SUPPORTING INFORMATION

for

A family of readily synthesised phosphorescent platinum(II) complexes based on tridentate *N^N^O*-coordinating Schiff-base ligands

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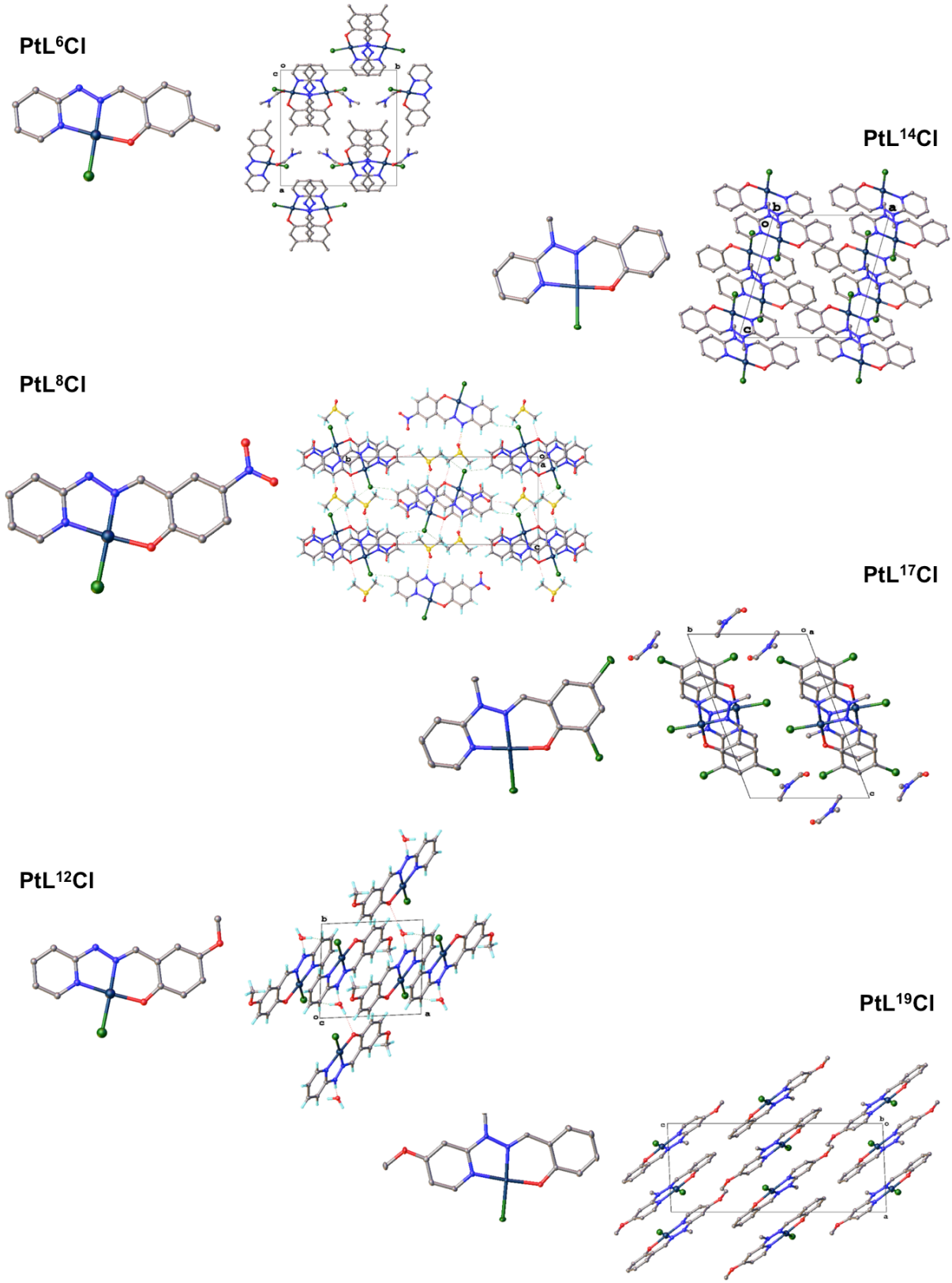

Figure S1 *The molecular and crystal structures of (left) the N–H hydrazone complexes PtL*^{6}*Cl, PtL*^{8}*Cl and PtL*^{12}*Cl, and (right) the N–Me hydrazone complexes PtL*^{14}*Cl, PtL*^{17}*Cl and PtL*^{19}*Cl. T = 120 K; H atoms are omitted for clarity.*

Table S1 Crystal data and structure refinement parameters

Identification code	PtL^1Cl	PtL^1CCAr	PtL^6Cl	PtL^8Cl	$PtL^{12}Cl$	$PtL^{14}Cl$	$PtL^{17}Cl$	$PtL^{19}Cl$	$PtL^{20}Cl$
Empirical formula	$C_{16}H_{11}ClN_2OPt$ x CH_2Cl_2	$C_{26}H_{14}F_6N_2OPt$ x 2 C_2H_6OS	$C_{13}H_{12}ClN_3OPt$ x C_3H_7NO	$C_{12}H_9ClN_4O_3Pt$ x C_2H_6SO	$C_{13}H_{14}ClN_3O_3Pt$	$C_{13}H_{12}ClN_3OPt$	$C_{13}H_{10}Cl_3N_3OPt$ x C_3H_7NO	$C_{14}H_{14}ClN_3O_2Pt$	$C_{14}H_{11}ClF_3N_3OPt$ x C_2H_6OS
Formula weight	562.73	835.74	529.89	565.90	490.81	456.80	598.78	486.82	602.92
Temperature/K	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	orthorhombic
Space group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/n$	P-1	$P2_1/c$	P-1	$P2_1/n$	Pnma
a/Å	7.8778(6)	16.5452(7)	14.4735(9)	7.0662(2)	8.5021(7)	11.1945(5)	8.5082(7)	8.3913(5)	11.5812(5)
b/Å	8.8726(8)	18.5441(7)	14.4419(9)	23.0266(5)	8.6034(7)	9.5950(4)	8.8816(7)	8.2576(5)	6.8946(3)
c/Å	13.2483(10)	9.7467(4)	8.3539(5)	11.1435(3)	10.4411(8)	12.2845(5)	13.2120(11)	19.9601(11)	23.2291(9)
α/°	75.787(7)	90	90.00	90.00	66.850(2)	90.00	108.748(2)	90	90
β/°	72.823(7)	91.0751(14)	96.170(2)	106.773(2)	88.962(3)	105.6722(14)	100.964(3)	92.4713(19)	90
γ/°	74.302(8)	90	90.00	90.00	86.218(3)	90.00	97.584(3)	90	90
Volume/$Å^3$	837.79(12)	2989.9(2)	1736.06(18)	1736.02(8)	700.68(10)	1270.44(9)	907.91(13)	1381.79(14)	1854.79(13)
Z	2	4	4	4	2	4	2	4	4
$\rho_{calc}g/cm^3$	2.231	1.857	2.027	2.165	2.326	2.388	2.190	2.340	2.159
μ/mm^{-1}	8.859	4.906	8.253	8.384	10.216	11.248	8.189	10.355	7.868
F(000)	532.0	1632.0	1016.0	1080.0	464.0	856.0	572.0	920.0	1152.0
Reflections collected	17866	65412	21653	34017	15145	27170	18871	22080	39498
Independent refl., R_{int}	4252, 0.0856	8719, 0.0488	4619, 0.0703	4619, 0.0784	4080, 0.0387	3706, 0.0275	5283, 0.0418	4032, 0.0527	2910, 0.0295
Data/restraints/parameters	4252/0/217	8719/7/405	4619/0/220	4619/0/228	4080/0/194	3706/0/174	5283/0/238	4032/0/192	2910/192/158
Goodness-of-fit on F^2	0.990	1.039	1.026	1.204	1.059	1.082	1.044	1.041	1.188
Final R_1 indexes [$I \geq 2\sigma(I)$]	0.0388	0.0243	0.0334	0.0408	0.0187	0.0114	0.0230	0.0268	0.0212
Final wR_2 [all data]	0.0693	0.0429	0.0720	0.0749	0.0410	0.0240	0.0474	0.0461	0.0384

