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Supporting Information

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Outer-Sphere Coordination Chemistry: Selective Extraction and Transport of the $[PtCl_6]^{2-}$ Anion

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Full experimental details

The benzylated tren cap **1** was prepared according to the literature procedure[12] involving the reductive amination of tren with benzaldehyde. Acylation of **1** with 2-phthalimidoacetyl chloride gave **2**, followed by deprotection with hydrazine hydrate to afford **3**. L^1 was prepared by reaction of **3** with 4-*tert*-butylbenzoyl chloride. The urea-containing ligands L^2-L^5 and L^{10} were synthesised in >80% yield by the reaction of tren with the appropriate isocyanate, [13] and amides L^6-L^9 were synthesized in >65% yields by reaction of tren with the respective benzoyl chlorides under basic conditions.[14-15] Dimethoxy- and trimethoxy-substitution of the pendant phenyl groups was necessary to ensure solubility of the reagents and, most importantly, of their complexes with anions in water-immiscible solvents.

All solvents and reagents were commercially available from Aldrich or Fisher. ^{1}H and ^{13}C NMR spectra were obatiined on Bruker ARX 250, DPX 360 or DPX 300 spectrometers. The chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent signal in $CDCl_3$ (δ_H 7.26 and δ_C 77.0), [d_6]-DMSO (δ_H 2.50 and δ_C 39.5), [d_4]-methanol (δ_H 3.31 and δ_C 49.0) or [d_2]-1,1,2,2-tetrachloroethane (δ_H 5.91 and δ_C 74.2). Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS50TC instrument in a 3-nitrobenzyl alcohol (NOBA) matrix. Electrospray (ES) mass spectra were recorded on a VG Autospec instrument. ICP-OES was carried out using the Perkin Elmer Optima 5300DV Spectrometer. For pH-measurements an AR50 (Fisher scientific) pH meter was used.

Ligand Synthesis

Tris[2-(benzylamino)ethyl]amine **1**[12] and 2-phthalimidoacetyl chloride[17] were synthesised as described previously.

General Procedure A – Urea synthesis.

Tren (0.20 cm^3, 1.35 mmol) was dissolved in dry thf (30 cm^3) under N_2. The appropriate phenyl isocyanate (4.20 mmol) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 2 h during which time a white precipitate formed. The precipitate was collected by filtration and dried *in vacuo*. L^5 was purified by column chromatography eluting with 7%MeOH, 93% $CHCl_3$.

General Procedure B – Amide synthesis.

Tren (0.40 cm^3, 2.70 mmol) was dissolved in water (20 cm^3) containing NaOH (0.33 g, 8.25 mmol). The appropriate benzoyl chloride (7.66 mmol) dissolved in diethyl ether for L^6 or CH_2Cl_2 for L^7-L^9 (10 cm^3) was added slowly and the reaction stirred at room temperature for 2 days. The off-white solid that formed was collected by filtration, washed with a portion of Et_2O (10 cm^3) and dried *in vacu*o.

Tris(2-(*N*-benzyl-*N*-(2-phthalimidoacetyl)amino)ethyl)amine 2

To a solution of tris[2-(benzylamino)ethyl]amine **1** (10.0 g, 24.0 mmol) in $CHCl_3$ (300 cm^3) containing triethylamine (20.9 cm^3, 150 mmol) at 0 °C was added a solution of 2-phthalimidoacetyl chloride (22.4 g, 100 mmol) in $CHCl_3$ (200 cm^3) over a period of 30 mins. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography eluting with 0% to 100% ethyl acetate / CH_2Cl_2 to give the product **2** as a pale brown product (17.0 g, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.0-7.6 (m, 12H, phthalimido-H_{Ar}), 7.5-7.1 (m, 15H, benzyl-H_{Ar}), 4.7-4.4 (overlapping m, 12H, $COCH_2$ and CH_2Ar), 3.5-3.2 (m, 6H, NCH_2CH_2NCO), 2.7-2.4 (m, 6H, NCH_2CH_2NCO). MS (FAB): *m/z* 979 $[M+H]^+$.

