45 (1H, m, $^2J_{H-Pt}$ ~ 100 Hz, H_l), 2.97 (m, H_j), 2.52 (m, H_k), 2.42 (m, $PCH_2CH_2CH_2CH_3$), 1.82 (m, $PCH_2CH_2CH_2CH_3$), 0.99 (6H, m, $PCH_2CH_2CH_2CH_3$), 0.42 (3H, d, $^3J_{H-H}$ = 7 Hz, $^3J_{H-Pt}$ = 38Hz, H_m).

Note, strong correlation of Pt to H_m, H_h and H_l when HMBC Pt-H coupling parameter set to 100 Hz, but no correlation of Pt to H_l when this parameter is set to 50Hz or less. When same parameter set to 10 Hz, we see an additional correlation to signal for H_o.

δ_F (263K, $CDCl_3$): -112.37, -107.45 ($^4J_{F-Pt}$ = 14 Hz). δ_P (263K, $CDCl_3$): 39.34 ($^1J_{P-Pt}$ = 3140 Hz). δ_{Pt} (263K, $CDCl_3$): -2570 (d, $^1J_{P-Pt}$ ~3100 Hz).

HR-MS (ESI): found *m/z* 660.2114, 696.1868; calc for $C_{29}H_{35}F_2NP^{194}Pt$ [M-2Cl-H] 660.2096, $C_{29}H_{36}F_2N^{35}ClP^{194}Pt$ [M-Cl] 696.1863.

Final complex 5



δ_H : 7.86 (2H, d,$^3J_{H-H}$ = 4.5 Hz, $H_{b,b'}$), 7.84 (2H, m, $H_{o/o'}$)*, 7.73 (1H, dd, $^3J_{H-H}$ = 8.5, $^4J_{H-F}$ = 5.5 Hz, H_e), 7.32 (3H, m, $H_{h,a}$), 7.14 (2H, t, $^3J_{H-H}$ = $^3J_{H-F}$ = 9Hz, $H_{p/p'}$)**, 6.95 (1H, dt, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5, $^4J_{H-H}$ = 2 Hz, H_f), 3.59 (1H, q,$^3J_{H-H}$ = 7Hz, $^2J_{H-Pt}$ = 75 Hz, H_l), 2.43 (1H, m, Bu), 1.98 (1H, m, H_j), 1.84 (1H, m, H_k), 1.61 (2H, m, H_j), 1.44 (3H, d,$^3J_{H-H}$ = 6.5 Hz, 36 Hz $^3J_{H-Pt}$, Me_m), 1.32 (2H, m, Bu), 1.20 (1H, m, H_k), 1.00 (4H, m, Bu), 0.93 (2H, m, Bu), 0.89 (3H, t, $^3J_{H-H}$ = 7 Hz, H_{Me}), 0.87 (2H, m, Bu), 0.68 (3H, t, $^3J_{H-H}$ = 7 Hz, H_{Me}) ppm.

*At 298K, at 400 MHz, both H_o and $H_{o'}$ form a single peak (28Hz FWHM). This peak does not correlate to anything in a COSY spectrum. At 253K this broad multiplet has separated into two broad lumps, and at 233K these lumps can be assigned chemical shifts of 8.31 (21 Hz FWHM) and 7.31ppm. Heating the sample to 328K narrows the peak substantially (9 Hz FWHM), and the peak now correlates to $H_{p,p'}$ in a COSY spectrum.

**At 298K, at 400 MHz, this peak is a triplet. At 253K the triplet loses shape, becoming a broad lump (28 Hz FWHM). At 233K the broad lump has now separated into two, about 44 Hz apart (7.19 and 7.08 ppm, 32 and 22 Hz FWHM respectively).

