Palladium Complexes of Phosphane-Functionalised Carbosilane Dendrimers as Catalysts in a Continuous-Flow Membrane Reactor

Debby de Groot,[a] Joost N. H. Reek,*[a] Paul C. J. Kamer,[a] and Piet W. N. M. van Leeuwen*[a]

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Phosphane-functionalised carbosilane dendrimers **9**, **10**, **11**, **12**, **13**, **19** and **20** have been synthesised, and their palladium complexes have been used as catalysts in the allylic substitution reaction. The catalytic sites at the periphery of the dendrimer support are readily accessible to the substrate, which is reflected – also for the larger dendrimeric systems – in the high catalytic activity. Moreover, the higher generations are sufficiently large to be retained by a nanofilter, and dendrimeric catalysts **13** and **20** have been applied in a continuous-flow membrane reactor. The stability of the palladium complexes of the phosphane-functionalised dendrimers is crucial for application in a continuous process of this type, and appeared to be very sensitive to small changes in the dendrimeric structure.

Introduction

Since the first reports by Vögtle,[1] Newkome,[2] and Tomalia,[3] the field of dendrimers has been explored intensively.[4−7] The synthesis of these highly ordered, tree-like structures has been a challenge to many chemists, resulting in new molecules with unique properties. Many different dendrimers have been synthesised, with a variety of functional groups in the chains,[8−14] in the core[15−21] and at the periphery.[22−28] One of the main applications of dendrimers[29−32] is their use in catalysis,[16,33−35] enabling recycling of the homogeneous catalysts by means of nanofiltration.[36−40]

Palladium complexes have been used as catalysts in many reactions that are of great importance to synthetic chemists.[41−43] Key issues in the development of easily applicable palladium catalysts include catalyst stability and recycling. Generally, palladium catalysts are not very stable, and the formation of palladium metal is often observed. Nevertheless, polymer-immobilised systems that can be used in consecutive batchwise reactions have been reported.[44−50] An even greater challenge would be the use of supported palladium catalysts in continuous processes, since small inactive palladium species would be washed out of the reactor, whereas these may be reactivated in batch reactions. Indeed, the so far reported palladium-functionalised dendrimers applied in continuous processes showed deactivation of the catalyst. Eggeling and co-workers observed catalyst deactivation when using a first generation phosphane−ester-functionalised carbosilane dendrimer in the palladium-catalysed hydrovinylation of styrene in a continuous-flow membrane reactor.[51] They reported precipitation of palladium metal in the reactor and on the surface of the membrane. The deactivation was attributed to the formation of multiply coordinated phosphane complexes and multinuclear phosphane-bridged complexes, possibly as a result of the high local concentration of phosphane at the periphery of the dendrimer. Brinkmann and co-workers reported leaching of palladium when using a fourth generation poly(propylene imine) dendrimer functionalised with diphenylphosphane−Pd end groups in a palladium-catalysed allylic substitution reaction performed in a continuous-flow membrane reactor.[38] They compensated for the loss of palladium by adding (allyl)palladium chloride in the feed, which resulted in product formation for a longer period. The formation of (ligand)$PdCl_2$ complexes was suggested as partly being responsible for the observed deactivation.

The goal of the work presented here is the exploration of palladium-functionalised dendrimers as catalysts for application in a continuously operated membrane reactor. For this purpose we functionalised carbosilane dendrimers[52−57] with diphenylphosphane end groups, and used the palladium complexes of these systems as catalysts. The dendrimers are large enough to enable their use in a continuous-flow membrane reactor. Previously, we had found that the second generation dendrimer with a calculated molecular volume of 2414 Å^3 [39] already displayed a retention of 98.1% when THF was used as a solvent[39] (99.7% for dichloromethane). The dendrimers used for catalysis in the membrane reactor are much larger, as is clearly

[a] Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

shown in Figure 1, and so should display an even higher retention. Catalyst stability is of crucial importance when reactions are performed in a continuous-flow membrane reactor, and this appeared to be very sensitive to small changes in the dendrimeric structure.

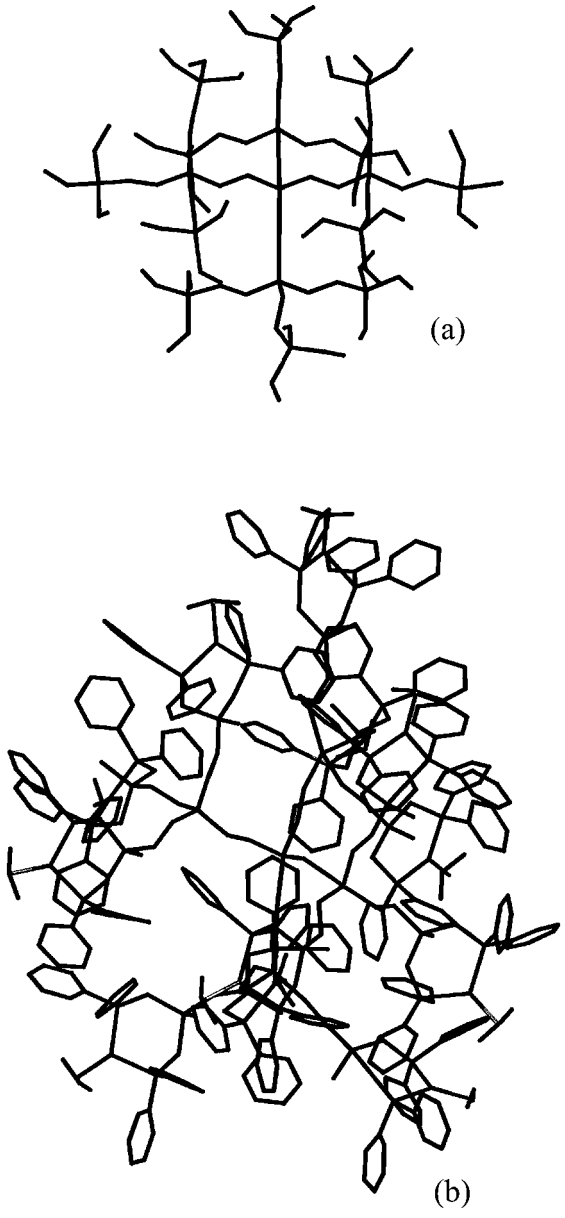
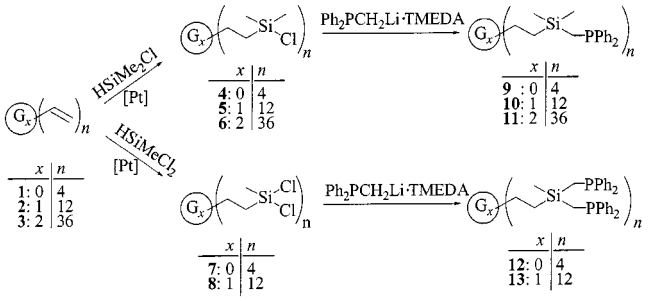


Figure 1. Crystal structure of the second generation dendrimer **3** (a) and a modelled structure[58] of the (allyl)Pd complex of **13** (b); hydrogen atoms and counter ions have been omitted for clarity

