Allylpalladium Complexes with *P*-Stereogenic Monodentate Phosphines. Application in the Asymmetric Hydrovinylation of Styrene

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A group of *P*-stereogenic monodentate phosphines *S*-PPhRR′ (R = 1-naphthyl, 9-phenanthryl, or *o*-biphenylyl and R′ = CH_3−, *i*-C_3H_8−, and Ph_3SiCH_2−) have been prepared by succesive substitution reactions on the oxazaphospholidineborane obtained from (−)-ephedrine and bis(*N*,*N*-diethylamino)phenylphosphine. The reaction with binuclear allyl compounds [Pd(*μ*-Cl)(allyl)]$_2$ gives neutral [PdCl(allyl)P*] complexes. When allyl = 2-CH_3-C_3H_4 (**5**), two isomers appeared in solution due to the *R*- or *S*-geometry around the palladium atom. The discrimination effect of the phosphines is small and the maximum isomeric ratio is observed for PPh(*o*-Ph_2)(CH_2SiPh_3). The molecular structure determined by X-ray diffraction of two complexes with P* = PPh(*o*-Ph_2)(*i*-Pr) and PPh(*o*-Ph_2)(OMe) showed a very similar nonsymmetric coordination of the allyl moiety according to the greater *trans* influence of the phosphorus atom. When allyl = 1-C_6H_5-C_3H_4 (**6**), the NMR spectroscopy showed up to four isomers due to the *R*- or *S*-geometry around palladium and the *Z*- or *E*-disposition of P* and the phenyl substituent of the allyl moiety. The *E*-isomers are the major species in solution, unique with PPh(*o*-Ph_2)(CH_2SiPh_3). The usual, well-defined dynamic exchanges by *π*−*σ*−*π* and pseudorotation of the allyl moiety have been observed. The codimerization reaction between styrene and ethylene has been tested using filtered CH_2Cl_2 solutions of [PdCl(2-CH_3-C_3H_4)P*] (**5**) complexes and $AgBF_4$ as catalytic precursors. Moderate activity (TOF < 225 h^{-1} at 25 °C) and good selectivities to 3-Ph-1-butene (∼90% at 80% conversion) are obtained. The ee is moderate (<40% ee) and different from the discrimination effects observed in the solutions of neutral complexes [PdCl(ally)P*]. The reaction carried out with deuterated styrene shows the clean C−H addition to the vinyl double bond of stryrene and confirms the irreversible nature of the insertion of styrene in the palladium hydride intermediate. The hydrovinylation reaction using substituted styrene with a potentially secondary coordination atom occurs only when the substitution is in the phenyl ring and without significant improvements of the ee.

Introduction

The reaction of hydrovinylation is a very effective and highly stereoselective carbon−carbon bond forming catalytic reaction that can be considered the addition of a carbon−hydrogen bond from a vinyl group to an olefin. The reaction, recently reviewed,[1] is catalyzed by a variety of transition metals, with nickel and palladium compounds being the most used, although ruthenium[2] is also an alternative. The scope of the reaction is limited by the nature of the olefin since excellent stereoselectivity is achieved only with conjugated dienes or strained olefins or in intramolecular reactions.[3]

The process shows a number of singularities, probably the most important being the monodentate nature of the unique stabilizing ligand supported by the catalytic cycle on nickel and palladium systems. Allylic precursors thus proved to be very useful since the metal/phosphine ratio is 1/1. The basic mechanism is relatively

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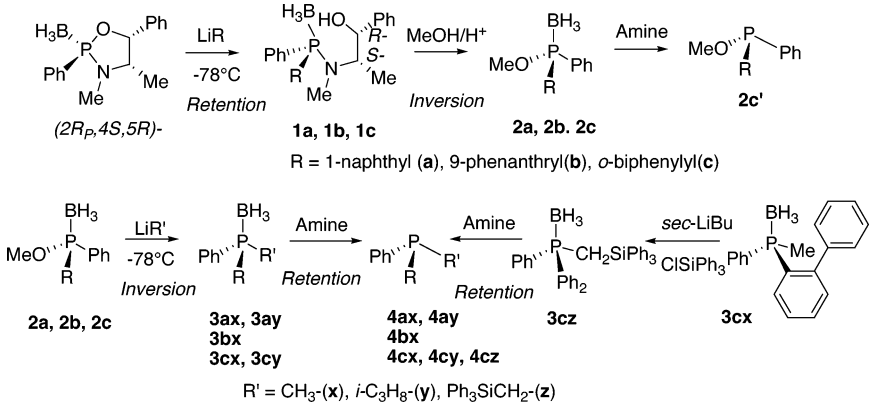
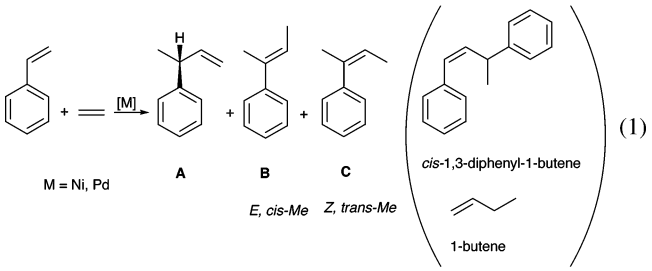
Scheme 1



well defined and involves a cationic metal hydride intermediate that initiates the heterodimerization. The study of the stereoselectivity in this singular system with a slightly crowded metal environment is attractive since the use of prochiral olefins produces a stereogenic center.

The model reaction of the process involves codimerization between styrene or vinylnaphthalene and ethylene (eq 1). When these types of vinylarenes are used as prochiral olefins, the excellent regioselectivities obtained originate in the allylic nature of the intermediate. However, the control of the reaction's enantioselectivity is more difficult, and it is probably an excellent process for evaluating the hemilability or potential secondary interactions of ligands anchored in one coordination position around the metal.[4] Impressive enantioselectivities were initially obtained by Wilke[5] (95.2% ee) and more recently by the groups of Vogt[6] (86% ee), Gibson[7] (92% ee), Rajanbabu (87% ee,[8] 91% ee[4d]), and Leitner[9] (94.8 ee) using phosphines, planar chiral chromium phosphines, phosphinites, or phosphoramidites as stabilizing ligands with nickel systems. However, the factors determining the discrimination ability of the ligands in this reaction remain poorly defined.



(1)

The final efficiency of the process is determined by the delicate competition between the olefins present in the reaction and all the species contained in the reaction medium that could potentially operate as ligands. These species are important in controlling the homo-heterodimerization reaction and the possible isomerization of the initial reaction product.

The excellent reaction yields using nickel systems lead to the proposal of a protocol for the synthetic application of the process.[10] Catalyst recovery using dendritic materials functionalized with P-O hemilabile ligands has been studied in a pressure membrane reactor.[11] The hydrovinylation carried out with palladium systems in this way showed less activity than the corresponding model molecular compounds.[11,12] The efficiency of supercritic CO_2 or ionic liquid/CO_2 systems has also been tested.[13]

Recently, we investigated the model reaction (eq 1) using nickel and palladium precursors.[14,15] The initial work provided evidence of the blocking effect of inert bidentate ligands. Further research with allylic palladium precursors containing *P*-stereogenic phosphines enabled the enantioselective version of the process to be studied. The *P*-stereogenic phosphines could be assumed to show good discrimination ability in the coordination and insertion reaction (Scheme 1) since they are close to the benzylic group in the allyl intermediate.[6] Precursor compounds [Pd(η^3-2-Me-C_3H_4)ClP*] containing the phosphines *S*-PBnMesPh and *S*-PBnCyPh gave *S*-3-Ph-1-butene with 40% and 60% ee, respectively.[15] Two diastereoisomers of the allylic precursors were observed in solution in a similar ratio (54−53/46−47), so the discrimination ability of the phosphine in the reaction could not be inferred from this ratio.

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Since the phosphines tested differed only in the mesityl and cyclohexyl groups, in this work we obtained a group of *P*-stereogenic phosphines by changing two different substituents. Hence, we prepared organometallic precursors containing the η^3-2-Me-C_3H_4 and the bulkier nonsymmetric η^3-1-Ph-C_3H_4 allyl ligands to see whether it was possible to evaluate the efficiency of the phosphine ligand in the hydrovinylation reaction with the isomer distribution of the allyl complexes in solution. Perdeuterated styrene was used to support the proposed mechanism. Some functionalized styrene derivatives were also tested to check the effect of a secondary coordination position in the substrate.

Results and Discussion

Phosphine Preparation. *P*-Stereogenic phosphines have been prepared by several methods,[16] such as the resolution of racemates,[15,17] stereoselective synthesis, and asymmetric catalysis.[18] In direct synthesis, the use of stoichiometric chiral auxiliaries is needed. The reported methods are based on the pairs (−)-menthol/phosphine,[19] sparteine/dimethylphosphines,[20] dynamic resolution with sparteine-*n*-BuLi,[21] the adduct ephedrine/dihalophosphine,[22] and the Michaelis-Arbuzov and the Staudinger reaction to obtain *P*-stereogenic phosphine oxides.[23]

We used the method developed by Jugé[22] and reported by several groups[24] (Scheme 1). Initially, the amino alcohol (1*R*,2*S*)-ephedrine and the most rigid (1*R*,2*S*)-1-amino-2-indanol were tested to achieve the best diastereomer discrimination in the reaction with PPh-$(NEt_2)_2$. The crude solutions of the oxazaphospholidine adducts showed a diastereomeric excess of 92% and 88%, respectively.[22b,c,25] The solid compounds separated were pure diastereomers. Since the use of the aminoindanol did not represent any advantage, it was more convenient to continue using the ephedrine as chiral auxiliary.

