Dendrimers as homogeneous transition metal catalysts.
de Groot, D.

Citation for published version (APA):

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Diphenylphosphine-functionalised carbosilane dendrimers 23-32 have been synthesised and used as ligands in the rhodium catalysed hydroformylation of 1-octene. The activity of the system depends on the size and flexibility of the dendrimeric ligand. The largest dendrimeric ligand with an ethylene-spacer between the terminal silicon atom and the phosphorus atom induces a slightly higher selectivity towards the linear aldehyde.

**Chapter 3**

**Introduction**

During the last two decades the field of dendrimers has gone through a rapid development. The specific shape of these systems has inspired many chemists towards the synthesis of new dendrimeric molecules, and a variety of applications has been envisaged.\(^1\)-\(^6\) An important potential application of dendrimers is their use in catalysis,\(^7\)-\(^12\) as dendrimers allow easy recycling of the homogeneous catalyst by means of nanofiltration.\(^12\)-\(^16\) Hydroformylation is a widely used, homogeneously catalysed process to produce aldehydes and alcohols.\(^17\),\(^18\) However, people are still searching for better ways to recycle the catalyst. So far the use of dendrimeric catalysts for hydroformylation reactions has been reported only scarcely. Reetz et al. reported preliminary results of the hydroformylation of 1-octene using diphenylphosphine-functionalised poly(propylene imine) dendrimers.\(^9\) They found a selectivity of 60:40 for the formation of the linear and branched aldehydes, which was similar to that of their model compounds. Cole-Hamilton and co-workers used phosphine-functionalised carbosilane dendrimers with silsesquioxane cores, containing Si(CH\(_2\)PR\(_2\))\(_3\) endgroups.\(^12\) For the hydroformylation of 1-hexene they observed a high selectivity towards the alcohol when applying trialkylphosphine ligands. For PE\(_2\)T-functionalised dendrimers they found a slightly higher linear/branched ratio (3.1) than for the model ligand PE\(_3\) (l/b = 2.4). They did not observe this increase in l/b ratio for PMe\(_2\)- and PPh\(_2\)-functionalised dendrimers. Surprisingly, when they used dendrimers with Si(CH\(_3\))(CH\(_2\)CH\(_2\)PPh\(_2\))\(_2\) endgroups, they observed an increase in l/b ratio (up to l/b = 13.9) for the larger systems.\(^19\) They attributed this effect to the size of the P-Rh-P ring; steric crowding makes eight-membered ring bidentate coordination favourable. Alper and co-workers reported the use of rhodium-complexed diphenylphosphine-functionalised poly(amo no amido) dendrimers anchored to a silica-gel support for the hydroformylation of several olefins (for octene: l/b = 2).\(^11\) These heterogenised systems are recyclable via microporous filtration, but the catalytic activity decreased significantly for higher generation dendrimers. They also anchored dendrimeric ligands to polystyrene beads and used these systems as catalysts in the hydroformylation of styrene.\(^20\) Here they report a higher activity for the second generation dendrimer than for the first generation, but the reason for this increased activity is not clear. Xi and co-workers performed two-phase hydroformylation reactions catalysed by rhodium-complexed water-soluble third generation poly(amo no amido) dendrimers (l/b = 1.3-4.2 for the hydroformylation of 1-
Rhodium catalysed hydroformylation using carbosilane dendrimers

octene). In this chapter we describe the use of phosphine-functionalised carbosilane dendrimers as ligands in the rhodium catalysed hydroformylation of 1-octene. The influence of size and flexibility of the dendrimeric ligands on the catalytic activity and selectivity was investigated.

Results & discussion

Synthesis

Previously, we and others reported the synthesis of carbosilane dendrimers with diphenylphosphine endgroups. As a backbone we used carbosilane dendrimers with two carbon atoms between the silicon branching points. In order to investigate the effect of compactness and flexibility of the dendrimers on their performance in catalysis, we report here the synthesis of phosphine-functionalised carbosilane dendrimers with three carbon atoms between the branching points. Model compounds (H₂C)₃SiCH₂PPh₂ (33) and (H₂C)₂Si(CH₂PPh₂)₂ (34) were used for comparison.

We synthesised the phosphine-functionalised dendrimers as described in chapter 1. Hydrosilylation of the various generations of carbosilane dendrimers with chlorodimethylsilane or dichloromethylsilane followed by a reaction with the tetramethylethylenediamine complex of (diphenylphosphino)methyl lithium (scheme 1) yielded the desired compounds. For the synthesis of dendrimers with Si(CH₃)₂CH₂PPh₂ endgroups we also applied an alternative route. After hydrosilylation of the unsaturated endgroups with chloromethyldimethylsilane the phosphine-terminated dendrimers were obtained by reaction with potassium diphenylphosphide (scheme 1). Chloromethylsilane-groups are less sensitive towards hydrolysis than chlorosilane-groups, and therefore this synthetic route was preferred. After stirring the reaction mixture for three hours all the chloromethylsilane-groups had reacted. The dendrimers were obtained as oils, becoming more viscous for higher generations. Characterisation by ¹H- and ³¹P-{¹H}-NMR spectroscopy and MALDI-TOF mass spectrometry showed that the SiCH₃PPh₂-functionalised dendrimers were obtained in at least 95% purity. Impurities are probably due to hydrolysis of the Si-Cl to give Si-OH and Si-O-Si or to decomposition to give CH₃PPh₂ (see chapter 2).

When comparing the structures of the C₂- and C₃-dendrimers (see chapter 1 for clarification of these names), we can see from figure 4 in chapter 1 that the second
generation C₂-dendrimer is smaller and more compact than the same generation C₃-dendrimer. We expect that upon functionalisation with phosphines the P-atoms will be forced closer together in the C₂-dendrimers than in the same generation C₃-dendrimers.

