

Concerted reductive coupling of an alkyl chloride at Pt(IV)

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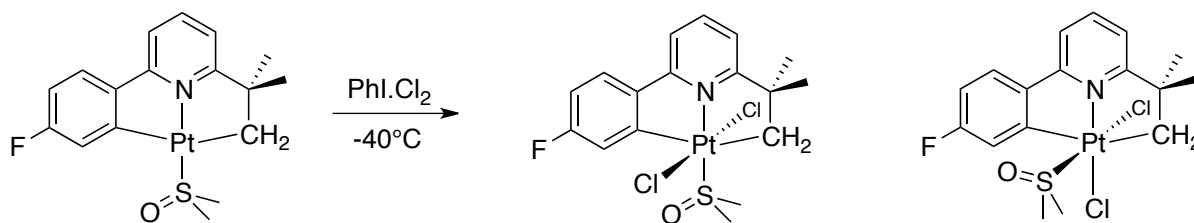
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Supporting Information.

Experimental

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400, 500 or 600 MHz spectrometer in CDCl₃ or D₆-acetone (these solvents were used as supplied and not dried); ¹H and ¹³C shifts are referenced to external TMS, assignments being made with the use of decoupling, NOE and the HMBC, HMQC, DEPT and COSY pulse sequences. ¹⁹F chemical shifts are quoted from the directly observed signals and are referenced to external CFCl₃. ¹H-¹⁹⁵Pt correlation spectra were recorded using a variant of the HMBC pulse sequence with the ¹⁹⁵Pt chemical shifts quoted taken from the 2D HETCOR spectra and referenced to external Na₂PtCl₆. All accurate mass spectra were run on a Bruker MaXis mass spectrometer and X-ray crystal structures were collected on an Oxford Diffraction Gemini four-circle system with Ruby CCD area detector. The synthesis of **1** has been reported previously (S. H. Crosby, G. J. Clarkson and J. P. Rourke, *J. Am. Chem. Soc.*, 2009, **131**, 14142-14143; *Organometallics*, 2011, **30**, 3603-3609.)

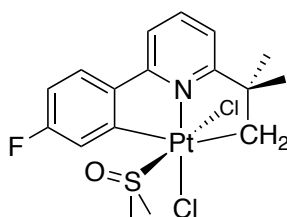
Oxidation of Complex 1



A small quantity of the Pt(II) complex **1** (approximately 10 mg) was dissolved in 0.7 ml of either CDCl₃ or acetone-d₆ inside an NMR tube. The sample was taken down to -40°C inside the appropriate NMR spectrometer and a variety of spectra run on the starting material. The tube was removed from the spectrometer and immediately placed in a dry ice/acetone bath; iodobenzene dichloride (1 eq or excess depending on the experiment) was added. The solution was mixed and the tube placed back inside the spectrometer and allowed to warm to -40°C. Reactions were monitored by ¹H, ¹⁹F, ¹³C and ¹⁹⁵Pt-NMR. When required for structural characterisation other 2D techniques were also carried out along with GOESY experiments. The temperature inside the spectrometer was raised in increments and NMR spectra obtained at each temperature.

When CDCl₃ was used as a solvent the reaction proceeded to give a mixture of two complexes identified as *cis* and *trans* **2**, in a 3:1 ratio at -40°C. When the same reaction was carried out in acetone d₆ the reaction proceeded to give 95% *cis* **2**.

cis-**2**



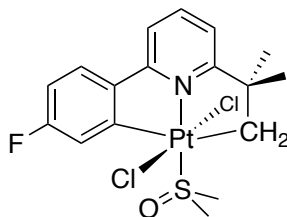
δ_{H} (600 MHz, 233 K, CDCl₃): 7.93 (1H, t, ³J = 7.7 Hz, H_f), 7.89 (1H, dd, ³J = 9.6 Hz, ⁴J = 2.5 Hz, H_h), 7.45 (1H, d, ³J = 8 Hz, H_g), 6.88 (1H, d, ³J = 8 Hz, H_e), 3.75 (3H, s, H_{i/j}), 3.72 (3H, s, H_{i/j}), *3.71 (1H, d, ²J = 8 Hz, H_{c/d}) 3.33 (1H, d, ²J = 8 Hz, ²J_{H-Pt} = 72 Hz, H_{c/d}) 2.12 (3H, s, H_{b/a}), *1.15 (1H, s, H_{b/a}) ppm.

*same face of molecule

δ_{F} (375 MHz, 233 K, CDCl₃): -105.5 (⁴J_{F-Pt} = 41 Hz) ppm.

δ_{Pt} (233 K, CDCl₃): -2092 ppm. (233 K, CD₃COCD₃): -2080 ppm.

trans-2



δ_{H} (600 MHz, 298 K, CDCl_3): 7.91 (1H, dd, $^3J_{\text{H-F}} = 8.3$ Hz, $^4J = 2.6$ Hz, H_m), 7.79 (1H, t, $^3J = 7.9$ Hz, H_f), 7.74 (1H, dd, $^3J = 8.6$ Hz, $^4J_{\text{H-F}} = 5.1$ Hz, H_j), 7.59 (1H, d, $^3J = 7.8$ Hz, H_g), 7.03 (1H, dd, $^3J = 7.8$ Hz, $^4J = 1.1$ Hz, H_e), 6.86 (1H, td, $^3J_{\text{H-H, H-F}} = 8.7$ Hz, $^4J = 2.7$ Hz, H_k), 3.56 (6H, s, $^3J_{\text{H-Pt}} = 13$ Hz, H_o), 2.64 (2H, s, $^3J_{\text{H-Pt}} = 48$ Hz, H_b), 1.55 (6H, s, H_a) ppm.

δ_{C} (150 MHz, 298 K, CDCl_3): 176.4 (C_d), 167.0 (d, $^4J_{\text{C-F}} = 4.3$ Hz, C_n), 163.4 (d, $^1J_{\text{C-F}} = 258$ Hz, C_l), 160.6 (C_h), 140.5 (d, $^4J_{\text{C-F}} = 2$ Hz, C_i), 139.1 (C_f), 126.4 (d, $^3J_{\text{C-F}} = 8.7$ Hz, C_j), 120.1 (C_e), 120.0 (C_m), 116.8 ($^3J_{\text{C-Pt}} = 25$ Hz, C_g), 111.5 (d, $^2J_{\text{C-F}} = 24$ Hz, C_k), 51.4 (C_c), 42.4 ($^2J_{\text{C-Pt}} = 32.5$ Hz, C_o), 40.1 ($^1J_{\text{C-Pt}} = 335$ Hz, C_b), 33.8 (C_a) ppm.

δ_{F} (375 MHz, 298 K, CDCl_3): -106.8 ($^4J_{\text{F-Pt}} = 14$ Hz) ppm.

δ_{Pt} (233K, CDCl_3): -1926 ppm.

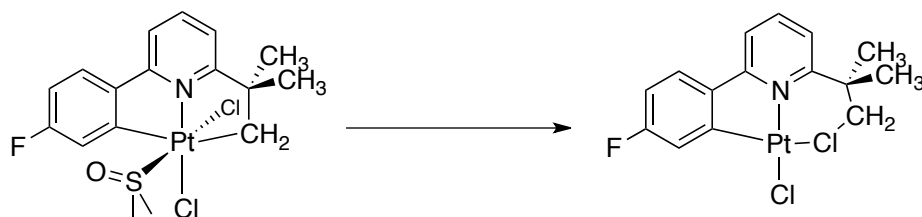
Elemental Analysis: Found (calculated) C 35.34 (35.73); H 3.72 (3.53); N 2.68 (2.45).

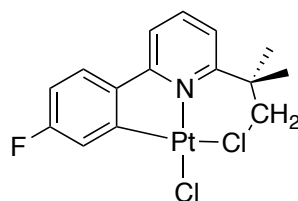
HR-MS (ESI): m/z 570.0325, calculated for $\text{C}_{17}\text{H}_{21}^{35}\text{Cl}_2\text{FNO}^{194}\text{PtS} = (\text{M}+\text{H})^+$ 570.0326; 592.0148, calculated for $\text{C}_{17}\text{H}_{20}^{35}\text{Cl}_2\text{FNNO}^{194}\text{PtS} = (\text{M}+\text{Na})^+$ 592.0145.

As the temperature of the reaction mixture was increased, at 0°C new species were observed in the NMR spectrum depending on the quantity of iodobenzene dichloride added at the start of the reaction.

