Summary

Catalysis is immensely important for the chemical industry to meet the demands of modern society in terms of chemical products. Whenever selectivity is an issue, it might be attractive to have the possibility to change the selectivity of a chemical process to meet a change in demand. Supramolecular chemistry gives the possibility to change the reactivity of a catalyst by simple self-assembly, and in some cases the changes can be quite spectacular. A supramolecular catalyst system for hydroformylation, published by our group some years ago certainly falls in this category. These catalysts consist of a rhodium center ligated by pyridylphosphine(s) through phosphorus. Each pyridine group is coordinating to a building block containing a Lewis acidic, but not catalytically active metal center. One of the most successful members of this catalyst family in changing the reactivity compared to the non-associated system is the system depicted in Figure 1. Here, the ligand is tris-*meta*-pyridylphosphine, and zinc(II)tetraphenyl-porphyrin building blocks encapsulate the catalytic center. This catalyst is ten times more active than the non-encapsulated counterpart, and preferentially produces the branched product (l/b =

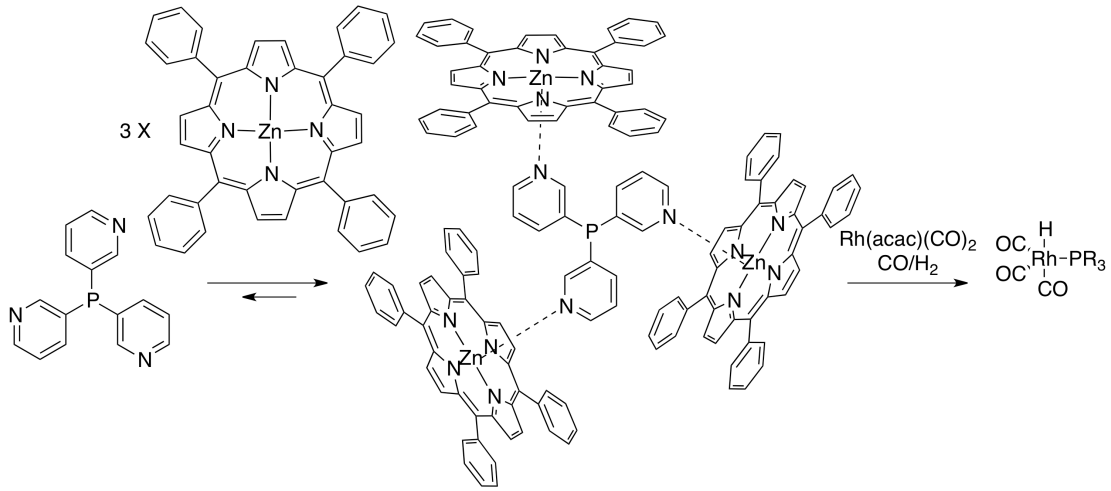

Figure 1. The self-assembly of the tris-*meta*-pyridylphosphine/Zn(II)porphyrin capsule followed by coordination of rhodium to form the active hydroformylation catalyst.

0.6), whereas the non-encapsulated catalyst preferentially produces the linear product (l/b = 2.8). Spectroscopic studies showed that the encapsulated catalyst exists as a monoligated (by phosphine) rhodium species, which is unusual, but conceptually easily understood: There is simply no space for a second ligand. This thesis deals with experimental and theoretical studies, aimed at gaining a better understanding of the mechanism by which these catalysts operate, focusing on the rate acceleration and the high branched-selectivity.

Chapter 1 gives an introduction to several aspects of hydroformylation in general, as well as to the supramolecular systems described above.

In chapter 2, DFT calculations are presented on the parent triphenylphosphine catalyst system. Although this system is well known, it has never been thoroughly determined how the reactivity changes when going from the bisligated to the monoligated catalyst. Experimentally this is not possible because the monoligated rhodium is in equilibrium with both the bisligated and the non-ligated species, so that under conditions where appreciable amounts of monoligated species are present, also the other complexes are present. The full catalytic cycles were calculated for the hydroformylation of ethene using non-dispersion-corrected DFT. However, these calculations showed some inconsistencies in the relative stability of the mono- and bisligated species, as well as in the relative reaction rates compared to what is known from experiments. Therefore, the key hydride migration step was recalculated with propene as the substrate and using dispersion corrections. This removed said inconsistencies, and allowed us to model the selectivity. The DFT calculations confirm that the monoligated catalyst is more active, and indeed the acceleration that was calculated matches with those observed for the encapsulated catalyst. The calculated l/b ratio is lower for the monoligated species than for the bisligated species, but the reduction is much smaller than that observed experimentally with the encapsulation of the catalyst. This means that the change in activity observed in the encapsulated catalyst can be fully attributed to the change in ligand coordination mode, but the change in selectivity cannot. Interactions between the substrate and the building blocks might additionally play a role in pushing the selectivity towards the branched product.