Tris(2-(*N*-benzyl-*N*-(2-aminoacetyl)amino)ethyl)amine 3

A suspension of **2** (4.5 g, 4.6 mmol) in EtOH (300 cm^3) was treated with a minimum amount of $CHCl_3$ to dissolve the solid. Hydrazine hydrate (2.2 cm^3, 46.0 mmol) was added and the reaction mixture was stirred for 16 h and then refluxed for 2 h and allowed to cool. The reaction mixture was filtered to

remove the white precipitate which washed with EtOH and $CHCl_3$. The combined filtrates were evaporated *in vacuo*, and he residue purified by column chromatography eluting with 0.5% $NH_4OH_{(aq)}$/5% MeOH/CH_2Cl_2 to 2% $NH_4OH_{(aq)}$/20% MeOH/ CH_2Cl_2 to give the product **3** as a colourless oil which was dried under high vacuum (2.5 g, 93%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.4-7.0 (m, 15H, H_{Ar}), 4.6-4.3 (m, 6H, CH_2Ar), 3.6-3.0 (m, 12H, $COCH_2$ and NCH_2CH_2NCO), 2.7-2.3 (m, 6H, NCH_2CH_2NCO). MS (FAB): *m/z* 588 $[M+H]^+$.

Tris(2-(*N*-benzyl-*N*-(2-((4-*tert*-butylbenzoyl)amino)acetyl)amino)ethyl)amine L^1

To a solution of **3** (2.45 g, 4.17 mmol) in $CHCl_3$ (200 cm^3) containing Et_3N (2.04 cm^3, 14.6 mmol) at 0 °C was added a solution of *tert*-butylbenzoyl chloride (2.70 g, 13.8 mmol) in $CHCl_3$ (100 cm^3) over a period of 2 h. The reaction mixture was allowed to warm to room temperature and then stirred for 16 h. The solvent was removed *in vacuo* and the residue purified by column chromatography eluting with 2% to 5% MeOH / CH_2Cl_2 to give the product L^1 as a colourless glass (4.4 g, 99%). The ^{1}H NMR spectrum of this material was extremely complex, showing severe splitting and broadening of signals due to the large number and slow rotation of amide rotamers. This was clarified by acquiring the ^{1}H NMR spectrum at 80 ^{o}C in [d_6]-DMSO, resulting in broad, but separate signals for each set of non-equivalent protons with the correct integration of signals. High resolution FAB mass spectrometry of this material was also consistent with the proposed structure.

^{1}H NMR (360 MHz, [D_6]-DMSO, 80°C): δ 8.17 (br s, 3H, NH), 7.79 (d, 6H, $^3J_{HH}$ = 11.2 Hz, H_{Ar} *ortho* to the amide), 7.45 (d, 6H, $^3J_{HH}$ = 11.2 Hz, H_{Ar} *ortho* to the ^{t}Bu group), 7.27 (br s, 15H, H_{Ar}), 4.58 (br s, 6H, $ArCH_2$), 4.20 (br s, 6H, $NCOCH_2$), 3.35 (br s, 6H, NCH_2CH_2NCO), 2.63 (br s, 6H, NCH_2CH_2NCO), 1.31 (s, 27H, CH_3). ^{13}C NMR (90 MHz, [D_6]-DMSO, 110°C): δ 168.3, 165.8, 153.6, 137.0, 131.2, 127.8, 126.6, 126.42, 126.40, 124.2, 51.7 (br), 49.2 (br), 44.9, 40.6, 33.9, 30.3. MS (FAB): *m/z* 1068.63445 $[M+H]^+$; $C_{66}H_{81}N_7O_6$ requires 1068.63211 $[M+H]^+$.

