Transition metals enclosed in supramolecular capsules: assembly, characterization and application in catalysis

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Chapter 4

Control of the Coordination Geometry Around Platinum by a Supramolecular Capsule
4.1 Introduction

Catalytic properties of transition metal complexes depend on ligand parameters such as steric and electronic properties, bite angle and chirality. Supramolecular chemistry provides novel strategies for influencing ligand parameters and consequently the properties of their transition metal complexes.1 Reek and co-workers have encapsulated transition metals by applying pyridylphosphine ligands which coordinate to the transition metal via the phosphorus atom, and at the same time, the nitrogen atoms of the pyridyl groups selectively coordinate to Zn(II)-porphyrins or Zn(II)-salphen, resulting in a hemispherical ligand-template capsule around the transition metal (Figure 1a).2 When tris(m-pyridyl)phosphine is applied, the created sterical hindrance around the metal results in decoordination of one of the two pyridylphosphine ligands. These encapsulated rhodium complexes were shown to have unusual reactivity and selectivity in the hydroformylation of terminal and internal alkenes. Interestingly, addition of 6 equivalents of Zn(II)-salphen to cis-[Pt(PA)2Cl2] (PA = tris(p-pyridyl)phosphine) gave rise to the exclusive formation of the encapsulated trans-Pt-complex trans-[Pt[(Zn)3·PA]2Cl2].2d This cis-to-trans isomerism is induced by the second coordination sphere around the transition metal.

Chelating (hetero)bidentate ligands can be assembled from two monodentate ligands by equipping them with complementary binding motifs or by applying a template that contains two binding sites for the two monodentate ligands.3 Reek and co-workers have studied the template-induced formation of chelating bidentate ligands by the selective self-assembly of two monodentate pyridylphosphine ligands (PB) on a rigid bis-zinc(II) salphen template with two identical binding sites (Figure 1b).3b Addition of the template to cis-[Pt(PB)2Cl2] resulted in a mixture of the templated cis-Pt-complex (15%) and the templated trans-Pt-complex (85%). The templated trans-Pt-complex is the thermodynamic product and is stabilized by the formation of a bidentate chelating ligand.

![Figure 1](image_url) Hemispherical ligand-template capsule (a) and templated chelating bidentate ligand (b).

In this chapter we report a supramolecular diphosphine capsule, which controls the coordination geometry around a platinum atom. Supramolecular capsules are composed of two or more, not necessarily identical, building blocks programmed to self-assemble in solution into the desired structure.1b,4 We have previously reported capsule A·C, which is formed by ionic...
interactions and composed of a tetracationic xantphos-type diphosphine A and a tetraanionic calix[4]arene C (Figure 2). Encapsulation of a transition metal within this capsule is achieved by using the palladium complex of the tetracationic diphosphine ligand for the assembly process. The encapsulated metal is still available for catalytic transformations as it is not involved in the assembly process.

![Figure 2 Ionic-based capsule A·C, composed of diphosphine A and calix[4]arene C.](image)

The class of xantphos ligands have large natural bite angles, typically between 100° and 120° (phosphorus-metal-phosphorus angle), which enables it to act as a cis- and trans-chelating ligand in square-planar palladium(II) and platinum(II) complexes, as is shown by van Leeuwen and coworkers. Kollar and co-workers have synthesized the cis-[Pt(xantphos)Cl2] complex by refluxing [PtCl2(PhCN)2] and xantphos in a 1:1 ratio in benzene (Scheme 1). Addition of a second equivalent of xantphos to the cis-Pt-complex at room temperature resulted in a cis-to-trans rearrangement, to give the ionic trans-[Pt(xantphos)(η1-xantphos)Cl]Cl complex with the ‘second’ xantphos ligand coordinating in a monodentate fashion. The platinum-xantphos-tin(II)chloride system, which is a mixture of cis- and trans-complexes, has been applied as a hydroformylation catalyst. Van Leeuwen and co-workers, Matt and co-workers and den Heeten have reported trans-[PtCl2(diphosphine)]-complexes by the use of trans-spanning diphosphine ligand SPANphos, and trans-spanning diphosphines based on a cyclodextrin cavity and a cyclic bisxantphos, respectively. To our knowledge, a platinum dichloride complex containing one trans-coordinating xantphos-type ligand, i.e. trans-[Pt(xantphos)Cl2], has not been reported in the literature.

![Scheme 1 Platinum(II)-xantphos complexes.](image)
4.2 Platinum complexes

Here we describe the reaction between the tetracationic xantphos-type ligand A and [PtCl₂(MeCN)₂], and in section 4.3 we report the same reaction with the diphosphine capsule A·C. The tetraammonium diphosphine tetrakis(p-diethylbenzylammonium)-xantphos tetratosylate A-HOTs (A) was synthesized by selective N-protonation of tetrakis(p-diethylbenzylamine)-xantphos a with four equivalents of p-toluenesulfonic acid (PTSA) in methanol (Scheme 2). Application of non-protic solvents such as dichloromethane resulted in a mixture of ammonium and phosphonium salts.

