Template directed assembly of transition metal catalysts
Slagt, V.F.

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Chapter Seven

Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts
Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts

7.1 Introduction

Nature provides many examples of proteins that form their functional structure by bringing together the components involved via a self-assembly process. As a result of this combination of monomer units by self-assembly, natural systems are able to generate, for example, an immense number of structures that are utilized for selective substrate recognition from relatively few components.\(^1\) Supramolecular chemistry includes approaches along similar lines aiming at large well-defined architectures with added functions such as molecular devices, (bio)materials and catalysis.\(^2\) A range of different approaches has been explored for the association of two or more components in the formation of these supramolecular structures and the number of examples is expanding rapidly.\(^5\) The first approaches to assemble monomeric compounds were mainly based on hydrogen bonding.\(^8\) More recently, the use of coordination chemistry as valuable tool for the formation of multidentate complex structures has evolved into one of the most widely used techniques for exploiting various transition metal centers as molecular building blocks.\(^9\) The huge interest in the transition metal-directed synthesis of supramolecular compounds lies in the ease with which many of these structures can be prepared and the large variety of building blocks that are available. For the formation of multi-component assemblies the use of porphyrins has been widely applied.\(^11\) In particular meso-phenyl zinc(II) porphyrin offers readily accessible building blocks for the construction of supramolecular assemblies, utilizing the axial coordination site for complexation of nitrogen based ligands to the zinc(II) ion. Additionally, numerous synthetic methodologies for the functionalization of porphyrin systems have been developed.\(^12\) Interesting examples include the formation of metalloporphyrins molecular sieves from meso-pyridine zinc(II) porphyrin building blocks,\(^13\) and the self-assembly of controllable supramolecular architectures based on various pyridine functionalized porphyrins.\(^14\)

An exiting application of these superstructures based on transition metal building blocks is the design and construction of supramolecular catalysts.\(^15\) Early examples of such systems are the cyclic tris porphyrin of Sanders that showed that catalytically active transition metal catalysts can be combined with strategically placed receptor/host moieties, metal ions, functional groups and/or steric bulk in order to enhance the selectivity and activity in catalysis.\(^16\) The group of Hupp applied zinc(II) porphyrin-pyridine interactions for the introduction of steric bulk around a chiral manganese(III) salen based catalysts. The presence of the zinc(II) porphyrin moieties in the vicinity of the catalyst improved its activity and lifetime.\(^18\) A more complex system based on assemblies of zinc(II) and manganese(III) porphyrins, held together by coordination of rhenium atoms, showed shape selectivity in epoxidation experiments of functionalized cis-stilbenes. Smaller substrates were epoxidized preferentially over the bulky substrates.\(^19\) In contrast to supramolecular catalysts for ester hydrolysis and oxidation
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reactions, supramolecular catalysts for carbon-carbon bond formation are far less developed. One of the few examples is a cyclophane-type host molecule functionalized with a bisoxazoline ligand incorporated in the macrocyclic ring that was applied in the copper(I) catalyzed cyclopropanation of styrene with diazoacetate. This supramolecular catalyst showed high enantiomeric excess and high diastereoselectivities. The few promising examples validate the development and exploration of new supramolecular catalyst systems containing transition metal catalysts for carbon-carbon bond formations.

![Figure 1. Schematic representation of multi-component assembly resulting in novel self-organized catalyst systems, P = monodentate phosphorus ligand, Template = ditopic ligand that selectively coordinates to two porphyrin moieties and M = transition metal catalyst.](image)

Recently, we reported the self-assembly of encapsulated transition metal catalysts. Zinc(II) porphyrin building blocks have been assembled on pyridine phosphorus ligands, using selective nitrogen-zinc interactions. It has been shown that the encapsulation of transition metal catalyst leads to mono-phosphorus coordinated metal centers, which together with the encapsulation effect, result in a significantly improvement of the catalyst properties. Here we report on a new concept to prepare new ligand systems using self-assembly processes thereby controlling the catalyst properties of transition metals. For this approach we use monomeric compounds that upon mixing form new highly structured self-assembled ligand systems (figure 1). Two monodentate phosphite ligands that are functionalized with a zinc(II) porphyrin molecule are selectively assembled on a ditopic template via selective nitrogen zinc interactions. As a result a new self-organized bidentate ligand system is created, which forms transition metal complexes with specific catalytic properties. Variation of the ditopic template and monodentate zinc(II) porphyrin phosphite ligands yields a series of new, assembled ligands formed by just mixing the components. In addition, a tris zinc(II) porphyrins phosphite ligand with three coordination sites that are utilized for the binding of multiple ditopic template molecules has been prepared and it is shown that upon addition of transition metal template a (self)-organized sandwich-type structure is formed. These assembled catalyst superstructures form more rigid bidentate ligand systems, caused by the triple binding of
ditopic template molecules, and as a consequence yield high selectivities in rhodium-catalyzed hydroformylation of 1-octene.\textsuperscript{23,24}

7.2 Results and discussion

Self-organized bidentate catalyst systems

The multi-component assemblies (forming the new bidentate catalyst systems) are build up from three basic components; 1) monodentate zinc(II) porphyrin ligand 1, which was easily prepared in reasonable yields via a reaction of the phosphorochloridite\textsuperscript{25} with the monohydroxyl zinc(II) porphyrin (scheme 1),\textsuperscript{26} 2) ditopic template ligands based on two nitrogen donor atoms b-i (chart 1), 3) transition metals that selectively coordinate to the two phosphorus donor atoms of the zinc(II) porphyrin ligands forming the catalytically active complex. For this purpose we used rhodium and palladium precursors.