^{13}C NMR (500MHz, $CDCl_3$, 298K) δ= 13.12 (C_{Me}), 13.43 (C_{Me}), 20.95 (d, $^1J_{C-P}$ = 33Hz, $^2J_{C-Pt}$ = 45.5 Hz, C_{alkyl}), 20.62 (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 15.5 Hz, C_{alkyl}), 23.93 (d, $^1J_{C-P}$ = 39 Hz, $^2J_{C-Pt}$ = 70 Hz, C_j), 24.26 (C_{alkyl}), 26.11 ($^2J_{C-Pt}$ = 26 Hz, C_m), 37.47 (d, $^2J_{C-P}$ = 2.5 Hz, $^2J_{C-Pt}$ = 16.9 Hz, C_k), 53.79 (d, $^2J_{C-P}$ = 3.5 Hz, $^1J_{C-Pt}$ = 572 Hz, C_l), 112.87 (d, $^2J_{C-F}$ = 23 Hz, C_f), 114.84 (d, $^2J_{C-F}$ = 22 Hz, $C_{p.p'}$), 116.53 (d, $^2J_{C-F}$ = 21 Hz, $^2J_{C-Pt}$ = 30 Hz, C_h), 118.21 ($^2J_{C-Pt}$ = 9 Hz, $C_{b'}$), 126.06 (C_a), 128.22 (d, $^3J_{C-f}$ = 9 Hz, $^3J_{C-Pt}$ = 39.6 Hz, C_e), 135.64 (d, $^4J_{C-F}$ 3.5 Hz, C_n), 138.71 (C_b), 139.07 (d, 2.5 Hz, C_d), 141.71 (d, $^3J_{C-f}$ = 6 Hz, $^1J_{C-Pt}$ = 844 Hz, C_i), 162.45 (J_{C-Pt} = 48Hz, $C_{c/c'}$), 163 (d,$^1J_{C-F}$ = 255 Hz, $^3J_{C-Pt}$ = 70 Hz, C_g), 163.74 (d, $^1J_{C-Pt}$ = 248 Hz, C_q), 164.02 ($C_{c/c'}$). δ_F : -108.28 ($^4J_{F-Pt}$ 43.5 Hz), -112.88. δ_P : 40.02 ($^1J_{P-Pt}$ 2945 Hz). δ_{Pt} -2721 ($^1J_{Pt-P}$ ~ 3010 Hz). HR-MS (ESI): found *m/z* 660.2092, 696.183; calc for $C_{29}H_{35}F_2NP^{194}Pt$ [M-2Cl-H] 660.2096, $C_{29}H_{36}F_2N^{35}ClP^{194}Pt$ [M-Cl] 696.186.

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Fig S4 and Tables 1, 8 and 9.

Table 1: Xray Crystal Data

	1a	**1b**	**2c(t)**	**2c(c)**	**5**
Crystal form	yellow block	yellow block	yellow block	yellow needle	yellow needle
Dimensions/mm	0.80x0.14x0.12	0.22x0.2x0.10	0.35×0.35×0.2	0.32×0.12×0.03	0.16×0.08×0.02
Emp. Formula	$C_{20}H_{16}Cl_3F_2NOPtS$	$C_{20}H_{18}F_2NPPt$	$C_{59}H_{73}Cl_7F_4N_2P_2Pt_2$	$C_{29}H_{36}Cl_2F_2NPPt$	$C_{29}H_{36}Cl_2F_2NPPt$
Mw	657.84	536.41	1586.46	733.55	733.55
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1$	C2/c	$P2_1/c$	Pbca	$Pna2_1$
a/Å	5.897(2)	23.9938(6)	42.5003(7)	14.9738(3)	17.9634(6)
b/Å	13.924(5)	12.5106(3)	8.95573(17)	15.8809(4)	13.9987(4)
c/Å	12.852(4)	12.1687(3)	15.7762(2)	24.6498(8)	11.0698(4)
α/°	90	90	90	90	90
β/°	96.001(10)	107.325(3)	92.9490(14)	90	90
γ/°	90	90	90	90	90
U/Å^3	1049.4(6)	3487.04(15)	5996.83(17)	5861.7(3)	2783.66(16)
T/K	180(2)	150(2)	150(2)	150(2)	150(2)
Z	2	8	4	8	4
D_{calc}/Mg m^{-3}	2.082	2.044	1.757	1.662	1.750
F(000)	628	2048	3128	2896	1448
μ(MoKα)/mm^{-1}	7.196	8.161	5.078	5.056	5.323
θ max/°	28.81	37.64	30.81	31.17	61.50
Refl. Measured	3773	33119	39740	45707	19220
Unique data	3532	8858	17255	8857	7402
*R*1 [$I > 2\sigma(I)$]	0.0285	0.0214	0.0365	0.0309	0.0406
*wR*2	0.0642	0.0484	0.0647	0.0611	0.0771
Data/rest/param	3773/1/266	8858/0/229	17255/0/691	8857/50/359	7402/1/328

The Xray Structure of **1a**

The asymmetric unit contained one molecule of the complex composed of a ligand, a DMSO and the Pt(II) and a chloroform molecule of crystallisation.

