## Supporting Information:

# A Comparison of the Selectivity of Extraction of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ by Mono-, Bi- and Tripodal Receptors that Address its Outer Co-ordination Sphere 

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1. Additional extraction data. The results presented in Figures S1-S6 demonstrate that extractants differing only in having 3,4-dimethoxy substitution rather than 3,5-dimethoxy substitution on the benzene rings show very similar loadings of $\left[\mathrm{PtCl}_{6}\right]^{2-}$.


Figure SI1. Plot of percentage of the total platinum extracted as $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from aqueous 0.6 M HCl into $\mathrm{CHCl}_{3}$ as a function of the [L]:[Pt] ratio for the tripodal ureas: $\mathbf{L}^{\mathbf{1}}$ (3,4-methoxy substituted) and $\mathbf{L}^{\mathbf{2}}(3,5-$ methoxy substituted).


Figure SI2. Plot of percentage of the total platinum extracted as $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from aqueous 0.6 M HCl into $\mathrm{CHCl}_{3}$ as a function of the [L]:[Pt] ratio for the tripodal amides: $\mathbf{L}^{3}$ (3,4-methoxy substituted) and $\mathbf{L}^{4}(3,5-$ methoxy substituted).


Figure SI3. Plot of percentage of the total platinum extracted as $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from aqueous 0.6 M HCl into $\mathrm{CHCl}_{3}$ as a function of the $[\mathrm{L}]:[\mathrm{Pt}]$ ratio for the bipodal ureas: $\mathbf{L}^{\mathbf{6}}$ (3,4-methoxy substituted) and $\mathbf{L}^{7}(3,5-$ methoxy substituted).


Figure SI4. Plot of percentage of the total platinum extracted as $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from aqueous 0.6 M HCl into $\mathrm{CHCl}_{3}$ as a function of the [L]:[Pt] ratio for the bipodal amides: $\mathbf{L}^{8}$ (3,4methoxy substituted) and $\mathbf{L}^{9}$ (3,5-methoxy substituted).


Figure SI5. Plot of percentage of the total platinum extracted as $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from aqueous 0.6 M HCl into $\mathrm{CHCl}_{3}$ as a function of the [L]:[Pt] ratio for the monopodal ureas: $\mathbf{L}^{\mathbf{1 1}}$ (3,4-methoxy substituted) and $\mathbf{L}^{12}$ (3,5-methoxy substituted).


Figure SI6. Plot of percentage of the total platinum extracted as $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from aqueous $0.6 \mathrm{M} \mathrm{HCl}^{2}$ into $\mathrm{CHCl}_{3}$ as a function of the $[\mathrm{L}]:[\mathrm{Pt}]$ ratio for the monopodal amides: $\mathrm{L}^{13}$ (3,4-methoxy substituted) and $\mathbf{L}^{14}$ (3,5-methoxy substituted).

