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Modular Approach to New Chiral Monodentate Diamidophosphite Ligands. Application in Palladium-Catalyzed Asymmetric Hydrovinylation of Styrene

Isabel Ayora, Rosa M. Ceder, Mauricio Espinel, Guillermo Muller, Mercè Rocamora,* and Marta Serrano

Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain

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A new group of chiral monodentate diamidophosphite ligands (2 P−N/1 P−O bond) based on diazaphospholidine backbones derived from *N*,*N*′-dibenzylcyclohexane-1,2-diamine (**7**) and *N*, *N*′-dimethylcyclohexane-1,2-diamine (**8**), and diazaphosphepine backbones derived from *N*, *N*′-dimethyl-[1,1′-binaphthyl]-2,2′-diamine (**9**) and various chiral alkoxy groups (coming from phenylethanol **a**, borneol **b**, methyllactate **c**, allylic alcohol **d**, and methanol **e**) were prepared. The ligands have a highly modular structure, which is well suited to the synthesis of a small library. Preparation was readily accomplished by the successive addition of pure enantiomeric substituted diamine and pure enantiomeric alcohol to phosphorus trichloride. The corresponding diamidophosphite selenides **Se**(**7**−**9**) were prepared and the J_{PSe} was calculated in order to evaluate the σ-donor ability of the new ligands. The reaction of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}CH_3C_3H_4)]_2$ with the new diamidophosphite ligands (**7**−**9**) led to the monomeric allylic neutral complexes **11**−**13**. Two isomers appeared in solution due to the *R*- or *S*-geometry around the palladium atom. The molecular structure determined by X-ray diffraction of the neutral complex $[PdCl(\eta^3\text{-}2\text{-}CH_3C_3H_4)(\mathbf{7a})]$ (**11a**-(S,S,S_{al})) showed a nonsymmetric coordination of the allyl moiety due to the greater *trans* influence of the phosphorus atom. The asymmetric hydrovinylation reaction between styrene and ethylene was tested using filtered CH_2Cl_2 solutions of $[PdCl(\eta^3\text{-}2\text{-}CH_3C_3H_4)L]$ complexes and $AgBF_4$ as catalytic precursors. The reaction performed at 15 °C and 15 bar of ethylene starting pressure led to good selectivities and moderate to good activities of 3-phenyl-1-butene. The best results were obtained when the cationic catalytic precursor contained the **9b**-(R,S_{al}) diamidophosphite with a binaphthyl backbone and bornyloxy as the third substituent. With this system the TOF reached 595 h^{-1} of 3-phenyl-1-butene, whereas the ee was 90% toward the *R*-isomer.

Introduction

Transition-metal-catalyzed asymmetric transformations play an important role in the synthesis of organic molecules and in the industrial production of fine chemicals.[1] In general, a chiral ligand is used both to influence the reactivity of the metal and to direct the stereochemical course of the catalyzed reaction. Chiral phosphorus ligands are the most widely used and have played a major role since the pioneering work of Knowles,[2] Kagan,[3] and Noyori.[4] In particular, both monophosphane and diphosphane ligands have been synthesized, with the latter being the best represented and most successful of the ligands used in asymmetric catalysis.[5] In recent years, however, monophosphorus chiral ligands have received renewed interest, particularly those structures that possess one or more P−heteroatom bonds. The vast majority of them contain a cyclic structure in which the phosphorus atom is a component of the heterocyclic ring, and this feature is responsible for an increase in ligand stability. Particularly interesting are chiral phosphonites, phosphites, and phosphoramidites, all based on the BINOL backbone, and these have been successfully applied in several metal-catalyzed asymmetric transformations.[6−9]

*Corresponding author. E-mail: merce.rocamora@qi.ub.es.

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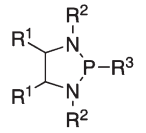
Less research has been reported on the synthesis and application of chiral diamidophosphite ligands with two P−N bonds and one P−O bond. It is presumed that these compounds have different properties from phosphoramidites or phosphites when applied as ligands in asymmetric catalysis. For example, nitrogen substituents create more steric bulk around the phosphorus than oxygen, since nitrogen substitution may be greater. Furthermore, diamidophosphites are assumed to have more electron-rich phosphorus than phosphoramidites or phosphites.

