Template directed assembly of transition metal catalysts
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Chapter Six

Supramolecular ligands as versatile components in transition metal catalyst libraries
6.1 Introduction

During the past decades combinatorial chemistry has evolved in an incredible manner and has been applied especially in pharmacy for drug discovery and optimization. This technology requires the micro-scale synthesis and screening of vast libraries of compounds, which has resulted in great improvements in the efficiency of testing new molecules and has clearly proven its value. Since the mid 1990’s, the making and testing of large libraries has been extended to other areas, leading to combinatorial approaches for the development and optimization of inorganic materials with superconductivity, giant magnetoresistance and luminescence properties as well as biochemical tools to analyze protein-protein interactions. Combinatorial approaches in combination with high-throughput screening methods have also been recognized as promising tool in the search for new catalyst systems. The preparation of large libraries of heterogeneous catalyst systems in a combinatorial manner has proven to be successful since it resulted in new and improved catalysts. To screen catalyst libraries several traditional screening techniques, like NMR (nuclear magnetic resonance) spectroscopy, IR (infrared) spectroscopy, MS (mass spectroscopy) and HPLC (high-pressure liquid chromatography), have been optimized and modified to automated processes in order to decrease screening times. Recently, several new, effective methods to screen catalyst libraries have also been reported.

The construction of libraries of biocatalysts and homogeneous chemo-catalysts has also been explored. The biocatalyst libraries consist of enzymes that are varied by mutagenesis / expression of enzymes. In the field of enzyme catalysis enormous progress has been made by applying molecular biological methods such as directed evolution, which resulted in large libraries of enzyme mutants (variants). The success in finding hits clearly increases upon expanding the size and the variation of the catalyst libraries. Therefore, the development of these homogeneous catalysts using combinatorial techniques involves two distinct challenges: 1) devising strategies and methods for the preparation of large libraries of ligands and/or catalyst displaying high degrees of structural diversity, 2) developing high-throughput screening techniques for the reaction of interest. A lot of effort has been put in the development of new screening techniques for homogeneous catalyst libraries and various methods have proven successful. In the search for new transition metal catalysts the preparation of catalyst libraries has mainly focused on variation of ligands, which are based on commercially available ligands or are prepared via conventional synthetic pathways and/or divergent methods using parallel synthesis. The synthesis of large libraries of new ligands indeed yields a major challenge and so far only a limited number of methodologies have been reported. Until now, library synthesis of ligands is based on combinatorial organic synthesis followed by metal complexation. This approach utilizes advanced solid and
solution phase combinatorial synthetic methodologies\textsuperscript{22,23} including parallel synthesis, split-pool techniques,\textsuperscript{24} encoding/deconvolution\textsuperscript{25} and polymer-supported reagents.\textsuperscript{26,27} Methods such as split pool techniques are much faster than traditional serial approaches and enable the preparation of relatively large numbers of compounds but often lack control over the purity and mixtures of compounds entering the assay screen. In contrast, the methods based on parallel or array syntheses yield intermediate libraries of pure compounds. Although these combinatorial techniques to construct ligand libraries have proven to be valuable, the preparation and evaluation of truly large numbers of potentially (enantio)selective catalysts has not been reported and the application is still limited to a few catalytic reactions. Moreover, the preparation of important multidentate ligands, like promising diphosphorus ligands, faces synthetic challenges, especially when sophisticated chiral entities are required for asymmetric catalysis (figure 1).\textsuperscript{28,29,30} New tools should be developed to efficiently deal with these synthetic challenges.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Schematic representation of covalently linked bidentate ligands with different phosphorus donor atoms (L1, L2), M = transition metal catalyst and a chiral phosphine-phosphite ligand BINAPHOS.}
\end{figure}

Here we report such a tool, which involves new effective supramolecular techniques to construct bidentate ligands, which can be formed by just mixing the monomeric compounds (figure 2). A phosphorus monodentate ligand L1, equipped with a zinc(II) porphyrin template, can selectively bind monodentate ligands L2 that have a nitrogen donor atom. These selective metal-ligand interactions (Zn-N) are utilized for the assembly of bidentate ligand systems and yield novel transition metal catalysts. Upon variation of the phosphorus monodentate compounds (i.e. 6 L1 and 9 L2) a matrix of new self-assembled bidentate ligands (54 L1-L2) can be created easily. This novel supramolecular strategy to prepare new assembled bidentate ligands is successfully applied in a combinatorial fashion and clearly simplifies the construction of catalyst libraries based on sophisticated phosphite-phosphine chelating ligands.
6.1 Results and discussion

Synthesis of the building blocks
To study our supramolecular approach of assembled bidentate ligands we synthesized six porphyrin functionalized phosphite ligands and nine different phosphorus ligands with a nitrogen donor atom. The phosphite zinc(II) porphyrin template ligands 1-6 were obtained via a reaction of the phosphorochloridite with the mono-hydroxyl zinc(II) porphyrin (chart 1). The phosphorus ligands with nitrogen donor atoms a-i were prepared according to standard procedures (chart 2). All new compounds were fully characterized with $^1$H-NMR, $^{31}$P-NMR and $^{13}$C-NMR spectroscopy, elemental analysis and mass-spectroscopy.

![Diagram](image)

**Figure 2.** Schematic representation of the assembly of monomeric ligands (L1, L2) to an *in situ* assembled bidentate complex (M = transition metal catalyst).