**Scheme 1.** Synthesis of diphenylphosphine-functionalised carboxilane dendrimers with a methylene-spacer between the Si-atom and the P-atom.

\[
\begin{align*}
G_0 \quad & \xrightarrow{\text{HSiMe}_2\text{CH}_2\text{Cl}} \quad G_1 \quad & \xrightarrow{\text{Ph}_2}\text{PK} \quad G_2 \\
1: x = 0, n = 0, m = 4 & \quad 7: x = 0, n = 0, m = 4 \\
2: x = 1, n = 0, m = 12 & \quad 8: x = 1, n = 0, m = 12 \\
3: x = 2, n = 0, m = 36 & \quad 9: x = 2, n = 0, m = 36 \\
4: x = 0, n = 1, m = 4 & \quad 10: x = 0, n = 1, m = 4 \\
5: x = 1, n = 1, m = 12 & \quad 11: x = 1, n = 1, m = 12 \\
6: x = 2, n = 1, m = 36 & \quad 12: x = 2, n = 1, m = 36 \\
\end{align*}
\]

\[
\begin{align*}
G_0 \quad & \xrightarrow{\text{HSiMe}_2\text{CH}_2\text{Cl}} \quad G_1 \quad & \xrightarrow{\text{Ph}_2}\text{PCH}_2\text{Li.TMEDA} \quad G_2 \\
13: x = 0, n = 0, m = 4 & \quad 19: x = 0, n = 0, m = 4 \\
14: x = 1, n = 0, m = 12 & \quad 20: x = 1, n = 0, m = 12 \\
15: x = 2, n = 0, m = 36 & \quad 21: x = 0, n = 1, m = 4 \\
16: x = 0, n = 1, m = 4 & \quad 22: x = 1, n = 1, m = 12 \\
17: x = 1, n = 1, m = 12 & \quad 23: x = 0, n = 0, m = 4 \\
18: x = 2, n = 1, m = 36 & \quad 24: x = 1, n = 0, m = 12 \\
\end{align*}
\]

\[
\begin{align*}
G_0 \quad & \xrightarrow{\text{HSiMe}_2\text{CH}_2\text{Cl}} \quad G_1 \quad & \xrightarrow{\text{Ph}_2}\text{PCH}_2\text{Li.TMEDA} \quad G_2 \\
25: x = 2, n = 0, m = 36 & \quad 29: x = 0, n = 0, m = 4 \\
26: x = 0, n = 1, m = 4 & \quad 30: x = 1, n = 0, m = 12 \\
27: x = 1, n = 1, m = 12 & \quad 31: x = 0, n = 1, m = 4 \\
28: x = 2, n = 1, m = 36 & \quad 32: x = 1, n = 1, m = 12 \\
\end{align*}
\]

\(G_x\) is the generation x of the carboxilane dendrimer, e.g. \(G_0 = \text{tetraallylsilane or tetravinylsilane}\)

In addition to dendrimers with Si(CH₃)₂CH₂PPh₂ and Si(CH₃)(CH₂PPh₂)₂ endgroups (containing a methylene-spacer between the terminal Si-atom and P-atom), dendrimers with Si(CH₃)₂CH₂CH₂PPh₂ endgroups have been synthesised (scheme 2). The allylic endgroups of the zeroth and first generation C₃-dendrimers were hydrosilylated with chloromethyltrdimethylsilane and subsequently reacted with the tetramethylethlenediamine complex of (diphenylphosphino)methyl lithium to give dendrimers with an ethylene-spacer between the terminal silicon atom and the phosphorus atom. The model compounds \((\text{H}_3\text{C})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2 (35)\) and \((\text{H}_3\text{C})_2\text{Si(CH}_2\text{CH}_2\text{PPh}_2)_2 (36)\) were prepared by reaction of chloromethyltrimethylsilane and bis(chloromethyl)dimethylsilane with the tetramethylethlenediamine complex of (diphenylphosphino)methyl lithium.

We have now presented three synthetic procedures to obtain diphenylphosphine-functionalised carbosilane dendrimers. The first method using chlorosilane-terminated dendrimers and Ph₂PCH₂Li.TMEDA led to a functionalisation of ~95% of the endgroups of the dendrimers. The second procedure was a reaction of chloromethylsilane-terminated dendrimers with potassium diphenylphosphide to give Si(CH₃)₂CH₂PPh₂-functionalised dendrimeric molecules. This method was expected to give purer compounds, since chloromethylsilane groups are less sensitive towards hydrolysis than chlorosilane groups. However, these dendrimers were also not completely functionalised and the presence of small amounts of methylidiphenylphosphine was observed. The only explanation for the presence of CH₃PPh₂ is decomposition of the SiCH₂PPh₂ endgroups of the dendrimer. The third method consists of a reaction of chloromethylsilane-terminated dendrimers with Ph₂PCH₂Li.TMEDA to give dendrimers with Si(CH₃)₂CH₂CH₂PPh₂ endgroups. This procedure led to the formation of pure compounds according to NMR spectroscopy and mass spectrometry.

Catalysis

The diphenylphosphine-terminated carbosilane dendrimers were used as ligands in the rhodium catalysed hydroformylation of 1-octene (scheme 3). The catalyst was prepared in situ by mixing (acetylacetonato)dicarbonylrhodium(I) and the dendrimeric ligand under a H₂/CO pressure of 20 bar.
When using the dendrimers with Si(CH$_3$)$_2$CH$_2$PPh$_2$ ("SiP") and Si(CH$_3$)(CH$_2$PPh$_2$)$_2$ ("SiP$_2$") endgroups as ligands, the selectivity for the linear and branched aldehydes (70:30) of the dendrimeric systems is the same as that of the model systems 33 and 34. Neither isomerisation of 1-octene nor hydrogenation to alkanes and alcohols is observed during the catalytic reactions. The dendrimeric structure, i.e. the different generations of dendrimers with SiP and SiP$_2$ endgroups, has no influence on the selectivity of the reaction. However, we did observe differences in reaction rates between the various dendrimeric ligands.

In general, a higher phosphine/rhodium ratio led to a slower reaction. Rhodium complexes with three or four coordinating phosphine ligands or dimeric rhodium complexes can be formed which show little or no activity. In contrast, the model compound (CH$_3$)$_3$SiCH$_2$PPh$_2$ (33) gives a more active catalyst at a higher P/Rh ratio (table 1a). Since the reaction is much faster than for the other ligands, it was already stopped after 30 minutes. During this time catalyst formation might not have been complete. This would explain the lower conversions for lower P/Rh ratios.

