SUMMARY

The homogeneously catalysed hydroformylation is an industrially applied reaction. Alkenes are converted into aldehydes under high pressures of CO/H_2 and in the presence of a transition metal complex as a catalyst. The transition metal complex often contains phosphorus ligands in order to enhance the stability of the catalyst complex so the reaction can be performed at milder conditions (low pressure, low temperature). Variation of the phosphorus ligands can effect the activity and selectivity. A high selectivity can imply the chemoselectivity, the regioselectivity and the enantioselectivity. When a high chemoselectivity is reached, little side products such as isomerisation— and hydrogenation products are obtained. When the formyl group adds selectively to one of the sp^2 carbon atoms, a high regioselectivity is obtained. Whether the preferred product is the linear or the branched aldehyde depends on the substrate.

This thesis contains studies on the rhodium catalysed hydroformylation with bulky phosphites as modifying ligands. Aim of this study is to gain more insight in the catalytic cycle and the complexes involved.

Chapter 2, 3 and 4 describe the application of the rhodium carbonyl catalyst with the bulky monophosphite **1** as modifying ligand. Chapter 2 contains the hydroformylation of oct-1-ene, styrene and cyclohexene with this catalyst. This phosphite ligand forms the catalyst complex **2**. For all three substrates a very high activity has been obtained compared to the rates that have been found with the conventional PPh_3 modified catalyst. Cyclohexene is even hardly hydroformylated with the latter catalyst system. This has been explained by the nature of **2**; because only one phosphite ligand is coordinated to the rhodium centre, enough space is left for the alkenes to coordinate with ease. Addition of the alkene to the rhodium is now very fast resulting in the observed high activity. The selectivity to the linear nonanal, respectively the branched 2-phenylpropanal is moderate, about 68%.
The kinetic behaviour for the three substrates has been studied. For oct-1-ene it has been found that the rate determining step is the last step in the reaction cycle, the reaction of H_2 with the acylrhodium compound. For cyclohexene the addition of the substrate to the rhodiumhydrido complex is the rate-limiting step. The kinetic behaviour of styrene is less staightforward. The kinetics for the formation of the linear aldehyde resemble those observed for oct-1-ene, meaning that the H_2 reaction is the rate-determining step. For the formation of the branched aldehyde, the kinetics strongly depend on the CO pressure. At low CO pressures, addition of CO to the proposed (η^3-1-phenylethyl)rhodium intermediate is slow. At higher CO pressures, hydrogenolysis of the rhodium acyl intermediate is the rate-determining step and the rate

decreases with increasing CO. An important side reaction is β-H elimination. For oct-1-ene, occurrence of this reaction results in the formation of isomerisation products. For styrene an enhanced amount of linear aldehydes is obtained.

Chapter 3 contains an *in-situ* infrared study of the reaction that is described in Chapter 2. Due to the very high reaction rates observed for the bulky posphite modified hydroformylation of 1-alkenes up to now the dominant species during the catalysis could never be characterised. A new *in-situ* IR autoclave has been developed of which the autoclave itself contains the IR windows. It is now possible to record infrared spectra of the reacting compounds under high pressures and temperatures. Preliminary studies that were performed for oct-1-ene with a rapid scan technique point towards the presence of an acyl compound as the most abundant species. The spectrum has been assigned to the saturated acylrhodium complex as was concluded earlier in Chapter 2 from the kinetic behaviour of this catalyst. For styrene and pentafluorostyrene, using regular FTIR, species were observed with similarly patterned IR spectra. The acyl band, if present, is obscured by the intensive aldehyde absorption. These equally patterned but shifted spectra are indicative of a substrate coordinated complex present as dominant species, in accordance with the results obtained with oct-1-ene. It is suggested therefore that for the three substrates $RhC(O)R(\mathbf{1})(CO)_3$ is observed.

In Chapter 4 the results are presented of the hydroformylation of several substituted 1-alkenes catalysed by **2**. The reaction rate appeared to be hardly dependent of the amount of substitution of the alkenes. This is in contrast with the results obtained with the PPh_3 modified rhodium catalyst. Here, the rate regularly decreased with increasing substitution of the alkene. For **2** the reaction rate remains independent of the substrate concentration up to 3,3-dimetyl-1-butene, the alkene studied with the highest degree of substitution. The selectivity to the linear aldehyde increases when the substituents are located closer to the C=C bond. However, the amount of isomerised alkenes remains substantial. This has been explained by the kinetic equation of the catalyst system. The rate-determining step is the reaction of the acylrhodium complex with H_2. Under the conditions used, the acyl compound, while "waiting" for the H_2 to react with, can give deinsertion of CO and subsequent β-H elimination, leading to isomerisation, can occur. For the Rh/PPh_3 catalyst, the rate-limiting step is the addition of the alkene to the hydridorhodium complex after which hydride migration occurs directly. A reverse reaction is not possible.

