
Conclusions

The conclusions of Chapter 2, *Carbohydrate derivative diphosphite ligands in asymmetric catalysis*, can be summarised as follows:

- New diphosphite ligands (**74-76**) with C_2 -symmetry and a tetrahydrofuran backbone have been synthesised in moderate to good yields starting from D-glucosamine, D-glucitol and (2*S*,3*S*)-diethyl tartrate. The structure of diphosphite ligands **74-76** was determined by one-dimensional ^1H , ^{13}C and ^{31}P NMR. Monocrystals of **74a** suitable for X-ray diffraction were obtained and the structure of **74a** could be proved unambiguously by single crystal X-ray diffraction. The tetrahydrofuran backbone showed a twisted conformation.
- The Rhodium cationic complexes of diphosphite ligands of general formula $[\text{Rh}(\text{cod})(\text{L})]\text{BF}_4$, (L= **74a-c**, **74'a,b**, **75a**, **75'a** and **76a-b**) were prepared by reacting $[\text{Rh}(\text{cod})_2]\text{BF}_4$ with the respective ligands. The structure of the rhodium complexes **90-92** was elucidated by NMR spectroscopic techniques. Monocrystals of the complexes $[\text{Rh}(\text{cod})(\text{74a})]\text{BF}_4$ (**90a**) and $[\text{Rh}(\text{cod})(\text{75'a})]\text{BF}_4$ (**91'a**), suitable for X-ray diffraction, were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. The rhodium atom is coordinated in both molecules in a slightly distorted square planar geometry.
- This new family of diphosphite ligands has been applied to the rhodium-catalysed asymmetric hydroformylation of styrene and related substituted vinyl arenes. High regioselectivities to the branched aldehyde (up to 90%) and moderate enantioselectivities (up to 46%ee) were obtained in the asymmetric hydroformylation of styrene. In the hydroformylation of *p*-methoxystyrene was obtained 60% of enantioselectivity. The configuration and substitution of the remote stereocenters at positions 2 and 5 of the tetrahydrofuran ring were observed to have a considerable influence on the enantioselectivity. The most significant result is that the configuration of



the major isomer obtained in the hydroformylation reaction can be controlled by changing the configuration of these stereocenters.

- The intermediate species in hydroformylation with diphosphite ligands **74a**, **74b**, **74'a**, **75a**, **75'a** and **76a** were studied by high pressure-NMR spectroscopy. These species were prepared *in situ* under hydroformylation conditions, observing that the formation of the hydridorhodiumcarbonyl specie was very slow. The small $^2J_{P-H}$ coupling constants (2.0 to 9.0 Hz) and the large $^1J_{Rh-P}$ coupling constants (230.0 to 234.1 Hz) indicate that the ligands coordinate in an equatorial-equatorial fashion in the trigonal-bipyramidal hydridorhodiumcarbonyl species. The low temperature study of the hydridorhodiumcarbonyl species under hydroformylation conditions detected that the phosphorous atoms were non equivalent, which proved the C_1 -symmetry of these complexes.
- Rhodium complexes were tested in the asymmetric hydrogenation of methyl acetamidoacrylate. The conversions and the enantioselectivities were low and were mainly influenced by the substitution in the biphenyl moiety and by the configuration of the remote centres at positions 2 and 5 of the tetrahydrofuran ring.

The conclusions of Chapter 3, *Rhodium-diphosphite catalysed hydroformylation of allylbenzene and propenylbenzene derivatives*, can be summarised as follows:

- The use of rhodium-diphosphite based systems in the hydroformylation of *trans*-anethole **1a** and estragole **2a** has not been previously reported. In this study, rhodium-diphosphite system **6** was used in the hydroformylation of *trans*-anethole **1a** and led to high selectivities on aldehyde **3a** (as high as 86%) under mild conditions (60°C, 40 bar). This is not so different from the diphosphine ligands used before which afforded up to 93% of aldehyde **3a** with BISBI ligand. We also observed that our diphosphite **6** based system is more active in this reaction than phosphine ligands in similar reaction conditions. When rhodium-diphosphite **7** was used in the *trans*-anethole **1a** hydroformylation, the regioselectivity was lower than when

diphosphite **6** was used. We attributed this to the formation of a seven-seven member chelate ring of diphosphite **7** when it coordinates to the rhodium. On the other hand, in the hydroformylation of this substrate new chiral centers (in aldehydes **3a** and **4a**) are formed by the introduction of formyl groups. We also studied the asymmetric induction of the two diphosphite chiral ligands **6** and **7** in this reaction. We only observed low enantioselectivities in the case of diphosphite **6** in *trans*-anhetole **1a** hydroformylation.

