Phosphino Carboxylic Acid Ester Functionalized Carbosilane Dendrimers: Nanoscale Ligands for the Pd-Catalyzed Hydrovinylation Reaction in a Membrane Reactor

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Phosphino carboxylic acid ester terminated G_0 compounds $Si\{(CH_2)_3SiMe_2(C_6H_4CH_2OC(O)(CH_2)_n-CH_2PPh_2\}_4$ (**9a** and **9b**; $n = 1, 2$) and the carbosilane dendrimers $Si\{(CH_2)_3Si((CH_2)_3SiMe_2(C_6H_4-CH_2OC(O)(CH_2)_nCH_2PPh_2)_3\}_4$ (**10a** and **10b**; $n = 1, 2$) have been prepared as hemilabile nanoscale ligands for the palladium-catalyzed codimerization of olefins. The hydrovinylation of styrene was carried out in a continuously operated nanofiltration membrane reactor. Under continuous conditions, the selectivity of the reaction is increased considerably. Monomeric model complexes and the dendritic catalysts were compared for their activity and selectivity in batch reactions. The Pd catalyst complexes were prepared in situ from the dendritic ligands and an (allyl)palladium(II) precursor.

Introduction

It remains a crucial feature for the commercialization of a catalytic process to separate catalysts from the reaction mixture. For most of the applications seen in industry today it was not until an efficient strategy for catalyst recovery was developed that they were used in chemical production. Depending on the productivity of the catalyst, in fine chemicals synthesis the recycling of sophisticated ligands can be as an important economic factor as the separation of the noble metal used. Therefore, there is currently considerable interest in the development of organometallic catalysts anchored on supports such as dendrimers.[1−7] Taking into account the enormous structural variety of these well-defined large molecules, several potential applications in homogeneous catalysis[8−10] and supported synthesis[11,12] have been envisaged, and several groups have started to explore the potential of functionalized dendritic materials. Because of their nanoscopic size these molecularly enlarged dendritic compounds have the potential to be removed from the product mixture via ultra- or nanofiltration techniques.[13−15]

C−C-coupling reactions that offer the opportunity to convert cheap carbon feedstocks into valuable chemical compounds are of high current interest. Major interest focuses on homogeneous catalytic versions with their adjustable regio- and stereoselectivity.[16]

For example, the hydrovinylation reaction (the codimerization with ethylene) of olefins opens easy access to building blocks for fine chemicals.[17] Since the first report of a hydrovinylation reaction with a $RhCl_3$ catalyst,[18] several metals were used as catalysts in hydrovinylation reactions,[19−20] among which nickel[21−25] and palladium[26−28] were the most successful ones.

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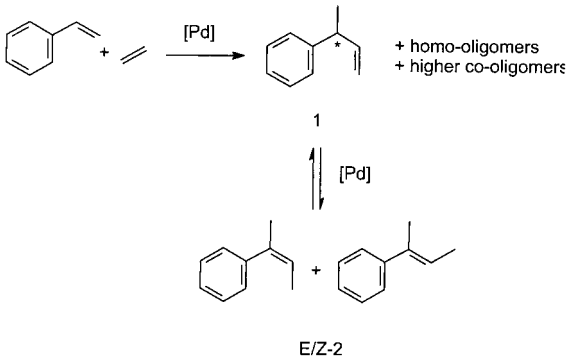
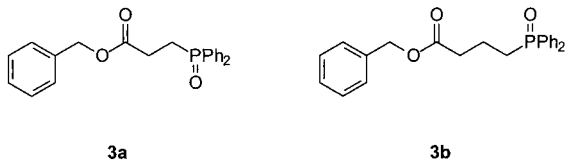
Scheme 1. Hydrovinylation of Styrene and Side Reactions



In case of nickel, a nickel halide salt activated by a Lewis acid together with a chiral azaphospholene ligand reported by Wilke is still the most efficient system for this reaction.[29] But progress has been made recently: RajanBabu et al. obtained good results using hemilabile MOP ligands. By use of a weakly coordinating counteranion, the Lewis acid could be replaced.[30,31] Via a similar route, Leitner et al. were able to apply the successful Wilke-system in supercritical CO_2, yielding promising results also in view of an immobilization of the catalyst.[32]

In case of palladium, for sufficient activity the halide has to be abstracted by a silver salt of a noncoordinating anion resulting in a cationic palladium complex. Due to their lower reactivity, the use of palladium catalysts allows moderate reaction conditions between 0 °C and room temperature. We could obtain good results in the asymmetric hydrovinylation of styrene (Scheme 1) using a ligand bearing a stereogenic phosphorus atom as well when applying bulky α-chiral (*R*)-tricarbonyl(η^6-ethylbenzene)−chromium complexes as asymmetric ligands.[33,34] Recently, the chiral benzylcyclohexylphenylphosphine has been reported by Muller et al. to catalyze the hydrovinylation of styrene with moderate selectivities and the hydrovinylation of 2-vinylnaphthalene with good selectivities.[35]

It is known that phosphino carboxylic acid derivatives lead to efficient and selective catalytic systems for C−C coupling reactions.[36] In the hydrovinylation of styrene high activity and selectivity toward 3-phenylbut-1-ene **1** were observed applying various phosphino esters.[37]



3a **3b**

Figure 1.

However, at higher conversions isomerization of the product to internal achiral olefins *E*/*Z*-**2** takes place. Therefore, it would be useful to be able to run the reaction continuously at lower conversion.

Herein we report on the synthesis of dendritic carbosilanes[38] functionalized with various diphenylphosphino carboxylic acid ester end groups. These dendritic hemilabile ligands were applied in the palladium-catalyzed hydrovinylation of styrene. The new Pd catalysts derived from G_0 compounds and G_1 dendritic P,O ligands are relatively stable under the reaction conditions, compared to similar complexes of monodentate ligands that decompose rapidly after formation to give palladium black. For the first time, the hydrovinylation was carried out continuously in a pressure membrane reactor using a nanofiltration membrane, giving rise to the selective formation of the desired, chiral 3-phenylbut-1-ene **1**.

Results and Discussion

Synthesis and Characterization of Model and Dendritic Ligands. Model studies were undertaken to determine the most efficient reaction conditions for periphery functionalization of the dendritic support. Coupling of benzylic alcohol with phosphinoxy carboxylic acid chlorides $ClC(O)(CH_2)_nCH_2P(O)Ph_2$ (n = 1, 2)[39] in the presence of 4-(dimethylamino)pyridine in DMF afforded compounds **3a** and **3b** (Figure 1).

Compound **3a** is a colorless crystalline solid, and **3b** is a slightly yellow viscous oil. Both were isolated in good yields (57−95%). The ^{1}H NMR spectrum of **3a** shows a multiplet for the methylene protons $C(O)(CH_2)_2P(O)Ph_2$ at 2.65 ppm, and the ^{1}H NMR spectrum of **3b** shows three well-resolved resonances at 2.00, 2.37, and 2.52 ppm. The ^{13}C and ^{31}P NMR spectra show the respective resonances at the expected chemical shifts. The GC-MS spectra of **3a** and **3b** show M^+ peaks at respectively 364 and 378 mass units.

The compound $Si\{(CH_2)_3SiMe_2(C_6H_4CH_2OH)\}_4$, G_0-$(OH)_4$ (**4**), and first generation carbosilane dendrimer $Si\{(CH_2)_3Si((CH_2)_3SiMe_2(C_6H_4CH_2OH))_3\}_4$, G_1-$(OH)_{12}$ (**5**), have been used as inert support material. Coupling of the carbosilane supports **4** and **5** with $ClC(O)(CH_2)_n$-$(CH)_2P(O)Ph_2$ (n = 1, 2), under the same conditions as described above, resulted in the formation of G_0 phosphine oxides **6a**,**b** and dendritic G_1 phosphine oxides **7a**,**b** as viscous oils, which were isolated in 43−85% yield (Schemes 2 and 3).