The limitations of the Jugé method in terms of the type and order of the successive introduction of different substituents preclude the preparation of a series of ligands containing −Me, −*i*-Pr, and −*t*-Bu groups. Although the *t*-Bu substituent can be introduced as the first one over the ephedrine adduct, the subsequent methanolysis does not occur.[26] As the second substituent, the associative nature of the substitution reaction blocked the process. Furthermore, the preparation of isopropyl phosphines is very slow, about 12 h being required to complete the reaction compared with 2 h for methyl substitution. To overcome this problem, the formation of P-Cl intermediates has been proposed.[27] Selection of the groups to be attached to the phosphorus atom seeks to increase regularly the steric hindrance of the phosphine and also modify the conformation of the biphenylyl substituent with respect to the P−B bond. The methylphosphines *S*-PPhMeR (R = *o*-Ph_2 and 1-Naph) have been prepared before,[28a,b] although PPhMe-(9-Phen) was obtained in racemic form.[28c]

The crystal structure of *P*-borane adducts **3bx**, **3cx**, and **3cy** (b = 9-Phen, c = *o*-Ph_2, x = Me, y = *i*-Pr) was determined to confirm the expected *S*-isomer geometry of the stereogenic center. The distances and angles measured (Table 1) were similar to those reported for analogous molecules.[28a,29] The disposition of the biphenylyl group is not modified by changing the methyl (**3cx**) for the *i*-Pr (**3cy**) alkyl substituents (Figure 1). The relative steric hindrance of the three substituents can be envisaged using the mean value of the three BPC angles. Smaller angles should represent higher steric hindrance, so the order proves to be **3cx** ∼ **3cy** > **3d** > **3bx** > **3ax** (113.9°)[28a] (a = Naph, b = 9-Phen, c = *o*-Ph_2, x = Me, y = *i*-Pr).

When the preparation of the isopropyl-phenanthryl-protected phosphine was attempted using the standard protocol, a new, different product was obtained (Scheme 2).

The addition of a slight excess of 2-propyllithium gave a mixture of the starting protected phosphinite **2b** (δ_P

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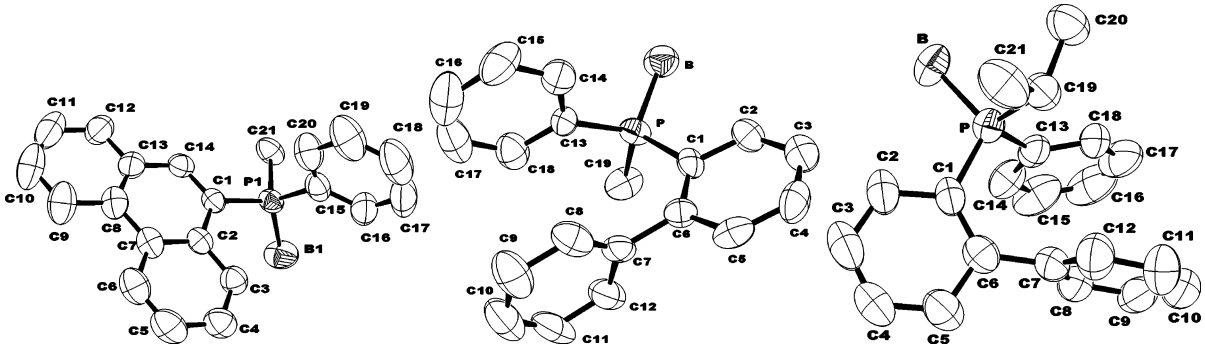
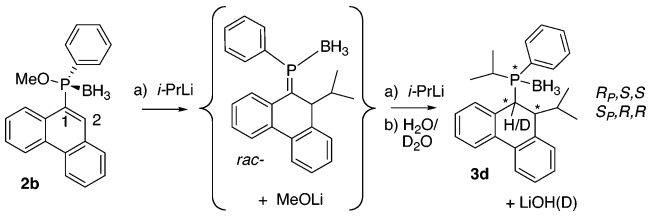


Figure 1. ORTEP drawing of the molecular structures of the phosphine-boranes **3bx**, **3cx**, and **3cy** (b = 9-Phen; c = *o*-Ph_2; x = Me; y = *i*-Pr**)** shown at 50% probability. Hydrogen atoms omitted for clarity.

Table 1. Selected Distances (Å) and Angles (deg) of the *P*-Borane Adducts 3cx, 3cy, 3bx, and 3d

P(BH_3)Ph(aryl)(alkyl)	**3cx** (*o*-Ph_2)Me	**3cy** (*o*-Ph_2)(*i*-Pr)	**3bx** (9-Phen)Me	**3d** (***R*$_P$*SS*) (9-PhenH_2*)(*i*-Pr)
P−alkyl	1.806(4)	1.829(2)	1.796(2)	1.939(5)
P−Ph	1.801(5)	1.788(2)	1.817(2)	1.835(3)
P−Aryl	1.822(5)	1.816(2)	1.814(2)	1.815(3)
P−B	1.919(8)	1.911(3)	1.934(2)	1.867(3)
Alkyl−P−B	109.7(3)	111.49(13)	107.23(11)	110.4(2)
Ph−P−B	111.8(3)	109.74(11)	117.74(12)	111.0(2)
Aryl−P−B	112.5(3)	112.93(12)	115.18(10)	117.5(2)
Σ/3	111.33	111.38	113.38	112.96
dihedral				
B−P−C(13)−C(14)	57.9(2)	64.21(12)		
C(1)−C(6)−C(7)−C(12)	82.3(2)	92.3(3)		

Scheme 2. Proposed Formation of 3d



= 111.5 ppm) and a new compound (δ_P = 10 ppm), and after the addition of an excess of 2-propyllithium the conversion to the new compound was complete. The final washing with water changed the chemical shift to δ_P = 25 ppm. The proton NMR spectrum of the isolated white solid showed the presence of two independent isopropyl fragments, one coupled with the phosphorus atom. Two new signals of aliphatic protons appeared at 3.75 (pseudotriplet, 4.0 Hz) and 2.78 (ddd, 3.2, 10.8, 34.8 Hz). The integration of the signals and NOESY experiment were coherent with the protected phosphine **3d**. The ^{31}P-decoupled proton NMR spectrum modifies the signals at 3.75 (d, ∼ 4 Hz), 2.78 (dd, 3.2, 10.8), and those of the *i*-Pr group attached to the phosphorus atom. The signal at 3.75 ppm disappears when D_2O is used as the washing solvent, and accordingly the signal at 2.78 reduced the multiplicity. Therefore, the initial signal at 10 ppm belongs to an anionic phosphine that captures the necessary hydrogen atom from the solvent.

Crystals of sufficient quality to confirm the proposed structure were obtained from mixtures of CH_2Cl_2 and hexane. The unit cell contains two enantiomers, R_PSS and S_PRR, of the phosphine-borane **3d** ((BH_3)PPh(9-PhenH_2*)(*i*-Pr)); Figure 2 shows the R_PSS isomer. Furthermore, optical rotation measurements of solutions of the crude product gave values close to zero that were consistent with the clean ^{1}H and ^{13}C NMR spectra observed. Thus, the isomerization of the initial protected phosphinite and the selective formation of the **3d** enantiomers could be interpreted as a concerted process where the reactive 1,2 bond of the phenanthrene moiety is initially attacked by the nucleophile, giving an undetected active intermediate. The phosphorus racemization is probably produced in the second nucleophilic attack assuming a P−C double bond as proposed in Scheme 2.

Allyl Palladium Compounds, [PdCl(η^3-allyl)(P)] (5 and 6). Neutral allyl complexes [PdCl(η^3-2-Me-C_3H_4)(P)] (**5**) and [PdCl(η^3-1-Ph-C_3H_4)(P)] (**6**) were obtained by reaction of the dinuclear complexes [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ and [Pd(η^3-1-Ph-C_3H_4)(μ-Cl)]$_2$ with the appropriate phosphine ligand as reported (see Scheme 3).[30] ^{1}H NMR and ^{31}P NMR spectra for allyl complexes at room temperature showed broad signals for the

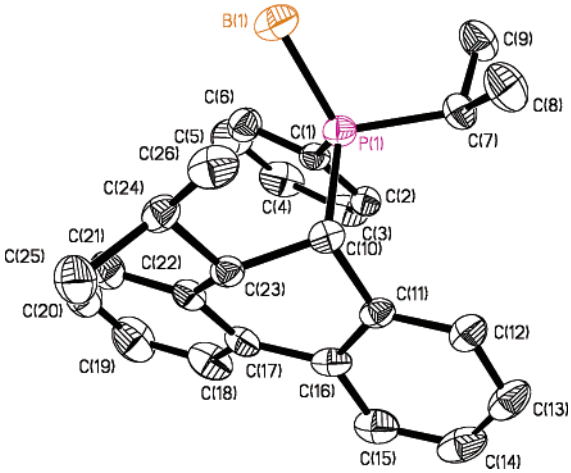


Figure 2. ORTEP drawning, of the molecular structure of the isomer R_PSS of **3d** ((BH_3)PPh(9-PhenH_2*)(*i*-Pr)) shown at 50% probability. Hydrogen atoms omitted for clarity.