In Chapter 5, the rhodium catalysed hydroformylation of styrene and oct-1-ene with several bulky diphosphites is described. Furthermore, a study of the characterisation of the catalyst complexes is presented. It is found that catalysts with rigid diphosphites which contain a diphenoxy bridge between the two phosphorus atoms hydroformylate oct-1-ene very selectively to the linear nonanal; a regioselectivity up to 96% is observed. From NMR and IR studies and an X-ray structure determination it has been shown that during the catalysis these diphosphites are coordinated to the rhodium in a bisequatorial fashion which results in a very crowded rhodium centre. After π-coordination of the alkene hydride migration that leads to the formation of the linear alkylrhodium complex is preferred, giving rise to a high regioselectivity. Flexible and bisequatorially coordinating diphosphites as well as diphosphites that coordinate in an axial-equatorial manner react with a high rate but a moderate regioselectivity is now obtained (≈60%). For styrene the preference for the linear aldehyde to be formed with the rigid diphosphites leads

to a decreased branched to normal ratio (≈1). However, the property of this catalyst can be exploited to obtain an unusually high selectivity to the linear aldehyde. When the reaction temperature is increased to 120 °C, β-H elimination dominates the hydroformylation reaction resulting in a selectivity for the linear 3-phenylpropanal of 84%. Cyclohexene barely reacts to the product aldehyde with this catalyst. The internal alkene is too sterically hindered to react with the crowded rhodium centre.
For oct-1-ene as the substrate the kinetic behaviour has been determined with the catalyst obtained with one of the bisequatorially coordinating diphosphites. The rate-determining step is the addition of oct-1-ene to the initial hydridorhodium complex.

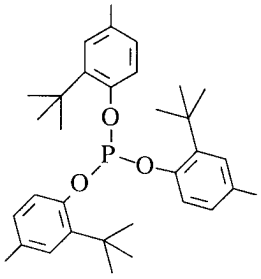
In Chapter 6, complex **3**, characterised in Chapter 5 and was found to be stable at 1 bar for some time, has been made to react with allyldiphenylphosphine in order to "trap" intermediates in the catalytic cycle of the hydroformylation reaction. The diphosphite-phosphine complex is formed with three phosphorus atoms coordinated equatorially. Heating of this compound results in hydride migration towards the sp^2 carbon atoms of the allyldiphenylphosphine and hence formation of a rhodium-phosphine heterocyclic ring complex. The ring size has been determined by ^{31}P NMR and the complexes have been characterised. Subsequently, the linear alkyl 5-membered ring and the branched acyl 5-membered ring are formed, and after reaction with CO, the 6-membered linear acyl ring is observed. The latter complex is only stable at high CO pressures or low temperature (253K). Reaction of the acyl compounds with H_2 leads to the reverse reaction resulting in the starting diphosphite-phosphine complex. Presumably this occurs via deinsertion of CO and subsequent β-H elimination. The second product obtained is the starting complex where the allyl group is hydrogenated to the propyl group. No complexes are observed that contain a formyl group.

In Chapter 7 the results are presented of the hydroformylation with phosphorus amidites as modifying ligands. In phosphorus amidites, one oxygen atom of the phosphite is substituted by a nitrogen atom in order to bring more bulk in proximity of the phosphorus atom and hence to the rhodium centre. Bulky monophosphorus amidites and bulky diphosphorus amidites have been applied for oct-1-ene and styrene as the substrates. The mono coordinating ligands react in general more slowly than phosphites and with a lower regioselectivity. From characterisation experiments it has been shown that the precursors are converted very slowly into the active catalysts and the conversion is not complete. These ligands are possibly too bulky and too sterically hindering to form the catalyst complex with ease. The diphosphorus amidite ligands give good results. They react more slowly than bulky diphospites but a comparable selectivity to the linear nonanal is reached, 91%. The applied diphosphorus amidites all coordinate bisequatorially to the rhodium centre, as has been shown by NMR spectroscopy.

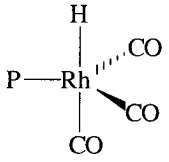
It can be concluded that bulky phosphite ligands are good modifying ligands in the rhodium catalysed hydroformylation of the used alkenes. Phosphites are easy too synthesise and almost insensitive towards oxidation. Particularly the diphosphites give rise to stable and hence identifiable complexes. Especially the studies on intermediates in the reaction cycle (Chapter 5) and on the diphosphorus amidites as modifying ligands (Chapter 7) are recommended to be

extended. To characterise different intermediate complexes, intramolecular reactions can be performed with various phosphines containing a C=C bond.

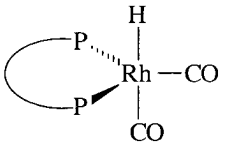
The phosphorus amidites require an extensive mechanistic study and adjustment of the structure of the ligands in order to enhance the activity and the selectivity of the reaction. Phosphorus amidites can be easily obtained in a chiral form. This can make these ligands especially attractive for the performance of asymmetric catalysis.



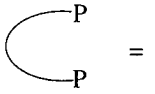
(1)



(2)



3



=