
Summary

The work described in this thesis is part of an NWO/CW project that was initiated to investigate the principles that are fundamental to dendrimeric transition metal catalysis and to develop potential applications of these dendrimeric systems. Other researchers within the project group focussed on periphery-functionalized dendrimeric catalysts. Well-known homogeneous catalysts have been anchored to the periphery of carbosilane dendrimers, after which these systems have been applied as catalysts in several important reactions.^[1] In this thesis the approach of core-functionalized dendrimeric catalysts is explored, and a concise overview of the results is given here.

In the introduction (*Chapter 1*) the history and the current state of dendrimeric transition metal catalysis are reviewed. The chapter includes a brief discussion of the position of dendrimeric catalysts in comparison with homogeneous and heterogeneous catalyst systems. Several concepts such as periphery-, core-, and focal point-functionalization are discussed. Furthermore, an overview of the reported application of dendrimeric transition metal catalysts in continuous processes and in asymmetric catalysis is presented. A closer look at the literature references shows that the majority of the reports on dendrimeric catalysis has appeared in the last five year, that is, since the initiation of the project reported in this thesis, which shows that this field is advancing rapidly and still has to mature.

Chapter 2 describes the synthesis and characterization of allyl-terminated carbosilane dendrimeric wedges. After coupling these wedges to a ferrocenyl diphosphine core a series of core-functionalized dendrimeric ligands was obtained. Palladium complexes of the dppf-type ligands were prepared, and even for the largest dendrimer **A** (see Chart) a facile formation of the bidentate complex was observed. Application of the ligands in the palladium-catalyzed allylic alkylation of several allylic substrates using diethyl 2-sodio-2-methylmalonate revealed an interesting dendrimeric effect; when higher generation dendrimers were used, formation of the branched alkylation product was promoted at the expense of the linear trans product. The change in regioselectivity was attributed to the apolar microenvironment around the catalytic center created by the dendrimeric encapsulation. The encapsulation imposed a disadvantageous effect on the catalytic activity, which was ascribed to the reduced accessibility of the catalytic center located at the core.

The largest dendrimeric catalyst **A** was applied in the allylic alkylation reaction in a continuous-flow membrane reactor. A constant activity and an unchanged selectivity were observed for at least 20 reactor volumes. This shows for the first time that core-functionalized dendrimeric catalysts are well-applicable in continuous processes.

Chapter 3 presents a direct comparison of the catalytic properties of dendrimeric systems with dppf derivatives located at the core (**B**, see Chart) and at the periphery (**C**). Palladium complexes of the two different kinds of functional dendrimers were applied as catalysts in the Grignard cross-coupling and the allylic amination reactions. When the core-functionalized dendrimers were employed, a decrease of the rate was observed for both catalytic reactions. This is in contrast to what we found for the systems with the catalysts attached to the dendrimer surface, which is directly related to the accessibility of the catalytic sites. In the allylic amination reaction no detrimental effect was observed. In the Grignard cross-coupling reaction a slightly lower rate is observed when dendrimer **C** is used compared to the monomeric analogue, which presumably is caused by interactions between the peripheral catalytic sites. This shows that, depending on the reaction studied, the interaction between the peripheral catalysts can change the catalytic performance.

The largest core-functionalized dendrimer **B** induced a change in the product selectivity of the Grignard cross-coupling reaction compared to that of the monomeric parent catalysts. Also a slower isomerization reaction, which is a side reaction after the allylic amination reaction has gone to completion, was observed. Such effects were not detected for the peripheral sites.

Allylic amination experiments in the continuous-flow reactor clearly show the differences between the encapsulated and peripheral catalysts. The latter are much more active than the less accessible sites at the core, while at the same time the dendrimeric encapsulation leads to a more stable catalyst.

The preparation of core-functionalized dendrimers containing xantphos (**D**) and triphenylphosphine (**E**) backbones is described in *Chapter 4*. Rhodium complexes of these and the dppf-based ligands (**B**) were applied as catalysts in the hydroformylation of oct-1-ene. Only a slight decrease of the reaction rate was observed when the higher generation dendrimers were employed. The regioselectivities induced by the three different types of phosphine ligands were similar to those obtained with the corresponding parent ligands. Apparently the regioselectivity of the hydroformylation of oct-1-ene is solely determined by the ligand backbone, be it a monophosphine, a rigid diphosphine, or a flexible diphosphine.

When the more bulky substrate 4,4,4-triphenylbut-1-ene was used, the decrease of activity along the dendrimeric ferrocenyl series was more pronounced. This shows clearly that

steric interactions between the substrate and the dendrimeric branches are responsible for the reduced activities. Additionally, when higher generations were applied as ligands a higher rate of isomerization was observed. The amount of linear aldehyde remained constant.

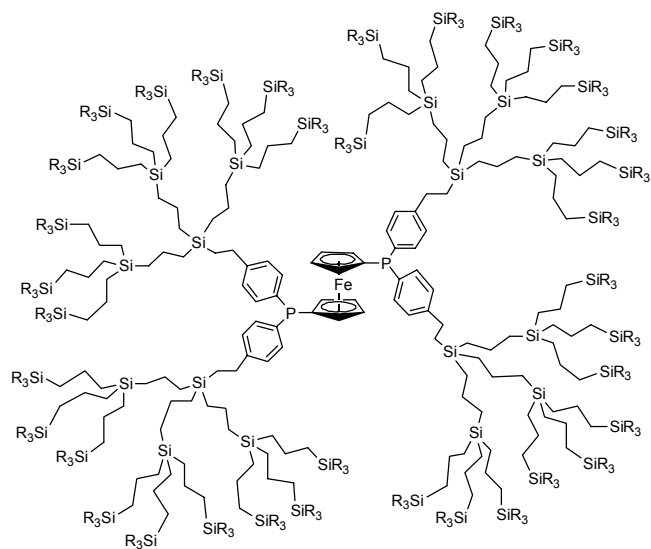
Rhodium complexes of the dppf-type dendrimeric ligands were also applied in the batchwise and continuous hydrogenation of dimethyl itaconate. The catalysts were active under mild conditions (room temperature, 5 bar H₂) and the rate of reaction was independent of the dendrimer used. Application of the dendrimeric hydrogenation catalyst in a continuous-flow membrane reactor showed the high stability of the dppf-rhodium catalyst and the high retention compared to the non-dendrimeric complex.

