Carbosilane Dendrons Containing a P-Stereogenic Phosphine at the Focal Point. Catalytic Behavior of Their Allylpalladium Complexes in the Asymmetric Hydrovinylation of Styrene

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Two carbosilane dendrons functionalized in the focal point by the P-stereogenic phosphine (*S*)-MePPh(2-biphenylyl) were synthesised and reacted with $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ to give the corresponding palladodendrons. The latter were tested as catalysts in the asymmetric hydrovinylation of styrene. The excellent catalytic results in terms of enantiomeric excesses were compared with those obtained with a model compound and with the related carbosilane dendrimers containing the palladium units on the periphery.

Introduction

Catalytic versions of asymmetric C−C coupling reactions are attracting high current interest. In most of the cases, a transition-metal complex containing chiral phosphines is required as a catalyst, although an alternative method involving the use of chiral dendrimers as ligands has emerged in the last few years.[1] Dendrimers have some advantages as compared with their monomeric catalysts. For example, they permit the regulation of the number and location of the catalytic entities attached to them and, significantly, they might favor the separation and reuse of the catalysts from the products. In spite of this, relatively few examples using metallodendrimers in stereoselective carbon−carbon bond formation have been reported and the goal of this paper is to increase the knowledge in this area.

Recently, we have described the first examples of carbosilane dendrimers functionalized with P-stereogenic monophosphines and the catalytic properties of their allylpalladium complexes in the asymmetric hydrovinylation of styrene.[2] The results showed no dramatic differences in terms of conversion, selectivity, and enantiomeric excess among the different dendrimer generations studied. This behavior is probably due to the almost identical environment around the peripheral metal centers throughout the dendrimer generations. In view of these results, the aim of this work was the synthesis of carbosilane dendrons, functionalized at the focal point with the P-stereogenic fragment P(2-biphenylyl)PhCH_2, capable of coordinating transition-metal centers. We expected that the specific nanoenvironment of the catalytic core site created by the dendritic structure could modulate its catalytic behavior, because of the restricted access to the metal center,[3] and as a result, the reactivity and selectivity of a metallodendron could depend on its particular generation. In fact, several examples of a positive dendritic effect have been reported.[4]

Here we describe the synthesis of two palladodendrons and their good catalytic properties exhibited in the hydrovinylation of styrene.

Results and Discussion

The synthesis of the model compound **2** and the new reported dendrons is shown in Schemes 1 and 2. As the core molecule we chose trichlorophenylsilane (**3**), from which the dendron growth was achieved by an alternating sequence of allylation and hydrosilylation steps.[5] The chloro-terminated dendrons **5** and **7** were then treated with BrMgMe to give the species **8** and **9**, containing methyl end groups. The functionalization of the latter molecules at the focal point was achieved by using a previously successful method.[6,7]In this, the phenyl group is selectively converted to a highly reactive triflato group, which in turn is readily substituted by a number of nucleophiles. The acidolytic cleavage of the Si−phenyl units in **8** or **9** was carried out using trifluoromethanesulfonic acid in a 1:1 molar ratio at 0 °C in CH_2Cl_2. Then the mixture was allowed to reach room temperature. The quantitative conversion was monitored by ^{1}H NMR spectroscopy, which showed no traces of phenyl resonances at the end of the reaction.

Displacement of the triflate ion from **10** and **12** by the chiral phosphine was achieved by reaction of the dendrons with the lithiated derivative Li[$CH_2P(BH_3)$(2-biphenylyl)Ph] in THF at −78 °C (Scheme 2). The latter may be synthesized by direct

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(3) See, for example: (a) Ribourdouille, Y.; Engel, G. D.; Gade, L. H. *C. R. Chim* **2003**, *6*, 1087. (b) Oosterom, E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1829. (c) Caminade, A. M.; Majoral, J. P. *Coord. Chem. Rev.* **2005**, *17/18*, 1917. (d) Caminade, A. M.; Maraval, A.; Majoral, J. P. *Eur. J. Inorg. Chem.* **2006**, 887.