Fig S1

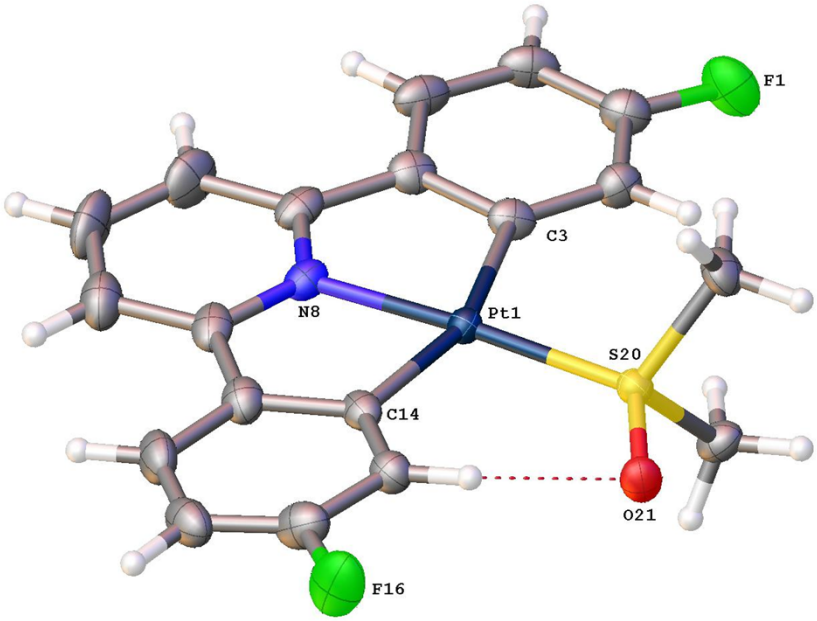


Table 2. Selected bond lengths [A] and angles [deg] for **1a**.

Pt1-N8	2.021(6)
Pt1-C14	2.069(7)
Pt1-C3	2.104(7)
Pt1-S20	2.1922(18)
F1-C1	1.353(9)
S20-O21	1.472(5)
S20-C23	1.768(7)
S20-C22	1.779(7)
N8-Pt1-C14	79.9(3)
N8-Pt1-C3	79.9(3)
C14-Pt1-C3	159.8(3)
N8-Pt1-S20	176.28(18)
C14-Pt1-S20	98.9(2)
C3-Pt1-S20	101.4(2)
C7-N8-C9	123.3(7)
C7-N8-Pt1	118.2(5)
C9-N8-Pt1	118.4(5)
O21-S20-C23	106.5(3)
O21-S20-C22	103.8(3)
C23-S20-C22	101.9(4)
O21-S20-Pt1	119.4(2)
C23-S20-Pt1	111.9(3)
C22-S20-Pt1	111.7(3)

The Xray Structure of **1b**

The asymmetric unit contains the complex. There are 8 complexes in the unit cell. The complexes forms pi stacked dimers related by an inversion centre. Pi stacking is defined by the angle between mean planes through interacting pi systems and closest atomic contact. As the pi systems are related by an inversion centre the mean planes through the interacting pi systems are parallel.

The closest atomic contact is 3.3679 (0.0030)

The pi stacking doesn't extend any further than this and the crystal packing is formed from these dimers stacking roughly orthogonal to each other.

Fig S2

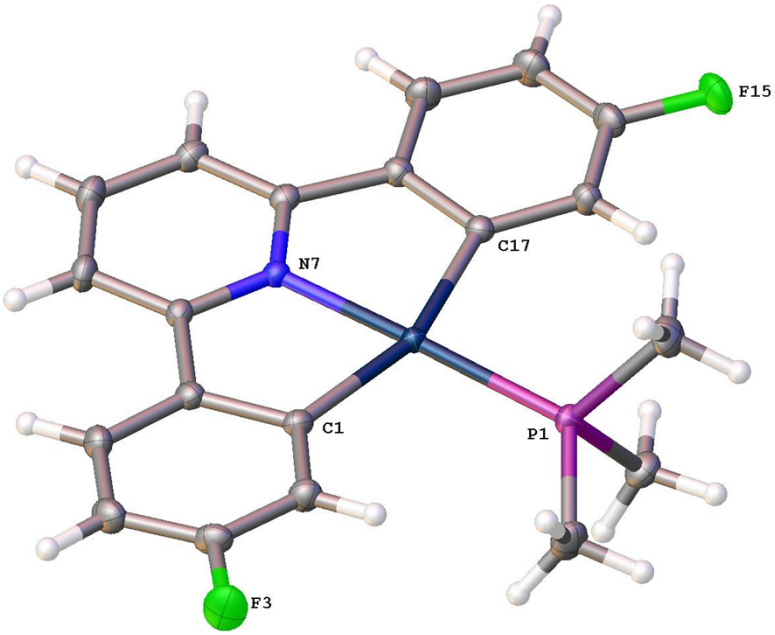


Table 3. Selected Bond lengths [A] and angles [deg] for **1b**.