Scheme 3. Allyl Compounds of Type 5 and 6 Obtained and Their Isomeric Composition in $CDCl_3$

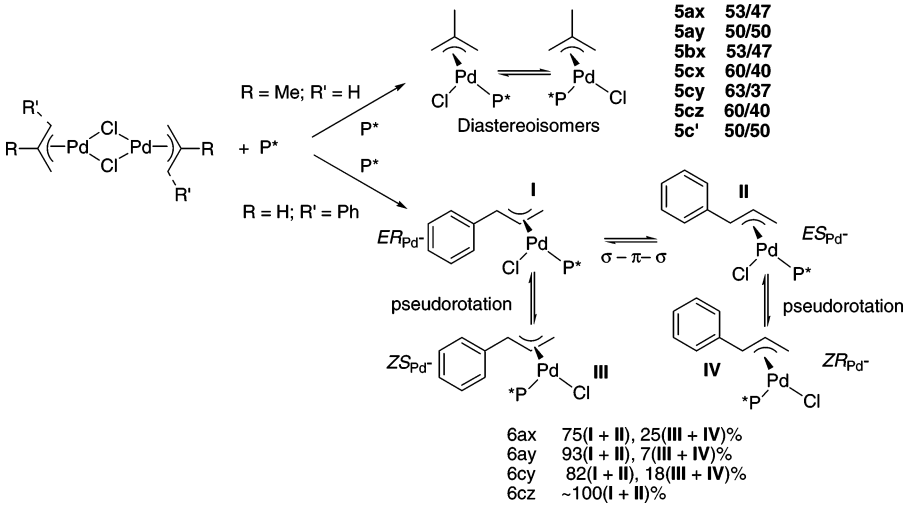


Table 2. ^{31}P and Selected ^1H NMR ($CDCl_3$, 298 K, 101.2 and 500.0 MHz) Data[a] (δ in ppm) for Complexes [Pd(η^3-(2-Me-C_3H_4)ClP] (5)

complex	^{31}P δ	P-CH_n	allyl-Me	*syn*-tP	*anti*-tP	*syn*-cP	*anti*-cP	P-X-CH_3
5ax								
major 1.1	3.62	2.19 (d, 9.0)	1.72	4.42 (m)	3.47 (d, 10.0)	2.66	2.58	
minor 1	3.10	2.22 (d, 9.0)	1.82	4.42 (m)	3.43 (d, 10.0)	2.71	2.39	
5ay[b]								
isomer a 1.1	23.72	3.05 (m)	1.66	4.32 (m)	3.41 (d, 10.0)	2.61	2.18	1.05, 1.31 (dd, 15.5, 7.0)
isomer b 1	22.71	3.05 (m)	1.56	4.32 (m)	3.34 (d, 10.0)	2.30	2.42	1.12, 1.39 (dd, 15.5, 7.0)
5bx								
major 1.1	5.70	2.29 (d, 8.4)	1.75	4.45 (m)	3.50 (d, 11.2)	2.75	2.59	
minor 1	4.50	2.22 (d, 8.8)	1.82	4.45 (m)	3.45 (d, 12.0)	2.75	2.38	
5cx								
major 1.5	6.21	1.88 (d, 8.0)	1.72	4.22 (dd, 7.5, 2.5)	2.80 (d, 11.0)	2.68	1.66	
minor 1	8.45	1.60 (d, 8.5)	1.85	4.37 (dd, 7.5, 2.5)	3.27 (d, 9.5)	2.97	2.08	
5cy								
major 1.7	33.46	2.49 (ds, 8.5, 6.5)	1.85	4.36 (dd, 7.0, 3.0)	3.12 (d, 10.0)	3.00 (m)	1.87	0.94, 1.17 (dd, 18.5, 7.0)
minor 1	33.51	2.31 (ds, 8.0, 7.0)	1.86	4.41 (dd, 6.5, 3.0)	3.22 (d, 9.5)	3.08 (m)	2.24	0.93, 1.07 (dd, 19.0, 7.0)
5cz								
major 1.5	19.32	3.27, 2.30 (dd, 13.6, 11.2)	1.79	4.26 (m)	2.77 (d, 9.6)	2.98 (d, 2.5)	1.64	
minor 1	12.45	2.73, 2.59 (pt, 14.8)	1.39	4.26 (m)	2.93 (d, 10.0)	3.00 (d, 2.5)	1.61	
5c'[b]								
isomer a 1	122.25		1.81	4.36 (m)	3.09 (d, 11.0)	3.17	1.88	3.53 (d, 14.0)
isomer b 1	118.07		1.84	4.36 (m)	2.95 (d, 11.0)	2.96	1.95	3.73 (d, 14.0)

[a] Multiplicity (b, broad; d, doublet; m, multiplet; q, quartet; s, septet; t, triplet, p pseudo), J_{PH} and J_{HH} coupling constants (in Hz). [b] ^{31}P and ^1H signals of both isomers not experimentally related.

unsymmetrical allyl **6** complexes due to their dynamic behavior. Only complexes **6cz** and **5** (c = *o*-Ph_2, z = CH_2-$SiPh_3$) gave sharp signals at room temperature. On cooling to 273 K the signals sharpened sufficiently and spin−spin interactions could be observed.

The spectra of compounds **5** showed the presence of two isomers, *R* and *S*-Pd, which are in equilibrium. The ^{31}P and ^1H data and isomeric composition are collected in Table 2; the relative ratio of isomers was independent of the temperature in chloroform. The discrimination effect of the naphthyl- and phenanthryl-substituted phosphines is negligible; only in those containing the *o*-biphenylyl group is the discrimination moderate, and even here it is not possible to establish any scale based on steric factors, as shown in the group of complexes containing PPh(*o*-Ph_2)R (R = Me, OMe, *i*-Pr).

^{31}P NMR spectra of the complexes showed the presence of both isomers, but when the isomeric ratio is 1/1 the signals cannot be associated with those of the ^1H NMR spectra since the $^{31}P-^{13}C$ correlations have not been carried out.

The ^1H NMR spectra are more informative, with two sets of signals for each pair of *syn* and *anti* protons being observed for each pair of isomers of all compounds **5**. The assignations were carried out using the relative amounts of the major and minor isomer, coupling with ^{31}P in *trans* position, and NOESY measurements (Table 2). The diastereomeric nature of the methylene protons P-CH_2-Si in **5cz** (c = *o*-Ph_2, z = CH_2SiPh_3) is clearly defined. NOE contacts between *syn* allyl protons and the central methyl group and each pair of *syn* and *anti*

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Table 3. ^{13}C NMR ($CDCl_3$, 298 K, 100.6 MHz) Data[a] (δ in ppm) for Complexes [Pd(η^3-(2-Me-C_3H_4)ClP] (5)

complex	P-CH_n	C_{allyl}-Me	C1-tP	C3-cP	P−X−CH_3
5ax[b]					
major 1.1	13.30 (d, 27.0)	23.15	76.90[c] (d, 34.4)	58.65	
minor 1	13.85 (d, 27.0)	23.15	75.65[c] (d, 34.2)	59.15	
5ay					
isomer a 1	26.44 (d, 22.9)	23.01	78.58 (d, 31.5)	59.40	18.55, 20.70 (d, 8.5)
isomer b 1	25.75 (d, 23.0)	22.91	78.15 (d, 31.4)	60.45	18.70, 20.96 (d, 7.6)
5bx					
major 1.1	13.50 (d, 26.8)	23.00	76.60 (d, 33.0)	58.85	
minor 1	14.00 (d, 26.8)	23.12	76.80 (d, 35.5)	59.45	
5cx					
major 1.5	15.00 (d, 26.8)	23.47	76.15 (d, 34.5)	59.50	
minor 1	15.70 (d, 26.0)	23.56	76.70 (d, 34.5)	56.90	
5cy					
major 1.7	26.00 (d, 21.4)	23.22	77.95 (d, 32.3)	58.45	19.32, 20.58 (d, 6.8)
minor 1	26.85 (d, 21.4)	23.22	78.55 (d, 31.4)	58.59	19.00, 20.30 (d, 7.6)
5cz					
major 1.5	14.58 (d, 12.3)	23.07	~76.8 ov	58.30	
minor 1	13.18 (d, 10.7)	22.56	~77.2 ov	56.70	
5c′					
isomer a 1		23.44	79.85 (d, 36.0)	58.50	57.26
isomer b 1		23.44	79.30 (d, 36.0)	56.60	56.16

[a] Multiplicity (d, doublet; m, multiplet; ov, overlapped), coupling constants J_{PC} in Hz). [b] Measured at 50.3 MHz. [c]In acetone-d_6.

protons attached to one carbon allowed us to assign the complete set of signals. The phase-sensitive NOESY spectra at 298 K with a mixing time of 500 ms showed the well-known $\eta^3-\eta^1-\eta^3$ isomerization process. The exchange between *syn/anti* allyl methylene proton pairs was observed selectively with the pair *cis* to the phosphorus atom. The pair that is *trans* only exchange between *syn*−*syn* and *anti*−*anti* protons, in accordance with a selective opening of the allyl ligand *trans* to the phosphorus atom as observed in analogous compounds.[30c,31] Less important cross-peaks that could be assigned to the whole apparent allyl rotation were also observed. Thus, for instance, the pair *syn*−*anti trans* to phosphorus of one isomer exchanges with the same pair *trans* to the chloride ligand of the other isomer. The signals of the alkyl groups of the phosphine and the methyl group of the allyl group showed the exchange between both isomers.

