Summary

The rhodium-catalysed hydroformylation using phosphorus ligands is one of the most extensively studied catalytic processes. One of the highlights of these studies is the development of new ligands in order to obtain highly active and selective catalysts. Important aspects of the investigations are the steric and electronic ligand properties and for bidentate ligands the bite angle. Not only the catalyst performance has been important, but also the reaction mechanism and the solution structure of the catalyst have been studied in great detail. Although several intermediates of the unmodified rhodium catalyst have been characterised, only a small number of intermediates proposed for the phosphorus-modified catalyst has been identified and very little is known about the reactivity of the reaction intermediates and the reversibility of the reaction steps proposed.

In this thesis studies on the rhodium-catalysed hydroformylation using phosphorus diamide ligands are presented. The nitrogen substituents on the phosphorus atom are introduced to form ligands that combine steric bulk with π-acidity. This combination of steric and electronic properties results in bulky, electron-poor catalysts. Because this type of ligands is relatively new in the hydroformylation reaction only few studies have been performed concerning the catalyst structure formed under hydroformylation reaction conditions. No studies on the reaction kinetics and the structure of the intermediates present during the reaction have been published until now.

In chapter two, several monodentate and bidentate phosphorus diamide ligands derived from a 1,3,5-N,N',N''-trisubstituted biuret structure are presented. This type of ligands combines steric bulk with π-acidity. Investigation of the rhodium complexes formed under hydroformylation reaction conditions revealed that the monodentate ligands form mixtures of $HRhL_2(CO)_2$ and $HRhL(CO)_3$. The ratio $HRhL_2(CO)_2$:$HRhL(CO)_3$ depends on the ligand concentration and its bulkiness. The bidentate ligands form hydride complexes with the structure $HRhL\frown L(CO)_2$. Both monodentate and bidentate ligands have been tested in the hydroformylation reaction of 1-octene. The monodentate ligands form very active catalysts but the linear-to-branched ratio of the product is moderate. The bidentate ligands show improved selectivity compared to the monodentate ligands and an activity that is only slightly lower.

In chapter three, a detailed study of the stoichiometric hydroformylation reaction of allyldiphenylphosphine is presented using the monodentate triethylbiuret-phenylphosphorus

diamide (ligand **1**, Figure 1). Coupling of the ligand and substrate functions in one molecule stabilises the intermediates of the hydroformylation reaction and enables the characterisation of the complexes using NMR spectroscopy. Reaction of the rhodium-hydride complex $HRhL_3CO$ (L = triethylbiuret-phenylphosphorus diamide) with allyldiphenylphosphine results in the formation of $HRhL_2(allylPPh_2)CO$. Hydride migration in the absence of CO led to complete conversion of the rhodium-hydride complex to the linear rhodium-alkyl complex. Deuterium labelling studies showed, that the hydride migration is reversible and that both the linear and the branched rhodium-alkyl complex had been formed. The linear rhodium-alkyl complex was shown as the thermodynamically stable product formed after longer reaction times. When carbon monoxide is added to the rhodium-alkyl complex, ligand exchange and CO insertion occurred, leading to the formation of $\overline{Rh(CO)CH_2CH_2CH_2PPh_2}L(CO)_2$, a cyclic rhodium-acyl complex. Addition of hydrogen completes the cycle forming the coordinated hydroformylated allyldiphenylphosphine ligand. The aldehyde-functionalised phosphine ligand is hydrogenated to the corresponding alcohol.

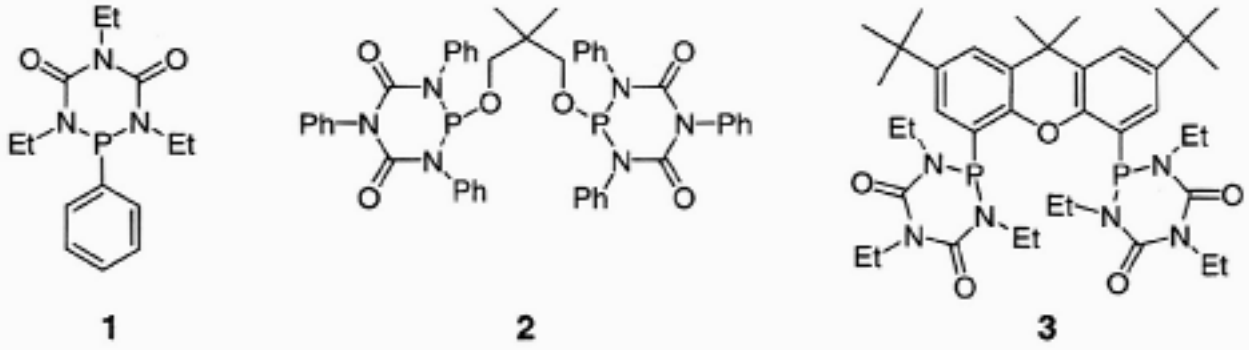

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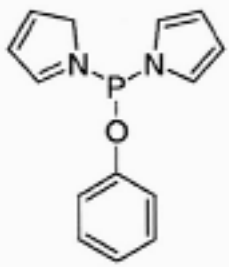
Figure 1. Several Monodentate and Bidentate Biuret-Based Phosphorus Diamide Ligands