When 1 equivalent of iodobenzene dichloride was used:

Once the reaction mixture reached room temperature the solvent was removed; column chromatography, loading silica and eluting with chloroform, resulted in the isolation of complex **3** as fraction 1. Complex *trans* **2** was also isolated as fraction 3.





Complex 3

δ_{H} (600 MHz, 298 K, CDCl_3): 7.79 (1H, t, $^3J = 8$ Hz, H_d), 7.54 (1H, dd, $^3J_{\text{H-F}} = 9.8$ Hz, $^4J = 2.6$ Hz, H_h), 7.57 (1H, dd, $^3J = 8$ Hz, $^4J = 1.1$ Hz, H_e), 7.30 (1H, dd, $^3J = 8.6$ Hz, $^4J_{\text{H-F}} = 5.5$ Hz, H_f), 7.24 (1H, dd, $^3J = 8$ Hz, $^4J = 1.3$ Hz, H_c), 6.78 (1H, td, $^3J_{\text{H-H}}, \text{H-F} = 8.5$ Hz, $^4J = 2.6$ Hz, H_g), 3.89 (2H, s, H_b), 1.75 (6H, s, H_a) ppm.

δ_{C} (150 MHz, 298 K, CDCl_3): 139.2 (C_d), 125.8 (d, $^3J_{\text{C-F}} = 9.3$ Hz, C_f), 119.6 (d, $^2J_{\text{C-F}} = 21.6$ Hz, C_h), 118.8 (C_c), 117.9 (C_e), 112.0 (d, $^2J_{\text{C-F}} = 23.3$ Hz, C_g), 52.7 (C_b), 27.8 (C_a) ppm.

δ_{F} (375 MHz, 298 K, CDCl_3): -106.9 ($^4J_{\text{F-Pt}} = 62$ Hz) ppm.

δ_{Pt} (298K, CDCl_3): -3577 ppm.

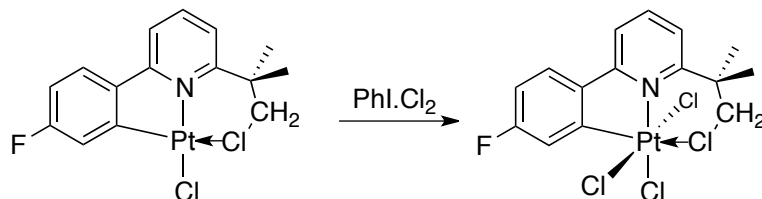
Elemental Analysis: Found (calculated) C 36.39 (36.52); H 2.94 (2.86); N 2.91 (2.84).

HR-MS (ESI): m/z 264.0959, calculated for $\text{C}_{15}\text{H}_{16}^{35}\text{ClFN}$ 264.0955; 266.0936, calculated for $\text{C}_{15}\text{H}_{16}^{37}\text{ClFN}$ 266.0925; 514.0019, calculated for $\text{C}_{15}\text{H}_{14}^{35}\text{Cl}_2\text{FNNa}^{194}\text{Pt} = (\text{M}+\text{Na})^+$ 514.0006.

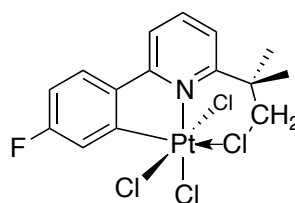
The coordination of the Cl to the platinum has not been proved, but the alternative of an agostic interaction from either the CH_2 , or the remaining two Me groups, can be ruled out from variable temperature NMR experiments which show no significant interactions between these protons and the ^{195}Pt nucleus.

When 2 equivalents of iodobenzene dichloride were used:

Once the reaction mixture reached room temperature the solvent was removed and column chromatography loading and eluting with chloroform resulted in the isolation of complex 4 as fraction 1. Complex *trans* 2 was also isolated as fraction 3.



Alternatively complex 4 could be synthesised by the addition of 1 equivalent of iodobenzene dichloride to a chloroform solution of complex 3.



Complex 4

δ_{H} (400 MHz, 233 K, CDCl_3): 7.97 (1H, t, $^3J = 8$ Hz, H_{g}), 7.87 (1H, dd, $^3J = 8$ Hz, $^4J = 1.1$ Hz, H_{h}), 7.70 (1H, dd, $^3J = 8$ Hz, $^4J = 1.3$ Hz, H_{f}), 7.65 (1H, dd, $^3J_{\text{H-F}} = 9$ Hz, $^4J = 2.5$ Hz, H_{k}), 7.57 (1H, dd, $^3J = 8.8$ Hz, $^4J_{\text{H-F}} = 5.5$ Hz, H_{i}), 7.02 (1H, td, $^3J_{\text{H-H, H-F}} = 8.4$ Hz, $^4J = 2.5$ Hz, H_{j}), 4.96 (1H, br, $H_{\text{b/c}}$), 4.01 (1H, br, $H_{\text{b/c}}$), 1.81 (6H, s, H_{a}) ppm.

At RT the CH_2 peak appears broad at 4.43 ppm

δ_{C} (125 MHz, 298 K, CDCl_3): 164.2 (C_{e}), 141.5 (C_{g}), 127.0 (d, $^3J_{\text{C-F}} = 9.2$ Hz, C_{i}), 123.0 (C_{f}), 120.6 (C_{h}), 118.6 (d, $^2J_{\text{C-F}} = 25$ Hz, C_{k}), 115.2 (d, $^2J_{\text{C-F}} = 23$ Hz, C_{j}), 55.3 (C_{b}), 44.9 (C_{d}), 30.3 (C_{a}) ppm.

δ_{F} (375 MHz, 253 K, CDCl_3): -101.2 ($^4J_{\text{F-Pt}} = 31$ Hz) ppm.

δ_{Pt} (298K, CDCl_3): -1148 ppm.

Elemental Analysis: Found (calculated) C 31.41 (31.93); H 2.46 (2.50); N 1.99 (2.48).

HR-MS (ESI): m/z 583.9381, calculated for $\text{C}_{15}\text{H}_{14}^{35}\text{Cl}_4\text{FNNa}^{194}\text{Pt} = (\text{M}+\text{Na})^+$ 583.9389.

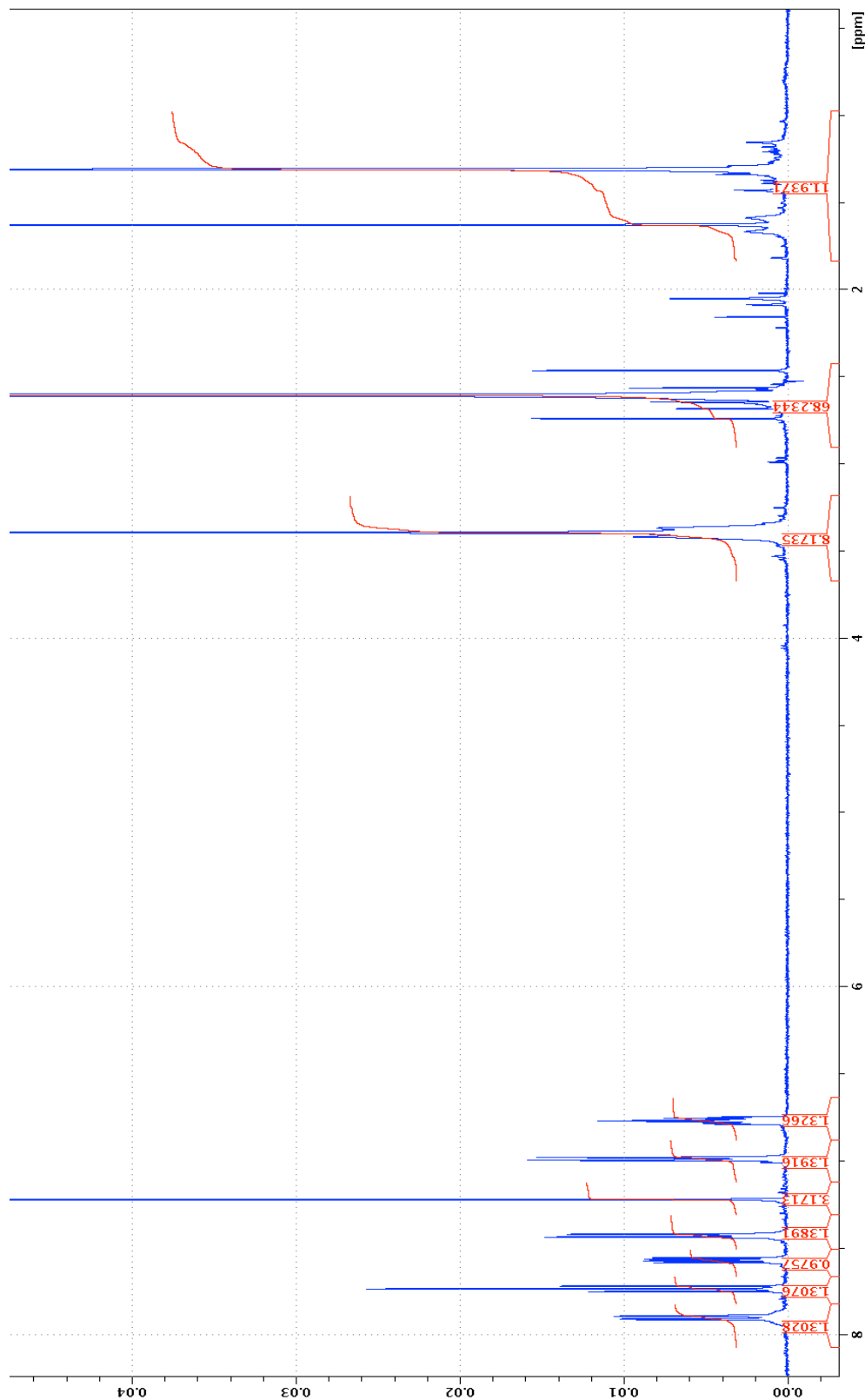
Crystals of **4** suitable for single crystal analysis were formed by slow evaporation of solvent from a chloroform solution.