***N,N',N"*-(nitrilotri-2,1-ethanediyl)tris[*N'*-phenylurea] L^2**

This was prepared using General Procedure A by the reaction of tren with phenyl isocyanate Yield: 95%. ^{1}H NMR (270 MHz, [d$_4$]-methanol): δ 7.26 (d, 6H, $^3J_{HH}$ = 7.6 Hz, H_{Ar}), 7.21–7.16 (m, 6H, H_{Ar}), 6.95 (t, 3H, $^3J_{HH}$ = 8.1 Hz, H_{Ar}), 3.54 – 3.48 (m, 6H, CH_2), 2.68 (t, 6H, $^3J_{HH}$ = 5.4 Hz, CH_2). ^{13}C NMR (68 MHz, [d$_6$]-DMSO): δ 156, 141, 129, 122, 118, 55, 37. MS (ES$^+$): *m/z* 504 $[M+H]^+$, 526 $[M+Na]^+$. IR (KBr, cm^{-1}): 3334 ($?_{(NH)}$), 1650 ($?_{(C=O)}$). Anal. calc. for $C_{27}H_{33}N_7O_3$: C, 64.40; H, 6.60; N, 19.47. Found: C, 64.29; H, 6.78; N, 19.11%.

***N,N',N"*-(Nitrilotri-2,1-ethanediyl)tris(*N'*-3,4-dimethoxyphenyl urea) L^3**

This was prepared using General Procedure A by the reaction of tren with 3,4-dimethoxyphenyl isocyanate. Yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (s, 3H, NH), 6.91 (s, 3H, H_{Ar}), 6.57 (d, 3H, $^3J_{HH}$ = 8.6 Hz, H_{Ar}), 6.49 (d, 3H, $^3J_{HH}$ = 9.0 Hz, H_{Ar}), 6.14 (br t, 3H, NH), 3.76 (s, 9H, OCH_3), 3.68 (s, 9H, OCH_3), 3.08 (br, 6H, CH_2), 2.35 (br, 6H, CH_2). ^{13}C NMR (75 MHz, [d$_6$]-DMSO): δ 156, 149, 144, 135, 113, 110, 104, 56, 55, 54, 37. MS (ES$^+$): *m/z* 684.33 $[M+H]^+$. IR (solid, cm^{-1}): 3299 ($?_{(N-H)}$), 2935 ($?_{(C-H)}$), 2834 ($?_{(C-H)}$), 1627 ($?_{(C=O)}$), 1205 ($?_{(C-O)}$). Anal. calc. for $C_{33}H_{45}N_7O_9$: C, 57.97; H, 6.63; N, 14.34. Found: C, 58.07; H, 6.69; N, 14.36%.

***N,N',N"*-(Nitrilotri-2,1-ethanediyl)tris(*N'*-3,5-dimethoxyphenyl urea) L^4**

This was prepared using General Procedure A by the reaction of tren with 3,5-dimethoxyphenyl isocyanate. Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 3H, NH), 6.44 (s, 6H, H_{Ar}), 6.10 (br t, 3H, NH), 6.06 (s, 3H, H_{Ar}), 3.64 (s, 18H, OCH_3), 3.22 (br, 6H, CH_2), 2.38 (br, 6H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162, 156, 142, 96, 93, 56, 55, 48. MS (ES$^+$): *m/z* 684.34 $[M+H]^+$. IR (solid, cm^{-1}): 3333 ($?_{(N-H)}$), 2942 ($?_{(C-H)}$), 2836 ($?_{(C-H)}$), 1647 ($?_{(C=O)}$), 1148 ($?_{(C-O)}$). Anal. calc. for $C_{33}H_{45}N_7O_9$: C, 57.97; H, 6.63; N, 14.34. Found: C, 57.74; H, 6.61; N, 14.10%.

***N,N',N"*-(Nitrilotri-2,1-ethanediyl)tris(*N'*-3,4,5-trimethoxyphenyl urea) L[5]**

This was prepared using General Procedure A by the reaction of tren with 3,4,5-trimethoxyphenyl isocyanate and purified by column chromatography on silica gel using 7% MeOH, 93 % $CHCl_3$ Yield: 74%. ^{1}H NMR (300 MHz, dmso-d_6): δ 8.50 (s, 3H, NH), 6.72 (s, 6H, HAr), 6.12 (t, 3H, $^3J_{HH}$ = 6.4 Hz, NH), 3.68 (s, 18H, OMe), 3.57 (s, 9H, OMe), 3.18 - 3.16 (m, 6H, CH_2), 2.57 (t, 6H, $^3J_{HH}$ = 5.3 Hz, CH_2). ^{13}C NMR (75 MHz, dmso-d_6): 156, 154, 138, 133, 96, 61, 56, 54, 37. IR (solid): 3336 ($?_{(N-H)}$), 1650 ($?_{(C=O)}$), 1603 ($?_{(C=C)}$, Ar), 1122 cm^{-1} ($?_{(C-O)}$). MS (ES$^+$): *m/z* 774 $[M+H]^+$