The coordination properties of the ligand assemblies to transition metals was investigated using high-pressure NMR-spectroscopy. Mixing two equivalents of zinc(II) porphyrin phosphite 1 and [Rh(acac)(CO)\textsubscript{2}] in toluene-d\textsubscript{8} under 20 bars of syngas (CO/H\textsubscript{2} = 1/1) resulted in the exclusive formation of the hydrido rhodium bis(zinc(II) porphyrin phosphite 1) biscarbonyl complex 2 (table 1). The addition of a stoichiometric amount of diaza-[2.2.2]-
bicyclooctane g (= dabco) to this mixture resulted in a shift of the phosphite donor atoms in the $^{31}$P-NMR spectrum. $^1$H-NMR-spectroscopy showed an up field shift for the rhodium-hydride and a large shift to high field was observed for the protons of the dabco template g ($\Delta \delta^H = 7.3$ ppm). This large shift is typical of the binding of dabco g to two equivalents of zinc(II) porphyrin\textsuperscript{27} and corroborates the formation of the self-organized bidentate ligand complex 3 (figure 2).

Table 1. Selected $^1$H- and $^{31}$P-NMR data of high-pressure NMR-spectroscopy of various rhodium complexes.

<table>
<thead>
<tr>
<th>complex</th>
<th>$\delta(^{31}$P)-phosphite (ppm)</th>
<th>$J_{\text{Rh-P}}$ (Hz)</th>
<th>$\delta(^1$H)-Rh-hydride (ppm)</th>
<th>$\delta(^1$H)-dabc o (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g (dabco, free ligand)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>2.5</td>
</tr>
<tr>
<td>2 [HRh(CO)$_2$(1)$_2$]</td>
<td>150.2</td>
<td>263</td>
<td>9.3</td>
<td>---</td>
</tr>
<tr>
<td>3 [HRh(CO)$_2$(g(1)$_2$)]</td>
<td>149.5</td>
<td>264</td>
<td>9.6</td>
<td>-4.8</td>
</tr>
</tbody>
</table>

Figure 2. Self-organized bidentate catalyst system consisting of two zinc(II) porphyrin phosphite 1 units, dabco g as the ditopic template and a rhodium metal center.

To show that these assemblies indeed show chelating behavior we performed UV-vis spectroscopic titrations to determine binding constants of the ditopic template-zinc(II) porphyrin complex in the presence and absence of rhodium phosphine complexes. If the chelate effect is nil we expect to find similar binding constants for both experiments, whereas any chelate effect would increase the binding constant if the rhodium complex is present. UV-vis spectroscopic titrations of zinc(II) porphyrin phosphite 1 and dabco g showed that g binds two monomeric zinc(II) porphyrin phosphite 1 units with high binding constants, $K_1 = 5.9 \times 10^4$ M$^{-1}$ and $K_2 = 1.6 \times 10^4$ M$^{-1}$ respectively. UV-vis spectroscopic titrations of an in situ
formed rhodium complex,\(^{28}\) using HRh(CO)(1)\(_2\)(PPh\(_3\)), showed that the binding constant of ditopic template dabcog, forming the 1:1 complex HRh(CO)(g(1)\(_2\))(PPh\(_3\)), increased considerably, \(K = 4.4 \times 10^5 \text{ M}^{-1}\) (table 2). This shows that the pre-organization of the two porphyrins via coordination to the rhodium metal indeed leads to increased binding of the ditopic template, indicating that there is a positive cooperative binding effect. The cooperativity effect translates to a chelating effect if the phosphite ligands are pre-organized by the ditopic template, an effect that can clearly affect the catalytic performance of the rhodium complex. The ditopic template ligand 4-4'-bipyridyl gave similar results and yielded also an increase in binding constant in the presence of a rhodium complex.

**Table 2.** Binding constants calculated for zinc(II) porphyrin phosphite 1 and dinitrogen based template ligands under various conditions based on UV-vis spectroscopic titrations.

<table>
<thead>
<tr>
<th>assembled porphyrin system</th>
<th>(K_1 (\text{M}^{-1}))</th>
<th>(K_2 (\text{M}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>g(1)(_2)(^{a})</td>
<td>5.9 \times 10^4</td>
<td>1.6 \times 10^3</td>
</tr>
<tr>
<td>[Rh(acac)(g(1)(_2))](^{a})</td>
<td>2.9 \times 10^5</td>
<td></td>
</tr>
<tr>
<td>[HRh(CO)(g(1)(_2))(PPh(_3))]</td>
<td>4.4 \times 10^5</td>
<td></td>
</tr>
<tr>
<td>i(1)(_2)(^{b})</td>
<td>7.9 \times 10^3</td>
<td>1.1 \times 10^3</td>
</tr>
<tr>
<td>[HRh(CO)(i(1)(_2))(PPh(_3))]</td>
<td>8.8 \times 10^4</td>
<td></td>
</tr>
</tbody>
</table>