![Scheme 2 Synthesis of the tetraammonium-xantphos A-HOTs.](image)

Depending on the conditions used, reaction of [PtCl₂(MeCN)₂] with A in methanol led to the formation of cis-[Pt(A)Cl₂] (B₁) and trans-[Pt(A)(η¹-A)Cl]Cl (B₂), vide infra, as is indicated by in situ $^{31}$P{¹H} NMR spectroscopy and ESI-MS (Scheme 3 and Table 2). The $^{31}$P{¹H} NMR spectrum of cis-B₁ shows a characteristic 1/4/1 pattern consisting of a singlet at 6.2 ppm, flanked by $^{195}$Pt satellites with a coupling constant $J_{Pt-P}$ of 3728 Hz (Table 1 and Figure 3b). This coupling constant indicates that a chloride ligand is present trans to the phosphorus, in line with the cis-chelation of A. The $^{31}$P{¹H} NMR spectrum of trans-B₂ shows the presence of three different phosphorus atoms (Table 1 and Figure 3c). A triplet signal for Pₓ at 15.9 ppm (1P) flanked by $^{195}$Pt satellites with $J_{Pₓ-P}$ of 4074 Hz. A doublet signal for Pᵧ at 15.0 ppm (2P) flanked by $^{195}$Pt satellites with $J_{Pₓ-P}$ of 2679 Hz, indicating that two phosphorus atoms are trans to each other. The triplet and doublet signals have a cis coupling constant $J_{Pₓ-P}$ of 18.1 Hz. The singlet signal at –22.6 ppm (1P) is assigned to Pₚ the non-coordinating phosphorus of the monodentate coordinating ligand.

| $^{31}$P{¹H} NMR data of the diphosphines, the platinum complexes and the capsules. |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                  | δPₓ (ppm)       | δPᵧ (ppm)       | δPₚ (ppm)       | $^1$J(Pₓ,Pᵧ) (Hz) | $^2$J(Pₓ,Pᵧ) (Hz) | $^2$J(Pₓ,Pᵧ) (Hz) |
| A                                 | –16.9 (s)       | –               | –               | –                | –                | –                |
| A·C                               | –17.5 (s)       | –               | –               | –                | –                | –                |
| B₁: cis-[Pt(A)Cl₂]                | 6.2 (s)         | –               | –               | 3728             | –                | –                |
| B₁·C                              | 6.6 (s)         | –               | –               | 3727             | –                | –                |
| B₂: trans-[Pt(A)(η¹-A)Cl]Cl       | 15.9 (t)        | 15.0 (d)        | –22.6 (s)       | 4074             | 2679             | 18.1             |
| B₂·(C)                            | 15.2 (br s)     | 15.2 (br s)     | –24.1 (s)       | 4091             | 2652             | –                |

* Spectra were measured in CD₃OD. * Multiplicities are given for the central lines. * The triplet and doublet resonances of Pₓ and Pᵧ coalescence as one broad central line.
Phosphorus numbering of $\text{trans-}B_2$:

\[
\begin{array}{c}
\text{Cl} \\
\text{P} \\
\text{P} \\
\text{Pr} \\
\text{Cl}
\end{array}
\]

Figure 3 In-situ $^{31}\text{P}\{^1\text{H}\}$ NMR experiments in CD$_3$OD of [PtCl$_2$(MeCN)$_2$] and diphosphine A to give $\text{cis-}B_1$ and $\text{trans-}B_2$.

Scheme 3 Reaction of [PtCl$_2$(MeCN)$_2$] with diphosphine A to give $\text{cis-}B_1$ and $\text{trans-}B_2$ (mol ratio).
Reaction of [PtCl₂(MeCN)₂] with one equivalent of A in CD₃OD at 20 °C resulted after two hours in the disappearance of A and the formation of cis-B₁ (79%) and trans-B₂ (21%) (Scheme 3 and Figure 3a). We have observed a slow transformation of trans-B₂ to cis-B₁ at 20 °C, as after three more hours at 20 °C their ratio changed into B₁ (81%) and B₂ (19%). Upon heating the NMR tube to 60 °C, B₂ transformed immediately and quantitatively into B₁ (Scheme 3 and Figure 3b).

Subsequently, we have added excess ligand to the metal precursor in order to study the effect on the product distribution. Reaction of [PtCl₂(MeCN)₂] with two equivalents of A in CD₃OD at 20 °C resulted after two hours in consumption of 53% of the initially present diphosphine A and in a larger amount of trans-B₂, i.e. cis-B₁ (9%) and trans-B₂ (91%) (Scheme 3 and Figure 3c). A very slow transformation of B₁ to B₂ at 20 °C is observed, as after one night at 20 °C their ratio changed into B₁ (7%) and B₂ (93%). Upon heating the NMR tube to 60 °C for five hours, a large amount of B₂ transformed into B₁, i.e. B₁ (51%) and B₂ (49%), which of course was accompanied with an increase in the amount of free ligand A (Scheme 3).

In summary, upon reaction of A with the Pt-precursor, cis-B₁ is formed as the major product at lower and higher temperatures (20 °C and 60 °C) while trans-B₂ is formed as the major product only when two equivalents of ligand are applied at lower temperatures (20 °C). These results imply that, under the given conditions, cis-B₁ is the thermodynamic product and trans-B₂ is the kinetic product (at a Pt/PP ratio of 1:1).

4.3 Platinum capsules

4.3.1 Platinum capsules by self-assembly of pre-formed metal complexes

Platinum encapsulation can be achieved by self-assembly of a platinum complex containing the tetracationic diphosphine A and the tetraanionic calix[4]arene C, or by the reaction between a platinum precursor and a diphosphine capsule. Self-assembly of the platinum capsules was carried out by mixing methanol solutions of the pre-charged platinum complex (B₁ or B₂) and the tetrasulfonato-calix[4]arene tetrasodiumsalt C-SO₃Na (Scheme 4). The platinum capsules B₁·C and B₂·(C)₂ are formed instantaneously and NaOTs salt is formed as a side-product. The platinum complexes cis-B₁ and trans-B₂ contain one respectively two equivalents of the tetracationic diphosphine ligand A. Hence, capsule (cis-B₁)·C contains one calix[4]arene C, while capsule (trans-B₂)·(C)₂ contains two calix[4]arenes C.