***N,N',N"*-(nitrilotri-2,1-ethanediyl)tris-benzamide L[6]**

This was prepared using General Procedure B by the reaction of tren with benzoyl chloride. Yield: 74%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 3H, $^3J_{HH}$ = 6.0 Hz, H_{Ar}), 7.33 (t, 6H, $^3J_{HH}$ = 9.0 Hz, H_{Ar}), 7.18 (br, 3H, NH), 7.07 (t, 6H, $^3J_{HH}$ = 9.0 Hz, H_{Ar}), 3.60–3.55 (m, 6H, CH_2), 2.76 (t, 6H, $^3J_{HH}$ = 6.0 Hz, CH_2). ^{13}C NMR (68 MHz, $CDCl_3$): δ 168, 134, 131, 128, 127, 54, 38. MS (ES$^+$): *m/z* 459 $[M+H]^+$. IR (solid, cm^{-1}): 3345 ($?_{(NH)}$), 3286 ($?_{(NH)}$), 1536 ($?_{(C=O)}$). Anal. calc. for $C_{27}H_{30}N_4O_3$: C, 70.72; H, 6.59; N, 12.22. Found: C, 70.86; H, 6.61; N, 12.24%.

***N,N',N"*-(Nitrilotri-2,1-ethanediyl)tris-3,4-dimethoxybenzamide L[7]**

This was prepared using General Procedure B by the reaction of tren with 3,4-dimethoxybenzoyl chloride. Yield: 66%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (br, 3H, NH), 7.28 (s, 3H, H_{Ar}), 7.12 (d, 3H, $^3J_{HH}$ = 8.4 Hz, H_{Ar}), 6.31 (d, 3H, $^3J_{HH}$ = 8.4 Hz, H_{Ar}), 3.81 (s, 9H, OCH_3), 3.79 (s, 9H, OCH_3), 3.60 (m, 6H, CH_2), 2.77 (t, 6H, $^3J_{HH}$ = 5.2 Hz, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168, 155, 153, 147, 126, 120, 110, 109, 56, 54, 39. MS (ES$^+$): *m/z* 639.30 $[M+H]^+$. IR (solid, cm^{-1}): 3291 ($?_{(N-H)}$), 2936 ($?_{(C-H)}$), 2836 ($?_{(C-H)}$), 1628 ($?_{(C=O)}$), 1264 ($?_{(C-O)}$). Anal. calc. for $C_{33}H_{42}N_4O_9$: C, 62.06; H, 6.63; N, 8.77. Found: C, 61.97; H, 6.55; N, 8.69%.

***N,N',N"*-(Nitrilotri-2,1-ethanediyl)tris-3,5-dimethoxybenzamide L[8]**

This was prepared using General Procedure B by the reaction of tren with 3,5-dimethoxybenzoyl chloride.Yield: 74%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (t, 3H, $^{3}J_{HH}$ = 5.4 Hz, NH), 6.87 (s, 6H, H_{Ar}), 6.38 (s, 3H, H_{Ar}), 3.63 (s, 18H, OCH_3), 3.47 (m, 6H, CH_2), 2.66 (t, 6H, $^{3}J_{HH}$ = 5.1 Hz, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168, 161, 105, 103, 55, 54, 39. MS (ES^+): *m/z* 639.30 $[M+H]^+$. IR (solid, cm^{-1}): 3304 (?$_{(N-H)}$), 2938 (?$_{(C-H)}$), 2837 (?$_{(C-H)}$), 1637 (?$_{(C=O)}$), 1151 (?$_{(C-O)}$). Anal. calc. for $C_{33}H_{42}N_4O_9$: C, 62.06; H, 6.63; N, 8.77. Found: C, 61.98; H, 6.81; N, 8.59%.