(a) in CH\(_2\)Cl\(_2\), (b) in toluene

**Supramolecular transition metal catalysis based on multi-component assemblies**

The self-organized bidentate ligands were studied in the asymmetric rhodium-catalyzed hydrogenation of dimethyl itaconate (scheme 2). For the multi-component assemblies chiral zinc(II) porphyrin phosphite 1 was used in combination with several dinitrogen template molecules. The rhodium complexes based on phosphite ligand 1 in the absence of a template resulted in moderate activity and a poor enantioselectivity \(16\%\) (S) (table 3). The use of tetramethylethylenediamine e as template ligand, forming the self-organized bidentate ligand e(1)\(_2\), gave rhodium complexes that resulted in a higher enantiomeric excess (24\% (S)) at the cost of a decrease in activity. The use of ligand assembly e(1)\(_2\) resulted in very slow catalyst systems, whereas the use of g(1)\(_2\) increased the activity considerably and complete conversion of the substrate was observed. The catalyst assemblies based on e(1)\(_2\), e(1)\(_2\) and g(1)\(_2\) show large differences in activity in the hydrogenation reaction, which clearly demonstrates the viability of the approach.

\[
\text{MeOOC} = \text{COOMe} \xrightarrow{[\text{Rh}] \text{H}_2} \text{MeOOC} \xrightarrow{\text{H}} \text{COOMe} + \text{MeOOC} \xrightarrow{\text{H}} \text{COOMe}
\]

**Scheme 2.**
Table 3. Hydrogenation of dimethyl itaconate using different rhodium catalyst assemblies: variation of ditopic template ligands.a

<table>
<thead>
<tr>
<th>ligand</th>
<th>conversion (%)</th>
<th>e.e. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46</td>
<td>15 (S)</td>
</tr>
<tr>
<td>e(1)2</td>
<td>28</td>
<td>24 (S)</td>
</tr>
<tr>
<td>e(1)2</td>
<td>4</td>
<td>24 (S)</td>
</tr>
<tr>
<td>g(1)2</td>
<td>100</td>
<td>19 (S)</td>
</tr>
</tbody>
</table>

(a) [Rh(nbd)_2(BPh_4)] = 1.0 mmol/l, [dimethyl itaconate] = 200 mmol/l, pressure = 5 bar hydrogen, T = 40 °C, (b) [1] = 3.0 mmol/l, [ditopic template] = 1.5 mmol/l (c) the reaction was stopped after 16 hours (d) e.e. = percent enantiomeric excess.

The second reaction studied using this new ligand system was the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-allyl acetate and dimethyl malonate (scheme 3). Palladium complexes based on monodentate zinc(II) porphyrin phosphite 1 in absence of ditopic template ligands resulted in low enantioselectivity (19 % (S)) and full conversion (table 4). The use of ditopic template ligand e and e, forming bidentate ligand e(1)2 and e(1)2, gave palladium catalysts that resulted in higher enantiomeric excess (29 % (S) and 27 % (S)) and for both ligand systems full conversion was observed. The enantiomeric excess was further increased upon using g(1)2 as a templating ligand to 39% (S) ee, along with complete conversion at room temperature. The self-organized catalyst systems have both proven to be successful in rhodium-catalyzed asymmetric hydrogenation as well as the palladium-catalyzed asymmetric allylic alkylation by changing important catalyst key-features like activity and (enantio)selectivity, but the ee’s obtained so far cannot compete yet with those reported in literature.

Scheme 3.

Table 4. Palladium catalyzed allylic alkylation: variation of ditopic template ligands.a

<table>
<thead>
<tr>
<th>ligand</th>
<th>conversion (%)</th>
<th>e.e. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt;99</td>
<td>19 (S)</td>
</tr>
<tr>
<td>e(1)2</td>
<td>&gt;99</td>
<td>29 (S)</td>
</tr>
<tr>
<td>e(1)2</td>
<td>&gt;99</td>
<td>27 (S)</td>
</tr>
<tr>
<td>g(1)2</td>
<td>&gt;99</td>
<td>39 (S)</td>
</tr>
</tbody>
</table>

(a) [Pd(allyl)Cl]_2 = 0.100 mmol/l, the reaction was stopped after 16 hours, T = 25 °C, (b) [1] = 0.6 mmol/l, [ditopic template] = 0.3 mmol/l (c) e.e. = percent enantiomeric excess.
Another important reaction for carbon-carbon bond formation is the rhodium-catalyzed hydroformylation of alkenes (scheme 4). The ligand assemblies based on zinc(II) porphyrin phosphite 1 and several ditopic templates were studied in the rhodium-catalyzed hydroformylation of 1-octene (table 5). Monodentate zinc(II) porphyrin phosphite 1 yields a rhodium catalyst with substantial activity (T.O.F. = 1.0*10^3) and a concomitant regioselectivity of 1/b = 2.5. The assembled bidentate c(1)_2 shows a small decrease in selectivity for the linear product, along with an increase in isomerization. Interestingly, hardly any change in activity was observed for this ligand system compared to the catalyst system based on monodentate 1. In contrast to c(1)_2, the rhodium catalyst based on the bidentate assembly g(1)_2 did show a decrease in activity (T.O.F. = 7.8*10^2). The concomitant selectivity for the linear product was further decreased and higher isomerization was observed. The assembly based on i(1)_2 yielded comparable results as found for g(1)_2. The bidentate assemblies based on zinc(II) porphyrin phosphite 1 and the ditopic template ligands did affect the catalytic properties of the rhodium catalyst. However, only small changes in selectivity and activity have been observed. This is most likely caused by the large flexibility in the backbone of the assembled ligand system and more rigidity in the ligand systems is needed to affect the catalyst properties to a larger extend.

\[
\text{RH}_2 / \text{CO} \xrightarrow{[\text{Rh}]} \text{R}^- \text{R}^+ \xrightarrow{[\text{Rh}]} \text{R}^- \text{R}^+ \xrightarrow{[\text{Rh}]} \text{R}^- \text{R}^+ + \text{R}^- \text{R}^+ + \text{R}^- \text{R}^+
\]

