

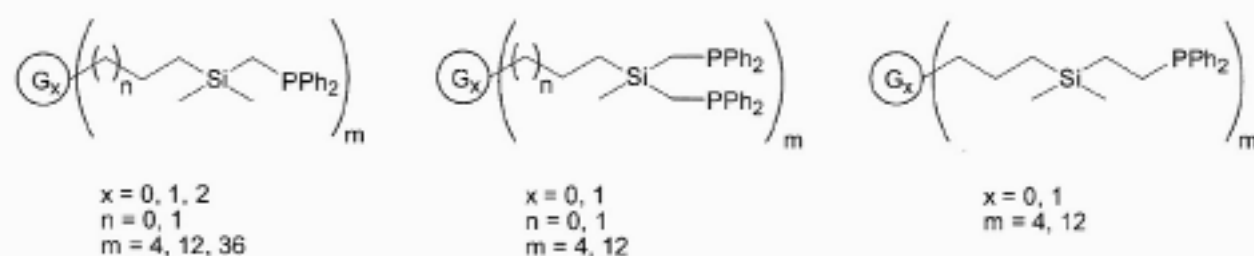
Summary

During the last two decades the field of dendrimers has gone through a rapid development. The specific tree-like structure of these systems has inspired many chemists to synthesise new dendrimeric molecules and a variety of applications has been envisaged. An important potential application of dendrimers is their use as catalyst support, as the size of the dendrimers enables easy recycling of the homogeneous catalyst by means of nanofiltration. The research described in this thesis involves the development of transition metal based dendrimeric catalysts and their use in a continuous-flow membrane reactor. We concentrated on periphery functionalised dendrimers and studied the influence of the dendrimer on the catalytic activity and selectivity as well as the stability in a continuous-flow reactor.

Initially, we focussed on carbosilane dendrimers as a catalyst support because of their inertness in catalysis and the easy modification of size and flexibility of these molecules. The optimised synthesis of carbosilane dendrimers containing a branch multiplicity of three and branch lengths of two and three carbon atoms is described in chapter 1. The structures have been studied using molecular modelling and for the second generation C_2 -dendrimer an X-ray crystal structure has been obtained. The membrane reactor set-up that has been used for the continuous experiments is presented in chapter 1. The retentions of various dendrimers were measured using different solvents. The retentions of linear polystyrene molecules were comparable to those of the dendrimers. We found a large solvent effect for the carbosilane dendrimers using the Koch/SelRO MPF-60 NF membrane in the continuous set-up. Dichloromethane is the best solvent tested so far and the presence of substrates in the solvent lowers the retention of the dendrimers. It is clear that the application of the Koch/SelRo MPF-60 NF membrane is limited.

When this research was started, not much was known about the functionalisation of dendrimers and dendrimeric catalysts. It was important to find synthetic procedures for the complete functionalisation of the dendrimers. In this thesis we describe several synthetic routes that lead to carbosilane dendrimers containing diphenylphosphine groups at the periphery. A series of carbosilane dendrimers containing $Si(CH_3)_2CH_2PPh_2$, $Si(CH_3)(CH_2PPh_2)_2$, $Si(CH_3)_2CH_2CH_2PPh_2$ and $Si(CH_2CH_2CH_2PPh_2)_3$ endgroups have

been synthesised (chapters 2, 3 and 4). The first three types were prepared by reaction of the TMEDA complex of (diphenylphosphino)methyl lithium with chlorosilane endgroups of the dendrimers or by reaction of potassium diphenylphosphide with chloromethylsilane endgroups. The $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ functionalised dendrimers were prepared by a reaction of diphenylphosphine with allylic endgroups of the dendrimers.



The $\text{SiCH}_2\text{PPh}_2$ -functionalised carbosilane dendrimers with a branch length of two carbon atoms have been used in the palladium catalysed hydrovinylation reaction and allylic substitution reactions (chapter 2). The largest systems have been used in a continuous-flow membrane reactor. A major problem in the use of these systems in continuous processes is deactivation of the catalyst. When using dendrimeric ligands with $\text{Si}(\text{CH}_2\text{PPh}_2)_2$ endgroups, the yield for allylic substitution reactions dropped rapidly during continuous experiments and became nearly zero (<0.1%) after the reactor was flushed with substrate solution approximately fifteen times. When a dendrimeric ligand with $\text{SiCH}_2\text{CH}_2\text{PPh}_2$ endgroups was used, a much more stable catalyst was obtained. During the experiment the yield only decreased from ~90% to ~75% after fifteen reactor volumes were pumped through the reactor. This corresponds to a retention of 98.5-99%, as may be expected for this size of supported catalyst. Hence, changing the endgroups of the dendrimeric ligand has a large impact on the catalyst stability.