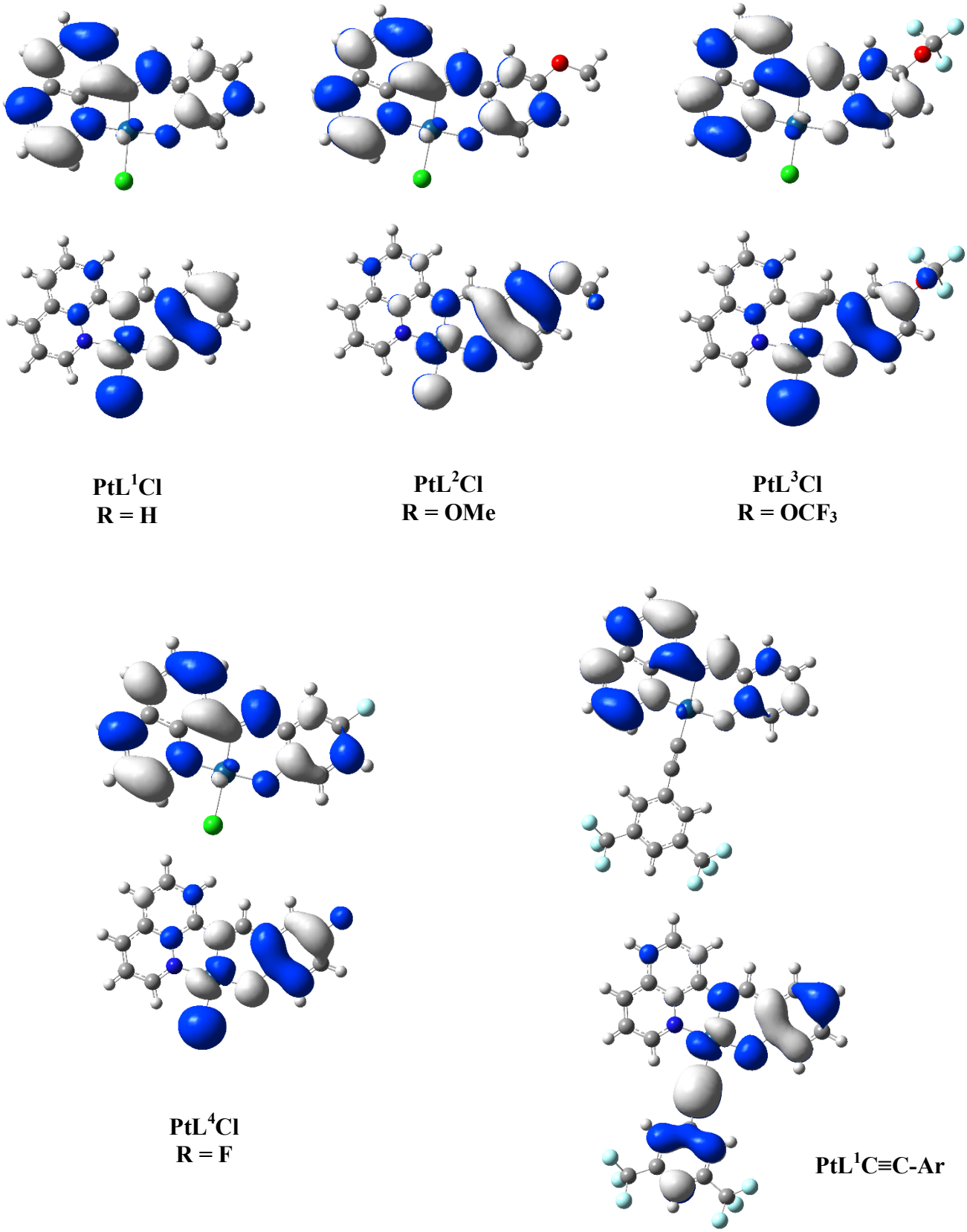

Figure S2 *Molecular orbital plots for the HOMO and LUMO (bottom and top in each case) of PtL$^{1–4}$Cl and PtL^{1}-C≡C-Ar calculated at the energy-minimised S_0 geometry.*

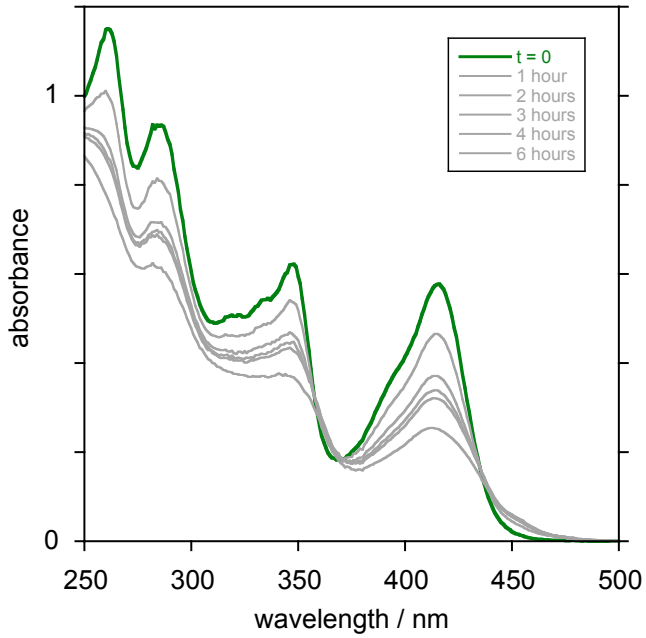

Figure S3 *UV-visible absorption spectra of PtL^9Cl in MeCN at 295 K (green line), and its evolution upon exposure to sunlight, monitored at hourly intervals.*

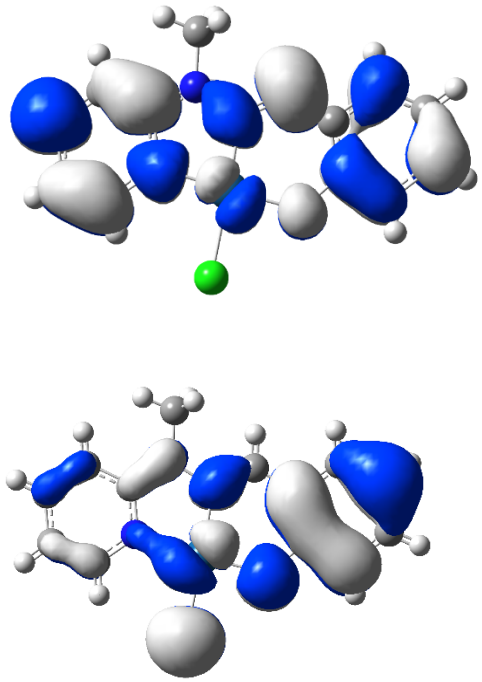

Figure S4 *Molecular orbital plots for the HOMO (bottom) and LUMO (top) of $PtL^{14}Cl$ at the energy-minimised S_0 geometry.*

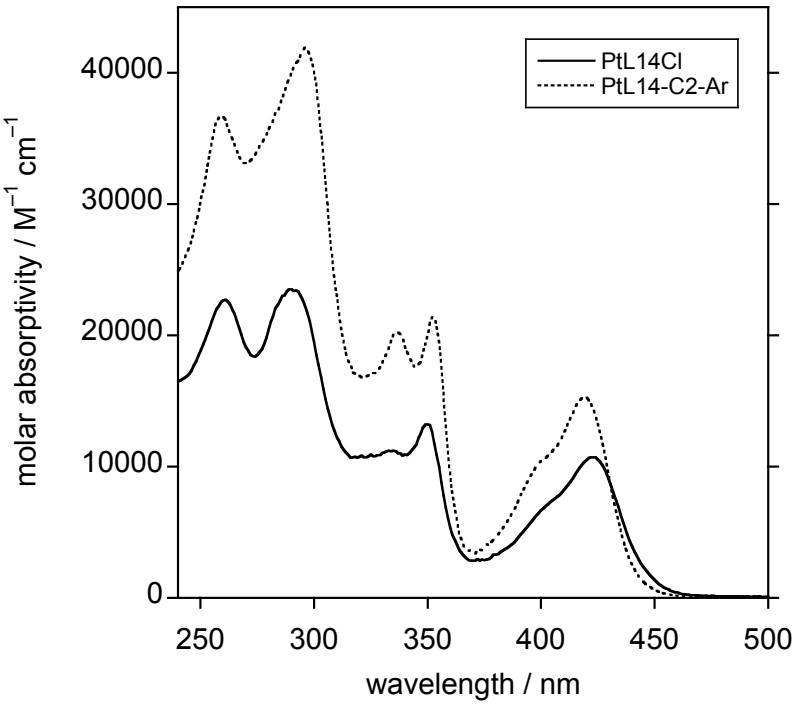

Figure S5 *UV-visible absorption spectra of $PtL^{14}Cl$ and PtL^{14}-C≡C-Ar in CH_2Cl_2 at 295 K (solid and dotted lines respectively).*