Is “*cis-2*” actually *cis-2*, or is it the hydrated complex crystallised and depicted in Fig 1?

It is possible to explain the ^1H nmr of “*cis-2*” as arising from a complex like that depicted in Fig 1. However, we are confident that it is not the hydrated complex shown in Fig 1 because that complex does not react in the same way (it is as inert as *trans-2*), and we can make *cis-2* in anhydrous chloroform. We have considerable experience with identifying water complexes (see *Organometallics* 2010, **29**, 1966) and are fully confident that we do not have any here (as a matter of course we look at the very low temperature nmr spectra of all our complexes, in order to look for any fluxional process). The suggestion that “*cis-2*” is a solvento complex, and thus a chloroform complex in chloroform, but an acetone complex in acetone can be discounted from a consideration of the ^{195}Pt nmr shift: that of *cis-2* is only 170ppm different from that of *trans-2*. Compare our earlier work (*Organometallics* 2010) where we see a difference of 143ppm between two dmsO isomers of a cyclometallated pyridine (complexes **2a** and **4a** in that paper), but a difference of 685ppm between complexes with one ligand changed (S-bound dmsO vs O-bound dmsO, complexes **2a** vs **3a**) and 881ppm difference between a dmsO and a water complex with the other ligands remaining unchanged. Even more

convincingly, the ^{195}Pt shift of “*cis-2*” is only 12ppm different in chloroform and acetone (-2092 vs -2080ppm) – whereas we would expect the difference in the shifts to be vastly greater for a chloroform complex in chloroform and an acetone complex in acetone.

A copy of the spectrum of unreacted **1**, with XS dmsO (~8 equiv) is included for reference.



Additional NMR studies - Kinetics

Further experiments were conducted: a solution of **1** in CDCl₃ was split into four samples and these were oxidised at -40°C. One sample was then warmed to +5°C and the rate of the disappearance of the *cis* **2** monitored. To the other samples 2 equivalents of Bu₄NCl, Bu₄NBr, or Bu₄NI were added before they were warmed to +5°C and once again the rate of the disappearance of the *cis* **2** was monitored.

Another sample of a different concentration was used and yet another sample was treated with additional DMSO (10 equivalents), before oxidation.

Spectra were recorded roughly every 140 secs (total time elapsed up to 40 mins) at +5°C.

The accumulation of **3** mirrors the consumption of *cis*-**2**, but we could not measure the amount of **3** anywhere near as accurately: **3** does not have any coordinated DMSO peaks to observe, and its other resonances overlap with those from the other complexes present, meaning it is difficult to measure an integral in the NMR.

Applying a simple kinetic analysis, using the integral of the DMSO peaks of the *cis* **2** we observed first order kinetics. Within 15%, the rates at which the *cis* **2** was consumed was the same in all samples. Rate constant = $0.00091 \pm 0.00015 \text{ s}^{-1}$, i.e. a half-life of 760s.

Solvent	Additive	Rate
CDCl ₃	none	0.000941
CDCl ₃	CDCl ₃ (dilute sample)	0.000923
CDCl ₃	Bu ₄ NCl (2 equiv)	0.000841
CDCl ₃	Bu ₄ NBr (2 equiv)	0.000843
CDCl ₃	Bu ₄ NI (2 equiv)	0.000954
CDCl ₃	DMSO (10 equiv)	0.000941
Acetone	none	0.000950*

* not used to calculate mean rate constant as this rate must be a composite one from reductive elimination and isomerisation

Fig1: the graph for the unadulterated sample. X axis is in thousand of seconds, with the y axis the ln(relative integral)