The ESI-MS spectra of the platinum capsules B₁·C and B₂·(C)₂ confirm their formation and stabilities in the gas-phase (Figure 4 and Table 2 entry’s 2 and 4). Prominent ion peaks are observed for the platinum capsules in CH₃OH. The charge on the capsules is created by loss of chlorides from the platinum complex and/or by addition of protons or sodium cations from the solution. The ESI-MS spectra of capsules B₁·C and B₂·(C)₂ confirm that the Pt-complexes B₁
and $B_2$ remain intact upon capsule formation. The Pt-capsules $B_1 \cdot C$ and $B_2 \cdot (C)_2$ give very broad proton resonances in their $^1H$ NMR spectra and therefore could not be characterized by proton NMR.$^{5c,7}$

![Scheme 4](image)

**Scheme 4** Platinum encapsulation: self-assembly of capsules $B_1 \cdot C$ (a) and $B_2 \cdot (C)_2$ (b).

<table>
<thead>
<tr>
<th>#</th>
<th>Compound</th>
<th>Assignment</th>
<th>Elemental composition</th>
<th>Found m/z</th>
<th>Calc. m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$B_1$</td>
<td>$[B_1 - 2\text{OTs}]^{2+}$</td>
<td>C$<em>{73}$H$</em>{94}$Cl$_2$N$_4$O$_7$P$_2$PtS$_2$</td>
<td>765.25</td>
<td>765.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[B_1 - \text{Cl} - 2\text{H} - 3\text{OTs}]^{2+}$</td>
<td>C$<em>{66}$H$</em>{85}$ClN$_4$O$_4$P$_2$PtS$_5$</td>
<td>661.26</td>
<td>661.26</td>
</tr>
<tr>
<td>2.</td>
<td>$B_1 \cdot C$</td>
<td>$[B_1 \cdot C + \text{Cl} + \text{H}]^{3+}$</td>
<td>C$<em>{103}$H$</em>{133}$ClN$_4$O$_21$P$_2$PtS$_4$</td>
<td>1091.36</td>
<td>1091.36</td>
</tr>
<tr>
<td></td>
<td>(B$_1 + C \rightarrow$)</td>
<td>$[B_1 \cdot C - \text{Cl} + \text{Na} + \text{H}]^{3+}$</td>
<td>C$<em>{103}$H$</em>{133}$ClN$_4$O$_21$P$_2$PtS$_4$Na</td>
<td>735.24</td>
<td>735.24</td>
</tr>
<tr>
<td>3.</td>
<td>$B_2$</td>
<td>$[B_2 - 2\text{Cl} - \text{H} - 3\text{OTs}]^{3+}$</td>
<td>C$<em>{153}$H$</em>{194}$ClN$<em>8$O$</em>{17}$S$_5$P$_4$Pt</td>
<td>977.06</td>
<td>977.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[B_2 - \text{Cl} - \text{H} - 4\text{OTs}]^{4+}$</td>
<td>C$<em>{146}$H$</em>{178}$ClN$<em>8$O$</em>{14}$S$_4$P$_4$Pt</td>
<td>690.03</td>
<td>690.03</td>
</tr>
<tr>
<td>4.</td>
<td>$B_2 \cdot (C)_2$</td>
<td>$[B_2 \cdot (C)_2 - \text{Cl} + 2\text{Na}]^{4+}$</td>
<td>C$<em>{206}$H$</em>{264}$ClN$<em>8$O$</em>{42}$P$_4$PtS$_8$Na$_2$</td>
<td>1393.48</td>
<td>1393.49</td>
</tr>
<tr>
<td></td>
<td>(B$_2 + 2C \rightarrow$)</td>
<td>$[B_2 \cdot (C)_2 - \text{Cl} + 2\text{H} + \text{Na}]^{4+}$</td>
<td>C$<em>{206}$H$</em>{266}$ClN$<em>8$O$</em>{42}$P$_4$PtS$_8$Na</td>
<td>1039.87</td>
<td>1039.89</td>
</tr>
<tr>
<td>5.</td>
<td>$B_2 \cdot (C)_2$</td>
<td>$[B_2 \cdot (C)_2 - \text{Cl} + 2\text{H}]^{3+}$</td>
<td>C$<em>{206}$H$</em>{266}$ClN$<em>8$O$</em>{42}$P$_4$PtS$_8$</td>
<td>1378.83</td>
<td>1378.83</td>
</tr>
<tr>
<td></td>
<td>(Pt + A·C $\rightarrow$)</td>
<td>$[B_2 \cdot (C)_2 - \text{Cl} + 3\text{H}]^{3+}$</td>
<td>C$<em>{206}$H$</em>{267}$ClN$<em>8$O$</em>{42}$P$_4$PtS</td>
<td>1034.39</td>
<td>1034.38</td>
</tr>
<tr>
<td>6.</td>
<td>$B_2 \cdot (C)_2$</td>
<td>$[B_2 \cdot (C)_2 - \text{Cl} - 2\text{Cl} - 2\text{H}]^{4+}$</td>
<td>C$<em>{212}$H$</em>{210}$ClN$<em>8$O$</em>{22}$P$_4$Pt</td>
<td>767.08</td>
<td>767.08</td>
</tr>
<tr>
<td></td>
<td>d (Pt + A·C $\rightarrow$)</td>
<td>$[B_2 \cdot (C)_2 - \text{Cl} - \text{Cl} - \text{H}]^{4+}$</td>
<td>C$<em>{212}$H$</em>{211}$ClN$<em>8$O$</em>{22}$P$_4$Pt</td>
<td>776.07</td>
<td>776.07</td>
</tr>
</tbody>
</table>

a The ESI-MS spectra were measured in CH$_3$OH. b The reaction equations given in the brackets describe the way the Pt-capsules were formed. c OTs = C$_7$H$_7$SO$_3$. d The same ion peaks of capsule $B_2 \cdot C$ were also observed in the esi-ms spectrum of capsule $B_2 \cdot (C)_2$ formed by self-assembly, i.e. $B_2 + 2C$. 
Figure 4 ESI-MS spectra of platinum capsules $\mathbf{B}_1\cdot\mathbf{C}$ ($\mathbf{B}_1 + \mathbf{C} \rightarrow \top$) (Top) and $\mathbf{B}_2\cdot\mathbf{C}_2$ (Pt + A·C $\rightarrow \bot$) (Bottom) in CH$_3$OH (insets: measured isotope patterns).
4.3.2 Platinum capsules by coordination to pre-formed ligand capsule