The methylene protons of the $SiCH_2CH_2CH_2Si$ units appear as three well-resolved resonances for the G_0

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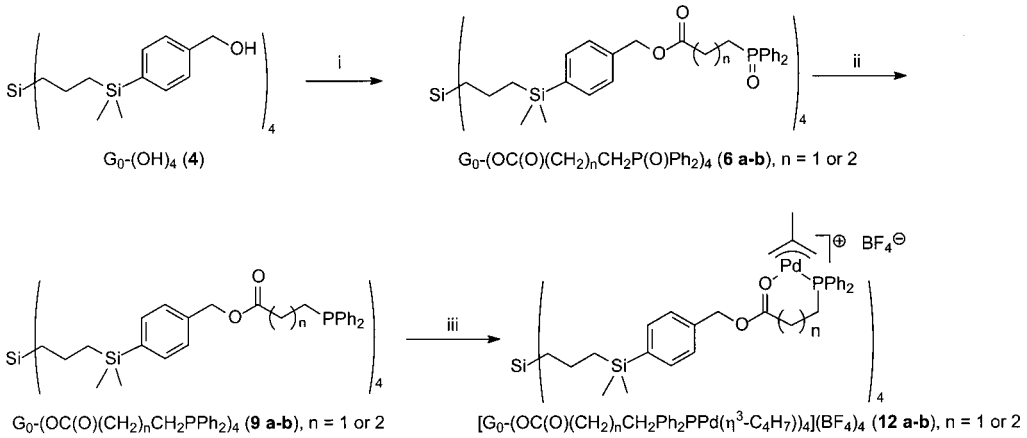
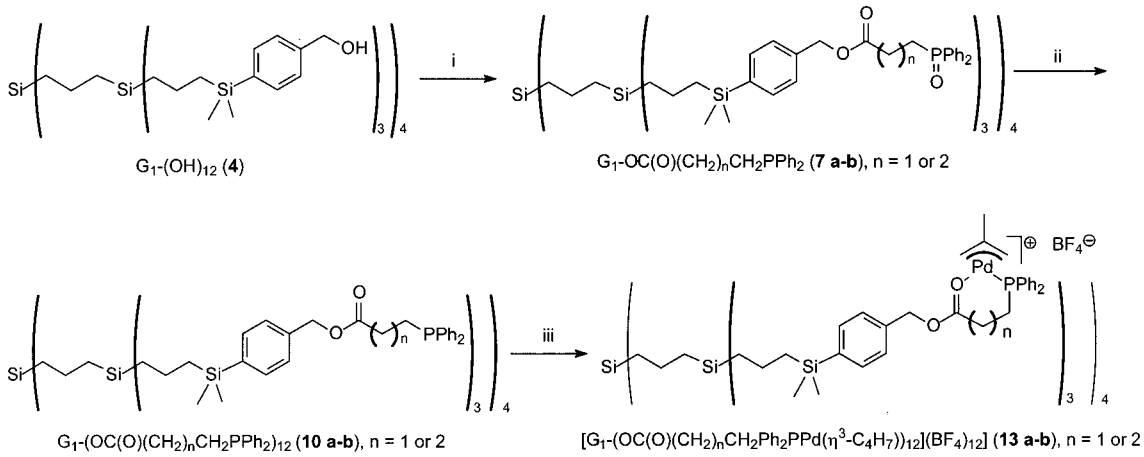
Scheme 2[a]



[a] Reagents and conditions: (i) 6.0 equiv. $Ph_2P(O)CH_2(CH_2)_nC(O)Cl$, 4-(dimethylamino)pyridine, DMF, 23 °C, 16 h; (ii) $HSiCl_3$, NEt_3, benzene, reflux, 17 h. (iii) $[(\eta^3\text{-}C_4H_7)Pd(cod)]BF_4$, CH_2Cl_2, 0 °C, 1 h.

Scheme 3[a]



[a] Reagents and conditions: (i−iii) following similar procedures to those used for the synthesis of **6a**,**b** in Scheme 2.

compound (24 H) as well as for the G_1 dendrimer (96 H). In the $^{13}C\{^1H\}$ NMR spectra of **7a** and **7b** two of the inner core methylene carbons of the G_1 dendrimer are visible while the third resonance occurs together with resonances of one of the outer methylene carbons. MALDI-TOF-MS spectra of **7a** and **7b** show signals at *m*/*z* 5974.1 and 6142.6 corresponding to $[G_1\text{-}(OC(O)(CH_2)_2\text{-}P(O)Ph_2)_{12} + 1Ag]^+$ (calcd 5974.2) and $[G_1\text{-}(OC(O)(CH_2)_3\text{-}P(O)Ph_2)_{12} + 1Ag]^+$ (calcd 6142.4), respectively. A solution of silver(I) trifluoroacetate in THF was added to the samples in order to improve the peak resolution.

The model compounds **3a**,**b** and the phosphine oxides **6a**,**b** and **7a**,**b** were converted into the phosphino compounds **8a**,**b**, **9a**,**b**, and **10a**,**b**, respectively, by reduction with trichlorosilane in benzene.

The ^1H NMR spectra of the reduced compounds show no significant shift of the benzylic protons. The aromatic regions of the phosphino compounds **8a**,**b**, **9a**,**b**, and **10a**,**b** show one multiplet. The $^{31}P\{^1H\}$ NMR spectra of the phosphino compounds **8a**,**b**, **9a**,**b**, and **10a**,**b** confirm that quantitative reaction has occurred as indicated by a shift of the phosphorus resonance to higher field, i.e., from 30 to −16 ppm. The FAB-MS spectra of compounds **9a** and **9b** show signals at *m*/*z* 1850 and 1889 corresponding to $[G_0\text{-}(OC(O)(CH_2)_2PPh_2)_4 + 2O]^+$ (calcd 1851) and $[G_0\text{-}(OC(O)(CH_2)_3PPh_2)_4 + 1O]^+$ (calcd 1889), respectively. Due to their air sensitivity, no elemental analysis of the phosphines could be obtained.

The model and dendritic catalysts were prepared in situ by treatment of the ligands with equimolar amounts of $[(\eta^3\text{-}C_4H_7)Pd(cod)]BF_4$ (cod = 1,5-cyclooctadiene) or $[(\eta^3\text{-}C_3H_5)PdI]_2/AgSbF_6$.

Catalytic Hydrovinylation of Styrene. High selectivity to the codimers was observed when the resulting catalysts **8a**,**b**, **9a**,**b**, and **10a**,**b** were applied in batch reactions (Table 1).

The ligands derived from diphenylphosphino propionic acid ($n = 1$) forming a six-membered hemilabile Pd(P∧O) chelate ring were generally less active than their diphenylphosphino butyric acid analogues ($n = 2$) forming a seven-membered hemilabile Pd(P∧O) chelate ring (**8a** vs **8b**, entries 1 and 5; **9a** vs **9b**, entries 3 and 8; **10a** vs **10b**, entries 4 and 10). The differences in activity are supposed to be due to the higher lability of the seven-membered chelate ring, which makes the catalysts more active.

The monomeric model compounds $PhCH_2OC(O)CH_2\text{-}(CH_2)_nPPh_2$ ($n = 1, 2$) showed a much higher activity than the corresponding G_0 and G_1 dendritic phosphino esters (compare **8a**, **9a**, and **10a**, entries 2, 3, and 4; as well as **8b**, **9b**, and **10b**, entries 5, 6, and 9). This effect might be due to increasing steric hindrance at the catalytic

Table 1. Hydrovinylation of Styrene: Comparison of Dendritic Ligands and Model Compounds[a]

entry	ligand	*t* (h)	conv[b] (%)	yield[c] (%)	$S_{(1+2)}$[d] (%)	$S_{(1)}$[e] (%)
1	$C_6H_5CH_2OC(O)(CH_2)_2PPh_2$ (**8a**)	3	20	14	73	98
2	$C_6H_5CH_2OC(O)(CH_2)_2PPh_2$ (**8a**)	17	97	50	91	56
3	G_0-$OC(O)(CH_2)_2PPh_2$ (**9a**)	17	68	57	97	86
4	G_1-$OC(O)(CH_2)_2PPh_2$ (**10a**)	17	1	1	97	93
5	$C_6H_5CH_2OC(O)(CH_2)_3PPh_2$ (**8b**)	3	100	4	93	<1
6	G_0-$OC(O)(CH_2)_3PPh_2$ (**9b**)	3	3	3	95	100
7	G_0-$OC(O)(CH_2)_3PPh_2$ (**9b**)	10	40	36	97	94
8	G_0-$OC(O)(CH_2)_3PPh_2$ (**9b**)	17	100	<1	92	<1
9	G_1-$OC(O)_(CH_2)_3PPh_2$ (**10b**)	3	2	1	nd	100
10	G_1-$OC(O)(CH_2)_3PPh_2$ (**10b**)	17	72	57	100	89

[a] Conditions: $T = 23$ °C; initial pressure 30 bar; P/Pd = 1; styrene/Pd = 700, CH_2Cl_2 (20 mL), styrene (4 mL; 34.8 mmol). [b] Conversion of styrene. [c] Yield of **1**. [d] $S_{(1+2)}$ = [(yield (**1**) + yield (**2**)/conv] × 100. [e] $S_{(1)}$ = [(yield (**1**)/(yield (**1**) + yield (**2**))] × 100. [f] $t = 3$ h.