***N,N',N"*-(Nitrilotri-2,1-ethanediyl)tris-3,4,5-trimethoxybenzamide L[9]**

This was prepared using General Procedure B by the reaction of tren with 3,4,5- trimethoxybenzoyl chloride. Yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (t, 3H, $^{3}J_{HH}$ = 4.6 Hz, NH), 7.00 (s, 6H, H_{Ar}), 3.78 (s, 3H, OCH_3), 3.63 (s, 6H, OCH_3), 3.44 (br, 6H, CH_2), 2.61 (br, 6H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168, 153, 141, 129, 105, 61, 56, 55, 39. MS (ES^+): *m/z* 729 $[M+H]^+$. IR (solid, cm^{-1}): 3304 (?$_{(N-H)}$), 2939 (?$_{(C-H)}$), 2836 (?$_{(C-H)}$), 1636 (?$_{(C=O)}$), 1120 (?$_{(C-O)}$). Anal. calc. for $C_{36}H_{48}N_4O_{12}$: C, 59.33; H, 6.64; N, 7.69. Found: C, 59.21; H, 6.58; N, 7.71%.

***N,N',N"*-(nitrilotri-2,1-ethanediyl)tris[*N'*-tertbutyl urea] L[10]**

Tren (0.20 cm^3, 1.35 mmol) was dissolved in dry thf (30 cm^3) under N_2. *Tert*-butylisocyanate (0.46 cm^3, 4 mmol) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 20 h and the solvent removed under vacuum to yield a white solid. No further purification was required. Yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$): 5.79 (br, 3H, N<u>H</u>), 5.15 (m, 3H, N<u>H</u>), 3.13 (br, 6H, C<u>H</u>$_2$), 2.46 (br, 6H, C<u>H</u>$_2$), 1.33 (s, 27H, ^{t}<u>Bu</u>). ^{13}C NMR (68 MHz, $CDCl_3$): 160, 56, 50, 30. MS (ES^+): *m/z* 444 $[M+H]^+$, 467 $[M+Na]^+$. IR (KBr, cm^{-1}): 3350 (?$_{(N-H)}$),1650 (?$_{(C=O)}$). Anal. calc. for $C_{21}H_{45}N_7O_3$: C, 56.86; H, 10.22; N, 22.10. Found: C, 56.50; H, 10.24; N, 20.58%.

Complex Synthesis

$(L^1H)_2[PtCl_6]$

A solution of ligand L^1 (0.53 g, 0.50 mmol) in MeOH (10 cm^3) was added to a solution of H_2PtCl_6 (0.13 g, 0.25 mmol) in MeOH (5 cm^3) and the solution was allowed to slowly evaporate to ~5 cm^3. The resulting pale orange solid was filtered, washed with cold MeOH and dried under high vacuum. ^{1}H NMR (360 MHz, [d_2]-1,1,2,2-tetrachloroethane): δ 7.81 (m, 12H, H_{Ar}), 7.67 (br s, 6H, CONH), 7.35 (m, 6H, H_{Ar}), 7.3-7.0 (m, 30H, H_{Ar}), 6.75 (br s, 2H, N^+H), 4.35 (br s, 12H, CH_2), 3.91 (br s, 12H, CH_2), 3.60 (br s, 24H, CH_2), 1.18 (br s, 54H, CH_3). ^{13}C NMR (90 MHz, [D_2]-1,1,2,2-tetrachloroethane, 80 °C): δ 172.5, 168.0, 155.7, 135.4, 131.1, 129.4, 128.3, 127.5, 127.4, 125.7, 54.4, 51.8, 42.5, 42.0, 35.0, 31.3.