- In the hydroformylation of estragole **2a**, we used rhodium-diphosphite **6** ligand. In this case, regioselectivities on the branched aldehyde **4a** were low (47% of **4a** and 53% of **5a**) when excess of ligand was added. We also investigated the enantioselectivity but we did not observe asymmetric induction in the conditions studied.

The conclusions of Chapter 4, *Metal nanoparticles stabilized by chiral ligands with carbohydrate backbone*, can be summarised as follows:

- New palladium, ruthenium and rhodium nanoparticles have been successfully synthesised in the presence of carbohydrate derivative ligands (**1-4**). We observed that the shape, size and dispersion of the nanoparticles depend strongly on the metal precursor and the stabiliser used.
- Palladium nanoparticles were synthesised from $[\text{Pd}_2(\text{dba})_3]$ with phosphite ligands **2** and **3** and phosphine-phosphite ligand **4** as stabilisers. The synthesis was done following the organometallic approach, at room temperature and under 3 bars of hydrogen pressure. In the presence of diphosphite ligands, small nanoparticles (diameter *ca.* 3.5-4 nm) well-crystallised and contain a few agglomerates were obtained. When phosphine-phosphite ligand **4** was used as stabiliser, smaller nanoparticles could be prepared. This indicates that the nature of the ligand has a strong influence on the morphology of the nanoparticles synthesised. We also studied the effect of the temperature and the palladium/ligand ratio on the nanoparticles stabilised with phosphine-phosphite ligand **4**. We observed



that an increase in the temperature or the quantity of ligand did not improve the results and led to more agglomeration and no well crystallisation.

- Ruthenium nanoparticles have also been synthesised by the organometallic approach using $[\text{Ru}(\text{C}_8\text{H}_{10})(\text{C}_8\text{H}_{12})]$ as metal precursor and diphosphite ligands **1** and **3** as stabilisers, at room temperature under 3 bars of hydrogen pressure. When diphosphite ligand **1** was used as stabiliser, nanoparticles were well-crystallised with a mean diameter *ca.* 3 nm. However, when diphosphite ligand **3** was used not well-crystallised nanoparticles were obtained.
- Rhodium nanoparticles were obtained by decomposition of two different rhodium precursors, $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ and $[\text{Rh}(\mu\text{-OMe})(\text{COD})]_2$, following the organometallic approach. The rhodium nanoparticles produced from $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ were synthesised in tetrahydrofuran in the presence of diphosphite ligands **1** and **3** as stabilisers at room temperature and under 3 bars of hydrogen pressure. In these conditions small and well-crystallised nanoparticles were obtained. The rhodium nanoparticles synthesised from the precursor $[\text{Rh}(\mu\text{-OMe})(\text{COD})]_2$ were stabilised with PVP (polyvinylpyrrolidone MW= 40000) and diphosphite ligands **1** and **3**, giving rise, respectively, to small and well-crystallised nanoparticles with PVP and large particles with diphosphite ligands. Although further study is required if it is to be determined whether these particles are really large, porous and polycrystalline or whether they consist of small individual nanoparticles, we can conclude that the nature of the metal precursor affects the particles synthesised.
- In collaboration with the Universitat de Barcelona and Laboratoire de Chimie de Coordination CNRS (Toulouse), we have studied the application of palladium nanoparticles stabilised with diphosphite ligands **2** and **3**, **Coll.2** and **Coll.3**, respectively, in palladium-catalysed allylic alkylation of rac-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate. **Colloid.2** system was not stable under catalytic conditions showing not reproducible results.

Colloid.3 system led to an enantiomeric excess of >98%(S) in II with high kinetic resolution in the substrate (rac-I) (98% (S) in the remaining substrate) at 73% of conversion after 9 hours of reaction. This behaviour is similar to that of the previously reported for **Colloid.1**.

- We studied the use of rhodium nanoparticles, synthesised from $[\text{Rh}(\mu\text{-OMe})(\text{COD})]_2$ in the presence of diphosphite ligands **1** and **3** (**Colloid.12** and **Colloid.13**, respectively), as catalyst in the styrene hydroformylation reaction. In both cases the activities were very low. The introduction of an excess of ligand increased the regioselectivity and enantioselectivity. The respective molecular system of **Colloid.12**, **Molecular.12**, and the poisoning test were studied in order to exclude the possible formation of homogeneous catalyst in the colloidal system. The results are difficult to analyse and further analysis are needed to be able to clearly conclude.