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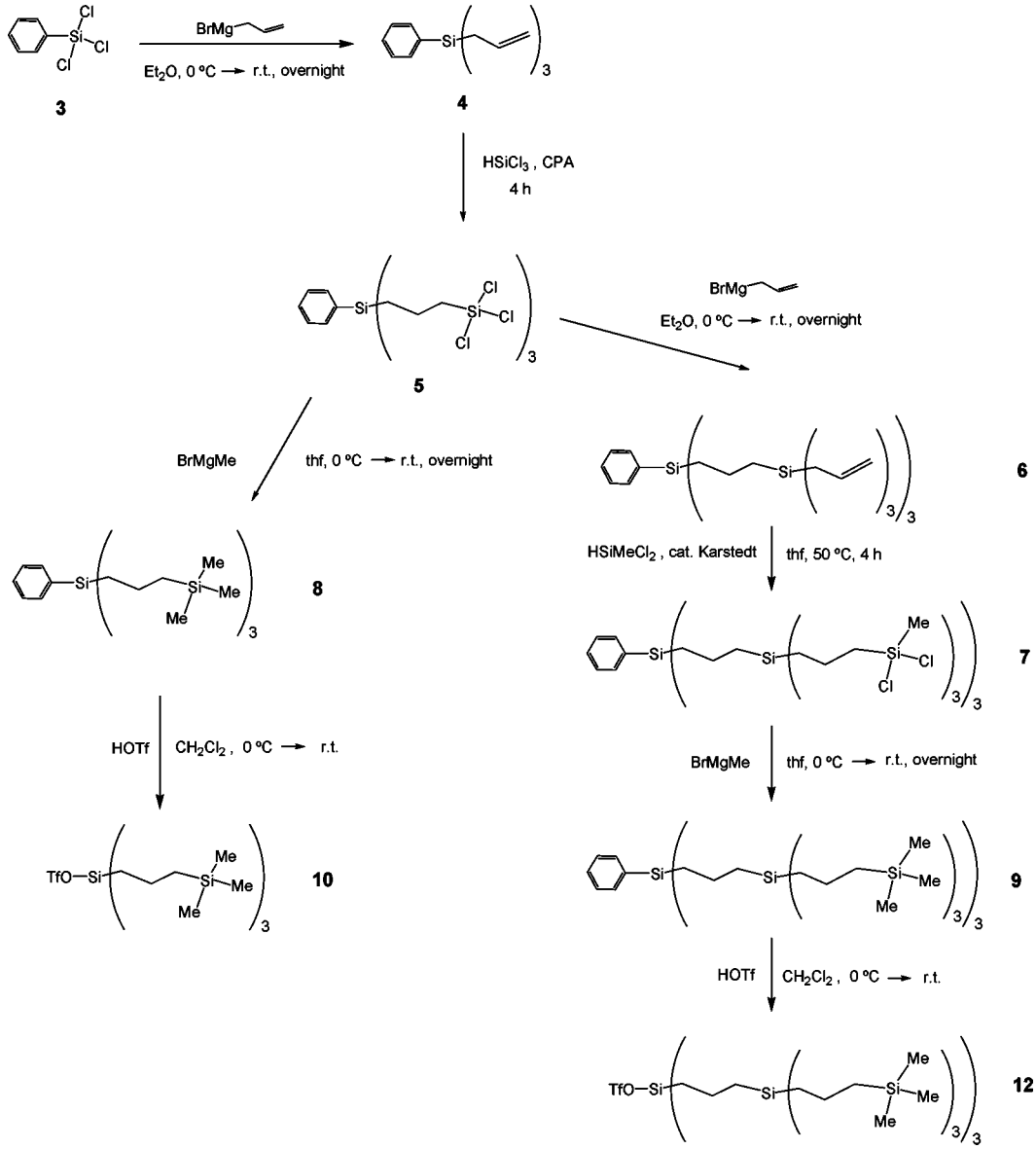
Scheme 1



lithiation of $P(BH_3)$(2-biphenylyl)PhMe with *sec*-BuLi.[8] Deprotection of the resulting species with morpholine, followed by purification with column chromatography, allowed us to obtain **11** in moderate yields. **13** was obtained in a similar manner, although in this case the phosphinodendron was previously isolated in its BH_3-protected form as a white solid in good yield.

Both **11** and **13** were characterized by multinuclear NMR spectroscopy, including HSQC $^1H-^{13}C$ experiments in order to assign the aliphatic protons and the carbon signals. The palladium allyl complexes were prepared in nearly quantitative yield, following a well-established method,[9] by stirring the ligand **1**, **11**, or **13** with the dinuclear allyl complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in CH_2Cl_2 at room temperature. The ^{31}P NMR of the reaction solution showed the disappearance of the free phosphine signal at about –29 ppm and the emergence of two singlets at 12.8 and 9.8 ppm for **14** and at 13.6 and 11.0 ppm for **15**, which revealed the presence of two expected palladium isomers, which are in equilibrium. The yellow compounds were pure within the limits of the NMR spectroscopic detection. They are soluble in moderately polar and nonpolar organic solvents and were characterized by NMR spectroscopy, including HSQC $^1H-^{13}C$ and NOESY $^1H-^1H$ experiments and electrospray mass spectrometry. The ^1H NMR of the palladium compounds **14** and **15** contained two sets of signals due to the presence of the two isomers. The integration showed isomeric ratios of 1:2, similar to those found for **2** and for the palladodendrimers containing peripheral P*(PdCl(η^3-2-MeC_3H_4)) units,[2] indicating the high steric hindrance induced by the phosphine. The diastereotopic character of the methylene protons $SiCH_2P$ was also evidenced by ^1H NMR spectroscopy by the presence of different signals for the two nuclei in each isomer. Thus, for example, for **14**, a proton signal for the major and the minor isomers appeared overlapped in the region of 2.01–1.85 ppm with the anti-cis H signal of the allyl unit, while the other proton signal appeared at 1.58 (dd, $J = 17.0$ Hz, $J = 13.0$ Hz; major isomer) and at 1.46–1.25 ppm as a multiplet (minor isomer). The ^{13}C NMR spectra in the aliphatic region contained two doublets corresponding to CH_2P of each isomer at 14.4 ppm ($^1J_{C-P} = 10.6$ Hz; minor isomer) and 12.2 ppm