Results and Discussion

Synthesis of the Dendrimeric Ligands

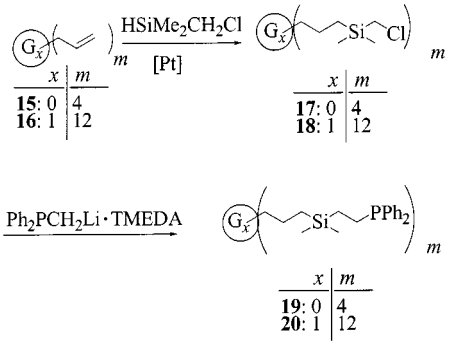
The phosphane-functionalised carbosilane dendrimers were synthesised by hydrosilylation of the double bonds of the various generations (G_0, G_1, G_2) with chlorodimethylsilane or dichloro(methyl)silane, followed by treatment with the tetramethylethylenediamine (TMEDA) complex of [(diphenylphosphanyl)methyl]lithium (Scheme 1). The hydrosilylation step was performed with an excess of chlorosilane as the solvent and tetrabutylammonium hexachloroplatinate as the catalyst.[59] Ph_2PCH_2Li·TMEDA was synthesised as described by Schore et al.[60] and obtained as a yellow solid after lithiation of Ph_2PCH_3 with *n*-butyllithium and TMEDA. A solution of Ph_2PCH_2Li·TMEDA in THF was added to the chlorosilane dendrimer. After stirring overnight, the reaction mixture was filtered through silica, and the excess of Ph_2PCH_3 was removed in vacuo. All the phosphane-functionalised dendrimers were obtained as oils or wax-like solids. Characterisation by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and MALDI-TOF mass spectrometry showed that the phosphane-functionalised dendrimers were obtained in at least 95% purity (see Exp. Sect. for details). Impurities were probably due to hydrolysis of the Si−Cl bond to give Si−OH and Si−O−Si. The MALDI-TOF mass spectra of the larger dendrimers (**11** and **13**) showed very broad signals in the expected range [for **11**: m/z = 8000−12000 (calcd. 11202); for **13**: m/z = 3000−6000 (calcd. 5888)]. Similar broad signals for larger functionalised dendrimers have been observed by Van Koten and co-workers.[40,61] A model compound, $(CH_3)_2Si(CH_2PPh_2)_2$ (**14**), was prepared by treatment of bis(chloromethyl)dimethylsilane with potassium diphenylphosphide. Previously, Alyea et al. reported the synthesis of this compound by treatment of chlorodiphenylphosphane with the Grignard reagent of bis(chloromethyl)-dimethylsilane.[62]



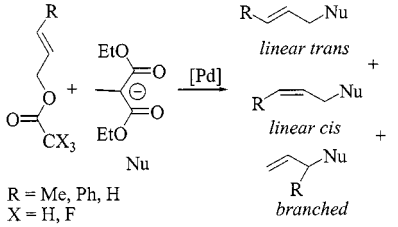
Scheme 1. Synthesis of diphenylphosphane-functionalised carbosilane dendrimers with a methylene spacer between Si atom and P atom

To obtain dendrimers with two carbon atoms between the terminal silicon atom and the phosphorus atom, carbosilane dendrimers (G_0, G_1) were hydrosilylated with (chloromethyl)dimethylsilane, followed by treatment with Ph_2PCH_2Li·TMEDA (Scheme 2).

Dendrimers **12** and **13** have four and twelve end groups, respectively, each containing an $SiMe(CH_2PPh_2)_2$ bis(phosphane) ligand. These units can be viewed as analogues of $Me_2Si(CH_2PPh_2)_2$ and dppp [= bis(diphenylphosphanyl)-propane]. The dendrimers **9**, **10**, **11**, **19** and **20** have end groups with $SiMe_2(CH_2)_yPPh_2$ (y = 1, 2) phosphane ligands, and bis(coordinated) metal complexes can only be formed between the phosphane units of different end groups.



Scheme 2. Synthesis of diphenylphosphane-functionalised carbosilane dendrimers with an ethylene spacer between the Si atom and the P atom



Scheme 3. Pd-catalysed allylic alkylation with sodium diethyl 2-methylmalonate as the nucleophile

Formation of the Palladium Complexes

In order to investigate complex formation between the dendrimeric ligand and the palladium ion, the phosphane-functionalised dendrimers were mixed with solutions of (COD)MePdCl (COD = 1,5-cyclooctadiene) to give the (dendrimer)MePdCl complexes (P/Pd = 2). The dendrimers **9**, **10** and **11** formed *trans* complexes according to $^{31}P\{^{1}H\}$ NMR spectroscopy, as singlets were observed at $\delta = 19$. These signals were broader for the higher generations [the signal for **11**-$(PdMeCl)_{18}$ was more than 165 Hz wide], which was probably a result of the many different conformations of the larger system and the different P−Pd−P rings formed. Dendrimers **12** and **13** coordinated in a *cis* fashion, similarly to the complexes formed by dppp.[63] The two doublets in the $^{31}P\{^{1}H\}$ NMR spectrum of **12**-$(PdMeCl)_4$ (at $\delta = 31.3$ and 2.75; $J = 39.0$ Hz) clearly showed the coupling of the inequivalent phosphorus atoms. For **13**-$(PdMeCl)_{12}$ the coupling between these atoms could not be observed, because the signals had broadened significantly. However, the two signals found in the $^{31}P\{^{1}H\}$ NMR spectrum at $\delta = 30.8$ and 2.38 suggested that *cis* complexes were formed.

(Allyl)palladium complexes were synthesised by treatment of the dendrimers with $[(\eta^3\text{-}C_3H_7)PdCl]_2$. According to the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra, the phosphane dendrimers **12** and **13** coordinated in a bidentate fashion, resulting in well-defined Pd complexes (both products gave broad signals at $\delta = 11.1$ in their $^{31}P\{^{1}H\}$ NMR spectra), whereas the monodentate phosphane dendrimers **9** and **11** gave rise to mixtures of products (as indicated by the presence of several signals in the $^{31}P\{^{1}H\}$ NMR spectra).

Catalysis

The Allylic Alkylation Reaction

Batch Process

The (allyl)Pd complexes of dendrimers **9**, **11**, **12** and **13** were used as catalysts in the allylic alkylation[41] of substituted allyl acetates with the sodium salt of diethyl 2-methylmalonate (Scheme 3).

The catalysts possessing dendrimeric ligands with large bridges between the P atoms (**9** and **11**) had very low activity compared to the catalysts containing **12** and **13** as ligands (Table 1). The selectivity towards the linear *trans* product was the same for all catalysts, and was also similar to that induced by palladium complexes of dppp [= bis(diphenylphosphanyl)propane] or dppb [= bis(diphenylphosphanyl)butane].[64] The second generation dendrimer **13** gave a slightly slower catalyst for the reaction with crotyl acetate than did its smaller analogue **12**. For cinnamyl acetate these dendrimeric catalysts showed similar activities.

Table 1. Pd-catalysed allylic alkylation of crotyl acetate or cinnamyl acetate and sodium diethyl 2-methylmalonate with (allyl)Pd complexes of **9**, **11**, **12**, **13**

Substrate	Ligand	Conversion (%)	*trans* (%)	*cis* (%)	Branched (%)
Crotyl acetate[a]	**9**	2	80	5	15
	11	2	78	6	16
	12	30	80	5	15
	13	22	80	5	15
Cinnamyl acetate[b]	**9**	0.6	99	0	1
	11	0.6	100	0	0
	12	10	97	0	3
	13	10	96	0	4

[a] Room temperature; solvent: THF; volume: 5 mL; [crotyl acetate] = 0.2 M; [sodium diethyl 2-methylmalonate] = 0.1 M; [Pd] = 0.05 mM; conversion after 2 h. [b] Room temperature; solvent: THF; volume: 20 mL; [cinnamyl acetate] = 46 mM; [sodium diethyl 2-methylmalonate] = 25 mM; [Pd] = 12.5 μM; conversion after 1 h.