$(L^2H)_2[PtCl_6]$

Ligand L^2 (0.019 g, 0.039 mmol) was dissolved in MeCN (2 cm^3). To this solution was added H_2PtCl_6 (0.010 g, 0.019 mmol) dissolved in MeCN (1 cm^3). An orange precipitate instantly formed which was collected by filtration and dried under vacuum. ^{1}H NMR (300 MHz, [D_6]-DMSO): δ 9.61 (br, 1H, NH^+), 8.80 (s, 3H, NH), 7.40 (d, 6H, $^3J_{HH}$ = 8.7 Hz, H_{Ar}), 7.19 (t, 6H, $^3J_{HH}$ = 8.4 Hz, H_{Ar}), 6.92 (t, 3H, $^3J_{HH}$ = 7.3 Hz, H_{Ar}), 6.45 (t, 3H, $^3J_{HH}$ = 5.6 Hz, NH), 3.51 (m, 6H, CH_2), 3.37 (m, 6H, CH_2). Anal. calc. for $C_{54}H_{68}Cl_6N_{14}O_6Pt$: C, 45.77; H, 4.84; N, 13.84. Found: C, 44.97; H, 4.71; N, 13.56%, IR: 3347 ($?_{N-H}$), 1661 ($?_{C=O}$), 1598 cm^{-1} (? C=C, Ar).

$(L^5H)_2[PtCl_6]$

This compound was prepared in a similar manner to that described for $(L^2H)_2[PtCl_6]$ and precipitated as a yellow powder. ^{1}H NMR (300 MHz, [d_6]-DMSO): δ 9.87 (br, 1H, NH^+), 8.81 (t, 3H, $^3J_{HH}$ = 5.2 Hz, NH), 7.81 (d, 6H, $^3J_{HH}$ = 7.10 Hz, H_{Ar}), 7.54 (t, 3H, $^3J_{HH}$ = 7.3 Hz, H_{Ar}), 7.47 (t, 6H, $^3J_{HH}$ = 7.1 Hz, H_{Ar}), 3.72 (d, 6H, $^3J_{HH}$ = 5.5, CH_2), other CH_2 obscured by H_2O signal. Anal. calc. for $C_{54}H_{62}Cl_6N_8O_6Pt$: C, 48.88; H, 4.71; N, 8.44. Found: C, 49.15; H, 4.63; N, 8.37%.

$[(L^{10}H)_2PtCl_6]$

L^{10} (0.039 mmol) was dissolved in MeCN (2 cm^3) and to this solution was added H_2PtCl_6 (0.019 mmol) dissolved in MeCN (1 cm^3). An orange precipitate formed immediately which was collected by filtration and dried under vacuum. ^{1}H NMR (270 MHz, d_6-dmso): 10.05 (br, 1H, N<u>H</u>$^+$), 6.05 (br, 3H, N<u>H</u>), 4.31 (br, 3H, N<u>H</u>), 3.31 (br, 6H, C<u>H</u>$_2$), 3.20 (br, 6H, C<u>H</u>$_2$), 1.25 (s, 27H, ^{t}<u>Bu</u>). Anal. calc. for $C_{42}H_{92}Cl_6N_{14}O_6Pt$: C, 38.89; H, 7.15; N, 15.12. Found: C, 38.82; H, 7.09; N, 15.03%.

General Experimental Procedure for Extractions

Analytical grade chloroform from a commercial source was used to prepare ligand solutions without further purification. Water used to prepare H_2PtCl_6 solutions was purified using a commercial filtration system and reported a resistance of ~18O. $H_2PtCl_6{\cdot}6H_2O$, purchased from Aldrich, was dried over P_2O_5 to obtain a yellow solid. Calibration curves for ICP-OES were prepared by dilution of commercially available standards.

Solutions of ligand were prepared at varying concentrations between 0.0005 - 0.01 M by weighing aliquots of 0.01 M ligand stock solution in $CHCl_3$ into 5 cm^3 volumetric flasks and diluting to the mark with $CHCl_3$. Solutions of H_2PtCl_6 were prepared by weighing $H_2PtCl_6{\cdot}6H_2O$ (0.03 g) into a 50 cm^3 volumetric flask and diluting to the mark with water or 0.1 M HCl or 0.6M HCl.

