
SUMMARY

The hydroformylation process is one of the most important industrial applications of homogeneous catalysis. Hydroformylation involves the reaction of hydrogen and CO with an alkene, thereby generating an aldehyde. Starting from a terminal alkene, both normal and branched aldehydes are formed. In general, the normal product is the desired one. It is converted to solvent alcohols, plasticiser alcohols and detergents. Industrially, cobalt and rhodium derived catalysts are used: cobalt mainly for the hydroformylation of higher alkenes and rhodium for low molecular weight alkenes, such as propene. The main obstacle for commercial exploitation of the far more active and selective rhodium catalysts in the hydroformylation of *higher* alkenes is separation of the rhodium metal from the high-boiling aldehydes. The required high distillation temperatures give rise to substantial catalyst loss which is economically feasible for cobalt but not for rhodium, which is several thousands of times as expensive.

Several concepts concerning the separation of the rhodium catalyst from the high-boiling aldehydes, other than distillation, have been investigated. Promising methods are immobilisation of the catalyst by either anchoring onto a support or by confinement to a solvent immiscible with the solvent containing the products. The latter field can be divided into two basically different approaches. The most extensively studied approach is two-phase catalysis, in which usually the catalyst is located in water and the reagents in an organic solvent. The other approach involves the extraction concept in which the catalyst is extracted from a homogeneous reaction medium in a second step.

This thesis describes a study of a process for the rhodium catalysed hydroformylation of higher alkenes. The rhodium catalyst is recycled via extraction into an aqueous phase using amphiphilic ligands. The corresponding amphiphilic rhodium catalysts have the advantage that they can switch between an organic and an aqueous phase by varying the pH of the system. Hence, the catalysis can be conducted in a homogeneous, organic phase with a concomitantly high reaction rate. After (partial) conversion of the alkene, the catalyst is extracted into an aqueous layer of the appropriate pH, thus allowing separation of the catalyst and the organic product. The rhodium catalyst is recovered by neutralisation of the aqueous layer and subsequent extraction into a new batch of organic solvent and/or substrate. The rhodium recycling procedure has been investigated and optimised using a series of amphiphilic ligands based on PPh_3 (Chapter 2 and 3). However, a commercial rhodium-based hydroformylation process of higher alkenes also calls for the highest possible yield of normal aldehydes. Therefore, a high ratio of normal and branched aldehydes (n/b) is pivotal while isomerisation of the double bond, a disturbing side reaction in the rhodium

catalysed hydroformylation, should be minimised. In the last decade, several ligand systems have been reported which give rise to selectivities higher than those obtained with systems based on PPh_3 . Hence, the research has been extended to the synthesis of novel amphiphilic analogues of these diphosphines, which are depicted in Figure 1 (Chapter 4, 5, and 6).

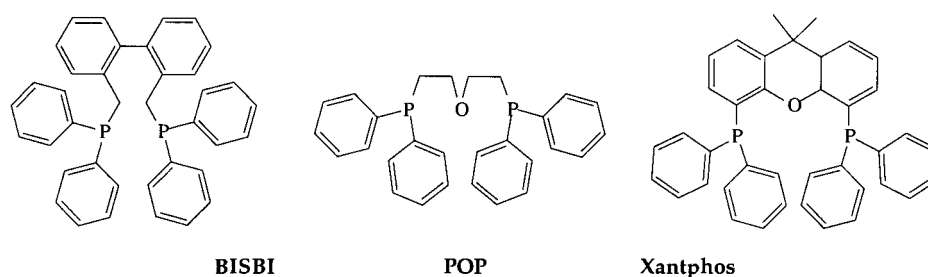


Figure 1—The diphosphines inducing high selectivity

Chapter 2 describes the syntheses of the amphiphilic PPh_3 -based ligands comprising Ph_2ArP (Ar=3-hydroxyphenyl, 4-carboxyphenyl), $\text{Ph}_n\text{Ar}_{3-n}\text{P}$ (Ar=4- $\text{C}_6\text{H}_4\text{CH}_2\text{X}$, X=NEt₂, NMePh, NPh₂; n=1-2) and $\text{Ph}_n\text{Ar}_{3-n}\text{P}$ (Ar=3/4-pyridyl; n=1-2). In the hydroformylation of oct-1-ene most ligands have reaction rates comparable with that of triphenylphosphine, whereas the pyridyl-phosphines are up to two times faster. The selectivity of the hydroformylation is not affected by the modifications and in all cases aldehydes are formed with a n/b-ratio of 2.8. $\text{Ph}_2\text{P}(4\text{-C}_6\text{H}_4\text{COOH})$ shows low catalytic activity under standard conditions. This has been ascribed to the formation of polymeric rhodium carboxylate structures under reaction conditions. Preliminary experiments have shown that $\text{PhP}(4\text{-C}_6\text{H}_4\text{CH}_2\text{NEt}_2)_2$ in its protonated, water-soluble form does not produce an active hydroformylation catalyst.

Chapter 3 contains the results of the rhodium recycling using the modified PPh_3 ligands. First of all, the pH-depending distribution has been determined of each *free* ligand in a biphasic system, consisting of water and Et₂O. These data give a good indication of the distribution behaviour of the corresponding rhodium complex and are, therefore, useful in determining the required extraction conditions. The recycling procedure has been optimised using $\text{PhP}(4\text{-C}_6\text{H}_4\text{CH}_2\text{NEt}_2)_2$. This ligand allows the extraction of rhodium and excess ligand into an aqueous solution of H₂SO₄ at pH 5 and separation of the product aldehydes. After neutralisation to pH 7 by the addition of NaHCO₃, rhodium is almost quantitatively (97 %) recovered in a new organic phase, as determined by rhodium analysis using ICP-AES. It has been demonstrated that the catalytically active rhodium hydrides decompose during the acidic extraction step. The structure of the recovered rhodium complexes has not been

elucidated by NMR- and IR-spectroscopy. Pressurising the recovered rhodium and excess ligand to 20 bar syngas at 80 °C results in substantial regeneration of the original, catalytically active species. A retention of catalytic activity up to 87 % has been achieved. When $\text{PhP}(3\text{-pyridyl})_2$ is used only 57 % of the rhodium charge is recycled.