**Chart 1.**
The assembly of phosphine-phosphite ligands

By just mixing two monomeric compounds, i.e. ortho-phosphite zinc(II) porphyrin 1 and meta-pyridyldiphenylphosphine b, an assembled bidentate ligand 1•b is formed in situ. UV-vis titrations33,34 in toluene and NMR-spectroscopy experiments show that the pyridyl moiety of b selectively coordinates to zinc(II) porphyrin 1 with high binding constant, \( K_{1.b} = 1.6 \times 10^3 \) M\(^{-1}\). The binding constant of meta-phosphite zinc(II) porphyrin 2 and b is slightly higher, \( K_{2.b} = 2.1 \times 10^3 \) M\(^{-1}\). These results show that via selective pyridine-zinc interactions two mono-dentate phosphorus ligands form a bidentate ligand assembly. We have shown previously that the binding of the nitrogen donor atoms to the zinc(II) porphyrin is very selective; the phosphorus donor atoms do not coordinate to the zinc and are available for transition metal coordination.35 In order to investigate the coordination properties of these new type of ligands their rhodium complexes were studied with high-pressure NMR-spectroscopy. The NMR-spectroscopy experiments in toluene-d\(_8\) under 20 bars of H\(_2\)/CO show that these ligand systems indeed coordinate to transition metals in a bidentate fashion.
Table 1. Selected $^1$H- and $^{31}$P-NMR data of high-pressure NMR-spectroscopy of various rhodium complexes at T = 25 °C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta(^{31}$P)-phosphine ($\text{ppm}$)</th>
<th>$\delta(^{31}$P)-phosphite ($\text{ppm}$)</th>
<th>$J_{\text{Rh-P}}$ ($\text{Hz}$)</th>
<th>$J_{\text{Rh-PO}_3}$ ($\text{Hz}$)</th>
<th>$J_{P-\text{PO}_3}$ ($\text{Hz}$)</th>
<th>$\delta(^1$H)-Rh-H ($\text{ppm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 [Rh(acac)(CO)(I)]$^a$</td>
<td>c</td>
<td>127.8</td>
<td>c</td>
<td>300</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>8 [HRh(CO)$_2$(1•b)]</td>
<td>29.4</td>
<td>144.3</td>
<td>143</td>
<td>265</td>
<td>153</td>
<td>-10.6</td>
</tr>
<tr>
<td>9 [HRh(CO)$_2$(1)(a)]</td>
<td>30.1</td>
<td>179.8</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>-9.8</td>
</tr>
<tr>
<td>10 [HRh(CO)$_2$(a$_2$)]</td>
<td>37.9</td>
<td>c</td>
<td>140</td>
<td>c</td>
<td>c</td>
<td>-9.1</td>
</tr>
<tr>
<td>11 [HRh(CO)$_2$(2•b)]</td>
<td>c</td>
<td>150.4</td>
<td>c</td>
<td>243</td>
<td>c</td>
<td>-9.3</td>
</tr>
<tr>
<td>12 [HRh(CO)$_2$(2•b)]</td>
<td>31.4</td>
<td>148.6</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>-10.8</td>
</tr>
</tbody>
</table>

(a) the [Rh(acac)(CO)(I)] was used cause, no satisfactory NMR-data were observed for the HRh(CO)$_2$(1), due to solubility problems, (b) broad signals were observed, (c) not present.

Monomeric ortho-phosphate zinc(II) porphyrin 1 in the presence of a rhodium precursor forms a monoligated rhodium phosphate complex 7 (table 1), as is also formed for other bulky phosphate ligands.$^{36}$ The one-to-one mixture of 3-pyridyldiphenylphosphine b and 1, yielding the assembled bidentate phosphine-phosphate ligand 1•b, indeed forms predominantly a new bidentate phosphate-phosphine rhodium complex 8 (Scheme 1).

Scheme 1. Assembly of rhodium complex 8 [[[HRh(1•b)(CO)$_2$] (modeled structure) consisting of phosphate zinc(II) porphyrin template 1 and 3-pyridyldiphenylphosphine b, which can also be prepared from phosphate-phosphine complex 9 ([HRh(1)(a)(CO)$_2$]) (a = triphenylphosphine).
Chapter Six

Figure 3. Coordination modes of [HRh(P)(CO)2]: equatorial-equatorial (ee) and equatorial-apical (ea), P = phosphorus ligand.

The rhodium-phosphorus coupling constants show that the assembled bidentate phosphine-phosphite ligand 1•b coordinates in a equatorial-equatorial (ee) fashion to the rhodium metal center (figure 3). Ortho-phosphite zinc(II) porphyrin 1 in the presence of a stoichiometric amount of triphenylphosphine a yielded a mixture of two different rhodium complexes, respectively phosphine-phosphite complex 9 and small amount of bisphosphine complex 10 as was evident from the NMR spectra (figure 4). The coordination mode of phosphine-phosphite complex 9 was not as clear for complex 8 and was found to be a mixture of equatorial-equatorial (ee) and equatorial-apical (ea) coordination modes in fast exchange on NMR-spectroscopy time-scale.37 Interestingly, the addition of 3-pyridyldiphenylphosphine b to this mixture results in pyridine coordination to the zinc(II) porphyrin template of 1, giving 1•b, and subsequently the assembled phosphine-phosphite bidentate 1•b binds to the rhodium and the rhodium-triphenylphosphine bond dissociates, yielding predominantly bidentate complex 8.

Figure 4. High-pressure 31P-NMR in toluene-d8 of [HRh(I)(a)(CO)2] 9 and [HRh(a)(CO)2] 10 and the assembled bidentate complex 8 [HRh(1•b)(CO)2].