The synthesis and characterization of some diamidophosphites with different heterocyclic backbones have been reported by Pfaltz,[10] Tsarev,[11] Buono,[12] and Reetz[13] as well as some ligands that are structurally related, such as the diamidophosphines reported by Spilling,[14] Wills,[15] and Piarulli,[16] and the triamidophosphites reported by Piarulli[16] and Leitner.[17] All of these new ligands have been applied to different asymmetric processes, such as palladium-catalyzed allylic alkylation,[10−12,13b,14,15] rhodium hydroformylation and hydrogenation,[13] iridium hydrogenation,[10] and enantioselective copper-catalyzed conjugate addition of diethylzinc to cyclohexenone.[12,17] Alexakis[18] and co-workers developed the synthesis of diamidophosphites in order to determine the enantiomeric excess of chiral alcohols, amines, thiols, and carboxylic acids. Very few examples of the coordination chemistry of these kinds of ligands are reported in the literature; only Tsarev[11a] and Buono[12] synthesized allylic palladium complexes with diamidophosphite ligands, and Spilling[14] prepared some platinum coordination compounds with a diamidophosphine ligand.

Here, we report the synthesis and characterization of chiral diamidophosphite ligands of general formula **I** (Figure 1), with binaphthyl or cyclohexyl R^1 backbones and with various substituents R^2 and R^3, since they display several potential sites of diversity and their synthesis can be readily accomplished through two modular synthetic paths.



I

Figure 1. General structure of diamidophosphite ligands **I**.

These new modular chiral ligands **I** can be tested in several asymmetric catalytic processes, but their monodentate character prompted us to study their behavior in the asymmetric hydrovinylation of styrene, since this would serve as a prototypical test case. We carried out the preparation and characterization of the neutral allylic palladium(II) compounds to be used as catalytic precursors in the reaction.

The catalytic asymmetric hydrovinylation reaction is a heterodimerization between ethylene and an activated olefin, usually conjugated dienes (styrene and other vinylarenes) or strained olefins (norbornene), catalyzed by a transition metal complex.[19] The codimerization product contains a stereogenic carbon atom, so the reaction is amenable to enantiocontrol. The process is of much interest in enantioselective synthesis because it provides a short route to 2-arylpropionic acids, the most important family of nonsteroidal antiinflammatory drugs, including naproxen or ibuprofen.[20] More recently it has also been employed in the stereoselective construction of benzylic all-carbon quaternary stereocenters,[21] a structural motif present in pharmacologically important compounds, and in the short synthesis of natural products.[22] In spite of its enormous potential, hydrovinylation is still an underused reaction even in the synthesis of fine chemicals. This is due to the presence of some side reactions, dimerization and isomerization, which require a subtle fine-tuning of the catalyst to obtain good selectivity. This process is catalyzed by a variety of transition metal compounds, nickel and palladium being the most frequently used, and the catalytic cycle proposed for these metal systems shows that the active catalyst is most probably an unsaturated metal hydride stabilized by one monodentate phosphine.[19c,23a] It must be noted, however, that the presence of the nickel hydride intermediate has been recently questioned by a theoretical study of RajanBabu and co-workers,[23b] who suggest a direct β-H transfer instead of a β-elimination. Excellent regioselectivities are obtained with vinylarenes such as styrene or vinylnaphthalene due to the allylic nature of the intermediate proposed. Very good enantioselectivities were initially obtained by Wilke,[24] and more recently by the groups of Vogt

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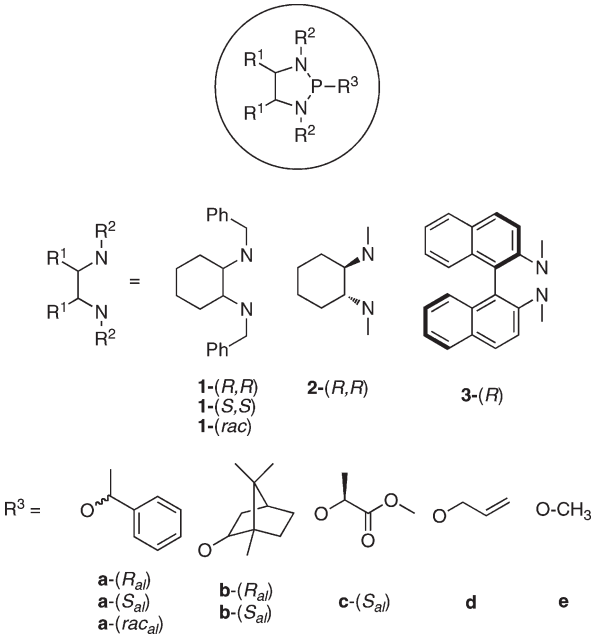
and Cavell,[25] Gibson,[26] Rajanbabu,[20b,21c,27] Leitner,[28] and Zhou,[29] using phosphines, planar chromium phosphines, phosphinites, or phosphoramidites as stabilizing ligands with nickel and palladium systems. Our research group studied the model reaction using nickel and palladium precursors. The initial study provided evidence of the blocking effect of inert bidentate ligands.[30a] Further research with allylic palladium precursors containing *P*-stereogenic phosphines[30b−e] and chiral aminophosphines[30f] enabled the enantioselective version of the process to be studied.