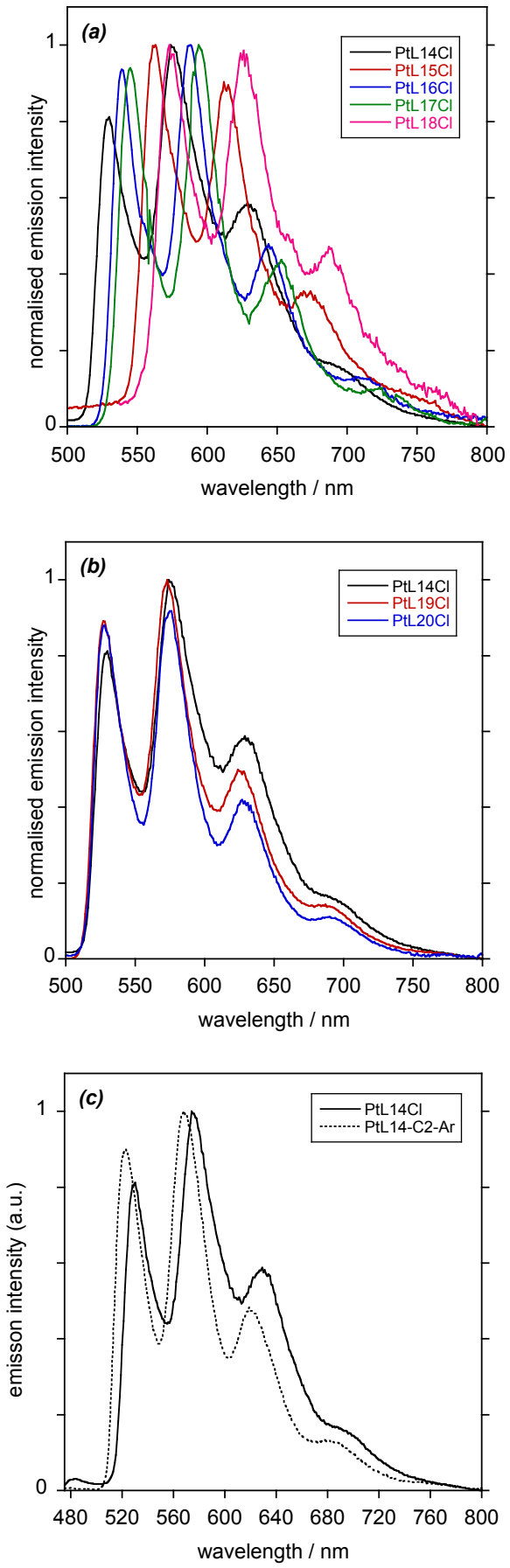

Figure S6 *Emission spectra in EPA glass at 77 K: (a) PtL$^{14–18}$Cl, (b) PtL$^{19–20}$Cl with PtL^{14}Cl also shown for comparision, (c) PtL^{14}Cl and PtL^{14}-C≡C-Ar.*

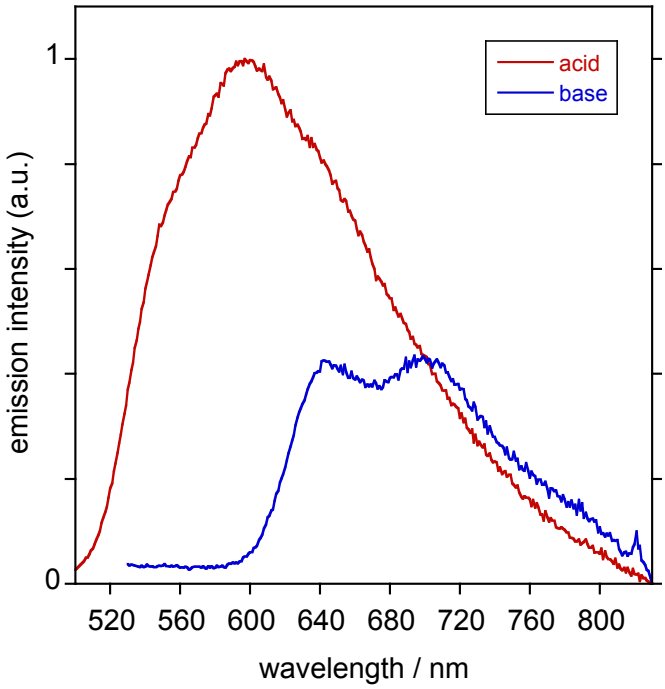

Figure S7 *Emission spectra of PtL^6Cl in deoxygenated MeCN at 295 K in the presence of CH_3CO_2H (to ensure the fully protonated form is present) and Et_3N (to generate the deprotonated form), shown in red and blue, respectively.*

Synthetic procedures and characterisation of compounds other than the representative examples described in the main text

The platinum precursor $Pt(COD)Cl_2$ was prepared by a standard procedure.[1] In the NMR assignments below, non-primed resonances indicate the quinoline or pyridine ring, primed resonances the phenol ring, double-primed the alkyne aromatic ring and triple-primed the alkyne bridge.

PtL^2Cl

8-Aminoquinoline (0.10 g, 0.69 mmol) and 2-hydroxy-5-methoxybenzaldehyde (107 mg, 0.70 mmol) were placed under vacuum and heated to 65°C for 2 h with stirring. The crude ligand, HL^2, was directly in the next step without purification. A mixture of HL^2 (31 mg, 0.11 mmol), $Pt(COD)Cl_2$ (42 mg, 0.11 mmol), anhydrous triethylamine (20 mg, 0.20 mmol) and anhydrous acetonitrile (1 mL) was stirred overnight at reflux under argon before allowing to cool to ambient temperature. The mixture was filtered and the precipitate washed with acetonitrile (2 × 1 mL) to give the title compound as a purple-red solid (43 mg, 11% over two steps). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.74 (1H, s, H^{imine}), 9.60 (1H, dd, J = 5 and 1, H^9), 8.84 (1H, dd, J = 8 and 1, H^8), 8.71 (1H, d, J = 8, H^4), 8.03 (1H, d, J = 8, H^6), 7.91 (1H, t, J = 8, H^5), 7.82 (1H, dd, J = 8 and 5, H^{10}), 7.27 – 7.25 (2H, m, $H^{3'}$ and $H^{5'}$), 6.91 (1H, d, J = 9, $H^{6'}$), 3.76 (3H, s, H^{OMe}). ^{13}C NMR (DMSO-d_6, 176 MHz): 159.2 ($C^{1'}$), 152.1 (C^9), 150.0 ($C^{4'}$), 148.4 (C^{imine}), 146.3 (C^3), 146.3 (C^2), 143.6 (C^8), 139.3 (C^8), 129.1 (C^7), 128.8 (C^5), 127.6 (C^6), 126.5 ($C^{3'}$), 123.7 (C^{10}), 122.4 ($C^{6'}$), 120.2 ($C^{2'}$), 118.7 (C^4), 113.1 ($C^{5'}$). MS (ES–): *m/z* 507 $[M–H]^+$. HRMS (ES^+) *m/z* 507.0394 $[M+H]^+$, calcd for 507.0371 $[C_{17}H_{14}N_2O_2Cl^{194}Pt]$.

PtL^3Cl

8-Aminoquinoline (0.10 g, 0.69 mmol) and 2-hydroxy-5-(trifluoromethoxy)benzaldehyde (144 mg, 0.70 mmol) were placed under vacuum and heated to 65°C for 2 h with stirring. The crude ligand, HL^3, was directly in the next step without purification. A mixture of HL^3 (37 mg, 0.11 mmol), $Pt(COD)Cl_2$ (42 mg, 0.11 mmol), anhydrous triethylamine (20 mg, 0.20 mmol) and anhydrous acetonitrile (1 mL) was stirred overnight at reflux under argon before allowing to cool to ambient temperature. The mixture was filtered and the precipitate washed with acetonitrile (2 × 1 mL) to give the title compound as an orange-red solid (35 mg, 9% over two steps). ^{1}H NMR (DMSO-d_6, 600 MHz): 9.85 (1H, s, H^{imine}), 9.57 (1H, d, J = 5, H^9), 8.84 (1H, d, J = 8, H^8), 8.70 (1H, d, J = 8, H^4), 8.06 (1H, d, J = 8, H^6), 7.91 (1H, t, J = 8, H^5), 7.84 – 7.79 (2H, m, H^{10} and $H^{3'}$), 7.53 (1H, dd, J = 9 and 3, $H^{5'}$), 7.00 (1H, d, J = 9, $H^{6'}$). ^{13}C NMR (DMSO-d_6, 151 MHz): 161.6 ($C^{1'}$), 152.2 (C^9), 149.1 (C^{imine}), 145.9 (C^3), 143.7 (C^2), 139.5 (C^8), 138.5 ($C^{4'}$), 129.1 (C^7), 128.8 (C^5), 128.6 ($C^{5'}$), 128.3 (C^6), 125.8 (C^{10} or $C^{3'}$), 123.8 (C^{10} or $C^{3'}$), 123.0 ($C^{6'}$), 121.0 ($C^{2'}$), 119.3 (C^4). MS (ES+): *m/z* 562 $[M-H]^+$; HRMS (ES+): *m/z* 561.0106 $[M+H]^+$; calculated for $[C_{17}H_{11}N_2O_2F_3ClPt]^+$ 561.0088.

