Carbosilane Dendrimers Peripherally Functionalized with P-Stereogenic Monophosphines. Catalytic Behavior of Their Allylpalladium Complexes in the Asymmetric Hydrovinylation of Styrene†

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Received October 21, 2005

The first dendrimers containing P-stereogenic monophosphines as peripheral groups were obtained by reacting the protected BH_3-$LiCH_2PPhR$ (R = 2-biphenylyl, 9-phenanthryl) with zeroth- and first-generation chlorocarbosilane dendrimers, followed by treatment with morpholine and subsequent chromatographic purification. The first-generation dendrimer with the 9-phenanthryl-substituted phosphine could not be obtained, due to the incomplete functionalization of all the arms of the dendrimer. The reaction of the chiral dendrimers with the dinuclear allyl complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ allowed us to graft $PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)$ units on their surface. Complete characterization of these species was achieved by multinuclear NMR spectra (including 2D experiments), mass spectrometry, and optical rotation determinations. The catalytic properties of the new palladodendrimers were tested in the asymmetric hydrovinylation of styrene. To evaluate possible dendritic effects, two model chiral compounds, $(CH_3)_3SiCH_2PPhR$, were prepared. The results in terms of activity, selectivity, and enantiomeric excess depend strongly on the nature of the phosphine and the halide abstractor. The best results were achieved with the employment of the first-generation dendrimer containing the 2-biphenylyl-substituted phosphine and NaBARF (79% ee toward the *S* enantiomer). In all experiments, the major enantiomer of 3-phenyl-1-butene had the absolute configuration *S*, with the exception of that catalyzed by the 9-phenanthryl-substituted phosphine dendrimer, which afforded (*R*)-3-phenyl-1-butene as the predominant enantiomer.

Introduction

One of the most interesting aims of metallodendrimer research is the preparation of novel and efficient catalytically active hyperbranched macromolecules. Some of these species have shown properties that differ significantly from those of the parent compounds, due to the distinct environment around the metal center created by the dendritic scaffold. Thus, a good number of examples of dendritic effects on catalyst properties have been reported in the literature.[1] However, the number of reports on asymmetric catalysis carried out by chiral dendritic systems is still very limited. Relevant examples include the amino alcohol−zinc alkyl compounds attached to PPI (phosphine-functionalized poly(propyleneimine)) by Meijer et al.,[2] the Ti-TADDOL systems studied by Seebach,[3] the chiral Salen systems reported by Jacobsen et al.,[4] the "pyrphos"-functionalized PPI dendrimers described by Gade et al.,[5] and the species reported by Togni et al. by grafting chiral ferrocenyl diphosphines ("Josiphos") into the periphery of a dendrimer.[6] Very recently, a third-generation chiral phosphorus-containing dendrimer has been described and used in Pd-catalyzed asymmetric allylic alkylation by Majoral et al.[7] In addition, a dendrimer displaying a Ru-BINAP chiral core is also known.[8] By far, chiral diphosphines have been the most successfully used ligands in catalysis, but unfortunately, they do not offer a straightforward method of functionalization that allows their attachment to dendrimers, thus restricting their use in this field. Moreover, in some catalytic reactions such as hydrovinylation, the presence of bidentate ligands inhibits the reaction.[9] Having in mind these precedents and the lack of dendrimers containing P-stereogenic phosphines, we undertook

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† Dedicated to Professor Victor Riera on the occasion of his 70th birthday.

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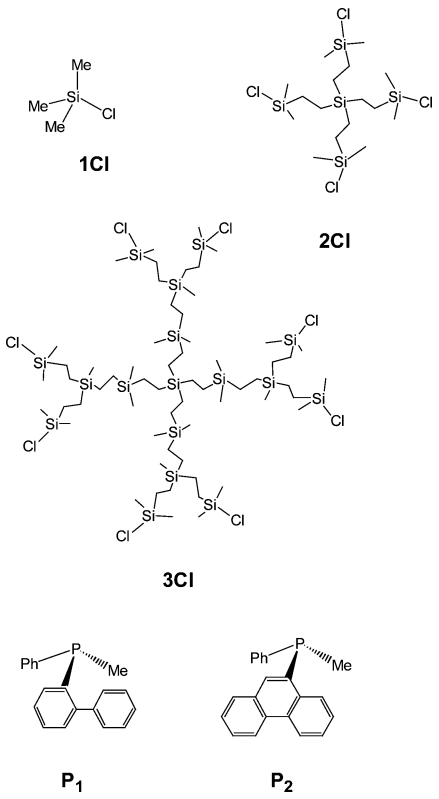
10.1021/om050915s CCC: $33.50
Publication on Web 02/11/2006

Chart 1



the synthesis of these kinds of compounds. For this, we took advantage of the clean synthesis of the chiral monodentate phosphines P*, (*S*)-MePPh(2-biphenylyl), and (*S*)-MePPh(9-phenanthryl), recently described by some of us.[10] These ligands are especially appropriate because of the presence of the methyl group, which permits the easy formation of the corresponding lithium derivatives. Thus, according to the previously developed methodology,[11] the reaction of the lithium species with the zeroth or first generation of chlorocarbosilane dendrimers enabled isolation of the targeted compounds. The catalytic properties of the related palladium dendrimers were tested in the hydrovinylation of styrene, which is an interesting process, because it opens up easy access to building blocks for fine chemicals.[12] The excellent results obtained in terms of selectivity and enantiomeric excess were compared with those of two mononuclear models prepared in order to detect dendritic effects.

Results and Discussion

Preparation of Chiral Phosphine Ended Carbosilane Dendrimers. The starting carbosilane dendrimers **2Cl** and **3Cl** and the chiral phosphine ligands $\mathbf{P_1}$ and $\mathbf{P_2}$ used in this work are represented in Chart 1, and they were obtained as described earlier.[10,11]

Two model compounds, $\mathbf{1P_1}$ and $\mathbf{1P_2}$, and three dendrimers peripherally functionalized with chiral phosphines, $\mathbf{2P_1}$, $\mathbf{2P_2}$, and $\mathbf{3P_1}$, were synthesized by following the protocol shown in Scheme 1.

In the first step, *sec*-BuLi was reacted with the protected P-BH_3 phosphines in thf at −78 °C to yield the corresponding lithiated derivatives LiP-BH_3. After 2 h, **1Cl**, **2Cl**, or **3Cl** was added to the solution to give ***n*P**-BH_3 ($n = 1-3$). In the case of the dendrimers, a slight excess of P-BH_3 with respect to *sec*-BuLi is needed to prevent the potential substitution of the chlorine atoms by *sec*-Bu groups. Moreover, the derivatives LiP-BH_3 formed must be in excess to complete the phosphorylation of all the arms of the dendrimer. These considerations are not necessary when model compounds are prepared, given that the mononuclear **1P**-BH_3 can be isolated by precipitation. The lithiated form of the phosphine and subsequent nucleophilic attack to the chloro compounds were carried out under the BH_3-protected form in order to increase the nucleophilicity of the deprotonated phosphine and to facilitate the workup.[13] Crystals suitable for an X-ray crystal structure determination of the borane adduct $\mathbf{1P_2}$-BH_3 were grown from a CH_2Cl_2/hexane solution. Figure 1 shows the molecular structure, confirming the expected *S*-isomer geometry of the stereogenic center. The distances and angles were similar to those reported for analogous molecules.[10] The ^{1}H NMR spectrum of ***n*P**-BH_3 ($n = 2, 3$) showed no traces of the external methyl groups of the starting carbosilane, indicating that it was completely consumed. In the phosphorylated dendrimers, these methyl groups appeared as two distinct singlets, confirming their diastereotopic character, as expected. In all cases, the molecules were made impure by the slight excess of P-BH_3. The second step involved the deprotection of this mixture with morpholine, followed by purification with column chromatography, which allowed us to isolate the desired compounds as pure white solids. The new compounds were characterized by multinuclear NMR spectroscopy (including HSQC ^{1}H−^{13}C experiments to unambiguously assign the aliphatic protons and the carbon signals), mass spectrometry, elemental analyses, and optical rotation determinations (Table 1).