^{13}C chemicals shifts for allylic carbons showed that the carbon atom located in *trans* position to phosphorus is more deshielded than the *cis* one, which usually coupled to the phosphorus atom as reported (Table 3).[32] The central atom resonates at a lower field than the terminal atoms but was not assigned. The methyl allyl group appears in nearly an almost identical position, showing a very small steric differentiation between the *R*- and *S*-Pd environment produced by the chiral phosphine.

Suitable monocrystals of **5cy** (c = *o*-Ph_2, y = *i*-Pr) and **5c′** (c = *o*-Ph_2, ′ = OMe) for X-ray diffraction measurements were obtained by slow diffusion of hexane over a dichloromethane solution of the complex. The molecular structure and selected bond lengths and angles are shown in Figure 3.

The selected crystals from which the structure determination has been carried out contain only one diastereomer, the configuration *S*-Pd *R*-P for the phosphine complex **5cy** (c = *o*-Ph_2, y = *i*-Pr) and the inverse, *R*-Pd *S*-P, for the phosphinite complex **5c′** (c = *o*-Ph_2, ′ = OMe). In both structures, the palladium atom showed a distorted square-planar coordination. Bond distances and angles are similar to those reported for related allyl compounds, and the longer Pd−C length *trans* to the phosphorus atom is in agreement with the stronger *trans* influence of the phosphorus ligand relative to the chloro ligand. The difference of the C−C distances in the allyl moiety is more pronounced, showing greater double-bond character in the *trans* position to the phosphorus atom in both complexes, although this difference could be reversed on changing from *S*-Pd to *R*-Pd isomers as reported.[15b,33] However, the difference between the phosphine and the phosphinite complexes is rather small and similar to crystal structures of analogous phosphinite[6b] or phosphine complexes.[34]

More interestingly, the *o*-biphenylyl arm in **5c′** is directed toward the allyl group, but the substituents at the phosphorus atom are not large enough to favor clearly this type of disposition that can be seen in **5cy**. Therefore, in **5c′** the allyl ligand is pushed out of the plane defined by the Pd−Cl−P atoms (C2 at 0.611 Å in **5c′** and 0.401 Å in **5cy** from the plane).

Although complexes containing a terminally monophenyl-substituted allyl can give rise to several isomers depending on the position occupied by the allyl phenyl group (*syn*/*syn, syn*/*anti*), NMR spectroscopy (I to IV in Scheme 3) reveals that complexes **6** appear as a mixture of four *syn*/*syn* isomers, and those with the phosphine and the phenyl allyl arm in opposite positions are the most favorable. In this type of allyl complex it is necessary to define the relative position of the asymmetric allyl substituent with respect to the two opposing and different ligands, the *syn*−*anti* allyl geometry of the allyl fragment and the inherent stereogenicity of the [M(allyl)AB] complex. Here, the *E*,*Z*

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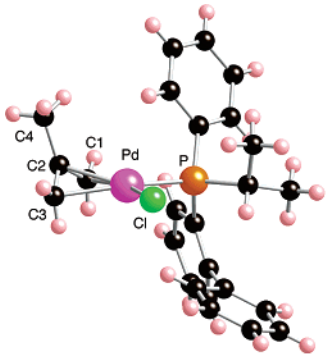

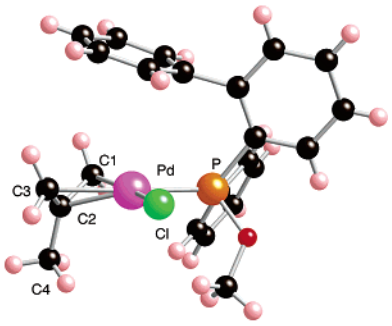

Compound **5cy** (c = *o*-Ph_2, y = *i*-Pr) isomer *S*-Pd		Compound **5c'** (c = *o*-Ph_2, ' = OMe) isomer *R*-Pd	
Pd-C1	2.098(3)	Pd-C1	2.103(6)
Pd-C2	2.188(3)	Pd-C2	2.157(5)
Pd-C3	2.201(3)	Pd-C3	2.186(5)
Pd-P	2.3047(7)	Pd-P	2.2705(13)
Pd-Cl	2.3707(7)	Pd-Cl	2.3730(15)
C2-C3	1.385(4)	C2-C3	1.382(8)
C1-C2	1.408(5)	C1-C2	1.406(8)
C2-C4	1.506(5)	C2-C4	1.499(9)
α	119.6°	α	112.8°
τ	3.24°	τ	3.05°

Figure 3. Molecular structures of complexes **5cy** and **5c'** and selected bond distances (Å) and structural parameters α (angle between planes C1C2C3 and PdClP) and τ (dihedral angle PClC3C1).[66]

Table 4. ^{31}P and Selected ^{1}H NMR Data[a] for Complexes [Pd(η^3-(1-Ph-C_3H_4)ClP] (6)

complex	^{31}P δ	H-central	*anti*-tP	*syn*-cP	*anti*-cP	P-CH_n	P-X-CH_3
6ay (273 K)							
major 1 (50%) 93%	35.52	5.47 (ddd, 12.0, 12.0, 7.0)	4.87 (dd, 13.0, J_{PH} = 10.0)	2.83 (d, 6.0)	2.34 (d, 12.0)	2.37 (m)	1.08, 0.99 (dd, 7.0, 20.0)
major 2 (43%)	36.42	5.34 (ddd, 12.0, 12.0, 7.0)	4.91 (dd, 13.0, J_{PH} = 10.0)	2.86 (d, 6.0)	2.42 (d, 12.0)	2.77 (m)	1.17, 0.95 (dd, 7.0, 20.0)
minor 1 (5%) **7**%	30.36						
minor 2 (2%)	28.94						
6cy (273 K)							
major 1 (43%) 82%	27.9	5.75 (m)	5.11 (dd, 10.2, J_{PH} = 13.2)	2.50 (d, 6.0)	2.65 (d, 12.0)	3.14 (m)	1.15, 1.44 (dd, 6.5, 19.8)
major 2 (39%)	27.6	5.75 (m)	5.19 (dd, 10.2, J_{PH} = 13.2)	2.81 (d, 6.0)	2.27 (d, 12.0)	3.08 (m)	1.08, 1.35 (dd, 6.5, 19.8)
minor 1 (12%) 18%	32.4						
minor 2 (6%)	29.8						
6cz (293 K)							
major 1 (75%) 100%	14.76	4.96 (ddd, 12.8, 12.0, 5.0)	4.18 (dd, 11.0, J_{PH} = 12.4)	2.48 (d, 6.8)	1.61 (d, 11.6)	3.42, 2.56 (pt, 12.0) (dd, 23.2, 16.8)	
major 2 (25%)	15.14	4.90 (m, ov)	4.62 (pt, 10.8)	2.76 (dd, 6.8)	~1.55 (ov)	2.92, ~1.55 (pt, ov, 12.4)	
6ax (273 K)							
major 1 (41%) 75%	8.90	5.78 (m)	5.23 (pt, 10)	2.69 (d, 8.5)	2.69 (d, 8.5)	2.19 (d, 8.5)	
major 2 (34%)	9.30	5.89 (ddd, 12.5, 12.0, 7.0)	5.21 (*pt*, 10.0)	2.94 (dd, 7.0, 1.5)	2.50 (d, 12.0)	2.26 (d, 8.5)	

		H-central	*syn*-tP	*anti*-tP	*anti*-cP	P-CH_n
minor 1 (13%) 25%	4.75	5.80 (m)	4.75 (pt, 10.0)	3.82 (d, 10.0)	4.05 (d, 11.5)	2.04 (d, 8.5)
minor 2 (12%)	4.60	5.95 (m)	4.73 (pt, 10.0)	3.79 (d, 10.0)	3.99 (d, 11.5)	1.72 (d, 8.5)

[a] δ in ppm, $CDCl_3$; multiplicity (d, doublet; t, triplet; m, multiplet; p pseudo; ov, overlapped), coupling constants (in Hz), J_{PH} and J_{HH}. ^{1}H measured at 400.0 or 500.0 MHz, ^{31}P measured at 101.2 MHz.

convention, the *syn*−*anti* description, and the *R*−*S* convention used recently by Faller[35] enable each isomer to be described. Unfortunately, it was not possible to obtain any crystals of sufficient quality to perform X-ray diffraction measurements. Isomers III and IV were not detected with the phosphine containing the $SiPh_3$ group, and only compound **6ax** (a = Naph, x = Me) displayed four sets of clear signals that could be assigned to the four isomers described in Scheme 3. The combined use of two-dimensional COSY and NOESY (τ_{mix} = 500 ms, 273 K) experiments enabled the relevant proton signals to be assigned and the dynamic behavior to be investigated (Table 4). By way of an example, the pattern of NOE contacts and exchange processes observed are displayed in Figure 4. Isomers I and II exchange by the $\eta^3-\eta^1-\eta^3$ mechanism, which is consistent with the interconversion between protons $H_{a'}$ and the pair H_s and H_a. This exchange was not detected between isomers III and IV. The conversion between major and minor isomers occurs in pairs, I with III and II with IV. The mechanism is a pseudorotation according to the interconversions observed between the same type of protons.