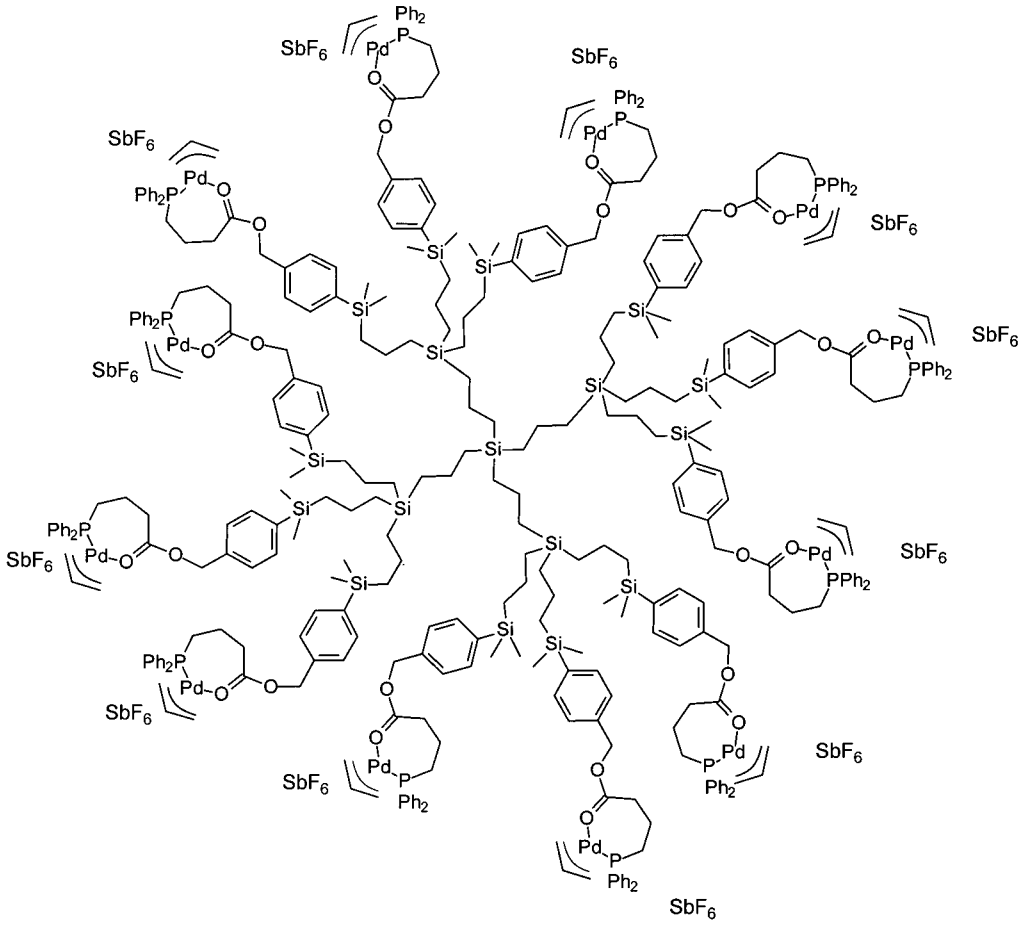


Figure 2. Dendritic catalyst complex **13b** with ligand G_1-$(OC(O)(CH_2)_3PPh_2)_{12}$ (**10b**).

sites, making access more difficult when going to higher generations. But also an special dendritic effect must be taken into account, leading to enhanced catalyst deactivation. Because of the close proximity of a large number of palladium centers, the formation of palladium black could be facilitated.

For the ligands derived from diphenylphosphino butyric acid **8b** and **9b** ($n = 2$) complete conversion and almost complete isomerization of 3-phenylbut-1-ene **1** to the *E*/*Z* mixture of achiral 2-phenylbut-2-ene *E*/*Z*-**2** was observed within 3 and 17 h, respectively (entries 5 and 8). However, as the isomerization is a consecutive reaction that with the phosphino carboxylic acid ester type of ligands occurs only at considerably high conversion, it can be efficiently suppressed by limiting the conversion (entry 7). This result suggests running the reaction at lower conversion in a continuously operating reactor.

As a result of the stability of the six-membered chelate ring, the G_0 and G_1 dendritic ligands **9a** and **10a** showed only little activity in the hydrovinylation reaction. On the other hand, ligands **9b** and **10b** were active enough to be tested in the continuous catalysis.

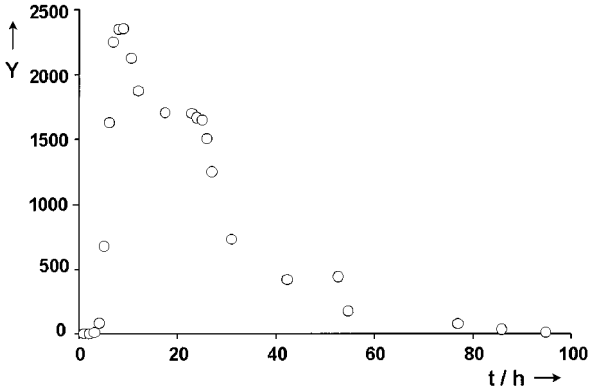
Therefore the next step was to run the catalysis in a continuously operated high-pressure-membrane-reactor with the new dendritic phosphine Pd catalysts derived from **9b** and **10b**. For the continuous catalysis a membrane reactor was used which has been developed especially for reactions under high pressure (see Figure 2). In preceding experiments the retention {defined as $R = 1 - [\text{permeate}]/[\text{retentate}]$} of the model compound G_0-$(OSi(Me)_2(^tBu))_4$ in the membrane reactor was determined to be $R = 85\%$. Although this retention is still far from being sufficient for practical purposes, the results of the catalysis using the dendritic Pd catalyst derived

Table 2. Hydrovinylation of Styrene: G_0 and Dendritic Ligands in a Continuous Process[a]

entry	ligand	conv (%)[b]	yield (%)[c]	$S_{(1+2)}$ (%)[d]	$S_{(1)}$ (%)[e]
1	G_0-OC(O)$(CH_2)_3PPh_2$ (**9b**)[f]	8.1	7.6	96	98
2	G_1-OC(O)$(CH_2)_3PPh_2$ (**10b**)[g]	40	27	80	85

[a] Conditions: T = 23 °C; p = 30 bar; P/Pd = 1; flow rates: ethene solution 2.5 mL h^{-1} (10 M), styrene solution 2.5 mL h^{-1} (1.8 M), MPF-60 NF membrane (Koch Int., Düsseldorf, Germany. [b] Conversion of styrene. [c] Yield of **1**. [d] $S_{(1+2)}$ = [(yield (**1**) + yield (**2**)/conv] × 100. [e] $S_{(1)}$ = [(yield (**1**)/(yield (**1**) + yield (**2**))] × 100. [f] t = 9 h. [g] t = 8 h.

Chart 1. Continuous Hydrovinylation of Styrene in a Membrane Reactor Using Ligand G_0-(OC(O)$(CH_2)_3PPh_2)_4$ (9b)[a]



[a] Conditions: T = 23 °C, p = 30 bar, 0.05 mmol Pd, L/Pd = 1, flow rates: ethylene solution 2.5 mL h^{-1} (10 M), styrene solution 2.5 mL h^{-1} (1.8 M), τ = 4 h, MPF-60 NF membrane (Koch Int., Düsseldorf, Ger.). Y) space time yield (mg $L^{-1}h^{-1}$).