Characteristic spectroscopic features are a unique signal for the phosphorus nucleus and four signals for the different silicon environments expected for $\mathbf{3P_1}$ with the external silicon coupled with the phosphorus atom ($J_{Si-P} = 14.0$ Hz). The MALDI-TOF spectrum of the dendrimers showed the molecular peak in all cases, with no indication of incomplete functionalization.

Attempts to obtain $\mathbf{3P_2}$ were unsuccessful, probably due to the rigidity and bulk of the phenanthryl moiety of the phosphine $\mathbf{P_2}$, resulting in only a partial functionalization of the dendrimer branches.

Allylpalladium Compounds [PdCl(η^3-2-Me-C_3H_4)(*n*$\mathbf{P_1}$)] (*n* = 1−3) and [PdCl(η^3-2-Me-C_3H_4)(*n*$\mathbf{P_2}$)] (*n* = 1, 2). The grafting of the Pd(η^3-2-MeC_3H_4)Cl units on the surface of the dendrimers was achieved in good yields by reaction of the dinuclear allyl complex [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$ with the corresponding phosphine derivatives in CH_2Cl_2 at room temperature (Scheme 2).[14]

The mononuclear model compounds $\mathbf{1P_1}$ and $\mathbf{1P_2}$ were obtained similarly. The synthesis was monitored by ^{31}P NMR spectroscopy. The free phosphine signal of the starting compounds (at about −33 ppm) completely disappeared after 20 min, and the emergence of two singlets (in the range of 2−8 ppm) was seen, indicative of the presence of the (*R*) and (*S*)-Pd isomers, which are in equilibrium. The yellow compounds were pure within the limits of the NMR spectroscopic detection. They are soluble in moderately polar organic solvents (CH_2Cl_2,

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Scheme 1

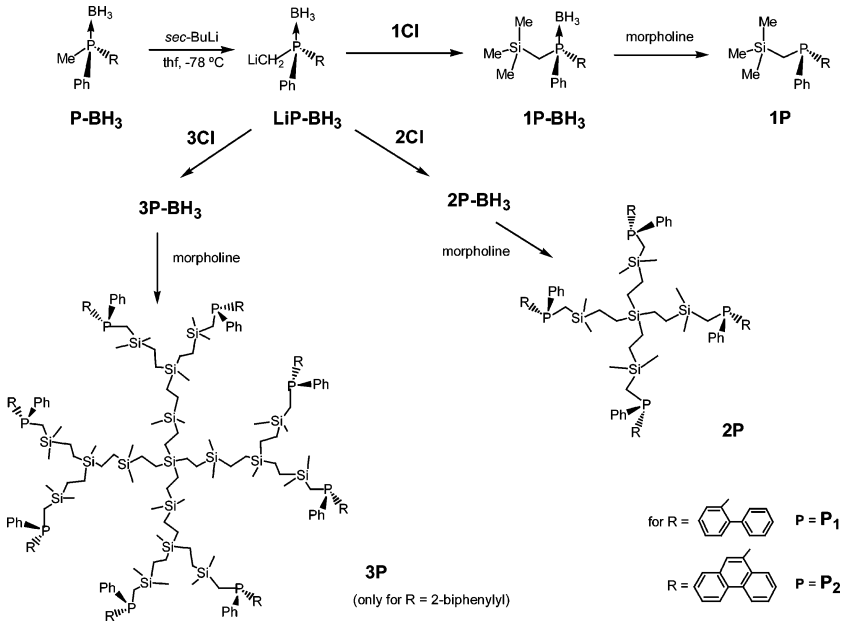


Table 1. Characteristic Features of Compounds $n\mathbf{P}_1$ (n = 1−3) and $n\mathbf{P}_2$ (n = 1, 2)

compd	^{1}H NMR (δ (ppm))[a] CH_2P	^{1}H NMR (δ (ppm))[a] $Si(CH_3)_2CH_2P$	^{13}C NMR (δ (ppm))[b] CH_2P	^{31}P NMR (δ (ppm))[c]	MS (MALDI-TOF) mol peak (m/z)	α (CH_2Cl_2) (deg)
$1P_1$	1.21 (pq, J = 7.5 Hz)[d]	−0.20 (s)[d]	15.1 (d, J = 28.4 Hz)[e]	−33.6 (s)	349.1 (349.5 calcd) $[M + H]^+$	−108.8
$2P_1$	1.18 (pq, J = 15.6 Hz)	−0.23 (s) −0.28 (s)	13.2 (d, J = 31.5 Hz)	−33.5 (s)	1473.5 (1474.2 calcd) $[M]^{\bullet+}$	−74.3
$3P_1$	1.20 (pq, J = 14.8 Hz)	−0.24 (s) −0.27 (s)	13.3 (d, J = 31.4 Hz)	−33.1 (s)	3549.6 (3549.8 calcd) $[M]^{\bullet+}$	−37.5
$1P_2$	1.21 (s (br))	0.03 (s)	14.6 (d, J = 29.9 Hz)	−33.2 (s)	597.3 (598.6 calcd) $[M + DTH]^{\bullet+}$	+87.9
$2P_2$	1.54 (s (br))	0.00 (s) −0.02 (s)	12.7 (d, J = 30.7 Hz)	−36.8 (s)	1570.9 (1570.2 calcd) $[M]^{\bullet+}$	+65.5

[a] Conditions (except as noted): $CDCl_3$, 400.1 MHz, 298 K. For all NMR spectra, abbreviations for multiplicity are as follows: s, singlet; d, doublet; p, pseudo; q, quartet; br, broad. [b] Conditions (except as noted): $CDCl_3$, 100.6 MHz, 298 K. [c] Conditions (except as noted): $CDCl_3$, 101.3 MHz, 298 K. [d] Conditions: $CDCl_3$, 250.1 MHz, 298 K. [e] Conditions: $CDCl_3$, 62.9 MHz, 298 K.

$CHCl_3$, acetone, thf) and were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as by fast atom bombardment (FAB) and electrospray mass spectrometry. The NMR data are collected in Table 2, and Figure 2 shows the scheme used for the assignation of the allylic fragment of the isomers.

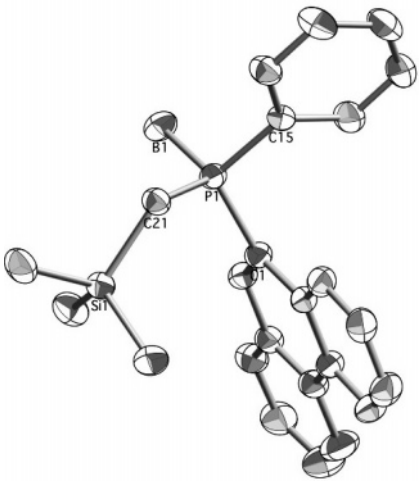
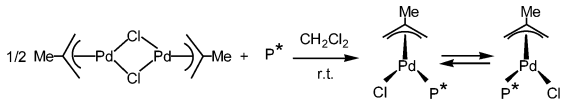


Figure 1. ORTEP view of $\mathbf{1P_2}$-BH_3, Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å): P1−C21, 1.801(2); P1−C1, 1.813(2); P1−C15, 1.813(2); P1−B1, 1.915(3); Si1−C21, 1.898(2).