Extractions were prepared by charging 100 cm^3 Schott flasks fitted with a magnetic stir bar with 5cm^3 of the ligand solution and 5 mL of H_2PtCl_6 solution. The extractions were stirred at 25ºC for 4 h, after which the phases were separated. Aqueous samples for ICP-OES analysis were prepared by weighing 2 cm^3 of the aqueous phase into 5 cm^3 volumetric flasks containing 0.8 cm^3 of 6M HCl and diluted to the mark with water. The organic phases (4.0 cm^3) were transferred into glass snap-top vials fitted with magnetic stir bars using a volumetric glass pipette. To this vial was added, an aliquot of 0.06 M aqueous NaOH such that there was a 2 mol equiv. of OH^- calculated relative to the amount of ligand

in the sample and enough water to make the final aqueous volume 4 cm^3. The two phases were contacted for 30 min then separated. Samples for ICP-OES analysis were prepared by weighing 2 cm^3 of the aqueous phase into 5 cm^3 volumetric flasks containing 0.8 cm^3 6M HCl and diluting to the mark with water. To determine the concentration of Pt in the stock solution by ICP-OES, samples were prepared by weighing in the same manner as the above aqueous extraction samples.

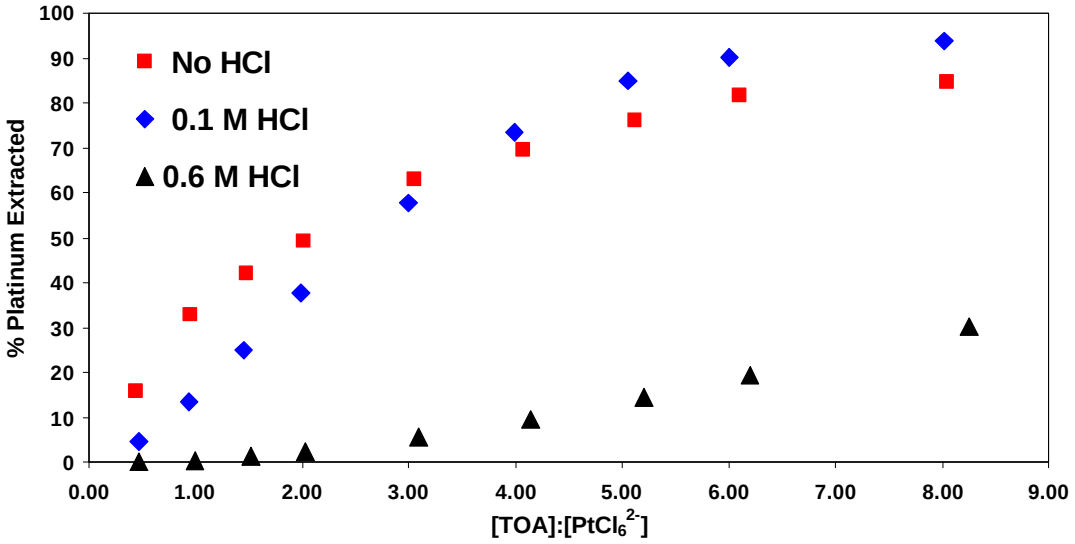

Figure S1: Platinum uptake into $CHCl_3$ solutions by TOA at varying concentrations from 0.001M aqueous solutions of H_2PtCl_6 containing 0, 0.1 or 0.6M HCl. 100% loading is based on the formation of a neutral 1:2 complex of $PtCl_6^{2-}$ with $TOAH^+$.