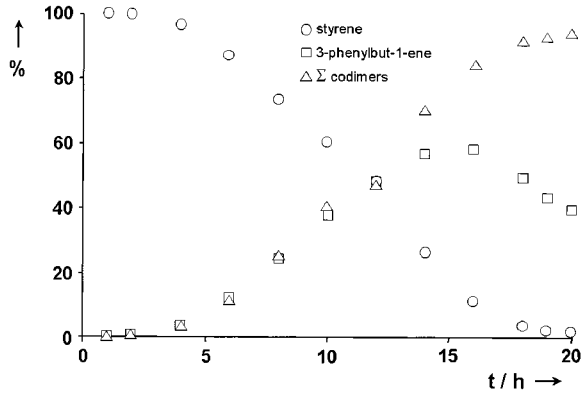
from ligand G_0-(OC(O)$(CH_2)_3PPh_2)_4$ **9b** look promising (Table 2, entry 1, Chart 1). It should be noted that the actual catalyst is already much larger (M_W = 2867.97 g mol^{-1}) than the model compound **4** (M_W = 1314.62 g mol^{-1}). Chart 1 shows the space-time yield as a function of time for a continuous run with the catalyst derived from G_0-(OC(O)$(CH_2)_3PPh_2)_4$ **9b**.

It takes about 9 h before the system reaches its maximum productivity of 2.3 g L^{-1} h^{-1}. The constant decline after the maximum cannot exclusively be explained by the moderate retention of the catalyst: with a residence time of τ = 4 h after 80 h, at least 20% of the catalyst should remain in the reactor. The effect of the washout is amplified by the deactivation of the catalyst visible by the precipitation of palladium black on the surface of the membrane. Although the catalyst possesses an acceptable stability in the batch reaction at low catalyst loading, palladium black formation is favored under continuous conditions.

However, although the retention of the G_0 compound is modest, the desired 3-phenylbut-1-ene **1** was produced over a period of 80 h. Most important is the observation that hardly any isomerization or other side products could be detected in the product solution (Table 2, entry 1).

Under these conditions using a G_0-Pd_4 catalyst and a continuous reaction mode, highly selective conversion is achieved, though the yields are quite low due to the decreased activity of this catalyst. Like in the continuous catalysis, a significant induction period is also found in the batch reaction (see Chart 2). The length of this period,

Chart 2. Induction Period in Batch Reaction Using G_0-(OC(O)$(CH_2)_3PPh_2)_4$ (9b)[a]



[a] Conditions: T = 23 °C, 30 bar initial pressure; P/Pd = 1; styrene/Pd = 700; styrene (4 mL, 34.8 mmol); 20 mL of CH_2Cl_2.

which can be ascribed to the formation of the active species, depends on the type of ligand used.

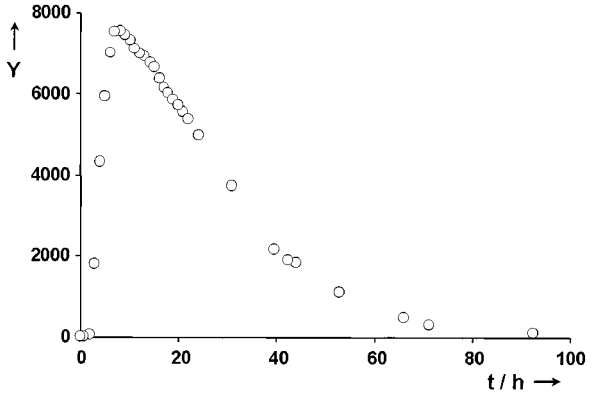
Since the induction periods in the batch reaction and in the continuous catalysis are of the same length, one can postulate that the catalytic complex undergoes the same activation steps in the membrane reactor as in the autoclave. This is confirmed by the results obtained when using a mononuclear phosphinite ligand.[33]

As a consequence of the results obtained with the G_0 catalyst **9b**, some conditions were changed applying the G_1-Pd_{12} catalyst **10b** (see Figure 2). The catalytic complex was not synthesized starting from the [(methallyl)Pd-(cod)]BF_4 precursor, but by reaction of the [(allyl)PdI]$_2$ dimer with the phosphine ligand and subsequent abstraction of the iodide using silver hexafluoroantimonate. This procedure ensures the formation of the hemilabile, seven-membered P∧O-chelate ring. We assume that the precipitation of palladium black is connected with a double or multiple complexation of the phosphino groups to the palladium, which would lead to a lack of ligand in the catalytic solution. Using the presynthesized hemilabile chelate complex as the catalyst precursor, the necessity of the displacement of the cyclooctadiene is avoided. As a consequence, a positive influence on the length of the induction period was expected.

Additionally, the amount of catalyst used was increased by 2.5 times in case of a positive concentration effect on the induction period. Due to both the higher concentration and the higher expected retention of the G_1 catalyst **10b**, the activity decrease caused by washout should only be of minor importance. Chart 3 shows the space−time yield obtained in the continuous catalysis in the presence of the G_1 dendritic catalyst **10b** as a function of time.

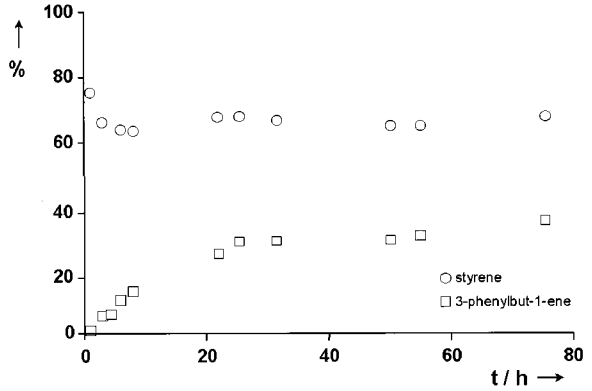
Despite the use of a different catalyst precursor and the higher retention of the G_1 dendritic catalyst, the time dependent product formation resembles almost perfectly the one found with the G_0 catalyst. The induction periods are nearly identical. Therefore, this period cannot be due to the displacement of the cyclooctadiene but to the formation of the palladium hydride species. After 8 h, the system achieves its maximum productivity of 7.5 g L^{-1} h^{-1}, which is 3.2 times higher than in the continuous catalysis in the presence of the G_0 ligand **9b**. This does not correspond completely to the increase in catalyst concentration, but it can be assumed that by use of the

Chart 3. Continuous Hydrovinylation of Styrene in a Membrane Reactor Using Dendrimer G_1-$(OC(O)(CH_2)_3PPh_2)_{12}$[a]



[a] Conditions: $T = 23$ °C, $p = 30$ bar, 0.13 mmol Pd, L/Pd = 1, flow rates: ethylene solution 2.5 mLh^{-1} (10 M), styrene solution 2.5 mL h^{-1} (1.8 M), $\tau = 4$ h, MPF-60 NF membrane (Koch Int., Düsseldorf, Ger.). Y) space time yield (mg $L^{-1}h^{-1}$).

Chart 4. Maximum Productivity of the Catalyst $[(allyl)Pd(G_1)]^+SbF_6^-$ [a]



[a] Conditions: $T = 23$ °C, $p = 30$ bar; P/Pd = 1; styrene/Pd = 10.400; styrene (30 mL, 260 mmol); 20 mL of CH_2Cl_2.

$[(allyl)PdI]_2/AgSbF_6$ system more active hydride species are available. At the maximum, the chemoselectivity amounts to 80% which is significantly lower than in the catalysis using the G_0 ligand **9b**. The selectivity drop can be ascribed to the different precursor system, as similar observations were made in corresponding batch reactions. The decrease of the activity in the continuous catalysis using the G_1 dendritic ligand **10b** is as rapid as with the G_0 ligand **9b**. Therefore, after 80 h the product fraction in the solution is minimal. Due to the similarity of the results obtained with the G_0 compound and the G_1 dendrimer, the activity drop can only secondarily be connected to the washout. The drastic decrease must rather be ascribed to a catalyst deactivation, which is independent of the precursor and starts within the first 10 h of the catalysis.