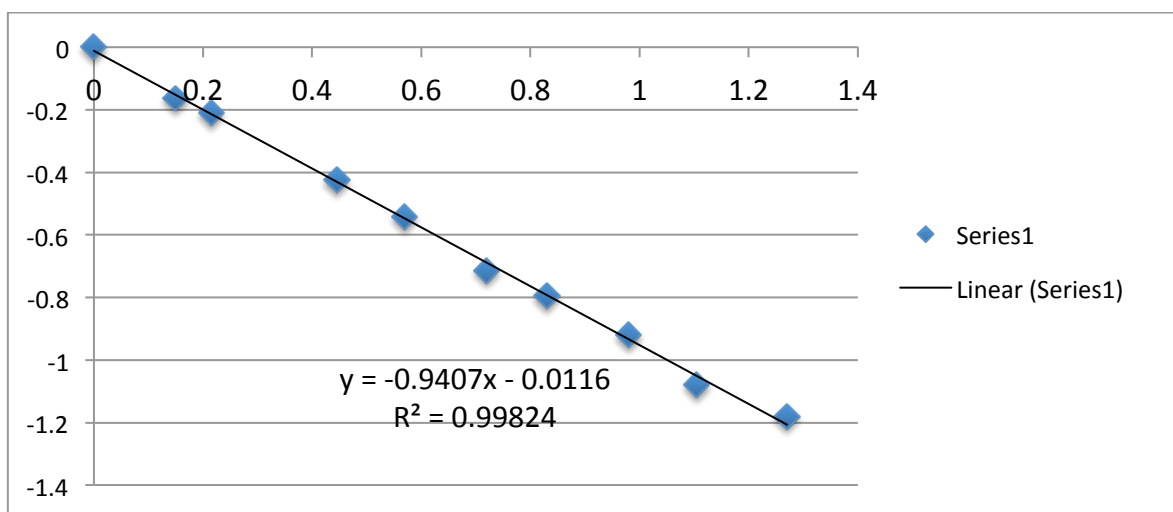


Fig 2: as fig 1, but the dilute sample

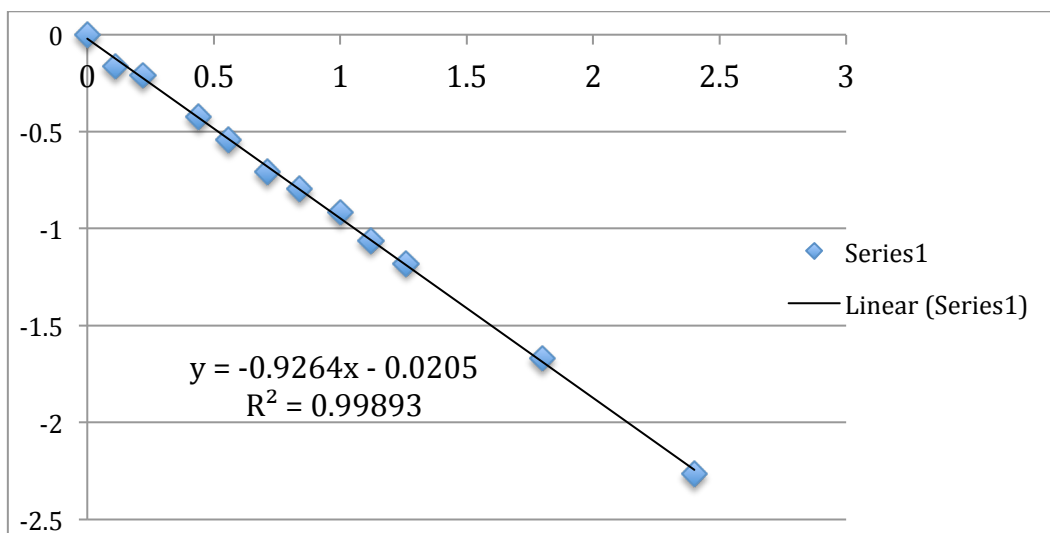


Fig 3: with chloride added

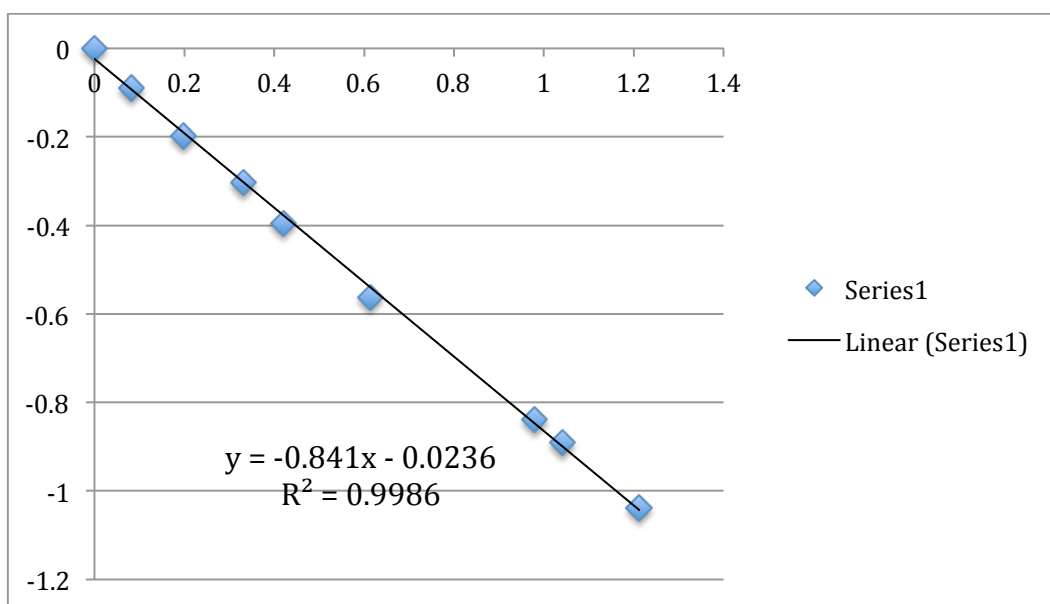


Fig 4 With bromide added

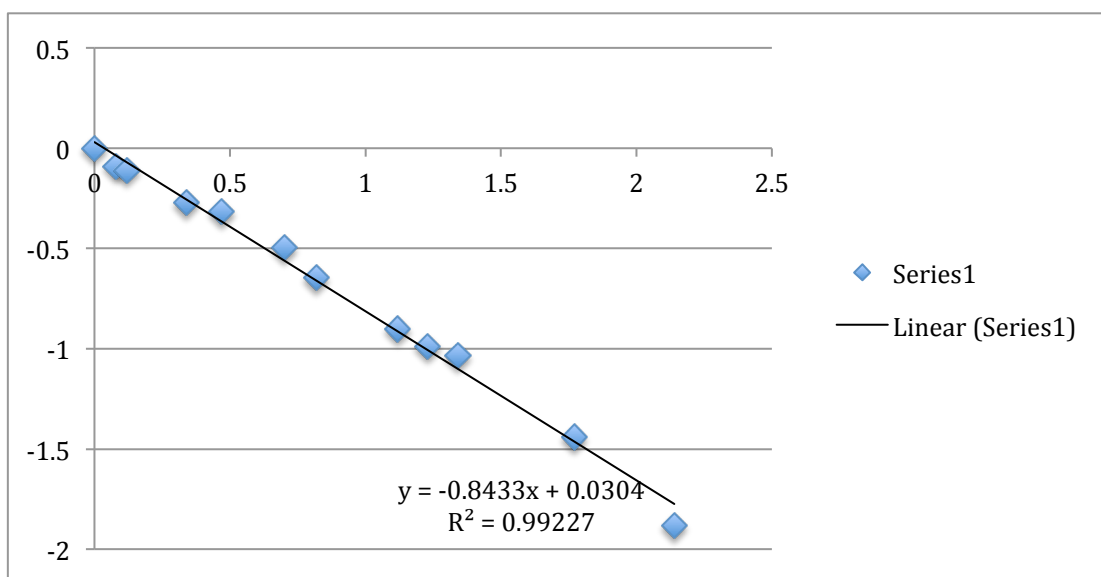


Fig 5 with iodide added

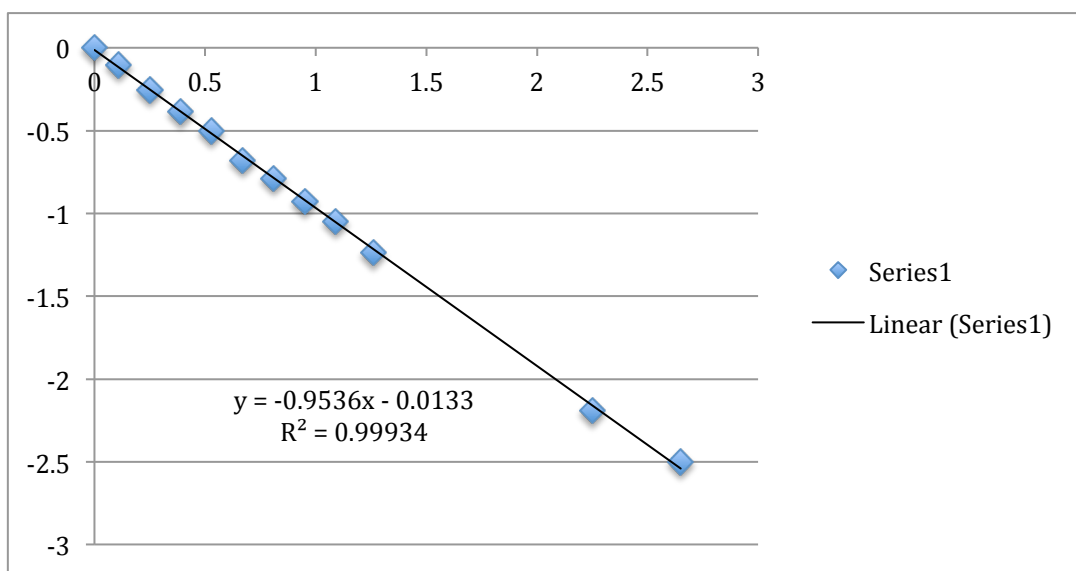


Fig 6 With dmsO

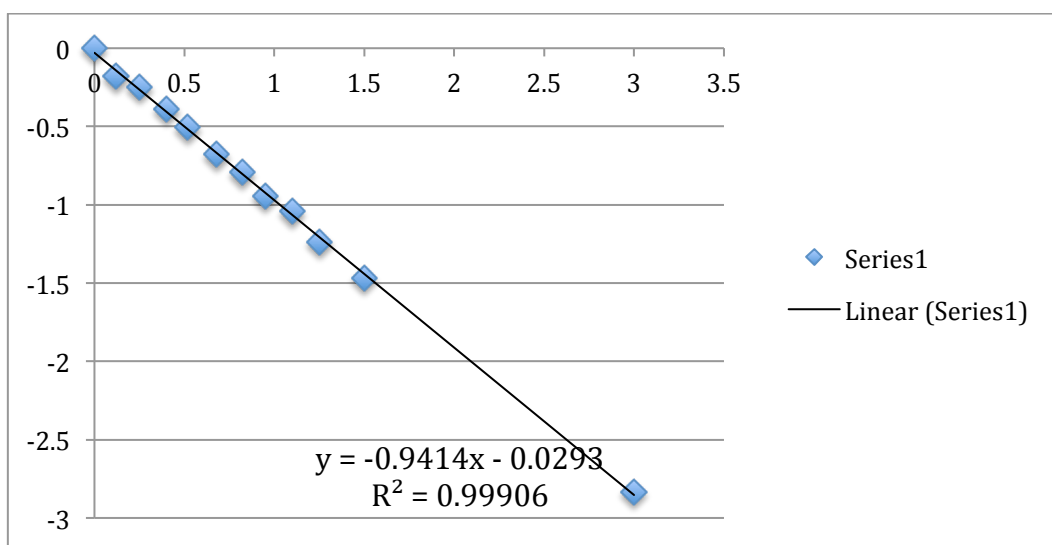
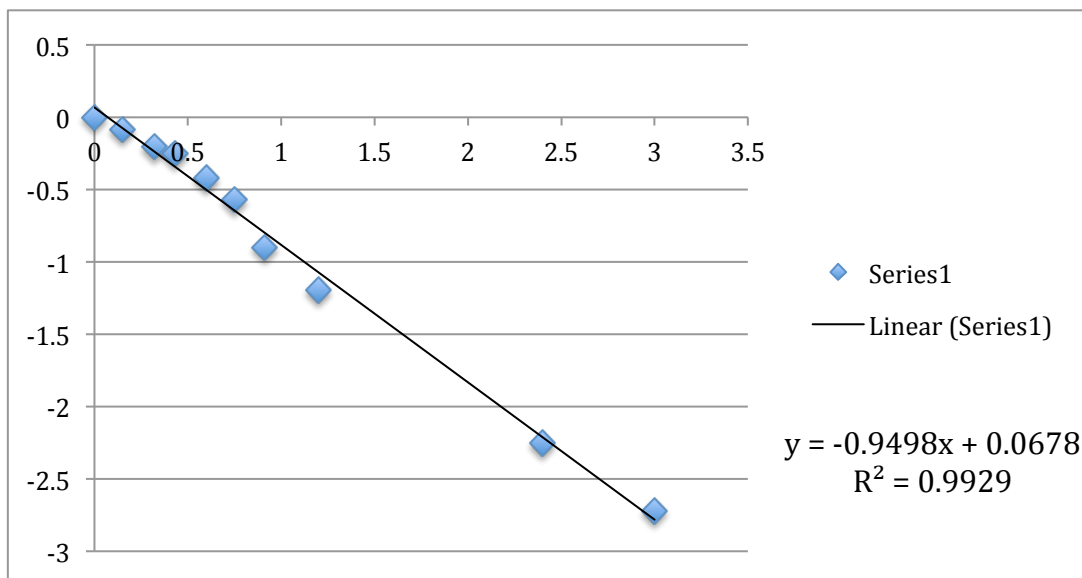


Fig 7 In acetone