The ^{1}H NMR spectra contained in all cases two sets of signals due to the presence of the two isomers. The integration revealed isomeric ratios of 1:2 for $\mathbf{P_1}$ species and 1:1.2 for those containing $\mathbf{P_2}$; no differences were noted between dendrimers and model compounds of each phosphine. The higher discrimination effect of the 2-biphenylyl-substituted phosphine versus the related 9-phenanthryl ligand indicates that the former induces higher steric hindrance. Although no contribution of the skeleton of the dendrimers is observed, it is worth noting that the silylated fragments $-Si(Me)_2CH_2-$ increase this discrimination effect in comparison to the methylphosphines in the $\mathbf{P_1}$ compounds.[10]

The diastereomeric character of the methylene protons $SiCH_2P$ was evidenced by different signals for the two nuclei in each isomer. For example, for the compounds [PdCl(η^3-2-MeC_3H_4)($n\mathbf{P_1}$)] one of these protons appears in the range 2.00−1.85 ppm, overlapped with other signals, whereas the other resonates as a multiplet at 1.70−1.50 ppm. The ^{13}C NMR spectra in the aliphatic region revealed two doublets (J_{C-P} about 10 Hz) corresponding to CH_2P of each isomer. The diastereotopic nature of the methyl groups in the Me_2Si fragments of the dendritic skeleton in both isomers is also observed. Confirmation of these assignations was obtained from NOESY ^{1}H−^{1}H and HSQC ^{1}H−^{13}C experiments. The two groups of signals of the allyl fragment for each pair of isomers were assigned by taking into account the relative amounts of the major and minor isomers, the coupling with ^{31}P in a trans position, and the two-dimensional NMR experiments (NOESY ^{1}H−^{1}H

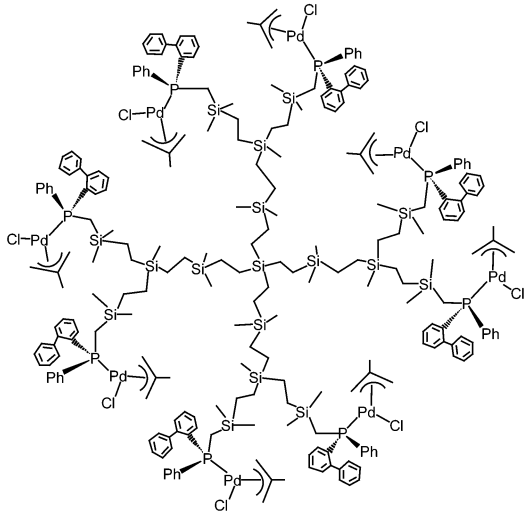
Scheme 2



for P* = $1P_1$: **Pd-1P$_1$** $1P_2$: **Pd-1P$_2$**

$2P_1$: **Pd-2P$_1$** $2P_2$: **Pd-2P$_2$**

$3P_1$: **Pd-3P$_1$**



Pd-3P$_1$

and HSQC $^1H-^{13}C$). ^{13}C chemical shifts for allylic carbons showed that the carbon atom located in a position trans to phosphorus is more deshielded than the cis carbon. The methyl allyl group appears in both isomers in nearly identical positions, indicating that there is a very small discrimination between (*R*)- and (*S*)-Pd environments produced by the chiral phosphine.

Notably, the phase-sensitive NOESY $^1H-^1H$ spectra of the palladium derivatives at 298 K with a mixing time of 500 ms showed the well-known $\eta^3-\eta^1-\eta^3$ dynamic exchange in all cases, while the pseudorotation mechanism was only detected for the **P$_2$** compounds. Both mechanisms allow the rapid interconversion of isomers at room temperature[15] (see the Supporting Information).

Hydrovinylation of Styrene. After the first report of a hydrovinylation reaction using a $RhCl_3$ catalyst,[16] several metals have been used, nickel[17] and palladium[18] being the most successful ones. However, the asymmetric version of the reaction has been much less studied.[9] In general, it has been observed that nickel-catalyzed hydrovinylation of olefins offers high regioselectivity and excellent enantioselectivity at very low temperatures.[19] On the other hand, the palladium catalysts are generally employed under moderate reaction conditions between 0 °C and room temperature, although the concomitant isomerization of the 3-aryl-1-butene to achiral 2-aryl-2-butenes complicates their use. Despite this, the choice of a suitable chiral ligand can surmount this drawback.[20]

Asymmetric hydrovinylation of vinylarenes to give 3-aryl-1-butenes and related derivatives with palladium is achieved by using [PdCl(allyl)L] (L = monodentate phosphine) as the precursor of the active species. Interestingly, the activity of the catalyst improves with the increasing bulk of L up to a certain point, beyond which a sharp decline is observed.[21] The preparation of dentritic precursors could be an alternative to be used in continuous homogeneous catalysis performed in a continuously operated membrane reactor.[22] With these precedents in mind, we focused our attention on the phosphine-containing palladium complexes reported here. We were mainly interested in determining the influence of the volume and nature of the ligand L on the activity, codimerization−homodimerization selectivity, isomerization of codimers, and enantioselectivity of the process. All the allylic precursors derived from **P$_1$** and **P$_2$** are stable. It is worth noting that this is the first report where chiral metallodendrimers have been used in catalytic asymmetric hydrovinylation.

(a) Systems Based on P$_1$. As the active catalysts in hydrovinylation reactions are cationic species, we began this study by preparing the precursors $[Pd(L)(\eta^3\text{-}2\text{-}MeC_3H_4)(n\mathbf{P_1})]\text{-}BF_4$ (L = solvent, styrene) in situ from **Pd-1P$_1$**, **Pd-2P$_1$**, or **Pd-3P$_1$**, styrene, and $AgBF_4$ in CH_2Cl_2. After the AgCl that formed was filtered out, the solution was introduced immediately in the reactor and was pressurized with ethylene. In none of the cases did we try to isolate the precursors (using CH_3CN as solvent for example), given that previous work in our laboratory with nonchiral palladodendrimers had shown that the compounds stabilized with acetonitrile were less effective in terms of activity.[14] The results shown in Table 3 were obtained as a mean value of at least three runs.

Gas chromatography and optical rotation measurements showed that (*S*)-3-phenyl-1-butene was obtained preferably from the (*S*)-phosphine-containing precursors in all experiments. No significant differences were found in comparing the behavior of the zeroth and first dendrimer generation. For example, at moderate conversions, the selectivities were almost identical, while the first generation showed a TOF that was slightly higher. The formation of styrene dimers was in all cases very low and, notably, the ee values found in both cases were excellent: 63% for **Pd-2P$_1$** and 65% for **Pd-3P$_1$**. The mononuclear model compound displayed similar behavior at moderate conversion. In this case, the ee was 68%. At higher conversions, the catalytic properties of dendrimers were similar. With both dendritic species a decrease of TOF was observed as a consequence of the deactivation of the active species, since the precipitation of

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Table 2. ^{31}P and Selected ^{1}H NMR ($CDCl_3$, 298 K, 101.3 and 400.1 MHz) and ^{13}C NMR ($CDCl_3$, 298 K, 100.6 MHz) Data (δ (ppm)) for the Complexes [PdCl(η^3-2-Me-C_3H_4)(*n*P)]

(a) ^{31}P and ^{1}H NMR[a]

		^{1}H					
complex	^{31}P	allyl-Me	*syn*-tP	*anti*-tP	*syn*-cP	*anti*-cP	CH_2P
Pd-1P$_1$							
minor	7.6	1.99 (s)	4.45 (m)	3.44 (d, 9.6)	3.27 (s (br))	2.49 (s (br))	1.99−1.87 (m), 1.70−1.50 (m)
major	6.7	1.89 (s)	4.41 (m)	3.21 (d, 10.4)	3.37 (s (br))	1.99−1.87	1.99−1.87 (m), 1.70−1.50 (m)
Pd-2P$_1$							
minor	7.3	1.97 (s)	4.42 (d (br), 6.4)	3.41 (d, 10.0)	3.28 (s (br))	2.47 (s (br))	1.96−1.87 (m), 1.67−1.53 (m)
major	6.4	1.87 (s)	4.37 (d (br), 7.2)	3.18 (d, 9.6)	3.33 (s (br))	1.96−1.87	1.96−1.87 (m), 1.67−1.53 (m)
Pd-3P$_1$							
minor	7.9	1.97 (s)	4.44 (d (br), 4.4)	3.43 (d, 9.6)	3.28 (s (br))	2.49 (s (br))	1.97−1.87 (m), 1.70−1.50 (m)
major	6.7	1.87 (s)	4.39 (d (br), 4.4)	3.19 (d, 10.0)	3.35 (s (br))	1.97−1.87	1.97−1.87 (m), 1.70−1.50 (m)
Pd-1P$_2$							
minor	7.9	1.82 (s)	4.41 (dd, 10.0, 2.8)	3.47 (d, 10.4)	3.24 (s)	2.53 (s)	2.10−1.92 (m)
major	4.0	1.53 (s)	4.37 (dd, 10.0, 2.8)	3.41 (d, 10.4)	2.83 (s)	2.54 (s)	2.17 (pt, 12.8), 2.10−1.92 (m)
Pd-2P$_2$							
minor	7.5	1.79 (s)	4.39−4.29 (m)	3.42 (d, 10.0)	3.24 (s)	2.49 (s)	2.17−1.95 (m)
major	2.7	1.42 (s)	4.39−4.29 (m)	3.38 (d, 10.0)	2.70 (s)	2.56 (s)	2.23 (pt, 12.8), 2.17−1.92 (m)