Sodium acetate, which is not soluble in THF, was formed as a side-product during the above alkylation reaction. The precipitate formed might complicate the nanofiltration process if the reaction were performed in a continuous-flow membrane reactor. If allyl trifluoroacetate were used as a substrate, soluble sodium trifluoroacetate would be formed, which would prevent these potential complications. We studied this substrate in a batch process, and all the dendrimeric catalysts showed very high activity. With a substrate/Pd ratio of 2000, the yield after 5 min was approximately 50% and only small differences in reaction rates were observed for the different generations: The degrees of conversion after 5 min were 49%, 55%, 45% and 47% with ligands **9**, **11**, **12** and **13**, respectively. The activity did not

decrease with increasing generation, indicating that all active sites were acting as independent catalysts. From molecular modelling (Figure 1b) it is clear that all the (allyl)Pd groups indeed reside at the outer surface of the dendrimer and should be easily accessible to the nucleophile.

Addition of a second portion of substrate after a degree of conversion of over 90% had been reached showed that the catalyst remained active. Turnover numbers of over 15,000 were reached in the batch process with **13**-[Pd(allyl)Cl]$_{12}$, indicating that this is a stable dendrimeric catalyst that might perform very well in a continuous process if a membrane reactor was used.

Continuous Process

For the continuous process, a solution of allyl trifluoroacetate and sodium diethyl 2-methylmalonate in THF (with *n*-decane as an internal standard) was pumped through the reactor and **13**-[Pd(allyl)Cl]$_{12}$ was used as a catalyst.

In Figure 2 the yield is plotted as a function of the amount of substrate solution (expressed in reactor volumes) pumped through the reactor. The reaction started immediately after addition of the catalyst and reached its maximum yield after two reactor volumes. After this point the yield dropped and was nearly zero after approximately fifteen times the reactor volume of substrate solution had been pumped through the reactor. In view of the size of the system and the stability of the catalyst in batch reactions, this decrease was unexpectedly rapid. The retention of the dendrimeric catalyst was determined to be 99.7% in dichloromethane (vide infra). On the basis of this retention, the yield should have decreased by less than 5%. The retention of the dendrimeric catalyst in THF has not been determined, but the retention of the second generation dendrimer **3**, which is much smaller than the catalyst, was 98.1% with THF as a solvent. The observed rapid decrease in yield was therefore ascribed to decomposition of the palladium catalyst and not to leaching of the dendrimer. This was in agreement with the observation that samples taken from the product flow were catalytically inactive, indicating that no *active* palladium catalyst had passed through the membrane. When the experiment was stopped after 39 reactor volumes of substrate solution had been flushed through the reactor, the contents of the reactor and the solution that had passed through the membrane were analysed for palladium. ICP-AES showed that all the palladium had passed through the membrane.

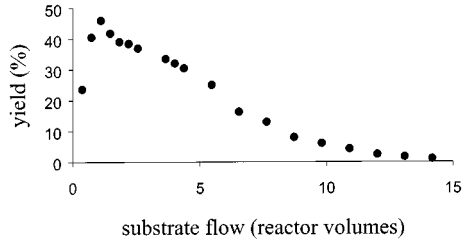


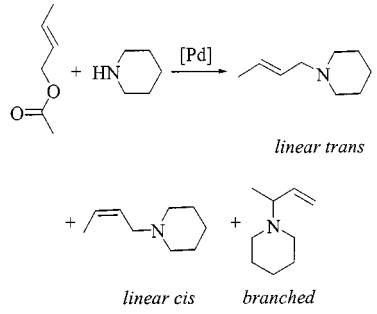
Figure 2. Application of dendrimeric ligand **13** in the allylic alkylation of allyl trifluoroacetate and sodium diethyl 2-methylmalonate in a continuous-flow membrane reactor (yield in % conversion of allyl trifluoroacetate in the product stream)

The deactivation observed in the continuous process was in sharp contrast with the stability of the catalyst when applied in a batch reaction. This suggested that the deactivation was induced either by interactions with the membrane or by leaching of small inactive palladium species. The former explanation can be ruled out, since batch experiments performed in the presence of pieces of membrane material gave results similar to those without membrane. Thus, one of the intermediate palladium complexes of the catalytic cycle was less strongly bound to the phosphane ligand and leached out of the reactor as a complex that showed little or no activity.

Allylic Amination

Batch Process

We were interested in the effect of the reaction conditions on the performance of these dendrimeric catalysts in the continuous-flow membrane reactor. An allylic substitution reaction was performed with an amine as the nucleophile and dichloromethane as the solvent. When the (allyl)Pd−dendrimer complexes of **9**, **11**, **12** and **13** were used as catalysts in the allylic amination reaction[42] between crotyl acetate and piperidine (Scheme 4, Table 2), dendrimers **12** and **13** gave more active catalysts than **9** and **11** did, as was also observed for the allylic alkylation reaction between crotyl acetate with sodium diethyl 2-methylmalonate. The selectivity induced by the dendrimers with SiMe(CH$_2$PPh$_2$)$_2$ end groups (**12** and **13**) was slightly differ-



Scheme 4. Pd-catalysed allylic amination with piperidine as the nucleophile

Table 2. Pd-catalysed allylic amination of crotyl acetate and piperidine with (allyl)Pd complexes of **9**, **11**, **12**, **13**

Ligand	Conversion[a][b] (%)	*trans* (%)	*cis* (%)	Branched (%)
9	26	24	6	70
11	26	31	5	64
12	59[c]	42	5	53
13	79	44	5	51

[a] Room temperature; solvent: CH_2Cl_2; volume: 5 mL; [crotyl acetate] = 0.12 M; [piperidine] = 0.25 M; [Pd] = 2 mM. [b] Conversion after 1 h. [c] The conversion is slightly lower due to partly decomposed catalyst.

ent from that generated by the dendrimers with Si-$Me_2CH_2PPh_2$ end groups (**9** and **11**).

Continuous Process

When palladium complexes of **13** were applied in a continuous process, deactivation of the catalyst during the experiment was again observed (Figure 3). The reaction started immediately after injection of the catalyst, and the maximum yield was reached after approximately three reactor volumes of substrate solution had been pumped through the reactor. The activity of the catalytic system decreased even more rapidly than that of the continuous allylic alkylation in THF.

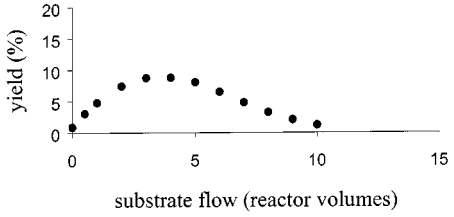


Figure 3. Application of dendrimeric ligand **13** in the allylic amination of crotyl acetate and piperidine in a continuous-flow membrane reactor (yield in % conversion of crotyl acetate in the product stream)

The retention of the second generation dendrimer (**3**) was high, also when the substrate solution was used as the solvent (98.2% versus 99.7% for pure CH_2Cl_2). Therefore, washing out of the dendrimeric system cannot account for the fast decrease in catalytic activity during the continuous process. Brinkmann and co-workers reported deactivation of the palladium catalyst in a continuous allylic amination reaction and observed the formation of an inactive (ligand)$PdCl_2$ complex, probably resulting from a reaction with dichloromethane.[38] To study this reaction, a model compound $\{(CH_3)_2Si(CH_2PPh_2)_2\}(\eta^3\text{-}C_3H_7)PdCl$ was prepared by treatment of $(CH_3)_2Si(CH_2PPh_2)_2$ (**14**) and 0.5 equiv. of $[(\eta^3\text{-}C_3H_7)PdCl]_2$. Decomposition of this complex was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and the formation of $\{(CH_3)_2Si(CH_2PPh_2)_2\}PdCl_2$ was observed. However, $\{(CH_3)_2Si(CH_2PPh_2)_2\}PdCl_2$ was only slightly less active than $\{(CH_3)_2Si(CH_2PPh_2)_2\}(\eta^3\text{-}C_3H_7)PdCl$ in the allylic amination of crotyl acetate and piperidine. Complete conversion was reached after 2 h. Therefore, the formation of $\{(CH_3)_2Si(CH_2PPh_2)_2\}PdCl_2$ by reaction with the solvent cannot account for the fast deactivation of the catalyst.

