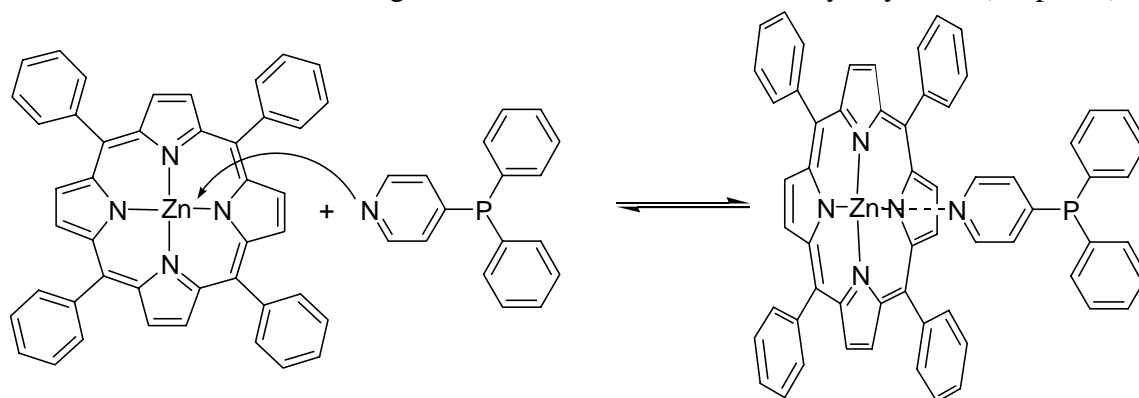


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# Summary

The main objective of this research project has been the development and exploration of novel, supramolecular catalyst systems that are formed by the assembly of several components using non-covalent interactions. The supramolecular strategy involves the multi-component assembly of a transition metal catalyst and various building blocks into a new supramolecular catalyst system. For the preparation of these assembled catalysts selective metal-ligand interactions have been used that control the coordination geometry around the catalytically active metal center and the final shape of the supramolecular catalyst system. Suitable homogeneous transition metal catalysts in combination with properly chosen molecular building blocks led to assembled catalyst systems that improve catalytic properties such as activity and selectivity. Metalloporphyrins and various phosphorus ligands were selected as well-suited building blocks for these assembled catalyst systems (chapter 1).



**Figure 1.**

Zinc(II) porphyrins and phosphorus ligands containing additional nitrogen donor atoms were found to assemble into well-defined supramolecular ligands using selective zinc-nitrogen interactions (figure 1). The phosphorus donor atom remains available for transition metal catalyst coordination, leading to a new, supramolecular catalyst system. Strategic placement of the porphyrins and phosphorus donor ligands enables the formation of larger catalyst assemblies and changes the environment of the coordinating transition metal catalyst. Three porphyrins were assembled around a phosphorus donor ligand, which after the coordination of transition metal catalyst, led to complete encapsulation of the active catalyst. In the rhodium catalyzed hydroformylation of 1-octene this encapsulation yielded ten-fold increase in activity and a high selectivity towards the branched product (~68%) was observed. These catalyst properties cannot be explained by changes in the coordination mode of the catalyst system only and are ascribed to the encapsulation effect of the catalyst (chapter 2).

The major advantage of this non-covalent approach of catalyst preparation is the easy ligand variation and the large number of new ligand systems that becomes accessible by variation of template molecules and phosphorus-nitrogen building blocks. This supramolecular tool enables simple modification of steric and electronic functionalities on the backbone of ligand and template molecule. Importantly, modifications of these properties in a supramolecular fashion have similar effects as those introduced via covalently linked functionalities. Interesting changes have been observed in the enantioselective rhodium-catalyzed hydrogenation of dimethyl itaconate. The ligand assemblies based on zinc(II) porphyrin with electron-withdrawing substituents led to a twelve-fold increase in activity and an increase in enantioselectivity from 17 to 50%. The first examples of assemblies based on non-chiral ligands and chiral zinc(II) porphyrin template molecules show proof of principle in yielding enantiomeric excess in the palladium-catalyzed asymmetric allylic alkylation (e.e. = 18.6 %) (chapter 3).

Selective metal-ligand interactions have also been used to prepare assembled bidentate ligands. Bidentate ligands were easily prepared by mixing monodentate ligands with a suitable template, which were proven to indeed form chelating ligands by selective coordination to the template. For these assemblies pyridine phosphorus ligands and a zinc(II) porphyrin dimer were used. In the rhodium-catalyzed hydroformylation of 1-octene and styrene high selectivities have been observed for some of the assembled bidentate ligand systems. In the palladium catalyzed asymmetric allylic alkylation similar effects were observed; the enantioselectivity increased by using a bisporphyrin template (chapter 4).

The preparation of supramolecular catalyst systems based on selective metal ligand interactions is not limited to selective zinc-nitrogen interactions, since selective ruthenium-nitrogen (chapter 2) or tin-oxygen interactions can just as easily be applied for the multi-component catalyst assemblies. It was shown that dihydroxotin(IV) porphyrin and carboxylic phosphorus ligands assembly into new supramolecular ligands. The phosphorus donor atom coordinated transition metal catalysts and give rise to active supramolecular catalyst systems (chapter 5).

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 and phosphorus ligands containing nitrogen donor atoms have been prepared. Upon mixing these monomeric compounds self-assembled bidentate ligands are formed instantaneously, via selective nitrogen-zinc interactions. From 16 monodentate ligands only, a catalyst library of 60 bidentate assembled ligands has been prepared and they were applied successfully 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 the components of the assembled catalyst affected the enantioselectivity enormously. Assembled bidentate ligands have also been used to make catalyst libraries to find new rhodium catalysts for hydrogenation and hydroformylation reactions (chapter 6).

Multi-component assemblies of monomeric zinc(II) porphyrin phosphite ligands and ditopic template ligands have also been investigated, enabling the formation of new series of self-assembled bidentate ligands. In this approach the variation of the ditopic template ligand should control the shape of the assembled bidentate catalyst systems. It was found that variation of the ditopic template in assembled bidentate ligands steers important key features in several catalytic reactions, changing activity and (enantio)selectivity. Impressive chelate effects were obtained using catalyst assemblies based on two tris zinc(II) porphyrin phosphite and three ditopic templates (dabco), yielding highly symmetrical sandwich type rhodium complexes. Titration experiments monitored by the rhodium-catalyzed hydroformylation of 1-octene showed that variation of the phosphite and dabco ratio results in major changes in activity and selectivity for the assembled bidentate catalyst systems. Furthermore, it was found that the 3:2 sandwich type complex resulted in very high linear/branched ratios, comparing very well with known selective diphosphite ligand systems (chapter 7).

In conclusion, it was demonstrated in this thesis that the assembly of phosphorus ligands, metalloporphyrin building blocks and transition metals form a new, promising class of supramolecular catalyst systems that are effective in various catalytic reactions. These assembled catalyst systems have proven to control key features of catalysts such as activity and selectivity and supramolecular catalysts are a serious alternative for traditional catalysts based on covalently linked ligand systems. The synthesis of the molecular building blocks is relatively simple and is modular in nature, thereby enabling the creation of large varieties of the supramolecular catalyst systems. We expect that this supramolecular approach in catalyst preparation is important for future applications in metal-catalyzed reactions.