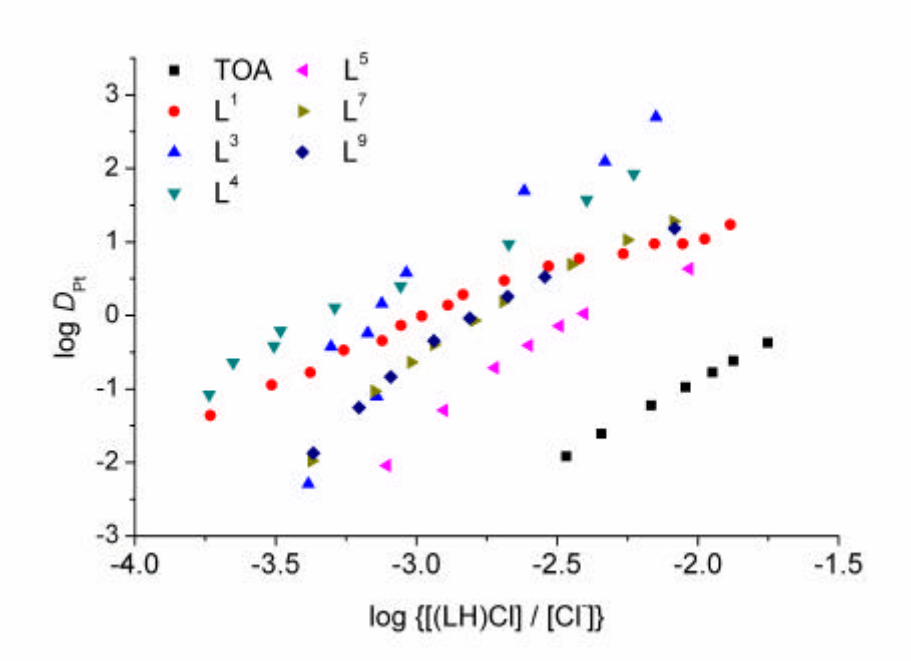

Figure S2: Plot of log D_{Pt} vs log{[(LH)Cl]/[Cl^-]} for a range of receptors with loss of linearity observed.

Crystal Structure of $[(L^{10}H)_2PtCl_6]$

Single crystals of the complex were grown by mixing two equivalents of L^{10} in MeCN with one equivalent of H_2PtCl_6 in MeCN. Slow evaporation from the solution led to the formation of crystals as yellow tablets. The complex crystallises in the triclinic space group *P*i with one $[(L^{10}H)_2PtCl_6]$ unit per unit cell. The extended crystal structure of $[(L^{10}H)_2PtCl_6]$ shows there is a hydrogen-bonded chain arrangement of the type …{L^{10}…$[PtCl_6]^{2-}$…L^{10}}…{L^{10}…$[PtCl_6]^{2-}$…L^{10}. Each molecule of $[HL^{10}]^+$ interacts with one $[PtCl_6]^{2-}$ and another molecule of $[HL^{10}]^+$. The L^{10}…L^{10} bifurcated H-bonding occurs between N7-H7A…O1 and N6-H6A…O1. The details of the H-bonding interactions are shown in Table S1.

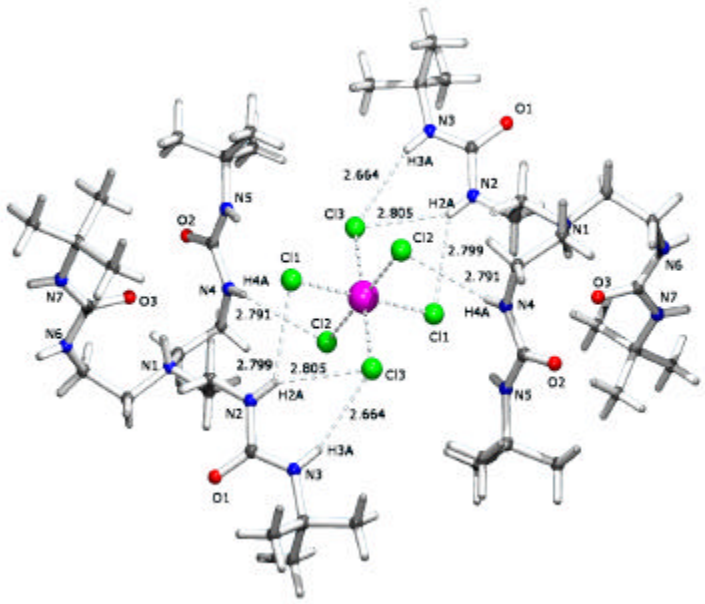

Figure S3: View of structure of $[(L^{10}H)_2PtCl_6]$

Table S1. Hydrogen-bonds present in $[(L^{10}H)_2PtCl_6]$ (D = donor, A = acceptor, d = distance).

D-H…A	d(D-H) Å	d(H…A) Å	d(D…A) Å	<(DHA) °
N2-H2A…Cl1	0.86	2.80	3.4390	132
N2-H2A…Cl3	0.86	2.80	3.5778	150
N3-H3A…Cl3	0.86	2.66	3.4951	163
N4-H4A…Cl2	0.86	2.79	3.3629	125
N6-H6A…O1	0.86	2.10	2.832	143
N7-H7A…O1	0.86	2.18	2.951	149