(b) ^{13}C NMR[a]

complex	C_{allyl}-Me	C-tP	C-cP	CH_2P
Pd-1P$_1$				
minor	23.5 (s)	77.8−77.0	58.3 (s)	18.3 (d, 10.8)
major	23.7 (s)	77.8−77.0	56.0 (s)	16.2 (d, 10.8)
Pd-2P$_1$				
minor	23.5 (s)	77.8−77.0	58.4 (s)	16.9 (d (br), ∼10)
major	23.8 (s)	77.8−77.0	57.0 (s)	14.6 (d (br), ∼10)
Pd-3P$_1$				
minor	23.4 (s)	77.6−76.9	58.1 (s)	16.6 (d (br), ∼10)
major	23.7 (s)	77.6−76.9	56.7 (s)	14.4 (d, 11.0)
Pd-1P$_2$				
minor	23.4 (s)	77.7−77.0	59.3 (s)	16.7 (d, 10.8)
major	23.0 (s)	77.7−77.0	60.3 (s)	16.0 (d, 11.5)
Pd-2P$_2$				
minor	23.4 (s)	77.7−76.9	59.4 (s)	15.3 (d (br), ∼9)
major	22.9 (s)	77.7−76.9	60.8 (s)	14.6 (d (br), ∼10)

[a] Abbreviations for multiplicity are as follows: s, singlet; d, doublet; p, pseudo; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants *J* are given in Hz.

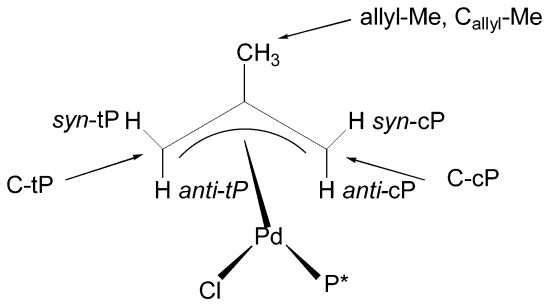

Figure 2. Nomenclature used in ^{1}H and ^{13}C NMR of the allylic fragment.

metallic palladium in the reactor was observed. Moreover, the isomerization of 3-phenyl-1-butene to 2-phenyl-2-butene, favored at high conversions, produced loss of selectivity. In contrast, the catalytic properties of the mononuclear **Pd-1P$_1$** remained unaltered with an increase in the conversion.

Studies performed on Ni-catalyzed asymmetric hydrovinylation by RajanBabu[19c] and by Leitner and co-workers[19d] detected an interesting counterion effect. A similar effect has recently been described in palladium-catalyzed hydrovinylation,[23] showing that the catalysis with the weakly coordinating anion triflate, TfO^-, gives poorer results in terms of reactivity and enantioselectivity than do bulkier and even more weakly coordinating anions, such as BF_4^-, PF_6^-, and SbF_6^-. The highest enantioselectivity was achieved with the (fluoroaryl)borate anion $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ ($BARF^-$). Therefore, we tried to optimize the reaction conditions for asymmetric hydrovinylation of styrene by using the sodium salt of this coactivator. Thus, the chloride anion was extracted by stirring the styrene/precursor

Table 3. Hydrovinylation of Styrene Catalyzed by [Pd(L)(η^3-2-MeC_3H_4)(*n*P$_1$)]BF_4 Precursors[a]

run	catalytic precursor	*t* (h)	conversn[b] (%)	selectivity[c] (%)	oligomers (%)	TOF[d] (h^{-1})	ee (%)
1	**Pd-1P$_1$**	2	38.6	96.9	0.5	97	68 (*S*)
2		3	62.1	93.9	0.3	104	68 (*S*)
3	**Pd-2P$_1$**	2	31.3	97.4	0.5	77	63 (*S*)
4		6	55.7	77.3	1.5	46	56 (*S*)
5	**Pd-3P$_1$**	2	34.0	95.6	0.8	85	65 (*S*)
6		6	53.8	77.9	0.2	45	58 (*S*)

[a] Conditions: reactions carried out at 25 °C, 15 bar of initial pressure of ethylene, 10 mL of CH_2Cl_2, styrene/Pd/$AgBF_4$ ratio 500/1/1. [b] Conversion is the total amount of codimers formed. [c] Selectivity is the percent of 3-phenyl-1-butene with respect to the codimers. [d] TOF is calculated as the total amount of phenylbutenes formed.

(23) Shi, W.; Xie, J.; Zhou, Q. *Tetrahedron: Asymmetry* **2005**, *16*, 705.

Table 4. Hydrovinylation of Styrene Catalyzed by [Pd(L)(η^3-2-MeC$_3$H$_4$)(nP$_1$)]BARF Precursors[a]

run	catalytic precursor	t (h)	conversn[b] (%)	selectivity[c] (%)	oligomers (%)	TOF[d] (h^{-1})	ee (%)
1[e]	**Pd-2P$_1$**	2	19.8	98.0	0.5	47	77 (*S*)
2		2	29.5	98.5	1.0	74	75 (*S*)
3		6	58.4	92.0	1.8	48	75 (*S*)
4	**Pd-3P$_1$**	2	27.4	98.6	1.1	69	79 (*S*)

[a] Conditions (unless otherwise noted): 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] Conversion is the total amount of codimers formed. [c] Selectivity is the percent of 3-phenyl-1-butene with respect to the codimers. [d] TOF is calculated as the total amount of phenylbutenes formed. [e] Styrene/Pd/NaBARF ratio 500/1/1.

mixture with the stoichiometric amount of NaBARF for 20 min. The catalytic results are listed in Table 4.

The analysis of Table 4 (run 1) shows that better selectivity (98%) and enantiomeric excess (77% ee) were achieved. However, in contrast with the results reported in the literature, the activity of the catalyst decreased. One possible explanation could be that the concentration of the cationic precursor is lower than that expected, due to incomplete halide abstraction. Thus, the reaction was repeated using double the amount of NaBARF with the same stirring time to avoid the deactivation of the catalyst. Under these conditions, the activity of the system was comparable to that found with the use of the silver salt, whereas the selectivity and the enantioselectivity were maintained at excellent levels (75% for **Pd-2P$_1$** and 79% for **Pd-3P$_1$**). The behavior of **Pd-2P$_1$** at higher conversion was also examined (run 3, Table 4) and compared with that exhibited by using $AgBF_4$. As can be seen, the use of NaBARF improved the selectivity (92% versus 77%), while the enantioselectivity continued to be higher (77% ee versus 56% ee). However, the use of the sodium salt did not avoid the destabilization of the catalyst, evidenced by the decrease of the TOF. In conclusion, the **Pd−P$_1$** dendrimers/NaBARF catalyst constitutes a very selective and enantioselective system for the hydrovinylation reaction and is comparable to the best palladium systems reported so far,[24] but making use, in this case, of more accessible systems.

(b) Systems Based on P$_2$. The palladium precursors based on **P$_2$** were analogously prepared as described for those based on **P$_1$**.

The catalytic results obtained using $AgBF_4$ as halide abstractor are listed in Table 5.

The most remarkable feature is the extraordinary activity of **Pd-1P$_2$**, already observed with similar phosphines.[10] Thus, run 1 shows that all the 3-phenyl-1-butene formed was consumed and run 2 demonstrates that the enantiomeric excess is the result of the kinetic resolution of the isomerization to 2-phenyl-2-butene.[23,25] Run 3 shows moderate selectivity and permits an estimation of the TOF value, although the enantioselectivity is null. The activity of **Pd-2P$_2$** was somewhat more reduced, the selectivity was consequently better, and as in the case of **Pd-1P$_2$**, it was unable to induce chirality (0% ee). In both systems, the amount of styrene dimers formed was considerable (3−7%), but less for the dendritic system, as expected on the basis of steric arguments.