PtL^4Cl

8-Aminoquinoline (0.10 g, 0.69 mmol) and 2-hydroxy-5-fluorobenzaldehyde (98 mg, 0.70 mmol) were placed under vacuum and heated to 65°C for 2 h with stirring. The crude ligand, HL^4, was directly in the next step without purification. A mixture of HL^4 (29 mg, 0.11 mmol), $Pt(COD)Cl_2$ (42 mg, 0.11 mmol), anhydrous triethylamine (20 mg, 0.20 mmol) and anhydrous acetonitrile (1

mL) was stirred overnight at reflux under argon before allowing to cool to ambient temperature. The mixture was filtered and the precipitate washed with acetonitrile (2 × 1 mL) to give the title compound as an orange-red solid (28 mg, 9% over two steps). ^{1}H NMR (DMSO-d_6, 600 MHz): 9.74 (1H, s, H^{imine}), 9.54 (1H, dd, J = 5 and 1, H^{9}), 8.81 (1H, dd, J = 8.5 and 1, H^{8}), 8.67 (1H, d, J = 8, H^{4}), 8.02 (1H, d, J = 8.5, H^{6}), 7.88 (1H, t, J = 8, H^{5}), 7.79 (1H, dd, J = 8 and 5.5, H^{10}), 7.54 (1H, dd, J = 9.5 and 3, $H^{3'}$), 7.44 (1H, ddd, J = 9.5, 8 and 3, $H^{4'}$), 6.91 (1H, dd, J = 9 and 5, $H^{6'}$). ^{13}C NMR (DMSO-d_6, 151 MHz): 160.0 ($C^{1'}$), 152.6 ($C^{4'}$), 152.1 (C^{9}), 148.5 (C^{imine}), 145.9 (C^{3}), 143.6 (C^{2}), 139.3 (C^{8}), 129.1 (C^{7}), 128.8 (C^{5}), 128.0 (C^{6}), 123.7 ($C^{5'}$), 122.8 (C^{10}), 120.3 ($C^{6'}$), 119.1 ($C^{2'}$), 117.0 ($C^{3'}$). MS (ES+): *m/z* 496 $[M–H]^+$. HRMS (ES^+) *m/z* 495.0161 $[M+H]^+$, calcd for 495.0171 $[C_{16}H_{11}N_2OFCl^{194}Pt]$.

HL[7]

3,5-Dichlorosalicylaldehyde (361 mg, 1.89 mmol) was added slowly to a stirred solution of 2-hydrazinopyridine (206 mg, 1.89 mmol) in MeOH (30 mL). The resulting yellow suspension was heated to reflux and stirred for 1 h. The mixture was allowed to cool to room temperature, filtered and washed with hexane (2 x 5 mL) to give the title compound as a yellow solid (471 mg, 89%). The experimental data were consistent with those previously reported by Li *et. al.*[2]

HL[8]

2-Hydroxy-5-nitrobenzaldehyde (154 mg, 0.93 mmol) was added slowly to a stirred solution of 2-hydrazinopyridine (100 mg, 0.92 mmol) in MeOH (8 mL). The resulting yellow slurry was heated to reflux and stirred for 1 h. The resulting mixture was allowed to cool to room temperature, filtered and washed with hexane (2 × 2 mL) to give the title compound as a bright yellow solid (188 mg, 79%). The synthesis of this compound had been reported previously,[3] but no charcterisation data was provided. ^{1}H NMR (DMSO-d_6, 600 MHz): 11.77 (1H, s, H^{OH}), 11.14 (1H, s, H^{NH}), 8.55 (1H, d, J = 3, $H^{3'}$), 8.31 (1H, s, H^{imine}), 8.14 (1H, d, J = 5, H^{3}), 8.07 (1H, dd, J = 9 and 3, $H^{5'}$), 7.68 (1H, ddd, J = 9, 7 and 2, H^{4}), 7.16 (1H, d, J = 8, H^{6}), 7.06 (1H, d, J = 9, $H^{6'}$), 6.81 (1H, dd, J = 7 and 5, H^{5}). ^{13}C NMR (DMSO-d_6, 151 MHz): 161.2 (C^{OH}), 156.3 (C^{2}), 147.9 (C^{3}), 140.1 ($C^{4'}$), 138.1 (C^{4}), 134.2 (C^{imine}), 125.0 ($C^{5'}$), 122.0 ($C^{2'}$), 121.4 ($C^{3'}$), 116.5 ($C^{6'}$), 115.5 (C^{5}), 106.5 (C^{6}). MS (ES-): *m/z* 257 [M–H].

HL[9]

5-Fluorosalicylaldehyde (133 mg, 0.95 mmol) was added slowly to a stirred solution of 2-hydrazinopyridine (100 mg, 0.92 mmol) in MeOH (8 mL). The resulting yellow slurry was heated to reflux and stirred for 1 h. The mixture was allowed to cool to room temperature, filtered and washed with hexane (2 × 5 mL) to give the title yellow as a bright yellow solid (109 mg, 51%).
^{1}H NMR (DMSO-d_6, 700 MHz): 10.97 (1H, s, H^{OH}), 10.22 (1H, s, H^{NH}), 8.24 (1H, s, H^{imine}), 8.12 (1H, dd, J = 5 and 1, H^{3}), 7.64 (1H, ddd, J = 8, 7 and 2, H^{5}), 7.43 (1H, dd, J = 10 and 3, $H^{3'}$), 7.14 (1H, d, J = 8, H^{6}), 7.00 (1H, td, J = 9 and 3, $H^{5'}$), 6.86 (1H, dd. J = 9 and 5, $H^{6'}$), 6.77 (1H, ddd, J = 7, 5 and 1, H^{4}). ^{13}C NMR (DMSO-d_6, 176 MHz): 156.5 (C^{OH}), 155.0 (C^{2}), 151.90 ($C^{2'}$), 147.8 (C^{3}), 138.0 (C^{5}), 136.0 (C^{imine}), 122.1 ($C^{4'}$), 117.1 ($C^{6'}$), 115.9 ($C^{5'}$), 115.2 (C^{5}), 111.5 ($C^{3'}$), 106.4 (C^{6}). MS (ES-): *m/z* 230 $[M–H]^–$; HRMS (ES+) m/z = 232.0884 $[M+H]^+$; calculated for $[C_{12}H_{11}N_3OF]^+$ 232.0886.

HL[10]

5-Chlorosalicylaldehyde (151 mg, 0.96 mmol) was added slowly to a stirred solution of 2-hydrazinopyridine (104 mg, 0.95 mmol) in MeOH (8 mL). The resulting white slurry was heated to reflux and stirred for 1 h. The mixture was allowed to cool to room temperature, filtered and washed with hexane (2 × 2 mL) to give the title compound as a white solid (165 mg, 70%). The synthesis of this compound has been reported previously but characterisation was limited to the IR spectrum.[4] ^{1}H NMR (DMSO-d_6, 700 MHz): 11.00 (1H, s, H^{OH}), 10.52 (1H, s, H^{NH}), 8.23 (1H, s, H^{imine}), 8.12 (1H, ddd, J = 5, 2 and 1, H^{3}), 7.67 (1H, d, J = 3, H^{5}), 7.64 (1H, ddd, J = 8, 7 and 2, $H^{3'}$), 7.18 (1H, dd, J = 9 and 3, $H^{5'}$), 7.13 (1H, d, J = 8, H^{6}), 6.89 (1H, d, J = 7, $H^{6'}$), 6.78 (1H, ddd, J = 7, 5 and 1, H^{4}). ^{13}C NMR (DMSO-d_6, 176 MHz): 156.4 (C^{OH}), 154.4 (C^{2}), 147.8 (C^{3}), 138.0 ($C^{3'}$), 135.6 (C^{imine}), 128.9 ($C^{5'}$), 125.1 (C^{5}), 123.1 ($C^{4'}$), 122.8 ($C^{2'}$), 117.7 ($C^{6'}$), 115.2 (C^{4}), 106.4 (C^{6}). MS (ES-): *m/z* 246 $[M–H]^–$.

HL[11]

2,4-Dihydroxybenzaldehyde (134 mg, 0.97 mmol) was added slowly to a stirred solution of 2-hydrazinopyridine (106 mg, 0.97 mmol) in MeOH (8 mL). The resulting orange slurry was heated to reflux and stirred for 1 h. The mixture was allowed to cool to ambient temperature, then cooled to 5 °C before being filtered and washed with hexane (2 × 5 mL) to give the title compound as an orange solid (97 mg, 44%). The synthesis of this compound had been reported previously, but characterisation was limited to a melting point.[5] ^{1}H NMR (DMSO-d_6, 700 MHz): 10.66 (2H, s, H^{OH}), 9.69 (1H, s, H^{NH}), 8.16 (1H, s, H^{imine}), 8.10 (1H, ddd, J = 5, 2 and 1, H^{3}), 7.61 (1H, ddd, J = 8, 7 and 2, H^{5}), 7.31 (1H, d, J = 8, $H^{3'}$), 6.92 (1H, d, J = 8, H^{6}), 6.72 (1H, ddd, J = 7, 5 and 1, H^{4}), 6.32 – 6.30 (2H, m, $H^{6'}$ and $H^{4'}$). ^{13}C NMR (DMSO-d_6, 176 MHz): 159.3 ($C^{5'}$), 157.7 ($C^{1'}$), 156.4 (C^{2}), 147.9 (C^{3}), 140.4 (C^{imine}), 137.9 (C^{5}), 129.0 ($C^{3'}$), 114.5 (C^{4}), 111.9 ($C^{2'}$), 107.5 ($C^{6'}$), 105.7 (C^{6}), 102.5 ($C^{4'}$). MS (ES-): *m/z* 228 $[M–H]^–$.