Figs 8 and 9 overleaf show the spectra for the unadulterated sample, and that with Bu₄NCl.

Key assignments:

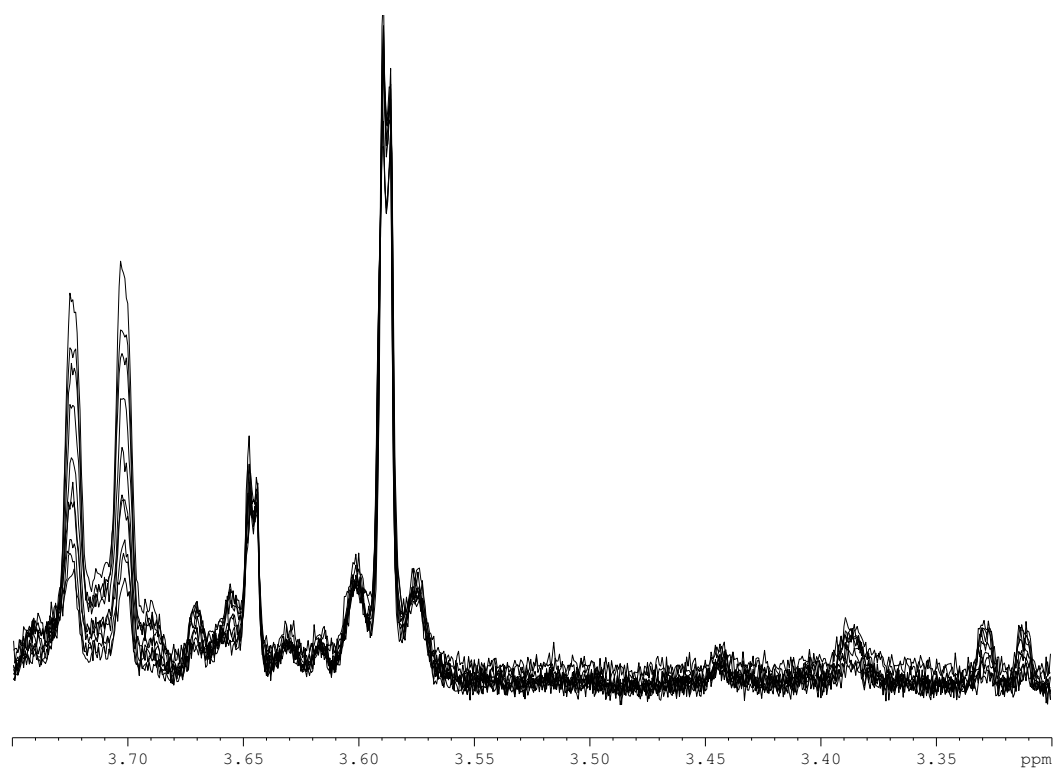
3.72 and 3.70 ppm: DMSO peaks of the *cis* **2** (i and j in the above assignment)

3.59 ppm: DMSO peaks of *trans* **2** (o in the above assignment)

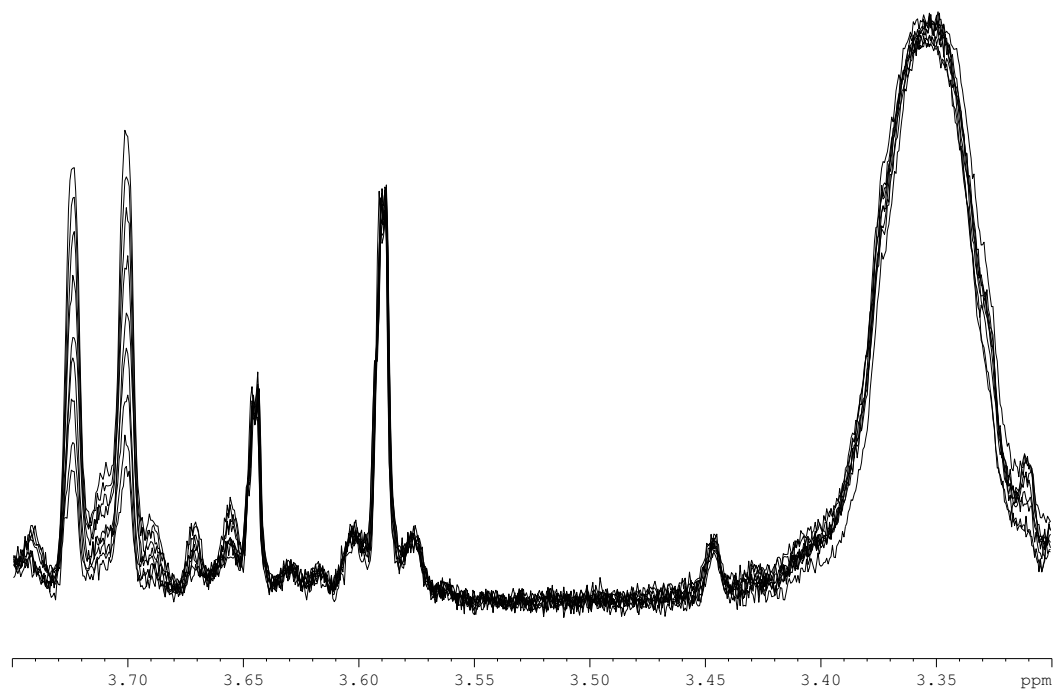
3.66/3.67 (doublet) and 3.31/3.33 ppm (doublet): CH₂ peaks of *cis* **2** (c and d in the above assignment)

3.36 ppm: N(CH₂CH₂CH₂CH₃)₄⁺

SI Fig 8: without Bu₄NCl.