Pt(1)-N(7)	2.0223(14)
Pt(1)-C(17)	2.0718(17)
Pt(1)-C(1)	2.0768(16)
Pt(1)-P(1)	2.2277(5)
P(1)-C(18)	1.809(2)
P(1)-C(19)	1.8193(19)
P(1)-C(20)	1.820(2)
F(3)-C(3)	1.363(2)
N(7)-Pt(1)-C(17)	80.06(6)
N(7)-Pt(1)-C(1)	79.89(6)
C(17)-Pt(1)-C(1)	159.83(7)
N(7)-Pt(1)-P(1)	172.66(4)
C(17)-Pt(1)-P(1)	96.51(5)
C(1)-Pt(1)-P(1)	103.66(5)
C(18)-P(1)-C(19)	100.71(11)
C(18)-P(1)-C(20)	100.18(10)

C(19)-P(1)-C(20)	104.48(10)
C(18)-P(1)-Pt(1)	120.36(7)
C(19)-P(1)-Pt(1)	116.70(7)
C(20)-P(1)-Pt(1)	112.02(7)
C(7)-N(7)-C(11)	122.65(15)
C(7)-N(7)-Pt(1)	118.65(12)
C(11)-N(7)-Pt(1)	118.54(11)

The Xray Structure of **2c(c)**

The asymmetric unit contains the complex, there are 8 complexes in the unit cell. Two of the butyl chains were modelled as disordered over two positions. In the chain terminating with C25, the terminal C25 was modelled as disordered over two positions and refined to a ration 53:47. In the chain terminating with C29, the terminal atoms C28 and C29 were modelled as disordered over two positions and also refined to a ration 53:47. Several SIMU and DELU restraints were used to give the disordered components reasonable thermal parameters.

Fig S3

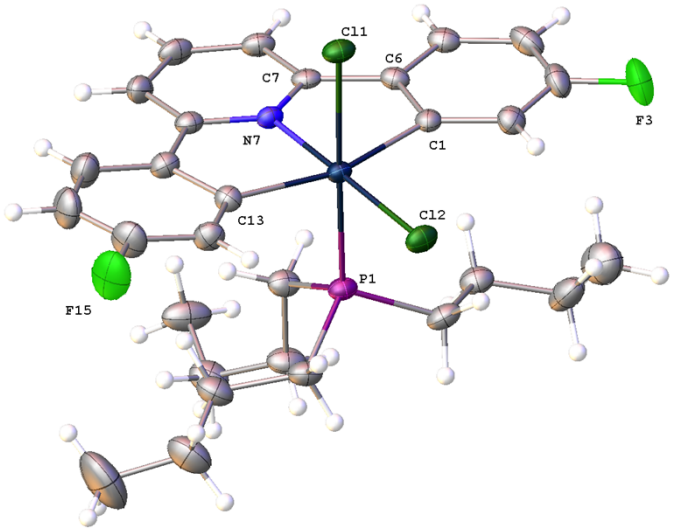


Table 4 bond lengths for **2c(c)**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Pt1	2.066(3)	C10	C11	1.388(4)
C1	C2	1.391(4)	C11	C12	1.477(4)
C1	C6	1.419(4)	C12	C13	1.420(4)
Cl1	Pt1	2.4098(7)	C12	C17	1.393(5)
P1	Pt1	2.2901(7)	C13	C14	1.389(4)
P1	C18	1.810(3)	C14	C15	1.381(5)
P1	C22	1.825(3)	C15	F15	1.363(4)
P1	C26	1.808(3)	C15	C16	1.368(5)
Pt1	Cl2	2.3324(7)	C16	C17	1.384(5)
Pt1	N7	1.979(2)	C18	C19	1.537(5)
Pt1	C13	2.074(3)	C19	C20	1.517(5)
C2	C3	1.382(5)	C20	C21	1.505(5)
C3	F3	1.368(4)	C22	C23	1.529(5)
C3	C4	1.374(5)	C23	C24	1.527(5)
C4	C5	1.385(5)	C24	C25	1.503(15)
C5	C6	1.392(4)	C24	C25A	1.540(18)
C6	C7	1.474(4)	C26	C27	1.541(4)
C7	N7	1.354(4)	C27	C28	1.507(8)
C7	C8	1.387(4)	C27	C28A	1.543(8)

N7	C11	1.356(4)	C28	C29	1.40(2)
C8	C9	1.380(5)	C28A	C29A	1.54(2)
C9	C10	1.387(5)			