# Section 2. Additional information on crystal structures and contact distances defining intermolecular H-bonds. 

Proligand $\mathbf{L}^{\mathbf{1 1}}$ : The extended structure shows inter-molecular hydrogen-bonding in $\mathbf{L}^{\mathbf{1 1 ( a )}}$ with $\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A}^{\cdots} \mathrm{O} 2\left(\mathrm{H}^{\cdots} \mathrm{A}=2.121 \AA\right.$ ) and $\mathrm{N} 3-\mathrm{H} 3 \mathrm{~A}^{\cdots} \mathrm{O} 2\left(\mathrm{H}^{\cdots} \mathrm{A}=2.092 \AA\right.$ (Figure 2). The molecules of $\mathbf{L}^{\mathbf{1 1 ( a )}}$ have an alternating orientation and form a chain with each molecule of $\mathbf{L}^{11(\text { a) }}$ being linked to the next through bifurcated hydrogen-bonds between the urea moieties. There are analogous inter-molecular interactions between the $\mathbf{L}^{\mathbf{1 1 ( b )}}$ molecules with $\mathrm{N} 7-\mathrm{H} 7 \mathrm{~A}^{\cdots} \mathrm{O} 4\left(\mathrm{H}^{\cdots} \mathrm{A}=2.056 \AA\right)$ and $\mathrm{N} 8 — \mathrm{H} 8 \mathrm{~A}^{\cdots} \mathrm{O} 4\left(\mathrm{H}^{\cdots} \mathrm{A}=2.140 \AA\right)$. Further data are included in Table S1.
$\left[\left(\mathbf{L}^{11} \mathbf{H}\right)_{2} \mathbf{P t C l}_{6}\right]$ : The complex crystallises in the monoclinic space group $\mathrm{P} 2_{1} / \mathrm{c}$ with one $\left[\mathrm{PtCl}_{6}\right]^{2-}$ anion lying on a centre of inversion and two receptor cations related by the inversion centre. The $\mathbf{L}^{\mathbf{1 1}}$ molecules are protonated at the bridgehead position (N1) to give the receptor $\mathrm{a}+1$ charge and for each $\left[\mathrm{PtCl}_{6}\right]^{2-}$ anion present there are two $\left(\mathbf{L}^{11} \mathrm{H}\right)^{+}$ cations ensuring that the structure has a net charge of zero and confirming the expected 2 : $1\left(\mathbf{L}^{11} \mathrm{H}\right)^{+}$to $\left[\mathrm{PtCl}_{6}\right]^{2-}$ stoichiometry of the complex. Disorder around the NMe fragment involving $\mathrm{N} 1, \mathrm{C} 1$ and C 2 was modelled over two half-occupied sites with distance restraints and was refined with isotropic atomic displacement parameters.

The structure determination reveals extensive hydrogen-bonding between the urea moieties of $\left(\mathbf{L}^{11} \mathrm{H}\right)^{+}$and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and also between the $\left(\mathbf{L}^{11} \mathrm{H}\right)^{+}$cations. Each $\left[\mathrm{PtCl}_{6}\right]^{2-}$ anion accepts three hydrogen-bonds from two $\left(\mathbf{L}^{11} \mathrm{H}^{+}\right)$cations giving a total of six
$\mathrm{NH}^{\cdots} \mathrm{Cl}$ interactions per anion with $\mathrm{N} 4 — \mathrm{H}^{2} 4 \mathrm{~A}^{\cdots} \mathrm{Cl} 2\left(\mathrm{H}^{\cdots} \mathrm{A}=2.604 \AA\right), \mathrm{N} 4 — \mathrm{H} 4 \mathrm{~A}^{\cdots} \mathrm{Cl} 3$ $\left(\mathrm{H}^{\cdots} \mathrm{A}=2.745 \AA\right)$ and $\mathrm{N} 5-\mathrm{H} 5 \mathrm{~A}^{\cdots} \mathrm{Cl} 2\left(\mathrm{H}^{\cdots} \mathrm{A}=2.729 \AA\right)$ (Figure 3). The N4—H4A donor group is located between the Cl 2 and Cl 3 atoms and the $\mathrm{N} 5-\mathrm{H} 5 \mathrm{~A}$ group is located approximately in the centre of a triangular face defined by $\mathrm{Cl} 1, \mathrm{Cl} 2$ and Cl 3 . These correspond to areas of highest electron density surrounding $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and are locations predicted to be targeted by NH groups. ${ }^{15}$