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Supramolecular ligands as versatile components in transition metal catalyst libraries

Meta-phosphate zinc(II) porphyrin 2 in the presence of a rhodium precursor forms of a bis-ligated rhodium phosphate complex 11. The addition of 3-pyridylidiphénylphosphïne b to this mixture results also in the formation of an assembled bidentate phosphate-phosphate ligand 2•b, yielding bidentate phosphate-phosphate rhodium complex 12. In contrast with ligand 1 the one-to-one mixture of 2 and a in presence of rhodium does not yield a phosphate-phosphate complex but only bisphosphate rhodium complex 10. However, the addition of b yields the assembled phosphate-phosphate ligand 2•b and complex 12 was formed predominantly. This proves unambiguously that this type of assembled bidentate ligands show chelating behavior in a similar fashion as their covalently linked analogues.

Table 2. Binding constants as determined with UV-vis spectroscopy of phosphate zinc(II)porphyrin templates and meta-pyridyl diphenylphosphine in dichloromethane.

<table>
<thead>
<tr>
<th>complex</th>
<th>binding constant (K-value, M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1•b</td>
<td>3.8 * 10⁻¹</td>
</tr>
<tr>
<td>1•b + [HRh(a)₃(CO)]</td>
<td>64.5 * 10⁻¹</td>
</tr>
<tr>
<td>2•b</td>
<td>6.9 * 10⁻¹</td>
</tr>
<tr>
<td>2•b + [HRh(a)₃(CO)]</td>
<td>43.0 * 10⁻¹</td>
</tr>
</tbody>
</table>

To obtain further prove that these assemblies indeed show chelating behavior we performed UV-vis titrations to determine binding constants of the pyridine-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 titrations on ortho-phosphate zinc(II) porphyrin 1 and 3-pyridylidiphénylphosphïne b in dichloromethane show that the presence of a rhodium complex [HRh(a)₃(CO)] indeed increased the association constant with a factor of seventeen (K = 3.8*10⁻¹ M⁻¹ to K = 64.5*10⁻¹ M⁻¹) (table 2). For meta-phosphate zinc(II) porphyrin 2 and b a similar increase was observed. The NMR and UV-vis studies show that selective metal-ligand interactions are a powerful tool to form self-assembled bidentate ligands that are easily accessible by just mixing monomeric compounds and show chelating behavior.

Catalysis

Now we have proven that bidentate ligands formed by self-assembly indeed show chelating behavior the next question to be answered was if these assemblies were sufficiently strong and stable to impose their typical behavior in catalysis. For this purpose we studied the assemblies in several different reactions that require various conditions.
The first reaction studied was the rhodium-catalyzed hydroformylation of styrene, which was performed in toluene at 40 °C and 80 °C under 20 bars of H₂/CO (1/1). The results show that the chelating assembled ligands were stable under catalytic conditions (scheme 2) and key features like selectivity and activity vary considerably by using different building blocks (table 3). Monodentate ortho-phosphite zinc(II) porphyrin 1 yields a rhodium catalyst with high activity and poor regioselectivity in the rhodium-catalyzed hydroformylation of styrene (T.O.F. = 2900 and b/l = 2.6). The assembled bidentate 1•b shows an increase in selectivity for the branched product and a decrease in activity of the catalyst, which shows that the assembly behaves as a bidentate ligand. Mixing triphenylphosphine a and 1 yield different activity and selectivity. The low turn over frequency for this complex in the hydroformylation is attributed to [HRh(CO)₂(I)(a)] 9 as observed in the high-pressure NMR spectroscopy experiments. In the mixture of the three monomeric compounds triphenylphosphine a, b and 1 (in equal amounts) the chelating assembled bidentate ligand will predominantly coordinate to rhodium center and indeed similar catalytic results were observed as for 1•b in the absence of a. The assembly 1•j based on 3-pyridyldiphenylphosphinoxide does not coordinate in a
bidentate fashion to the rhodium metal center and hardly any influence in catalysis was observed as for 1 in the absence of J. The meta-phosphite zinc(II) porphyrin 2 results in bisphosphite rhodium complex 11, which gives reasonable activity and low selectivity in the hydroformylation of styrene (T.O.F. = 1060 and b/l = 3.6). Addition of triphenylphosphine a yields predominately [HRh(CO)₂(a)] 10, as was evident from high-pressure NMR spectroscopy experiments. Consequently, using such a mixture in the rhodium-catalyzed hydroformylation of styrene similar activity and selectivity as in the absence of 2 is observed. In contrast, the activity and selectivity changes upon using the assembled bidentate ligand 2·b giving comparable results as observed for 1·b. The presence of a to the solution of bidentate assembled ligand 2·b does not change the catalytic properties of the assembled rhodium complex based on 2·b, again showing the chelating effect under catalytic conditions.

Asymmetric catalysis
Introducing chirality in the phosphite of the zinc(II) porphyrin template molecule enables the assembly of various chiral bidentate ligand systems. One of the first questions to be answered was if the bidentate ligand formed by assembly would indeed result in a sufficiently chiral environment to induce enantioselectivity. In the rhodium-catalyzed hydroformylation of styrene the metal complex based on chiral monodentate phosphite zinc(II) porphyrin 3 resulted in low enantiomeric excess (7 % (R)) (table 4). The bidentate assembly of 3-pyridyldiphenylphosphine b and 3 changed the ligand properties in this reaction and, surprisingly, the rhodium complex based on 3·b slightly favored the formation of the other enantiomer (7 % (S)). The use of rhodium complexes based on 3·d improved the enantioselectivity to yield 19 % e.e. (S). These first results do not give very selective catalysts, but corroborate that assembly of bidentate ligands is a promising approach to form new chiral catalytic systems.

| Table 4. Hydroformylation of styrene using different rhodium catalyst assemblies.² |
|-----------------|------|------|------|
| Ligand         | T.O.F. | b/l  | e.e. (%) |
| 3          | 8     | >100 | 7 (R) |
| 3 + a       | 5     | >100 | 7 (R) |
| 3·b         | 11    | 15   | 7 (S) |
| 3·d         | 13    | 11   | 19 (S) |