Chart 1. Building Blocks for the Synthesis of Diamidophosphite Ligands



Results and Discussion

Diamidophosphite Preparation. The structure of the chiral diamidophosphite ligands allows easy adjustment of steric and electronic properties, through modification of the nature and chirality of the C_2 diamine backbone (R^1), the nature of the amine substituent (R^2), and the nature and chirality of the alkoxy group (R^3) (Chart 1).

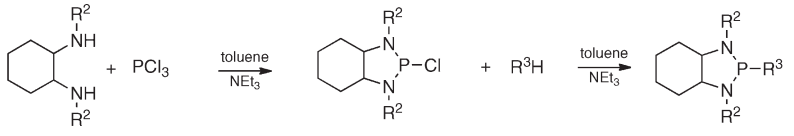
Chiral diamidophosphite ligands were prepared as reported in the literature,[10a,11a,13a,18d] via a two-step reaction (Scheme 1).

The reaction of phosphorus trichloride with the enantiomerically pure chiral disubstituted diamine in the presence of excess triethylamine led to the preparation of the heterocyclic chloride derivative. The formation of **4**, **5**, and **6** was monitored by phosphorus NMR spectroscopy (**4**, **5**: δ = 174.5 ppm and **6**: δ = 204.9 ppm). When the PCl_3 signal disappeared, the stoichiometric amount of the corresponding chiral alcohol (R^3H) was added until completion of the reaction. The last step produced the diamidophosphites **7a**−**d**, **8b**, and **8e** with a diazaphospholidine backbone and **9b** with a diazaphosphepine backbone.

The four diastereomers of ligands **7a** (**7a**-(*R,R,R*$_{al}$), **7a**-(*R,R,S*$_{al}$), **7a**-(*S,S,S*$_{al}$), **7a**-(*S,S,R*$_{al}$)) and two diastereoisomers of ligands **7b** (**7b**-(*R,R*$_{al}$), **7b**-(*R,S*$_{al}$)) and **9b** (**9b**-(*R,R*$_{al}$), **9b**-(*R,S*$_{al}$)) were prepared in order to study the *match*/*mismatch* effects of the two chiral units in the catalytic asymmetric process. The racemic **7a**-(*rac,rac*$_{al}$) and **7a**-(*rac,S*$_{al}$) ligands were prepared in order to study the separation of the corresponding diastereomeric allyl palladium complexes by fractional crystallization. Ligands **7c** and **7d** were prepared to test the potential hemilability coming from a second donating group, the double bond and oxygen atom, respectively.

Compounds **7a**−**d**, **8b**, **8e**, and **9b** were obtained as sensitive pure oils, stored under nitrogen atmosphere, and used in the synthesis of palladium(II) complexes without further treatment. The new ligands have been characterized by mass

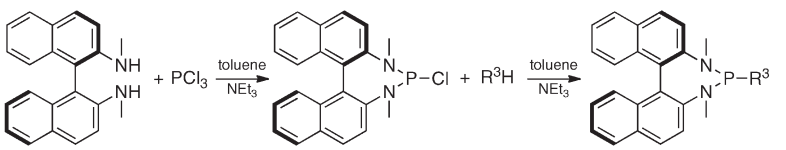
Scheme 1



1-(*R,R*), R^2= $CH_2C_6H_5$
1-(*S,S*), R^2= $CH_2C_6H_5$
1-(*rac*), R^2= $CH_2C_6H_5$
2-(*R,R*), R^2= CH_3

4-(*R,R*), R^2= $CH_2C_6H_5$
4-(*S,S*), R^2= $CH_2C_6H_5$
4-(*rac*), R^2= $CH_2C_6H_5$
5-(*R,R*), R^2= CH_3

7a-(*R,R,R*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **a**-(*R*$_{al}$)
7a-(*R,R,S*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **a**-(*S*$_{al}$)
7a-(*S,S,S*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **a**-(*S*$_{al}$)
7a-(*S,S,R*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **a**-(*R*$_{al}$)
7a-(*rac,rac*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **a**-(*rac*$_{al}$)
7a-(*rac,S*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **a**-(*S*$_{al}$)
7b-(*R,R,R*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **b**-(*R*$_{al}$)
7b-(*R,R,S*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **b**-(*S*$_{al}$)
7c-(*R,R,S*$_{al}$), R^2= $CH_2C_6H_5$, R^3= **c**-(*S*$_{al}$)
7d-(*R,R*), R^2= $CH_2C_6H_5$, R^3= **d**
8b-(*R,R,S*$_{al}$), R^2= CH_3, R^3= **b**-(*S*$_{al}$)
8e-(*R,R*), R^2= CH_3, R^3= **e**