A *total turnover number* of 260 is obtained in the continuous catalysis. The next step was the correlation of this value to the maximum efficiency of the system obtained in the batch reaction. For this reason, catalytic runs with a high catalyst loading (styrene/palladium = 10400) were conducted with both the G_1 dendritic ligand **10b** and the mononuclear model compound **8b**. The courses of conversion and yield are given in Chart 4. The graph shows clearly that also these systems possess only a limited efficiency. Complete conversion is not achieved under these conditions. As in the continuous runs, within the first 10 h the catalyst reaches its maximum productivity. Afterward, the conversion falls off and after about 30 h no further conversion is obtained. With the G_1 dendritic system a *total turnover number* of 3273 is obtained, whereas with the mononuclear compound the *total turnover number* comes to 6027. The dendritic system therefore is even less stable than the mononuclear compound. This is supposed to be due to the flexibility of the dendritic arms bringing the phosphino end groups close to each other. This facilitates the formation of diphosphine complexes leading to a deactivation of the catalyst followed by the precipitation of palladium black.

Concluding Remarks

In conclusion, the model complexes used have a limited efficiency resulting from a restricted lifetime. Despite the stabilization by the hemilabile coordination, within 10 h the dendritic catalyst complexes start to deactivate. This is indicated by the precipitation of palladium black in the reactor and on the membrane surface. The deactivation process must be ascribed to double or multiple phosphine complexation. The multiple coordination surely is facilitated by the low space-filling properties of the diphenylphosphino groups. However, NMR investigations with the freshly prepared catalyst solutions suggest that independently of the precursor used, initially the pure monophosphine complex is formed. The deactivation process therefore occurs during the catalysis. Since the deactivation process takes a similar course but different turnovers are reached in the batch reaction as well as in the continuous catalysis, it can be excluded that it is correlated to the amount of converted styrene or solvent contacted.

Experimental Section

General Data. All reactions were carried out using standard Schlenk techniques under an inert atmosphere of dry, oxygen-free nitrogen unless otherwise stated. DMF was dried on molecular sieves (4 Å) prior to use, Et_2O, THF, and hexane were carefully dried and distilled from Na/benzophenone prior to use, and CH_2Cl_2 was distilled from CaH_2. The carbosilane functionalized compounds **4** and **5** were prepared according to a literature procedure.[12] Styrene was purchased from Fluka and distilled from CaH_2 under argon. The ethene used has a purity of >99.5%. $[(\eta^3\text{-}C_3H_5)PdI]_2$ was prepared by a literature procedure.[40] All other standard chemicals were purchased from ACROS Chimica or Aldrich Chemical Co. and used without further purification. Catalytic experiments under pressure were carried out in 75 mL stainless steel autoclaves equipped with a magnetic stirring bar. Mass spectra obtained under electron ionization (EI) conditions (70 eV) were recorded by linear scanning from m/z 50−500. FAB-MS spectra were recorded either on a (1) JEOL JMS SX/SX 102A four-sector mass spectrometer, operated at 10 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 5 mA emission current, producing a beam of 6 keV xenon atoms or a (2) JEOL JMS AX 505 spectrometer, operated at 3 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 10 mA emission current, producing a beam of 6 keV xenon atoms. The spectra were obtained from the Analytical Chemical Department of the University of Utrecht. MALDI-TOF-MS spectra were acquired using a Voyager-DE BioSpectrometry Workstation (PerSeptive Bio-

(40) White, D. A. *Inorg. Synth.* **1972**, *13*, 55.

systems Inc., Framingham, MA) mass spectrometer equipped with nitrogen laser emitting at 337 nm. The instrument was operated in the linear mode at an accelerating voltage in the range 23000−25000 V. External calibration was performed using insulin (bovine), and detection was done by means of a linear detector and a digitizing oscilloscope operating at 500 MHz. Sample solutions with (30 mg/mL) in THF were used, and the matrix was 3,5-dihydroxybenzoic acid in THF (34 mg/mL). A solution of silver(I) trifluoroacetate in THF was added in order to improve the peak resolution. The sample solution (0.2 mL) and the matrix solution (0.2 mL) were combined and placed on a gold MALDI target and analyzed after evaporation of the solvents. Elemental microanalyses were obtained from Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Synthesis of Phosphine Oxide Ligands. Diphenylphosphinoxy carboxylic acids were prepared following a literature procedure.[39] These were then converted to the acid chlorides by treatment with a 0.5 M solution of thionyl chloride in THF. The acid chlorides were not isolated but used directly after evaporation to dryness.

Diphenylphosphinoxy Propionic Benzyl Ester (3a). To a solution of 4-(dimethylamino)pyridine (0.63 g, 5.16 mmol) in DMF (15 mL) was added a solution of diphenylphosphinoxy propionyl chloride (1.50 g, 5.13 mmol) in DMF (10 mL) at room temperature. Subsequently, a solution of benzylic alcohol (0.4 g, 3.7 mmol) in DMF (10 mL) was added to the orange solution. The mixture was stirred overnight and filtered. Ice−water was added, and the mixture was extracted with Et_2O. The combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed in vacuo, and after purification by column chromatography (silica/CH_2Cl_2) colorless crystals were obtained. Yield: 1.27 g, 3.5 mmol, 95%. Mp: 96 °C. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.74 (m, 4H), 7.49 (m, 6H), 7.32 (m, 5H), 5.07 (s, 2H), 2.65 (m, 4H). ^{13}C{^{1}H}-NMR: ($CDCl_3$, 298 K): δ = 172.1 (d, $^3J_{CP}$ = 17.1, 1C), 135.5 (s, 1C), 132.1 (d, $^1J_{CP}$ = 99.8, 2C), 131.9 (d, $^4J_{CP}$ = 2.8, 2C), 130.7 (d, J_{CP} = 9.4, 4C), 128.7 (d, J_{CP} = 11.6, 4C), 128.5 (s, 2C), 128.2 (s, 1C), 128.1 (s, 2C), 66.7 (s, 1C), 26.4 (d, $2J_{CP}$ = 1.8, 1C), 25.0 (d, $^1J_{CP}$ = 72.6, 1C). ^{31}P{^{1}H}-NMR: ($CDCl_3$; 298 K): δ = 31.9 (s). GC-MS: (rel intensity): *m/z* 364 (<1%, M^+; 257 (10), 230 (15), 202 (100), 183 (10), 155 (10), 91 (40). IR ($CHCl_3$): 1740 cm^{-1} (C═O), 1179 cm^{-1} (P═O). Anal. Calcd for $C_{22}H_{21}O_3P$ (mw: 364.38): C, 72.52; H, 5.81; P, 8.50. Found: C, 72.35; H, 5.83; P, 8.38.

Diphenylphosphinoxy Butyric Benzyl Ester (3b). The synthetic procedure was identical to that described for **3a**, starting from benzyl alcohol (0.65 g, 6.0 mmol), 4-(dimethylamino)pyridine (1.46 g, 12.0 mmol) and diphenylphosphinoxy butyric acid chloride (2.75 g, 9.00 mmol). A slightly yellow oil was obtained. Yield: 1.28 g, 3.4 mmol, 57%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.74 (m, 4H, *ortho* PAr*H*), 7.47 (m, 6H), 7.32 (m, 5H), 5.08 (s, 2H), 2.48 (t, *J* = 6.8, 2H), 2.32 (m, 2H), 1.97 (m, 2H). ^{13}C{^{1}H}-NMR: ($CDCl_3$, 298 K): δ = 172.7 (s, 1C), 136.1 (s, 1C), 133.0 (d, $1J_{CP}$ = 105.6, 2C), 132.0 (d, $^4J_{CP}$ = 3, 2C), 131.0 (d, J_{CP} = 9.2, 4C), 128.9 (d, J_{CP} = 11.1, 4C), 128.8 (s, 2C), 128.5 (s, 1C), 128.5 (s, 2C), 66.5 (s, 1C), 34.9 (d, $^3J_{CP}$ = 14.3, 1C), 29.2 (d, $^1J_{CP}$ = 71.9, 1C), 17.6 (d, $^2J_{CP}$ = 3.7, 1C). ^{31}P{^{1}H}-NMR: ($CDCl_3$; 298 K): δ = 33.2 (s). GC-MS: (rel intensity): *m/z* 378 (10), M^+; 271 (20), 243 (40), 215 (100), 202 (70), 183 (10), 155 (10), 91 (70). IR (CHCl): 1745 cm^{-1} (C═O), 1188 cm^{-1} (P═O). Anal. Calcd for $C_{23}H_{23}O_3P$ (mw: 378.41): C, 73.00; H, 6.13; P, 8.19. Found: C, 73.18; H, 6.20; P, 8.06.