There are also intra- and inter-ligand $\mathrm{NH}^{\cdots} \mathrm{O}$ interactions $\mathrm{N} 1-\mathrm{H} 1 \mathrm{D} \cdots \mathrm{O} 2\left(\mathrm{H}^{\cdots} \mathrm{A}=\right.$ $2.103 \AA), \mathrm{N} 2-\mathrm{H} 2 \mathrm{~A}^{\cdots} \mathrm{O} 1\left(\mathrm{H}^{\cdots} \mathrm{A}=2.069 \AA\right.$ ) and $\mathrm{N} 3-\mathrm{H}^{\circ} \mathrm{A}^{\cdots} \mathrm{O} 1\left(\mathrm{H}^{\cdots} \mathrm{A}=2.141 \AA\right)$. The extended structure shows that one urea group in each $\left(\mathbf{L}^{11} \mathrm{H}^{+}\right)$cation hydrogen-bonds to $\left[\mathrm{PtCl}_{6}\right]^{2-}$ while the other forms hydrogen-bonds to an adjacent $\left(\mathbf{L}^{11} \mathrm{H}^{+}\right)$molecule to give
 hydrogen-bonds present in this structure are given in Table S2.

The configuration of the ligand is different in $\mathbf{L}^{11}$ and $\left.\left(\mathbf{L}^{11} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right]$. In $\mathbf{L}^{\mathbf{1 1}}$ the two pendant arms have a parallel orientation with a bifurcated intra-ligand hydrogenbond between the urea moieties on the pendant arms. The arms are aligned less in $\left[\left(\mathbf{L}^{11} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right]$ and there are no intra-ligand hydrogen-bonds between the urea moieties.

It was thought that a bipodal receptor would form fewer hydrogen-bonds to $\left[\mathrm{PtCl}_{6}\right]^{2-}$ than a tripodal urea receptor because there are fewer NH donor groups available. The structure $\left[\left(\mathbf{L}^{11} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right]$ shows that two out of four functionalised arms interact with the anion and there are six $\mathrm{NH}^{\cdots} \mathrm{Cl}$ hydrogen-bonds to each $\left[\mathrm{PtCl}_{6}\right]^{2-}$. This suggests that the number of functionalised pendant arms does not play a significant part in determining the number of hydrogen-bonds that are formed to $\left[\mathrm{PtCl}_{6}\right]^{2-}$ in the solid state. This is true also for the other structures.
$\left[\left(\mathbf{L}^{13} \mathbf{H}\right)_{\mathbf{2}} \mathbf{P t C l}_{6}\right]$ : The $\mathbf{L}^{13} \mathrm{H}^{+}$units present in the structure are protonated at the tertiary amine position (N1) giving them a +1 charge and as the $\left(\mathbf{L}^{\mathbf{1 3}} \mathrm{H}\right)^{+}:\left[\mathrm{PtCl}_{6}\right]^{2-}$ ratio is 2: 1 the crystal has a net charge of zero. The structure also contains four molecules of disordered MeCN in the unit cell. These have been omitted in Figure 4.