HL[12]

2-Hydroxy-5-methoxybenzaldehyde (150 mg, 0.98 mmol) was added slowly to a stirred solution of 2-hydrazinopyridine (102 mg, 0.94 mmol) in MeOH (8 mL). The resulting whte slurry was heated to reflux and stirred for 1 hour. The mixture was allowed to cool to room temperature, filtered and washed with hexane (2 × 5 mL) to give the title compound as a white solid (133 mg, 58%). The synthesis of the compound was described previously but no characterisation data were provided.[3]
^{1}H NMR ($CDCl_3$, 700 MHz): 10.25 (1H, br s, H^{OH}), 9.10 (1H, br s, H^{NH}), 8.18 (1H, d, J = 5, H^{3}), 7.91 (1H, s, H^{imine}), 7.66 (1H, t, J = 8, H^{5}), 7.09 (1H, d, J = 8, H^{6}), 6.94 (1H, d, J = 9, $H^{3'}$), 6.87 – 6.84 (2H, m, H^{4} and $H^{5'}$), 6.71 (1H, d, J = 3, $H^{6'}$), 3.79 (3H, s, H^{OMe}). ^{13}C NMR ($CDCl_3$, 176 MHz): 155.6 (C^{2}), 152.8 ($C^{4'}$), 151.5 ($C^{1'}$), 147.5 (C^{3}), 142.9 (C^{imine}), 139.0 (C^{5}), 118.3 ($C^{2'}$), 117.5 ($C^{3'}$), 117.1 ($C^{5'}$), 116.5 (C^{4}), 114.2 ($C^{6'}$), 107.0 (C^{6}). MS (ES+): *m/z* 244 $[M+H]^+$.

2-(1-methylhydrazinyl)pyridine

Bromopyridine (3.3 g, 21 mmol) was added under a stream of argon to methyl hydrazine (14.5 g, 315 mmol) to form a pale-yellow solution. The solution was heated to reflux and stirred under argon for 4 hours. The solution was allowed to cool to room temperature and the solvent removed in vacuo to give a yellow oil. The crude product was washed with sat. aq. Na_2CO_2 (40 mL) and extracted into EtOAc (3 × 50 mL). The combined organic layers were washed with brine (2 × 40 mL), dried over anhydrous magnesium sulphate and filtered. The solvent was removed to yield the

title compound as a yellow oil (1.19 g, 96%). The experimental data were consistent with those previously reported by Leung *et. al.*[6]

HL[15]

2-Hydroxy-5-methoxybenzaldehyde (93 mg, 0.61 mmol) was added to a stirring solution of 2-(1-methylhydrazinyl)pyridine (75 mg, 0.61 mmol) in MeOH (3 mL). The resulting yellow solution was heated to reflux and stirred for 30 min, forming a lemon slurry. The mixture was allowed to cool to room temperature, filtered and washed with cold MeOH (2 × 5 mL) to give the title compound as a white solid (104 mg, 66%). ^{1}H NMR ($CDCl_3$, 700 MHz): 10.77 (1H, s, H^{OH}), 8.27 (1H, dd, J = 8 and 1, H^{3}), 7.76 (1H, s, H^{imine}), 7.63 (1H, ddd, J = 8.5, 7 and 2, H^{5}), 7.27 (1H, d, J = 8.5, H^{6}), 6.93 (1H, d, J = 9, $H^{3'}$), 6.85-6.83 (2H, m, $H^{5'}$ and H^{4}), 6.80 (1H, d, J = 3, $H^{6'}$), 3.80 (3H, s, H^{OMe}), 3.71 (3H, s, H^{NMe}). ^{13}C NMR ($CDCl_3$, 176 MHz): 156.6 (C^{2}), 152.8 ($C^{4'}$), 151.0 ($C^{1'}$), 147.5 (C^{3}), 138.3 (C^{5}), 138.0 (C^{imine}), 119.3 ($C^{2'}$), 117.3 ($C^{3'}$), 116.4 (C^{4} or $C^{5'}$), 116.3 (C^{4} or $C^{5'}$), 114.5 ($C^{6'}$), 108.8 (C^{6}), 56.1 (C^{OMe}), 29.6 (C^{NMe}). MS (ES+): m/z 258 $[M+H]^+$.

HL[16]

2-Hydroxy-5-(trifluoromethoxy)benzaldehyde (343 mg, 1.66 mmol) was added to a stirring solution of 2-(1-methylhydrazinyl)pyridine (205 mg, 1.66 mmol) in MeOH (2 mL). The resulting yellow solution was heated to reflux and stirred for 30 min. The solution was allowed to cool to room temperature and placed in the fridge overnight. The resulting yellow slurry was filtered and washed with cold MeOH (2 × 2 mL) to yield the title compound as a lemon solid (192 mg, 37%). ^{1}H NMR ($CDCl_3$, 600 MHz): 11.23 (1H, s, H^{OH}), 8.29 (1H, ddd, J = 5, 2 and 1, H^{3}), 7.74 (1H, s, H^{imine}), 7.65 (1H, ddd, J = 8.5, 7 and 2, H^{5}), 7.25 (1H, d, J = 8.5, H^{6}), 7.14 (1H, d, J = 2.5, $H^{3'}$), 7.09 (1H, dd, J = 9 and 2.5, $H^{5'}$ or $H^{6'}$), 6.98 (1H, d, J = 9, $H^{5'}$ or $H^{6'}$), 6.87 (1H, ddd, J = 7, 5 and 1,H^{4}), 3.71 (3H, s, H^{NMe}). ^{13}C NMR ($CDCl_3$, 151 MHz): 156.4 (C^{2}), 155.4 ($C^{1'}$), 147.7 (C^{3}), 141.8 ($C^{4'}$), 138.4 (C^{5}), 136.6 (C^{imine}), 122.8 ($C^{5'}$ or $C^{6'}$), 122.4 ($C^{3'}$), 121.6 (C^{OCF_3}), 119.8 ($C^{2'}$), 117.7 ($C^{5'}$ or $C^{6'}$), 116.7 (C^{4}), 108.7 (C^{6}), 29.7 (C^{NMe}). MS (ES–): m/z 310 $[M–H]^–$; HRMS (ES–): *m/z* 310.0798 $[M–H]^–$; calculated for $[C_{14}H_{11}N_3O_2F_3]^–$ 310.0803.

HL[17]

3,5-Dichlorosalicylaldehyde (150 mg, 0.79 mmol) was added to a stirring solution of 2-(1-methylhydrazinyl)pyridine (95 mg, 0.77 mmol) in MeOH (5 mL). The resulting lemon slurry was heated to reflux and stirred for 30 min. The mixture was allowed to cool to room temperature, filtered and washed with cold MeOH (2 × 5 mL) to give the title compound as a white solid (169 mg, 74%). ^{1}H NMR ($CDCl_3$, 700 MHz): 11.85 (1H, s, H^{OH}), 8.29 (1H, ddd, J = 9.5, 2 and 1, H^{3}). 7.68 (1H, s, H^{imine}), 7.66 (1H, ddd, J = 9, 7 and 2, H^{5}), 7.31 (1H, d, J = 2, $H^{5'}$), 7.28 (1H, d, J = 8.5, H^{6}), 7.18 (1H, d, J = 2.5, $H^{3'}$), 6.90 (1H, ddd, J = 7, 5 and 1, H^{4}), 3.71 (3H, s, H^{NMe}). ^{13}C NMR ($CDCl_3$, 176 MHz): 156.1 (C^{2}), 151.3 ($C^{1'}$), 147.7 (C^{3}), 138.6 (C^{5}), 135.5 (C^{imine}), 129.4 ($C^{5'}$), 127.7 ($C^{3'}$), 124.3 ($C^{2'}$), 122.2 ($C^{6'}$), 121.3 ($C^{4'}$), 117.2 (C^{4}), 108.9 (C^{6}), 29.9 (C^{NMe}). MS (ES+): m/z 296 $[M+H]^+$; HRMS (ES+): *m/z* 296.0362 $[M+H]^+$; calculated for $[C_{13}H_{12}N_3OCl_2]^+$ 296.0357.

