

Summary

The work reported in this thesis describes the use of calixarene frameworks as bulky platforms for the synthesis of novel phosphorus-containing bidentate ligands. The introduction (Chapter 1) gives an overview on the most recent phosphorus-modified calixarenes reported in literature, which have been investigated for their complexation properties towards transition metal centres and have been applied as ligands in metal-catalysed transformations.

In the other chapters, various calix[4]arene-based phosphites are described together with one series of phosphorus ligands built up on large calix[8]arene macrocycles. In both types of bidentates, at least one μ_3 -bridging phosphite unit was introduced at the lower rim the calixarene cavity. It is known that the combination of a triple *O,O,O*-bridging phosphorus atom with a calixarene framework leads to robust calixarene-based phosphites that exhibit higher thermal and hydrolytic stability compared with other triaryphosphites and thus, represent an attractive class of ligands to be applied in homogenous catalysis.

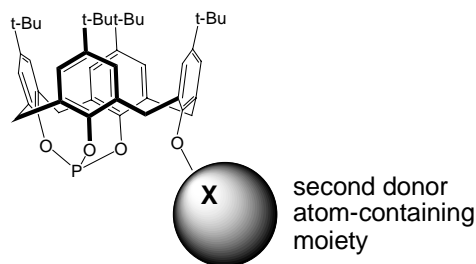


Figure 1. General structure of calix[4]arene-based bidentate ligands.

Different phosphorus-based ligands have been generated on the basis of the general structure depicted in Figure 1, through a semi-modular approach that consists in the variation of the properties of the auxiliary function. In order to obtain bidentate ligands with chelating properties and thus, calixarene frameworks characterised by an overall *cone* conformation, a general two-step synthesis was developed. All the ligands have been conformationally characterised by means of spectroscopic techniques (^1H , ^{13}C , ^{31}P and ^{15}N NMR) and, in some cases, using X-ray crystallography.

Chapter 2 describes the synthesis of a series of extremely bulky bidentate ligands obtained by lower rim-coupling of two calix[4]arene cavities (Figure 2). Six ligands, characterised by different bridging units, have been obtained and their coordination properties towards Pd(II), Pt(II) complexes investigated. When biscalic[4]arene diphosphites were applied in the rhodium-catalysed hydroformylation of 1-octene, the corresponding catalytic systems showed good activity but very poor regioselectivity towards linear aldehydes.

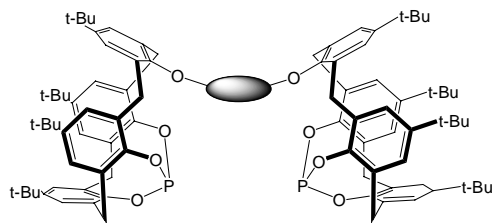


Figure 2. General structure of bis(calix[4]arene)-based diphosphites.

In *Chapter 3*, we used a quinoline fragment as a nitrogen donor atom-containing moiety, obtaining the first heterofunctionalised P,N- ligand built up on a calix[4]arene matrix (Figure 3). Due to the intrinsic hemilability of this ligand, different coordination modes have been observed depending on the nature of the transition metal precursor employed. Upon extensive complexation studies, it was found that spectroscopic parameters, such as the chemical shift of the proton H^{δ} of the quinoline unit as well as the signals of the methylene bridges of the cavity (ArCH₂Ar) in the ¹H NMR spectra, can give a clear indication about the mono- or bidentate behaviour of the P,N-ligand in the various complexes. The coordination modes of the calix[4],quinoline-based ligand were also deduced from ¹⁵N NMR data and, for some complexes, from X-ray crystal structure analysis.

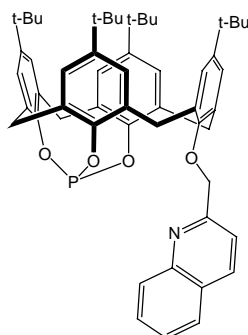


Figure 3. Calix[4],quinoline-based P,N-ligand.

Chapter 4 described the synthesis of novel C_1 -symmetric diphosphite ligands built up on a calix[4]arene backbone (Figure 4). These ligands, which contain a BINOL- or a TADDOL-based phosphite moiety, can coordinate to transition metal centres in a chelating manner, as it was established by NMR spectroscopy and X-ray crystallography. When applied in the rhodium-catalysed hydrogenation of prochiral olefins, the chiral ligands have been found to lead to active and enantioselective catalytic systems reaching excellent enantioselectivities in the hydrogenation of dimethyl itaconate and methyl α -acetamidoacrylate. In the asymmetric hydroformylation of styrene hardly any enantiomeric excess could be obtained. Studies of hydridorhodium

[HRh(CO)₂(P₁[∧]P₂)] complexes under syngas pressure revealed fluxional behaviour on the NMR time scale, which is believed to be responsible for the low asymmetric induction observed in catalysis. The mechanism proposed for the structural rearrangement operates via a rapid exchange of the axially-coordinated phosphorus atom between the axial and the equatorial position.

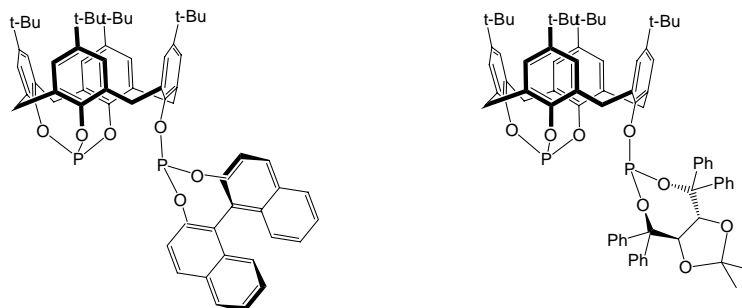


Figure 4. Chiral calix[4],BINOL- and calix[4],TADDOL-based diphosphites.

In *Chapter 5* the larger calix[8]arenes have been considered as bulky backbones for the construction of bidentates (Figure 5). Analogously to the previously reported calix[4]-based ligands, μ_3 -bridging phosphorus atoms tethered at the lower rim of the cavity, have been chosen for the construction of robust diphosphites.

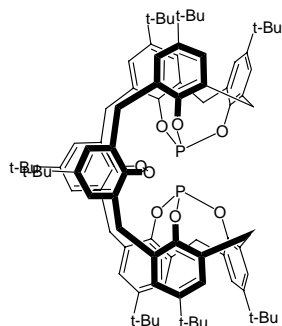


Figure 5. General structure of calix[8]arene-based diphosphite ligands.

In order to obtain diphosphite ligands with the proper structural features, the macrocycle was selectively 1,5-intrabridged prior to P-functionalisation. NMR spectroscopy and X-ray crystallography proved unambiguously that the diphosphite ligands obtained via this route exist as two different stereoisomers, in which the two μ_3 -bridging phosphite units can be *SYN* or *ANTI* oriented with respect to the main calixarene reference plane.