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

Homogeneous transition metal catalysis is applied in industry for the production of bulk and fine chemicals and leads to new and more efficient synthetic pathways. The key point in optimizing these homogeneous catalyzed reactions lies in controlling the environment around the transition metal catalyst, which depends on the ligands. Implementing supramolecular strategies in transition metal catalysis results in new means for influencing the nano-environment around the active site. In this thesis we describe a new strategy in supramolecular transition metal catalysis, which comprises the encapsulation of a transition metal inside a self-assembled capsule. This hetero-dimeric capsule is based on one functionalized traditional ligand (or the metal complex thereof) and one calix[4]arene. The capsule’s building blocks associate with one another by the formation of noncovalent bonds. In this thesis we also report that the novel nano-environment created around the encapsulated catalyst influences its catalytic performance. In Chapter 1 (review) we described the application of self-assembled nanocapsules with well-defined cavities as nanoreactors for organic and metal catalyzed transformations.

In Chapters 2 and 3 we described the self-assembly and characterization of novel heterodimeric diphosphine capsules formed by multiple ionic interactions and composed of a tetracationic diphosphine ligand and a complementary tetraanionic calix[4]arene (Scheme 1). Encapsulation of a palladium atom within the diphosphine capsule is achieved by using the metal complex of the tetracationic diphosphine ligand for the assembly process (Scheme 1). In this templated approach to metal encapsulation, the transition metal complex is an integrated part of the capsule with the transition metal located inside the capsule and it is not involved in the assembly process. We showed that the encapsulated palladium retains its reactivity. The scope of the diphosphine- and the metallo-diphosphine capsules is easily extended by applying tetracationic diphosphine ligands with different backbones and cationic binding motifs. These tetracationic building blocks with different flexibilities and shapes, readily associate into capsules with the proper capsular structure.

**Scheme 1** Self-assembly of a metallo-diphosphine capsule.
In Chapter 4 we demonstrated that the coordination geometry around a platinum atom can be controlled by a diphosphine capsule composed of a tetracationic xantphos-type ligand and a tetraanionic calix[4]arene. Reaction of the diphosphine capsule with a platinum precursor yields the bis-calix[4]arene bisligated trans-platinum capsule, while the same diphosphine in the absence of calix[4]arene prefers the formation of the monoligated cis-platinum complex (Scheme 2). The two calix[4]arenes stabilize the kinetic product (trans-Pt), and thereby slow the formation of the thermodynamic product (cis-Pt).

\[ \text{Scheme 2 Control of the coordination geometry around platinum by a diphosphine capsule.} \]

In Chapter 5 we demonstrated that the approach for metal encapsulation inside ionic-based diphosphine capsules, can easily be extended to give bismetallo-capsules. We reported on the encapsulation of a rhodium metal inside a diphosphine capsule composed of a novel tetraanionic diphosphine ligand and a tetracationic calix[4]arene (Figure 1a). In addition, we described bis-diphosphine capsules, composed of two oppositely charged diphosphine ligands (Figure 1b). Replacing the two oppositely charged ligands with their corresponding transition metal complexes results in the simultaneous encapsulation of two different transition metals in one cavity (Figure 1c). These bismetallo-capsules are potentially useful as bimetallic catalysts.

\[ \text{Figure 1 Metallo-diphosphine capsule (a), bis-diphosphine capsule (b), bis-metallo capsule (c).} \]
In Chapter 6 we described the encapsulation of a rhodium catalyst within a diphosphine capsule composed of a tetracationic xantphos-type ligand and a tetraanionic calix[4]arene, and its application as a homogeneous catalyst for the hydroformylation of styrene, 1-octene and 4,4,4-triphenylbut-1-ene (Scheme 3). Catalyst encapsulation protects the metal center against rhodium dimer formation, induce substrate selectivity and product chemoselectivity and results in lower activity and in different product regioselectivities compared with the non-encapsulated analogue. Catalysis results and molecular modeling studies show that the substrate is not necessarily encapsulated during the catalysis. The restricted nano-environment around the rhodium catalyst dictates the orientation of the alkene and reduces the substrate’s rotational freedom which is required for the selectivity determining hydride migration. The product inhibition observed upon catalyst encapsulation is likely caused by interactions of the aldehydes with the capsule’s ionic substituents and/or due to a higher affinity of the aldehyde for the capsule’s cavity compared to the alkene. A kinetic study shows an exceptional almost second-order in styrene concentration (1.70) for the encapsulated catalyst, which suggests that two styrene molecules are involved in the catalytic cycle: one which undergoes hydroformylation and a second non-coordinating styrene molecule accommodated inside the capsule’s cavity.

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\text{Scheme 3 Alkene hydroformylation catalyzed by encapsulated rhodium.}
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In Chapter 7 we reported the synthesis of novel xantphos-type ligands functionalized with four identical hydrogen bonding motifs, i.e. tetraglycoluril-xantphos and tetraurea-xantphos (Figure 2). In non-competitive solvents the self-complementary ligands form disordered aggregates. Apparently, a better pre-organization of the building blocks is required to form selectively defined supramolecular architectures such as dimeric capsules. However, further study is needed in order to find out the exact nature of the assembly’s in solution.

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\text{Figure 2 Tetraglycoluril-xantphos and tetraurea-xantphos.}
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In this thesis we have successfully introduced a new supramolecular strategy in transition metal catalysis for creating a well defined nano-environment around a transition metal catalyst. Encapsulation of a transition metal catalyst inside a self-assembled capsule influences the catalyst’s performance in the hydroformylation reaction. The capsules presented here are accessible by using building blocks with different shapes and flexibilities, and therefore can be broadly applied. The approach for metal encapsulation presented in this thesis can be extended to create a specific, defined cavity around catalyst and substrate, which may mimic the cavity of an enzyme, and this way introduce new opportunities for catalysis.