In Chapter 5 the synthesis and characterization of NCN pincer ligands coupled to the focal point of a series of carbosilane dendrimeric wedges (**F**) is described. The Suzuki coupling between the ligand precursor and the boronic acid-functionalized wedge of generation three failed. The NCN pincer-nickel complexes up to generation two were applied in the Kharasch addition reaction of CCl₄ to methyl methacrylate. The preliminary catalytic results reveal that these focal point systems have no effect on the reaction rate or on the stability of the catalyst is observed. Molecular modeling confirmed that the second-generation wedge does not lead to encapsulation of the catalytic center. Retention measurements indicate that the size of ligand **F** is sufficiently large for the application in a continuous-flow membrane reactor.

References

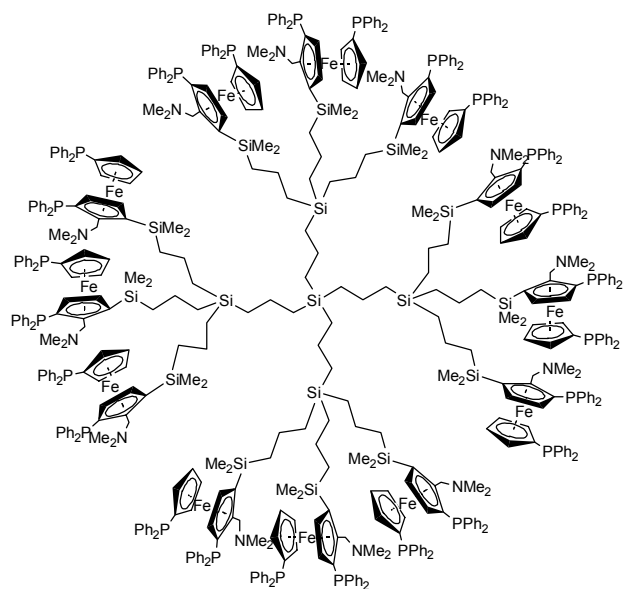
- [1] a) N. J. Hovestad, *Periphery Functionalized Dendrimers: Organic Synthesis and Homogeneous Catalysis*, Ph.D. thesis, Utrecht University, Utrecht, The Netherlands, **1999**; b) A. W. Kleij, *Supramolecular Homogeneous Catalysts Derived from Metallodendrimers*, Ph.D. thesis, Utrecht University, Utrecht, The Netherlands, **2000**; c) D. de Groot, *Dendrimers as Homogeneous Transition Metal Catalysts*, Ph.D. thesis, University of Amsterdam, Amsterdam, The Netherlands, **2001**; see also the publications of these researchers cited throughout this thesis.

Chart

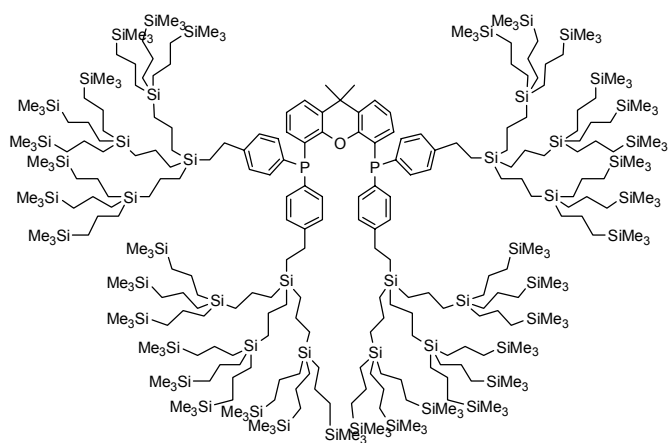


A, R = CH₂CH=CH₂

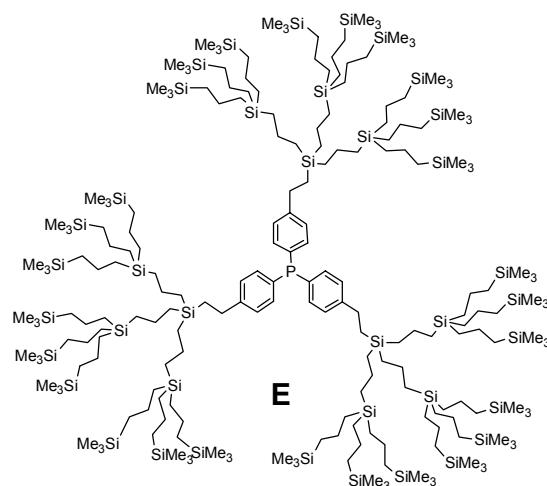
B, R = CH₃



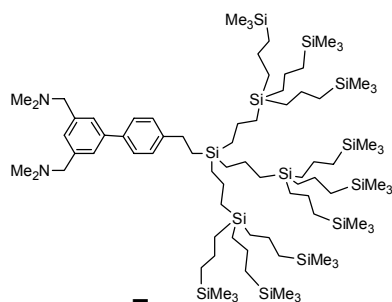
C



D



E



F