When comparing table 1a with 1b it can be seen that the dendrimers with SiP endgroups (23-28) give faster catalysts than the dendrimers with SiP$_2$ endgroups (29-32), a difference that is also observed for the model compounds (33 and 34). Note that the reaction times for the dendrimeric catalysts containing SiP$_2$ endgroups and a P/Rh ratio of 5 or 10 are 4 hours, while the other reaction times are 1 hour.
Table 1. Rhodium catalysed hydroformylation of 1-octene using various dendrimeric ligands.a

a) dendrimers with Si(CH$_3$)$_2$CH$_2$PPh$_2$ endgroups

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<th>ligand</th>
<th>P/Rh</th>
<th>time (h)</th>
<th>conversion (%)</th>
<th>l/b</th>
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b) dendrimers with Si(CH$_3$)(CH$_2$PPh$_2$)$_2$ endgroups

<table>
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<th>ligand</th>
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<td>1</td>
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aT = 80°C, solvent: toluene, p$_{CO}$=p$_{H2}$=10 bar, [Rh] = 1 mM, [1-octene] = 637 mM; bA lot of isomerisation was observed for ligand 29 when P/Rh = 2.5.
For P/Rh ratios of 5 and 2.5 the catalysts containing the dendrimeric ligands with SiP₂ endgroups give very similar conversions (table 1b), all being about three times as low as the conversion of the model compound (34) after the same reaction time. In the case of a P/Rh ratio of 5 this might be explained by a higher local concentration of phosphines for the dendrimers compared to the model compound and thus an increase in the amount of inactive rhodium surrounded by three or four P-atoms. When a P/Rh ratio of 2.5 is used, however, the excess of phosphines is small and the formation of Rh-complexes containing three or four phosphines is not very likely. The low activity might be caused by the formation of inactive rhodium dimers. The high isomerisation observed for ligand 29 indicates the presence of free rhodium. For a P/Rh ratio of 10 there is a slight decrease in activity upon going from the first generation to the second generation dendrimers (30<29 and 32<31), while the difference between the first generation dendrimers (29 and 31) and the model compound (34) is negligible. At higher phosphine concentrations the amounts of inactive Rh-complexes are more likely to be similar for the smaller dendrimers and the model compound, while the larger dendrimers have a higher local concentration of phosphine, which might lead to the formation of more inactive rhodium complexes such as dimers.

When considering the dendrimers functionalised with SiP endgroups (table 1a), the C₃-dendrimers (26, 27, 28) give generally faster catalysts than the more compact C₂-dendrimers (23, 24, 25) (see also figure 1). This effect is less pronounced for the first generation dendrimers (23 and 26). For a P/Rh ratio of 5 and 2.5 the activities of these systems are similar. However, for a P/Rh ratio of 10 the C₃-dendrimer (26), in which the phosphines are further apart than in the more compact C₂-dendrimer, gives a more active catalyst than 23 (40% conversion versus 24%). For the second and third generation dendrimers, where the local concentration of phosphines is higher, the more compact C₂-dendrimers (24 and 25) give slower catalysts than the more flexible C₃-dendrimers (27 and 28).

The larger SiP-terminated C₃-systems resulted in lower activities than their smaller analogues (28<27<26), especially when P/Rh = 2.5 (conversions are 41%, 59% and 64%, respectively). For higher phosphine concentrations (P/Rh = 10, 5) the first generation dendrimer (26) gives a faster catalyst than 27 and 28, but the second and third generation
dendrimers, both with high local concentrations of phosphorus atoms, are very similar (conversions are 18-23%). Figure 1 gives a graphic representation of these results.

**Figure 1.** Conversion of the Rh-catalysed hydroformylation of 1-octene using various generations of SiP-terminated C₂- and C₃-dendrimers with P/Rh = 10, 5 and 2.5.

Alper and co-workers performed hydroformylation reactions using rhodium complexes of N(CH₂PPh₂)₂-functionalised poly(amido amine) dendrimers on silica. They reported an increase in activity for dendrimers with a larger chain length. The similarity of the results using the SiP₂-terminated dendrimers (29, 30, 31 and 32) indicates that in the homogeneous phase we do not observe such a difference. The change in activity for the dendrimeric catalysts with SiP endgroups is likely to be due to the distance between the individual phosphines and thus the ring size of the (dendrimer)P-Rh-P ring. In the compact C₂-dendrimers the phosphines are forced in even closer proximity to each other in higher generations than in the C₃-dendrimers, which is reflected in a generally lower activity for the former. It is interesting to note that for the second and third generation C₂-dendrimers (24 and 25) the activity of the catalyst (for P/Rh = 2.5) falls in the range of that of the catalysts with dendrimeric ligands having SiP₂ endgroups. In order to visualise this effect, the results are summarised in a graph (figure 2).
**Figure 2.** Conversion of the Rh-catalysed hydroformylation of 1-octene (P/Rh = 2.5) using various carbosilane dendrimers.

![Graph showing conversion of Rh-catalysed hydroformylation of 1-octene using various carbosilane dendrimers.](image)

**Table 2.** Rhodium catalysed hydroformylation of 1-octene using dendrimeric ligands with an ethylene-spacer.

<table>
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<th>Ligand</th>
<th>P/Rh</th>
<th>Time (h)</th>
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*a*T = 80°C, solvent: toluene, p_{CO}=p_{H2}=10 bar, [Rh] = 1 mM, [1-octene] = 637 mM.

Table 2 shows the hydroformylation results of the SiCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}-dendrimers. When comparing tables 1 and 2, it can be seen that the SiCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}-model compounds (35 and 36) give very similar results to the SiCH\textsubscript{3}PPh\textsubscript{2}-model compounds (33 and 34). The dendrimeric ligands (37 and 38), however, give much slower catalysts than their
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SiCH$_2$PPh$_2$-analogues (26 and 27). Apparently, the larger ring-size of the SiCH$_2$CH$_2$PPh$_2$-dendrimers is not very favourable for the reaction rate of the hydroformylation of 1-octene. The dendrimeric ligand with twelve SiCH$_2$CH$_2$PPh$_2$ endgroups (38) induces a slightly higher selectivity towards the linear aldehyde ($l/b = 4.9$). Cole-Hamilton and co-workers also observed an increase in $l/b$ for dendrimeric systems containing Si(CH$_3$)(CH$_2$CH$_2$PPh)$_2$ endgroups ($l/b = 13.9$ for a silsesquioxane based carbosilane dendrimer with 16 phosphines).$^{19}$ They performed the reaction at a lower pressure (10 bar H$_2$/CO) and higher temperature (120°C) using a P/Rh ratio of 6. When we used those conditions for the hydroformylation of 1-octene catalysed by the Rh-complex of 38, we obtained a slightly higher $l/b$ compared to our standard conditions ($l/b = 5.3$ at 60% conversion after 1 hour). However, under these conditions also isomerisation towards internal alkenes (5%) was observed. The selectivity towards the linear aldehyde is actually slightly lower (80%) under these conditions than when using our standard conditions (83%). It should be noted that we used dendrimers with SiCH$_2$CH$_2$P endgroups, while Cole-Hamilton and co-workers performed these reactions with Si(CH$_2$CH$_2$P)$_2$ dendrimeric ligands. Hence, the (dendrimer)P-Rh-P rings are different.