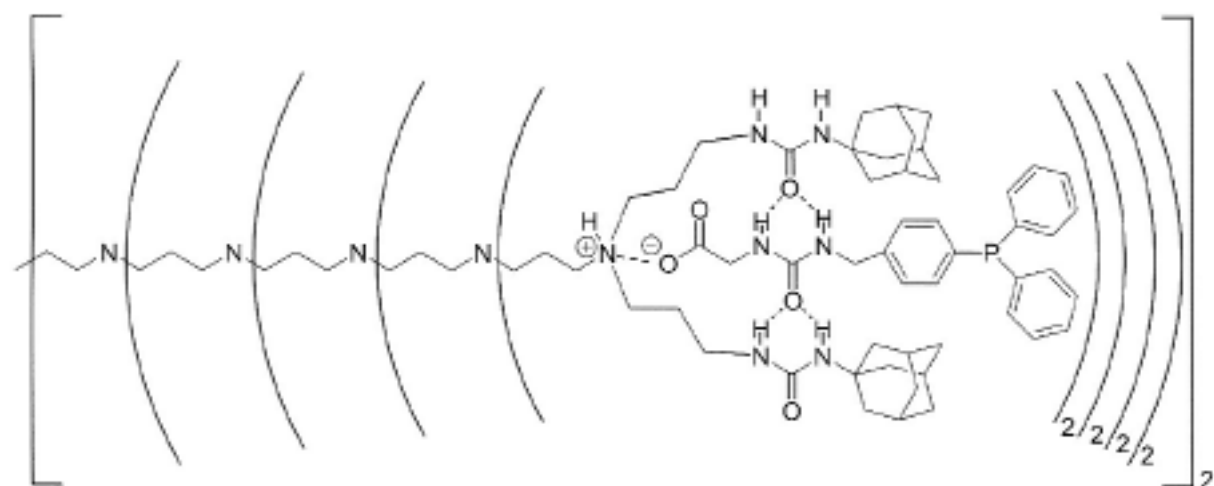
The $\text{SiCH}_2\text{PPh}_2$ and $\text{SiCH}_2\text{CH}_2\text{PPh}_2$ functionalised carbosilane dendrimers with branch lengths of two and three carbon atoms have been used as ligands in the rhodium catalysed hydroformylation of 1-octene (chapter 3). The influence of the size and flexibility of the dendrimeric structure on the catalytic activity and selectivity has been investigated. The dendrimeric ligands with $\text{Si}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2$ and $\text{Si}(\text{CH}_3)(\text{CH}_2\text{PPh}_2)_2$ endgroups induce the same selectivity as their smaller analogues, $(\text{CH}_3)_3\text{SiCH}_2\text{PPh}_2$ and $(\text{CH}_3)_2\text{Si}(\text{CH}_2\text{PPh}_2)_2$. The activity of the system does depend on the size and flexibility of the dendrimeric support. The catalyst becomes less active when the phosphines are forced in closer

proximity, i.e. for higher generation dendrimers and for the more compact C₂-dendrimers. The dendrimeric ligands with Si(CH₃)₂CH₂CH₂PPh₂ endgroups give catalysts that are less active than those of the dendrimeric ligands containing a methylene-spacer between the terminal silicon and phosphorus atom. The largest dendrimeric ligand with an ethylene-spacer between the terminal Si-atom and P-atom induces a slightly higher selectivity towards the linear product (*l/b* = 4.9 compared to 2.3). Although this is a small effect, it is interesting that the selectivity of the hydroformylation reaction can be improved by changing the structure of the support. Detailed insight in this effect might provide a tool to prepare more selective catalysts.

The Si(CH₂CH₂CH₂PPh₂)₃ functionalised carbosilane dendrimers were prepared by a photochemically activated addition reaction of diphenylphosphine to the olefinic endgroups of the dendrimer (chapter 4). This reaction is believed to proceed *via* a radical mechanism, in which the primary step is the formation of a PR₂-radical. The possibility of a photochemically activated [2+2] addition mechanism has been investigated experimentally and by using DFT calculations. DFT calculations show that the energy barrier for a reaction proceeding *via* a cyclic transition state is very low, suggesting that this might be a likely pathway. Calculations also give low energy barriers for a radical mechanism. Experimental results point towards a radical mechanism, but a [2+2] addition mechanism cannot be excluded.

Up to now only covalently functionalised dendrimers have been discussed. A disadvantage of this approach is that functionalisation is irreversible. Non-covalent functionalisation of the dendrimers would be an elegant solution for this drawback and would simplify the route towards dendrimer supported catalysts. The reversible nature of non-covalent catalyst anchoring allows controlled de- and re-functionalisation of the support. Such a non-covalent approach, using a combination of ionic interactions and hydrogen bonding, has been used for the functionalisation of poly(propylene imine) dendrimers (chapter 5). A fifth generation dendrimer functionalised with urea-adamantyl endgroups is used as a host, and urea-acid-functionalised triphenylphosphine guest molecules are assembled at its periphery. Palladium complexes of the resulting supramolecular multidentate phosphine ligand have been used as catalysts in the allylic amination of crotyl acetate and piperidine. The activity and selectivity of the dendrimeric catalyst are similar to those of the monomeric system, indicating that there is no decrease in activity as a result of the

immobilisation. The retention of the supramolecular catalyst is high (99.4%) and the system can be applied in a continuous-flow membrane reactor. Similar to the covalently functionalised systems of chapter 2, the catalyst stability is an important issue that needs to be addressed.



In general, dendrimers appear to be quite suitable as a catalyst support. The dendrimeric catalysts described in this thesis are active in several catalytic reactions. For palladium catalysed reactions both the activity and the selectivity of the different generations of the dendrimers are similar to those of the monomeric compounds, indicating that the catalytic sites are readily accessible to the substrate. For the rhodium catalysed hydroformylation reaction there is an effect on the activity, but not on the selectivity of the system. When the phosphines are forced in closer proximity inactive rhodium complexes are formed leading to a decrease in activity.

These dendrimeric catalysts can be used in a continuous-flow membrane reactor. However, for industrial applications much higher retentions are required (>99.99%), so higher generation dendrimers should be used. Catalyst stability is an important issue to avoid decomposition and leaching of the transition metal. Furthermore, new membrane materials that are less dependent on the solution and temperature should be developed.