To study other possible deactivation pathways, we explored the stability of the **13**-$[Pd(allyl)Cl)]_{12}$ catalyst system by performing retention measurements in dichloromethane. The reactor was flushed with 10 reactor volumes and the amounts of palladium and phosphorus on both sides of the membrane were determined by ICP-AES. The retention of **13**-$[Pd(allyl)Cl]_{12}$ was 99.7%, indicating that the catalyst, which was in the Pd^{II} state, was stable under these conditions. During the catalytic cycle the catalyst also becomes Pd^0, and so we attempted a retention measurement of the catalyst in the Pd^0 state. By addition of 1 equiv. of diethylamine[65] we expected that, after nucleophilic attack, the Pd^{II} would have changed to Pd^0. Palladium and phosphorus analysis revealed a retention of 99.5%. The retention was still as high as 98.5% upon changing the solvent to a mixture of diethylamine and dichloromethane.

Apparently, the catalyst was stable under conditions very similar to those of the catalysis experiments; only the allyl acetate substrate was absent. We therefore conclude that the decomposition was stimulated by the presence of the allyl acetate. One possible deactivation pathway is through the formation of (allyl)Pd acetate complexes. Another possibility is that the alkene product or the alkene starting material might be stabilising the zerovalent (alkene)(P−P)Pd intermediate and causing the formation of $(alkene)_2Pd$ complexes.

We also prepared dendrimers with ethylene spacers between the terminal silicon atom and the phosphorus atom (**19** and **20**). The larger dendrimer (**20**) was applied as a ligand in the continuous allylic amination reaction. Figure 4 shows that the maximum yield was reached after approximately five reactor volumes of substrate solution had been pumped through the reactor. To our surprise, this dendrimeric catalyst was much more stable, and the formation of product was fairly constant during the next ten reactor volumes. After this period the degree of conversion was still more than 70% of the maximum reached. This decrease would correspond to a retention of the dendrimeric catalyst of more than 98%.

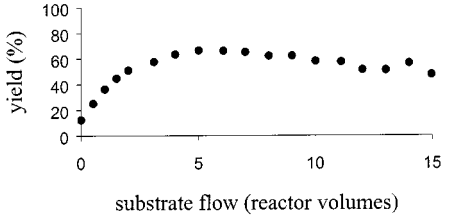


Figure 4. Application of dendrimeric ligand **20** in the allylic amination of crotyl acetate and piperidine in a continuous-flow membrane reactor (P/Pd = 2, yield in % conversion of crotyl acetate in the product stream)

In order to increase the activity and stability of the catalyst even further, the P/Pd ratio was increased from 2 to 4.[66] The batchwise allylic amination reaction between crotyl acetate and piperidine with dendrimeric ligand **20** and $[(crotyl)PdCl]_2$ as palladium precursor, with a P/Pd ratio of 4, appeared to be very fast: Over 65% conversion was obtained after 5 min under the same conditions as for the other dendrimeric ligands. This was nearly five times as fast as for **13**-$[Pd(allyl)Cl]_{12}$ with a P/Pd ratio of 2, and 25 times faster than for **9**-$[Pd(allyl)Cl]_4$ or **11**-$[Pd(allyl)Cl]_{36}$ (P/Pd = 2). We also performed the continuous process with a P/Pd ratio of 4 (Figure 5). The maximum yield obtained during the reaction was higher for P/Pd = 4 than for P/Pd = 2, showing that the catalyst was also more active under continuous-flow conditions, since the palladium concentration was the same in both experiments. In addition, the stability of the catalysts was very high. The slight decrease in yield

during this experiment (P/Pd = 4) is attributed to very small amounts of dendrimeric catalyst passing through the membrane. From the curve in Figure 5, the retention of the dendrimeric complex was estimated to be 98.5−99%, which is indeed in the range of the expected values. In contrast to **13**-[Pd(allyl)Cl]$_{12}$, the **20**-[Pd(allyl)Cl]$_3$ catalyst did not show decomposition during the continuous allylic amination reaction. The dendrimeric ligands with ethylene spacers between the terminal Si atom and P atom give catalysts that are more stable in the continuous process than the dendrimeric ligands with methylene spacers between Si and P. This might be due to the higher stability of the $SiCH_2CH_2P$ unit compared to $SiCH_2P$ (we have observed decomposition of this type of dendrimer to yield Ph_2PCH_3; see Exp. Sect.). More probably, the $SiCH_2CH_2PPh_2$ dendrimers give more stable Pd complexes than the $Si(CH_2PPh_2)_2$ dendrimers. If the reason for decomposition lies in an equilibrium between coordination of the phosphane ligand in the zerovalent (alkene)Pd complex and stabilisation of this complex by another alkene, then ligand **20** might possibly favour the coordinated complex, while the equilibrium might be shifted in the opposite direction for ligand **13**.

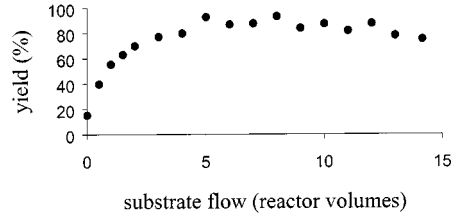


Figure 5. Application of dendrimeric ligand **20** in the allylic amination of crotyl acetate and piperidine in a continuous-flow membrane reactor (P/Pd = 4, yield in % conversion of crotyl acetate in the product stream)

In general, the stability of the catalyst is very important when considering its application in a continuous process. We have shown that small changes in the periphery of the dendrimer can have a huge impact on the stability of these catalytic systems, possibly through the formation of more stable palladium complexes.

Conclusions

We have described several routes to phosphane-functionalised carbosilane dendrimers, resulting in systems that differ in the number of phosphane units per silicon atom of the end group [$SiCH_3(CH_2PPh_2)_2$ versus $Si(CH_3)_2CH_2PPh_2$] and the number of carbon atoms between the phosphane unit and silicon end groups [$Si(CH_3)_2CH_2PPh_2$ versus $Si(CH_3)_2CH_2CH_2PPh_2$]. Palladium complexes of phosphane-functionalised carbosilane dendrimers were active as catalysts in the allylic substitution reaction and, as expected, the number of phosphane units per end group had an impact on the activity and selectivity in the allylic amination reaction. Interestingly, the activity was hardly influenced by the dendrimer size, making these dendrimers attractive as catalyst supports. These dendrimeric catalysts were sufficiently large to enable their application in a continuous-flow membrane reactor, as indicated by the retention of 99.7% for the dendrimeric catalyst **13**-[Pd(allyl)Cl]$_{12}$ in dichloromethane. When dendrimeric ligands with $Si(CH_2PPh_2)_2$ end groups were used, the yields for allylic substitution reactions dropped rapidly during continuous experiments, due to catalyst deactivation. When dendrimeric ligands with $SiCH_2CH_2PPh_2$ end groups were used, stable catalysts were obtained, that were successfully applied in the continuous-flow membrane reactor. During the experiment the yield of the reaction decreased to some extent, which was in line with a retention of 98.5−99%. The important message is that small changes in the dendrimeric ligand had a large impact on the catalyst stability. High catalyst stability is pivotal for successful application in continuous-flow membrane reactors.