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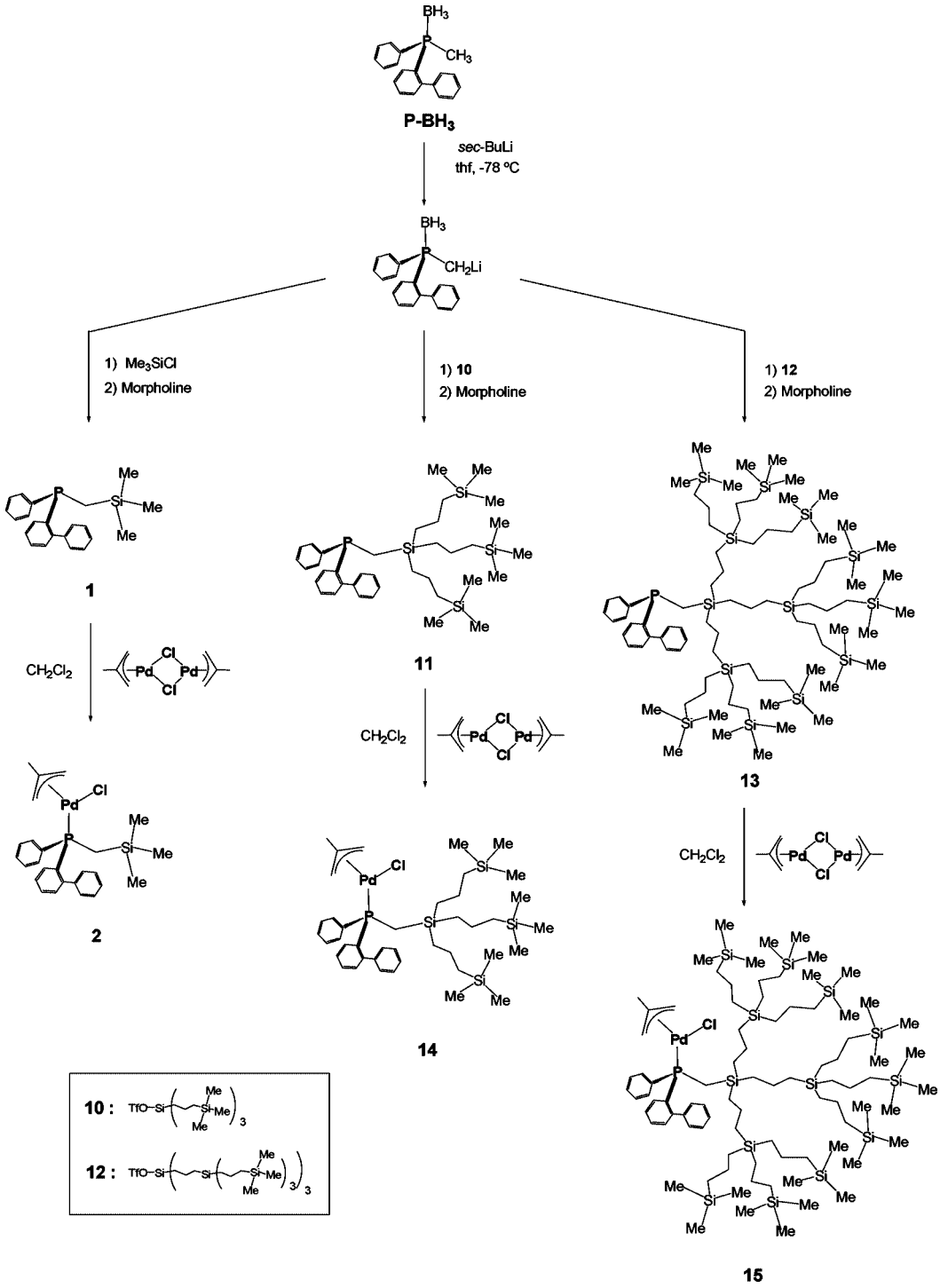
Scheme 2



($^1J_{C-P}$ = 10.1 Hz; major isomer). The ESI mass spectrum revealed the molecular peak in both cases, and Figure 1-S (Supporting Information) gives the spectrum of **15** with the expected and experimental isotopic distributions. Finally, the phase-sensitive NOESY $^1H-^1H$ spectra of **14** and **15** at 298 K with a mixing time of 500 ms showed the $\eta^3-\eta^1-\eta^3$ dynamic exchange and the pseudorotation mechanisms, typical for these kinds of complexes[10] (see the Supporting Information).