A potential application of these dendrimeric catalysts is their use in continuous processes.$^{13-16}$ Preliminary experiments using a commercially available membrane with a molecular weight cut-off of 400 Dalton, which should be suitable for this size of dendrimers (Koch/SelRO MPF-60 NF)$^{27}$ showed that this membrane is not compatible to our standard hydroformylation conditions due to its temperature and solvent restrictions (see chapter 1).

**Conclusions**

Diphenylphosphine-functionalised carbosilane dendrimers are active in the rhodium catalysed hydroformylation of 1-octene. The dendrimeric ligands with Si(CH$_3$)$_2$CH$_2$PPh$_2$ and Si(CH$_3$)(CH$_2$PPh$_2$)$_2$ endgroups induce the same selectivity as their smaller analogues. The activity of the system depends on the size and flexibility of the dendrimeric ligand. The catalyst becomes less active when the phosphines are forced closer together, i.e. for higher generation dendrimers and for the more compact C$_2$-dendrimers. The dendrimeric ligands with Si(CH$_3$)$_2$CH$_2$CH$_2$PPh$_2$ endgroups give catalysts that are less active than the
catalysts with dendrimeric ligands containing a methylene-spacer between the terminal silicon atom 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. The (dendrimer)P-Rh-P ring is an important parameter for this effect and the selectivity might be tuned even further.

**Experimental section**

**General data.** All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were distilled under N₂ from sodium/benzophenone (toluene, THF, diethyl ether, hexane, pentane) or calcium hydride (dichloromethane) prior to use. TMEDA was distilled from n-butyllithium. Chemicals were purchased from Aldrich Chemical Co. and Acros Chimica and were used without further purification. The 1-octene was filtered over neutral alumina prior to use. Silica 60 (SDS Chromagel, 70-200 μm) was used for filtration of the reaction mixtures. Tetrabutylammonium hexachloroplatinate,²⁸ methylidiphenylphosphine,²⁹ and the tetramethylethlenediamine complex of (diphenylphosphino)methyl lithium³⁰ were prepared according to literature procedures. 

¹H+, 

¹³C-¹H₁-,

and 

³¹P-¹H₁-NMR spectra were recorded on a Bruker AMX 300 and on a Varian Mercury 300. The 

¹³C-¹H₁-NMR spectra for 35, 36, 37 and 38 were measured on a Varian Inova 500. The chemical shifts are given in ppm relative to TMS for 

¹H- and 

¹³C-NMR and relative to 

H₃PO₄ for 

³¹P-NMR. 

²⁹Si-¹H₁-NMR spectra were measured on a Bruker AC 100 and on a Bruker DRX 300 spectrometer. The chemical shifts are given in ppm relative to TMS. Matrix Assisted Laser Desorption Ionisation (MALDI) Time-of-Flight (TOF) mass spectrometry was performed using a Perkin Elmer/PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer (PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction. A 337nm UV Nitrogen laser producing 3ns pulses was used and the mass spectra were obtained in the linear and reflectron mode. Samples were prepared in an Atmosbag (Aldrich) filled with argon by mixing 10 μl of dichloromethane solution of the sample with 30 μl of a solution of 3 mg/l 2,5-dihydroxybenzoic acid (DHB) or Dithranol (DIT) in dichloromethane. One μl of the solution was loaded on a gold-sample plate, the solvent was removed and the sample transferred to the vacuum of the mass spectrometer for analysis. Fast atom bombardment (FAB) mass spectrometry was carried out using a JEOL SX/SX 102A (Tokyo, Japan) four-sector tandem mass spectrometer (B₁E₁B₂E₂ geometry), coupled to a JEOL MS/MP9021D/UPD data system. The samples were loaded in a nitrobenzylalcohol
solution onto a stainless steel probe and bombarded with xenon atoms with an energy of 8 KeV. During the high-resolution FAB-MS measurements a resolving power of 5,000-10,000 (10% valley definition) was used. Polyethyleneglycol (PEG) 300 and 600 was used to calibrate the mass spectrometer. Elemental analyses were measured on an Elementar Vario EL apparatus. Gas chromatography was performed on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB1 30 m column, film thickness 3.0 mm, carrier gas: 70 kPa He, F.I.D. detector).

The synthesis of the chloro-terminated dendrimers 13, 14, 15, 19 and 20, of the chloromethyl-terminated dendrimers 10 an 11, of model compound 34 and of the diphenylphosphine-functionalised dendrimers 23, 24, 25, 29, 30, 37 and 38 has been described in chapter 2. The Si(CH$_3$)$_2$PPh$_2$-functionalised dendrimers 23, 24 and 25 have also been synthesised using method B, starting from the chloromethyl-terminated dendrimers 7, 8 and 9.

Typical procedure for the preparation of the chloromethyl-terminated dendrimers:

**Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl)$_4$:**

7: The reaction was performed under N$_2$. To 0.257 g (1.89 mmol) tetravinylsilane (1) 5.6 μL 0.134 M [Bu$_4$N]$_2$[PtCl$_6$] solution in CH$_2$Cl$_2$ was added, followed by 1.8 mL (15 mmol) chloromethyldimethylsilane. The reaction mixture was stirred over the weekend at 40°C. Excess of chloromethyldimethylsilane was removed in vacuo. Product 7 was obtained as an off-white wax-like solid in 0.952 g (88%) yield. $^1$H-NMR (300 MHz, CDCl$_3$): δ 2.79 (s, 8H, SiC#$\equiv$Cl), 0.46 (s, 16H, SiCH$_2$CH$_2$Si), 0.09 (s, 24H, SiCH$_3$).