Experimental Section

General Data: All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were distilled under N_2 from sodium/benzophenone (THF, diethyl ether, hexane, pentane) or calcium hydride (dichloromethane) prior to use. TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was distilled from *n*-butyllithium. Chemicals were purchased from Aldrich Chemical Co. and Acros Chimica and were used without further purification. Silica 60 (SDS Chromagel, 70−200 μm) was used for filtration of the reaction mixtures. The various generations of dendrimers (**1**, **2**, **3**, **15** and **16**) were prepared as described by Van der Made et al.[52] Tetrabutylammonium hexachloroplatinate,[59] methyldiphenylphosphane,[67] the tetramethylethylenediamine complex of (diphenylphosphanyl)methyllithium,[60] (COD)MePdCl,[68] [(η^3-C_4H_7)(COD)Pd][BF_4],[69] [(crotyl)PdCl]$_2$ [70] and [(allyl)PdCl]$_2$ [70] were prepared according to literature procedures. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker AMX 300 and a Varian Mercury 300. ^{13}C{^{1}H} NMR spectra were measured with a Bruker AMX 300 and a Varian Inova 500. The chemical shifts are given in ppm relative to TMS for ^{1}H and ^{13}C NMR and relative to H_3PO_4 for ^{31}P NMR. Matrix Assisted Laser Desorption Ionisation (MALDI) Time-of-Flight (TOF) mass spectrometry was performed with a Perkin−Elmer/PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer (PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction. A 337-nm UV nitrogen laser producing 3-ns 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; 1 μL of the solution was loaded onto a gold sample plate, the solvent was removed, and the sample was transferred to the vacuum of the mass spectrometer for analysis. Fast atom bombardment (FAB) mass spectrometry was carried out with a JEOL SX/SX 102A (Tokyo, Japan) four-sector tandem mass spectrometer ($B_1E_1B_2E_2$ geometry), coupled to a JEOL MS/MP9021D/UPD data system. The samples, in nitrobenzyl alcohol solution, were loaded onto a stainless steel probe and bombarded with xenon atoms with an energy of 8 keV. A resolving power of 5000−10000 (10% valley definition) was used during the high-resolution FAB-MS measurements. Polyethylene glycol (PEG) 300 and 600 were used to calibrate the mass spectrometer. Elemental analyses were measured with an Elementar Vario EL

apparatus. The amounts of palladium and phosphorus were determined with induced coupled argon plasma − atomic emission spectrometry (ICP-AES). The ICP-AES measurements were performed by a literature procedure,[71] with a sequential Jarrell Ash upgraded (Model 25) Atomscan model 2400 ICP scanning monochromator and a Perkin−Elmer Optima 3000 XL instrument. The measured atomic lines of Pd and P were 340.458 nm and 213.618 nm, respectively. Gas chromatography was performed with 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 GPC measurements were performed with a Shimadzu apparatus equipped with a Waters Styragel Column HR 1, HR 2 and HR 4 in series and with a RID-10A refractive index detector and a SPD-10A VP UV/Vis detector. The membrane reactor set-up contained a Gilson Piston Pump Model 303/10SC and a Gilson Model 802C Manometric Module. The reactor volume was 5 mL and the diameter of the membrane was 23 mm. A Koch/SelRO MPF-60 NF membrane (Koch Membrane Systems, Düsseldorf, Germany) with a molecular weight cut-off (MWCO) of 400 Dalton was used for the continuous experiments.

Typical Procedure for the Preparation of the Chloro-Terminated Dendrimers

Si[$CH_2CH_2Si(CH_3)_2Cl$]$_4$ (4): The reaction was performed under N_2. A few drops of a concentrated solution of $[Bu_4N]_2[PtCl_6]$ in technical ethanol were added to a solution of tetravinylsilane (**1**; 0.526 g, 3.86 mmol) in chlorodimethylsilane. After this had been stirred overnight, the solvent was evaporated. Product **4** was obtained as a white solid in 92% yield (1.82 g, 3.53 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7−0.5 (m, 16 H, SiCH_2CH_2Si), 0.42 (s, 24 H, SiCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 2.34 (s, SiCH_3), 3.47 (s, SiCH_2CH_2SiCl), 12.7 (s, SiCH$_2$$CH_2$SiCl). No further purification was performed, and product **4** was converted immediately into **9**.

Si{CH_2CH_2Si[$CH_2CH_2Si(CH_3)_2Cl]_3$}$_4$ (5): This compound was prepared from **2** (0.510 g, 0.883 mmol) according to the same procedure as for **4**, to yield a white solid (1.52 g, 0.887 mmol, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7−0.5 (m, 64 H, SiCH_2CH_2Si), 0.42 (s, 72 H, SiCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 2.40 (s, SiCH_3), 3.37 (s, SiCH_2CH_2SiCl), 12.9 (s, SiCH$_2$$CH_2$SiCl).

Si(CH_2CH_2Si{CH_2CH_2Si[$CH_2CH_2Si(CH_3)_2Cl]_3$}$_3$)$_4$ (6): This compound was prepared from **3** (0.322 g, 0.170 mmol) according to the same procedure as for **4** (a longer reaction time was necessary; conversion was monitored by ^{1}H NMR), to yield a white solid (0.676 g, 0.127 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7−0.4 (m, 208 H, SiCH_2CH_2Si), 0.42 (s, 216 H, SiCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 2.69 (s, SiCH_3), 3.41 (s, SiCH_2CH_2SiCl), 12.9 (s, SiCH$_2$$CH_2$SiCl).

Si[$CH_2CH_2Si(CH_3)Cl_2$]$_4$ (7): The reaction was performed under N_2. A few drops of a concentrated solution of $[Bu_4N]_2[PtCl_6]$ in technical ethanol were added to a solution of tetravinylsilane (**1**; 0.138 g, 1.01 mmol) in dichloromethylsilane. After this had been stirred overnight, the solvent was evaporated. Product **7** was obtained as a white solid in 97% yield (0.587 g, 0.985 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (s, 12 H, SiCH_3), 0.78−0.71 (m, 8 H, SiCH_2CH_2Si), 1.01−0.95 (m, 8 H, SiCH_2CH_2Si). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 1.5 (s, SiCH_3), 4.2 (s, SiCH_2CH_2SiCl), 13.9 (s, SiCH$_2$$CH_2$SiCl). No further purification was performed, and product **7** was converted immediately into **12**.

Si{CH_2CH_2Si[$CH_2CH_2Si(CH_3)Cl_2]_3$}$_4$ (8): This compound was prepared from **3** (0.162 g, 0.281 mmol) according to the same procedure as for **7**, to yield a white solid (0.562 g, 0.287 mmol, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (s, 36 H, SiCH_3), 0.46 0.77−0.70, 1.01−0.95 (m, 64 H, SiCH_2CH_2Si). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 1.5 (s, SiCH_3), 4.2 (s, SiCH_2CH_2SiCl),14.2 (s, SiCH$_2$$CH_2$SiCl).

Typical Procedure for the Preparation of the Diphenylphosphane-Terminated Dendrimers

Si[$CH_2CH_2Si(CH_3)_2CH_2PPh_2$]$_4$ (9): A solution of Ph_2PCH_2Li·TMEDA (2.43 g, 7.54 mmol) in THF (40 mL) was added to **4** (0.7565 g, 1.47 mmol). After stirring overnight, the reaction mixture was filtered through silica, and the excess of Ph_2PCH_3 was removed in vacuo (100 °C, 10^{-5} mbar, overnight). The slightly yellow liquid was obtained in 97% yield (1.67 g, 1.43 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.10 (s, 24 H, SiCH_3), 0.26 (s, 16 H, SiCH_2CH_2Si), 1.40 (s, 8 H, SiCH_2P), 7.3 (m, 24 H, ArH), 7.5 (m, 16 H, ArH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = −20.8 (s). MALDI-TOF-MS: *m*/*z* = 1170 [M^+] (calcd. 1169.8), 986 [M^+ − CH_2PPh_2 + OH]. $C_{68}H_{88}P_4Si_5$: calcd. C 69.81, H 7.59; found C 69.33, H 7.59.