Catalytic Results. Palladium-catalyzed reactions using dendrimer-based catalysts is an expanding area, due to the variety of transformations they are able to catalyze, in particular the possibilities offered for carbon−carbon formation.[11] The hydrovinylation of styrene and ethylene to produce 3-phenyl-1-butene is a well-known process. However, the asymmetric version of the reaction has been much less studied,[12] due probably to the concomitant isomerization of the hydrovinylation product to achiral species. In fact, the only report in the area of dendrimers has been reported by our group, involving the use

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Table 1. Catalytic Reactions[a]

run	catalytic precursor	*t* (h)	conversn[b] (%)	selectivity[c] (%)	dimers (%)	TOF[d] (h^{-1})	ee (%)
1	**2**	2	29.3	99.9	0.9	72	83(*S*)
2		6	70.4	97.7	1.4	58	83(*S*)
3	**14**	2	25.9	99.1	1.8	64	81(*S*)
4		6	61.6	97.0	0.4	51	82(*S*)
5	**15**	2	23.4	99.0	0.4	58	73(*S*)
6		6	61.3	97.5	1.1	49	73(*S*)

[a] Conditions: reactions carried out at 25 °C, 15 bar of initial pressure of ethylene, 10 mL of CH_2Cl_2, styrene/Pd/NaBARF ratio 500/1/2. [b] Total amount of codimers formed. [c] Percent of 3-phenyl-1-butene with respect to the codimers. [d] Calculated as the total amount of phenylbutenes formed.

of carbosilane dendrimers functionalized peripherally with the chiral ligands (*S*)-MePPh(2-biphenylyl) and (*S*)-MePPh(9-phenanthryl).[2] The best results in terms of enantiomeric excess (79%) were obtained by using the third-generation carbosilane dendrimer functionalized with (*S*)-MePPh(2-biphenylyl) in the presence of NaBARF (BARF = $B[3,5\text{-}(CF_3)_2C_6H_3]_4$) as a halide abstractor.

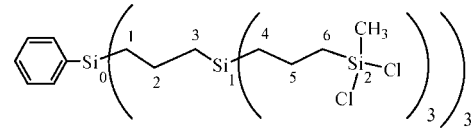
These precedents prompted us to investigate the catalytic properties of the palladium compounds reported here. It is generally accepted that the key intermediate is a cationic Pd(II) hydride complex, which reacts with the olefin to afford a metal−alkyl bond stabilized, in the case of vinyl aromatic derivatives, in the form of an η^3-benzylic complex. This is the step where the asymmetric discrimination operates.[13] Consequently, since the active catalysts are cationic species, they were prepared in this work in situ from **2**, **14**, and **15** by reaction with NaBARF in CH_2Cl_2. In a typical experiment, after filtration of the NaCl formed, the solution was introduced immediately into the reactor and the reactor was pressurized with ethylene, whereupon the active hydride catalyst was formed. In no case were the cationic precursors previously isolated. The styrene/Pd/NaBARF ratio was 500/1/2, and we used 15 bar of initial ethylene pressure and a reaction temperature of 25 °C. The conversion was monitored by GC. The results given in Table 1 were obtained as a mean of at least three runs.

All the palladium complexes were catalytically active, and (*S*)-3-phenyl-1-butene was the species obtained in excess. A decrease in the TOF was clearly observed on going from the mononuclear model compound **2** to the palladodendrimers **14** and **15**; this change might be due to the increasing steric bulk of the dendron, hindering the attack of the nucleophile on the palladium center, as found by other groups.[4] Interestingly, the selectivity was good and the formation of styrene dimers was in all cases very low. Moreover, the enantiomeric excesses found were better than those found for the dendrimers containing the palladium allyl units on the periphery.[2] The best results were obtained with the model compound **2** (83%) and the dendrimer **14** (81–82%). A negative effect was detected on going to **15** (73%). It is clear that the increase of the dendron generation strongly affects the catalytic activity, as expected, in contrast with our observations based on their palladodendrimer congeners. However, in terms of ee value, the results reported here are better than or comparable with those reported for the best palladium systems described so far.[14]

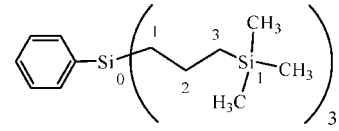
In conclusion, the combination of the palladium carbosilane dendrons with NaBARF has been proved to be an active and enantioselective system for the hydrovinylation reaction of styrene. Thus, these materials have interesting potential as catalysts in a continuous-pressure membrane reactor using a nanofiltration membrane,[15] although problems derived from leaching of palladium metal can not be underestimated.

Experimental Section

General Data. All manipulations were performed under purified nitrogen using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were obtained on Bruker DXR 250, Varian Unity 300, and Varian Mercury 400 spectrometers. Bidimensional NMR spectra (NOESY $^1H-^1H$ and HSQC $^1H-^{13}C$) were recorded on a Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^1H, ^{13}C, and ^{29}Si, CF_3COOH for ^{19}F, and 85% H_3PO_4 for ^{31}P), and coupling constants are given in Hz. MS ESI(+) spectra were recorded in a LC/MSD-TOF (Agilent Technologies) spectrometer. MS MALDI-TOF spectra were recorded with a Voyager DE-RP (Perspective Biosystems) spectrometer using DTH (dithranol; 1,8,9-trihydroxianthracene) or DBH (2,5-dihydroxybenzoic acid) as a matrix. The routine GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column, 5% phenylmethylsilicone and 95% dimethylsilicone) with an FID detector. Optical rotations were measured on a Perkin-Elmer 241MC spectropolarimeter at 23 °C. Enantiomeric excesses were determined by GC on a Hewlett-Packard 5890 Series II gas chromatograph (30 m Chiraldex DM column) with a FID detector. $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$, **P-BH$_3$**, **2**, **4**−**6**, and **12** were prepared as previously described.[1,6,7] Other reagents were used as received from commercial suppliers.