Si(CH$_2$CH$_2$Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl)$_3$)$_4$:  

8: This compound was prepared from 2 (0.267 g, 0.463 mmol) and chloromethyldimethylsilane (1.35 mL, 11 mmol) using the same procedure as for 7, yielding a white solid (0.791 g, 91%). Some dichloromethane (1.5 mL) was necessary to keep everything in solution. $^1$H-NMR (300 MHz, CDCl$_3$): δ 2.77 (s, 24H, SiCH$_2$Cl), 0.45 (s, 64H, SiCH$_2$CH$_2$Si), 0.07 (s, 72H, SiCH$_3$).

Si(CH$_2$CH$_2$Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl)$_3$)$_4$:  

9: This compound was prepared from 3 (0.261 g, 0.137 mmol) and chloromethyldimethylsilane (1.2 mL, 9.9 mmol) using the same procedure as for 7 (longer stirring was necessary; conversion was followed by $^1$H-NMR), yielding a thick oil (0.398 g, 50%, some product was lost by preparation of NMR samples to check for complete
conversion). The solid dendrimer was first dissolved in the chloromethylidimethylsilane before addition of the catalyst. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 2.76 (s, 72H, SiCH$_2$Cl), 0.48 (s, 208H, SiCH$_2$CH$_2$Si), 0.09 (s, 216H, SiCH$_3$).

**Si(CH$_2$CH$_2$CH$_2$Si(CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl)$_3$**:

12: This compound was prepared from 6 (0.502 g, 0.191 mmol) and chloromethylidimethylsilane (1.7 mL, 14 mmol) using the same procedure as for 7 (longer stirring was necessary; conversion was followed by $^1$H-NMR), yielding a colourless oil (0.894 g, 72%). $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 2.73 (s, 72H, SiCH$_2$Cl), 1.35 (m, 104H, SiCH$_2$CH$_2$Si), 0.69 (m, 104H, SiCH$_2$CH$_2$Si), 0.56 (m, 104H, SiCH$_2$CH$_2$Si), 0.08 (s, 216H, SiCH$_3$). Anal. calcd. for C$_{260}$H$_{801}$Si$_{15}$Cl$_{16}$: C 48.48; H 9.25. Found: C 48.91; H 9.48.

Typical procedure for the preparation of the chloro-terminated dendrimers:

**Si(CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Cl)$_4$**:

16: The reaction was performed under N$_2$, but the dendrimer was saturated with air before use. To a solution of 1.127 g (5.87 mmol) tetraallylsilane (4) in chlorodimethylsilane (3.5 mL, 32 mmol) a few drops of a concentrated solution of [Bu$_4$N]$_2$[PtCl$_6$] in technical ethanol were added. After stirring overnight the solvent was evaporated. Product 16 was converted into 26 without further purification. Product 16 was obtained as a colourless liquid in 3.24 g (97%) yield. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 1.45 (m, 8H, SiCH$_2$CH$_2$CH$_2$Si), 0.90 (m, 8H, SiCH$_2$CH$_2$CH$_2$Si), 0.62 (m, 8H, SiCH$_2$CH$_2$CH$_2$Si), 0.41 (s, 24H, SiCH$_3$). $^{13}$C-$^1$H-NMR (75 MHz, CDCl$_3$): $\delta$ 23.4 (s, SiCH$_2$CH$_2$CH$_2$SiCl, $J_{C-Si} = 58$ Hz), 17.6 (s, SiCH$_2$CH$_2$CH$_2$SiCl), 16.4 (s, SiCH$_2$CH$_2$CH$_2$SiCl, $J_{C-Si} = 49$ Hz), 1.6 (s, SiCH$_3$). $^{13}$C-$^1$H-NMR (19.9 MHz, CDCl$_3$): $\delta$ 32.1 (s, 4 Si, SiCl), 1.2 (s, 1 Si, core Si).

**Si(CH$_2$CH$_2$CH$_2$Si(CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Cl)$_3$**:

17: This compound was prepared from 5 (1.01 g, 1.26 mmol) using the same procedure as for 16, yielding a colourless oil (2.33 g, 96%). $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 1.45 (m, 32H, SiCH$_2$CH$_2$CH$_2$Si), 0.89 (m, 32H, SiCH$_2$CH$_2$CH$_2$Si), 0.60 (m, 32H, SiCH$_2$CH$_2$CH$_2$Si), 0.40 (s, 72H, SiCH$_3$). $^{13}$C-$^1$H-NMR (75 MHz, CDCl$_3$): $\delta$ 23.5 (s, SiCH$_2$CH$_2$CH$_2$SiCl), 18.4 (s, CH$_2$ inner ring), 17.6 (s, SiCH$_2$CH$_2$CH$_2$SiCl + CH$_2$ inner ring), 17.4 (s, CH$_2$ inner ring), 16.5 (s, SiCH$_2$CH$_2$CH$_2$SiCl), 1.7 (s, SiCH$_3$). $^{29}$Si-NMR (59.6 MHz, CDCl$_3$): $\delta$ 31.2 (s, 12 Si, SiCl), 0.9 (s, 12 Si, Si of branching point), 0.5 (s, 1 Si, core Si).
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Si(CH$_2$CH$_2$CH$_2$Si(CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Cl)$_3$)$_4$:

18: This compound was prepared from 6 (0.224 g, 0.0850 mmol) using the same procedure as for 16, yielding a colourless oil (0.52 g, 100%). $^1$H-NMR (300 MHz, CDCl$_3$): δ 1.46 (m, 72H, SiCH$_2$CH$_2$CH$_2$Si inner rings), 0.90 (m, 72H, SiCH$_2$CH$_2$CH$_2$SiCl), 0.61 (m, 136H, SiCH$_2$CH$_2$CH$_2$Si + SiCH$_2$CH$_2$CH$_2$Si inner rings), 0.42 (s, 216H, SiCH$_3$). $^{13}$C-$^1$H-$^1$H-NMR (75 MHz, CDCl$_3$): δ 23.5 (s, SiCH$_2$CH$_2$CH$_2$Si), 18.5 (s, SiCH$_2$CH$_2$CH$_2$Si), 16.5 (s, SiCH$_2$CH$_2$Si), 1.8 (s, SiCH$_3$).