Table 5 bond angles for **2c(c)**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	Pt1	130.3(2)	C8	C7	C6	128.3(3)
C2	C1	C6	118.7(3)	C7	N7	Pt1	117.8(2)
C6	C1	Pt1	111.0(2)	C7	N7	C11	124.4(3)
C18	P1	Pt1	112.64(11)	C11	N7	Pt1	117.7(2)
C18	P1	C22	105.32(15)	C9	C8	C7	118.8(3)
C22	P1	Pt1	111.73(11)	C8	C9	C10	121.9(3)
C26	P1	Pt1	112.71(10)	C9	C10	C11	118.4(3)
C26	P1	C18	106.40(16)	N7	C11	C10	118.3(3)
C26	P1	C22	107.56(16)	N7	C11	C12	113.8(3)
C1	Pt1	Cl1	87.62(8)	C10	C11	C12	127.9(3)
C1	Pt1	P1	92.41(8)	C13	C12	C11	115.9(3)
C1	Pt1	Cl2	98.27(9)	C17	C12	C11	122.9(3)
C1	Pt1	C13	162.29(12)	C17	C12	C13	121.1(3)
P1	Pt1	Cl1	178.12(3)	C12	C13	Pt1	110.9(2)
P1	Pt1	Cl2	85.55(3)	C14	C13	Pt1	130.4(2)
Cl2	Pt1	Cl1	92.58(3)	C14	C13	C12	118.4(3)
N7	Pt1	C1	81.41(11)	C15	C14	C13	118.7(3)
N7	Pt1	Cl1	88.78(7)	F15	C15	C14	118.3(3)
N7	Pt1	P1	93.08(7)	F15	C15	C16	118.1(3)
N7	Pt1	Cl2	178.58(7)	C16	C15	C14	123.6(3)
N7	Pt1	C13	81.50(11)	C15	C16	C17	118.8(3)
C13	Pt1	Cl1	87.43(8)	C16	C17	C12	119.4(3)
C13	Pt1	P1	93.08(8)	C19	C18	P1	117.6(2)
C13	Pt1	Cl2	98.93(9)	C20	C19	C18	111.2(3)
C3	C2	C1	118.2(3)	C21	C20	C19	113.7(3)
F3	C3	C2	117.6(3)	C23	C22	P1	116.6(2)
F3	C3	C4	118.3(3)	C24	C23	C22	111.3(3)
C4	C3	C2	124.0(3)	C23	C24	C25A	110.9(8)
C3	C4	C5	118.2(3)	C25	C24	C23	112.7(6)
C4	C5	C6	119.8(3)	C27	C26	P1	113.9(2)
C1	C6	C7	116.1(3)	C26	C27	C28A	112.7(4)
C5	C6	C1	120.9(3)	C28	C27	C26	113.3(4)
C5	C6	C7	123.0(3)	C29	C28	C27	116.4(11)
N7	C7	C6	113.5(3)	C29A	C28A	C27	115.4(10)
N7	C7	C8	118.1(3)				

The Xray Structure of **2c(t)**

There are two complexes and a molecule of chloroform in the asymmetric unit. Four times all this in the unit cell. There is a shortish contact between the chloroform CH and one of the bound chlorides but nothing really to discuss in the crystal packing.