Synthesis of 7. To a solution in thf (25 mL) of **6** (1.95 g, 2.99 mmol) were added an excess of $HSiMeCl_2$ (6.2 mL, 1.105 g/mL, 99%, 59.2 mmol) and 3 drops of the Karstedt catalyst. After the solution was stirred for 4 h at 50 °C, the volatiles were removed. A colorless oil was obtained in quantitative yield (4.89 g). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.49–7.42 (m, *o*-C_6H_5, 2H), 7.36–7.31 (m, *m*-C_6H_5 + *p*-C_6H_5, 3H), 1.55–1.46 (m, C^5H_2, 18H), 1.40–1.30 (m, C^2H_2, 6H), 1.16 (t, $^3J_{HH}$ = 8.0 Hz, C^6H_2, 18H), 0.95–0.82 (m, C^1H_2, 6H), 0.76 (s, CH_3Si, 27H), 0.64–0.60 (m, C^3H_2 + C^4H_2, 24H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 137.7 (s, *i*-C_6H_5), 134.2 (s, *o*-C_6H_5), 129.1 (s, *p*-C_6H_5), 128.0 (s, *m*-C_6H_5), 26.1 (s, C^6H_2), 18.7 (s, C^2H_2), 17.7 (s, C^1H_2), 17.6 (s, C^5H_2), 17.4 (s, C^3H_2), 16.2 (s, C^4H_2), 5.7 (*s*, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K; δ (ppm)): 32.1 (s, Si^2), 1.2 (s, Si^1), −4.0 (*s*, Si^0).



Synthesis of 8. This product was prepared by following literature procedures[6,7] with some experimental modifications. To a stirred

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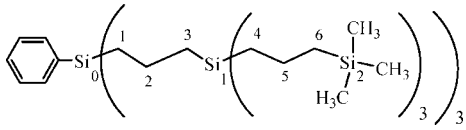
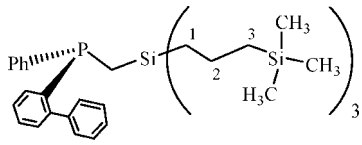
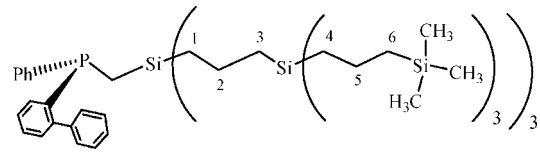
solution in thf of MeMgCl (3 M, 50 mL, 150.0 mmol) at 0 °C, a solution of **5** (6.70 g, 10.6 mmol, 100 mL of thf) was added, drop by drop, for 30 min. The mixture was stirred and warmed to room temperature overnight. A saturated aqueous solution of NH_4Cl (100 mL) was added to hydrolyze MeMgCl in excess, and thf was removed in vacuo. The remaining suspension was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic portions were dried with anhydrous sodium sulfate. After the CH_2Cl_2 was evaporated to dryness, the product was purified by column chromatography (SiO_2, hexane) and it was obtained as a colorless oil. Yield: 3.47 g (73%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.51–7.47 (m, *o*-C_6H_5, 2H), 7.37–7.33 (m, *m*-C_6H_5 + *p*-C_6H_5, 3H), 1.44–1.36 (m, $^2CH_2$, 6H), 0.87 (t, $^3J_{HH}$ = 8.4 Hz, C^1H_2, 6H), 0.60 (t, $^3J_{HH}$ = 8.2 Hz, C^3H_2, 6H), −0.02 (s, CH_3Si, 27H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 138.5 (s, *i*-C_6H_5), 134.3 (s, *o*-C_6H_5), 128.8 (s, *p*-C_6H_5), 127.8 (s, *m*-C_6H_5), 21.8 (s, C^3H_2), 18.7 (s, C^2H_2), 17.5 (s, C^1H_2), −1.3 (s, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K; δ (ppm)): 0.6 (s, Si^1), −3.9 (s, Si^0).



Synthesis of 9. This product was prepared using the same procedure as for **8**, starting from 5.05 g (2.93 mmol) of **7** and 30 mL of a 3 M solution of MeMgCl in thf (90.0 mmol). The desired product was obtained as a colorless oil. Yield: 2.79 g (70%). ^{1}H NMR (4001 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.47–7.43 (m, *o*-C_6H_5, 2H), 7.32–7.30 (m, *m*-C_6H_5 + *p*-C_6H_5, 3H), 1.39–1.21 (m, C^2H_2 + C^5H_2, 24H), 0.85–0.78 (m, C^1H_2, 6H), 0.59–0.50 (m, C^3H_2 + C^4H_2 + C^6H_2, 42H), −0.04 (s, CH_3Si, 81H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 138.4 (s, *i*-C_6H_5), 134.2 (s, *o*-C_6H_5), 128.8 (s, *p*-C_6H_5), 127.8 (s, *m*-C_6H_5), 21.9 (s, C^4H_2/C^6H_2), 18.8 (s, C^2H_2 + C^5H_2), 18.1 (s, C^3H_2), 17.9 (s, C^1H_2), 17.6 (s, C^4H_2/C^6H_2), −1.3 (s, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K; δ (ppm)): 0.6 (s, Si^2), −4.2 (s, Si^1), −4.7 (s, Si^0).