Platinum encapsulation can also be achieved by the reaction of a platinum precursor and the diphosphine capsule \( A \cdot C \). The ionic-based diphosphine capsule \( A \cdot C \) consists of the tetracationic diphosphine \( A \) and the complementary tetraanionic calix[4]arene \( C \) (Scheme 5).\(^{5b-c}\) Mixing methanol solutions of the neutral building blocks tetraamine-diphosphine \( a \) and tetratsulfonicacid-calix[4]arene \( C\text{-SO}_3\text{H} \) results in quantitative protonation of \( a \) by \( C\text{-SO}_3\text{H} \), leading to capsule \( A \cdot C \), without salt formation.\(^{11}\)

\[
\text{Scheme 5 Self-assembly of capsule } A \cdot C.
\]

Depending on the conditions used, reaction of \([\text{PtCl}_2(\text{MeCN})_2]\) with capsule \( A \cdot C \) in methanol led to the formation of the platinum capsules (\( \text{cis-B1}\cdot C \) and (\( \text{trans-B2}\cdot (C)_2 \)), \textit{vide infra}, as is indicated by \textit{in situ} \(^{31}\text{P\{1H\}}\) NMR spectroscopy and ESI-MS (Scheme 6 and Table 2). The chemical shifts in the \(^{31}\text{P\{1H\}}\) NMR spectra of the Pt-capsules are comparable to those of their corresponding Pt-complexes but the signals of the Pt-capsules are broad.\(^{5c}\) The phosphorus resonances of capsule (\( \text{cis-B1}\cdot C \) show a characteristic 1/4/1 pattern consisting of a singlet at 6.6 ppm, flanked by \(^{105}\text{Pt}\) satellites with a coupling constant \( J_{\text{Pt-P}} \) of 3727 Hz (Table 1 and Figure 5b). The \(^{31}\text{P\{1H\}}\) NMR spectrum of (\( \text{trans-B2}\cdot (C)_2 \) consists of one singlet at \(-24.1\) ppm (1P) assigned to the non-coordinating \( P_Z \), and one singlet at 15.2 ppm (3P) assigned to \( P_X \) and \( P_Y \) (Table 1 and Figure 5a). As a result of signal broadening, the resonances of \( P_X \) and \( P_Y \) coalesce into one broad singlet. Still, the Pt-satellites of \( \text{B2}\cdot (C)_2 \) are visible (\( P_X: J_{\text{P-Pt}} = 4091 \) Hz and \( P_Y: J_{\text{P-Pt}} = 2652 \) Hz) confirming that \( \text{B2} \) has the same structure in its capsular form.

The ESI-MS spectrum of capsule \( \text{B2}\cdot (C)_2 \) formed by the reaction of \([\text{PtCl}_2(\text{MeCN})_2]\) with capsule \( A \cdot C \) supports the presence of two calix[4]arenes \( C \) around \( \text{B2} \) (Table 2 entry 5). Interestingly, in the ESI-MS spectrum of \( \text{B2}\cdot (C)_2 \) we have also observed ion peaks corresponding to [capsule \( \text{B2}\cdot C \)]\(^{4+}\) \textit{i.e.} \([\text{B2}\cdot (2)_2 - \text{C} - 2\text{Cl} - 2\text{H}]^{4+}\) and \([\text{B2}\cdot (C)_2 - \text{C} - \text{Cl} - \text{H}]^{4+}\) (Table 2 entry 6). We assume that [capsule \( \text{B2}\cdot C \)]\(^{4+}\) is formed by abstraction of one tetraanionic calix[4]arene \( C \) from \( \text{B2}\cdot (C)_2 \) during the ionization process.
Figure 5 In-situ $^{31}$P{$^1$H} NMR experiments in CD$_3$OD of [PtCl$_2$(MeCN)$_2$] and diphosphine capsule A·C to give Pt-capsules B$_1$·C and B$_2$·(C)$_2$.

Scheme 6 Platinum encapsulation by reaction of [PtCl$_2$(MeCN)$_2$] with capsule A·C to give capsules B$_1$·C and B$_2$·(C)$_2$ (b) (mol ratio).

Reaction of [PtCl$_2$(MeCN)$_2$] with one equivalent of capsule A·C in methanol at 20 °C resulted after three hours in the disappearance of A·C and the formation of capsule (cis-B$_1$)·C (2%) and capsule (trans-B$_2$)(C)$_2$ (98%) (Scheme 6 and Figure 5a). We have observed a slow transformation of B$_2$·(C)$_2$ to B$_1$·C at 20 °C, as after one night at 20 °C their ratio changed into B$_1$·C (9%) and B$_2$·(C)$_2$ (91%). Upon heating the NMR tube to 60 °C, capsule B$_2$·(C)$_2$ continued to transform into the capsule B$_1$·C up to B$_1$·C (82%) and B$_2$·(C)$_2$ (18%) (Scheme 6 and Figure
5b). This ratio is reached after seven hours at 60 °C and did not change even after eight more hours.

In summary, at lower temperatures (20 °C) the reaction of \([\text{PtCl}_2(\text{MeCN})_2]\) with capsule \(\text{A·C}\) results in \((\text{trans-B}_2)\cdot(\text{C})_2\) as the major product (98%) while the same reaction with diphosphine \(\text{A}\) results in \(\text{cis-B}_1\) as the major product (79%). At higher temperatures (60 °C) both capsule \(\text{A·C}\) and diphosphine \(\text{A}\) have a preference towards the \(\text{cis}\)-species, i.e. \((\text{cis-B}_1)\cdot\text{C}\) (82%) and \(\text{cis-B}_1\) (100%), respectively. The difference in product selectivity between \(\text{A·C}\) and \(\text{A}\) at low temperatures shows that the presence of two calix[4]arenes around the platinum complex stabilizes the kinetic product, i.e. the \(\text{trans-B}_2\) species. This stabilization is supported by the fact that at high temperatures only the capsule results in incomplete transformation to the \(\text{cis-Pt}\)-complex (82%).