Fig S4

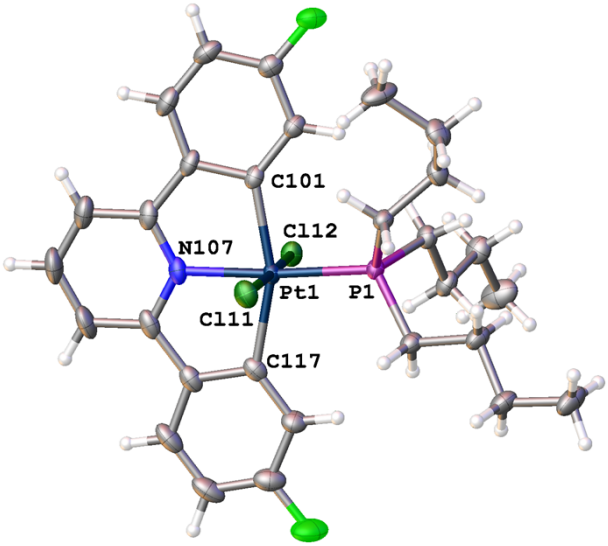


Table 6 Bond Lengths for 2c(t).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	Cl11	2.3327(9)	Pt2	C201	2.102(3)
Pt1	Cl12	2.3267(8)	Pt2	N207	2.046(3)
Pt1	C101	2.102(4)	Pt2	C217	2.127(3)
Pt1	N107	2.043(3)	Pt2	P2	2.3112(9)
Pt1	C117	2.123(4)	C201	C202	1.396(5)
Pt1	P1	2.3084(9)	C201	C206	1.415(5)
C101	C102	1.394(5)	C202	C203	1.378(5)
C101	C106	1.419(5)	C203	F203	1.359(4)
C102	C103	1.382(5)	C203	C204	1.366(5)
C103	F103	1.361(4)	C204	C205	1.382(5)
C103	C104	1.375(6)	C205	C206	1.391(5)
C104	C105	1.372(6)	C206	C207	1.463(5)
C105	C106	1.396(6)	C207	N207	1.350(4)
C106	C107	1.460(6)	C207	C208	1.395(5)
C107	N107	1.349(5)	N207	C211	1.349(4)
C107	C108	1.400(5)	C208	C209	1.390(6)
N107	C111	1.348(5)	C209	C210	1.366(6)
C108	C109	1.370(7)	C210	C211	1.393(5)
C109	C110	1.385(7)	C211	C212	1.462(5)
C110	C111	1.396(6)	C212	C213	1.398(5)
C111	C112	1.455(6)	C212	C217	1.423(5)
C112	C113	1.392(5)	C213	C214	1.374(6)
C112	C117	1.432(5)	C214	C215	1.365(6)
C113	C114	1.369(7)	C215	F215	1.366(4)
C114	C115	1.370(6)	C215	C216	1.380(5)
C115	F115	1.365(5)	C216	C217	1.387(5)
C115	C116	1.388(5)	P2	C218	1.822(3)
C116	C117	1.386(6)	P2	C222	1.831(4)
P1	C118	1.841(4)	P2	C226	1.818(4)
P1	C122	1.827(4)	C218	C219	1.526(5)
P1	C126	1.818(4)	C219	C220	1.519(5)
C118	C119	1.531(5)	C220	C221	1.514(5)
C119	C120	1.521(6)	C222	C223	1.526(5)
C120	C121	1.515(6)	C223	C224	1.506(6)

C122	C123	1.520(5)	C224	C225	1.529(6)
C123	C124	1.525(5)	C226	C227	1.515(5)
C124	C125	1.501(6)	C227	C228	1.537(6)
C126	C127	1.531(5)	C228	C229	1.503(6)
C127	C128	1.518(5)	C30	Cl31	1.750(5)
C128	C129	1.519(6)	C30	Cl32	1.746(4)
Pt2	Cl21	2.3234(8)	C30	Cl33	1.761(5)
Pt2	Cl22	2.3298(8)			

Table 7 Bond Angles for 2c(t).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl12	Pt1	Cl11	177.06(3)	C201	Pt2	Cl22	86.35(9)
C101	Pt1	Cl11	92.45(10)	C201	Pt2	C217	159.21(13)
C101	Pt1	Cl12	87.50(10)	C201	Pt2	P2	104.83(9)
C101	Pt1	C117	159.34(15)	N207	Pt2	Cl21	89.97(8)
C101	Pt1	P1	95.57(10)	N207	Pt2	Cl22	87.31(8)
N107	Pt1	Cl11	89.10(9)	N207	Pt2	C201	79.50(12)
N107	Pt1	Cl12	87.99(9)	N207	Pt2	C217	79.71(12)
N107	Pt1	C101	79.68(14)	N207	Pt2	P2	175.57(8)
N107	Pt1	C117	79.80(14)	C217	Pt2	Cl21	91.05(9)
N107	Pt1	P1	174.05(10)	C217	Pt2	Cl22	92.81(9)
C117	Pt1	Cl11	89.56(10)	C217	Pt2	P2	95.95(10)
C117	Pt1	Cl12	89.45(10)	P2	Pt2	Cl21	89.22(3)
C117	Pt1	P1	105.06(11)	P2	Pt2	Cl22	93.83(3)
P1	Pt1	Cl11	87.53(3)	C202	C201	Pt2	131.6(3)
P1	Pt1	Cl12	95.41(3)	C202	C201	C206	116.7(3)
C102	C101	Pt1	131.7(3)	C206	C201	Pt2	111.6(2)
C102	C101	C106	116.9(3)	C203	C202	C201	119.8(3)
C106	C101	Pt1	111.3(3)	F203	C203	C202	117.7(3)
C103	C102	C101	119.9(4)	F203	C203	C204	118.5(3)
F103	C103	C102	117.9(4)	C204	C203	C202	123.8(3)
F103	C103	C104	118.5(3)	C203	C204	C205	117.6(4)
C104	C103	C102	123.6(4)	C204	C205	C206	120.4(4)
C105	C104	C103	117.2(4)	C201	C206	C207	117.1(3)
C104	C105	C106	121.3(4)	C205	C206	C201	121.7(3)
C101	C106	C107	117.1(3)	C205	C206	C207	121.2(3)
C105	C106	C101	121.0(4)	N207	C207	C206	113.8(3)
C105	C106	C107	121.8(4)	N207	C207	C208	118.5(3)
N107	C107	C106	114.0(3)	C208	C207	C206	127.7(3)
N107	C107	C108	118.2(4)	C207	N207	Pt2	117.7(2)
C108	C107	C106	127.7(4)	C211	N207	Pt2	118.0(2)
C107	N107	Pt1	117.7(3)	C211	N207	C207	124.2(3)
C111	N107	Pt1	118.0(3)	C209	C208	C207	118.5(4)
C111	N107	C107	124.3(3)	C210	C209	C208	121.2(4)
C109	C108	C107	119.2(4)	C209	C210	C211	119.6(4)
C108	C109	C110	121.1(4)	N207	C211	C210	118.0(3)
C109	C110	C111	119.2(4)	N207	C211	C212	114.0(3)
N107	C111	C110	118.0(4)	C210	C211	C212	128.0(3)
N107	C111	C112	114.3(3)	C213	C212	C211	121.4(3)
C110	C111	C112	127.7(4)	C213	C212	C217	120.8(4)
C113	C112	C111	121.9(4)	C217	C212	C211	117.7(3)
C113	C112	C117	120.5(4)	C214	C213	C212	120.9(4)
C117	C112	C111	117.6(3)	C215	C214	C213	117.7(3)
C114	C113	C112	121.5(4)	C214	C215	C216	123.4(4)
C113	C114	C115	117.4(4)	F215	C215	C214	118.7(3)
C114	C115	C116	123.9(4)	F215	C215	C216	117.8(4)
F115	C115	C114	118.6(4)	C215	C216	C217	120.4(4)
F115	C115	C116	117.5(4)	C212	C217	Pt2	110.3(2)
C117	C116	C115	119.4(4)	C216	C217	Pt2	132.9(3)
C112	C117	Pt1	110.3(3)	C216	C217	C212	116.7(3)
C116	C117	Pt1	132.4(3)	C218	P2	Pt2	113.10(13)
C116	C117	C112	117.3(3)	C218	P2	C222	110.16(17)
C118	P1	Pt1	110.24(12)	C222	P2	Pt2	111.11(12)