(a) [Rh(acac)(CO)₂] = 0.83 mmol/l, pressure = 20 bar (CO/H₂ = 1/1), T = 40 °C. (b) phosphite / rhodium = 25, phosphite/phosphine = 1. (c) T.O.F. = turn over frequency = (mol aldehyde)(mol Rh)⁻¹h⁻¹, the reaction was stopped after 16 hours. (d) b/l = branched/linear. (e) e.e. = enantiomeric excess.
After these initial results we decided to prepare small series of phosphite porphyrins and nitrogen containing phosphorus ligands in order to prepare a catalyst library by self-assembly. The mono-dentate phosphorus ligands a-i were selectively assembled via coordination of the nitrogen donor atom to the zinc(II) porphyrin binding site of phosphites 1-6, by simply mixing the stock-solutions of the different monomeric compounds. The matrix of the newly assembled bidentate ligands and the monomers 1-6 yielded a catalyst library of 60 new catalyst systems that was based on 16 monomeric compounds that were synthesized. In addition to this synthetic advantage, the number of precise weighing is reduced to 16 (the stock solutions), compared to 60 in the case of traditional one ligand per vessel approach. Therefore the assembled ligand systems can easily be adapted for automation. The catalysts library was screened in a parallel fashion in the asymmetric palladium allylic alkylation (scheme 3).  

Figure 5. Results in enantioselective palladium catalyzed allylic alkylation of 1,3-diphenylallyl acetate and dimethyl malonate obtained from a matrix of 1-6 and a-i, yielding a catalyst library of self-assembled bidentate ligands.
The results are depicted in figure 5 and the enantiomeric excess of each ligand assembly is given. For the tested catalysts the enantiomeric excess ranged from 87 % (S) to 86 % (R). Importantly, both ligand components were important for the enantioselectivity, which shows the power of the combinatorial approach using supramolecular techniques.

<table>
<thead>
<tr>
<th>ligand</th>
<th>conversion (%)</th>
<th>e.e. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>56</td>
<td>97 (S)</td>
</tr>
<tr>
<td>3*b</td>
<td>100</td>
<td>60 (R)</td>
</tr>
<tr>
<td>3*c</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>3*d</td>
<td>100</td>
<td>44 (S)</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>96 (R)</td>
</tr>
<tr>
<td>4*b</td>
<td>100</td>
<td>60 (S)</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>42 (S)</td>
</tr>
<tr>
<td>5*b</td>
<td>40</td>
<td>70 (S)</td>
</tr>
</tbody>
</table>

(a) [[Pd(allyl)Cl]₂] = 0.100 mmol/l, [phosphite] = 0.6 mmol/l, [phosphine] = 0.6 mmol/l, the reaction was stopped after 43 hours, T = -20 °C (b) e.e. = enantiomeric excess.

After selection of the “hits” from the catalyst library, the catalytic conditions for these catalyst systems was further optimized, by performing the catalysis at -20 °C (table 5). It was found, that under these conditions the palladium catalyst based on monodentate (S)-ortho-phosphite zinc(II) porphyrin 3 yielded a very high enantioselectivity (97 % (S)). In the presence of 3-pyridyldiphenylphosphine b, giving the assembled phosphine-phosphite ligand 3*b, unexpectedly the configuration of product changed giving enantiomeric excess of 60 % (R). In addition a much higher conversion was obtained. Variation of the b/3 ratio does not influence the enantioselectivity (figure 6), indicating that palladium coordinates exclusively to the chelating assembled bidentate ligand 3*b under catalytic conditions.

Figure 6. Palladium catalyzed allylic alkylation at 25 °C upon variation of 3/b ratio (3/palladium = 1).
The catalyst based on the bidentate assembly of 3-pyridylmethylidiphenylphosphine \( d \) and 3 resulted in the formation of the S-product with an enantiomeric excess of 44%. The assembly 3\( ^e \) did not give enantioselectivity in the palladium catalyzed allylic alkylation. Likely, the conformation of the assembly does not allow bidentate chelation to palladium and as a result the catalysis is dominated by non-chiral palladium phosphine \( d \) species.\(^{34} \) These results show that small changes in the monodentate phosphorus ligands have huge impact on the assembled catalyst systems, as can be concluded from the large variety in enantiomeric excess.

Changing the monomeric phosphite zinc(II) porphyrin ligand from (S)-ortho 3 to (S)-meta 5 affected also the catalytic results. Monodentate ligand 5 gave moderate enantioselectivity in the allylic alkylation (42 % (S)), but the presence of phosphine \( b \) amends the selectivity substantially. Intriguing is the large difference in enantioselectivity found between the bidentate assembled ligands 3\( ^b \) and 5\( ^b \), giving 60 % (R) and 70 % (S) respectively. This shows that small changes in the assembly of the phosphite zinc(II) porphyrin and the phosphorus ligands \( a-i \) change the enantioselectivity induced by the assembled catalyst systems. Apparently, the diversity of the supramolecular catalyst library is sufficient to give catalyst with selectivities ranging from 97 % (S) to 60 % (R).