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Table 5. Hydrovinylation of Styrene Catalyzed by [PdL(allyl)(PPhRR′)]BF_4 Precursors[a]

PPhRR′	conversion %	codimers %	selectivity toward 3-Ph-1-butene	TOF h^{-1}	ee %	isomer ratio **5**	isomer ratio **6**[b]
Ph_2, *i*-Pr	16.1	16.0	98.9	160	40 (*S*)	63/37	43/39
Ph_2, *i*-Pr[c]	59.0	58.8	96.2	120	40 (*S*)	63/37	43/39
Ph_2, *i*-Pr[d]	98.8	98.6	70.6	125	40 (*S*)	63/37	43/39
Ph_2, Me	10.5	10.0	97.2	100	23 (*S*)	60/40	
Ph_2, $SiPh_3$	8.0	7.8	98.6	77	38 (*S*)	60/40	75/25
Ph_2, OMe	18.1	17.7	95.9	178	12 (*R*)	50/50	
Naph, *i*-Pr[e]	99.9	93.0	10.2	>2800		50/50	50/43
Naph, *i*-Pr[e,f]	94.0	92.0	80.5	2780	22 (*S*)	50/50	50/43
Naph, Me	28.5	24.0	96.3	240	~0 (−)	53/47	41/34
Phen, Me	25.0	22.5	94.4	225	20 (*S*)	53/47	
Bn, Mes[15b]	64.0		92.5	625	40 (*S*)		
Bn, Cy[15a]	61.5	56.0	98.0	1290	60 (*S*)		
Menth, *t*-Bu[6]	95.0				86 (*S*)		

[a] Reaction carried out at 25 °C, and 15 bar of initial pressure of ethylene, 1 h, in 10 mL of CH_2Cl_2; ratio styrene/Pd 1000/1; TOF/h calculated as the total amount of phenylbutenes formed. Conversion: conversion of starting styrene. Codimer: total amount of codimers. Selectivity: % of 3-phenyl-1-butene with respect to the codimers. [b]Only relative amounts of the more stable *Z*-isomers are represented. [c]5 h. [d]8 h. [e]20 min. [f]15 °C.

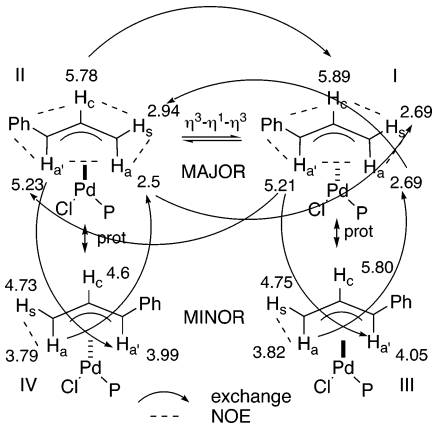


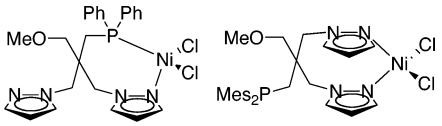
Figure 4. NOE contacts and exchange peaks observed for 6ax (a = Naph, x = Me).

The pattern showed that the accessibility of the $\eta^3-\eta^1-\eta^3$ mechanism is limited to the opening of the allyl carbon bond *trans* to the phosphorus atom when it contains the phenyl substituent. This path is less favorable for the minor isomers because the rotation on the η^1-carbon *cis* to the phosphine requires the displacement of the phenyl ring, giving the *anti* isomer.

Hydrovinylation Reactions. Hydrovinylation Results. [PdL(η^3-2-Me-C_3H_4)(PPhRR′)]BF_4 precursors were prepared in situ from compounds **5** and $AgBF_4$ in CH_2Cl_2 solution, where L may be solvent or styrene. The solution was introduced immediately into the reactor and was pressurized with ethylene. The results obtained as a mean value of at least three runs are shown in Table 5. Good reproducibility and excellent selectivity toward codimers at low conversions were obtained, in accordance with previous research.[15] Only with the precursor containing the phosphine **4ay** (a = Naph, y = *i*-Pr) did a very fast reaction occur, thus preventing direct comparison of the activity with the other precursors. Despite the slightly faster reactions with the similar naphthyl or phenanthryl phosphines, this huge difference cannot be discussed without further structural data. Thus, the activity observed is difficult to relate to a single steric parameter.

Some features may, however, to be highlighted. For example, under ethylene pressure dimerization of styrene is negligible and palladium black appears only after total conversion of styrene. Very small amounts

Chart 1



of 2-phenyl-2-butene isomers were formed at about 20% conversion of ethylene, suitable conditions to compare the discrimination ability of the phosphines avoiding kinetic resolution in the consecutive isomerization reaction.[36] However, the hydrovinylation was followed at higher conversions with precursor **5cy** (c = *o*-Ph_2, y = *i*-Pr) to check the efficiency of this type of catalyst. The catalytic system remains similarly selective toward *S*-3-Ph-1-butene at high conversion (run at 5 h). At almost total conversion (run at 8 h) the codimers are present in a relative composition of A/B/C = 70.5/23.8/4.2% (eq 1), similar to other systems,[6] and the ee drops by about 5%, showing the inverse effect to that already reported.[36] The catalytic system remains stable since similar TOF values were obtained until almost total conversion.

The subtle difference in coordinating ability between styrene and 3-Ph-1-butene could be varied by changing the phosphine substituents, as shown in Table 5. The better selectivity of the codimer toward 3-Ph-1-butene may be associated with the increased steric hindrance of the phosphine.

Examples reported in the literature show that when nickel complexes, containing not very labile bidentate ligands (Chart 1), were activated with MAO and used as precursors in the hydrovinylation reaction, the isomers of 3-phenyl-1-butene or styrene dimers were not obtained; however, at complete conversion of styrene, around 70% of trimers and tetramers were obtained. This ilustrates that with these ligands a second insertion of ethylene competes well with the β-elimination after formation of the heterodimer.[37]

The ee's obtained here are moderate, showing a range of enantioselectivities from 10% to 40% ee that can be related to pure steric discrimination since secondary

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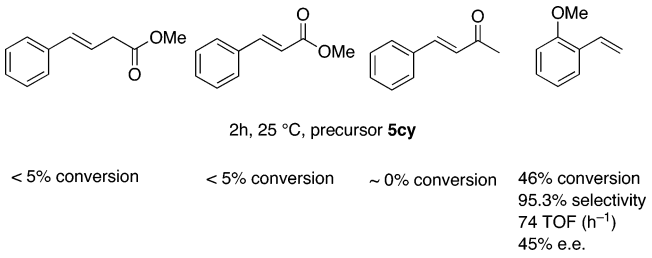
Scheme 4



interactions are not expected with this type of phosphine substituent.[38]

The *ortho*-biphenylyl phosphines are slightly better than the naphthyl and phenanthryl analogues. The increased steric hindrance of the alkyl groups attached to the phosphorus atom also induced greater discriminative power in the phosphine. Major discriminative power could be expected for biphenylyl-containing phosphines, but crystal structures of the allyl precursors showed that the differences in size of the different substituents, methyl or isopropyl groups, are not enough to direct the biphenylyl arm toward the metal center; thus, the environments generated by this group of phosphines are similar.

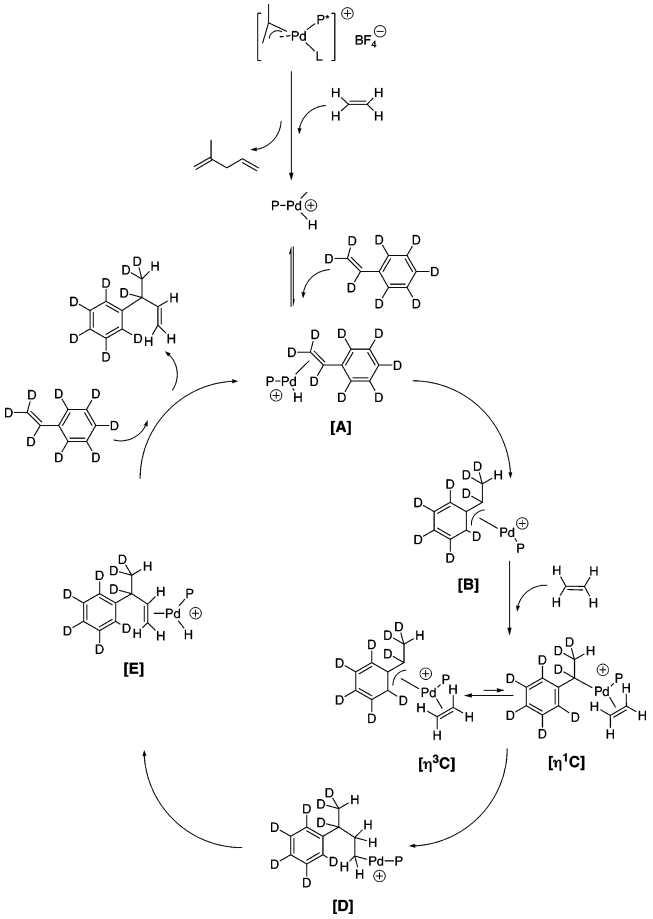
Although the relative amounts of epimers in the substituted **6** allyl precursors provide accurate information about the discriminative power of the palladium-phosphine unit, the discrimination ability of the phosphine ligands in the hydrovinylation of styrene cannot be deduced from the isomer ratio of the palladium complexes. Neither is it possible to obtain a reasonable precise match with the ee's of the reaction from the compounds **5**, whose allyl moiety is small and too symmetric to be an effective reporter group, nor from the isomers of compounds **6**. When the substrate used contains a second potentially coordinating atom, the hydrovinylation reactions were observed to some extent only with the aryl-substituted styrene. The results shown in Scheme 4 do not suggest any important secondary coordination of the substrate that could improve the ee.