Si(CH$_2$CH$_2$CH$_2$Si(CH$_3$)Cl)$_4$:

21: The reaction was performed under N$_2$, but the dendrimer was saturated with air before use. To a solution of 0.901 g (4.69 mmol) tetraallylsilane (4) in dichloromethylsilane (3 mL, 30 mmol) a few drops of a concentrated solution of [Bu$_4$N]$_2$[PtCl$_6$] in technical ethanol were added. After stirring overnight the solvent was evaporated. Product 7 was converted into 12 without further purification. Product 7 was obtained as a colourless liquid in 2.89 g (95%) yield. $^1$H-NMR (300 MHz, CDCl$_3$): δ 1.55 (m, 8H, SiCH$_2$CH$_2$Si), 1.20 (m, 8H, SiCH$_2$CH$_2$Si), 0.78 (s, 12H, SiCH$_3$), 0.69 (m, 8H, SiCH$_2$CH$_2$Si). $^{13}$C-$^1$H-$^1$H-NMR (75 MHz, CDCl$_3$): δ 25.7 (s, SiCH$_2$CH$_2$Si), 17.1 (s, SiCH$_2$CH$_2$Si), 15.6 (s, SiCH$_2$CH$_2$Si), 5.3 (s, SiCH$_3$).

Si(CH$_2$CH$_2$CH$_2$Si(CH$_2$CH$_2$Si(CH$_3$)Cl)$_2$)$_4$:

22: This compound was prepared from 5 (0.516 g, 0.643 mmol) using the same procedure as for 21, yielding a colourless oil (1.40 g, 100%). $^1$H-NMR (300 MHz, CDCl$_3$): δ 1.55 (m, 24H, SiCH$_2$CH$_2$CH$_2$Si), 1.3 (m, 8H, SiCH$_2$CH$_2$CH$_2$Si inner ring), 1.19 (m, 24H, SiCH$_2$CH$_2$CH$_2$SiCl), 0.78 (s, 36H, SiCH$_3$), 0.67 (m, 24H, SiCH$_2$CH$_2$CH$_2$SiCl), 0.61 (m, 16H, SiCH$_2$CH$_2$CH$_2$Si inner ring). $^{13}$C-$^1$H-$^1$H-NMR (75 MHz, CDCl$_3$): δ 25.7 (s, SiCH$_2$CH$_2$CH$_2$SiCl outer-ring), 18.3 (s, CH$_2$ inner ring), 17.4 (s, CH$_2$ inner ring), 17.3 (s, CH$_2$ inner ring), 17.2 (s, SiCH$_2$CH$_2$Si), 15.8 (s, SiCH$_2$CH$_2$SiCl), 5.3 (s, SiCH$_3$).

Typical procedure for the preparation of the diphenylphosphine-terminated dendrimers:

Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)$_4$:

23: Method B: To a solution of 0.880 g of the chloromethyl-terminated dendrimer 7 (1.54 mmol) in 4 mL THF 12.4 mL 0.5 M KPPH$_2$ (6.2 mmol) in THF was added dropwise at -70°C. After stirring for 4 hours, during which the temperature was increased to room temperature, the reaction mixture was filtered over silica. The excess of KPPH$_2$ was removed in vacuo
((room temperature, $10^{-5}$ mbar, overnight). The colourless oil was obtained in 75% yield (1.34 g, 1.15 mmol).

**Si(CH$_2$CH$_2$Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)$_3$**

24: Method B: This compound was prepared from 8 (0.7186 g, 0.382 mmol) and KPPh$_2$ (9.2 mL 0.5 M in THF, 4.6 mmol) using the same procedure as for 23, yielding a slightly yellow oil (1.23 g, 0.335 mmol, 88%).

**Si(CH$_2$CH$_2$Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)$_3$**

25: Method B: This compound was prepared from 9 (0.3855 g, 0.0663 mmol) and KPPh$_2$ (4.8 mL 0.5 M in THF, 2.4 mmol) using the same procedure as for 23, yielding a white wax-like solid (0.7025 g, 0.0627 mmol, 95%).

**Si(CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)$_4$**

26: Method A: A solution of Ph$_2$PCH$_2$Li.TMEDA (1.505 g, 4.67 mmol) in 20 mL THF was added to 16 (0.3409 g, 0.597 mmol). After stirring overnight the reaction mixture was filtered over silica, and the excess of Ph$_2$PCH$_3$ was removed *in vacuo* (100°C, $10^{-5}$ mbar, overnight). The slightly yellow liquid was obtained in 96% yield (0.7024 g, 0.573 mmol).

Method B: This compound was prepared from 10 (0.3610 g, 0.576 mmol) and KPPh$_2$ (4.65 mL 0.5 M in THF, 2.3 mmol) using the same procedure as for 23, yielding a colourless oil (0.5337 g, 0.435 mmol, 76%).

$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.5 (m, 16H, ArH), 7.3 (m, 24H, ArH), 1.39 (s, 8H, SiCH$_2$P), 1.31 (m, 8H, SiCH$_2$CH$_2$Si), 0.56 (m, 16H, SiCH$_2$CH$_2$Si), -0.06 (s, 24H, SiCH$_3$). $^{31}$P-1$^1$H-NMR (121.5 MHz, CDCl$_3$) δ -21.6. For $^{13}$C NMR spectra overnight measurements were necessary. Unfortunately, the P-functionalised dendrimers decomposed during a night in solution in the NMR-tube. Anal. calc'd. for C$_{72}$H$_{96}$P$_4$Si$_{10}$ (partly oxidised): C 69.64; H 7.79. Found: C 69.45; H 7.95.