In Chapter four, the hydroformylation mechanism using the monodentate triethylbiuret-phenylphosphorus diamide ligand (Figure 1) has been investigated under catalytic conditions. A detailed kinetic study and (*in situ*) spectroscopic techniques revealed that several of the elementary reaction steps are involved in the hydroformylation rate control. Which step is rate determining depends strongly on the conditions used. Deuterioformylation showed that alkene coordination followed by hydride migration is irreversible under the conditions studied. The rhodium-hydride complex $HRhL_2(CO)_2$ and several rhodium-acyl complexes were observed during the hydroformylation reaction, using *in situ* HP IR spectroscopy. The structures of the rhodium-acyl complexes have been characterised using ^{31}P, ^{13}C, and ^{103}Rh NMR spectroscopy. The rhodium-acyl complexes observed contain

phosphorus ligands coordinated in both the **ee** and **ea** coordination mode, although in the hydride complex the phosphorus ligands are coordinated exclusively in the equatorial plane. These results show that formation of a hydride complex having *bis*-equatorially coordinated phosphorus ligands does not guarantee a high linear-to-branched ratio in the product, since the monodentate ligands may well have the flexibility to form **ea** complexes for the more hindered branched-alkyl and acyl complexes.



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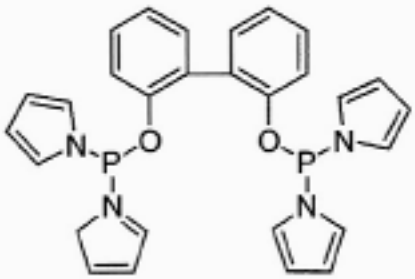

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Figure 2. Monodentate and Bidentate Pyrrolyl-Containing Ligands

In chapter five, novel monodentate and bidentate phosphorus amidite ligands that contain two pyrrolyl substituents have been synthesised (Figure 2). The performance of the hydroformylation catalyst based on these ligands has been compared to similar diphenyl substituted phosphinite ligands. These phosphinite ligands have analogous steric properties but they differ in terms of π-acidity. Using these ligands, the electronic effect on the catalyst performance can be investigated with a minimal change in steric properties. Spectroscopic studies showed, that under hydroformylation conditions the monodentate ligands form mixtures of $HRhL_2(CO)_2$ and $HRhL_3CO$ depending on the ligand and rhodium concentrations and the CO pressure. The bidentate ligands form mixtures of $HRh(L\frown L)(CO)_2$ and $HRh(L\frown L)(L\frown L')CO$, having one L⌒L' coordinated as a monodentate, depending on the reaction conditions used. All ligands have been tested in the hydroformylation reaction. Increasing the π-acidity of the ligand resulted in an increase of the hydroformylation rate. The monodentate ligands showed high activity but moderate selectivity for the linear aldehyde. The catalyst formed using the bidentate phosphorus amidite ligand **3** revealed high regioselectivity for the linear aldehyde together with a high isomerisation rate. The reaction mechanism using the bidentate pyrrolyl-based phosphorus amidite ligand was studied by a deuterioformylation experiment. The results showed that the hydride migration is a reversible step under these hydroformylation reaction conditions. Both linear and branched rhodium-alkyl complexes prefer β-hydride elimination instead of CO insertion resulting in a high

percentage of 2-alkenes. The linear rhodium-alkyl finally undergoes CO-insertion leading to high linear-to-branched ratios.

From the work presented in this thesis, it can be concluded, that the introduction of bulky, electron-withdrawing nitrogen substituents leads to π-acidic phosphorus ligands that show increased activity compared to phosphines in the hydroformylation reaction. Spectroscopic studies of the catalyst structures formed using these ligands revealed that the type of complexes formed under syn-gas pressure is sensitive to the electronic and steric ligand properties. Slight changes in these properties give rhodium-hydride complexes containing either one, two or three phosphorus ligands. The type of complexes present during catalysis influence strongly the catalyst activity and selectivity. Investigation of the reaction mechanism using these π-acidic phosphorus ligands by deuterioformylation or kinetic studies revealed that the relative rate of the subsequent reaction steps proposed in the reaction mechanism is strongly depending on the conditions used. Especially the *in situ* spectroscopic study using the monodentate biuret-based ligand showed that the rate-determining step of the reaction can be changed easily from early to late in the catalytic cycle by changing the reaction conditions and therefore the colloquial expression "the rate-determining step of the reaction" does not apply.