G_0-(OC(O)(CH$_2$)$_2$P(O)Ph$_2$)$_4$, Si{(CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$CH$_2$OC(O)(CH$_2$)$_2$P(O)Ph$_2$}$_4$ (6a). The synthetic procedure was identical to that described for **3a**, starting from diphenylphosphinoxy propionic acid chloride (5.18 g, 17.7 mmol), 4-(dimethylamino)pyridine (2.47 g, 20.2 mmol), and **4** (2.13 g, 2.48 mmol). A slightly yellow oil was obtained. Yield: 2.0 g, 1.1 mmol, 43%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.69 (m, 16H), 7.53−7.41 (m, 32H), 7.27−7.25 (d, *J* = 7.6, 8H), 5.05 (s, 8H), 2.65 (m, 16H) 1.27 (m, 8H), 0.77 (m, 8H), 0.54 (m, 8H), 0.18 (s, 24H). ^{13}C-{^{1}H}-NMR: ($CDCl_3$, 298 K): δ = 172.1 (d, $^3J_{CP}$ = 17.1, 4C), 140.0 (s, 4C), 135.8 (s, 4C), 133.7 (s, 8C), 132.1(d, $^1J_{CP}$ = 99.8, 8C), 131.9 (d, $^4J_{CP}$ = 2.8, 8C), 130.7 (d, J_{CP} = 9.4, 16C), 128.7 (d, J_{CP} = 11.9, 16C), 127.4 (s, 8C), 66.7 (s, 4C), 26.4 (s, 4C), 24.9 (d, $^1J_{CP}$ = 72.6, 4C), 20.4 (s, 4C), 18.4 (s, 4C), 17.3 (s, 4C), −3.0 (s, 8C). ^{31}P{^{1}H}-NMR: ($CDCl_3$; 298 K): δ = 32.1 (s). FAB-MS: (rel intensity): *m/z* 1906 ($G_0(CH_2)_2P(O)Ph_2$ + Na)$^+$, 1883 ($G_0(CH_2)_2P(O)Ph_2$ + H)$^+$. IR ($CHCl_3$): 1732 cm^{-1} (C═O), 1179 cm^{-1} (P═O). Anal. Calcd for $C_{108}H_{128}O_{12}P_4Si_5$ (mw: 1882.54): C, 68.91; H, 6.85; P, 6.58; Si, 7.46. Found: C, 68.78; H, 6.88; P, 6.66; Si, 7.41.

G_0-(OC(O)(CH$_2$)$_3$P(O)Ph$_2$)$_2$, Si{(CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$CH$_2$OC(O)(CH$_2$)$_3$P(O)Ph$_2$}$_4$ (6b). The synthetic procedure was identical to that described for **3a**, starting from diphenylphosphinoxy butyric acid chloride (2.30 g, 7.5 mmol), 4-(dimethylamino)pyridine (1.23 g, 10.0 mmol), and **4** (1.08 g, 1.26 mmol). A slightly yellow oil was obtained. Yield: 1.29 g, 0.67 mmol, 53%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.74 (m, 16H), 7.53−7.43 (m, 32H), 7.27 (d, *J* = 8.1, 8H), 5.05 (s, 8H), 2.49 (t, *J* = 7.0, 8H), 2.31 (m, 8H), 1.97 (m, 8H) 1.29 (m, 8H), 0.75 (t, *J* = 8.0, 8H), 0.52 (t, 8H), 0.20 (s, 24H). ^{13}C{^{1}H}-NMR: ($CDCl_3$, 298 K): δ = 172.7 (s, 4C), 140.2 (s, 4C), 136.4 (s, 4C), 134.0 (s, 8C), 133.0 (d, $^1J_{CP}$ = 100.6, 8C), 131.9 (d, $^4J_{CP}$ = 2.4, 8C), 131.0 (d, J_{CP} = 9.2, 16C), 128.9 (d, J_{CP} = 12.0, 16C), 127.7 (s, 8C), 66.5 (s, 4C), 34.9 (d, $^3J_{CP}$ = 14.3, 4C), 29.2 (d, $^1J_{CP}$ = 71.8, 4C), 20.7 (s, 4C), 18.8 (s, 4C), 17.6 (d, $^2J_{CP}$ = 4.1, 4C), 17.5 (s, 4C), −2.6 (s, 8C). ^{31}P{^{1}H}-NMR: ($CDCl_3$; 298 K): δ = 33.1 (s). FAB-MS: (rel intensity): *m/z* 1961.0 ($G_0(CH_2)_3P(O)Ph_2$ + Na)$^+$, 1939.0 ($G_0(CH_2)_3P(O)Ph_2$ + H)$^+$. IR ($CHCl_3$): 1749 cm^{-1} (C═O), 1171 cm^{-1} (P═O). Anal. Calcd for $C_{112}H_{136}O_{12}P_4Si_5$ (mw: 1938.64): C, 69.39; H, 7.07; Si, 7.24. Found: C, 69.19; H, 7.02; Si, 7.36.

G_1-(OC(O)(CH$_2$)$_2$P(O)Ph$_2$)$_{12}$, Si{(CH$_2$)$_3$Si((CH$_2$)$_3$SiMe$_2$-(C$_6$H$_4$CH$_2$OC(O)(CH$_2$)$_2$-P(O)Ph$_2$)$_3$}$_4$ (7a). The synthetic procedure was identical to that described for **3a**, starting from diphenylphosphinoxy propionic acid chloride (1.34 g, 4.58 mmol), 4-(dimethylamino)pyridine (0.61 g, 5.00 mmol), and **5** (0.71 g, 0.25 mmol). A slightly yellow oil was obtained. Yield: 1.27 g, 0.22 mmol, 85%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.72 (m, 48H), 7.59−7.31 (m, 96H), 7.24 (d, *J* = 7.8, 24H), 5.00 (s, 24H), 2.62 (m, 48H), 1.29 (m, 32H), 0.77 (m, 24H), 0.54 (m, 40H), 0.17 (s, 24H). ^{13}C{^{1}H}-NMR: ($CDCl_3$, 298 K): δ = 172.3 (d, $^3J_{CP}$ = 17.1, 12C), 140.2 (s, 12C), 136.2 (s, 12C), 134.3 (s, 24C), 132.2 (d, $^1J_{CP}$ = 101.3, 24C), 132.2 (d, $^4J_{CP}$ = 2.7, 24C), 131.0 (d, J_{CP} = 9.2, 48C), 129.0 (d, J_{CP} = 11.5, 48C), 127.7 (s, 24C), 66.9 (s, 12C), 26.7 (s, 12C), 25.2 (d, $^1J_{CP}$ = 73.2, 12C), 20.7 (s, 12C), 18.9 (s, 16C), 18.4 (4C), 18.1 (4C), 17.7 (s, 12C), −2.6 (s, 24C). ^{31}P{^{1}H}-NMR: ($CDCl_3$; 298 K): δ = 32.8 (s). MALDI-TOF-MS: *m/z* 5974.1 [$G_1(CH_2)_2P(O)Ph_2$ + Ag]$^+$ (calcd 5974.2). IR ($CHCl_3$): 1738 cm^{-1} (C═O), 1175 cm^{-1} (P═O). Anal. Calcd for $C_{108}H_{128}O_{12}P_4Si_5$ (mw: 1882.54): C, 68.73; H, 7.00; P, 6.33; Si, 8.13. Found: C, 68.79; H, 6.99; P, 6.26; Si, 8.21.