**Si(CH$_2$CH$_2$CH$_2$Si(CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)$_3$**

27: Method A: This compound was prepared from 17 (0.5649 g, 0.292 mmol) and Ph$_2$PCH$_2$Li.TMEDA (1.970 g, 6.11 mmol) using the same procedure as for 26, yielding a colourless oil (0.935 g, 0.240 mmol, 82%).
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Method B: This compound was prepared from 11 (0.2252 g, 0.107 mmol) and KPPh₂ (2.6 mL 0.5 M in THF, 1.3 mmol) using the same procedure as for 23, yielding a colourless oil (0.3039 g, 0.0779 mmol, 73%).

\[^{1}H\]-NMR (300 MHz, CDCl₃) δ 7.43 (m, 48H, ArH), 7.26 (m, 72H, ArH), 1.29 (s, 24H, SiCH₂P), 1.24 (m, 32H, SiCH₂CH₂CH₂Si), 0.50 (m, 64H, SiCH₂CH₂CH₂Si), -0.16 (s, 72H, SiCH₃). \[^{31}P\]-\[^{1}H\]-NMR (121.5 MHz, CDCl₃) δ -21.6. MALDI-TOF-MS: m/z 4008 ([M+Ag]⁺) (calcd. 4010.0) , 3825 (M⁺+Ag-CH₂PPh₂+OH). Anal. calcd. for C₁₂₂H₃₂P₂Si₃₀ (partly oxidised): C 68.77; H 7.90. Found: C 68.57; H 8.03.

Si(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₃)₂CH₂PPh₂)₃)₄:

28: Method B: This compound was prepared from 12 (0.5507 g, 0.0842 mmol) and KPPh₂ (6.1 mL 0.5 M in THF, 3.0 mmol) using the same procedure as for 23, yielding a colourless oil (0.9469 g, 0.0794 mmol, 94%). \[^{1}H\]-NMR (300 MHz, CDCl₃) δ 7.4-7.0 (m, 360H, ArH), 1.19 (s (br.), 176H, SiCH₂P + SiCH₂CH₂CH₂Si), 0.44 (s (br.), 208H, SiCH₂CH₂CH₂Si), -0.23 (s (br.), 216H, SiCH₃). \[^{31}P\]-\[^{1}H\]-NMR (121.5 MHz, CDCl₃) δ -22.5 (s). Anal. calcd. for C₆₉₆H₉₆₀P₃₆Si₅₃O₁₆ (partly oxidised): C 68.60; H 7.94. Found: C 68.56; H 7.52.

Si(CH₂CH₂CH₂SiCH₃(CH₂PPh₂)₃)₄:

31: This compound was prepared from 21 (0.4164 g, 0.638 mmol) and Ph₂PCH₂Li.TMEDA (2.795 g, 8.67 mmol) using the same procedure as for 26, yielding a white oil (0.993 g, 0.506 mmol, 79%). \[^{1}H\]-NMR (300 MHz, CDCl₃) δ 7.5-7.1 (m, 80H, ArH), 1.20 (s, 16H, SiCH₂P), 1.15 (m, 8H, SiCH₂CH₂CH₂Si), 0.44 (m, 8H, SiCH₂CH₂CH₂Si), 0.28 (m, 8H, SiCH₂CH₂CH₂Si), -0.31 (s, 12H, SiCH₃). \[^{31}P\]-\[^{1}H\]-NMR (121.5 MHz, CDCl₃) δ -22.3. MALDI-TOF-MS: m/z 2068.5 ([M+Ag]⁺) (calcd. 2070.5), 1962 (M⁺), 1884 (M⁻-CH₂PPh₂+OH+Ag), 1778 (M⁻-CH₂PPh₂+OH).

Si(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₃)₂CH₂PPh₂)₃)₄:

32: This compound was prepared from 22 (0.4972 g, 0.228 mmol) and Ph₂PCH₂Li.TMEDA (3.387 g, 10.5 mmol) using the same procedure as for 26, yielding a slightly yellow oil (1.009 g, 0.165 mmol, 72%). \[^{1}H\]-NMR (300 MHz, CDCl₃) δ 7.5-7.1 (m, 240H, ArH), 1.14 (s (br.), 80H, SiCH₂P + SiCH₂CH₂CH₂Si), 0.3-0.5 (m (br.), 64H, SiCH₂CH₂CH₂Si), -0.35 (s (br.), 36H, SiCH₃). \[^{31}P\]-\[^{1}H\]-NMR (121.5 MHz, CDCl₃) δ -22.3. MALDI-TOF-MS: m/z 6110.3 (M⁺) (calcd. 6112.3), 5925.9 (M⁺-PPh₂, fragmentation).
Chapter 3

(H\textsubscript{3}C)\textsubscript{3}SiCH\textsubscript{2}PPh\textsubscript{2}:  

33: This compound was prepared from (H\textsubscript{3}C)\textsubscript{3}SiCH\textsubscript{2}Cl (0.9433 g, 7.69 mmol) and KPPh\textsubscript{2} (10 mL 0.5 M in THF, 5.0 mmol) using the same procedure as for 23, yielding a yellow liquid (1.300 g, 4.77 mmol, 95%). In this procedure an excess of (H\textsubscript{3}C)\textsubscript{3}SiCH\textsubscript{2}Cl is used because it can be easily removed in vacuo. \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.45 (m, 4H, ArH), 7.28 (m, 6H, ArH), 1.36 (d, 2H, SiCH\textsubscript{2}P, \( \text{J}_{\text{CP}} \) = 1.8 Hz), -0.08 (s, 9H, SiCH\textsubscript{3}). \textsuperscript{31}P-\textsuperscript{1}H-NMR (121.5 MHz, CDCl\textsubscript{3}) \( \delta \) 21.8. FAB-MS: \( m/z \) 272 (M\textsuperscript{+}, 100%), 257.1 (M\textsuperscript{+}-CH\textsubscript{3}), 73.0 (Me\textsubscript{3}Si), HRMS (FAB\textsuperscript{+}): \( m/z \) calc for C\textsubscript{16}H\textsubscript{22}SiP [M+H\textsuperscript{+}]: 273.1228. Found: 273.1232. Anal. calcd. for C\textsubscript{16}H\textsubscript{22}SiP (partly oxidised): C 69.33; H 7.64. Found: C 69.29; H 7.85.