4-Methoxy-2-(1-methylhydrazinyl)pyridine

2-Chloro-4-methoxypyridine (126 mg, 0.88 mmol) was added under a stream of argon to methyl hydrazine (2.63 g, 57 mmol) to form a pale-yellow solution. The solution was heated to reflux and stirred under argon for 24 h. The solution was allowed to cool to room temperature, diluted with

water (10 mL) and extracted with Et_2O (3 × 30 mL). The combined organic later were dried over anhydrous magnesium sulphate, filtered and the solvent removed in vacuo to yield the title compound as a pale orange oil (130 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.98 (1H, d, J = 6), 6.49 (1H, d, J = 6), 6.24 (1H, dd, J = 6 and 2), 4.02 (2H, br s), 3.83 (3H, s), 3.27 (3H, s). MS (ES+): m/z 154 $[M+H]^+$.

HL[19]

Salicylaldehyde (130 mg, 1.06 mmol) was added to a stirring solution of 4-methoxy-2-(1-methylhydrazinyl)pyridine (120 mg, 0.78 mmol) in MeOH (2.5 mL). The resulting orange solution was heated to reflux and stirred for 3 h. The solution was allowed to cool to room temperature and placed in the fridge overnight. The resulting white slurry was filtered and washed with cold methanol (2 × 2 mL) to yield the title compound as a white crystalline solid (51mg, 19%). ^{1}H NMR ($CDCl_3$, 700 MHz): 11.19 (1H, s, H^{OH}), 8.08 (1H, d, J = 6, H^3), 7.80 (1H, s, H^{imine}), 7.27-7.23 (2H, m, $H^{4'}$ and $H^{5'}$), 7.00 (1H, d, J = 8, $H^{6'}$), 6.93 (1H, td, J = 7.5, $H^{3'}$), 6.75 (1H, d, J = 2, H^6), 6.44 (1H, dd, J = 6, 2), 3.89 (3H, s, H^{OMe}), 3.70 (3H, s, H^{NMe}). ^{13}C NMR ($CDCl_3$, 176 MHz): 167.8 (C^4), 158.6 (C^2), 157.0 ($C^{1'}$), 148.4 (C^3), 138.4 (C^{imine}), 130.2 ($C^{4'}$ or $C^{5'}$), 130.0 ($C^{4'}$ or $C^{5'}$), 119.7 ($C^{3'}$), 119.4 ($C^{2'}$), 116.7 ($C^{2'}$), 105.2 (C^5), 92.6 (C^6), 55.3 (C^{OMe}), 29.9 (C^{NMe}). MS (ES+): m/z 258 $[M+H]^+$; HRMS (ES+): *m/z* 258.1245 $[M+H]^+$; calculated for $[C_{14}H_{16}N_3O]^+$ 258.1243.

2-(1-Methylhydrazinyl)-4-(trifluoromethyl)-pyridine

2-Bromo-4-(trifluoromethyl)pyridine (200 mg, 0.88 mmol) was added under a stream of argon to methyl hydrazne (2.63 g, 57 mmol) to form a pale-yellow solution. The solution was heated to reflux and stirred under argon for 24 hours. The solution was allowed to cool to room temperature, diluted with water (10 mL) and extracted with Et_2O (3 × 30 mL). The combined organic later were dried over anhydrous magnesium sulphate, filtered and the solvent removed in vacuo to yield the title compound as a pale yellow oil (100 mg, 59%). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.22 (1H, d, J = 5), 7.30-7.28 (1H, m), 6.72 (1H, dd, J = 5 and 1), 4.00 (2H, br s), 3.32 (3H, s). MS (ES+): m/z 192 $[M+H]^+$.

HL[20]

Salicylaldehyde (105 mg, 0.89 mmol) was added to a stirring solution of 2-(1-methylhydrazinyl)-4-(trifluoromethyl)-pyridine (169 mg, 0.86 mmol) in MeOH (2.5 mL). The resulting yellow solution was heated to reflux and stirred for 3 h. The solution was allowed to cool to room temperature and placed in the fridge overnight. The resulting white slurry was filtered and washed with cold methanol (2 × 2 mL) to yield the title compound as a crystalline white solid (188 mg, 72%).
^{1}H NMR (CDCl3, 700 MHz): 10.83 (1H, br s, H^{OH}), 8.40 (1H, d, J = 5, $H^?$), 7.89 (1H, s, H^3), 7.43 (1H, s, H^{imine}), 7.28-7.25 (2H, m, $H^{4'}$ and $H^{5'}$), 7.04-7.00 (2H, m, $H^{6'}$ and $H^{3'}$), 6.93 (1H, td, J = 7.5 and 1, H^5), 3.73 (3H, d, J = 1, H^{NMe}). ^{13}C NMR ($CDCl_3$, 176 MHz): 156.8, 148.7, 140.4, 130.5, 130.4, 125.2 , 123.6, 122.1, 119.6, 118.7, 116.7, 111.2, 104.4, 29.7. MS (ES+): *m/z* 296 $[M+H]^+$; HRMS (ES+): *m/z* = 296.1011 $[M+H]^+$; calculated for $[C_{14}H_{13}F_3N_3O]^+$ = 296.2672.

PtL[5]Cl

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^5 (26 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting mustard yellow slurry was separated

by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5mL) and Et_2O (5 mL) to isolate a green solid. The crude product was then extracted into hot MeCN, filtered through celite and the solvent removed in vacuo to give the title compound as a yellow solid (32 mg, 60%). The synthesis of this compound had been reported previously, but characterisation was limited to the IR spectrum.[4] ^{1}H NMR (DMSO-d_6, 700 MHz): 8.86 (1H, ddd, J = 6, 2 and 1, H^3), 8.70 (1H, s, H^{imine}), 7.97 (1H, ddd, J = 8.5, 7 and 1.5, H^5) 7.70 (1H, dd, J = 8 and 2, $H^{3'}$), 7.45 (1H, ddd, J = 8.5, 6.5 and 2, $H^{4'}$), 7.23 (1H, t, J = 8.5, H^6), 7.09 (1H, d, J = 8.5, $H^{6'}$), 7.01 (1H, ddd, J = 7, 6 and 1, H^4), 6.77 (1H, ddd, J = 8, 7 and 1, $H^{5'}$). ^{13}C NMR (DMSO-d_6, 176 MHz): 159.2 ($C^{1'}$), 153.8 (C^2), 145.2 (C^3), 138.4 (C^5), 138.3 (C^{imine}), 132.8 ($C^{3'}$), 132.3 ($C^{4'}$), 120.7 ($C^{6'}$), 118.6 ($C^{2'}$), 116.0 ($C^{5'}$), 115.2 (C^4), 107.0 (C^6). MS (ES+): *m/z* 442 $[M+H]^+$; HRMS (ES+): *m/z* 442.0206 $[M+H]^+$; calculated for $[C_{12}H_{11}N_3OPtCl]^+$ 442.0217.

PtL^{7}Cl

A solution of potassium tetrachloroplatinate (300 mg, 0.73 mmol) in deionised water (5 mL) was added to a solution of HL^7 (200 mg, 0.71 mmol) in EtOH (15 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting yellow slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give a mustard yellow solid. The crude product was recrystallized in hot DMF to give the title compound as a bright yellow solid (223 mg, 61%). ^{1}H NMR (DMSO-d_6, 600 MHz): 8.84 (1H, d, J = 6, H^3), 8.72 (1H, s, H^{imine}), 7.99 (1H, ddd, J = 8.5, 7 and 1.5, H^5), 7.88 (1H, d, J = 3, $H^{3'}$), 7.72 (1H, d, J = 3, $H^{5'}$), 7.24 (1H, d, J = 8.5, H^6), 7.03 (1H, t, J = 6.5, H^4). ^{13}C NMR (DMSO-d_6, 151 MHz): 154.3 (C^{OH}), 152.8 (C^2), 145.3 (C^3), 138.7 (C^5), 137.4 (C^{imine}), 130.8 ($C^{5'}$), 130.3 ($C^{3'}$), 125.7 ($C^{4'}$ or $C^{6'}$), 120.5 ($C^{2'}$), 118.2 ($C^{4'}$ or $C^{6'}$), 115.4 (C^4), 107.3 (C^6). MS (ES-): *m/z* 510 $[M-H]^-$. HRMS (ES^+) *m/z* 509.9453 $[M+H]^+$, calcd for 509.9438 $[C_{12}H_9N_3OCl_3{}^{194}Pt]$.