The kinetics of the hydroformylation reaction have been studied rigorously in the past, and two simple models exist to describe the two most common kinetic types

found in hydroformylation (type I and type II). These models do not say anything about selectivity however, and more problematically, they are not able to describe the kinetics of the tris-*meta*-pyridylphosphine/zinc(II)tetraphenylporphyrin system (as shown in chapter 4). In chapter 3 a general model for hydroformylation is described that explicitly takes the linear and branched cycles into account. It is shown that the kinetics of each cycle influence the kinetics of the other, resulting in a complex system. This model can be used to describe systems displaying both type I and type II kinetics, as shown by fitting it to data from the literature.

In chapter 4 experiments are described to measure the kinetics of the tris-*meta*-pyridylphosphine/zinc(II)tetraphenylporphyrin system using gas-uptake measurements. Several steady-state models are compared in their ability to describe the hydroformylation kinetics, and it is shown that the standard type I and type II models do not describe the experimental results adequately. The model from chapter 3 works much better, but an even better description can be obtained by moving away from the steady-state approximation using a fully dynamic model. Both the steady-state and the dynamic model show that the branched acyl species is the dominant resting state, and that its formation is (almost) irreversible. Because of this, the catalyst has to pass through the hydrogenolysis to produce the branched product before entering the linear cycle. This, in combination with a fast branched cycle, causes the high branched selectivity.

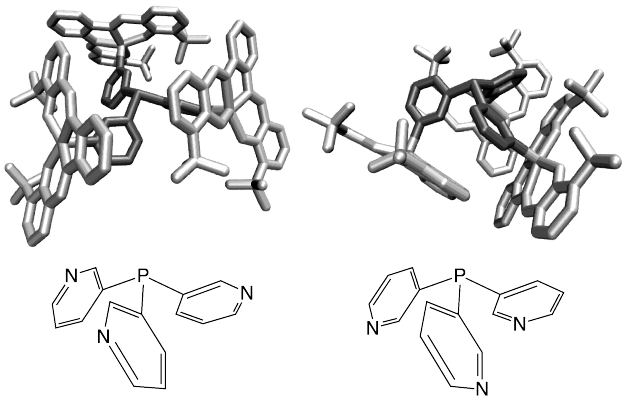

Figure 2. The assembly of tris-*meta*-pyridylphosphine with a zn(II)salphen building block exhibits two conformations in the solid state.

In chapter 5 experimental and theoretical studies are described of catalysts making use of zinc(II)salphens instead of porphyrins. These catalysts show the same trends upon association of the building blocks as the porphyrins, but the changes are less

pronounced. An X-ray crystal structure of the pyridylphosphine with the salphen building blocks showed the co-crystallization of two conformers alternating in the crystal lattice (Figure 2). This shows that multiple conformations are accessible, but not to what extent they play a role in solution. This was investigated with NMR studies and molecular dynamics simulations. From these it was concluded that conformational exchange is very fast, even without dissociation of the building blocks, and that therefore multiple conformations are indeed accessible in solution. As a consequence, the salphen complexes do not result in fully encapsulated ligands, and mixtures of mono- and bisligated rhodium complexes are formed during catalysis. This results in lower branched-selectivity and a lower rate acceleration.

To summarize, we have studied supramolecular catalysts making use of both experimental and theoretical approaches. In this manner we were able to understand the behavior of these supramolecular complexes at the molecular level. We were able to give an explanation for both the increase in activity and the change in selectivity when the porphyrin building blocks are used. At the same time we were able to show why these changes are much less pronounced when using the salphen building blocks. Hopefully, understanding how these catalysts work facilitates the design and development of the next generation of hydroformylation catalysts.