There are $\mathrm{N}-\mathrm{H}^{\cdots} \mathrm{Cl}-\mathrm{Pt}$ interactions between both amide NH groups in $\left(\mathbf{L}^{\mathbf{1 3}} \mathrm{H}^{+}\right)$ and two separate molecules of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ with $\mathrm{N} 2 — \mathrm{H} 2 \mathrm{~A}^{\cdots} \mathrm{Cl} 2\left(\mathrm{H}^{\cdots} \mathrm{A}=2.464 \AA\right)$ and $\mathrm{N} 3-$ $\mathrm{H} 3 \mathrm{~A}^{\cdots} \mathrm{Cl} 3\left(\mathrm{H}^{\cdots} \mathrm{A}=2.581 \AA\right)$. There is a centre of inversion at Pt1 resulting in each $\left[\mathrm{PtCl}_{6}\right]^{2-}$ anion accepting one hydrogen-bond from four different $\left(\mathbf{L}^{13} \mathrm{H}^{+}\right)$cations. The H3A atom hydrogen-bonds to Cl 3 but the $\mathrm{H} 3 \mathrm{~A}^{\cdots} \mathrm{Cl} 1$ distance $\left(\mathrm{H}^{\cdots} \mathrm{A}=2.990 \AA\right.$ ) is slightly too long to be classed as a close interaction. The H3A atom is located between the Cl 1 and Cl 3 atoms but is slightly out of the plane defined by $\mathrm{Pt} 1, \mathrm{Cl} 1$ and Cl 3 . There are also inter-ligand interactions $\mathrm{N} 1-\mathrm{H} 1 \cdots \mathrm{O} 5\left(\mathrm{H}^{\cdots} \mathrm{A}=2.038 \AA\right.$ ) and $\mathrm{N} 1-\mathrm{H} 1 \cdots \mathrm{O} 1\left(\mathrm{H}^{\cdots} \mathrm{A}=2.569\right.$ A). Further information on the hydrogen-bonds present are given in Table S3.
[ $\left.\left(\mathbf{L}^{23} \mathbf{H}\right)_{\mathbf{2}} \mathbf{P t C l}_{6}\right]$ : Orange blocks of $\left[\left(\mathbf{L}^{23} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right]$ obtained by slow evaporation of an aqueous methanolic solution of $\mathbf{L}^{23}, \mathrm{H}_{2} \mathrm{PtCl}_{6}$ and HCl have the triclinic space group P-1. The NH unit of the protonated tertiary amine nitrogen atom forms a H -bond to the neighbouring amide oxygen atom to form a 6-membered "proton chelate". The chelated proton does not make close contacts with $\left[\mathrm{PtCl}_{6}\right]^{2-}$ ions but the chelate ring structure determines which polarised $\mathrm{N}-\mathrm{H}$ and $\mathrm{C}-\mathrm{H}$ bonds are available to address the outer coordination sphere of a chloridoplatinate through $\mathrm{N}-\mathrm{H} \cdots \mathrm{Cl}$ and $\mathrm{C}-\mathrm{H} \cdots \mathrm{Cl} \mathrm{H}$-bonding interactions. A polymeric structure results in which chloridoplatinate shows twelve long
range interactions (within $3 \AA$ ) between five of its chloride atoms: two amido $\mathrm{N}-\mathrm{H} \cdots \mathrm{Cl}$ interactions, $\mathrm{N} 5 \mathrm{~A}-\mathrm{H} 5 \mathrm{~A} \cdots \mathrm{Cl4C}(\mathrm{H} 5 \mathrm{~A} \cdots \mathrm{Cl4C}=2.637 \AA)$ and $\mathrm{N} 5 \mathrm{~B}-\mathrm{H} 5 \mathrm{~B} \cdots \mathrm{Cl} 6 \mathrm{C}$ $(\mathrm{H} 5 \mathrm{~B} \cdots \mathrm{Cl} 6 \mathrm{C}=2.468 \AA)$ and a further ten $\mathrm{C}-\mathrm{H} \cdots \mathrm{Cl}$ interactions between 2.768 and $2.903 \AA \mathrm{H} \cdots \mathrm{Cl}$ length. A list if the X-H $\cdots \mathrm{Cl}$ contacts shorter than $3 \AA$ is given in Table S4.
$\left[\left(\mathbf{L}^{24} \mathbf{H}\right)_{2} \mathbf{P t C l}_{6}\right]$ : Preliminary details of this structure have been published. ${ }^{7}$ Figure 6 provides a comparison with those described for the first time in this work. The assembly formed by $\left[\mathrm{L}^{24} \mathrm{H}\right]^{+}$is fundamentally different in having only $\mathrm{C}-\mathrm{H} . . . \mathrm{Cl}$ interactions because it does not contain any amido $\mathrm{N}-\mathrm{H}$ groups and the ammonium proton is not available as it is chelated by the amido $\mathrm{C}=\mathrm{O}$ group. Four $\mathrm{C}-\mathrm{H}$ groups $\alpha$ to the ammonium nitrogen atoms form close contacts ( 2.641 to $2.993 \AA$, see Table S5). A further four interactions with aryl $\mathrm{C}-\mathrm{H}$ donors are observed.