To extend the scope of catalytic reactions the library of assembled bidentate ligand systems was also used in the rhodium-catalyzed asymmetric hydrogenation of dimethyl itaconate (scheme 4). The catalysts based on the bidentate assemblies of phosphorus ligands \( a-i \) and phosphite zinc(II) porphyrin 3 and 5 showed large differences in conversion and enantioselectivity (table 6). In general, the bidentate assemblies based on phosphite zinc(II) porphyrin 5 resulted in catalysts with lower activity and slight increase in enantioselectivity compared to catalysts based on 5 only. The bidentate assemblies based on phosphite zinc(II) porphyrin 3 resulted also in decrease of activity. Interestingly, the catalysts based on 3\( ^e \) and 3\( ^h \), presenting a match/mis-match correlation between the chiral bidentate assemblies based on (S)- and (R)-pyridyl phosphite ligands \( g \) and \( h \), indeed give different selectivity 24 (S) and 35 (S) respectively.\(^{42} \) Notable are the results obtained with the bidentate assembly based on 3\( ^e \), which in contrast with other assemblies based on 3, showed complete conversion and improved the enantioselectivity of the catalyst significantly 66 % (S).

\[
\text{Scheme 4. Rhodium-catalyzed hydrogenation of dimethyl itaconate.}
\]
Table 6. Rhodium-catalyzed hydrogenation of dimethyl itaconate.\(^a\)

<table>
<thead>
<tr>
<th>ligand</th>
<th>Conversion (%)</th>
<th>ee(^b) [%]</th>
<th>Conversion (%)</th>
<th>ee(^b) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>28</td>
<td>20 (S)</td>
<td>88</td>
<td>16 (S)</td>
</tr>
<tr>
<td>a</td>
<td>14</td>
<td>9 (S)</td>
<td>82</td>
<td>19 (S)</td>
</tr>
<tr>
<td>b</td>
<td>4</td>
<td>18 (S)</td>
<td>19</td>
<td>18 (S)</td>
</tr>
<tr>
<td>c</td>
<td>5</td>
<td>13 (S)</td>
<td>13</td>
<td>25 (S)</td>
</tr>
<tr>
<td>d</td>
<td>1</td>
<td>17 (S)</td>
<td>9</td>
<td>19 (S)</td>
</tr>
<tr>
<td>e</td>
<td>100</td>
<td>66 (S)</td>
<td>13</td>
<td>24 (S)</td>
</tr>
<tr>
<td>f</td>
<td>22</td>
<td>5 (S)</td>
<td>15</td>
<td>21 (S)</td>
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<td>g</td>
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<td>24 (S)</td>
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<tr>
<td>h</td>
<td>1</td>
<td>35 (S)</td>
<td>10</td>
<td>19 (S)</td>
</tr>
<tr>
<td>i</td>
<td>6</td>
<td>6 (S)</td>
<td>19</td>
<td>16 (S)</td>
</tr>
</tbody>
</table>

\(^a\) [Rh(nbd)\(_2\)BPh\(_4\)] = 1.0 mmol/l, [porphyrin] = 3.0 mmol/l, [phosphorous (a-i)] = 3.0 mmol/l, T = 40 °C, the reaction was stopped after 18 hours (b) ee = enantiomeric excess.

6.3 Conclusion

A new effective strategy to simplify the construction of catalysts, facilitating the preparation of larger libraries, is presented. These catalysts are constructed using assembly processes based on selective metal-ligand interactions, which are utilized to assemble monodentate ligands to form a new class of chelating bidentate ligands. For the construction of these catalysts monomeric phosphite zinc(II) porphyrin template molecules 1-6 and phosphorus ligands a-i have been prepared. Upon mixing these monomeric compounds instantaneously self-assembled bidentate ligands are formed, via selective nitrogen-zinc interactions, as has been proven by NMR and UV-vis spectroscopy. From only 16 monodentate ligands a catalyst library based on 60 bidentate assembled ligands has been prepared and was successfully tested in the palladium catalyzed asymmetric allylic alkylation. Some hits were identified and these promising catalyst systems gave high enantioselectivities up to 97 % after optimization. Moreover, for this reaction it was found that small changes in components of the assembled catalyst affected the enantioselectivity enormously. For example, the assembly of 3-pyridyldiphenylphosphine b and phosphite zinc(II) porphyrin 3, preferentially forms the R-product (60 % ee), whereas the catalyst based on 3 gives the S-product 97 % ee. The use of assembled bidentate ligands to make catalyst libraries can also be used to find new rhodium catalysts for hydrogenation and hydroformylation reactions. So far we only showed the phosphite zinc(II) porphyrin 1-6 and the nitrogen donor ligands a-i, but many other (a)chiral building blocks can be used for the ligand assemblies.
6.4 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 benzophenone 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 30m column, film thickness 3.0 μm, carrier gas 70kPa He, FID Detector) equipped with a Hewlett Packard Data system (Chrom-Card). Chiral GC separations were conducted with a chirasil-L-Val capillary column (0.25 mm x 25 m). Chiral HPLC analyses were carried out using a Daicel Chiralcel-OD column (0.46 x 25 cm). 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 compound were synthesized according to published procedures: phosphorochloridites,²⁹ pyridylphosphines b and c,³² phosphines d-f,⁴³ pyridyl phosphites g-i,⁴⁴ hydroxy l porphyrins³¹ and zinc(II) porphyrins were prepared according to the method of Adler.⁴⁵

Synthesis of 5-(2-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin

Salicylaldehyde (200 mmol) and benzaldehyde (200 mmol) were dissolved in 1.0 l of propionic acid and heated till reflux. Under an air flow and vigorous stirring pyrrole (400 mmol) was added and the solution was refluxed for 1 hour. The reaction mixture was cooled to 60 °C and 200 ml of methanol was added. The reaction was stored overnight at 4 °C, allowing the porphyrin to precipitate. The reaction mixture was filtered and washed several times with methanol until the filtrate was colorless. The porphyrin was purified using column chromatography (basic alumina, CH₂Cl₂, upgrade 1 % MeOH in CH₂Cl₂), giving I (1.05 g, 1.66 mmol, 1.7 %).
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**Synthesis of 5-(3-hydroxyphenyl)-10,15,20-tris(phenyl) porphyrin**

3-hydroxybenzaldehyde (6.35 g, 52.0 mmol) and benzaldehyde (15.8 ml, 156 mmol) were dissolved in 750 ml of propionic acid and heated till reflux. Under an air flow and vigorous stirring pyrrole (14.4 ml, 208 mmol) was added and the solution was refluxed for 1 hour. The reaction mixture was cooled to 60 °C and 100 ml of methanol was added. The reaction was stored overnight at 4 °C, allowing the porphyrin to precipitate. The reaction mixture was filtered and washed several times with methanol until the filtrate was colorless. The porphyrin was purified using column chromatography (basic alumina, CH₂Cl₂, upgrade 2% MeOH in CH₂Cl₂), giving 2 (1.09 g, 1.73 mmol, 3.3%).