Table 5. Hydrovinylation of Styrene Catalyzed by [Pd(L)(η^3-2-MeC$_3$H$_4$)(nP$_2$)]BF$_4$ Precursors[a]

run	catalytic precursor	t (h)	conversn[b] (%)	selectivity[c] (%)	oligomers (%)	TOF[d] (h^{-1})	ee (%)
1[e]	**Pd-1P$_2$**	2	92.9[g]	0	7.1		
2[f]		1	94.4[g]	11.7	5.6		16 (*S*)
3		1/2	59.5	95.6	6.3	1785	∼0
4	**Pd-2P$_2$**	1	80.8	89.7	3.0	1214	∼0
5		1/2	47.4	96.9	3.4	1425	∼0

[a] Conditions (unless otherwise noted): reactions carried out at 15 °C, 15 bar of initial pressure of ethylene, 10 mL of CH_2Cl_2, styrene/Pd/$AgBF_4$ ratio 1500/1/1. [b] Conversion is the total amount of codimers formed. [c] Selectivity is the percent of 3-phenyl-1-butene with respect to the codimers. [d] TOF is calculated as the total amount of phenylbutenes formed. [e] Styrene/Pd/$AgBF_4$ ratio 500/1/1, 25 °C. [f] Styrene/Pd/$AgBF_4$ ratio 1000/1/1. [g] Total conversion of starting styrene.

Table 6. Hydrovinylation of Styrene Catalyzed by [Pd(L)(η^3-2-MeC$_3$H$_4$)(nP$_2$)]BARF Precursors[a]

run	catalytic precursor	t (h)	conversn[b] (%)	selectivity[c] (%)	oligomers (%)	TOF[d] (h^{-1})	ee (%)
1	**Pd-1P$_2$**	1/2	87.5[e]	6.9	12.5		38 (*S*)
2	**Pd-2P$_2$**	1/2	17.4	93.5	4.3	524	16 (*R*)
3		1	40.6	93.2	5.2	610	18 (*R*)

[a] Conditions: reactions carried out at 15 °C, 15 bar of initial pressure of ethylene, 10 mL of CH_2Cl_2, styrene/Pd/NaBARF ratio 1500/1/2. [b] Conversion is the total amount of codimers formed. [c] Selectivity is the percent of 3-phenyl-1-butene with respect to the codimers. [d] TOF is calculated as the total amount of phenylbutenes formed. [e] Total conversion of starting styrene.

The use of NaBARF did not improve the results (Table 6).

For the model compound **Pd-1P$_2$**, the reaction was extremely rapid, producing total conversion, so that a study of the process could not be performed. Moreover, a large amount of styrene dimers was observed. The results obtained with the dendrimer were more fruitful. By using **Pd-2P$_2$** the rate of the process decreased significantly, the selectivity was good (93.2%), and the ratio of styrene dimers was comparable with that found with the silver salt. The most remarkable difference, however, lies in the enantioselectivity of the process. In all the experiments described above, the major enantiomer of the 3-phenyl-1-butene had the absolute configuration *S*, but surprisingly, in this case the *R* isomer was found to be predominant. At this point, there is no evidence of how the formation of ionic pairs can modify the nature of the dendritic system in comparison with the simple molecular one. In fact, in the present report and in others,[26] the results obtained with NaBARF as halide abstractor are in some cases erratic and unreliable. Therefore, much work is still needed to establish the implications of its use. Finally, it should be noted that the dendritic system **Pd-2P$_2$**/NaBARF remarkably decreases the amount of styrene dimers formed.

Conclusions

In summary, we have established a new efficient system for palladium-catalyzed asymmetric hydrovinylation of styrene using carbosilane dendrimers peripherally functionalized with P-stereogenic monophosphines. The results in terms of activity, selectivity, and enantiomeric excess strongly depend on the nature of the phosphine and the halide abstractor. Thus, for the palladium species containing the 2-biphenylyl-substituted phos-

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phine (**P_1**), the use of the sodium salt of $BARF^-$ instead of $AgBF_4$ increased notably the chemoselectivity and the enantioselectivity of the process. The best results in terms of ee (79% toward the *S* isomer) were obtained with **Pd-3P_1**. On the other hand, the systems **Pd-P_2**/$AgBF_4$ were found to be extraordinarily active, although they were unable to induce enantioselectivity. Surprisingly, the system **Pd-2P_2**/NaBARF gave (*R*)-3-phenyl-1-butene as the predominant isomer, in contrast to its analogous model system **Pd-1P_2**/NaBARF, which yielded (*S*)-3-phenyl-1-butene, as did the other systems studied in this paper. More experiments are needed to elucidate this fact.

Experimental Section

General Data. All manipulations were performed under purified nitrogen using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were obtained on Varian Gemini 200, Bruker DRX 250, Varian Unity 300, and Varian Mercury 400 spectrometers. 2D NMR spectra (NOESY ^{1}H−^{1}H and HSQC ^{1}H−^{13}C) were recorded on a Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^{1}H, ^{13}C, and ^{29}Si, BF_3·Et_2O for ^{11}B, and 85% H_3PO_4 for ^{31}P), and coupling constants are given in Hz. MS (FAB and ES) spectra were recorded with a Fisions VGQuattro spectrometer using NBA (3-nitrobenzyl alcohol) as a matrix for FAB spectra. MALDI-TOF spectra were recorded with a Voyager DE-RP (Perspective Biosystems) spectrometer using DTH (dithranol; 1,8,9-trihydroxianthracene) 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. HPLC analyses were carried out in a Waters 717 Plus autosampler chromatograph with a Waters 996 multidiode array detector, fitted with a Chiracel OD-H chiral column. The eluent, in all the determinations, was a mixture of *n*-hexane and ^{i}PrOH (95/5). 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 an FID detector. Elemental analyses (C, H) were performed at the Servicio de Microanálisis del Centro de Investigación y Desarrollo del Consejo Superior de Investigaciones Científicas (CSIC) or at the Serveis Cientificotècnics of the Universitat Rovira i Virgili. The palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ and the starting carbosilane dendrimers **2Cl** and **3Cl** as well as the chiral phosphines **P_1**-BH_3 and **P_2**-BH_3 were prepared as previously described.[10,11,27] Other reagents were used as received from commercial suppliers.

Synthesis. 1P_1-BH_3. The phosphine−borane **P_1**-BH_3 (0.400 g, 1.380 mmol) was dissolved in 15 mL of thf and cooled to −78 °C. *sec*-Butyllithium (1.70 mL of 1.3 M cyclohexane/hexane solution, 2.210 mmol) was added slowly. After the resulting violet mixture was stirred for 2 h, 0.5 mL of the silane **1Cl** (0.857 g/mL, 3.944 mmol) was added by syringe. The temperature was maintained at −78 °C for 4 h, and then the mixture was stirred for 14 h, slowly reaching room temperature. Afterward, 20 mL of a solution HCl 1 M was added and the thf was removed in vacuo. The remaining aqueous suspension was extracted with dichloromethane (3 × 10 mL), and the combined organic portions were dried with anhydrous sodium sulfate. The solution was concentrated, and the addition of ethanol caused the precipitation of **1P_1**-BH_3 as a white solid. Yield: 0.230 g (46%). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 17.1 (pd (br), $^1J_{BP} \approx 74$ Hz). ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.21−6.75 (m, Ar, 14H), 1.60−0.30 (m, BH_3, 3H), 1.19−0.89 (m, CH_2P, 2H), −0.11 (s, CH_3Si, 9H). ^{13}C{^{1}H} NMR (50.0 MHz, $CDCl_3$, 298 K; δ (ppm)): 135.2−127.8 (Ar), 10.0 (d, $^1J_{CP} = 24.6$ Hz, CH_2P), 0.1 (s, CH_3Si). ^{11}B{^{1}H} NMR (80.2 MHz, $CDCl_3$, 298 K; δ (ppm)): −35.3 (d, $J_{BP} = 54.3$ Hz). Anal. Calcd for $BC_{22}H_{28}PSi$: C, 72.93; H, 7.79. Found: C, 72.26; H, 7.61. $[\alpha]_D = -2.7°$ ($c = 0.945$, $CHCl_3$). HPLC (t_R): 8.5 min.