(H\textsubscript{3}C)\textsubscript{3}SiCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}:  

35: A solution of Ph\textsubscript{2}PCH\textsubscript{2}Li.TMEDA (1.982 g, 6.15 mmol) in 15 mL THF was added dropwise to a solution of chloromethyltrimethylsilane (0.8777 g, 7.16 mmol) in 5 mL THF at -70°C. The reaction mixture was warmed to room temperature overnight. After filtration over silica, the solvent was evaporated. The excess of Ph\textsubscript{2}PCH\textsubscript{3} was removed in vacuo (100°C, 10\textsuperscript{-5} mbar, 2 hours). The colourless oil was obtained in 68% yield (1.1942 g, 4.17 mmol, some of the product was lost at the high vacuum). \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.49 (m, 4H, ArH), 7.35 (m, 6H, ArH), 2.06 (m, 2H, SiCH\textsubscript{2}CH\textsubscript{2}P), 0.65 (m, 2H, SiCH\textsubscript{2}CH\textsubscript{2}P), 0.06 (s, 9H, SiCH\textsubscript{3}). \textsuperscript{31}P-\textsuperscript{1}H-NMR (121.5 MHz, CDCl\textsubscript{3}) \( \delta \) 9.20. \textsuperscript{13}C-\textsuperscript{1}H-NMR (125.8 MHz, CDCl\textsubscript{3}) : \( \delta \) 139.3 (d, ipso-PhP, \( \text{J}_{\text{CP}} \) = 14.3 Hz), 133.0 (d, o-PhP, \( \text{J}_{\text{CP}} \) = 17.7 Hz), 128.7 (s, p-PhP), 128.7 (d, m-PhP, \( \text{J}_{\text{CP}} \) = 6.7 Hz), 22.0 (d, SiCH\textsubscript{2}CH\textsubscript{2}P, \( \text{J}_{\text{CP}} \) = 13.8 Hz), 12.5 (d, SiCH\textsubscript{2}CH\textsubscript{2}P, \( \text{J}_{\text{CP}} \) = 10.1 Hz), -1.6 (s, SiCH\textsubscript{3}). FAB-MS: \( m/z \) 286.1 (M\textsuperscript{+}, 100%), 271.1 (M\textsuperscript{+}-CH\textsubscript{3}), 209.1 (M\textsuperscript{+}-Ph), 73.0 (Me\textsubscript{3}Si), HRMS (FAB\textsuperscript{+}): \( m/z \) calc for C\textsubscript{17}H\textsubscript{24}SiP [M+H\textsuperscript{+}]: 287.1385. Found: 287.1385. Anal. calcd. for C\textsubscript{17}H\textsubscript{24}PSi: C 71.29; H 8.09. Found: C 70.84; H 8.16.

(H\textsubscript{3}C)\textsubscript{2}Si(CH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}):  

36: This compound was prepared from (H\textsubscript{3}C)\textsubscript{2}Si(CH\textsubscript{2}Cl\textsubscript{2}) (0.4376 g, 2.79 mmol) and Ph\textsubscript{2}PCH\textsubscript{2}Li.TMEDA (2.051 g, 6.36 mmol) using the same procedure as for 35, yielding a yellow oil (1.1892 g, 2.45 mmol, 88%). The excess of Ph\textsubscript{2}PCH\textsubscript{3} was removed in vacuo (100°C, 10\textsuperscript{-5} mbar, overnight). \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.25-7.42 (m, 20H, ArH), 1.92 (m, 4H, SiCH\textsubscript{2}CH\textsubscript{2}P), 0.60 (m, 4H, SiCH\textsubscript{2}CH\textsubscript{2}P), 0.00 (s, 6H, SiCH\textsubscript{3}). \textsuperscript{31}P-\textsuperscript{1}H-NMR (121.5 MHz, CDCl\textsubscript{3}) \( \delta \) -9.03. \textsuperscript{13}C-\textsuperscript{1}H-NMR (125.8 MHz, CDCl\textsubscript{3}) : \( \delta \) 138.8 (d, ipso-PhP, \( \text{J}_{\text{CP}} \) = 13.8 Hz), 132.7 (d, o-PhP, \( \text{J}_{\text{CP}} \) = 18.2 Hz), 128.5 (s, m-PhP), 128.3 (d, m-PhP, \( \text{J}_{\text{CP}} \) = 5.5 Hz), 21.6 (d, SiCH\textsubscript{2}CH\textsubscript{2}P, \( \text{J}_{\text{CP}} \) = 14.3 Hz), 10.3 (d, SiCH\textsubscript{2}CH\textsubscript{2}P, \( \text{J}_{\text{CP}} \) = 10.2 Hz), -3.8 (s, SiCH\textsubscript{3}). FAB-MS:
Rhodium catalysed hydroformylation using carbosilane dendrimers

$m/z$ 485.2 ([M+H$^+$]), 407.1 (M$^-$-Ph), 299.1 (M$^-$-PPh$_2$, 100%), HRMS (FAB$^-$): $m/z$ calcd for C$_{30}$H$_{34}$SiP$_2$ [M+H$^+$]: 485.1983. Found: 485.1916. Anal. calcd. for C$_{30}$H$_{34}$P$_2$SiO$_{0.2}$ (partly oxidised): C 73.86; H 7.03. Found: C 73.52; H 7.17.

Hydroformylation experiments. The hydroformylation reactions were carried out in a stainless steel autoclave, in which four small autoclaves were connected to perform four reactions simultaneously. The autoclaves were equipped with magnetic stirring bars and positioned in an oil bath. In a typical experiment the autoclaves were filled with 1 mL of 0.0030 M Rh(CO)$_2$(acac) solution (0.0030 mmol), 1 mL of dendrimer solution (0.0075 M = 0.0075 mmol, 0.015 M = 0.015 mmol, 0.018 M = 0.018 mmol or 0.030 M = 0.030 mmol) and 1 mL of substrate solution containing 1.9 M 1-octene (1.9 mmol) and 0.77 M n-decane (0.77 mmol) in toluene. Before adding the substrate solution the catalyst solution was flushed several times with CO/H$_2$ (1:1). Then the autoclaves were placed in the oil bath, which had already been heated to 80°C or 120°C, and pressurised to the appropriate pressure (20 or 10 bar). After the appropriate reaction time (1 or 4 hours) the reaction was stopped by cooling in an ice bath and subsequently a solution of tri-n-butylphosphite in ethanol was added. The conversion and product distribution were determined by GC analysis.

References


(27) Koch/SelRO MPF-60 NF membrane, Koch Membrane Systems, Düsseldorf, Germany, Molecular Weight Cut-off (MWCO) = 400 Dalton, maximum temp. = 40°C. Toluene: retention 6 = 80%, CH₂Cl₂: retention 6 = 99.5%.