### 4.4 Molecular modeling study

The modeled structures of the platinum complexes \(\text{B}_1\) and \(\text{B}_2\) (with xantphos ligand/s) were first calculated using DFT and subsequently the optimized structures were used as input for PM3 calculations. In order to calculate the structures of capsules \((\text{cis-B}_1)\cdot\text{C}\) and \((\text{trans-B}_2)\cdot(\text{C})_2\), the structures of the platinum complexes \(\text{B}_1\) and \(\text{B}_2\) were frozen, except the diethylammoniummethyl substituents, and calix[4]arene \(\text{C}\) molecule/s were added (modeled on the PM3-level). These structures were used as input for molecular mechanics calculations (MMFF) and subsequently the structure of capsule \((\text{cis-B}_1)\cdot\text{C}\) is also subjected to PM3 calculation (PM3 calculation of capsule \((\text{trans-B}_2)\cdot(\text{C})_2\) failed because it is too large). The modeled structure of the \(\text{cis}\)-platinum complex \(\text{B}_1\) (with a xantphos ligand) illustrates the square-planar geometry around platinum. The modeled structure of capsule \((\text{cis-B}_1)\cdot\text{C}\) illustrates that \(\text{B}_1\) and \(\text{C}\) are complementary, facing one another, as a result of interaction between the ammonium and sulfonato groups. In addition, the platinum metal is located inside the capsule (Figure 6a).

The modeled structure of the bisligated \(\text{trans}\)-platinum complex \(\text{B}_2\) (with two xantphos ligands) shows that the ionic Pt-complex adopts a distorted square-planar geometry with one diphosphine coordinating to the platinum in a \(\text{trans}\) fashion and a second diphosphine coordinating to the platinum in a monodentate fashion (Figure 6b). The monodentate coordinating ligand is situated partly between the two P(Ar)₂-groups of the bidentate coordinating ligand. Consequently, the calix[4]arene \(\text{C}\) can not interact solely with the bidentate ligand or solely with the monodentate ligand. The modeled structure of capsule \((\text{trans-B}_2)\cdot(\text{C})_2\) illustrates that two molecules of the rigid concave-like calix[4]arene interact with the platinum complex \(\text{B}_2\) (Figure 6c). One of the two tetraanionic calix[4]arenes interacts with four cationic groups of \(\text{B}_2\) that are situated on four different phosphorus atoms and the other calix[4]arene interacts with three cationic groups of \(\text{B}_2\) that are situated on three different phosphorus atoms. Hence, each calix[4]arene interacts simultaneously with both ligands. Consequently, capsule \(\text{B}_2\cdot(\text{C})_2\) is composed of two semi-capsules with a undefined capsular structure. The platinum
atom is situated between (and not within) these two semi-capsules, \textit{i.e.} the platinum atom is not directly encapsulated. Interestingly, capsule $\text{B}_2 \cdot (\text{C})_2$ has a sandwich-like structure with the two calix[4]arenes pointing towards one another and the platinum complex is situated in between. The modeled structure of capsule $\text{B}_2 \cdot (\text{C})_2$ displays only one of the possible conformations and therefore it is likely that the two calix[4]arenes interact with $\text{B}_2$ in more ways than presented here.

**Figure 6** Modeled structures and schematic pictures of capsule $(\text{cis-B}_1) \cdot \text{C}$ (a), $\text{trans-B}_2$ (with xantphos ligands) (b), and capsule $(\text{trans-B}_2) \cdot (\text{C})_2$ (c).

### 4.5 Discussion

We assume that upon reaction of $[\text{PtCl}_2(\text{MeCN})_2]$ with diphosphine $\text{A}$ or capsule $\text{A} \cdot \text{C}$, the kinetic products $\text{trans-B}_2$ and capsule $(\text{trans-B}_2) \cdot (\text{C})_2$ respectively, are the first products that are formed. Subsequently, upon coordination of the Pt-precursor to the non-coordinating phosphorus atom of $\text{B}_2$, the kinetic products transform into the thermodynamic products $\text{cis-B}_1$ and capsule $(\text{cis-B}_1) \cdot \text{C}$ respectively. The low solubility of $[\text{PtCl}_2(\text{MeCN})_2]$ in methanol results initially in excess of $\text{A}$ and $\text{A} \cdot \text{C}$ with respect to the metal, which enhance the formation of the kinetic product (as is observed by \textit{in situ} $^{31}\text{P}\{^{1}\text{H}\}$ NMR). The kinetic product capsule $(\text{trans-}$
B₂·(C)₂ is stabilized by the two molecules of calix[4]arene, and therefore the formation of the corresponding thermodynamic product (cis-B₁)·C is inhibited (at 20 °C, Pt/PP = 1, B₁·C 2% and B₂·(C)₂ 98%). In contrast, the kinetic product trans-B₂ is not stabilized by its eight tosylate counterions and therefore it transforms immediately to the corresponding thermodynamic product cis-B₁ (at 20 °C, Pt/PP = 1, B₁ 79% and B₂ 21%). A steric congestion is created around B₂ of capsule B₂·(C)₂ by the two calix[4]arenes. This inhibits the access of the Pt-precursor to the non-coordinating phosphorus atom of B₂ and consequently the formation of the thermodynamic product B₁·C is also inhibited. The modeled structure of B₂·(C)₂ implies that each tetraanionic calix[4]arene interacts with cationic groups of the two different ligands of B₂ and consequently fix the spatial orientation of the two ligands relative to each other which results in stabilization of the kinetic product. This stabilization of (trans-B₂)·(C)₂ compared to trans-B₂, leads to a higher energy barrier for transformation of the kinetic product (trans-B₂)·(C)₂ into the thermodynamic product (cis-B₁)·C. Stabilization of (trans-B₂)·(C)₂ explains the slow reaction to (cis-B₁)·C, and the shift in equilibrium to the trans-Pt species.