Table S1. Intra- and inter-molecular hydrogen-bonds $\mathrm{D}-\mathrm{H}^{\cdots} \mathrm{A}$ in $\mathbf{L}^{11}(\mathrm{D}=$ donor, $\mathrm{A}=$ acceptor, $\mathrm{d}=$ distance)

| D- ${ }^{*}$ * | $\mathbf{d}\left(\mathbf{D}_{\AA}^{\AA} \mathbf{H}\right) /$ | $\begin{gathered} \mathbf{d}\left(\mathbf{H}^{\cdots} \cdot \mathbf{A}\right) \\ / \AA \end{gathered}$ | $\begin{gathered} \mathbf{d}(\mathbf{D} \cdots \mathbf{A}) \\ / \AA \\ \hline \end{gathered}$ | $<(\underset{\mathbf{0}}{(\mathbf{D H A})} /$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N} 4-\mathrm{H} 4 \mathrm{~A} \cdots \mathrm{O} 1$ | 0.86 | 2.087 | 2.8821(14) | 153.5 |
| N5-H5A ${ }^{\text {O }}$ 1 | 0.86 | 2.127 | 2.9144(14) | 152.1 |
| $\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A} \cdots \mathrm{O} 2$ | 0.86 | 2.121 | 2.9044(14) | 151.2 |
| $\mathrm{N} 3-\mathrm{H} 3 \mathrm{~A} \cdots \mathrm{O} 2$ | 0.86 | 2.092 | 2.8868(14) | 153.4 |
| N9-H9A ${ }^{\text {O }}$ 3 | 0.86 | 2.161 | 2.9281(14) | 148.3 |
| $\mathrm{N} 10-\mathrm{H} 10 \mathrm{~A}^{\cdots} \mathrm{O} 3$ | 0.86 | 2.204 | $2.9404(14)$ | 143.6 |
| N7—H7A ${ }^{\text {O }}$ 4 | 0.86 | 2.056 | 2.8583(14) | 154.8 |


| $\mathrm{N} 8 — \mathrm{H} 8 \mathrm{~A}$ | O 4 | 0.86 | 2.140 | $2.9099(13)$ |
| :--- | :--- | :--- | :--- | :--- | 148.9

*symmetry codes $\mathrm{x}+1 / 2, \mathrm{y}+1 / 2,-\mathrm{z}+1 / 2,-\mathrm{x}+3 / 2, \mathrm{y}-1 / 2, \mathrm{z}+1 / 2$.

Table S2. Inter-molecular hydrogen-bonds in $\left[\left(\mathbf{L}^{11} \mathrm{H}\right){ }_{2} \mathrm{PtCl}_{6}\right](\mathrm{D}=$ donor, $\mathrm{A}=$ acceptor, d = distance).

| D- ${ }^{\cdots}$ * | $\mathrm{d}(\mathrm{D}-\mathrm{H})$ | $\begin{gathered} \mathrm{d}\left(\mathbf{H}_{/ \times} \cdot \mathbf{A}\right) \\ / \AA \end{gathered}$ | $\begin{gathered} \mathbf{d}\left(\mathbf{D}_{\text {® }} \mathbf{A} \mathbf{A}\right) \\ \hline \end{gathered}$ | $\underset{/{ }^{0}}{\langle(\text { DHA })}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{D} \cdots \mathrm{O} 2$ | 0.93 | 2.103 | 2.912(13) | 145 |
| $\mathrm{N} 2-\mathrm{H} 2 \mathrm{~A} \cdots \mathrm{O} 1$ | 0.88 | 2.069 | 2.885(7) | 154 |
| N3—H3A ${ }^{\text {- }}$ O1 | 0.88 | 2.141 | 2.937(7) | 150 |
| N4—H4A ${ }^{\text {Cl2 }}$ | 0.88 | 2.604 | 3.411(7) | 153 |
| N4- $\mathrm{H} 4 \mathrm{~A} \cdots \mathrm{Cl} 3$ | 0.88 | 2.745 | 3.386(9) | 131 |
| N5-H5A ${ }^{\text {c }} \mathrm{Cl} 2$ | 0.88 | 2.729 | 3.521(5) | 151 |

*symmetry codes $\mathrm{x},-\mathrm{y}+1 / 2, \mathrm{z}-1 / 2,-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+2$.