**Scheme 4.** Rhodium catalyzed-hydroformylation of alkenes.

**Table 5.** Hydroformylation of 1-octene using different rhodium catalysts and their porphyrin assemblies: variation ditopic template ligands.\(^a\)

<table>
<thead>
<tr>
<th>ligand (^b)</th>
<th>T.O.F. (^c)</th>
<th>1/b (^d)</th>
<th>isomers (%)</th>
<th>linear (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0*10^3</td>
<td>2.5</td>
<td>6.9</td>
<td>66.5</td>
</tr>
<tr>
<td>c(1)_2</td>
<td>9.8*10^2</td>
<td>2.1</td>
<td>10.2</td>
<td>60.8</td>
</tr>
<tr>
<td>g(1)_2</td>
<td>7.8*10^2</td>
<td>2.0</td>
<td>13.1</td>
<td>57.6</td>
</tr>
<tr>
<td>i(1)_2</td>
<td>8.4*10^2</td>
<td>1.8</td>
<td>14.5</td>
<td>55.3</td>
</tr>
</tbody>
</table>

\(^a\) [Rh(acac)(CO)\(_2\)] = 0.084 mmol/l in toluene, pressure = 20 bar (CO/H\(_2\) = 1/1), T= 80 °C, 1-octene/rhodium = 5160. (b) [I] = 2.1 mmol/l, [ditopic template] = 1.1 mmol/l. (c) T.O.F. = average turn over frequency = (mol aldehyde)/(mol Rh)^3 h^-1, the reaction was stopped after 1 hour. (d) 1/b = linear/branched ratio. (e) percent selectivity to isomerization to 2-, 3- and 4-octene and percent selectivity to linear aldehyde based on converted 1-octene.

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Multi-component assemblies based on tris zinc(II) porphyrin phosphite ligands

In order to have a better control over the ligand orientation by self-assembly we anticipated that more anchoring points in the assembly were required. Therefore tris zinc(II) porphyrin phosphite 4 was prepared, in reasonable yields from phosphorus trichloride and three equivalents of a mono-hydroxyl zinc(II) porphyrin (scheme 5).

Scheme 5. Synthesis of tris zinc(II) porphyrin phosphite 4.

This monomeric phosphite ligand 4 contains three zinc(II) porphyrin moieties that can be used as anchoring points for the simultaneous assembly of various ditopic template ligands (a-i). Before studying the assemblies in detail, mixtures 4 and template ligands a-i (nitrogen/zinc = 1/1) were used as ligands in the rhodium-catalyzed hydroformylation of 1-octene in a parallel fashion (table 6).

Figure 3. Ratio of linear over branched aldehydes formed in the rhodium-catalyzed hydroformylation of 1-octene, using assemblies of tris zinc(II) porphyrin phosphite 4 and various template ligands a-i.
Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts

Table 6. Hydroformylation of 1-octene using rhodium catalysts based on tris-zinc(II)porphyrin phosphite assemblies with various ditopic template ligands.\(^a\)

<table>
<thead>
<tr>
<th>ligand(^b)</th>
<th>template(^b)</th>
<th>temp. (°C)</th>
<th>T.O.F.(^c)</th>
<th>1/b (^d)</th>
<th>isomers(^f) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>---</td>
<td>80</td>
<td>2.0*10(^3)</td>
<td>2.5</td>
<td>10.6</td>
</tr>
<tr>
<td>4</td>
<td>a</td>
<td>80</td>
<td>3.4*10(^3)</td>
<td>1.9</td>
<td>16.1</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>80</td>
<td>2.1*10(^3)</td>
<td>2.3</td>
<td>11.2</td>
</tr>
<tr>
<td>4</td>
<td>c</td>
<td>80</td>
<td>2.4*10(^3)</td>
<td>2.7</td>
<td>14.1</td>
</tr>
<tr>
<td>4</td>
<td>d</td>
<td>80</td>
<td>3.4*10(^3)</td>
<td>2.1</td>
<td>14.7</td>
</tr>
<tr>
<td>4</td>
<td>e</td>
<td>80</td>
<td>3.2*10(^3)</td>
<td>2.1</td>
<td>14.4</td>
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<tr>
<td>4</td>
<td>f</td>
<td>80</td>
<td>1.9*10(^3)</td>
<td>3.4</td>
<td>10.4</td>
</tr>
<tr>
<td>4</td>
<td>g</td>
<td>80</td>
<td>1.1*10(^3)</td>
<td>15.1</td>
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<td>g</td>
<td>30</td>
<td>25</td>
<td>22.8</td>
<td>10.3</td>
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<tr>
<td>4</td>
<td>h</td>
<td>80</td>
<td>2.1*10(^3)</td>
<td>2.5</td>
<td>11.3</td>
</tr>
<tr>
<td>4</td>
<td>i</td>
<td>80</td>
<td>1.4*10(^3)</td>
<td>2.9</td>
<td>10.4</td>
</tr>
</tbody>
</table>

\(^{a}\) [Rh(acac)(CO)\(_2\)] = 0.084 mmol/l in toluene, pressure = 20 bar (CO/H\(_2\) = 1/1), 1-octene/rhodium = 5160.

\(^{b}\) [4] = 2.1 mmol/l, [a] = 6.3 mmol/l, [b-i] = 3.1 mmol/l.

\(^{c}\) T.O.F = average turnover frequency = (mol aldehyde)/(mol Rh) h\(^{-1}\), the reaction was stopped after 1 hour (80 °C) and 17 hours (30 °C).