4.6 Conclusions

In this Chapter, we have demonstrated that the coordination geometry around a platinum atom can be controlled by supramolecular capsules. The capsule used in this study is formed by ionic interactions and is composed of a tetracationic xantphos-type diphosphine ligand and a complementary tetraanionic calix[4]arene. Reaction of the diphosphine capsule with a platinum precursor yields the bisligated bis-calix[4]arene trans-Pt capsule, while the same diphosphine in the absence of calix[4]arene prefers the formation of the monoligated cis-Pt-complex, as is indicated by ³¹P{¹H} NMR and ESI-MS. The two calix[4]arenes stabilize the kinetic product, i.e. the trans-Pt species, and thereby slow the formation of the thermodynamic product, i.e. the cis-Pt species. This novel supramolecular strategy for controlling the reactivity of transition metal complexes opens up new opportunities to control the activity, stability and selectivity of the potential homogeneous catalysts.

4.7 Experimental section

General remarks. All reactions were carried out under a dry, inert atmosphere of purified nitrogen or argon using standard Schlenk techniques, unless stated otherwise. Solvents were dried and distilled under nitrogen prior to use. Diethyl ether was distilled from sodium/benzophenone. Methanol was distilled from CaH₂. Deuterated solvents were distilled from the appropriate drying agents. Unless stated otherwise, all chemicals were obtained from commercial suppliers and used as received. 4,5-Bis[bis(p-((diethylamino)methyl)phenyl)phosphino]-9,9-dimethylxanthene a⁵b, 5,11,17,23-tetakis(sulfonato)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene tetrasodiumsalt C-SO₃Na⁵b,¹² and 5,11,17,23-
tetrakis(sulfonicacid)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene $\text{C-SO}_3\text{H}^{5c}$ were synthesized according to reported procedures. NMR spectra were recorded on Varian Inova 500, Bruker Avance DRX 300 and Varian Mercury 300 NMR spectrometers. Chemical shifts are given relative to TMS ($^1\text{H}$ and $^{13}\text{C}$ NMR) and 85% H$_3$PO$_4$ ($^{31}\text{P}[^1\text{H}]$ NMR). Chemical shifts are given in ppm. High-resolution fast atom bombardment mass spectrometry (HRMS FAB) measurements were carried out on a JEOL JMS SX/SX 102A at the Department of Mass Spectrometry at the University of Amsterdam. Electrospray ionization mass spectrometry (ESI-MS) measurements were carried out on a Q-TOF (Micromass, Waters, Whyttenshawe, UK) mass spectrometer equipped with a Z-spray orthogonal nanoelectrospray source, using Econo Tips (New Objective, Woburn, MA) to create an off-line nanospray, at the Department of Mass Spectrometry of Biomacromolecules at the University of Amsterdam. Molecular modeling calculations were performed using Spartan '08 V1.0.3 software (B3LYP LACVP basic set).

**Synthesis**

4,5-Bis[bis(\(p\)-((diethylammoniumtosylate)methyl)phenyl)phosphino]-9,9-dimethylxanthene: A-HOTs (A)

$p$-Toluenesulfonic acid monohydrate (840.5 mg, 4.419 mmol) was added to a solution of 4,5-bis[bis(\(p\)-((diethylamino)methyl)phenyl)phosphino]-9,9-dimethylxanthene a (1.015 g, 1.105 mmol) in 50 ml methanol. The reaction mixture was stirred for 1 h at room temperature. After evaporation of the solvent *in vacuo* the product A-HOTs was obtained as an off-white sticky solid in quantitative yield. $^1\text{H}$ NMR (300 MHz, CD$_3$OD, 293 K): $\delta = 7.66$ (d, $J = 8.2$ Hz, 8H, OTs$^-$), 7.58 (d, $J = 7.9$ Hz, 2H, PC$_6$H$_3$), 7.49 (d, $J = 7.9$ Hz, 8H, PC$_6$H$_3$), 7.26 (m, 8H, PC$_6$H$_4$), 7.17 (d, $J = 7.9$ Hz, 8H, OTs$^-$), 7.01 (t, $J = 7.6$ Hz, 2H, PC$_6$H$_3$), 6.45 (d, $J = 7.3$ Hz, 2H, PC$_6$H$_3$), 4.32 (s, 8H, CH$_2$N), 3.17 (m, 16H, C$_2$H$_2$CH$_3$), 2.31 (s, 12H, CH$_3$, OTs$^-$), 1.66 (s, 6H, C(CH$_3$)$_2$), 1.29 (t, $J = 7.3$ Hz, 24H, CH$_2$CH$_3$); $^{31}\text{P}[^1\text{H}]$ NMR (121.5 MHz, CD$_3$OD, 293 K): $\delta = –16.9$ (s); $^{13}\text{C}[^1\text{H}]$ NMR (75 MHz, CD$_3$OD, 293 K): $\delta = 151.9$ (t, $J = 9.9$ Hz, CO), 142.3 (s, Cq, OTs$^-$), 140.4 (s, Cq, OTs$^-$), 138.9 (t, $J = 7.3$ Hz), 134.5 (t, $J = 10.8$ Hz), 131.4 (s), 130.9 (br s), 130.4 (s), 130.2 (s), 128.6 (s, CH, OTs$^-$), 127.5 (s), 125.6 (s, CH, OTs$^-$), 124.0 (t, $J = 8.8$ Hz), 123.8 (s), 55.5 (s, CH$_2$N), 46.7 (s, CH$_2$CH$_3$), 34.2 (s, CCH$_3$), 31.3 (s, CCH$_3$), 20.1 (s, CH$_3$ OTs$^-$) 7.8 (s, CH$_2$CH$_3$); HRMS (FAB–): found 1605.6255; calcd. for [C$_{87}$H$_{108}$N$_4$O$_{13}$P$_2$S$_4$ – H$^-$]– 1605.6193.