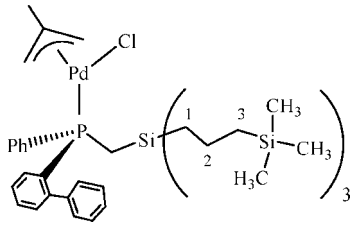
Synthesis of 11. A 158 μL portion of HOTf (1.696 g/ml, 99%, 1.774 mmol) was added at 0 °C to a solution of **8** (0.800 g, 1.774 mmol) in CH_2Cl_2 (10 mL). After 20 min at 0 °C, the stirring was maintained for a further 40 min at room temperature. Volatiles were removed in vacuo. **10** was obtained quantitatively as a colorless oil. On the other hand, the phosphine−borane **P-BH$_3$** (0.618 g, 2.129 mmol) was dissolved in 20 mL of thf, and the solution was cooled to −78 °C. *sec*-Butyllithium (1.50 mL, 1.3 M cyclohexane/hexane solution, 1.951 mmol) was added slowly. After the violet mixture that formed was stirred for 2 h, a precooled, recently prepared solution of **7** (0.246 g, 0.482 mmol) in thf (5 mL) was added. The temperature was maintained at −78 °C for 4–5 h, and after that the mixture was stirred for 14 h, slowly achieving room temperature. Afterward, 25 mL of a 0.5 M aqueous HCl solution was added and the thf was removed in vacuo. The remaining suspension was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic portions were dried with anhydrous sodium sulfate. After the CH_2Cl_2 was evaporated to dryness, the crude product was dissolved in morpholine (20 g, 20 mL) and the solution was stirred for 14 h at room temperature. Morpholine was then removed by vacuum, and the crude product was passed through a short column of alumina with toluene as eluent. A mixture of the dendron **11** and the free phosphine was obtained after the toluene was evaporated. The product was purified by flash chromatography under N_2 on a silica gel column with hexane/thf (100/1) as eluent. The desired compound was obtained as a colorless oil. Yield: 0.352 g (31%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −29.1 (*s*). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.49–7.16 (m, Ar, 14H), 1.20–1.07 (m, C^2H_2 + CH_2P, 8H), 0.39 (t, $^3J_{HH}$ = 8.2 Hz, C^3H_2, 6H), 0.35–0.31 (m, C^1H_2, 6H), −0.06 (s, CH_3Si, 27H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 147.7–127.0 (m, Ar), 21.7 (s, C^3H_2), 18.5 (s, C^2H_2), 18.3 (d, $^3J_{CP}$ = 4.0 Hz, C^1H_2), 10.9 (d, $^1J_{CP}$ = 32.7 Hz, CH_2P), −1.3 (s, CH_3Si). MS (MALDI-TOF, DBH; *m*/*z*): 649.2 (649.2 calcd) $[M]^{\bullet+}$.



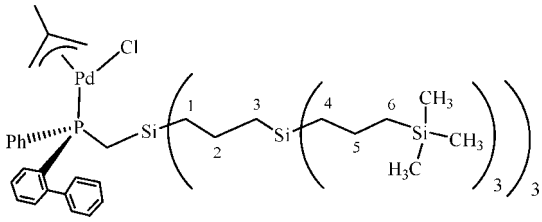
Synthesis of 13. A 40 μL portion of HOTf (1.696 g/mL, 99%, 0.499 mmol) was added at 0 °C to a solution of **9** (0.800 g, 1.774 mmol) in CH_2Cl_2 (10 mL). After 20 min at 0 °C, the stirring was maintained for other 40 min at room temperature. Volatiles were removed in vacuo. **12** was obtained quantitatively as a colorless oil. On the other hand, the phosphine-borane **P-BH$_3$** (0.195 g, 0.672 mmol) was dissolved in 10 mL of thf, and the solution was cooled to −78 °C. *sec*-Butyllithium (485 μl, 1.3 M cyclohexane/hexane solution, 0.630 mmol) was added slowly. After the violet mixture that formed was stirred for 2 h, a precooled solution of **12** (0.600 g, 0.421 mmol) in thf (5 mL) was added. The temperature was maintained at −78 °C for 4 h, and after that the mixture was stirred for 14 h, slowly achieving room temperature. Afterward, 25 mL of a 0.5 M aqueous HCl solution was added and the thf was removed in vacuo. The remaining suspension was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic portions were dried with anhydrous sodium sulfate. After the CH_2Cl_2 was evaporated to dryness, the crude product was extracted with 5 mL of cool hexane and the soluble fraction was purified by flash chromatography (SiO_2, starting with hexane and increasing the polarity to 100/5 hexane/thf). The protected phosphine−borane dendron was obtained as a colorless oil. Yield: 0.312 g (47%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 18.1 (s (br)). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.09–6.73 (m, Ar, 14H), 1.38–1.22 (m, C^5H_2, 18H), 1.17–1.00 (m, C^2H_2 + CH_2P, 8H), 0.62–0.50 (m, C^4H_2 + C^6H_2, 36H), 0.46–0.37 (m, C^1H_2 + C^3H_2, 12H), −0.03 (s, CH_3Si, 81H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 146.8–127.4 (m, Ar), 21.9 (s, C^4H_2/C^6H_2), 18.9 (d, $^3J_{CP}$ = 1.5 Hz, C^1H_2), 18.8 (s, C^5H_2), 18.6 (s, C^2H_2), 18.2 (s, C^3H_2), 17.6 (s, C^4H_2/C^6H_2), 7.6 (d, $^1J_{CP}$ = 24.0 Hz, CH_2P), −1.2 (s, CH_3Si). MS (MALDI-TOF, DBH; *m*/*z*): 1565.8 (1565.0 calcd) $[M + H]^+$, 1550.8 (1551.0 calcd) $[M - BH_3]^{\bullet+}$.