Estimation of the Purity: The vinyl-functionalised dendrimers were all purified by silica column chromatography, and these compounds were considered to be pure starting materials. The hydrosilylation reaction was quantitative, as evidenced by ^{1}H NMR (no vinyl signals were visible in any of the spectra). The reaction between the chlorosilane-terminated dendrimers and the lithium reagents {[(diphenylphosphane)methyl]lithium} was monitored by ^{1}H NMR, by monitoring the Si$(CH_3)_2$Cl signals (δ = 0.8), which were shifted to δ = −0.10 [−0.20 for SiMe$(CH_2PPh_2)_2$] after functionalisation. Unchanged Si$(CH_3)_2$Cl gave a clear peak at δ = 0.04 [δ = −0.13 for SiMeOR(CH_2PPh_2)] after hydrolysis. According to these NMR spectra at least 95% of the end groups had been functionalised with phosphanes, and the remaining end groups were hydrolysed chlorosilanes, giving Si$(CH_3)_2$OR. When dendrimers **9**, **10**, **11**, **12** and **13** and model compound **14** were stored in glass Schlenk flasks, either at room temperature or at −20 °C and with or without exclusion of light, slow decomposition took place to yield Ph_2PCH_3 and an insoluble polymeric substance.

Si{$CH_2CH_2Si[CH_2CH_2Si(CH_3)_2CH_2PPh_2]_3$}$_4$ (10): This compound was prepared from **5** (0.5355 g, 0.313 mmol) and Ph_2PCH_2Li·TMEDA (3.38 g, 10.49 mmol) according to the same procedure as for **9**, to yield a slightly yellow oil (0.944 g, 0.257 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.20 (br. s, 72 H, SiCH_3), 0.28 (s, 64 H, SiCH_2CH_2Si), 1.28 (br. s, 24 H, SiCH_2P), 7.2 (m, 72 H, ArH), 7.4 (m, 48 H, ArH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = −21.7 (s). MALDI-TOF-MS: *m*/*z* = 3682 [M^+] (calcd. 3677.7), 3498 [M^+ − CH_2PPh_2 + OH], 3322 [M^+ − 2 CH_2PPh_2 + 2 OH]. $C_{212}H_{280}P_{12}Si_{17}$: calcd. C 69.23, H 7.68; found C 68.51, H 7.66.

Si(CH_2CH_2Si{CH_2CH_2Si[$CH_2CH_2Si(CH_3)_2CH_2PPh_2]_3$}$_3$)$_4$ (11): This compound was prepared from **6** (0.4625 g, 0.0872 mmol) and Ph_2PCH_2Li·TMEDA (2.69 g, 8.33 mmol) according to the same procedure as for **9**, to yield a slightly yellow oil (0.8858 g, 0.0791 mmol, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.25 (br. s, 216 H, SiCH_3), 0.31 (br. s, 208 H, SiCH_2CH_2Si), 1.25 (br. s, 72 H, SiCH_2P), 7.5−7.0 (m, 360 H, ArH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = −22.0 (s). MALDI-TOF-MS: *m*/*z* = 8000−12000 (very broad) (calcd. 11201.6). $C_{644}H_{856}P_{36}Si_{53}$: calcd. C 69.05, H 7.71; found C 68.20, H 7.70.

Si[$CH_2CH_2SiCH_3(CH_2PPh_2)_2$]$_4$ (12): This compound was prepared from **7** (0.5716 g, 0.958 mmol) and Ph_2PCH_2Li·TMEDA (6.44 g,

20.0 mmol) according to the same procedure as for **9**, to yield a yellow liquid (1.098 g, 0.576 mmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.29 (br. s, 12 H, SiCH_3), 0.19 (m, 16 H, SiCH_2CH_2Si), 1.26 (br. s, 16 H, SiCH_2P), 7.5−7.1 (m, 80 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −22.5 (s). MALDI-TOF-MS: *m/z* = 1907 [M^+] (calcd. 1906.5), 1707 [$M^+ - CH_2PPh_2$, fragmentation]. $C_{116}H_{124}P_8Si_5$: calcd. C 73.08, H 6.56; found C 72.59, H 6.75.

Si{$CH_2CH_2Si[CH_2CH_2SiCH_3(CH_2PPh_2)_2]_3$}$_4$ (13): This compound was prepared from **8** (0.5628 g, 0.288 mmol) and Ph_2PCH_2Li·TMEDA (5.11 g, 15.9 mmol) according to the same procedure as for **9**, to yield a yellow oil (1.368 g, 0.232 mmol, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.38 (br. s, 36 H, SiCH_3), 0.35 (m, 64 H, SiCH_2CH_2Si), 1.12 (br. s, 48 H, SiCH_2P), 7.5−7.0 (m, 240 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −= 22.6 (s). MALDI-TOF-MS: *m/z* = 3000−6000 (very broad) (calcd. 5887.9). $C_{356}H_{388}P_{24}Si_{17}$: calcd. C 72.6, H 6.65; found C 70.08, H 6.82. The deviation was attributed to incomplete functionalisation of the dendrimer.

$(H_3C)_2Si(CH_2PPh_2)_2$ (14): $KPPh_2$ in THF (0.5 M, 20 mL, 10 mmol) was added dropwise at −70 °C to a solution of $(H_3C)_2Si(CH_2Cl)_2$ (0.7867 g, 5.01 mmol) in THF (2 mL). After stirring for 3 h, during which the temperature was increased to room temperature, the reaction mixture was filtered through silica. The excess of PPh_2 was removed in vacuo (room temperature, 10^{-5} mbar, overnight). A white oil was obtained in 64% yield (1.458 g, 3.19 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ = −0.20 (s, 6 H, SiCH_3), 1.27 (d, 4 H, SiCH_2P, $^2J_{HP}$ = 1.2 Hz), 7.27 (m, 12 H, ArH), 7.36 (m, 8 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ = −22.8. FAB-MS: *m/z* = 457.2 [M + H]$^+$, 379.1 [M^+ − Ph], 73.0 [Me_3Si]. HRMS (FAB$^+$): *m/z* calcd. for $C_{28}H_{31}SiP_2$ [M + H]$^+$: 457.1670; found 457.1676. $C_{28}H_{30}P_2Si$: calcd. C 73.65, H 6.63; found C 73.18, H 6.63.

Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Cl$]$_4$ (17): The reaction was performed under N_2. $[Bu_4N]_2[PtCl_6]$ solution in CH_2Cl_2 (0.134 M, 3.3 μL) was added to the dendrimer **15** (0.2105 g, 1.09 mmol), followed by (chloromethyl)dimethylsilane (1.0 mL, 8.2 mmol). The reaction mixture was stirred overnight at 45 °C. Excess (chloromethyl)dimethylsilane was removed in vacuo. Product **17** was obtained as a slightly yellow oil. ^{1}H NMR ($CDCl_3$): δ = 0.11 (s, 24 H, SiCH_3), 0.58 (m, 8 H, SiCH_2CH$_2$CH$_2$Si), 0.71 (m, 8 H, SiCH$_2$CH$_2$CH_2Si), 1.33 (m, 8 H, SiCH$_2$CH_2CH$_2$Si), 2.78 (s, 8 H, SiCH_2Cl). $C_{24}H_{56}Cl_4Si_5$: calcd. C 45.98, H 9.00; found C 45.64, H 9.01.

Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Cl]_3$}$_4$ (18): This compound was prepared from **16** (0.809 g, 1.01 mmol) and (chloromethyl)dimethylsilane (3.0 mL, 24 mmol) according to the same procedure as for **17**, to yield a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, 72 H, SiCH_3), 0.59 (m, 32 H, SiCH_2CH$_2$CH$_2$Si), 0.72 (m, 32 H, SiCH$_2$CH$_2$CH_2Si), 1.37 (m, 32 H, SiCH$_2$CH_2CH$_2$Si), 2.77 (s, 24 H, SiCH_2Cl). $C_{84}H_{192}Cl_{12}Si_{17}$: calcd. C 47.92, H 9.19; found C 47.82, H 9.14.

Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2CH_2PPh_2$]$_4$ (19): A solution of Ph_2PCH_2Li·TMEDA (2.070 g, 6.422 mmol) in 15 mL of THF was added dropwise at −70 °C to a solution of **17** (0.4166 g, 0.665 mmol) in 5 mL of THF. The reaction mixture was allowed to warm to room temperature overnight. After filtration through silica, the solvent was evaporated. The excess of Ph_2PCH_3 was removed in vacuo (100 °C, 10^{-5} mbar, overnight). A slightly yellow oil was obtained in 84% yield (0.7182 g, 0.560 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.07 (s, 24 H, SiCH_3), 0.51 (m, 24 H, SiCH_2CH$_2$CH_2Si + SiCH_2CH$_2$P), 1.23 (m, 8 H, SiCH$_2$CH_2CH$_2$Si), 1.95 (m, 8 H, SiCH$_2$CH_2P), 7.25−7.42 (m, 40 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ = −9.03. ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = −1.6 (s, SiCH_3), 11.0 (d, SiCH_2CH$_2$P, $^2J_{C,P}$ = 9.3 Hz), 17.4 (s, CH_2 of SiCH$_2$CH$_2$CH$_2$Si), 18.5 (s, CH_2 of SiCH$_2$CH$_2$CH$_2$Si), 19.8 (s, CH_2 of SiCH$_2$CH$_2$CH$_2$Si), 21.7 (d, SiCH$_2$CH$_2$P, $^1J_{C,P}$ = 13.5 Hz), 128.5 (s, *p*-PhP), 128.3 (d, *m*-PhP, $^3J_{C,P}$ = 6.3 Hz), 132.7 (d, *o*-PhP, $^2J_{C,P}$ = 18.2 Hz), 138.8 (d, *ipso*-PhP, $^1J_{C,P}$ = 14.2 Hz). FAB-MS: *m/z* = 1283 [M + H]$^+$, 1206 [M^+ − Ph], 1098 [M^+ − PPh_2], 1085 [M^+ − CH_2PPh_2], 1069 [M^+ − CH_2PPh_2-CH_3]. MALDI-TOF-MS: *m/z* = 1280.7 [M^+] (calcd. 1282.0), 1096 [M^+ − PPh_2, fragmentation]. $C_{76}H_{104}P_4Si_5$: calcd. C 71.20, H 8.18; found C 70.48, H 8.29.

Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_3)_2CH_2CH_2PPh_2]_3$}$_4$ (20): This compound was prepared from **18** (0.2153 g, 0.102 mmol) and Ph_2PCH_2Li·TMEDA (0.4386 g, 1.36 mmol) according to the same procedure as for **19**, to yield a colourless oil (0.1512 g, 0.0371 mmol, 36%, some product probably remained on the silica during the filtration). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.09 (s, 24 H, SiCH_3), 0.51 (m, 88 H, SiCH_2CH$_2$CH_2Si + SiCH_2CH$_2$P), 1.20 (m, 32 H, SiCH$_2$CH_2CH$_2$Si), 1.95 (m, 24 H, SiCH$_2$CH_2P), 7.25−7.41 (m, 120 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −9.16. ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = −3.2 (s, SiCH_3), 11.3 (d, SiCH_2CH$_2$P, $^2J_{C,P}$ = 10 Hz), 17.6 (s, CH_2 of SiCH$_2$CH$_2$CH$_2$Si),18.7 (s, CH_2 of SiCH$_2$CH$_2$CH$_2$Si), 20.1 (s, CH_2 of SiCH$_2$CH$_2$CH$_2$Si), 21.9 (d, SiCH$_2$CH$_2$P, $^1J_{C,P}$ = 13.8 Hz), 128.6 (d, *m*-PhP, $^3J_{C,P}$ = 6.8 Hz), 128.7 (s, *p*-PhP), 132.9 (d, *o*-PhP, $^2J_{C,P}$ = 17.7 Hz), 138.9 (s, *ipso*-PhP). MALDI-TOF-MS: *m/z* = 4064.8 [M^+] (calcd. 4070.5), 3880 [M^+ − PPh_2, fragmentation].

Si[$CH_2CH_2SiCH_3(CH_2PPh_2)_2$PdMeCl]$_4$: A toluene solution (4 mL) containing (COD)MePdCl (49.4 mg, 0.19 mmol = 0.5 equiv. with respect to the phosphane concentration) was slowly added to a solution of **12** (88.2 mg, 0.046 mmol), dissolved in 4 mL of toluene. The white suspension was stirred for 2.5 h, and, after filtration and subsequent washing with toluene (2 × 2.5 mL) and diethyl ether (4 × 4 mL), 95.5 mg of a white product was isolated (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.41 (br. s, 12 H, Pd CH_3), −0.37 (br. s, 12 H, SiCH_3), 0.57 (br., 16 H, SiCH_2CH_2Si), 1.24 and 1.61 (br., 16 H, SiCH_2P), 7.66, 7.42, 7.19 (br., 80 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, [D_6]DMSO): δ = 2.75 (d, *J* = 39.0 Hz), 31.28 (d, *J* = 39.0 Hz).

Si{$CH_2CH_2Si[CH_2CH_2SiCH_3(CH_2PPh_2)_2$PdMeCl]$_3$}$_4$: A toluene solution (4 mL) containing (COD)MePdCl (44 mg, 0.17 mmol = 0.5 equiv. with respect to the phosphane concentration) was slowly added to a solution of **13** (83 mg, 0.014 mmol) in 4 mL of toluene,. The white suspension was stirred for 2 h, and, after filtration and subsequent washing with toluene (2 × 2.5 mL) and diethyl ether (4 × 5 mL), 84 mg of a white powder was isolated (77%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = −0.65 (br. s, 36 H, Pd CH_3), −0.4 (br. s, 36 H, SiCH_3), 0.03 and 0.27 (br., 64 H, SiCH_2CH_2Si), 1.2 and 1.75 (br. s, 48 H, SiCH_2P), 7.42 and 7.52 (br., 240 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, [D_6]DMSO): δ = 2.38 (br.), 30.84 (br.).

Si[$CH_2CH_2SiCH_3(CH_2PPh_2)_2$Pd(allyl)Cl]$_4$: Compound **12** (62 mg, 0.033 mmol) and [(allyl)PdCl]$_2$ (24.1 mg, 0.07 mmol = 0.5 equiv. with respect to the phosphane concentration) were dissolved in 5 mL of dichloromethane. The yellow solution was stirred for 2 h, the solvent was evaporated, and the solid was subsequently washed with diethyl ether (2 × 5 mL) to yield 80 mg of the product (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.59 (br. s, 12 H, SiCH_3), 0.08 and 0.23 (br., 16 H, SiCH_2CH_2Si), 1.71 (s., 16 H, SiCH_2P), 3.56 (br., 16 H, allyl-H), 5.56 (br., 4 H, allyl H), 7.22, 7.37, 7.46, 7.68 (br., 80 H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 11.1 (br. s).