cis-[Pt(A)Cl$_2$]: B$_1$

Diphosphine A-HOTs (97.4 mg, 60.57 $\mu$mol) was added to a fine suspension of [PtCl$_2$(MeCN)$_2$] (21.08 mg, 60.57 $\mu$mol) in 8 ml methanol. After stirring for 1 h at room temperature, the clear reaction mixture was refluxed overnight at 70 °C. Next morning, the solvent was evaporated and the yellow solid was washed three times with diethyl ether. The product B$_1$ was obtained as a pale yellow microcrystalline powder. $^{31}\text{P}[^1\text{H}]$ NMR (121.5 MHz, CD$_3$OD, 293 K): $\delta = 6.2$ (s, $J_{\text{Pt-P}} = 3728$ Hz); $^1\text{H}$ NMR (300 MHz, CD$_3$OD, 293 K): $\delta = 7.87$ (d, $J = 7.5$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 8H, OTs$^-$), 7.61-7.14 (m, 20H), 7.25 (d, $J = 8.4$ Hz, 8H, OTs$^-$), 4.31 (s, 8H, CH$_2$N$_2$), 3.04 (m, 16H, NCH$_2$CH$_3$), 2.34 (s, 12H, OTs$^-$), 1.87 (s, 6H, C(CH$_3$)$_2$), 1.22 (t, $J = 7.8$ Hz, 24H, NCH$_2$CH$_3$). B$_1$ give broad carbon resonances in its $^{13}\text{C}[^1\text{H}]$ NMR spectrum and therefore could not be characterized by carbon NMR.
Self-assembly of capsule A·C
Methanol solution of the tetraacidic calix[4]arene C-SO₃H (1 equiv.) was slowly added to a methanol solution of the tetraamine diphosphine a (1 equiv.). The solution was stirred for 30 min. at room temperature and subsequently the solvent was evaporated resulting in capsule A·C. Observed upfield shifts of the proton resonances ($\Delta \delta_H$) of the CH$_2$NH+(CH$_2$CH$_3$)$_2$ protons of capsule A·C, with respect to those of the corresponding free A-HOTs, in CD$_3$OD: $\Delta \delta$(CH$_2$CH$_3$)$_2$ = 0.37, $\Delta \delta$(CH$_3$CH$_3$) = 0.34 and $\Delta \delta$(NCH$_3$) = 0.25 ppm (A/C = 1/1). ESI-MS (m/z, CH$_3$OH): [A·C + 2H]$^{2+}$ found 977.06, calcd. (C$_{103}$H$_{134}$N$_4$O$_{21}$P$_2$S$_4$) 976.90; [A·C + 3H]$^{3+}$ found 651.74, calcd. (C$_{103}$H$_{135}$N$_4$O$_{21}$P$_2$S$_4$) 651.60.

Self-assembly of capsule B$_1$·C
Equimolar methanol solutions of the platinum complex B$_1$ and the tetraanionic calix[4]arene C-SO$_3$Na were mixed at room temperature, resulting in the immediate formation of capsule B$_1$·C together with four equivalents of NaOTs.

Self-assembly of capsule B$_2$·(C)$_2$
Methanol solutions of the platinum complex B$_2$ (synthesized in situ) (1 equiv.) and the tetraanionic calix[4]arene C-SO$_3$Na (2 equiv.) were mixed at room temperature, resulting in the immediate formation of capsule B$_2$·(C)$_2$ together with eight equivalents of NaOTs.

In-situ VT $^{31}$P{$^1$H} NMR studies

\textit{cis-}[Pt(A)Cl$_2$]: B$_1$
A solution of [PtCl$_2$(MeCN)$_2$] (2.611 mg, 7.5 $\mu$mol, 1 equiv.) and A-HOTs (12.060 mg, 7.5 $\mu$mol, 1 equiv.) in 0.5 ml CD$_3$OD was vigorously stirred for 2 h at room temperature, to ensure that all the reactants dissolved. Subsequently, the reaction mixture was transferred into a NMR tube and the reaction was followed in time by $^{31}$P{$^1$H} NMR, i.e. 3 more hours at 20 °C and 3 hours at 60 °C.

\textit{trans-}[Pt(A)(η$^1$-A)Cl]Cl: B$_2$
A solution of [PtCl$_2$(MeCN)$_2$] (2.611 mg, 7.5 $\mu$mol, 1 equiv.) and A-HOTs (24.120 mg, 15.0 $\mu$mol, 2 equiv.) in 0.5 ml CD$_3$OD was vigorously stirred for 2 h at room temperature, to ensure that all the reactants dissolved. Subsequently, the reaction mixture was transferred into a NMR tube and the reaction was followed in time by $^{31}$P{$^1$H} NMR, i.e. 16 more hours at 20 °C and 5 hours at 60 °C.

Capsule B$_1$·C and Capsule B$_2$·(C)$_2$
A solution of [PtCl$_2$(MeCN)$_2$] (2.611 mg, 7.5 $\mu$mol, 1 equiv.) and capsule A·C (14.643 mg, 7.5 $\mu$mol, 1 equiv.) in 0.5 ml CD$_3$OD was vigorously stirred for 3 h at room temperature, to ensure that all the reactants dissolved. Subsequently, the reaction mixture was transferred into a NMR tube and the reaction was followed in time by $^{31}$P{$^1$H} NMR, i.e. 16 more hours at 20 °C and 20 hours at 60 °C.