PtL^{8}Cl

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^8 (31 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting orange-yellow slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give the title compound as an orange solid (44 mg, 75%). The synthesis of this compound had been reported previously, but characterisation was limited to the IR spectrum.[4]
^{1}H NMR (DMSO-d_6, 700 MHz): 8.88 (1H, s, H^{imine} or $H^{3'}$), 8.87 (1H, s, H^{imine} or $H^{3'}$), 8.80 (1H, d, J = 6, H^3), 8.22 (1H, dd, J = 9 and 3, $H^{5'}$), 7.98 (1H, ddd, J = 8, 7 and 1, H^5), 7.23 (1H, d, J = 8, H^6), 7.16 (1H, d, J = 9, $H^{6'}$), 7.01 (1H, t, J = 7, H^4). ^{13}C NMR (DMSO-d_6, 176 MHz): 163.7 (C^{OH}), 154.9 (C^2), 145.3 (C^3), 138.9 (C^5), 137.9 (C^{imine}), 137.0 ($C^{4'}$), 130.7 ($C^{3'}$), 125.6 ($C^{5'}$), 121.7 ($C^{6'}$), 118.9 ($C^{2'}$), 115.2 (C^4), 107.4 (C^6). MS (ES–): *m/z* 486 $[M–H]^–$.

PtL^{9}Cl

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^9 (27 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting orange slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give the title compound as a yellow solid (41 mg, 73%). ^{1}H NMR (DMSO-d_6, 700 MHz): 8.86 (1H, ddd, J = 6, 1.5 and 1, H^3), 8.68 (1H, s, H^{imine}), 7.98 (1H, ddd, J = 9, 7 and 1.5, H^5), 7.61 (1H, dd, J =

10 and 3, $H^{3'}$), 7.34 (1H, ddd, J = 11, 7 and 2, $H^{5'}$), 7.23 (1H, d, J = 8.5, H^{6}), 7.09 (1H, dd, J = 9 and 5, $H^{6'}$), 7.03 (1H, ddd, J = 7, 6 and 1, H^{4}). ^{13}C NMR (DMSO-d_6, 176 MHz): 156.6 ($C^{1'}$), 154.2 (C^{2}), 152.8 ($C^{4'}$), 145.7 (C^{3}), 138.9 (C^{5}), 137.9 (C^{imine}), 122.3 ($C^{6'}$), 120.7 ($C^{5'}$), 118.1 ($C^{2'}$), 116.2 ($C^{3'}$), 115.8 ($C^{4'}$), 107.6 (C^{6}). MS (ES+): *m/z* 460 $[M+H]^+$; HRMS (ES+): *m/z* 460.0113 $[M+H]^+$; calculated for $[C_{12}H_{10}N_3OFPtCl]^+$ 460.0123.

PtL^{10}Cl

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^{10} (29 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting yellow slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give the title compound as a yellow solid (43 mg, 75%). The synthesis of this compound had been reported previously, but characterisation was limited to the IR spectrum.[4] ^{1}H NMR (DMSO-d_6, 700 MHz): 8.82 (1H, d, J = 6, H^{3}), 8.67 (1H, s, H^{imine}), 7.95 (1H, ddd, J = 9, 7 and 1, H^{5}), 7.84 (1H, d, J = 3, $H^{3'}$), 7.41 (1H, dd, J = 9 and 3, $H^{5'}$), 7.20 (1H, d, J = 9, H^{6}), 7.07 (1H, d, J = 9, $H^{6'}$), 7.00 (1H, t, J = 7, H^{4}). ^{13}C NMR (DMSO-d_6, 176 MHz): 158.5 (C^{OH}), 154.5 (C^{2}), 145.7 (C^{3}), 138.9 (C^{5}), 137.8 (C^{imine}), 132.0 ($C^{5'}$), 131.3 ($C^{3'}$), 123.0 ($C^{6'}$), 120.1 ($C^{4'}$ or $C^{2'}$), 119.6 ($C^{4'}$ or $C^{2'}$), 115.7 (C^{4}), 107.6 (C^{6}). MS (ES–): *m/z* 476 $[M–H]^–$.

PtL^{11}Cl

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^{11} (27 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting brown slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give the title compound as a green solid (20 mg, 36%). ^{1}H NMR (DMSO-d_6, 700 MHz): 13.50 (1H, br s, H^{NH}), 9.94 (1H, s, H^{OH}), 8.78 (1H, ddd, J = 6, 2 and 1, H^{3}), 8.45 (1H, s, H^{imine}), 7.92 (1H, ddd, J = 9, 7 and 2, H^{5}), 7.48 (1H, d, J = 9, $H^{6'}$), 7.15 (1H, dt, J = 9 and 1, H^{6}), 6.94 (1H, ddd, J = 7, 6 and 1, H^{4}), 6.43 (1H, d, J = 3, $H^{4'}$), 6.31 (1H, dd, J = 9 and 2, $H^{3'}$). ^{13}C NMR (DMSO-d_6, 176 MHz): 161.8 ($C^{5'}$), 161.6 ($C^{1'}$), 153.8 (C^{2}), 145.2 (C^{3}), 138.20 (C^{imine}), 138.1 (C^{5}), 134.2 ($C^{6'}$), 114.7 (C^{4}), 112.0 ($C^{2'}$), 107.6 ($C^{3'}$), 106.7 (C^{6}), 104.4 ($C^{4'}$). MS (ES-): *m/z* 458 $[M–H]^–$.

PtL^{12}Cl

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^{12} (29 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 hours. The resulting yellow slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give the title compound as a yellow solid (41 mg, 72%). ^{1}H NMR (DMSO-d_6, 700 MHz): 8.86 (1H, ddd, J = 6, 2 and 1, H^{3}), 8.68 (1H, s, H^{imine}), 7.97 (1H, ddd, J = 9, 7 and 2, H^{5}), 7.23-7.22 (2H, m, H^{6} and $H^{3'}$), 7.14 (1H, dd, J = 9 and 3, $H^{5'}$), 7.04 (1H, d, J = 9, $H^{6'}$), 7.01 (1H, ddd, J = 7, 6 and 1, H^{4}), 3.75 (1H, s, H^{OMe}). ^{13}C NMR (DMSO-d_6, 176 MHz): 154.9 ($C^{1'}$), 153.6 (C^{2}), 149.6 ($C^{4'}$), 145.2 (C^{3}), 138.2 (C^{5}), 137.8 (C^{imine}), 122.4 ($C^{5'}$), 121.5 ($C^{6'}$), 117.3 ($C^{2'}$), 115.1 (C^{4}), 112.6 ($C^{3'}$), 107.0 (C^{6}), 55.7 (C^{OMe}). MS (ES-): *m/z* 471 $[M-H]^-$. HRMS (ES^+) *m/z* 472.0323 $[M+H]^+$, calcd for 472.0323 $[C_{13}H_{13}N_3O_2Cl^{194}Pt]$.

$PtL^{14}Cl$

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^{14} (27 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting mustard yellow slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5mL) and Et_2O (5 mL) to isolate a green solid. The crude product was then extracted into DCM, filtered through celite and the solvent removed in vacuo to give the title compound as a yellow solid (45 mg, 82%). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.06 (1H, ddd, J = 6, 2 and 0.5, H^3), 8.94 (1H, s, H^{imine}), 8.07 (1H, ddd, J = 9, 7 and 2, H^5), 7.82 (1H, dd, J = 8 and 2, $H^{3'}$), 7.48 (1H, d, J = 9, H^6), 7.45 (1H, ddd, J = 8.5, 6.5 and 2, $H^{6'}$), 7.09 (2H, m, H^4 and $H^{5'}$), 6.79 (1H, ddd, J = 8, 7 and 1, $H^{4'}$), 3.91 (3H, s, H^{NMe}). ^{13}C NMR (DMSO-d_6, 176 MHz): 159.3 (C^2), 152.9 ($C^{1'}$), 145.9 (C^3), 138.7 (C^5), 137.6 (C^{imine}), 133.7 ($C^{3'}$), 132.5 ($C^{5'}$), 120.5 ($C^{6'}$), 118.8 ($C^{2'}$), 116.1 ($C^{4'}$), 115.8 ($C^{4'}$), 108.7 (C^6), 34.03 (C^{NMe}). MS (ES+): *m/z* 462 $[M\text{-}Cl+MeCN]^+$; HRMS (ES+): *m/z* 461.0865 $[M+H]^+$; calculated for $[C_{15}H_{15}N_4OPt]^+$ 461.0878.

$PtL^{15}Cl$

A solution of potassium tetrachloroplatinate (75 mg, 0.18 mmol) in deionised water (1.5 mL) was added to a solution of HL^{15} (44 mg, 0.17 mmol) in EtOH (4 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting dark green slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give a green solid. The crude product was recrystallized in hot DMF to give the title compound as a bright yellow solid (36 mg, 43%). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.09 (1H, d, J = 6), 8.96 (1H, s), 8.08 (1H, ddd, J = 9, 7 and 2), 7.50 (1H, d, J = 9), 7.37 (1H, d, J = 3), 7.15 (1H, dd, J = 9 and 3), 7.10 (1H, t, J = 7), 7.05 (1H, d, J = 9). The material was not sufficiently soluble to obtain a ^{13}C NMR spectrum. MS (ES+): *m/z* 487 $[M+H]^+$. HRMS (ES^+) *m/z* 486.0472 $[M+H]^+$, calcd for 486.0480 $[C_{14}H_{15}N_5O_2Cl^{194}Pt]$.