1P_2-BH_3. This compound was prepared analogously to **1P_1**-BH_3. From the phosphine−borane **P_2**-BH_3 (0.600 g, 1.910 mmol), *sec*-butyllithium (2.35 mL, 1.3 M cyclohexane/hexane solution, 3.056 mmol), and **1Cl** (0.7 mL, 0.857 g/mL, 5.539 mmol), the product was obtained as a white solid. Yield: 0.719 g (97%). ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 13.9 (pd (br), $^1J_{BP} \approx 64$ Hz). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.74−7.26 (m, Ar, 14H), 2.00 (pt, $J \approx 13.6$ Hz, CH_2P, 1H), 1.78 (pt, $J \approx 13.6$ Hz, CH_2P, 1H), 1.60−0.80 (m, BH_3, 3H), −0.13 (s, CH_3Si, 9H). ^{13}C{^{1}H} NMR (50.0 MHz, $CDCl_3$, 298 K; δ (ppm)): 138.2−122.6 (Ar), 12.8 (d, $^1J_{CP} = 25.0$ Hz, CH_2P), 0.4 (s, CH_3Si). ^{11}B{^{1}H} NMR (80.2 MHz, $CDCl_3$, 298 K; δ (ppm)): −35.0 (s (br)). Anal. Calcd for $BC_{24}H_{28}PSi$: C, 74.61; H, 7.30. Found: C, 74.53; H, 7.51. $[\alpha]_D = -47.7°$ ($c = 1.010$, $CHCl_3$). HPLC (t_R): 21.3 min.

1P_1. 1P_1-BH_3 (0.120 g, 0.331 mmol) was dissolved in morpholine (15 g, 15 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 the product as a colorless oil. Yield: 0.100 g (87%). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −33.6 (s). ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.60−7.15 (m, Ar, 14H), 1.21 (pq, $J \approx 7.5$ Hz, CH_2P, 2H), −0.20 (s, CH_3Si, 9H). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 298 K; δ (ppm)): 148.1−127.4 (Ar), 15.1 (d, $^1J_{CP} = 28.4$ Hz, CH_2P), 0.1 (s, CH_3). Anal. Calcd for $C_{22}H_{25}PSi$: C, 75.82; H, 7.23. Found: C, 75.63; H, 7.16. $[\alpha]_D = -108.8°$ ($c = 0.85$, CH_2Cl_2). MS (MALDI-TOF; *m/z*): 349.1 (349.5 calcd) $[M + H]^+$.

1P_2. This product was prepared using the same procedure as for **1P_1**. With **1P_2**-BH_3 (0.350 g, 0.906 mmol) and morpholine (20 g, 20 mL) as starting materials, the product was obtained as a colorless oil. Yield: 0.270 g (80%). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −33.2 (s). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.65−7.23 (m, Ar, 14H), 1.53 (s (br), CH_2P, 2H), 0.03 (s, CH_3Si, 9H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 140.6−122.9 (Ar), 14.6 (d, $^1J_{CP} = 29.9$ Hz, CH_2P), 0.3 (d, $^3J_{CP} = 4.5$ Hz, CH_3Si). Anal. Calcd for $C_{24}H_{25}PSi$: C, 77.38; H, 6.76. Found: C, 77.51; H, 6.80. $[\alpha]_D = +87.9°$ ($c = 0.85$, CH_2Cl_2). MS (MALDI-TOF; *m/z*): 597.3 (598.6 calcd) $[M + DTH]^{\bullet+}$ (matrix aggregation, DTH), 373.2 (373.5 calcd) $[M + H]^+$.

2P_1. The phosphine−borane **P_1**-BH_3 (0.722 g, 2.487 mmol) was dissolved in 20 mL of thf, and the solution was cooled to −78 °C. *sec*-Butyllithium (1.84 mL of 1.3 M cyclohexane/hexane solution, 2.431 mmol) was added slowly. After the violet mixture that formed was stirred for 2 h, a precooled solution of the silane **2Cl** (0.246 g, 0.482 mmol) in thf 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 HCl solution was added and the thf was removed in vacuo. The remaining aqueous suspension was extracted with dichloromethane (3 × 10 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, and the crude product was passed through a short column of alumina with toluene as eluent. A mixture of the dendrimer **1P_1** and the free phosphine **P_1** was obtained after evaporating the toluene. The product was purified by flash chromatography under N_2 on a silica gel column with hexane/thf (10/1) as eluent. The title compound was finally obtained as a white foam. Yield: 0.290 g (41%). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −33.5 (s). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.50−7.16 (m, Ar, 56H), 1.18 (pq, $J \approx 15.6$ Hz, CH_2P, 8H), 0.11−0.01 (m, CH_2Si, 16H), −0.23 (s, CH_3Si, 12H), −0.28

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(s, CH_3Si, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 147.7−127.0 (Ar), 13.2 (d, $^1J_{CP}$ = 31.5 Hz, CH_2P), 8.7 (d, $^3J_{CP}$ = 3.8 Hz, CH_2Si_1), 2.5 (s, CH_2Si_0), −2.6 (d, $^3J_{CP}$ = 4.5 Hz, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K; δ (ppm)): 9.17 (s, Si_0), 3.49 (d, $^2J_{SiP}$ = 14.5 Hz, Si_1). Anal. Calcd for $C_{92}H_{104}P_4Si_5$: C, 74.96; H, 7.11. Found: C, 75.12; H, 7.20. $[\alpha]_D$ = −74.3° (c = 0.65, CH_2Cl_2). MS (MALDI-TOF; *m/z*): 1473.5 (1474.2 calcd) $[M]^{\bullet+}$, 1214.4 (1213.9 calcd) [M − phosphine + H]$^+$.

2P$_2$. The procedure was analogous to that used for **2P$_1$**. In the purification by chromatography, the eluent used was a mixture of hexane and thf (10/3). With **P$_2$**-BH_3 (0.956 g, 3.032 mmol), *sec*-butyllithium (2.24 mL of 1.3 M cyclohexane/hexane solution, 2.915 mmol), and **2Cl** (0.300 g, 0.583 mmol) as starting materials, the product was obtained as a white foam. Yield: 0.510 g (56%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −36.8 (s). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.85−7.21 (m, Ar, 56H), 1.54 (s (br), CH_2P, 8H), 0.41 (m, CH_2Si, 16H), 0.00 (s, CH_3Si, 12H), −0.02 (s, CH_3Si, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 140.6−122.8 (Ar), 12.7 (d, $^1J_{CP}$ = 30.7 Hz, CH_2P), 9.0 (d, $^3J_{CP}$ = 4.6 Hz, CH_2Si_1), 2.9 (s, CH_2Si_0), −2.1 (pt, $^3J_{CP} \approx$ 5.4 Hz, CH_3Si). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K; δ (ppm)): 9.55 (s, Si_0), 3.96 (d, $^2J_{SiP}$ = 14.6 Hz, Si_1). Anal. Calcd for $C_{100}H_{104}P_4Si_5$: C, 76.49; H, 6.68. Found: C, 76.52; H, 6.70. $[\alpha]_D$ = +65.5° (c = 2.1, CH_2Cl_2). MS (MALDI-TOF; *m/z*): 1570.9 (1570.2 calcd) $[M]^{\bullet+}$, 1793.9 (1796.3 calcd) [M + DTH]$^+$ (matrix aggregation, DTH), 1285.8 (1285.9 calcd) [M − phosphine + H]$^+$.

3P$_1$. This was prepared in the same way as **2P$_1$**. In the purification by chromatography, the eluent used was a mixture of hexane and thf (10/3). With **P$_1$**-BH_3 (0.714 g, 2.462 mmol), *sec*-butyllithium (1.81 mL of 1.3 M cyclohexane/hexane solution, 2.350 mmol), and **3Cl** (0.365 g, 0.224 mmol) as starting materials, the product was obtained as a white foam. Yield: 0.120 g (15%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): −33.1 (s). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.48−7.18 (m, Ar, 112H), 1.20 (pq, $J \approx$ 14.8 Hz, CH_2P, 16H), 0.40−0.00 (m, CH_2Si, 64H), −0.09 (s, CH_3Si_1, 48H), −0.24 (s (br), CH_3Si_3 + CH_3Si_2, 24H + 12H), −0.27 (s, CH_3Si_3, 24H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 147.7−127.2 (Ar), 13.3 (d, $^1J_{CP}$ = 31.4 Hz, CH_2P), 8.8 (d, $^3J_{CP}$ = 4.6 Hz, CH_2Si_3), 7.0−2.8 (m, CH_2Si), −2.4 (d, $^3J_{CP}$ = 5.3 Hz, CH_3Si_3), −4.1 (s, CH_3Si_1), −6.4 (s, CH_3Si_2). $^{29}Si\{^1H\}$ NMR (49.7 MHz, $CDCl_3$, 298 K; δ (ppm)): 9.43 (s, Si_0), 7.88 (s, Si_2), 5.66 (s, Si_1), 3.55 (d, $^2J_{SiP}$ = 14.0 Hz, Si_3). Anal. Calcd for $C_{212}H_{276}P_8Si_{17}$: C, 71.73; H, 7.84. Found: C, 71.89; H, 7.87. $[\alpha]_D$ = −37.5° (c = 1.90, CH_2Cl_2). MS (MALDI-TOF; *m/z*): 3549.6 (3549.8 calcd) $[M]^{\bullet+}$.