\(^{d}\) 1/b = linear/branched ratio.

\(^{e}\) percent selectivity to isomerization to 2-, 3- and 4-octene based on converted 1-octene.

The monomeric tris zinc(II) porphyrin phosphite 4 yields a rhodium catalyst with reasonable activity and poor regioselectivity in the rhodium-catalyzed hydroformylation of 1-octene (T.O.F. = 2.0*10\(^3\) and 1/b = 2.5). The addition of three equivalents of monotopic ligand a to 4 yields a more bulky ligand system 4(a)\(_3\). Consequently, the activity and the isomerization in the rhodium-catalyzed hydroformylation increased, upon using 4(a)\(_3\), and the concomitant selectivity decreased (T.O.F. = 3.4*10\(^3\) and 1/b = 1.9). Likely, the more bulky assembled 4(a)\(_3\) leads to rhodium monoligated phosphite complexes, which explains the increase in activity and decreases in selectivity.\(^{29}\) The use of ditopic template ligands b-i allows the formation bidentate ligand assemblies. In general, the ligand assemblies based on b-i and 4 showed small changes in selectivity and activity ranging from linear/branched = 2.1 to 3.4 (figure 3) (T.O.F. = 1.4*10\(^3\) to 3.4*10\(^3\)). The bidentate assembled ligand systems based on tris zinc(II) porphyrin phosphite 4 and dabco g is a clear exception since for this catalyst system a high linear over branched was found (1/b = 15.1) with maintenance of good activity. Surprisingly, lowering the temperature to 30 °C resulted in even a more selective catalyst and the linear to branched ratio increased to 1/b = 22.8. The latter is unexpected for the hydroformylation of alkenes, since lowering the temperature in general decreases the amount of linear aldehyde formed.\(^{31}\) This suggests that the assembled supramolecular catalyst system is stabilized at lower temperatures, which can be explained by higher binding constants of the nitrogen donor.
atoms to the zinc(II) porphyrin moieties. Since the assembly based on g as the template gave the most interesting results we decided to study this assembly in more detail.

**UV-vis titration experiments using tris zinc(II) porphyrin phosphite**

To obtain more insight in the structure of the supramolecular catalyst UV-vis spectroscopic titrations in toluene were performed to study the binding of ditopic template g to ligand 4 and its rhodium complex. The titration curve representing the binding of g to 4 shows two distinct inflecting points that indicate that there are two different binding modes for g to 4 (figure 4).

![Figure 4](image.png)

**Figure 4.** Plot of absorption (A) versus the dabco g/4 ratio taken from UV-vis spectroscopy experiments in toluene.

The first inflecting point is at the g/4 = 1/1 ratio and corresponds to the binding of dabco g to 4 in a ditopic fashion (I), which is facilitated by intramolecular binding via chelation of the zinc(II) porphyrin moieties of 4. The second inflection point at a 2/1 ratio shows the binding of the second dabco g to 4, which is monotopic (II), because only one binding site is left. At these concentrations the formation of larger assemblies is unlikely and indeed in non of the spectroscopic data we found indications for the formation of such species. The titration curve of g to complex Rh(acac)(4)$_2$ shows one inflection point only, indicating a different binding behavior of the dabco g to the complex (figure 5). The stoichiometry of the supramolecular complex formed is g/ Rh(acac)(4)$_2$ is 3/1 with $K_1 = K_2 = K_3$, which is in line with the assembly structure 8. Indeed, we were able to fit the titration curve with the equation for a complex with a 3 : 1 stoichiometry, giving an average high binding constant ($K = 1.9 * 10^7 \text{ M}^{-1}$) that is typical for ditopic complexation. The binding constant is somewhat lower than found by Hunter et. al., for zinc(II) porphyrin dimers and dabco. Some of the effects seen in dabco binding of porphyrin trimers and oligomers have also been seen by Sanders et. al.
Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts

Figure 5. Plot of absorption (A) versus the dabco g/Rh(acac)4 ratio taken from UV-vis spectroscopy experiments in toluene.

High-pressure NMR spectroscopy titration experiments on tris zinc(II) porphyrin phosphite

In order to investigate the coordination properties of these new type of ligand systems in more detail their rhodium complexes were studied with high-pressure NMR-spectroscopy at various g/4 ratios (figure 6). The NMR-spectroscopy experiments in toluene-d8 under 20 bars of H2/CO show that monomeric tris zinc(II) porphyrin phosphite 4 in the presence of a rhodium precursor forms the hydrido rhodium biscarbonyl diphosphite complex 5; 31P-1H-NMR spectroscopy showed the formation a doublet (δ = 148.0 ppm, J_{Rh-P} = 232 Hz) and a corresponding rhodium hydride signal A (δ = -9.3 ppm) in the 1H-NMR spectrum was observed, similar to other phosphite rhodium complexes under these conditions.29,35 The gradual addition of dabco g (g/4 ratio = 0-0.75) to this complex resulted in a decrease of intensity of A and the formation of a second rhodium hydride signal B (δ = -9.4 ppm) was observed. This shows that under these conditions two catalyst systems are in slow exchange on the NMR-spectroscopy timescale with complex 5, yielding only one average rhodium-hydride signal, which is not observed. This shows that the assembled bidentate rhodium complex 7 is predominantly formed over rhodium complex 6. The chelating effect of three anchoring points of the assembled catalyst 7 consists of two bridging dabco ligands and the rhodium metal center (dabco-porphyrin (2x) and phosphite-rhodium (1x)). Whereas, in 6...
the phosphites are not chelating and the dabco ditopic template is coordinated in intramolecular fashion in the phosphite ligand (dabco-porphyrin (2x)).