C122	P1	Pt1	112.98(13)	C226	P2	Pt2	119.49(13)
C122	P1	C118	107.78(17)	C226	P2	C218	99.75(16)
C126	P1	Pt1	116.46(13)	C226	P2	C222	102.21(17)
C126	P1	C118	103.29(17)	C219	C218	P2	120.8(2)
C126	P1	C122	105.33(18)	C220	C219	C218	110.7(3)
C119	C118	P1	116.8(3)	C221	C220	C219	113.4(3)
C120	C119	C118	112.1(3)	C223	C222	P2	116.3(3)
C121	C120	C119	114.6(4)	C224	C223	C222	111.5(3)
C123	C122	P1	114.7(3)	C223	C224	C225	113.5(4)
C122	C123	C124	110.8(3)	C227	C226	P2	117.8(3)
C125	C124	C123	112.9(4)	C226	C227	C228	113.1(3)
C127	C126	P1	115.8(3)	C229	C228	C227	114.0(4)
C128	C127	C126	111.0(3)	Cl31	C30	Cl33	110.0(2)
C127	C128	C129	113.3(4)	Cl32	C30	Cl31	110.7(3)
Cl21	Pt2	Cl22	174.81(3)	Cl32	C30	Cl33	110.3(3)
C201	Pt2	Cl21	88.81(9)				

The Xray Structure of **5**

The asymmetric unit contains the Pt complex with a metallated bis 2,6-bis(4-fluorophenyl)pyridyl ligand, two chlorides and a metallated tributylphosphine ligand. There is 4 times all this in the unit cell.

The molecule has crystallised in a polar space group [Pna2(1)] which means that the crystal itself has a polar axis because all the molecules are pointing in one overall direction (no inversion centre in this space group). There are however both enantiomers of the complex present.