$PtL^{16}Cl$

A solution of potassium tetrachloroplatinate (100 mg, 0.24 mmol) in deionised water (2 mL) was added to a solution of HL^{16} (62 mg, 0.20 mmol) in EtOH (5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 hours. The resulting dark green slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give a green solid. The crude product was recrystallized in hot DMF to give the title compound as a bright yellow solid (47 mg, 43%). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.03 (1H, dd, J = 6 and 1, H^3), 9.00 (1H, s, H^{imine}), 8.07 (1H, ddd, J = 9, 7 and 1.5, H^5), 7.88 (1H, d, J = 3, $H^{3'}$), 7.49 (1H, d, J = 9, H^6), 7.43 (1H, dd, J = 9 and 3, $H^{5'}$), 7.13 (1H, d, J = 9, $H^{6'}$), 7.09 (1H, ddd, J = 7, 6 and 1, H^4), 3.91 (3H, s, H^{NMe}). ^{13}C NMR (DMSO-d_6, 176 MHz): 157.8 ($C^{1'}$), 152.9 (C^2), 145.9 (C^3), 138.8 (C^5), 137.9 ($C^{2'}$), 136.9 (C^{imine}), 125.6 ($C^{4'}$), 124.8 ($C^{5'}$), 121.9 ($C^{3'}$), 119.7 (C^{OCF_3}), 118.5 ($C^{6'}$), 116.0 (C^4), 108.8 (C^6). MS (ES+): *m/z* 541 $[M+H]^+$; HRMS (ES+): *m/z* 540.0207 $[M+H]^+$; calculated for $[C_{14}H_{12}N_3O_2F_3PtCl]^+$ 540.0197.

$PtL^{17}Cl$

A solution of potassium tetrachloroplatinate (291 mg, 0.70 mmol) in deionised water (5 mL) was added to a solution of HL^{17} (200 mg, 0.68 mmol) in EtOH (15 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting dark green slurry was separated by

centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give a green solid. The crude product was recrystallized in hot DMF to give the title compound as a bright yellow solid (114 mg, 32%). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.03 (1H, dd, J = 6 and 1, H^3), 8.98 (1H, s, H^{imine}), 8.09 (1H, ddd, J = 9, 7 and 1.5, H^5), 7.92 (1H, d, J = 3, $H^{3'}$), 7.71 (1H, d, J = 3, $H^{5'}$), 7.79 (1H, d, J = 9, H^6), 7.11 (1H, ddd, J = 7, 6 and 1, H^4), 3.87 (3H, s, H^{NMe}). The material was not sufficiently soluble to obtain a ^{13}C NMR spectrum. MS (ES+): *m/z* 531 $[M\text{-}Cl+MeCN]^+$. HRMS (ES^+) *m/z* 529.0087 $[M\text{-}Cl+MeCN]^+$, calcd for 529.0093 $[C_{15}H_{13}N_4OCl_2{}^{194}Pt]$.

$PtL^{18}Cl$

A solution of potassium tetrachloroplatinate (75 mg, 0.18 mmol) in deionised water (1.5 mL) was added to a solution of HL^{18} (50 mg, 0.17 mmol) in EtOH (4 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting green slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5 mL) and Et_2O (5 mL) to give a green solid. The crude product was recrystallized in hot DMF to give the title compound as a yellow solid (30 mg, 35%). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.45 (1H, s), 9.06 (1H, d, J = 7), 8.41 (1H, d, J = 8.5), 8.08 (1H, t, J = 8), 7.92 (1H, d, J = 9), 7.85 (1H, d, J = 8), 7.61 (1H, t, J = 7.5), 7.56 (1H, d, J = 9), 7.36 (1H, t, J = 7), 7.30 (1H, d, J = 9), 7.10 (1H, t, J = 6). The material was not sufficiently soluble to obtain a ^{13}C NMR spectrum. MS (ES+): *m/z* 507 $[M+H]^+$

$PtL^{19}Cl$

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^{19} (27 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting green slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5mL) and Et_2O (5 mL) to isolate a green solid. The crude product was recrystallized in hot DMF to give the title compound as a yellow solid (17 mg, 32%). ^{1}H NMR (DMSO-d_6, 700 MHz): 8.85 (1H, s, H^{imine}), 8.75 (1H, d, J = 7, H^3), 7.75 (1H, dd, J = 8 and 2, $H^{3'}$), 7.40 (1H, ddd, J = 8.5, 7 and 2, H^5), 7.02 (1H, d, J = 8, $H^{6'}$), 6.88 (1H, d, J = 2.5, H^6), 6.76 – 6.72 (2H, m, H^5 and $H^{4'}$), 3.94 (3H, s, H^{OMe}), 3.86 (3H, s, H^{NMe}). ^{13}C NMR (DMSO-d_6, 176 MHz): 166.8 (C^4), 159.4 ($C^{1'}$), 154.7 (C^2), 146.6 (C^3), 137.3 (C^{imine}), 133.7 ($C^{3'}$), 132.4 ($C^{5'}$), 120.5 ($C^{6'}$), 118.9 ($C^{2'}$), 115.9 ($C^{4'}$), 105.5 (C^5), 91.6 (C^6). MS (ES+): *m/z* 492 $[M+H]^+$; HRMS (ES+): *m/z* 491.0976 $[M+H]^+$; calculated for $[C_{16}H_{17}N_4O_2PtCl]^+$ 491.0978.

$PtL^{20}Cl$

A solution of potassium tetrachloroplatinate (50 mg, 0.12 mmol) in deionised water (1 mL) was added to a solution of HL^{20} (29 mg, 0.12 mmol) in EtOH (2.5 mL) and the resulting pale pink solution was heated to reflux and stirred for 4 h. The resulting green slurry was separated by centrifuge and the precipitate washed with water (2 × 5 mL), EtOH (2 × 5mL) and Et_2O (5 mL) to isolate a green solid. The crude product was recrystallized in hot DMF to give the title compound as a yellow solid (22 mg, 38%). ^{1}H NMR (DMSO-d_6, 700 MHz): 9.31 (1H, d, J = 6), 9.07 (1H, s), 7.88 (1H, s), 7.86 (1H, dd, J = 8 and 1.5), 7.48 (1H, ddd, J = 85, 7 and 2), 7.40 (1H, dd, J = 6.5 and 1.5), 7.13 (1H, d, J = 8), 6.82 (1H, t, J = 7). The material was not sufficiently soluble to obtain a ^{13}C NMR spectrum. MS (ES+): *m/z* 530 $[M+H]^+$; HRMS (ES+): *m/z* 529.0762 $[M]^+$; calculated for $[C_{16}H_{14}N_4OF_3PtCl]^+$ 529.0746.

PtL^{14}-C≡C-Ar

A mixture of $PtL^{14}Cl$ (37 mg, 0.08 mmol), CuI (5 mg, 0.03 mmol), 1-ethynyl-3,5-bis(trifluoromethyl)benzene (30 mg, 0.12 mmol) and anhydrous NEt_3 (0.4 mL) in anhydrous DCM (7 mL) was heated to reflux for a period of 48 under argon. The resulting slurry was filtered and wash with DCM (3 × 2 mL) to give the title compound as a bright yellow solid (20 mg, 38%).
^{1}H NMR (DMSO-d_6, 600 MHz): 9.26 (1H, dd, J = 6 and 1, H^3), 8.91 (1H, s, H^{imine}), 8.10 (1H, ddd, J = 9, 7 and 1.5, H^5), 8.00 (2H, s, $H^{2''}$), 7.88 (1H, s, $H^{4''}$), 7.82 (1H, dd, J = 8 and 2, $H^{3'}$), 7.54 (1H, d, J = 9, H^6), 7.46 (1H, ddd, J = 8.5, 7 and 2, $H^{5'}$), 7.17 (1H, d, J = 8, $H^{6'}$), 7.08 (1H, t, J = 6.5, H^4), 6.81 (1H, t, J = 7, $H^{4'}$), 3.94 (3H, s, H^{NMe}). ^{13}C NMR (DMSO-d_6, 151 MHz): 159.8, 153.0, 149.1, 138.5, 138.4, 134.1, 132.3, 131.7, 130.5, 130.2, 124.2, 122.4, 121.1, 118.8, 116.3, 115.7, 109.1, 104.1, 33.6, 30.7, 7.2. MS (ES+): *m/z* 659 $[M+H]^+$.

Density functional theory

DFT calculations were carried out using the Gaussian 09 suite[7] of programs to predict energy-minimised structures of the singlet ground state. The LANL2DZ basis set was used for all atoms. Calculations were run using the B3LYP functional[8] in the gas phase. Geometries were optimised without symmetry constraints. Harmonic vibrational wavenumber calcualtions were performed to confirm that the structures obtained correspond to minima of the potential energy surface.

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