The Mechanism. Nickel and palladium compounds are usually used as catalysts in the hydrovinylation of styrene.

Nonlabile bidentate ligands are known to inhibit the reaction, so only monodentate or hemilabile ligands are used to stabilize the catalytic system. Consequently, allyl palladium complexes [Pd(Allyl)ClP] containing one monodentate ligand are convenient reaction precursors. The transition to the active hydride species involves two steps, initial generation of the cationic species using silver salts or NaBARF-type halide abstractors, followed by the insertion and β-elimination of either ethylene or styrene in the sigma form of the allyl ligand, giving the active hydride intermediate (Scheme 5).

The cationic precursors [Pd(Allyl)PP]BF_4, where PP is a bidentate phosphine or two monodentate phosphines,[39] were recovered unaltered after treatment with ethylene under the same catalytic conditions. However,

Scheme 5



[PdR(CH_3CN)P_2]BF_4 precursors are readily activated in the presence of ethylene. Consequently, it seems that ethylene is unable by itself to substitute certain phosphines or induce the $\eta^3-\eta^1$ shift on the allyl moiety.

Two reactions were carried out with deuterated styrene under standard conditions using the [PdCl(2-MeC_3H_4)PPh(*o*-Ph_2)(*i*-Pr)] (**5cy**) complex as the precursor, the first at low conversion, and the second at total conversion to study the isomerization of 3-Ph-1-butene. At low conversion the partially deuterated 3-phenyl-1-butene obtained showed an extremely clean C−H addition of the ethylene (Scheme 5). The proton NMR spectra obtained after standard workup and evaporation of the solvent confirmed the expected isotopomer. Mass spectroscopy confirmed the isotopic pattern without any H−D scrambling due to an equilibrium of insertion−β-elimination between species [**A**] and [**B**]. Accordingly, the insertion reaction of styrene is not reversible under the reaction conditions.

Isomerization of 3-phenyl-1-butene takes place at total conversion. The proton NMR spectrum of the crude product mainly showed the isomer *E*-2-Ph-2-butene [**F**] partially deuterated (Scheme 6). After initiation (reaction a of Scheme 6), the isomerization process must exclusively transfer the deuterium located in carbon 3 to carbon 1 in the 3-Ph-1-butene (reaction b of Scheme 6). However, the isotopomer obtained showed the transfer of hydrogen alone. Thus, it must be assumed that the scrambling of hydrogen between the palladium hydride and the free ethylene is very fast compared with the isomerization process (reaction c of Scheme 6), since

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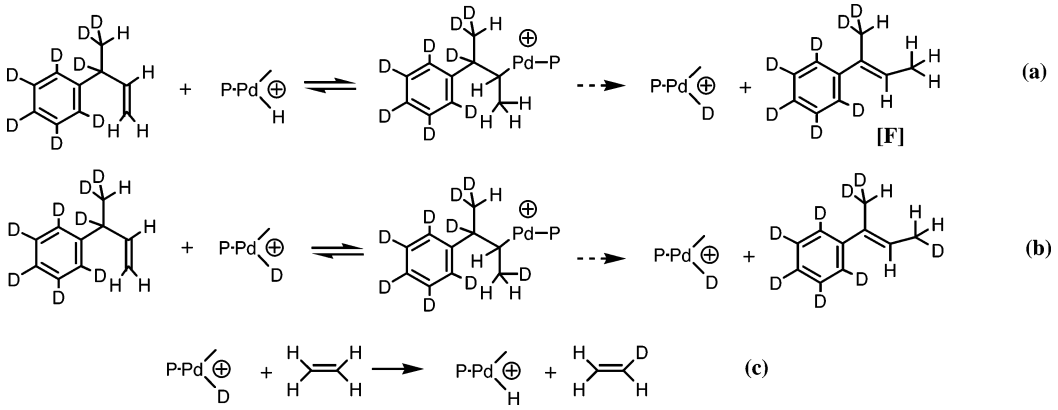
(39) Ceder, R. M.; García, C.; Muller, G.; Rocamora, M. Manuscript in preparation.

Scheme 6



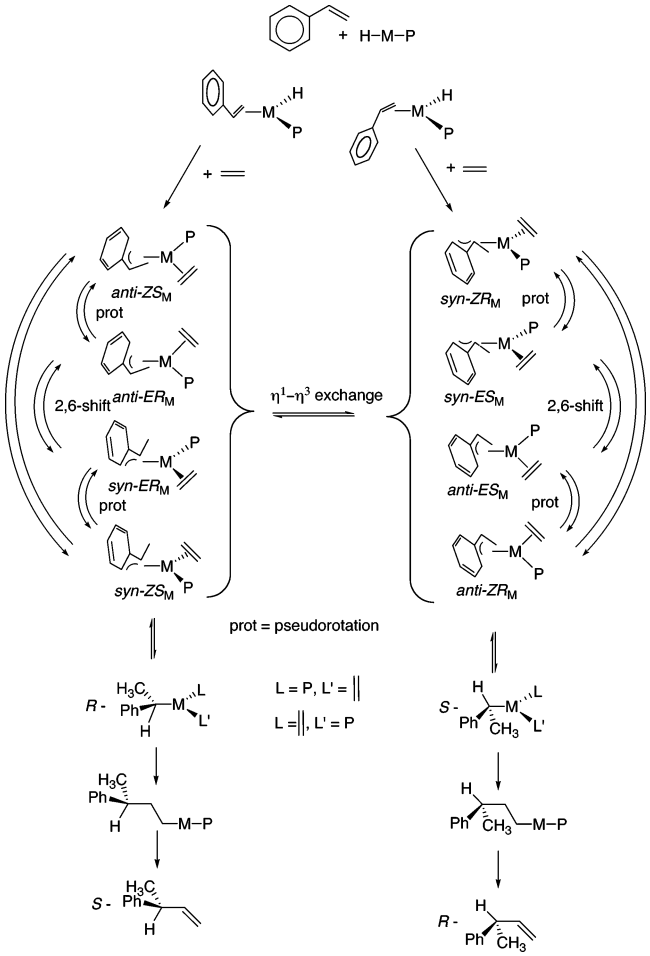
[**F**] is the only derivative detected. This fact has already been stated by Ozaki et al.,[40] who observed fast interchange of deuterium between mixtures of ethylene and deuterated ethylene using nickel precursors. The complementary results of the hydrovinylation reaction using deuterated ethylene could be rationalized in the same way.[41]

The presence of neutral or anionic species in the reaction medium can compete with ethylene[4c,10b] for the open coordination position. This kind of competition alters either the activity of the reaction or the selectivity between codimers. In this study the counterion was always BF_4^-, so this effect was not investigated. Therefore, in this case the nature of the anchored phosphine is the primary element that modifies the pattern of the free coordination position at the palladium center.

The enantioselectivity depends only on the discrimination ability between the stereoheterotopic faces of the olefin generated by the chiral phosphine if the subsequent ethylene insertion is faster than the reequilibration of the benzylic intermediate. The formally enantioselective step of the proposed mechanism, from [**A**] to [**B**], is nonreversible under the reaction conditions, so what needs to be clarified is the configuration stability of the benzylic complex [η^3**C**] responsible for the excellent regioselectivity of the reaction. This control must be complex in a system containing only one monodentate phosphine, so hemilabile ligands may play an important role in this reaction, as reported.[4]

All the experimental data suggest that the intermediate responsible for the enantioselectivity contains an η^3-benzylic group, one monodentate phosphine, and ethylene ([**C**] of Scheme 5), so Scheme 7 enables discussion of the process. The complex dynamics of these particular allyl complexes includes the well-known $\eta^3-\eta^1$ exchange and the pseudorotation of the allyl ligand, as well as a 2,6-suprafacial allyl shift, which is likely to be relatively faster.[42] The 2,6-shift can be considered as a natural alternative available for the σ-intermediate of the $\eta^3-\eta^1$ exchange accessible by the benzylic system. However, analysis of the different exchange between isomers showed that only the standard $\eta^3-\eta^1$ mechanism can modify the geometry of the final 3-Ph-1-butene product.

Scheme 7



The direct insertion of ethylene into the allyl moiety has been proposed by computational studies[43] in palladium allyl complexes containing one monodentate phosphine and ethylene, and in this case the insertion process would take place from the *Z*-isomers.