**Synthesis of (3,3'-5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)-(5-(phenyl-2-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin) phosphite 1**

5-(2-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin (1.59 g, 2.30 mmol), azeotropically dried with toluene (3x5 ml), and disopropylethylamine (4.0 ml, 23.0 mmol) were dissolved in THF (80 ml) and the solution was cooled to 0 °C. Freshly prepared (S)-2,2'-binaphthol phosphorochloridite (0.73 g, 2.09 mmol) was dissolved in THF (20 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 30 minutes. The reaction mixture was filtered and the solvent evaporated. The crude product was purified by flash column chromatography under Argon (basic alumina; CH₂Cl₂) to remove the excess of hydroxyl-porphyrin, giving 1 (0.887 g, 0.88 mmol, 42%) as a purple-red solid: ¹H NMR (300 MHz): δ 8.90 (m, 8H), 8.22 (m, 6H), 8.09 (m, 1H), 7.76 (m, 9H), 7.64 (m, 1H) 7.59 (m, 1H), 7.47 (m, 1H), 7.19 (d, 2H, J = 4.2Hz), 6.93 (d, 2H, J = 4.2Hz), 1.21 (s, 18H), 0.93 (s, 18H); ³¹P NMR (121.5 MHz): δ 133.4; ¹³C-ATP (75.465 MHz): δ 150.67, 150.41, 150.32, 146.63, 145.53, 143.35, 135.89, 134.71, 132.46, 132.46, 132.05, 129.27, 127.61, 126.96, 126.72, 126.68, 122.56, 121.85, 121.07, 35.24, 31.62, 30.95; HRMS (FAB+): m/z calcd. for C₇₂H₆₈N₄O₃PZn ([MH⁺]): 1131.4320; obsd.: 1131.4314; anal. calcd. for C₇₇H₆₂N₄O₃PZn: C, 76.35; H, 5.96; N, 4.95. Found: C, 76.26; H, 6.15; N, 5.06.

**Synthesis of (3,3'-5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)-(5-(phenyl-3-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin) phosphite 2**

This compound was prepared as described for 1, using 5-(3-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin. Yield (47%) as a purple-red solid: ¹H NMR (300 MHz): δ 8.96-8.94 (m, 8H), 8.25-8.20 (m, 6H), 8.01 (s, 1H), 7.95 (d, 1H, J = 8.7Hz), 7.82-7.77 (m, 9H), 7.67-7.62 (m, 1H), 7.49-7.45 (m, 1H), 7.42 (s, 2H), 7.23 (s, 2H), 1.50-1.47 (m, 18H), 1.36-1.32 (s, 18H); ³¹P NMR (121.5 MHz): δ 139.02; ¹³C-ATP (75.465 MHz): 150.77 (C), 150.48 (C), 150.22 (C), 146.98 (C), 144.66 (C), 143.04 (C), 140.42 (C), 137.02 (C), 136.09 (C).
(C), 134.67 (CH), 133.07 (C), 132.23 (CH), 130.68 (CH), 129.12 (CH), 128.45 (CH), 127.75 (CH), 126.80 (CH), 154.54 (CH), 125.07 (CH), 124.60 (CH), 122.56 (C), 122.39 (C), 122.13 (C), 121.41 (C), 119.73 (CH), 35.68 (C), 34.85 (C), 31.70 (CH), 31.47 (CH); HRMS (FAB+): m/z calcd. for C$_{72}$H$_{68}$N$_{4}$O$_{3}$PZn ([$\text{MH}^+$]): 1131.4321; obsd.: 1131.4329; anal. calcd. for C$_{72}$H$_{68}$N$_{4}$O$_{3}$PZn: C, 76.35; H, 5.96; N, 4.95. Found: C, 76.83; H, 6.35; N, 4.68.

**Synthesis of (S)-(1,1'-binaphthyl-2,2'-diyl)-(5-(phenyl-2-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin) phosphite 3**