In Chapter 4 novel amphiphilic diphosphines are discussed that are based on BISBI. The water-soluble, sulphonated BISBI has been reported by others to be highly active and selective in the two-phase hydroformylation of propene, but poorly active when hex-1-ene is used as substrate. When used in the hydroformylation of oct-1-ene, our amino or pyridyl modified BISBI ligands give rise to rhodium catalysts that are up to twice as active as those derived from the parent BISBI. High *n/b*-ratios (up to 51) are found with 6-8% of isomerised octenes. The influence of the *L/Rh*-ratio, temperature and substrate have been investigated as well as the kinetics of the reaction. NMR- and IR-spectroscopy have revealed that the diphosphines (PP) form $\text{HRh}(\text{CO})(\text{PPh}_3)\text{PP}$ and $\text{HRh}(\text{CO})_2\text{PP}$ complexes, analogously to BISBI, so that formation of P-N chelated complexes can be excluded. The amino modified BISBI (incorporating two benzylic diethylamino groups) enables rhodium recycling to the extent of 92 %. The recycled rhodium induces hydroformylation of a new batch of oct-1-ene with the same high selectivity and a reduced activity (72 %). In contrast, the pyridyl modified BISBI ligands are inapt for rhodium recycling experiments. Extraction into an acidic aqueous phase is effective, but neutralisation of the acidic phase results in formation of rhodium species which cannot be extracted from the aqueous layer.

Chapter 5 describes two novel amphiphilic diphosphines based on POP. The amino modified POP ligand and unmodified POP give identical results in the hydroformylation of oct-1-ene. Because of the moderate *n/b*-ratio of 7.3 and the complete absence of isomerisation activity, the yield of *n*-nonanal is almost equal to that obtained using the BISBI ligands. The isomerisation activity is absent even at 100 °C or at a low P_{CO} ($\text{H}_2/\text{CO}=10:5$ bar). An explanation for this behaviour, based on the flexibility of the POP ligand, is postulated. The pyridyl modified ligand gives a rhodium catalyst almost twice as active as that derived from POP. A higher *n/b*-ratio (9) is found but aldehyde formation is accompanied by 0.7 % isomerisation. Rhodium recycling experiments using the amino modified POP ligand has shown that rhodium is extracted into an acidic aqueous layer for more than 99.95 %, which allows complete separation of product aldehydes and catalyst. However, after neutralisation only 65 % of the rhodium is recovered, which gives rise to a 58 % retention of activity in the hydroformylation of a new batch of oct-1-ene.

In Chapter 6 the Xantham ligand is discussed, Xantphos functionalised with a benzylic diethylamino group on each phenyl ring. The crystal structure of Xantham illustrates that the additional amino groups cause a significant distortion of the structure found for Xantphos. The result is an increased P-P distance. Nevertheless, in the hydroformylation of oct-1-ene

both ligands give similar results; n/b-ratios of 50 are achieved (94 % *n*-nonanal) with 4 % of isomerised octenes, while Xantham is slightly more active. Solution structures of rhodium Xantham complexes have been studied by means of NMR- and IR-spectroscopy. The 5-coordinate Rh(Xantham)(CO)(acac) complex has been characterised. Xantham does not engage in P-N chelated rhodium complexes, since it forms HRh(Xantham)(PPh₃)(CO) and HRh(Xantham)(CO)₂ complexes, analogously to Xantphos. Fluxional processes have been detected in the latter complex; even at -80 °C the two CO ligands are in rapid exchange on the ¹³C NMR time scale. Rhodium (and excess Xantham) is extracted into an aqueous layer at pH 5-5.5 to the extent of 99.95 %, thus allowing complete separation of the aldehydes. After neutralisation of the aqueous phase, 98 % of the rhodium is re-extracted into a fresh organic layer. The retention of activity amounts to 86 %.

From this study, it can be concluded that the applied concept of recovering the rhodium catalyst from a hydroformylation reaction mixture, containing higher aldehydes, is effective. All novel amphiphilic (di)phosphines enable the complete separation of the rhodium catalyst plus excess ligand by simple acidic extraction. The benzylic diethylamino group is without exception the functional group of choice in the modification of the hydrophobic parent phosphines. Nonetheless, the pyridyl modified phosphines are an interesting class of hydroformylation ligands.

Rhodium can be recycled nearly quantitatively when Xantham is used, which makes this ligand highly suitable for the use in a rhodium catalysed hydroformylation process of higher alkenes. Such a process would be environmentally more benign than the conventional cobalt-based processes. The high selectivity of rhodium Xantham renders a maximal conversion of feedstock 1-alkenes to the desired linear aldehyde. Due to the lower operating pressures and temperatures, the energy demand is lower. In addition, the energy-consuming distillation is circumvented by the extraction and re-extraction concept. Since the rhodium Xantham system is recycled at nearly neutral pH, the amount of produced waste salts is minimal. For commercial application in a process producing commodity aldehydes, a rhodium recovery of at least 99.99 % is mentioned in literature. Given the simple experimental set-up we used, the rhodium recovery of 98 % is promising and employment in the production of fine-chemicals can be envisaged. The retention of activity of 86 % is high, though not satisfactory from an industrial point of view. Future research should focus on performing all recycling steps under syngas pressure to avoid *irreversible* catalyst decomposition.