Summary

In this thesis the research into the applications of calixarene based phosphites in homogeneous catalysis is described. The introduction (Chapter 1) describes how calixarenes were discovered, how they are synthesised en what their (physical) chemical properties are. Also a concise review of the, for this thesis relevant, literature is given. This mainly concerns complex chemistry with transition metals using sulfur and phosphorus containing calixarenes. At the end of Chapter 1 the aim of the research is explained.

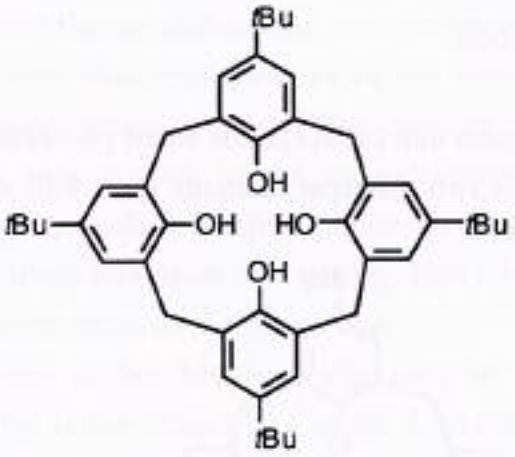

Figure 1 A calix[4]arene.

Chapter 2 describes the use of oxacalix[3]arene based phosphites in the rhodium catalysed hydroformylation of alkenes. An example of an oxacalix[3]arene phosphite is depicted in Figure 2.

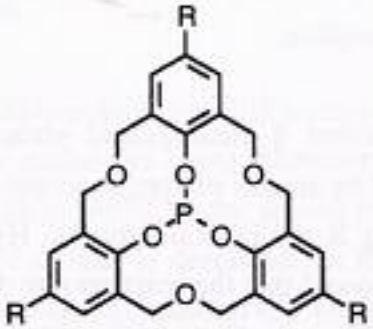

Figure 2 An oxacalix[3]arene phosphite.

Phosphites based on oxacalix[3]arenes can now be synthesised in high yield (ca. 80%). The structure of these phosphites is elucidated by means of NMR techniques and X-ray crystallography. These techniques show that the ligand has a shallow bowl shape. A metal atom that coordinates to the phosphite is embedded in this bowl and is shielded. This

leads to very high catalytic activities in the rhodium catalysed hydroformylation of alkenes to aldehydes with Turn-Over-Frequencies as high as 30,000 molecules per rhodium atom per hour. The selectivity towards the production of linear aldehydes is higher than that observed for equally fast catalysts that are based on other phosphites (see Figure 3).

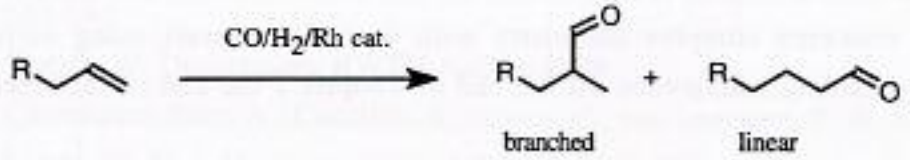

Figure 3 Hydroformylation.

In Chapter 3 the research into calix[4]arene based phosphites is described. In the synthesis of these phosphites two different methods were followed that yielded three types of phosphites.

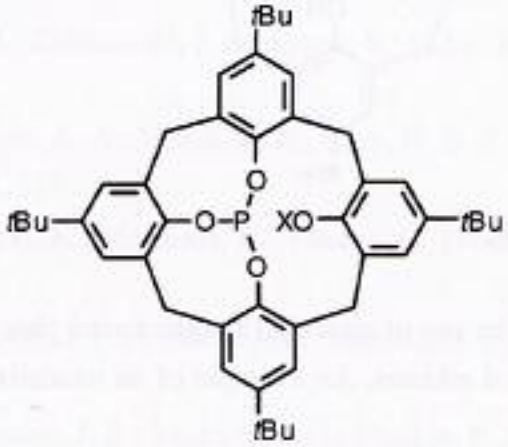

Figure 4 Calix[4]arene phosphite.

These three types have different 3-dimensional structures (conformation). This conformation was characterised by means of spectroscopic techniques (^{1}H, ^{13}C and ^{31}P NMR) and in some cases using X-ray crystallography. Hydroformylation experiments using 1-octene as a substrate, showed that the reaction rate depended on the conformation of the calix[4]arene phosphite. The selectivity of the catalyst for the linear product was, to a certain extent, influenced by the size of the substituent on the phosphite (X). How this selectivity is effected is not clear yet.

Chapter 4 describes the synthesis of *syn*-calix[6]arene diphosphite, the synthesis of complexes with this ligand and the use of a palladium complex in the homogeneous catalysed copolymerisation of carbon monoxide and ethene. The diphosphite can be synthesised in reasonable yield from calix[6]arene and PCl_3.

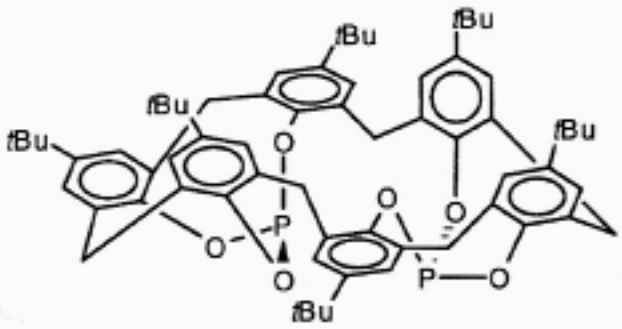

Figure 5 *syn*-Calix[6]arene diphosphite.

In the synthesis of calix[6]arene diphosphite two conformations were found. Only the conformation having both phosphite moieties on the same side of the molecule (*syn* conformation) was suitable for our purpose. This conformation is depicted in Figure 5. The diphosphite is a very suitable ligand for palladium and platinum. A cationic calix[6]arene diphosphite-palladium complex turned out to be a very active catalyst in the coploymerisation of carbon monoxide and ethene. This diphosphite is the only known phosphite that forms active catalysts in this reaction.

The calix[6]arene diphosphite was also used in two other, homogeneously catalysed reactions. This is the subject of Chapter 5. In the first part of Chapter 5, the nickel-catalysed reaction of styrene and HCN (hydrocyanation) is described.

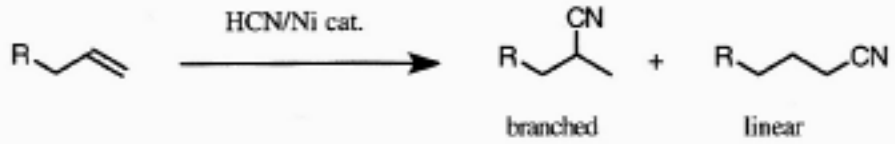

Figure 6 Hydrocyanation.

The catalyst, a calix[6]arene diphosphite-nickel(0) complex, was very active (Turn-Over-Frequency = 900 mol per mol nickel per hour). Moreover, the selectivity for the desired branched product was very high (> 99%). In the second part of this Chapter the rhodium-catalysed hydroformylation of styrene is described. In this reaction too a high rate was observed, together with a relatively high selectivity for the linear aldehyde. The activity and the selectivity of the catalyst were mainly dependent on the ligand/rhodium ratio that was applied, and the incubation time.