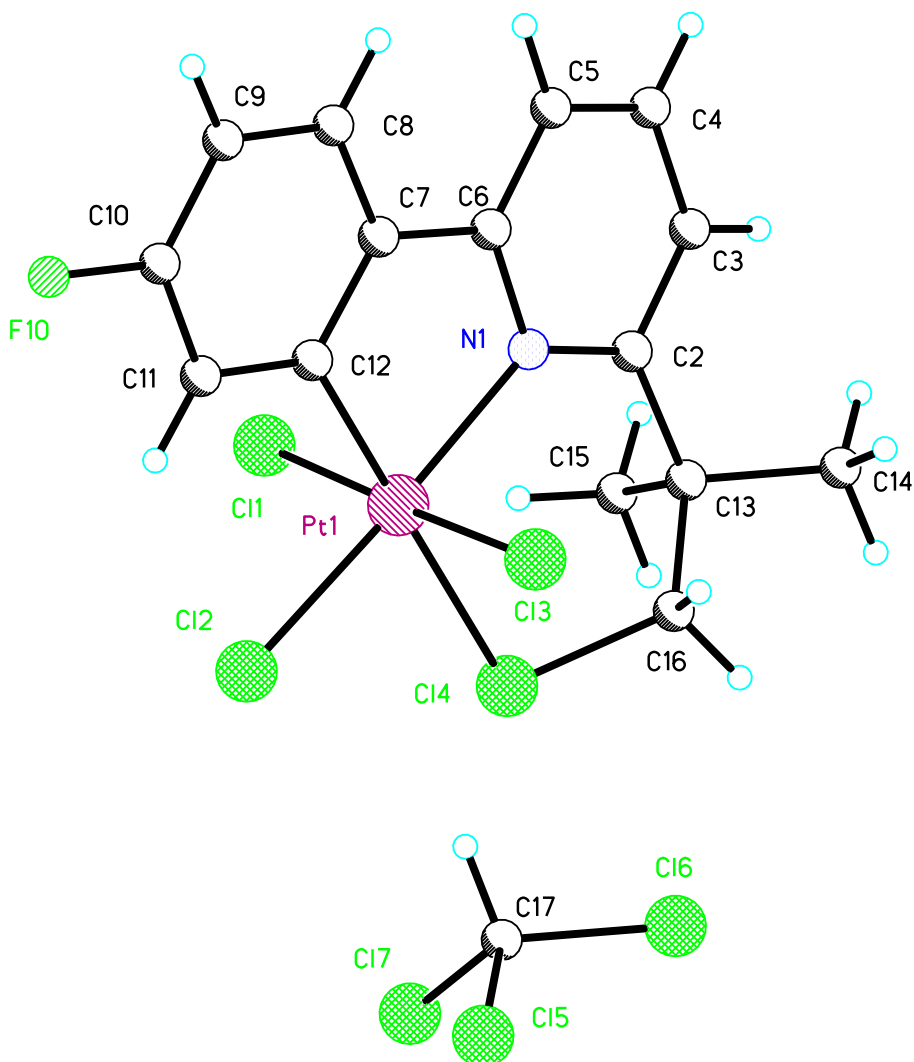
SI Fig 9: with Bu₄NCl.



Crystal Structures

Experimental data for 4

The asymmetric unit contains the complex and a solvent chloroform



Short contacts are detailed below.

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

D-H	H...A	D...A	<(DHA)	
1.00	3.17	3.578(4)	105.8	C17-H17A...Cl4
0.95	2.84	3.763(4)	165.1	C3-H3A...Cl2_\$1
0.95	2.70	3.538(4)	146.9	C5-H5A...Cl1_\$2
0.95	2.78	3.532(4)	136.6	C8-H8A...Cl1_\$3
0.98	2.54	3.222(5)	126.8	C15-H15C...F10_\$4

Pt Cl bond lengths

2.3027 (0.0009) Pt1 - Cl1

2.3051 (0.0009) Pt1 - Cl2

2.3112 (0.0009) Pt1 - Cl3

2.4915 (0.0009) Pt1 - Cl4

Twist angle between the pyridine (N1-C6) and phenyl (C7-C12) is 9.43(21)°

Crystal Data

C16 H15 Cl7 F N Pt, M = 683.53, Triclinic, space group P-1

a = 8.1614(3), b = 10.0416(4), c = 13.4119(6) Å ,

alpha = 83.023(3) deg., beta = 74.000(3) deg., gamma = 78.171(3) deg.,

U = 1031.67(7) Å³ (by least squares refinement on 6036 reflection positions),

T = 100(2)K, lambda = 0.71073 Å, Z = 2,

D(cal) = 2.200 Mg/m³, F(000) = 648.

mu(MoK-alpha) = 7.718 mm⁻¹.

Crystal character: yellow block.

Crystal dimensions 0.30 x 0.30 x 0.20 mm,

Data Collection and Processing.

Oxford Diffraction Gemini four-circle system with Ruby CCD area detector.

The crystal was held at 100(2)K with the Oxford Cryosystem Cryostream Cobra.

Maximum theta was 29.41°.

The hkl ranges were -9/ 10, -11/ 13, -13/ 17.

8310 reflections measured, 4812 unique [R(int) = 0.0294].

Absorption correction by Semi-empirical from equivalents;

minimum and maximum transmission factors: 0.53; 1.00.

no crystal decay

Structure Analysis and Refinement.

No systematic absences. Space group P-1 was chosen on the basis of intensity statistics and shown to be correct by successful refinement.

The structure was solved by direct methods using SHELXS (G. M. Sheldrick *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, Germany: 1997.) with additional light atoms found by Fourier methods.

Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl

hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The weighting scheme was calc $w=1/[\sigma^2(F_o^2)+(0.0251P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$.

Goodness-of-fit on F^2 was 0.972,

$R1$ [for 4275 reflections with $I>2\sigma(I)$] = 0.0260, $wR2$ = 0.0540.

Data / restraints / parameters 4812/ 0/ 237.

Largest difference Fourier peak and hole 1.319 and -1.402 e.Å⁻³.

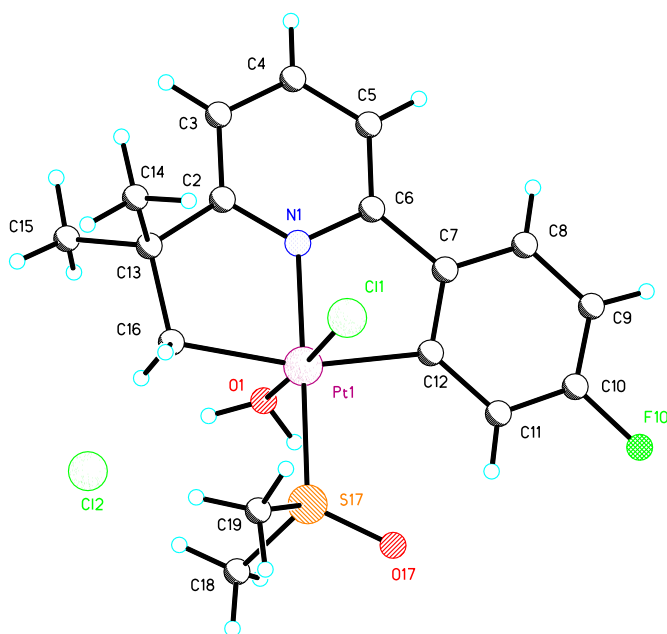
Table. Bond lengths [Å] and angles [deg] for 4.

Pt(1)-C(12)	1.996(4)
Pt(1)-N(1)	2.080(3)
Pt(1)-Cl(1)	2.3027(9)
Pt(1)-Cl(2)	2.3051(9)
Pt(1)-Cl(3)	2.3112(9)
Pt(1)-Cl(4)	2.4915(9)
Cl(4)-C(16)	1.804(4)
N(1)-C(2)	1.363(5)
N(1)-C(6)	1.370(5)
C(2)-C(3)	1.390(5)
C(2)-C(13)	1.539(5)
C(3)-C(4)	1.380(5)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.371(6)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.381(5)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.460(5)
C(7)-C(12)	1.389(5)
C(7)-C(8)	1.405(5)
C(8)-C(9)	1.383(6)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.369(6)
C(9)-H(9A)	0.9500
C(10)-F(10)	1.367(4)
C(10)-C(11)	1.371(5)
C(11)-C(12)	1.380(5)
C(11)-H(11A)	0.9500
C(13)-C(16)	1.525(5)
C(13)-C(14)	1.542(5)
C(13)-C(15)	1.543(5)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800