It remains unclear which benzylic disposition is the most stable, the methyl fragment in *syn* or *anti* position. The determined crystal structures containing similar allylic moieties in palladium compounds gave a *syn* disposition in tol-BINAP[44] or 2,2′-bipyridyl[45] stabilized

(40) Maruyama K.; Kuroki T.; Mizoroki T.; Ozaki A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2002.

(41) Kawakami, K.; Kawata, N.; Maruya, K.; Mizoroki, T.; Ozaki, A. *J. Catal.* **1975**, *39*, 134.

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(43) Cárdenas, D. J.; Alcamí, M.; Cossió, F.; Méndez, M.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 96.

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complexes and an *anti* disposition in a methylstyrene moiety stabilized by 1,10-phenanthroline.[46] Analogous platinum diphosphine species stabilized the benzyl ligand in *anti* conformation.[47]

Furthermore, the anti conformation is proposed as the most probable isomer following careful NMR analysis of a series of palladium and platinum η^3-methylbenzyl diphosphine complexes.[48] The isomers of type *E* with the bulkier phosphine and the phenyl ring in opposing positions are expected to be preferred.

Conclusions

A group of allyl [PdCl(allyl)P*] complexes (allyl = 2-CH_3-C_3H_4 (**5**) and 1-C_6H_5-C_3H_4 (**6**)) containing *P*-stereogenic phosphines has been obtained. The discrimination power of the phosphines was reflected in the relative amounts of diastereoisomers present in solution. The cationic derivatives $[PdS(2\text{-}CH_3\text{-}C_3H_4)P^*]^+$ were used as catalyst precursors in the hydrovinylation of styrene. However, the enantiomeric excess observed in the reactions were different compared to the isomeric proportions observed in the solutions of complexes **5** and **6**. The control of the enantioselectivity in the hydrovinylation reaction of vinylarenes seems to be done in benzylic intermediates, a particular type of allylic intermediates. Reactions carried out using deuterated styrene showed that the formation of the benzylic species by insertion of styrene is not reversible under the reaction conditions ([**B**] in Scheme 5). The dynamics of the benzylic intermediates is complex but only the $\eta^3-\eta^1-\eta^3$ exchange is able to modify the isomer ratio of the reaction products.

Consequently, it seems that in order to confirm the origin of the enantioselectivity in the hydrovinylation reaction, it is necessary to conduct further studies of η^3-methylbenzyl complexes in an asymmetric environment. The goal would be to ensure that the ethylene insertion reaction is faster than the $\eta^3-\eta^1-\eta^3$ exchange, to control the enantioselectivity just at the coordination of the olefin ([**A**] in Scheme 5). Here, the presence of an efficient hemilabile ligand could be the determining factor.[4,49]

Experimental Section

General Data. All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen. $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$[50] and $[Pd(\eta^3\text{-}1\text{-}Ph\text{-}C_3H_4)(\mu\text{-}Cl)]_2$[51] were prepared as previously described. The routine ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on either a Varian XL-500 or Mer-400 MHz (^1H, standard $SiMe_4$), Varian Gemini (^{13}C, 50.3 MHz, standard $SiMe_4$), and Bruker DRX-250 (^{31}P, 101.2 MHz) spectrometers in $CDCl_3$ unless otherwise specified. Chemical shifts were reported downfield from standards. The two-dimensional experiments were generally carried out with a Bruker DMX-500 or a Varian XL-500 instrument. IR spectra were recorded on the following spectrometers: FT-IR Nicolet 520, FT-IR Nicolet Impact 400, FT-IR Avatar 330, and FT-IR Nicolet 5700. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. 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 a FID detector. The GC/MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (50-m Ultra 2 capillary column) interfaced to a Hewlett-Packard 5971 mass selective 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/^{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 a FID detector. Elemental analyses were carried out by the Serveis Cientificotècnics of the Universitat Rovira i Virgili in an Eager 1108 microanalyzer.

Detailed synthetic procedures and characterization data of the *P*-stereogenic phosphines are collected in the Supporting Information. Only PPh(1-Naph)Me (**4ax**) has been obtained by the method of Jugé,[28a] but the phosphinites (*R*)-methoxy-(9-phenanthryl)phenylphosphine-P-borane(1/1) (**2b**), and (*R*)-(2-biphenylyl)methoxyphenylphosphine-P-borane(1/1) (**2c**) are already known.

Synthesis. Chloro(η^3-2-methylallyl)[(*R*)-methyl(1-naphthyl)phenylphosphine]palladium(II), 5ax. The phosphine **4ax** (0.501 g, 2.0 mmol) was dissolved in 20 mL of dichloromethane, and $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ (0.394 g, 1.0 mmol) was added in one portion. The yellow solution was stirred for 1 h. The dichloromethane was then removed, and the addition of ether (10 mL) caused the precipitation of the **5ax** complex as a pale yellow solid. This solid was filtrated and washed with ether and pentane. Yield: 0.800 g (90%). Anal. Calcd for $C_{21}ClH_{22}PPd$: C 56.40, H 4.96. Found: C 56.20, H 5.24. IR $\bar{\nu}$ (cm^{-1}): 3055 ν(C−H), 2977 ν(C−H), 2958 ν(C−H), 2914 ν(C−H), 1386, 1099, 900, 883, 801, 779, 725, 693, 456.

Chloro[(*R*)-isopropyl(1-naphthyl)phenylphosphine]-(η^3-2-methylallyl)palladium(II), 5ay. This complex was prepared with the same method used for **5ax**. From **4ay** (0.100 g, 0.36 mmol) and the dimer $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ (0.07 g, 0.18 mmol) a pale yellow solid was obtained. Yield: 0.100 g (60%). Anal. Calcd for $C_{23}ClH_{26}PPd$: C 58.12, H 5.51. Found: C 58.09, H 5.71. IR $\bar{\nu}$ (cm^{-1}): 3052 ν(C−H), 2955 ν(C−H), 2926 ν(C−H), 2908 ν(C−H), 2854 ν(C−H), 1504, 1435, 1381, 1031, 798, 776, 754, 703, 697, 634, 520, 479.

Chloro[(*R*)-(2-biphenylyl)methylphenylphosphine](η^3-2-methylallyl)palladium(II), 5cx. The procedure used was the same as for **5ax**. Starting from the phosphine **4cx** (0.379 g, 1.37 mmol) and the palladium dimer $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ (0.237 g, 0.60 mmol) a pale yellow solid was obtained. Yield: 0.270 g (48%). Anal. Calcd for $C_{23}ClH_{24}PPd$: C 58.37, H 5.11. Found: C 58.27, H 5.46. IR $\bar{\nu}$ (cm^{-1}): 3061 ν(C−H), 3042 ν(C−H), 2987 ν(C−H), 2959 ν(C−H), 1438, 891, 884, 751, 734, 699, 508.

Chloro[(*R*)-(2-biphenylyl)isopropylphenylphosphine]-(η^3-2-methylallyl)palladium(II), 5cy. This compound was prepared following the procedure used to obtain **5ax**. Starting from **4cy** (0.304 g, 1.0 mmol) and $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(\mu\text{-}Cl)]_2$ (0.197 g, 0.5 mmol) a pale yellow solid was obtained. Yield: 0.350 g (70%). Anal. Calcd for $C_{25}ClH_{28}PPd$: C 59.90, H 5.63. Found: C 59.42, H 5.84. IR $\bar{\nu}$ (cm^{-1}): 3049 ν(C−H), 2970 ν(C−H), 2925 ν(C−H), 2864 ν(C−H), 1463, 1436, 1380, 1097, 1043, 786, 765, 753, 701, 676, 631, 524, 462.

X-ray Diffraction. Yellow crystals were grown, at 4 °C, by slow diffusion of hexane over a solution of the complex in dichloromethane.

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(47) Crascall, L. E.; Litster, S. A.; Redhouse, A. D.; Spencer, J. L. *J. Organomet. Chem.* **1990**, *394*, C35.
(48) Crascall, L. E.; Spencer, J. L. *Dalton Trans.* **1992**, 3445.
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(50) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

Chloro(η^3-2-methylallyl)[(*R*)-methyl(9-phenanthryl)-phenylphosphine]palladium(II), 5bx. The procedure used was the same as for **5ax**. Starting from the phosphine **4bx** (0.400 g, 1.33 mmol) and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.210 g, 0.53 mmol) a pale yellow solid was obtained. Yield: 0.305 g (58%). Anal. Calcd for $C_{25}ClH_{24}PPd$: C 60.38, H 4.86. Found: C 60.10, H 5.22. IR $\bar{\nu}$ (cm^{-1}): 3065 ν(C−H), 3046 ν(C−H), 3023 ν(C−H), 1489, 1436, 1427, 1108, 793, 748, 726, 711, 700, 642.

Chloro[(*R*)-(2-biphenylyl)phenyl(2,2,2-triphenyl-2-silaethyl)phosphine](η^3-2-methylallyl), 5cz. The phosphine **4cz** (0.107 g, 0.2 mmol) was dissolved in 10 mL of dichloromethane, and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.039 g, 0.1 mmol) was added. After 1 h of stirring the solvent was removed and the pasty solid obtained was washed and stirred several times with pentane until the yellow solid **5cz** was obtained after filtration. Yield: 0.110 g (75%). Anal. Calcd for $C_{41}ClH_{38}PPdSi$: C 67.31, H 5.23. Found: C 67.72, H 5.54. IR $\bar{\nu}$ (cm^{-1}): 3046 ν(C−H), 3018 ν(C−H), 2957 ν(C−H), 2922 ν(C−H), 1427, 1108, 726, 711, 698, 515.