$Si\{CH_2CH_2Si[CH_2CH_2SiCH_3(CH_2PPh_2)_2Pd(allyl)Cl]_3\}_4$: Compound **13** (75 mg, 0.013 mmol) and $[(allyl)PdCl]_2$ (28 mg, 0.077 mmol = 0.5 equiv. with respect to the phosphane concentration) were dissolved in 5 mL of dichloromethane. The yellow solution was stirred for 2 h, the solvent was evaporated, and the solid material was subsequently washed with diethyl ether (2 × 5 mL) to yield 76 mg of the product (74%). ^1H NMR (300 MHz, $CDCl_3$): δ = −0.65 (br. s, 36 H, $SiCH_3$), 0.1 and 0.4 (br., 64 H, $SiCH_2CH_2Si$), 1.7 (br. s, 48 H, $SiCH_2P$), 3.5 (br., 48 H, allyl-H), 5.56 (br., 12 H, allyl H), 7−7.8 (br., 240 H, ArH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 11.1 (br. s).

Retention Measurements: The retention measurements with dichloromethane, diethylamine in dichloromethane (0.26 M), or the substrate solution for the allylic amination reactions were measured with the continuous-flow membrane reactor set-up as described elsewhere.[72] The retention measurement in THF was performed by using the reactor set-up as described by Eggeling.[73]

Typical Procedure for a Retention Measurement: The membrane was cut to the correct size for the reactor and stored in acetone for one night before being stored in methanol (for at least one night). After it had been adjusted in the membrane reactor, the membrane was flushed overnight with CH_2Cl_2. (When the substrate solution was used as a solvent, the reactor was first flushed overnight with CH_2Cl_2 before flushing with the desired solvent for the amount of time needed to flush the reactor with two reactor volumes.) The dendrimer was transferred into the reactor and the solvent was pumped through for a certain amount of time (e.g., 250 min at a flow rate of 12 mL/h in order to flush the reactor 10 times). The contents of the reactor and the solution that had been pumped through were both then analysed by GPC or NMR. For the retention measurements of [**13**-Pd(allyl)Cl], ICP-AES analyses of palladium and phosphorus were performed.

Allylic Alkylation Experiments: The allylic alkylation experiments were performed under N_2 at room temperature. The catalyst was prepared by mixing the diphenylphosphane-functionalised dendrimer with $[(\eta^3\text{-}C_3H_7)PdCl]_2$, with CH_2Cl_2 as a solvent (P/Pd = 2). After this had been stirred for 2 h, the solvent was evaporated and the resulting yellow solid was washed with diethyl ether. The sodium diethyl 2-methylmalonate was prepared by treatment of diethyl 2-methylmalonate with sodium hydride. The sodium hydride (dispersion in oil) was washed with pentane before use. The diethyl 2-methylmalonate (1.03 g, 5.9 mmol) was added dropwise to the solution of sodium hydride (0.141 g, 5.9 mmol) in THF at 0 °C, to obtain a 0.5 M solution of the sodium diethyl 2-methylmalonate.

Batch Process: Before the reaction, several stock solutions were prepared: a sodium diethyl 2-methylmalonate solution (0.5 M in THF), an *n*-decane solution (0.04 M in THF), a crotyl acetate solution (0.5 M in THF), a cinnamyl acetate solution (0.5 M in THF), an allyl trifluoroacetate solution (0.5 M in THF) and a catalyst solution (0.125 mM Pd in THF). The allylic alkylations with crotyl acetate as a substrate were performed in a total volume of 5 mL. To 2.0 mL of crotyl acetate solution, 1.0 mL of *n*-decane solution, 1.0 mL of sodium diethyl 2-methylmalonate solution and 2.0 mL of catalyst solution were added. Samples were quenched in an H_2O/Et_2O mixture. The conversion and product distribution were determined by GC analysis of the Et_2O layer. The allylic alkylations with cinnamyl acetate as a substrate were performed in a total volume of 20 mL. The stock solutions were added to 14 mL of THF in the following order: 1.0 mL of *n*-decane solution, 1.0 mL of sodium diethyl 2-methylmalonate solution, 2.0 mL of cinnamyl acetate solution and 2.0 mL of catalyst solution. Samples were quenched in an H_2O/Et_2O mixture. The conversion and product distribution were determined by GC analysis of the Et_2O layer. The allylic alkylations with allyl trifluoroacetate as a substrate were performed in a total volume of 20 mL. The stock solutions were added to 14 mL of THF in the following order: 1.0 mL of *n*-decane solution, 1.0 mL of sodium diethyl 2-methylmalonate solution, 2.0 mL of allyl trifluoroacetate solution and 2.0 mL of catalyst solution. Samples were quenched in a H_2O/Et_2O mixture. The conversion was determined by GC analysis of the Et_2O layer.

Continuous Process: The continuous experiment was performed by use of the reactor set-up described by Eggeling.[73] The membrane (stored in ethanol) was rinsed with acetone before being transferred into the membrane reactor. The membrane was first flushed overnight with THF and then with substrate solution. The substrate solution was prepared by mixing allyl trifluoroacetate (6.106 g, 39.6 mmol), sodium diethyl 2-methylmalonate (36.6 mL 0.547 M, 20.0 mmol) and *n*-decane (0.8 mL, 4.1 mmol, internal standard) in THF (total volume: 800 mL) and was pumped through the reactor with a flow rate of 43.6 mL/h. The catalyst (0.00025 mmol Pd) was dissolved in 2 mL of CH_2Cl_2 and transferred into the membrane reactor. Samples of the solution coming out of the reactor were taken continuously, quenched in H_2O/Et_2O and analysed by GC.

Allylic Amination Experiments: The allylic amination experiments were performed under N_2 at room temperature. The same catalysts as for the allylic alkylation reactions were used. The catalyst solution for ligand **20** was prepared by mixing either **20** (0.0142 g, 0.00349 mmol) (for P/Pd = 4) or **20** (0.0072 g, 0.00177 mmol) (for P/Pd = 2) and $[(crotyl)PdCl]_2$ (1.965 mg, 0.00499 mmol, 0.00998 mmol Pd) in 2 mL of CH_2Cl_2 and stirring for 1.5 h.

Batch Process: A substrate solution was prepared by mixing crotyl acetate (0.351 g, 3.07 mmol), piperidine (0.538 g, 6.32 mmol, filtered through neutral alumina) and *n*-decane (0.368 g, 2.59 mmol, internal standard) in CH_2Cl_2 (total volume: 5.0 mL). The catalyst (0.0100 mmol Pd) was dissolved in 4.0 mL of CH_2Cl_2, and 1.0 mL of substrate solution was added. Samples were quenched in DBA/Et_2O solution (DBA = dibenzylideneacetone). Conversion and product distribution were determined by GC analysis.

Continuous Process: The continuous experiment was performed with the continuous-flow membrane reactor set-up as described elsewhere.[72] The membrane was cut to the correct size for the reactor and stored in acetone for one night before being stored in methanol (for at least one night). After it had been transferred into the membrane reactor, the membrane was first flushed overnight with CH_2Cl_2 and then with substrate solution (approximately two reactor volumes). The substrate solution was prepared by mixing 1.5 mL of crotyl acetate, 2.47 mL of piperidine (after filtration over neutral alumina) and 2.44 mL of *n*-decane (as internal standard) in CH_2Cl_2 (total volume = 100 mL) and was pumped through the reactor with a flow rate of 9 mL/h. The catalyst (0.0100 mmol Pd) was dissolved in 2 mL of CH_2Cl_2 and transferred into the membrane reactor. Samples of the solution coming out of the reactor were taken continuously, quenched in DBA/Et_2O and analysed by GC.

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