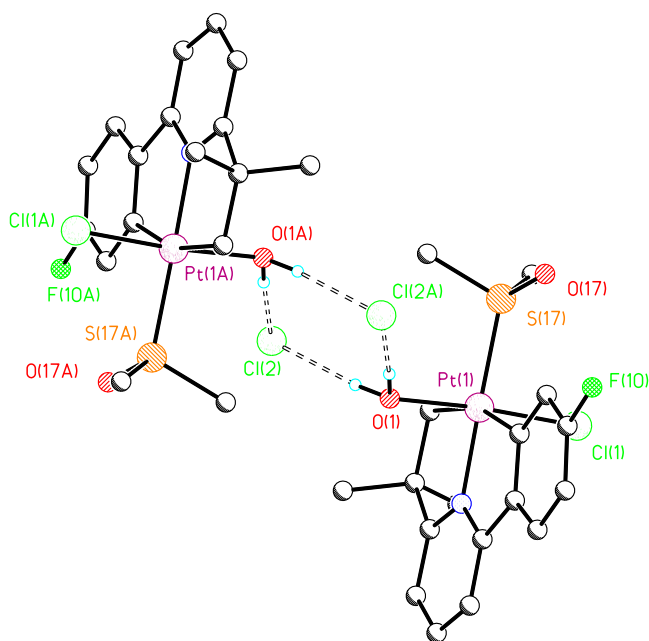
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-Cl(7)	1.759(4)
C(17)-Cl(5)	1.767(4)
C(17)-Cl(6)	1.772(4)
C(17)-H(17A)	1.0000
C(12)-Pt(1)-N(1)	83.20(14)
C(12)-Pt(1)-Cl(1)	90.28(11)
N(1)-Pt(1)-Cl(1)	87.54(9)
C(12)-Pt(1)-Cl(2)	94.84(11)
N(1)-Pt(1)-Cl(2)	177.64(9)
Cl(1)-Pt(1)-Cl(2)	91.18(3)
C(12)-Pt(1)-Cl(3)	89.05(11)
N(1)-Pt(1)-Cl(3)	91.00(9)
Cl(1)-Pt(1)-Cl(3)	178.46(3)
Cl(2)-Pt(1)-Cl(3)	90.26(3)
C(12)-Pt(1)-Cl(4)	179.59(11)
N(1)-Pt(1)-Cl(4)	96.64(8)
Cl(1)-Pt(1)-Cl(4)	90.09(3)
Cl(2)-Pt(1)-Cl(4)	85.34(3)
Cl(3)-Pt(1)-Cl(4)	90.57(3)
C(16)-Cl(4)-Pt(1)	95.18(13)
C(2)-N(1)-C(6)	119.9(3)
C(2)-N(1)-Pt(1)	129.0(2)
C(6)-N(1)-Pt(1)	110.9(2)
N(1)-C(2)-C(3)	118.6(3)
N(1)-C(2)-C(13)	124.6(3)
C(3)-C(2)-C(13)	116.8(3)
C(4)-C(3)-C(2)	121.5(4)
C(4)-C(3)-H(3A)	119.3
C(2)-C(3)-H(3A)	119.3
C(5)-C(4)-C(3)	119.2(4)
C(5)-C(4)-H(4A)	120.4
C(3)-C(4)-H(4A)	120.4
C(4)-C(5)-C(6)	119.0(4)
C(4)-C(5)-H(5A)	120.5
C(6)-C(5)-H(5A)	120.5
N(1)-C(6)-C(5)	121.7(3)
N(1)-C(6)-C(7)	116.1(3)
C(5)-C(6)-C(7)	122.2(3)
C(12)-C(7)-C(8)	119.1(4)
C(12)-C(7)-C(6)	117.4(3)
C(8)-C(7)-C(6)	123.5(4)
C(9)-C(8)-C(7)	119.6(4)
C(9)-C(8)-H(8A)	120.2
C(7)-C(8)-H(8A)	120.2
C(10)-C(9)-C(8)	118.4(4)
C(10)-C(9)-H(9A)	120.8

C(8)-C(9)-H(9A)	120.8
F(10)-C(10)-C(9)	118.2(3)
F(10)-C(10)-C(11)	117.5(3)
C(9)-C(10)-C(11)	124.4(4)
C(10)-C(11)-C(12)	116.5(4)
C(10)-C(11)-H(11A)	121.7
C(12)-C(11)-H(11A)	121.7
C(11)-C(12)-C(7)	122.0(3)
C(11)-C(12)-Pt(1)	125.9(3)
C(7)-C(12)-Pt(1)	112.1(3)
C(16)-C(13)-C(2)	115.9(3)
C(16)-C(13)-C(14)	102.7(3)
C(2)-C(13)-C(14)	109.8(3)
C(16)-C(13)-C(15)	111.5(3)
C(2)-C(13)-C(15)	108.1(3)
C(14)-C(13)-C(15)	108.7(3)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-Cl(4)	114.3(3)
C(13)-C(16)-H(16A)	108.7
Cl(4)-C(16)-H(16A)	108.7
C(13)-C(16)-H(16B)	108.7
Cl(4)-C(16)-H(16B)	108.7
H(16A)-C(16)-H(16B)	107.6
Cl(7)-C(17)-Cl(5)	110.7(2)
Cl(7)-C(17)-Cl(6)	110.3(2)
Cl(5)-C(17)-Cl(6)	110.2(2)
Cl(7)-C(17)-H(17A)	108.5
Cl(5)-C(17)-H(17A)	108.5
Cl(6)-C(17)-H(17A)	108.5

Crystals of the an analogue of the analogue of *trans* **2** suitable for Xray analysis were isolated from a solution of *cis* **2** in acetone that was held at -20°C ; note that we made no attempt to exclude atmospheric water from this solution. The asymmetric unit contains one molecule, a chloride and two disordered acetone molecules.



Solid state structure of **5** with atom numbering. The disordered molecules of acetone solvent have been removed for clarity.



Experimental data

The complex has a Pt surrounded by a fluorophenyl-t-butylpyridine also coordinated with a chloride, a DMSO and a water and two molecules of acetone (disordered). The hydrogens were located on the coordinated water. The hydrogens were also located on the metalated C16 carbon. These hydrogens were allowed to refine with distance restraints.

One molecule of acetone (C101-C103) was disordered about the 'a' axis in a 50:50 ratio. The other acetone (C201-C203/C301-C303) was modelled as disordered over two positions and refined to a ratio of 52:48. These disordered acetones were refined isotropically.

The coordinated water forms a dimer with a symmetry related complex across an inversion centre involving two bridging chlorides.

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

D-H	H...A	D...A	<(DHA)	
0.89(2)	2.11(2)	2.991(4)	170(5)	O1-H1A...Cl2
0.89(2)	2.07(2)	2.962(3)	176(5)	O1-H1B...Cl2_\$1
0.95	2.37	3.124(8)	136.1	C11-H11A...O17

Interesting distances

0.9236 (0.0225) C16 - H16A

0.8955 (0.0225) C16 - H16B

2.1182 (0.0049) Pt1 - C16

2.1071 (0.0051) Pt1 - Cl2

2.0031 (0.0041) Pt1 - N1

2.2878 (0.0012) Pt1 - Cl1

2.0665 (0.0034) Pt1 - O1

Symmetry operators used to generate equivalent atoms were \$1 -x+1, -y+1, -z+1

Crystal Data

C₂₁H₃₁Cl₂FN₃O_{3.5}PtS, M = 676.52, Triclinic, space group P-1

a = 9.8916(4), b = 10.3390(5), c = 13.0249(4) Å,

alpha = 103.566(4) deg., beta = 95.759(3) deg., gamma = 105.831(4) deg.,

U = 1226.38(9) Å³ (by least squares refinement on 15119 reflection positions),

T = 100(2)K, lambda = 0.71073 Å, Z = 2,

D(cal) = 1.832 Mg/m³, F(000) = 664.

mu(MoK-alpha) = 6.057 mm⁻¹.

Crystal character: orange plate.

Crystal dimensions 0.20 x 0.10 x 0.02 mm,

Data Collection and Processing.

Oxford Diffraction Gemini four-circle system with Ruby CCD area detector.

The crystal was held at 100(2) K with the Oxford Cryosystem Cryostream Cobra.

Maximum theta was 29.38 deg.

The hkl ranges were -13/ 13, -13/ 14, -16/ 17.

20461 reflections measured, 6025 unique [R(int) = 0.0362].

Absorption correction by Semi-empirical from equivalents;

minimum and maximum transmission factors: 0.73; 1.00.

no crystal decay

Structure Analysis and Refinement.

No systematic absences. Space group P-1 was chosen on the basis of intensity statistics and shown to be correct by successful refinement.

The structure was solved by direct methods using SHELXS (G. M. Sheldrick *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen, Germany: 1997.) with additional light atoms found by Fourier methods.

Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups except the CHs on C16 which were located in a difference map. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl and C16 hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The weighting scheme was $\text{calc } w=1/[\sigma^2(F_o^2)+(0.0475P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$.

Goodness-of-fit on F^2 was 1.102,

$R1[\text{for } 5401 \text{ reflections with } I > 2\sigma(I)] = 0.0302, wR2 = 0.0762.$

Data / restraints / parameters 6025/ 214/ 291.

Largest difference Fourier peak and hole 2.083 and -2.526 e. \AA^{-3} .

Table. Bond lengths [Å] and angles [deg] for 5.

Pt(1)-N(1)	2.003(4)
Pt(1)-O(1)	2.067(3)
Pt(1)-C(12)	2.107(5)
Pt(1)-C(16)	2.118(5)
Pt(1)-S(17)	2.2788(12)
Pt(1)-Cl(1)	2.2878(12)
N(1)-C(2)	1.350(7)
N(1)-C(6)	1.371(7)
O(1)-H(1A)	0.89(2)

O(1)-H(1B)	0.89(2)
C(2)-C(3)	1.394(7)
C(2)-C(13)	1.520(7)
C(3)-C(4)	1.391(8)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.370(8)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.383(8)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.466(8)
C(7)-C(12)	1.391(8)
C(7)-C(8)	1.402(8)
C(8)-C(9)	1.399(9)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.342(10)
C(9)-H(9A)	0.9500
F(10)-C(10)	1.370(7)
C(10)-C(11)	1.383(8)
C(11)-C(12)	1.408(8)
C(11)-H(11A)	0.9500
C(13)-C(15)	1.531(8)
C(13)-C(14)	1.541(7)
C(13)-C(16)	1.553(7)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.92(2)
C(16)-H(16B)	0.90(2)
S(17)-O(17)	1.461(4)
S(17)-C(18)	1.778(6)
S(17)-C(19)	1.781(6)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(101)-C(102)	1.48(2)
C(101)-H(10A)	0.9800
C(101)-H(10B)	0.9800
C(101)-H(10C)	0.9800
O(102)-C(102)	1.201(16)
C(102)-C(103)	1.53(2)
C(103)-H(10D)	0.9800
C(103)-H(10E)	0.9800
C(103)-H(10F)	0.9800
C(201)-C(202)	1.47(2)
C(201)-H(20A)	0.9800
C(201)-H(20B)	0.9800

C(201)-H(20C)	0.9800
O(202)-C(202)	1.222(16)
C(202)-C(203)	1.484(19)
C(203)-H(20D)	0.9800
C(203)-H(20E)	0.9800
C(203)-H(20F)	0.9800
C(301)-C(302)	1.56(2)
C(301)-H(30A)	0.9800
C(301)-H(30B)	0.9800
C(301)-H(30C)	0.9800
O(302)-C(302)	1.243(19)
C(302)-C(303)	1.46(2)
C(303)-H(30D)	0.9800
C(303)-H(30E)	0.9800
C(303)-H(30F)	0.9800

N(1)-Pt(1)-O(1)	86.32(16)
N(1)-Pt(1)-C(12)	80.4(2)
O(1)-Pt(1)-C(12)	88.52(18)
N(1)-Pt(1)-C(16)	82.51(18)
O(1)-Pt(1)-C(16)	88.42(17)
C(12)-Pt(1)-C(16)	162.8(2)
N(1)-Pt(1)-S(17)	177.90(13)
O(1)-Pt(1)-S(17)	95.38(9)
C(12)-Pt(1)-S(17)	100.85(16)
C(16)-Pt(1)-S(17)	96.30(14)
N(1)-Pt(1)-Cl(1)	89.60(13)
O(1)-Pt(1)-Cl(1)	175.92(9)
C(12)-Pt(1)-Cl(1)	90.60(15)
C(16)-Pt(1)-Cl(1)	91.26(15)
S(17)-Pt(1)-Cl(1)	88.69(4)
C(2)-N(1)-C(6)	123.9(4)
C(2)-N(1)-Pt(1)	118.8(3)
C(6)-N(1)-Pt(1)	117.3(3)
Pt(1)-O(1)-H(1A)	120(4)
Pt(1)-O(1)-H(1B)	116(4)
H(1A)-O(1)-H(1B)	104(5)
N(1)-C(2)-C(3)	118.3(5)
N(1)-C(2)-C(13)	116.4(4)
C(3)-C(2)-C(13)	125.2(5)
C(4)-C(3)-C(2)	118.7(5)
C(4)-C(3)-H(3A)	120.7
C(2)-C(3)-H(3A)	120.7
C(5)-C(4)-C(3)	121.4(5)
C(5)-C(4)-H(4A)	119.3
C(3)-C(4)-H(4A)	119.3
C(4)-C(5)-C(6)	119.6(5)
C(4)-C(5)-H(5A)	120.2
C(6)-C(5)-H(5A)	120.2
N(1)-C(6)-C(5)	118.0(5)
N(1)-C(6)-C(7)	113.9(5)

C(5)-C(6)-C(7)	128.1(5)
C(12)-C(7)-C(8)	122.4(5)
C(12)-C(7)-C(6)	117.0(5)
C(8)-C(7)-C(6)	120.6(5)
C(9)-C(8)-C(7)	118.8(6)
C(9)-C(8)-H(8A)	120.6
C(7)-C(8)-H(8A)	120.6
C(10)-C(9)-C(8)	117.9(5)
C(10)-C(9)-H(9A)	121.1
C(8)-C(9)-H(9A)	121.1
C(9)-C(10)-F(10)	117.6(5)
C(9)-C(10)-C(11)	125.3(6)
F(10)-C(10)-C(11)	117.1(6)
C(10)-C(11)-C(12)	117.9(6)
C(10)-C(11)-H(11A)	121.1
C(12)-C(11)-H(11A)	121.1
C(7)-C(12)-C(11)	117.8(5)
C(7)-C(12)-Pt(1)	111.4(4)
C(11)-C(12)-Pt(1)	130.8(4)
C(2)-C(13)-C(15)	108.4(5)
C(2)-C(13)-C(14)	106.7(4)
C(15)-C(13)-C(14)	109.3(4)
C(2)-C(13)-C(16)	112.0(4)
C(15)-C(13)-C(16)	110.6(5)
C(14)-C(13)-C(16)	109.6(4)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-Pt(1)	109.6(3)
C(13)-C(16)-H(16A)	108(4)
Pt(1)-C(16)-H(16A)	107(4)
C(13)-C(16)-H(16B)	112(4)
Pt(1)-C(16)-H(16B)	105(4)
H(16A)-C(16)-H(16B)	115(6)
O(17)-S(17)-C(18)	108.9(3)
O(17)-S(17)-C(19)	108.4(3)
C(18)-S(17)-C(19)	100.8(3)
O(17)-S(17)-Pt(1)	116.69(18)
C(18)-S(17)-Pt(1)	109.82(18)
C(19)-S(17)-Pt(1)	111.00(18)
S(17)-C(18)-H(18A)	109.5
S(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5

S(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
S(17)-C(19)-H(19A)	109.5
S(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
S(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(102)-C(102)-C(101)	122.1(13)
O(102)-C(102)-C(103)	121.8(14)
C(101)-C(102)-C(103)	116.0(12)
C(202)-C(201)-H(20A)	109.5
C(202)-C(201)-H(20B)	109.5
H(20A)-C(201)-H(20B)	109.5
C(202)-C(201)-H(20C)	109.5
H(20A)-C(201)-H(20C)	109.5
H(20B)-C(201)-H(20C)	109.5
O(202)-C(202)-C(201)	122.4(13)
O(202)-C(202)-C(203)	120.6(13)
C(201)-C(202)-C(203)	117.0(13)
C(302)-C(301)-H(30A)	109.5
C(302)-C(301)-H(30B)	109.5
H(30A)-C(301)-H(30B)	109.5
C(302)-C(301)-H(30C)	109.5
H(30A)-C(301)-H(30C)	109.5
H(30B)-C(301)-H(30C)	109.5
O(302)-C(302)-C(303)	121.8(15)
O(302)-C(302)-C(301)	122.7(15)
C(303)-C(302)-C(301)	115.5(14)
C(302)-C(303)-H(30D)	109.5
C(302)-C(303)-H(30E)	109.5
H(30D)-C(303)-H(30E)	109.5
C(302)-C(303)-H(30F)	109.5
H(30D)-C(303)-H(30F)	109.5
H(30E)-C(303)-H(30F)	109.5