Chloro[(*S*)-(2-biphenylyl)methoxyphenylphosphine]-(η^3-2-methylallyl)palladium(II), 5c′. This complex was prepared with the same method used for **5ax**. Starting from **2c′** (0.333 g, 1.14 mmol) and the palladium dimer [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.195 g, 0.49 mmol), the product was obtained as a very pale yellow solid. Yield: 0.323 g (67%). Anal. Calcd for $C_{23}ClH_{24}OPPd$: C 56.46, H 4.94. Found: C 56.49, H 5.35. IR $\bar{\nu}$ (cm^{-1}): 3052 ν(C−H), 2971 ν(C−H), 2926 ν(C−H), 2835 ν(C−H), 1433, 1099, 1034, 776, 737, 704.

X-ray Diffraction. Yellow crystals were grown, at 4 °C, by slow diffusion of hexane over a solution of the complex in dichloromethane.

Chloro[(*R*)-methyl(1-naphthyl)phenylphosphine](η^3-1-phenylallyl)palladium(II), 6ax. The procedure was the same as that used to prepare the complex **5cz**. From the phosphine **4ax** (0.525 g, 2.1 mmol) and the dimer [Pd(η^3-1-Ph-C_3H_4)(μ-Cl)]$_2$ (0.518 g, 1.0 mmol) the title product was obtained as a bright yellow solid. Yield: 0.605 g (60%). Anal. Calcd for $C_{26}ClH_{24}PPd$: C 61.32, H 4.75. Found: C 61.63, H 5.20. IR $\bar{\nu}$ (cm^{-1}): 3050 ν(C−H), 2969 ν(C−H), 2917 ν(C−H), 2852 ν(C−H), 1505, 1488, 1435 1385, 1101, 892, 800, 775, 751, 691, 522, 453. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 11.5 (CH_3), 14.7 (CH_3), 15.5 (CH_3), 53.6 (CH), 55.2 (CH), 55.4 (CH), 98.0 (CH), 99.1 (CH) 111.2 (CH), 111.4 (CH), 114.6 (CH), 124.8−136.8 (m, C, CH).

Chloro[(*R*)-isopropyl(1-naphthyl)phenylphosphine]-(η^3-1-phenylallyl)palladium(II), 6ay. This complex was obtained in the same way as **5cz**. Using the phosphine **4ay** (0.165 g, 0.59 mmol) and the dimer [Pd(η^3-1-Ph-C_3H_4)(μ-Cl)]$_2$ (0.154 g, 0.29 mmol) a bright yellow solid was obtained. Yield: 0.239 g (75%). Anal. Calcd for $C_{28}ClH_{28}PPd$: C 62.59, H 5.25. Found: C 61.83, H 5.42. IR $\bar{\nu}$ (cm^{-1}): 3050 ν(C−H), 2959 ν(C−H), 2926 ν(C−H), 2866 ν(C−H), 1504, 1435, 1386, 1097, 1029, 800, 776, 751, 699, 522, 480. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 18.6 (CH_3), 18.7 (CH_3), 20.5 (CH_3), 20.9 (CH_3), 26.7 (s, CH), 27.0 (s, CH), 55.3 (s, CH_2), 56.8 (s, CH_2), 99.6 (d, CH, J_{CP} = 27.6 Hz), 100.4 (d, CH, J_{CP} = 27.6 Hz), 124.9−136.7 (m, C, CH).

Chloro[(*R*)-(2-biphenylyl)isopropylphenylphosphine]-(η^3-1-phenylallyl)palladium(II), 6cy. This complex was obtained using the same procedure as for **5cz**. Starting from the phosphine **4cy** (0.205 g, 0.67 mmol) and the palladium dimer [Pd(η^3-1-Ph-C_3H_4)(μ-Cl)]$_2$ (0.163 g, 0.32 mmol), a bright yellow solid was obtained. Yield: 0.320 g (51%). Anal. Calcd for $C_{30}ClH_{30}PPd$: C 63.96, H 5.37. Found: C 63.72, H 5.83. IR $\bar{\nu}$ (cm^{-1}): 3051 ν (C−H), 2964 ν(C−H), 2960 ν(C−H), 2928 ν(C−H), 2924 ν(C−H), 2908 ν(C−H), 1434, 761, 695, 522, 513, 495. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm): 18.6 (s, CH_3), 18.7 (s, CH_3), 20.5 (s, CH_3), 20.9 (s, CH_3), 26.7 (s, CH), 27.0 (s, CH), 55.3 (s, CH_2), 56.8 (s, CH_2), 99.6 (d, CH, J_{CP} = 27.6 Hz), 100.4 (d, CH, J_{CP} = 27.6 Hz), 124.9−136.7 (m, C, CH, Ar).

Chloro[(*R*)-(2-biphenylyl)phenyl(2,2,2-triphenyl-2-silaethyl)phosphine](η^3-phenylallyl)palladium(II), 6cz. This complex was obtained through the same procedure as for **5cz**. From the phosphine **4cz** (0.200 g, 0.37 mmol) and the palladium dimer [Pd(η^3-1-Ph-C_3H_4)(μ-Cl)]$_2$ (0.088 g, 0.17 mmol), a bright yellow solid was isolated. Yield: 0.151 g (56%). Anal. Calcd for $C_{46}ClH_{40}PPdSi$: C 69.61, H 5.08. Found: C 69.85, H 5.47. IR $\bar{\nu}$ (cm^{-1}): 3065 ν(C−H), 3046 ν(C−H), 3023 ν(C−H), 1489, 1461, 1427, 1107, 793, 748, 727, 700, 492. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K), δ (ppm, major isomer): 15.9 (d, CH_2, J_{CP} = 12.2 Hz), 52.7 (s, CH_2), 97.7 (d, CH, J_{CP} = 29.7 Hz), 110.5 (d, CH, J_{CP} = 5.4 Hz), 127.2−146.4 (C, CH, Ar). δ (ppm, minor isomer): 13.9 (br, CH_2), 52.1 (s, CH_2), 98.9 (m, CH), 110.0−110.1 (m, CH), 127.2−146.4 (m, C, CH, Ar).

Structural Characterization. Suitable crystals of phosphine-borane adducts **3bx**, **3cy**, and **3d** and complexes **5c′** and **5cy** for X-ray characterization were mounted in a Bruker SMART CCD diffractometer. The data were collected using graphite-monochromated. Mo Kα radiation (λ = 0.71073 Å). SHELXTL software was used for solution and refinement.[52] Absortion corrections were made with the SADABS program.[53] The structures were refined by full-matrix least-squares on F^2.

Hydrovinylation Reactions. Hydrovinylation reactions were performed in a stainless steel autoclave fitted with an external jacket connected to an isobutanol bath, and the temperature was controlled using a thermostat to ±0.5 °C. Internal temperature and pressure were recorded as a function of time with a Linseis L-200 recorder.

A mixture of the suitable neutral palladium complex **5** (0.045 mmol), $AgBF_4$ (around 8.9 mg, 0.045 mmol), and styrene (4.7 g, 45 mmol) in 10 cm^3 of dry and freshly distilled CH_2Cl_2 was stirred for 5 min in the dark. After filtering off the AgCl formed, 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 in Table 4 for each reaction, the autoclave was slowly depressurized and NH_4Cl 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 were determined by GC analysis. Major components were characterized by ^1H NMR.

Characterization of Hydrovinylation Products. 3-Phenyl-1-butene. ^1H NMR (200.0 MHz, $CDCl_3$, 298 K): δ (ppm) 1.36 (d, J = 7.0 Hz, 3H), 3.47 (m, 1H), 5.03 (dd, J = 10.5 Hz, J = 1.4 Hz, 1H), 5.05 (dd, J = 17.0 Hz, J = 1.4 Hz, 1H), 6.01 (ddd, J = 17.0 Hz, J = 10.5 Hz, J = 6.8 Hz, 1H), 7.10−7.35 (m, 5H). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ (ppm) 20.7, 43.2, 113.1, 126.1, 127.2, 128.4, 143.2, 145.5.

(*E*)-2-Phenyl-2-butene. ^1H NMR (200.0 MHz, $CDCl_3$, 298 K): δ (ppm) 1.77 (d, J = 6.9 Hz, 3H), 2.01 (s, 3H), 5.85 (q, J = 6.9 Hz, 1H), 7.10−7.40 (m, 5H). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ (ppm) 14.3, 15.4, 122.4, 125.5, 126.4, 128.1, 135.5, 144.0.

The absolute configuration of the major enantiomer of 3-phenyl-1-butene was assigned by measuring the optical

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rotation of a reaction mixture and comparing the sign with the literature.[54]

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Supporting Information Available: Experimental details and characterization data for *P*-stereogenic phosphines, crystallographic data for palladium complexes **5cy** and **5c′**, ^{1}H and ^{13}C NMR spectra of the aromatic region of palladium complexes **5**, NMR spectra of partially deuterated 3-Ph-1-butene and 2-Ph-2-butene, and CIF files of phosphines **3bx**, **3cy**, and **3d** and complexes **5cy** and **5c′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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