5-(2-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin (1.59 g, 2.30 mmol), azeotropically dried with toluene (3x 5 ml), and diisopropylethylamine (4.0 ml, 23.0 mmol) were dissolved in THF (80 ml) and the solution was cooled to -40 °C. Freshly prepared (S)-2,2'-binaphtol phosphorochloridite (0.73 g, 2.09 mmol) was dissolved in THF (20 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 30 minutes. The reaction mixture was filtered and the solvent evaporated. The crude product was purified by flash column chromatography under Argon (basic alumina; CH$_2$Cl$_2$) to remove the excess of hydroxyl-porphyrin, giving 3 (0.887 g, 0.88 mmol, 42 %) as a purple-red solid: $^1$H NMR (300 MHz): δ 8.94 (d, 6H, J=4.5Hz), 8.89 (d, 1H, J=4.5Hz), 8.84 (d, 1H, J=4.5Hz), 8.23 (m, 6H), 8.13 (m, 2H), 7.77 (m, 11H), 7.66 (m, 2H), 7.55 (m, 1H), 7.16 (m, 1H), 6.91 (d, 1H, J=8.7Hz), 6.84 (m, 1H), 6.60 (d, 1H, J= 8.1Hz), 6.45 (m, 2H), 6.38 (m, 1H), 5.72 (d, 1H, J=8.7Hz), 5.60 (d, 1H, J= 8.4Hz); $^{31}$P NMR (121.5 MHz): δ 145.15; $^{13}$C-ATP (75.465 MHz): δ 150.62, 150.50, 150.22, 146.43, 145.32, 143.25, 135.79, 134.71, 132.42, 132.12, 131.50-130.22, 128.61, 127.53-126.63, 125.50, 125.21, 122.56, 121.07; HRMS (FAB+): m/z calcd. for C$_{64}$H$_{59}$N$_{4}$O$_{3}$PZn ([$\text{MH}^+$]): 1007.2130; obsd.: 1007.2144; anal. calcd. for C$_{64}$H$_{59}$N$_{4}$O$_{3}$PZn: C, 76.23; H, 3.90; N, 5.56. Found: C, 76.08; H, 4.16; N, 5.42.

**Synthesis of (R)-(1,1'-binaphthyl-2,2'-diyl)-(5-(phenyl-2-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin) phosphite 4**

This compound was prepared as described for 3, using freshly prepared (R)-2,2'-binaphtol phosphorochloridite. Yield (46 %) as a purple-red solid: $^1$H NMR (300 MHz): δ 8.94 (d, 6H, J=4.5Hz), 8.89 (d, 1H, J=4.5Hz), 8.84 (d, 1H, J=4.5Hz), 8.22 (d, 1H, J=4.5Hz) 8.14 (m, 2H), 7.78 (m, 11H), 7.64 (m, 2H), 7.55 (m, 1H), 7.16 (m, 1H), 6.91 (d, 1H, J=8.4Hz), 6.84 (m, 1H), 6.60 (d, 1H, J= 8.1Hz), 6.45 (m, 2H), 6.38 (m, 1H), 5.71 (d, 1H, J=8.7Hz), 5.59 (d, 1H, J= 8.4Hz); $^{31}$P NMR (121.5 MHz): δ 145.13; $^{13}$C-ATP (75.465 MHz): δ 150.62, 150.50, 150.22, 146.43, 145.32, 143.25, 135.79, 134.71, 132.42, 132.12, 131.50-130.22, 128.61, 127.53-126.63, 125.50, 125.21, 122.56, 121.85, 121.07; HRMS (FAB+): m/z calcd. for C$_{64}$H$_{59}$N$_{4}$O$_{3}$PZn
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\[\text{[MH]}^+\] \( \text{obsd.: } 1007.2130 \text{; anal. calcd. for } \text{C}_{64}\text{H}_{40}\text{N}_4\text{O}_3\text{PZn}: \text{C, 76.23; H, 3.90; N, 5.56. Found: C, 76.29; H, 4.14; N, 5.22.} \]

Synthesis of (S)-(1,1′-binaphthyl-2,2′-diyl)-(5-(phenyl-3-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin) phosphite 5

This compound was prepared as described for 3, using 5-(3-hydroxyphenyl)-10,15,20-tris(phenyl)-zinc(II) porphyrin and freshly prepared (S)-2,2′-binaphtol phosphorochloridite. Yield (39 %) as a purple-red solid: \(\text{\textsuperscript{1}H NMR (300 MHz): } \delta 8.97-8.94 (m, 6H), 8.83-8.78 (m, 2H), 8.24-8.21 (m, 6H), 8.04-7.79 (m, 6H), 7.77 (s, 9H) 7.70-7.15 (m, 10H); \text{\textsuperscript{31}P NMR (121.5 MHz): } \delta 142.49; \text{\textsuperscript{13}C-ATP (75.465 MHz): } \delta 150.53 (C), 150.28 (C), 144.83 (C), 143.01 (C), 134.67 (CH), 132.39 (CH), 132.02 (CH), 131.49 (C), 131.15 (CH), 130.76 (CH), 130.23 (CH), 128.61 (CH), 127.83 (CH), 127.31 (CH), 127.26 (CH), 126.83 (CH), 126.71 (CH), 126.63 (CH), 125.50 (CH), 125.23 (CH), 124.99 (CH), 121.49 (C), 120.19 (CH); \text{HRMS (FAB+): } m/z \text{ calcd. for } \text{C}_{64}\text{H}_{40}\text{N}_4\text{O}_3\text{PZn}: \text{[MH]}^+ \text{ calcd. for } \text{C}_{64}\text{H}_{40}\text{N}_4\text{O}_3\text{PZn}: \text{C, 76.23; H, 3.90; N, 5.56. Found: C, 76.29; H, 4.14; N, 5.22.} \]

Synthesis of (S)-(3,3′-bis(trimethylsilyl)-1,1′-binaphthyl-2,2′-diyl)-(5-(phenyl-2-yl)-10,15,20-tris(phenyl)-zinc(II) porphyrin) phosphite 6