Pd-1P$_1$. The model compound **1P$_1$** (0.100 g, 0.286 mmol) was dissolved in 15 mL of CH_2Cl_2, and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.056 g, 0.143 mmol) was added. After the mixture was stirred for 20 min, the solvent was removed and the resulting pasty solid was recrystallized from CH_2Cl_2/hexane. The product **Pd-1P$_1$** was obtained as a yellow solid. Yield: 0.150 g (96%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.6 (s, minor isomer), 6.7 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.00−6.90 (m, Ar, both isomers), 4.45 (m, H_{syn-tP}, minor isomer), 4.41 (m, H_{syn-tP}, major isomer), 3.44 (d, J = 9.6 Hz, $H_{anti-tP}$, minor isomer), 3.37 (s (br), H_{syn-cP}, major isomer), 3.27 (s (br), H_{syn-cP}, minor isomer), 3.21 (d, J = 10.4 Hz, $H_{anti-tP}$, major isomer), 2.49 (s (br), $H_{anti-cP}$, minor isomer), 1.99 (s, allyl-Me, minor isomer), 1.99−1.87 (m, CH_2P both isomers + $H_{anti-cP}$ minor isomer), 1.89 (s, allyl-Me, major isomer), 1.70−1.50 (m, CH_2P both isomers), −0.11 (s, CH_3Si, major isomer), −0.14 (s, CH_3Si, minor isomer). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 146.6−127.1 (Ar + allyl-C_q, both isomers), 77.8−77.0 (m, allyl-C_{tP}, both isomers), 58.3 (s (br), allyl-C_{cP}, minor isomer), 56.0 (s (br), allyl-C_{cP}, major isomer), 23.7 (s, allyl-Me, major isomer), 23.5 (s, allyl-Me, minor isomer), 18.3 (d (br), $^1J_{CP}$ = 10.8 Hz, CH_2P, minor isomer), 16.2 (d (br), $^1J_{CP}$ = 10.8 Hz, CH_2P, major isomer), 0.8 (d, $^3J_{CP}$ = 3.8 Hz, CH_3Si, both isomers). Anal. Calcd for $C_{26}H_{32}ClPPdSi$: C, 57.25; H, 5.91. Found: C, 57.31; H, 5.99. MS (FAB(+); *m/z*): 509.0 (510.0 calcd) [M − Cl]$^+$.

Pd-1P$_2$. This complex was obtained in the same way as for **Pd-1P$_1$**. With **1P$_2$** (0.210 g, 0.558 mmol) and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.110 g, 0.279 mmol) as starting materials, a pale yellow solid was obtained. Yield: 0.305 g (96%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.9 (s, minor isomer), 4.0 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.69−7.25 (m, Ar, both isomers), 4.41 (dd, J_1 = 10.0 Hz, J_2 = 2.8 Hz, H_{syn-tP}, minor isomer), 4.37 (dd, J_1 = 9.6 Hz, J_2 = 2.8 Hz, H_{syn-tP}, major isomer), 3.47 (d, J = 10.0 Hz, $H_{anti-tP}$, minor isomer), 3.41 (d, J = 10.4 Hz, $H_{anti-tP}$, major isomer), 3.24 (s, H_{syn-cP}, minor isomer), 2.83 (s, H_{syn-cP}, major isomer), 2.54 (s, $H_{anti-cP}$, major isomer), 2.53 (s, $H_{anti-cP}$, minor isomer), 2.17 (pt, J = 12.8 Hz, CH_2P, major isomer), 2.10−1.92 (m, CH_2P, both isomers), 1.82 (s, allyl-Me, minor isomer), 1.53 (s, allyl-Me, major isomer), 0.08 (s, CH_3Si, major isomer), 0.00 (s, CH_3Si, minor isomer). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 135.5−122.8 (Ar + allyl-C_q, both isomers), 77.7−77.0 (m, allyl-C_{tP}, both isomers), 60.3 (s, allyl-C_{cP}, major isomer), 59.3 (s, allyl-C_{cP}, minor isomer), 23.4 (s, allyl-Me, minor isomer), 23.0 (s, allyl-Me, major isomer), 16.7 (d, $^1J_{CP}$ = 10.8 Hz, CH_2P, minor isomer), 16.0 (d, $^1J_{CP}$ = 11.5 Hz, CH_2P, major isomer), 1.0 (d, $^3J_{CP}$ = 3.8 Hz, CH_3Si, major isomer), 0.9 (d, $^3J_{CP}$ = 3.0 Hz, CH_3Si, minor isomer). Anal. Calcd for $C_{28}H_{32}ClPPdSi$: C, 59.05; H, 5.66. Found: C, 59.27; H, 5.78%. MS (FAB(+); *m/z*): 533.0 (534.0 calcd) [M − Cl]$^+$.

Pd-2P$_1$. This complex was obtained using the same procedure as for **Pd-1P$_1$**. With **2P$_1$** (0.182 g, 0.123 mmol) and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.097 g, 0.246 mmol) as starting materials, a yellow solid was obtained. Yield: 0.265 g (95%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.3 (s, minor isomer), 6.4 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.00−7.00 (m, Ar, both isomers), 4.42 (d (br), J = 6.4 Hz, H_{syn-tP}, minor isomer), 4.37 (d (br), J = 7.2 Hz, H_{syn-tP}, major isomer), 3.41 (d, J = 10.0 Hz, $H_{anti-tP}$, minor isomer), 3.33 (s (br), H_{syn-cP}, major isomer), 3.28 (s (br), H_{syn-cP}, minor isomer), 3.18 (d, J = 9.6 Hz, $H_{anti-tP}$, major isomer), 2.47 (s (br), $H_{anti-cP}$, minor isomer), 1.97 (s, allyl-Me, minor isomer), 1.96−1.87 (m, CH_2P both isomers + $H_{anti-cP}$ major isomer), 1.87 (s, allyl-Me, major isomer), 1.67−1.53 (m, CH_2P, both isomers), 0.10-(−0.10) (m, CH_2Si + CH_3Si, both isomers), −0.37 (s, CH_3Si, minor isomer), −0.38 (s, CH_3Si, major isomer). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 146.5−127.2 (Ar + allyl-C_q, both isomers), 77.8−77.0 (m, allyl-C_{tP}, both isomers), 58.4 (s (br), allyl-C_{cP}, minor isomer), 57.0 (s (br), allyl-C_{cP}, major isomer), 23.8 (s, allyl-Me, major isomer), 23.5 (s, allyl-Me, minor isomer), 16.9 (d (br), $^1J_{CP} \approx$ 10 Hz, CH_2P, minor isomer), 14.6 (d (br), $^1J_{CP} \approx$ 10 Hz, CH_2P, major isomer), 9.4 (d, $^3J_{CP}$ = 4.5 Hz, CH_2Si_1, major isomer), 9.3 (d, $^3J_{CP} \approx$ 4 Hz, CH_2Si_1, minor isomer), 2.7 (s, CH_2-Si, both isomers), −1.3-(−2.1) (m, CH_3Si, both isomers). Anal. Calcd for $C_{108}H_{132}Cl_4P_4Pd_4Si_5$: C, 57.35; H, 5.88. Found: C, 57.56; H, 5.98. MS (ES(+); *m/z*): 2226.9 (2226.5 calcd) [M − Cl]$^+$.