G_1-OC(O)(CH$_2$)$_3$P(O)Ph$_2$, Si{(CH$_2$)$_3$Si((CH$_2$)$_3$SiMe$_2$(C$_6$H$_4$-CH$_2$OC(O)(CH$_2$)$_3$-P(O)Ph$_2$)$_3$}$_4$ (7b). The synthetic procedure was identical to that described for **3a**, starting from diphenylphosphinoxy butyric acid chloride (1.27 g, 4.13 mmol), 4-(dimethylamino)pyridine (0.61 g, 5.00 mmol), and **5** (0.64 g, 0.23 mmol). A slightly yellow oil was obtained. Yield: 1.12 g, 0.19 mmol, 81%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.75 (m, 48H), 7.60−7.34 (m, 96H), 7.24 (d, *J* = 6.6, 24H), 5.02 (s, 24H), 2.42 (t, *J* = 7.1, 24H), 2.30 (m, 8H), 1.97 (m, 8H), 1.31 (m, 32H), 0.75 (m, 24H), 0.54 (m, 40H), 0.18 (s, 24H). ^{13}C{^{1}H}-NMR: ($CDCl_3$, 298 K): δ = 172.7 (s, 12C), 140.1 (s, 12C), 136.6 (s, 12C), 133.9 (s, 24C), 133.0 (d, $^1J_{CP}$ = 97.6, 24C), 132.0 (d, $^4J_{CP}$ = 2.8, 24C), 131.0 (d, J_{CP} = 9.2, 48C), 128.9 (d, J_{CP} = 11.5, 48C), 127.7 (s, 24C), 66.4 (s, 12C), 34.8 (d, $^2J_{CP}$ = 14.3, 12C), 29.2 (d, $^1J_{CP}$ = 71.9, 12C), 20.8 (s, 12C), 18.9 (s, 16C), 18.5 (s, 4C), 18.1 (s, 4C), 17.7 (s, 12C), 17.6 (d, $^2J_{CP}$ = 3.3, 12C), −2.5 (s, 24C). ^{31}P{^{1}H}-NMR: ($CDCl_3$; 298 K): δ = 32.9 (s). MALDI-TOF-MS: *m/z* 6142.6 [$G_1(CH_2)_3P(O)Ph_2$ + Ag]$^+$ (calcd 6142.4). IR ($CHCl_3$): 1754 cm^{-1} (C═O), 1186 cm^{-1} (P═O). Anal. Calcd for $C_{112}H_{136}O_{12}P_4Si_5$ (mw: 1938.64): C, 69.19; H, 7.20; P, 6.15. Found: C, 69.25; H, 7.16; P, 6.06.

Synthesis of the Phosphine Ligands. Diphenylphosphino Propionic Benzyl Ester (8a). To a solution of **3a** (0.89 g, 2.44 mmol) in C_6H_6 (20 mL) were added degassed triethylamine (0.7 mL, 5.1 mmol) and trichlorosilane (2.3 mL, 23

mmol). The mixture was heated under reflux overnight and the solvent removed in vacuo. After addition of Et_2O (50 mL), a yellow suspension was obtained which was filtered under a nitrogen atmosphere. The filtrate was diluted with degassed water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to yield a pale yellow oil (0.5 g, 1.4 mmol, 60%). ^{1}H NMR (C_6D_6, 298 K): δ = 7.31 (m, 4H), 7.15 (m, 11H), 4.99 (s, 2H), 2.31 (m, 4H). $^{13}C\{^1H\}$-NMR: (C_6D_6, 298 K): δ = 172.7 (d, $^3J_{CP}$ = 15.0, 1C), 139.2 (s, 1C), 137.9 (d, $^1J_{CP}$ = 95.9, 2C), 133.4 (d, $^4J_{CP}$ = 18.8, 2C), 129.2 (s, 4C), 129.0 (d, J_{CP} = 7.3, 4C), 129.0 (s, 2C), 128.8 (s, 1C), 128.6 (s, 2C), 66.8 (s, 1C), 31.4 (d, $^2J_{CP}$ = 20.0, 1C), 23.9 (d, $^1J_{CP}$ = 13.1, 1C). $^{31}P\{^1H\}$-NMR: ($CDCl_3$; 298 K): δ = −15.1 (s). IR ($CHCl_3$): 1732 cm^{-1} (C═O). Anal. Calcd for $C_{22}H_{21}O_2P$ (mw: 348.38): C, 75.85; H, 6.08; P, 8.89. Found: C, 75.72; H, 6.00; P, 8.66.

Diphenylphosphino Butyric Benzyl Ester (8b). The synthetic procedure was identical to that described for **8a**, starting from **3b** (0.81 g, 2.14 mmol), degassed triethylamine (0.6 mL, 4.3 mmol), and trichlorosilane (2.2 mL, 21.4 mmol). A slightly yellow oil was obtained. Yield: 0.58 g, 1.6 mmol, 60%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.59−7.30 (m, 15H), 5.17 (s, 2H), 2.55 (t, J = 7.0, 2H), 2.15 (m, 2H), 1.88 (m, 2H). $^{13}C\{^1H\}$-NMR: ($CDCl_3$, 298 K): δ = 173.1 (s, 1C), 138.7 (d, $^1J_{CP}$ = 12.9, 2C), 136.3 (s, 1C), 133.0 (d, J_{CP} = 18.4, 4C), 128.8 (m, 6C), 128.8 (s, 2C), 128.7 (s, 1C), 128.5 (s, 2C), 66.5 (s, 1C), 35.7 (d, $^3J_{CP}$ = 13.4, 1C), 27.8 (d, $^1J_{CP}$ = 12.0, 1C), 21.9 (d, $^2J_{CP}$ = 18.4, 1C). $^{31}P\{^1H\}$-NMR: ($CDCl_3$; 298 K): δ = −15.8 (s). IR ($CHCl_3$): 1732 cm^{-1}, (C═O). Anal. Calcd for $C_{23}H_{23}O_2P$ (mw: 362.41): C, 76.23; H, 6.40; P, 8.55. Found: C, 76.09; H, 6.54; P, 8.39.

G_0-$(OC(O)(CH_2)_2PPh_2)_4$, Si$\{(CH_2)_3SiMe_2(C_6H_4CH_2OC(O)(CH_2)_2PPh_2\}_4$ (9a). The synthetic procedure was identical to that described for **8a**, starting from **6a** (0.67 g, 0.36 mmol), degassed triethylamine (0.40 mL, 2.9 mmol), and trichlorosilane (0.7 mL, 7.0 mmol). A colorless oil was obtained. Yield: 0.34 g, 0.19 mmol, 52%. ^{1}H NMR (C_6D_6, 298 K): δ = 7.46 (d, J = 8.1, 8H), 7.33 (m, 16H), 7.27 (d, J = 7.8, 8H), 7.03 (m, 24H), 5.00 (s, 8H), 2.34 (m, 16H), 1.47 (m, 8H), 0.85 (m, 8H), 0.63 (t, J = 8.3, 8H), 0.26 (s, 24H). $^{13}C\{^1H\}$-NMR: (C_6D_6, 298 K): δ = 172.8 (d, $^3J_{CP}$ = 14.6, 4C), 140.0 (s, 4C), 139.1 (d, $^1J_{CP}$ = 14.0, 8C), 137.7 (s, 4C), 134.4 (s, 8C), 133.4 (d, $^4J_{CP}$ = 18.9, 8C), 129.2 (s, 8C), 129.1 (m, 32C), 66.7 (s, 4C), 31.4 (d, $^2J_{CP}$ = 20.1, 4C), 23.8 (d, $1J_{CP}$ = 13.1, 4C), 21.2 (s, 4C), 19.5 (s, 4C), 18.2 (s, 4C), −2.4 (s, 8C). $^{31}P\{^1H\}$-NMR: (C_6D_6; 298 K): δ = −17.3 (s). FAB-MS: (rel intensity): m/z 1850 (M + 2O)$^+$, 1834 (M + O)$^+$, 1819 (M + H)$^+$. IR ($CHCl_3$): 1730 cm^{-1} (C═O).