Figure 6. High-pressure $^1$H-NMR-spectra (hydride region) of rhodium catalyst assemblies of tris zinc(II) porphyrin phosphite 4 and various amounts of dabco g.

The addition of more dabco g (g/4 ratio = 1-1.5) resulted in the rise of a new distinct rhodium hydride signal C ($\delta = -9.54$ ppm) and a decrease in intensity of B. The addition one equivalent of dabco g to complex 7 yields the sandwich type rhodium complex 8. In this complex the phosphites are fixed in space by the complexation of three ditopic templates. In the rhodium-catalyzed hydroformylation of 1-octene a very high linear/branched ratio has been observed at this dabco-concentration (g/4 ratio = 1.5) and the UV-vis spectroscopy titration curve showed that an highly symmetrical complex is formed upon mixing dabco g with Rh(acac)(4)2. All these data point at the formation of highly symmetrical sandwich type complex 8. Increasing the concentration of dabco showed that hydride-signal C was regularly shifted upfield giving hydride-signal D ($\delta = -9.6$ ppm, g/4 ratio = 3). This means that
complex 8 is in fast exchange on the NMR-spectroscopy timescale with another catalyst system, which is likely complex 9. This suggests that the binding of the third dabco g to the assembled bidentate catalyst system is weaker compared to the binding of the first two dabco g template ligands.

**Figure 7.** Schematic representation of the several assembled bidentate catalyst systems based on dabco g to tris zinc(II) porphyrin phosphite 4 (P = phosphite moiety and M = rhodium-catalyst).

*Titration experiments monitored by catalysis in the rhodium-catalyzed hydroformylation*

The preliminary hydroformylation experiments showed that the assemblies based on 4(g) resulted in very selective catalysts compared to the use of 4 as monodentates. UV-vis spectroscopic titrations and high-pressure NMR-spectroscopy experiments suggested the formation of an highly ordered sandwich type structure 8. To provide more evidence for the
existence of assembly 8 we decided to perform a titration that is monitored by catalysis, i.e. study the catalytic performance at different g/4 ratios. This obviously can only give information if a well-known catalytic reaction is studied that is sensitive to changes of the structure. The g/4 ratios were varied and tested in a parallel setup in the rhodium-catalyzed hydroformylation of 1-octene at 40 °C and the results are displayed in figure 8-10.

![Figure 8](image)

**Figure 8.** The linear/branched ratio of aldehydes formed in the rhodium-catalyzed hydroformylation of 1-octene using assemblies of tris zinc(II) porphyrin phosphite 4 and various amounts of dabco g.

![Figure 9](image)

**Figure 9.** The activity (initial turn over frequencies) of the assemblies formed from tris zinc(II) porphyrin phosphite 4 and various amounts of dabco g in the rhodium-catalyzed hydroformylation of 1-octene.

The rhodium catalyst based on monodentate tris zinc(II) porphyrin phosphite 4 (g/4 = 0) gives low selectivity in the hydroformylation of 1-octene (l/b = 2.9) and the addition of small quantities of dabco g to 4 (g/4 = 0-0.8) results in a small increase in selectivity only (figure 8). The presence of more than one equivalent of g to 4 (g/4 = 1-1.5) results in catalyst assemblies
that have high linear/branched ratios. In addition, a small increase in isomerization is detected. The addition of more than 1.5 equivalents of dabco to results in gradual decrease in the linear to branched ratio, but even at g/4 ratio of 4.5 the catalyst assembly is still more selective than the catalyst based on monomers 4. In contrast with the changes in the linear to branched ratios the catalyst shows a large decrease in activity upon addition of small amounts g to 4 (figure 9). This decrease in activity is typical of bidentate phosphorus ligands in the rhodium-catalyzed hydroformylation of 1-octene and confirms that the in situ assembly of g and 4 in the presence of rhodium catalyst yields a bidentate chelating ligand system (figure 7). An increase of the g/4 ratio does not change the catalyst activity, even upon addition of large excess of dabco, suggesting that chelating bidentate ligands are formed. The tremendous increase in selectivity in the rhodium-catalyzed hydroformylation of 1-octene is ascribed to the formation of sandwich type complex 8. The binding of third dabco molecule to the assembled bidentate catalyst yields a more rigid ligand system, increasing the catalyst selectivity to linear aldehyde. However, the binding of the third dabco molecule is weak compared to the first two dabco molecules as is evident from the decrease in selectivity in the hydroformylation in presence of excess dabco yielding the less selective complex 9. Noteworthy, the decrease in branched aldehyde formed, caused by the assembly of the complex 8, goes along with a small increase in isomerization (figure 10).

![Figure 10](image-url)

**Figure 10.** Percent branched aldehyde and isomerization formed in the rhodium-catalyzed hydroformylation of 1-octene using assemblies of tris zinc(II) porphyrin phosphite 4 and various amounts of dabco g.