Fig S5

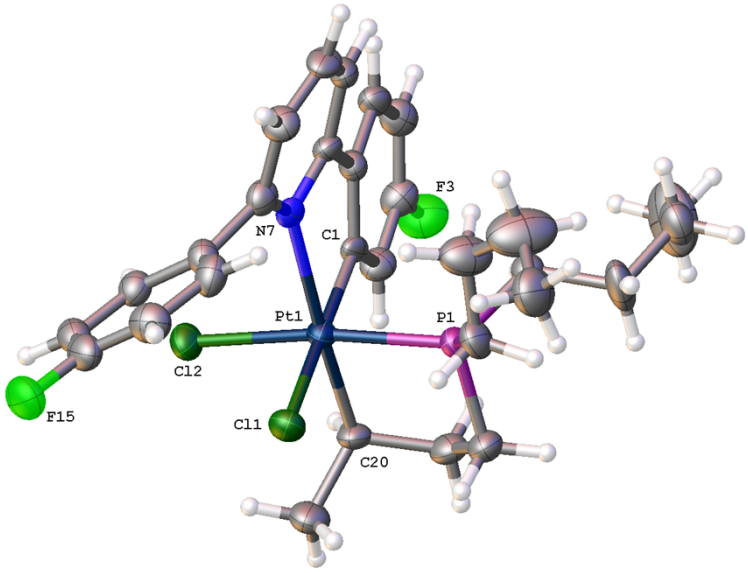


Table 8 Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Pt1	2.027(8)	C8	C9	1.357(12)
C1	C2	1.383(12)	C9	C10	1.362(14)
C1	C6	1.413(12)	C10	C11	1.384(13)
Cl1	Pt1	2.432(2)	C11	C12	1.488(13)
P1	Pt1	2.274(3)	C12	C13	1.391(13)
P1	C18	1.832(10)	C12	C17	1.388(13)
P1	C22	1.810(9)	C13	C14	1.397(14)
P1	C26	1.801(10)	C14	C15	1.357(15)
Pt1	Cl2	2.389(2)	C15	F15	1.359(11)
Pt1	N7	2.274(7)	C15	C16	1.375(13)
Pt1	C20	2.111(9)	C16	C17	1.383(13)
C2	C3	1.377(13)	C18	C19	1.518(13)
C3	F3	1.381(11)	C19	C20	1.518(14)
C3	C4	1.353(14)	C20	C21	1.531(13)
C4	C5	1.369(12)	C22	C23	1.529(13)
C5	C6	1.398(12)	C23	C24	1.506(13)
C6	C7	1.473(11)	C24	C25	1.503(15)
C7	N7	1.358(9)	C26	C27	1.494(15)

C7	C8	1.385(13)	C27	C28	1.464(17)
N7	C11	1.358(11)	C28	C29	1.483(16)

Table 9 Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	Pt1	128.0(7)	N7	C7	C6	115.7(7)
C2	C1	C6	117.7(8)	N7	C7	C8	121.9(8)
C6	C1	Pt1	114.3(6)	C8	C7	C6	122.4(8)
C18	P1	Pt1	100.9(3)	C7	N7	Pt1	108.9(5)
C22	P1	Pt1	115.0(3)	C7	N7	C11	117.2(7)
C22	P1	C18	106.1(5)	C11	N7	Pt1	131.4(6)
C26	P1	Pt1	119.4(4)	C9	C8	C7	119.7(8)
C26	P1	C18	108.5(5)	C8	C9	C10	119.0(9)
C26	P1	C22	106.0(5)	C9	C10	C11	120.0(9)
C1	Pt1	Cl1	174.4(2)	N7	C11	C10	121.4(9)
C1	Pt1	P1	91.5(2)	N7	C11	C12	120.0(8)
C1	Pt1	Cl2	88.5(2)	C10	C11	C12	118.3(8)
C1	Pt1	N7	79.4(3)	C13	C12	C11	120.1(9)
C1	Pt1	C20	92.8(4)	C17	C12	C11	120.9(8)
P1	Pt1	Cl1	85.74(9)	C17	C12	C13	118.7(9)
P1	Pt1	Cl2	171.07(9)	C12	C13	C14	120.1(10)
Cl2	Pt1	Cl1	94.95(9)	C15	C14	C13	118.8(10)
N7	Pt1	Cl1	96.02(17)	C14	C15	F15	118.0(9)
N7	Pt1	P1	96.23(19)	C14	C15	C16	123.2(9)
N7	Pt1	Cl2	92.56(19)	F15	C15	C16	118.7(10)
C20	Pt1	Cl1	91.8(3)	C15	C16	C17	117.4(10)
C20	Pt1	P1	84.6(3)	C16	C17	C12	121.8(9)
C20	Pt1	Cl2	86.5(3)	C19	C18	P1	103.8(6)
C20	Pt1	N7	172.2(3)	C18	C19	C20	110.3(8)
C3	C2	C1	119.5(9)	C19	C20	Pt1	111.8(7)
C2	C3	F3	117.4(9)	C19	C20	C21	111.1(8)
C4	C3	C2	123.8(9)	C21	C20	Pt1	114.2(7)
C4	C3	F3	118.8(8)	C23	C22	P1	116.0(7)
C3	C4	C5	117.9(9)	C24	C23	C22	113.6(9)
C4	C5	C6	120.8(9)	C25	C24	C23	115.3(11)
C1	C6	C7	118.5(7)	C27	C26	P1	115.5(7)
C5	C6	C1	120.3(8)	C28	C27	C26	118.7(11)
C5	C6	C7	121.2(8)	C27	C28	C29	118.8(13)