G_0-$(OC(O)(CH_2)_3PPh_2)_4$, Si$\{(CH_2)_3SiMe_2(C_6H_4CH_2OC(O)(CH_2)_3PPh_2\}_4$ (9b). The synthetic procedure was identical to that described for **8a**, starting from **6b** (0.61 g, 0.31 mmol), degassed triethylamine (0.40 mL, 2.9 mmol), and trichlorosilane (0.65 mL, 6.5 mmol). A colorless oil was obtained. Yield: 0.36 g, 0.19 mmol, 62%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.61−7.23 (m, 56H), 5.07 (s, 8H), 2.47 (t, J = 7.4, 8H), 2.11 (m, 8H), 1.80 (m, 8H) 1.26 (m, 8H), 0.80 (t, J = 7.8, 8H), 0.52 (t, J = 8.2, 8H), 0.21 (s, 24H). $^{13}C\{^1H\}$-NMR: ($CDCl_3$, 298 K): δ = 173.1 (s, 4C), 140.1 (s, 4C), 138.6 (d, $^1J_{CP}$ = 12.4, 8C), 136.6 (s, 4C), 134.0 (s, 8C), 132.9 (d, $^4J_{CP}$ = 18.4, 8C), 128.7 (m, 32C), 127.7 (s, 8C), 66.4 (s, 4C), 35.6 (d, $^3J_{CP}$ = 13.3, 4C), 27.8 (d, $^1J_{CP}$ = 12.0, 4C), 21.8 (d, $^2J_{CP}$ = 18.4, 4C), 20.8 (s, 4C), 18.8 (s, 4C), 17.7 (s, 4C), −2.6 (s, 8C). $^{31}P\{^1H\}$-NMR: ($CDCl_3$; 298 K): δ = −15.9 (s). FAB-MS: (rel intensity): m/z 1888.7 (M + O)$^+$. IR ($CHCl_3$): 1725 cm^{-1} (C═O). Anal. Calcd for $C_{112}H_{136}O_8P_4Si_5$ (mw: 1874.65): C, 71.76; H, 7.31; P, 6.61, Si, 7.49. Found: C, 71.84; H, 7.38; P, 6.49, Si, 7.38.

G_1-$(OC(O)(CH_2)_2PPh_2)_{12}$, Si$\{(CH_2)_3Si((CH_2)_3SiMe_2(C_6H_4CH_2OC(O)(CH_2)_2PPh_2)_3\}_4$ (10a). The synthetic procedure was identical to that described for **8a**, starting from **7a** (0.22 g, 3.75 × 10^{-5} mol), degassed triethylamine (0.13 mL, 9.4 × 10^{-4} mol), and trichlorosilane (0.45 mL, 4.5 mmol). A colorless oil was obtained. Yield: 0.17 g, 0.030 mmol, 80%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.61−7.20 (m, 168H), 5.00 (s, 24H), 2.46 (m, 48H), 1.25 (m, 32H), 0.75 (m, 24H), 0.53 (m, 40H), 0.17 (s, 24H). $^{13}C\{^1H\}$-NMR: ($CDCl_3$, 298 K): δ = 173.1 (d, $^3J_{CP}$ = 14.7, 4C), 140.1 (s, 12C), 138.0 (d, $^1J_{CP}$ = 12.4, 24C), 136.5 (s, 12C), 133.9 (s, 24C), 132.7 (d, J_{CP} = 18.9, 24C), 127.7 (s, 24C), 128.7 (m, 96C), 66.7 (s, 12C), 31.0 (d, $^2J_{CP}$ = 19.4, 4C), 23.2 (d, $^1J_{CP}$ = 12.0, 4C), 20.8 (s, 12C), 18.9 (s, 16C), 18.5 (s, 4C), 18.1 (s, 4C), 17.7 (s, 12C), −2.5 (s, 24C). $^{31}P\{^1H\}$-NMR: ($CDCl_3$; 298 K): δ = −14.8 (s). IR ($CHCl_3$): 1730 cm^{-1} (C═O).

G_1-$(OC(O)(CH_2)_3PPh_2)_4$, Si$\{(CH_2)_3Si((CH_2)_3SiMe_2(C_6H_4CH_2OC(O)(CH_2)_3PPh_2)_3\}_4$ (10b). The synthetic procedure was identical to that described for **8a**, starting from **7b** (0.13 g, 2.15 × 10^{-5} mol), degassed triethylamine (0.1 mL, 7.22 × 10^{-4} mol), and trichlorosilane (0.26 mL, 2.58 mmol). A colorless oil was obtained. Yield: 0.10 g, 1.7 × 10^{-5} mol, 80%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.58−7.16 (m, 168H), 5.04 (s, 24H), 2.45 (t, J = 7.0, 24H), 2.04 (m, 24H), 1.76 (m, 24H) 1.31 (m, 32H), 0.77 (m, 24H), 0.55 (m, 40H), 0.19 (s, 24H). $^{13}C\{^1H\}$-NMR: ($CDCl_3$, 298 K): δ = 173.1 (s, 12C), 140.0 (s, 12C), 138.5 (d, $^1J_{CP}$ = 12.4, 24C), 136.7 (s, 12C), 133.9 (s, 24C), 132.9 (d, $^4J_{CP}$ = 18.9, 24C), 128.7 (m, 96C), 127.7 (s, 8C), 66.3 (s, 12C), 35.5 (d, $^3J_{CP}$ = 13.4, 12C), 27.8 (d, $^1J_{CP}$ = 12.0, 12C), 21.8 (d, $^2J_{CP}$ = 18.4, 12C), 20.8 (s, 12C), 18.9 (s, 16C), 18.5 (4C), 18.1 (4C), 17.7 (s, 12C), −2.5 (s, 24C). $^{31}P\{^1H\}$-NMR: ($CDCl_3$; 298 K): δ = −15.7 (s). IR ($CHCl_3$): 1725 cm^{-1} (C═O).

Preparation of the Cationic [(methallyl)PdP]$^+BF_4^-$ Complexes. A solution of 1.00 equiv of the phosphorus P∧O ligand (0.05 mmol) in CH_2Cl_2 was added to a solution of 0.05 mmol of [(η^3-C_4H_7)Pd(cod)]BF_4[13] in CH_2Cl_2. After stirring for 60 min at 0 °C, the resulting solution was used for catalysis.

Preparation of the Cationic [(G_1-P_{12}) {(allyl)Pd}$_{12}$]$^{12+}$-(SbF_6^-)$_{12}$ Complex for the Continuous Process. A solution of 1.00 equiv of the phosphorus P∧O ligand (0.011 mmol) in CH_2Cl_2 was added to a solution of 0.065 mmol of [(η^3-C_3H_5)-PdI]$_2$ in 5 mL of CH_2Cl_2. After stirring for 30 min the solution was transferred to a flask containing 1.03 equiv of $AgSbF_6$ in 2 mL of CH_2Cl_2. Subsequently, the mixture was stirred for 5 min and filtered over Celite. The solvents were removed in vacuo, 2 mL of CH_2Cl_2 was added, and the mixture was injected in the membrane reactor.

Hydrovinylation Reaction

Batch Reaction. The cold catalyst solution (0.05 mmol of [(η^3-C_4H_7)Pd(P∧O)]BF_4 in 20 mL of CH_2Cl_2) was transferred into a 75 mL stainless steel autoclave via a syringe with a stainless steel needle. The autoclave was cooled in an ice bath. Chilled styrene (4 mL: 34.8 mmol) was added, and the autoclave was pressurized with ethene (30 bar initial pressure). After the reaction, the autoclave was slowly vented, and the reaction mixture separated from the catalyst and higher oligomers by flash chromatography over basic alumina. Products were analyzed by GC.

Continuous Catalysis. The membrane (MPF-60 NF membrane, Koch Int., Düsseldorf, Germany), stored in ethanol, was rinsed with acetone and carefully transferred into the membrane reactor. After the membrane had been thoroughly flushed by several 100 mL portions of CH_2Cl_2, the reactants (ethylene solution 1.8 M in CH_2Cl_2, flow rate 2.5 mLh^{-1}; styrene solution 10 M in CH_2Cl_2, flow rate 2.5 mLh^{-1}) were pumped through the reactor. The catalyst solution (0.05 mmol in 2 mL of CH_2Cl_2) was injected via an HPLC injection valve. Samples of the outcoming product solution were taken continuously and analyzed by GC.

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Supporting Information Available: Experimental part with all NMR peak assignments. This material is available free of charge via the Internet at http://pubs.org.org.

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