The protected phosphine−borane dendron (0.300 g, 0.192 mmol) was dissolved in morpholine (10 g, 10 mL), and the solution was stirred for 14 h at room temperature. The morpholine was then removed in vacuo, and the crude product was passed through a short column of alumina with toluene as eluent. Evaporation of the solvent furnished **13** as a colorless oil. Yield: 0.200 g (67%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −28.5 (s). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.52–7.12 (m, Ar, 14H), 1.35–1.26 (m, C^5H_2, 18H), 1.18–1.06 (m, C^2H_2 + CH_2P, 8H), 0.57–0.50 (m, C^4H_2 + C^6H_2, 36H), 0.38 (t, $^3J_{HH}$ = 8.0 Hz, C^3H_2, 6H), 0.31 (t, $^3J_{HH}$ = 8.0 Hz, C^1H_2, 6H), −0.03 (s, CH_3Si, 81H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 147.8–127.0 (m, Ar), 21.9 (s, C^4H_2/C^6H_2), 18.8 (s, C^5H_2), 18.6 (s (br), C^1H_2 + C^2H_2), 18.1 (s, C^3H_2), 17.7 (s, C^4H_2/C^6H_2), 10.7 (d, $^1J_{CP}$ = 32.7 Hz, CH_2P), −1.2 (s, CH_3Si). MS (MALDI-TOF, DBH; *m*/*z*): 1549.9 (1551.0 calcd) $[M]^{\bullet+}$.

Synthesis of 14. The dendron **11** (0.319 g, 0.491 mmol) was dissolved in 15 mL of CH_2Cl_2, and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.097 g, 0.246 mmol) was added. After the



mixture was stirred for 20 min, the solvent was removed. The product was obtained quantitatively as a yellow oil (0.416 g). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 12.8 (s, minor isomer), 9.8 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.95–6.92 (m, Ar, both isomers), 4.47 (dd, $J = 6.6$ Hz, $J = 2.9$ Hz, $H_{syn\text{-}tP}$, minor isomer), 4.40 (dd, $J = 7.0$ Hz, $J = 2.8$ Hz, $H_{syn\text{-}tP}$, major isomer), 3.49 (d, $J = 9.6$ Hz, $H_{anti\text{-}tP}$, minor isomer), 3.38 (s (br), $H_{syn\text{-}cP}$, both isomers), 3.21 (d, $J = 9.9$ Hz, H $H_{anti\text{-}tP}$, major isomer), 2.59 (s, H $H_{anti\text{-}cP}$, minor isomer), 2.01 (s, allyl Me, minor isomer), 2.01–1.85 (m, CH_2P both isomers + $H_{anti\text{-}cP}$ major isomer), 1.90 (s, allyl Me, major isomer), 1.58 (dd, $J = 17.0$ Hz, $J = 13.0$ Hz, CH_2P, major isomer), 1.46–1.25 (m, CH_2P minor isomer + C^2H_2 major isomer), 1.22–0.80 (m, $C^2H_2 + C^1H_2$, minor isomer), 0.65–0.28 (m, C^1H_2 major isomer + C^3H_2 both isomers), −0.08 (s, CH_3Si, minor isomer), −0.09 (s, CH_3Si, major isomer). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 146.2–127.0 (m, Ar + allyl C_q, both isomers), 77.7–76.9 (m, allyl C_{tP}, both isomers), 57.5 (s (br), allyl C_{cP}, minor isomer), 56.5 (d, $^2J_{CP} = 2.0$ Hz, allyl C_{cP}, major isomer), 23.8 (s, allyl Me, major isomer), 23.3 (s, allyl Me, minor isomer), 21.9 (s, C^3H_2, minor isomer), 21.7 (s, C^3H_2, major isomer), 18.9 (d, $^3J_{CP} = 3.4$ Hz, C^1H_2, minor isomer), 18.7 (s (br), C^1H_2 major isomer + C^2H_2 minor isomer), 18.6 (s, C^2H_2, major isomer), 14.4 (d, $^1J_{CP} = 10.6$ Hz, CH_2P, minor isomer), 12.2 (d, $^1J_{CP} = 10.1$ Hz, CH_2P, major isomer), −1.3 (s, CH_3Si, minor isomer), −1.3 (s, CH_3Si, major isomer). MS (ESI(+); *m*/*z*): 809.3 (809.3 calcd) $[M - Cl]^+$.