* The $\mathrm{NH}^{*} \mathrm{Cl}$ and $\mathrm{NH}^{*} \mathrm{O}$ interactions are separated by a horizontal line.

Table S3. Inter-molecular hydrogen-bonds in $\left[\left(\mathbf{L}^{\mathbf{1 3}} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right](\mathrm{D}=$ donor, $\mathrm{A}=$ acceptor, d $=$ distance).

| $\mathbf{D}-\mathbf{H}^{\cdots} \mathbf{A}$ | $\mathbf{d}(\mathbf{D}-\mathbf{H})$ <br> $/ \AA$ | $\mathbf{d}\left(\mathbf{H}^{\cdots} \mathbf{A}\right) / \AA$ | $\mathbf{d}(\mathbf{D} \cdots \mathbf{A}) / \AA$ | $<(\mathbf{D H A}) /{ }^{\circ}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N} 2 — \mathrm{H} 2 \mathrm{~A}^{\cdots} \mathrm{Cl} 2$ | 0.880 | 2.464 | 3.310 | 161.61 |
| $\mathrm{~N} 3 — \mathrm{H} 3 \mathrm{~A} \cdots \mathrm{Cl} 3$ | 0.880 | 2.581 | 3.365 | 148.84 |
| $\mathrm{~N} 1 — \mathrm{H} 1 \cdots \mathrm{O} 5$ | 0.845 | 2.038 | 2.751 | 141.67 |
| $\mathrm{~N} 1 — \mathrm{H} 1 \cdots \mathrm{O} 1$ | 0.845 | 2.569 | 3.154 | 127.26 |

*symmetry codes $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1,-\mathrm{x},-\mathrm{y}+1,-\mathrm{z}+2$.
*A horizontal line separates the $\mathrm{NH}{ }^{*} \mathrm{Cl}$ and $\mathrm{NH}{ }^{\circ} \mathrm{O}$ interactions

Table S4. Inter-molecular interactions in $\left[\left(\mathbf{L}^{23} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right](\mathrm{D}=$ donor, $\mathrm{A}=$ acceptor, $\mathrm{d}=$ distance).

| $\mathbf{D}-\mathbf{H} \cdots \mathbf{A}$ | $\mathbf{d}(\mathbf{D}-\mathbf{H}) / \AA$ | $\mathbf{d}(\mathbf{H} \cdots \mathbf{A}) / \AA$ | $\mathbf{d}(\mathbf{D} \cdots \mathbf{A}) / \AA$ | $<(\mathbf{D H A}) /{ }^{\circ}$ |
| :--- | :--- | :--- | :--- | :--- |
| N5B-H5B $\cdots \mathrm{Cl}$ C | 0.881 | 2.468 | 3.324 | 163.98 |
| N5A-H5A $\cdots \mathrm{Cl} 4 \mathrm{C}$ | 0.881 | 2.637 | 3.513 | 173.20 |


| C9B-H9B2 2 Cl6C | 0.990 | 2.768 | 3.321 | 115.77 |
| :---: | :---: | :---: | :---: | :---: |
| C3A-H3A1 ${ }^{\text {Cl3C }}$ | 0.990 | 2.832 | 3.713 | 148.65 |
| C17B-H17F ${ }^{\text {Cl4C }}$ | 0.979 | 2.834 | 3.557 | 131.32 |
| C17B-H17E ${ }^{\text {c }}$ Cl5C | 0.980 | 2.842 | 3.615 | 136.36 |
| C18A-H18B ${ }^{\text {Cl1C }}$ | 0.979 | 2.850 | 3.881 | 167.44 |
| C17A-H17B ${ }^{\text {Cl6 }}$ C | 0.980 | 2.861 | 3.794 | 159.28 |
| C15B-H15D ${ }^{\text {Cl3C }}$ | 0.991 | 2.862 | 3.817 | 162.06 |
| C13B-H13F ${ }^{\text {Cl3C }}$ | 0.981 | 2.889 | 3.556 | 126.15 |
| C11A-H11A ${ }^{\text {c }}$ Cl5C | 0.990 | 2.893 | 3.781 | 149.64 |
| C12B-H12B*Cl3C | 1.000 | 2.903 | 3.536 | 121.99 |