To further investigate the assembled bidentate catalyst systems based on dabco g in the rhodium-catalyzed hydroformylation of 1-octene, the catalyst assemblies were also studied in the presence of monopic quinuclidine j (table 7). The mixture of tris zinc(II) porphyrin phosphite 4 and quinuclidine j cannot form assembled chelating bidentate ligand systems and
in the rhodium-catalyzed hydroformylation only small changes in activity and selectivity were observed in presence and absence of quinuclidine j. In the presence of dabco \((g/4 = 0.5)\) the activity in catalysis decreases, which is caused by the formation of the bidentate assembled catalysts 7. The addition of j to this system yields only small changes in selectivity and activity and corroborates the stability of the bidentate assembled catalyst systems in the presence of compounds with only one nitrogen donor atom. However, the formation of the selective bidentate assembled complex 8, present in \(g/4\) ratios of 1 and 1.5, is disturbed in the presence of quinuclidine j and in the rhodium-catalyzed hydroformylation a significant decrease in selectivity is observed. Under these conditions the catalyst is still based on a bidentate assembly, because a similar activity is observed in presence as absence of j. Nevertheless, the presence of j suppresses the formation of complex 8, which corroborates the weaker binding of the third dabco molecule to the bidentate assembled catalyst system.

Table 7. Hydroformylation of 1-octene using rhodium catalyst assemblies based on tris
zinc(II)porphyrin phosphite 4 and various amounts of dabco g and quinuclidine j:

<table>
<thead>
<tr>
<th>g/4 ratio</th>
<th>j/4 ratio</th>
<th>T.O.F., (1.4\times10^2)</th>
<th>1/b</th>
<th>isomers (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.9</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>2.7</td>
<td>8.1</td>
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<tr>
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<td>0</td>
<td>57</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>40</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
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<td>0</td>
<td>34</td>
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</tr>
<tr>
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<td>1</td>
<td>36</td>
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<tr>
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</tr>
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<td>35</td>
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</tr>
<tr>
<td>1.5</td>
<td>2</td>
<td>36</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

(a) \([HRh(CO)(PPh_3)_3] = 0.05 \text{mmol/l in toluene, pressure} = 20 \text{bar (CO/H}_2 = 1/1), 1-octene/rhodium} = 8600, in none of the reactions hydrogenation was observed, temperature = \(40^\circ\text{C}\). (b) \([4] = 0.5 \text{mmol/l}. (c) T.O.F. = \text{average turn over frequency} = (\text{mol aldehyde})(\text{mol Rh})^{-1}\text{h}^{-1}, \text{the reaction was stopped after 16 hours (d) 1/b = linear/branched ratio, (e) percent selectivity to isomerization to 2-, 3- and 4-octene based on converted 1-octene.}

7.3 Conclusion

In conclusion a new supramolecular approach is presented to prepare self-organized transition metal catalyst systems. The multi-component assembly of monomeric ligands enables the formation of new series of self-assembled bidentate ligands, which can easily be varied by using different templates. For the formation of the catalyst assemblies, zinc(II) porphyrin phosphite ligands 1 and 4 have been used that can selectively coordinate to various ditopic template ligands, forming \textit{in situ} a self-assembled bidentate ligand systems as is proven by UV-vis and NMR-spectroscopy. The assembled bidentate catalyst systems control important
key features in several catalytic reactions, changing activity and (enantio)selectivity. Impressive chelate effects were obtained using catalyst assemblies based on tris zinc(II) porphyrin phosphite 4 and dabcog. UV-vis spectroscopy and high-pressure NMR titrations experiments showed that highly symmetrical sandwich type rhodium complexes can be formed. Titration experiments monitored by the rhodium-catalyzed hydroformylation of 1-octene showed that variation of the g/4 ratio results in major changes in activity and selectivity for the assembled bidentate catalyst systems and it was found that sandwich type complex 8 results in very high linear/branched ratios, which competes very well with known selective diphosphite ligand systems. This novel supramolecular approach of ligand preparation has proven to be very successful in transition metal catalysis and shows that these assembled catalyst systems can compete with covalently linked chemo-catalysts.

7.4 Experimental section

General Procedures. Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. THF, hexane and diethyl ether were distilled from sodium benzenophenone ketyl, CH₂Cl₂, isopropanol and methanol were distilled from CaH₂ and toluene was distilled from sodium under nitrogen. NMR spectra (¹H, ³¹P and ¹³C) were measured on a Bruker DRX 300 MHz and Varian Mercury 300 MHz; CDCl₃ was used as a solvent, if not further specified. Mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. UV-vis spectroscopy experiments were performed on a HP 8453 UV/Visible System. Elemental analyses were obtained on an Elementar Vario EL apparatus. Gas chromatographic analyses were run on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB-1 J&W 30 m column, film thickness 3.0 µm, carrier gas 70kPa He, FID Detector) equipped with a Hewlett Packard Data system (Chrom-Card). Molecular modeling was performed using semi-empirical (PM3-tm) calculations on a unix workstation using the Spartan software.

Materials. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Diisopropylethylamine and triethylamine were distilled from CaH₂ under argon. The following compounds were synthesized according to published procedures: phosphorochloridites,⁵ 5-(3-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin⁶,⁷ and phosphite porphyrin 1.⁸

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Synthesis of tris(5-(phenyl-2-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin)phosphite 4

5-(3-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin (1.23 g, 1.77 mmol), azeotropically dried with toluene (3x3 ml), and diisopropylethylamine (3.1 ml, 17.7 mmol) were dissolved in THF (80 ml) and the solution was cooled to -40°C. Freshly PCl₃ (44 µl, 0.51 mmol) was dissolved in THF (10 ml) and added dropwise, stirring was continued for 15 minutes. The cooling bath was removed and the solution was allowed to warm to room temperature, stirring was continued for 2 hours. The reaction mixture was filtered and the solvent evaporated. The crude product was purified by flash column chromatography under Argon (silica; toluene) to remove the excess of hydroxyl-porphyrin, giving 15 (0.341 g, 0.16 mmol, 32 %) as a purple-red solid: 