Pd-2P$_2$. This procedure was analogous to that used for **Pd-1P$_1$**. With **2P$_2$** (0.191 g, 0.122 mmol) and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.096 g, 0.244 mmol) as starting materials, a pale yellow solid was obtained using toluene instead of hexane to precipitate the product. Yield: 0.280 g (98%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.5 (s, minor isomer), 2.7 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 8.75−7.33 (m, Ar, both isomers), 4.39−4.29 (m, H_{syn-tP}, both isomers), 3.42 (d, J = 10.0 Hz, $H_{anti-tP}$, minor isomer), 3.38 (d, J = 10.0 Hz, $H_{anti-tP}$, major isomer), 3.24 (s, H_{syn-cP}, minor isomer), 2.70

(s, H_{syn-cP}, major isomer), 2.56 (s, $H_{anti-cP}$, major isomer), 2.49 (s, $H_{anti-cP}$, minor isomer), 2.23 (pt, $J = 12.8$ Hz, CH_2P, major isomer), 2.17−1.95 (m, CH_2P, both isomers), 1.79 (s, allyl-Me, minor isomer), 1.42 (s, allyl-Me, major isomer), 0.50−0.18 (m, CH_2Si, both isomers), 0.20 (s, CH_3Si, major isomer), 0.09 (s, CH_3Si, minor isomer), 0.02 (s, CH_3Si, major isomer), −0.08 (s, CH_3Si, minor isomer). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)): 135.6−122.9 (Ar + allyl-C_q, both isomers), 77.7−76.9 (m, allyl-C_{tP}, both isomers), 60.8 (s, allyl-C_{cP}, major isomer), 59.4 (s, allyl-C_{cP}, minor isomer), 23.4 (s, allyl-Me, minor isomer), 22.9 (s, allyl-Me, major isomer), 15.3 (d (br), $^1J_{CP} \approx 9$ Hz, CH_2P, minor isomer), 14.6 (d (br), $^1J_{CP} \approx 10$ Hz, CH_2P, major isomer), 9.6 (d (br), $^3J_{CP} \approx 4$ Hz, CH_2Si_1, both isomers), 3.0 (s (br), CH_2Si_0, both isomers), −1.1 (s (br), CH_3Si, major isomer), −1.2 (d, $^3J_{CP} = 4.0$ Hz, CH_3-Si, minor isomer), −1.6 (s (br), CH_3Si, major isomer), −1.7 (m, CH_3Si, minor isomer). Anal. Calcd for $C_{116}H_{132}Cl_4P_4Pd_4Si_5$: C, 59.08; H, 5.64. Found: C, 59.30; H, 5.78. MS (ES(+); *m*/*z*): 2323.4 (2322.6 calcd) $[M - Cl]^+$, 2125.4 (2125.6 calcd) $[M - Pd(2\text{-Me-}C_3H_4)Cl - Cl]^+$.

Pd-3P$_1$. This complex was obtained using the same procedure as for **Pd-1P$_1$**. With **3P$_1$** (0.111 g, 0.031 mmol) and the palladium dimer $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\mu\text{-Cl})]_2$ (0.049 g, 0.125 mmol) as starting materials, a yellow solid was obtained. Yield: 0.155 g (97%). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.9 (s, minor isomer), 6.7 (s, major isomer). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K; δ (ppm)): 7.95−7.00 (m, Ar, both isomers), 4.44 (d (br), $J = 4.4$ Hz, H_{syn-tP}, minor isomer), 4.39 (d (br), $J = 4.4$ Hz, H_{syn-tP}, major isomer), 3.43 (d, $J = 9.6$ Hz, $H_{anti-tP}$, minor isomer), 3.35 (s (br), H_{syn-cP}, major isomer), 3.28 (s (br), H_{syn-cP}, minor isomer), 3.19 (d, $J = 10.0$ Hz, $H_{anti-tP}$, major isomer), 2.49 (s (br), $H_{anti-cP}$, minor isomer), 1.97 (s, allyl-Me, minor isomer), 1.97−1.87 (m, CH_2P both isomers + $H_{anti-cP}$ major isomer), 1.87 (s, allyl-Me, major isomer), 1.70−1.50 (m, CH_2P, both isomers), 0.40-(−0.40) (m, CH_2Si + CH_3Si, both isomers). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K; δ (ppm)):146.4−127.2 (Ar + allyl-C_q, both isomers), 77.6−76.9 (m, allyl-C_{tP}, both isomers CH_2), 58.1 (s (br), allyl-C_{cP}, minor isomer), 56.7 (s (br), allyl-C_{cP}, major isomer), 23.7 (s, allyl-Me, major isomer), 23.4 (s, allyl-Me, minor isomer), 16.6 (d (br), $^1J_{CP} \approx 10$ Hz, CH_2P, minor isomer), 14.4 (d (br), $^1J_{CP} = 11.0$ Hz, CH_2P, major isomer), 9.2−2.8 (m, CH_2Si, both isomers), −1.4-(−6.4) (m, CH_3Si, both isomers). Anal. Calcd for $C_{244}H_{332}Cl_8P_8Pd_8Si_{17}$: C, 57.17; H, 6.53. Found: C, 57.32; H, 6.67.

Structural Characterization. A colorless crystal of **1P$_2$**-BH_3 (0.86 × 0.65 × 0.54 mm) was mounted in a Bruker SMART CCD diffractometer. Intensities were collected at 293(2) K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A total of 3701 unique reflections were collected, of which 3556 with $I > 2\sigma(I)$ were used in refinement. SHELXTL software was used for solution and refinement.[28] Absorption corrections were made with the SADABS program.[29] The structure was solved by direct methods and refined using full-matrix least squares on F^2. $R = 0.039$ and $R_w = 0.098$, with the Flack parameter[30] $\chi = 0.06(8)$. Crystal data for **1P$_2$**-BH_3: $BC_{22}H_{28}PSi$, molecular weight 386.33, monoclinic, space group $P2_1$, $a = 10.373(2)$ Å, $b = 9.943(2)$ Å, $c = 11.265(2)$ Å, $\beta = 107.692(4)°$, $V = 1106.9(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.159$ g cm^{-3}.

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.

The catalytic solutions were prepared with styrene/Pd molar ratios of 500/1 and 1000/1, using 0.02 and 0.04 mol of styrene, respectively, and 4.0×10^{-5} mol of Pd (4.0×10^{-5} mol of **Pd-1P** compounds, 1.0×10^{-5} mol of **Pd-2P** metallodendrimers, or 5×10^{-6} mol for **Pd-3P$_1$**). Catalytic solutions with the styrene/Pd molar ratio 1500/1 were prepared with 0.04 mol of styrene and 2.7×10^{-5} mol of Pd (2.7×10^{-5} mol of **Pd-1P$_2$** or 6.7×10^{-6} mol of **Pd-2P$_2$**).

(a) Catalytic Solutions Prepared with $AgBF_4$ as Halide Abstractor. A mixture of the suitable neutral palladium precursor, styrene, and $AgBF_4$ ($AgBF_4$/Pd ratio 1/1) in 10 mL of dry and freshly distilled CH_2Cl_2 was stirred for 10 min in the dark. After the AgCl 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 the desired temperature. Ethylene was admitted until a pressure of 15 bar was reached. After the time indicated for each reaction, the autoclave was slowly depressurized and HCl 10% solution (10 cm^3) 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.

(b) Catalytic Solutions Prepared with NaBARF as Halide Abstractor. A mixture of the suitable neutral palladium complex, styrene, and NaBARF (NaBARF/Pd ratio 2/1) 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 the desired temperature. Ethylene was admitted until a pressure of 15 bar was reached. After the time indicated for each reaction, the autoclave was slowly depressurized and HCl 10% solution (10 cm^3) 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.

Acknowledgment. We acknowledge support from the Ministerio de Ciencia y Tecnología (Projects BQU2003-01131 and CTQ2004-01546) and the CIRIT (Generalitat de Catalunya) (Project 2001SGR 00054). L-I.R. and A.G. are indebted to the Ministerio de Ciencia y Tecnología for a scholarship. We also thank Mr. Sebastian Gischig for the crystal structure determinations performed at the Department of Chemistry, ETH Hönggerberg, Zürich, Switzerland.

Supporting Information Available: CIF file giving crystal data for the phosphine **1P$_2$**-BH_3 and tables showing the NOESY $^1H-^1H$ cross-peaks between isomers of compounds **Pd-3P$_1$** and **Pd-2P$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050915S

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