Table S5. Inter-molecular interactions in $\left[\left(\mathbf{L}^{24} \mathrm{H}\right)_{2} \mathrm{PtCl}_{6}\right](\mathrm{D}=$ donor, $\mathrm{A}=$ acceptor, $\mathrm{d}=$ distance).

| $\mathbf{D}-\mathbf{H} \cdots \mathbf{A}$ | $\mathbf{d}(\mathbf{D}-\mathbf{H}) / \AA$ | $\mathbf{d}(\mathbf{H} \cdots \mathbf{A}) / \AA$ | $\mathbf{d}(\mathbf{D} \cdots \mathbf{A}) / \AA$ | $\left\langle(\mathbf{D H A}) /^{\mathbf{0}}\right.$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C} 45-\mathrm{H} 45 \mathrm{~B} \cdots \mathrm{Cl} 4$ | 0.990 | 2.938 | 3.438 | 113.33 |
| $\mathrm{C} 16-\mathrm{H} 16 \mathrm{~A} \cdots \mathrm{Cl} 2$ | 0.989 | 2.864 | 3.664 | 138.50 |
| $\mathrm{C} 47-\mathrm{H} 47 \cdots \mathrm{Cl} 2$ | 0.950 | 2.946 | 3.762 | 144.81 |
| $\mathrm{C} 52-\mathrm{H} 52 \mathrm{~B} \cdots \mathrm{Cl} 5$ | 0.990 | 2.993 | 3.923 | 178.51 |
| $\mathrm{C} 23-\mathrm{H} 23 \mathrm{~B} \cdots \mathrm{Cl} 6$ | 0.990 | 2.647 | 3.437 | 136.90 |
| $\mathrm{C} 22-\mathrm{H} 22 \cdots \mathrm{Cl6}$ | 0.950 | 2.883 | 3.788 | 156.76 |
| $\mathrm{C} 23-\mathrm{H} 23 \mathrm{~B} \cdots \mathrm{Cl} 6$ | 0.990 | 2.861 | 3.561 | 128.34 |
| $\mathrm{C} 22-\mathrm{H} 22 \cdots \mathrm{Cl} 3$ | 0.950 | 2.814 | 3.487 | 128.72 |
| $\mathrm{C} 32-\mathrm{H} 32 \cdots \mathrm{Cl} 3$ | 0.951 | 2.820 | 3.710 | 156.42 |

Section 3. ${ }^{1} \mathbf{H ~ n m r}$ data for all protons in titration of $\mathrm{L}^{4} \cdot \mathbf{H C l}$ with $\left[\left(\mathrm{Oct}_{4} \mathrm{~N}\right)_{2} \mathrm{PtCl}_{6}\right]$


Figure SI7. ${ }^{1} \mathrm{H}$ NMR titration of $\mathbf{L}^{4} \cdot \mathrm{HCl}(10 \mathrm{mM})$ with $\left[\left(\mathrm{Oct}_{4} \mathrm{~N}\right)_{2} \mathrm{PtCl}_{6}\right]$ in $\mathrm{CDCl}_{3}$. Chemical shift changes for the hydrogen atoms $(a-g)$ in the host are presented on arbitrary scales to show their different behaviour upon increasing concentration of the guest anion. The dotted lines mark the $2: 1$ host : guest ratio ( 0.5 eq. of guest added).

## Section 4. Listing of CIF files.

SI File: ic6b00848_si_001.pdf
SI File: ic6b00848_si_002.cif
SI File: ic6b00848_si_003.cif
SI File: ic6b00848_si_004.cif
SI File: ic6b00848_si_005.cif