1H NMR (300 MHz): δ 8.90-8.84 (m, 18H), 8.80 (d, 3H, J = 4.5 Hz), 8.68 (d, 3H, J = 4.5 Hz), 8.21-8.17 (m, 18H), 8.06 (s, 3H), 7.96 (m, 3H), 7.72-7.65 (m, 30H), 7.48 (m, 3H); 

31P NMR (121.5 MHz): δ 128.30;

13C-ATP (75.465 MHz): 158.19, 150.43, 150.24, 150.19, 142.81, 135.81, 135.43, 133-130, 127.48, 121.12, 121.07, 120.72; anal. calcd. for C₁₃₂H₈₁N₁₂O₃PZn₃: C, 75.13; H, 3.87; N, 7.96. Found: C, 75.08; H, 3.76; N, 8.05.

Catalysis.

The hydroformylation experiments were performed as follows. A stainless steel 25 ml autoclave, equipped with a teflon stirring bar, was charged with 0.42 µmol of [Rh(acac)(CO)₂], 10.4 µmol of phosphine and 0.017 µmol of dpea in 4.0 ml of toluene. The solution was incubated for 1 under 20 bar CO/H₂ (1:1). The pressure was reduced to 1 bar and a mixture of 0.34 ml 1-octene and 0.17 ml of decane in 0.67 ml of toluene was added. Subsequently the CO/H₂ pressure was repressurized to 20 bar. The mixture was stirred at for 1 hour (80 °C) and 17 hours (25 °C). Then the autoclave was cooled down to 0 °C in ice and the pressure was reduced to 1.0 bar. A sample was taken and the conversion was checked by GC measurement of the crude product after filtration over a plug silica to remove the catalyst.

Alternatively, a stainless steel 150 ml autoclave, equipped with 15 vessels and teflon stirring bars, was charged with 0.042 µmol of [Rh(acac)(CO)₂], 1.04 µmol of phosphorus and 0.0017 ml of dpea, 0.034 ml 1-octene and 0.017 ml of decane in 0.5 ml of toluene. The CO/H₂ pressure was adjusted to 20 bar. The mixture was stirred for 1 hour (80 °C) and 16 hours (40 °C). Then the autoclave was cooled down to 0 °C and the pressure was reduced to 1.0 bar.

The allylic alkylation experiments were performed as follows. Under Schlenk conditions 0.50 µmol of [Pd(allyl)Cl]₂, 3.0 µmol phosphite and 3.0 µmol phosphine were dissolved in 5.0 ml of CH₂Cl₂ and stirred for 30 minutes. Respectively, 50 µmol 1,3-diphenyl-allylacetic, 150 µmol dimethylmalonate, 150 µmol BSA and 50 µmol decane and a catalytic amount of KOAc were added. The mixture was stirred for 15 hours at 25 °C and subsequently stopped by
Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts

adding a saturated ammonium chloride solution of water. Subsequently, 5.0 ml of petroleum ether was added and the solution was washed once more with a saturated NH₄Cl solution. The organic phase was dried over Na₂SO₄, filtered and the conversion was checked by GC measurement. The solution was chromatographed (SiO₂; petroleum ether/CH₂Cl₂ = 1/1) to give analytically pure products.³⁸ Enantiomeric purities were determined by chiral HPLC (OD column, eluens 0.5 % isopropanol in hexane tₗ (R) = 33.2 min. and tₘ (S) = 34.9 min.).

Asymmetric hydrogenation reactions were performed as follows. A stainless steel 150 ml autoclave, equipped with 15 vessels and teflon stirring bars, was charged with 0.5 µmol of [Rh(nbd)₂(BPh₄)], 1.5 µmol of phosphine, 1.5 µmol of porphyrin, 1.0 µl of dipea, 100 µmol dimethyl itaconate and 50 µmol of decane in 0.5 ml of toluene. The H₂ pressure was adjusted to 5 bar, without incubation. The mixture was stirred, for 17 hours at 40 °C. Then the autoclave was cooled down to 0 °C and the pressure was reduced to 1.0 bar. The conversion was checked by GC measurement of the crude product after filtration over a plug of magnesium sulfate and subsequently silica. Enantiomeric purities were determined by chiral GC (Chirasil-L-Val, isothermal; T = 70 °C, tₗ (R) = 34.4 min. and tₘ (S) = 35.2 min.).

High-pressure NMR-experiments³⁹
In a typical experiment the high pressure NMR tube was filled with (8 µmol) of [Rh(acac)(CO)₂], (30 µmol) of zinc(II) porphyrin phosphite and 1.5 ml of toluene-d₈. The tube was purged three times with 20 bar of CO/H₂ (1:1), pressurized to approximately 20 bar, heated to 80 °C and incubated for 1 hour. Measurements were performed at 25 °C. For the titration experiments the tube was depressurized and certain amount of a solution of 0.75 M dabco in toluene-d₈ was added under flow of syngas, subsequently the tube was repressurized to 20 bars.
7.5 References and Notes


Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts

28 Rh(acac)(CO)₂ and HRh(CO)(PPh₃)₃ were mixed with zinc(II) porphyrin phosphite 1 in a 1:2 ratio, forming Rh(acac)(I₂) and HRh(CO)(PPh₃) respectively.

33 This complex was prepared in situ by mixing Rh(acac)(CO)$_2$ with zinc(II) porphyrin phosphite 4 in a 1:2 ratio.


37 See chapter six.


Supramolecular zinc(II) porphyrin phosphite assemblies as highly selective catalysts