This compound was prepared as described for 3, using freshly prepared (S)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridite. Yield (51 %) as a purple-red solid: \(\text{\textsuperscript{1}H NMR (300 MHz): } \delta 9.06 (d, 2H), 8.96 (d, 2H, J = 5.4Hz)), 8.85 (d, 2H , J = 5.1Hz), 8.83 (m, 2H), 8.66 (m, 1H), 8.49 (m, 3H), 8.23 (m, 2H), 8.12 (m, 1H), 7.94 (d, 2H, J = 5.4Hz), 7.84-7.55 (m, 9H), 7.45 (m, 1H), 7.37 (m, 2H), 7.22-7.11 (m, 4H), 6.63 (m, 1H), 8.94 (m, 1H), 5.06 (m, 1H), 4.50 (m, 1H), 0.51 (s, 3H), 0.03 (s, 3H); \text{\textsuperscript{31}P NMR (121.5 MHz): } \delta 150.03; \text{\textsuperscript{13}C-ATP (75.465 MHz): } \delta 150.7, 150.5, 150.4, 145.4, 135.7, 134.7, 132.4, 132.1, 131.5-130.2, 128.7, 127.6-126.5, 125.4, 125.1, 122.5, 121.9, 0.35, 0.20; \text{HRMS (FAB+): } m/z \text{ calcd. for } \text{C}_{70}\text{H}_{58}\text{N}_4\text{O}_3\text{PSi}_2\text{Zn}: \text{[MH]}^+ \text{ calcd. for } \text{C}_{70}\text{H}_{58}\text{N}_4\text{O}_3\text{PSi}_2\text{Zn}: \text{C, 72.93; H, 4.81; N, 4.86. Found: C, 72.96; H, 4.83; N, 4.71.} \]

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 \(\mu\text{mol of } \text{[Rh(acac)(CO)]}_2\), 10.4 \(\mu\text{mol of phosphine and 0.017 ml of dipea in 4.0 ml of toluene. The solution was incubated for 1 under 20 bar CO/H}_2 \text{ (1:1). The pressure was reduced to 1 bar and a mixture of 0.34 ml styrene and 0.17 ml of decane in 0.67 ml of toluene was added. Subsequently the CO/H}_2 \text{ pressure was pressurized to 20 bar. The mixture was stirred, depending on the temperature, for 1 hour (80°C) or 18 hours (40°C). 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 analysis of the crude product after filtration over a plug silica to remove the catalyst. The enantiomeric excess was determined after oxidation of the product to the corresponding alcohol. The crude product mixture of styrene was subjected to reduction with NaBH₄ by stirring in 5.0 ml methanol for 30 minutes. Quenching with water, extraction with a solution of ethyl acetate/hexane = 1/1, drying of the organic layer, filtrations and removal of solvent gave the corresponding alcohols, for which the enantiomeric purities were determined by chiral GC (Cyclosil-B, isothermal; T = 90°C, tᵣ (R) = 63.5 min. and tₛ (S) = 64.8 min.).

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-allylacetae, 150 μmol dimethylmalonate, 150 μmol BSA and 50 μmol decane and a pinch of KOAc were added. The mixture was stirred at 25°C (-20°C) and after 24 hours the reaction was stopped by adding a saturated ammoniumchloride 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 analysis. The solution was chromatographed (SiO₂; petroleum ether/CH₂Cl₂ = 1/1) to give analytically pure products.⁴⁶ Enantiomeric purities were determined by chiral HPLC (OD column, eluens 0.5 % iso-propanol in hexane tᵣ (R) = 33.2 min. and tₛ (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 phosphorus, 1.5 μmol of porphyrin, 1.0 μl of dipea, 50 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 18 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 over silica. Enantiomeric purities were determined by chiral GC (Chirasil-L-Val, isothermal; T = 70 °C, tᵣ (R) = 34.4 min. and tₛ (S) = 35.2 min.).

High-pressure NMR-experiments

In a typical experiment the high pressure NMR tube was filled with (30 μmol) of [Rh(acac)(CO)₂], (75 μmol) of phosphite zinc(II) porphyrin, (75 μmol) phosphine and 1.5 ml of toluene-d₈. The tube was purged three times with 15 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.

6.5 References and Notes

Chapter Six


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37 Low temperature $^{31}$P-NMR spectroscopy ($T = -20 \, ^\circ\text{C}$) of phosphine-phosphite complex 9 showed that the phosphine signal yielded a double doublet ($J_{P,P} = 131 \, \text{Hz}$, $J_{P,PO} = 111 \, \text{Hz}$). This suggest that the phosphine is coordinated in the equatorial plane of the rhodium complex. At the given temperature the phosphite signal still yielded a broadened multiplet and along with the phosphine-phosphite coupling constant ($J_{P,PO} = 111 \, \text{Hz}$), which suggests that the equatorial and apical phosphite coordination to the rhodium is in fast exchange on the NMR spectroscopy time-scale. The high phosphorus-signal of the phosphite ($\delta = 179.8 \, \text{ppm}$) is addressed to steric constraints in the ring-current, as is also found for several other phosphine-phosphite rhodium complexes.


39 It was anticipated that under catalytic conditions only phosphine-phosphite complex 9 was present, leading to high selectivity and poor activity in the presence of 1. Whereas, the presence of bisphosphine rhodium complex 10 would yield higher activity and poorer selectivity as found for complex 10 in absence of 1. In the high-pressure NMR-experiments also small amounts of bisphosphine complex 10 were detected, but this was attributed to the low phosphite/phosphine/rhodium ratio used in the NMR-experiments. Whereas, the presence of bisphosphine rhodium complex 10 would yield higher activity and less selectivity as found for complex 10 in absence of 1.

41 For triphenylphosphine a in presence or absence of a chiral phosphite porphyrin similar results were observed (e.e. = 0 %, complete conversion), which corroborates the formation of non-chiral palladium phosphine catalysts.

42 (S)- and (R)-(1,1'-binaphthyl-2,2'-diyl)-(3-pyridyl) phosphite g and h in absence of phosphite porphyrin yield in the rhodium-catalyzed hydrogenation of dimethyl itaconate an enantiomeric excess of 36 % (S) for g and 36 % (R) for h.


44 See chapter 3 and 4


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