ESI-MS
Samples of the Pt-complexes and of the capsules with initial concentrations of 100-250 $\mu$M were diluted in MeOH to a final concentration of 1%. ESI-MS analysis of B$_1$ was carried out with an isolated sample of B$_1$. ESI-MS analysis of B$_2$ was carried out with an in-situ sample of B$_2$ which was prepared by stirring.
a methanol solution of \([\text{PtCl}_2(\text{MeCN})_2]\) and \(A\) (two equivalents) overnight at 20 °C. ESI-MS analysis of capsule \(B_1\cdot C\) was carried out by mixing methanol solutions of \(B_1\) and \(C\), \textit{i.e.} self-assembly. ESI-MS analysis of capsule \(B_2\cdot(C)_2\) was done in two ways: (1) by mixing methanol solutions of \(B_2\) and \(C\), \textit{i.e.} self-assembly, and (2) by using an \textit{in-situ} sample of \(B_2\cdot(C)_2\) which was prepared by stirring a methanol solution of \([\text{PtCl}_2(\text{MeCN})_2]\) and \(A\cdot C\) overnight at 20 °C. No ion peaks for higher aggregates than 1:1 for \(B_1\cdot C\) and 1:2 for \(B_2\cdot(C)_2\) were detected. Comparison of the measured isotope patterns of the Pt-complexes capsules with the calculated ones confirms the elemental composition and charge state. The reported \(m/z\) correspond to the 100% ion peak (isotope with the highest intensity) (OTs = C\(_7\)H\(_7\)SO\(_3\)).

**Pt-complex \(B_1\)** (C\(_{87}\)H\(_{108}\)Cl\(_2\)N\(_4\)O\(_{13}\)P\(_2\)PtS\(_4\)) ESI-MS (\(m/z\), CH\(_3\)OH): \([B_1 – 2\text{OTs}\]^{2+}\) found 765.25, calcd. 765.25; \([B_1 – \text{Cl} – 2\text{H} – 3\text{OTs}]^{2+}\) found 661.26, calcd. 661.26; \([B_1 – \text{Cl} – 3\text{H} – 4\text{OTs}]^{2+}\) found 575.25, calcd. 575.25; \([B_1 – 3\text{OTs}]^{3+}\) found 453.17, calcd. 453.64; \([B_1 – \text{Cl} – \text{H} – 3\text{OTs}]^{3+}\) found 441.18, calcd. 441.17; \([B_1 – 3\text{OTs}]^{3+}\) found 395.84, calcd. 395.83; \([B_1 – \text{Cl} – 2\text{H} – 4\text{OTs}]^{3+}\) found 383.82, calcd. 383.83.

**Pt-complex \(B_2\)** (C\(_{174}\)H\(_{216}\)Cl\(_2\)N\(_8\)O\(_{26}\)S\(_8\)P\(_4\)Pt) ESI-MS (\(m/z\), CH\(_3\)OH): \([B_2 – \text{Cl} – \text{H} – 3\text{OTs}]^{3+}\) found 977.06, calcd. 977.05; \([B_2 – \text{Cl} – 2\text{H} – 4\text{OTs}]^{3+}\) found 919.71, calcd. 919.71; \([B_2 – \text{Cl} – 3\text{H} – 5\text{OTs}]^{3+}\) found 862.37, calcd. 862.37; \([B_2 – \text{Cl} – 4\text{H} – 6\text{OTs}]^{3+}\) found 805.04, calcd. 805.03; \([B_2 – \text{Cl} – \text{H} – 4\text{OTs}]^{4+}\) found 690.03, calcd. 690.03; \([B_2 – 2\text{Cl} – 4\text{H} – 6\text{OTs}]^{4+}\) found 594.79, calcd. 594.78.

**Capsule \(B_1\cdot C\)** (C\(_{103}\)H\(_{132}\)Cl\(_2\)N\(_4\)O\(_{21}\)P\(_2\)PtS\(_4\)) ESI-MS (\(m/z\), CH\(_3\)OH): \([B_1\cdot C]^{+} + 2\text{H}\]^{2+}\) found 1109.86, calcd. 1109.85; \([B_1\cdot C – \text{Cl} + \text{H}]^{2+}\) found 1091.36, calcd. 1091.36; \([B_1\cdot C – 2\text{Cl} + \text{H}]^{3+}\) found 715.93, calcd. 715.92; \([B_1\cdot C – 2\text{Cl} + \text{Na}]^{3+}\) found 723.23, calcd. 723.24; \([B_1\cdot C – \text{Cl} + 2\text{H}]^{3+}\) found 727.91, calcd. 727.91; \([B_1\cdot C – \text{Cl} + \text{Na} + \text{H}]^{4+}\) found 735.24, calcd. 735.24; \([B_1\cdot C – \text{Cl} + 2\text{Na}]^{3+}\) found 742.55, calcd. 742.56.

**Capsule \(B_2\cdot(C)_2\)** (C\(_{206}\)H\(_{264}\)Cl\(_2\)N\(_8\)O\(_{42}\)P\(_4\)PtS\(_8\)) ESI-MS (\(m/z\), CH\(_3\)OH): \([B_2\cdot(C)_2 – \text{Cl} + 2\text{H}]^{3+}\) found 1378.83, calcd. 1378.83; \([B_2\cdot(C)_2 – \text{Cl} + 3\text{H}]^{4+}\) found 1034.39, calcd. 1034.38; \([B_2\cdot(C)_2 – \text{Cl} + 2\text{H} + \text{Na}]^{4+}\) found 1039.87, calcd. 1039.89; \([B_2\cdot(C)_2 – \text{Cl} + \text{H} + 2\text{Na}]^{4+}\) found 1045.35, calcd. 1045.37; \([B_2\cdot(C)_2 – 2\text{Cl} + 3\text{Na}]^{4+}\) found 1050.86, calcd. 1050.86; \([B_2\cdot(C)_2 – 2\text{Cl} – \text{C} – 2\text{H}]^{4+}\) found 767.07, calcd. 767.07; \([B_2\cdot(C)_2 – \text{C} – 2\text{Cl} – \text{H}]^{4+}\) found 776.07, calcd. 776.07.

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4.9 References