Synthesis of 15. This complex was obtained in the same way as for **14**. With **13** (0.159 g, 0.103 mmol) and $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\mu\text{-Cl})]_2$ (0.020 g, 0.051 g) as starting materials, a yellow oil was obtained in quantitative yield (0.180 g). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 13.6 (s, minor isomer), 11.0 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.94–6.93 (m, Ar, both isomers), 4.47 (dd, $J = 6.4$ Hz, $J = 2.6$ Hz, $H_{syn\text{-}tP}$, minor isomer), 4.40 (dd, $J = 7.0$ Hz, $J = 2.6$ Hz, $H_{syn\text{-}tP}$, major isomer), 3.49 (d, $J = 9.5$ Hz, $H_{anti\text{-}tP}$, minor isomer), 3.39 (s (br), $H_{syn\text{-}cP}$, both isomers), 3.21 (d, $J = 9.9$ Hz, $H_{anti\text{-}tP}$, major isomer), 2.57 (s, $H_{anti\text{-}cP}$, minor isomer), 2.01 (s, allyl Me, minor isomer), 2.01–1.85 (m, CH_2P both isomers + $H_{anti\text{-}cP}$, major isomer), 1.90 (s, allyl Me, major isomer), 1.58 (dd, $J = 17.0$ Hz, $J = 13.0$ Hz, CH_2P, major isomer), 1.46–1.40 (m, CH_2P, minor isomer), 1.35–1.22 (m, C^5H_2, both isomers), 1.18–0.94 (m, C^2H_2, both isomers), 0.58–0.46 (m, C^4H_2 both isomers + C^6H_2 both isomers + C^1H_2 both isomers), 0.39–0.31 (m, C^1H_2 both isomers + C^3H_2 both isomers), −0.03 (s, CH_3Si, major isomer), −0.03 (s, CH_3Si, minor isomer). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 146.2–127.0 (m, Ar + allyl C_q, both isomers), 77.7–76.9 (m, allyl C_{tP}, both isomers), 57.3 (s (br), allyl C_{cP}, minor isomer), 56.4 (s (br), allyl C_{cP}, major isomer), 23.8 (s, allyl Me, major isomer), 23.3 (s, allyl Me, minor isomer), 21.9 (s, C^4H_2/C^6H_2, both isomers), 19.2 (d, $^3J_{CP} = 3.3$ Hz, C^1H_2, minor isomer), 19.0 (d, $^3J_{CP} = 2.7$ Hz, C^1H_2, major isomer), 18.8 (s, C^5H_2, both isomers), 18.7 (s, C^2H_2, minor isomer), 18.6 (s, C^2H_2, major isomer), 18.3 (s, C^2H_2, minor isomer), 18.2 (s, C^2H_2, major isomer), 17.6 (s, C^4H_2/C^6H_2, both isomers), 14.3 (d (br), $^1J_{CP} \approx 10$ Hz, CH_2P, minor isomer), 12.2 (d, $^1J_{CP} = 9.4$ Hz, CH_2P, major isomer), −1.2 (s, CH_3Si, both isomers). MS (ESI(+); *m*/*z*): 1710.0 (1710.0 calcd) $[M - Cl]^+$.

Hydrovinylation Reactions. Hydrovinylation reactions were performed in a stainless-steel autoclave fitted with an external jacket connected to an isobutyl alcohol bath, and the temperature was controlled using a thermostat to ±0.5 °C. The internal temperature was monitored using a thermopar coupled to a digital recorder, whereas the internal pressure was continuously measured as a function of time with a Linseis L-200 recorder.

A mixture of the suitable neutral palladium complex (4.0×10^{-5} mol), styrene (0.02 mol), and NaBARF (8.0×10^{-5} mol) in 10 mL of dry and freshly distilled CH_2Cl_2 was stirred for 20 min in the dark. After the NaCl that formed was filtered off, the solution was placed in the autoclave, which had previously been purged by successive vacuum/nitrogen cycles and thermostated at 25 °C. Ethylene was admitted until a pressure of 15 bar was reached. After the time indicated for each reaction (2 or 6 h), the autoclave was slowly depressurized and aqueous HCl 10% solution (10 mL) was added. The mixture was stirred for 10 min in order to quench the catalyst. The CH_2Cl_2 layer was decanted off and dried with Na_2SO_4. The quantitative distribution of products and their ee values were determined by GC analysis.

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Supporting Information Available: A figure giving ESI mass spectra of compound **15** and tables giving NOESY $^1H-^1H$ cross-peaks between the isomers of compounds **14** and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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