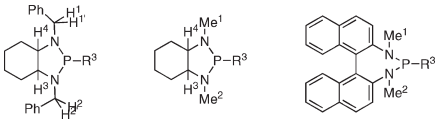


3-(*R*)
6-(*R*)
9b-(*R,R*$_{al}$), R^3= **b**-(*R*$_{al}$)
9b-(*R,S*$_{al}$), R^3= **b**-(*S*$_{al}$)

Table 1. Selected NMR Data[a] (δ in ppm, in $CDCl_3$) for Ligands 7−9

ligand	δ ^{31}P	δ ^{1}H (diamine backbone) H^1, H$^{1'}$, H^2, H$^{2'}$	H^3, H^4	δ ^{1}H (R^3) O−C*H*
7a-(*R,R,R*$_{al}$)	+135.2 (s)	4.17−4.04 (om, 2H)	2.91 (m)	4.95 (dq; J_{HH} = 8.8, J_{HP} = 6.4)
7a-(*S,S,S*$_{al}$)		3.96 (dd; J_{HH} = 15.6, J_{HP} = 12, 1H)	2.44 (m)	
		3.48 (dd; J_{HH} = 15.2, J_{HP} = 9.6, 1H)		
7a-(*R,R,S*$_{al}$)	+140.7 (s)	4.23 (pt, J_{HH} = J_{HP} = 13.5, 1H)	2.99 (m)	4.86 (m)
7a-(*S,S,R*$_{al}$)		4.17 (pt, J_{HH} = J_{HP} = 13.5, 1H)	2.46 (m)	
		3.82 (pt; J_{HH} = J_{HP} = 14.8, 1H)		
		3.52 (dd; J_{HH} = 15.2, J_{HP} = 10.4, 1H)		
7b-(*R,R,R*$_{al}$)	+135.9 (s)	4.28 (dd; J_{HH} = 15.3, J_{HP} = 11.7; 1H)	2.92 (m)	4.09 (m)
		4.20 (t, J_{HH} = J_{HP} = 14.1; 2H)	2.46 (m)	
		3.73 (dd; J_{HH} = 15.3, J_{HP} = 8.4; 1H)		
7b-(*R,R,S*$_{al}$)	+142.4 (s)	4.34 (dd; J_{HH} = 16, J_{HP} = 13.6; 1H)	2.95 (m)	3.98 (m)
		4.11 (dd; J_{HH} = 15, J_{HP} = 12; 2H)	2.47 (m)	
		3.76 (dd; J_{HH} = 15.2, J_{HP} = 10.8; 1H)		
7c-(*R,R,S*$_{al}$)	+140.4 (s)	4.40−4.15 (om; 2H)	3.07 (m)	4.40−4.15 (om)
		4.00−3.80 (om; 2H)	2.51 (m)	
7d-(*R,R*)[b]	+137.1 (s)	4.35−3.82 (om; 4H)	3.00 (m)	**O−C*H*$_2$**
			2.50 (m)	4.35−3.82 (om, 2H)
8b-(*R,R,S*$_{al}$)	+144.0 (s)	**Me^1**, **Me^2**	2.63 (m)	**O−C*H***
		2.60 (d; J_{HP} = 13.2; 3H)	2.29 (m)	4.02 (m)
		2.42 (d; J_{HP} = 14; 3H)		
8e-(*R,R*)	+136.0 (s)	2.61 (d; J_{HP} = 14; 3H)	2.65 (m)	**O−C*H*$_3$**
		2.48 (d; J_{HP} = 14; 3H)	2.24 (m)	3.36 (d; 9.6; 3H)
9b-(*R,R*$_{al}$)	+178.6 (s)	2.88 (d; J_{HP} = 12; 3H)		**O−C*H***
		2.81 (d; J_{HP} = 8; 3H)		4.32 (m)
9b-(*R,S*$_{al}$)	+177.6 (s)	2.91 (d; J_{HP} = 13.6; 3H)		4.27 (m)
		2.89 (d; J_{HP} = 9.6; 3H)		

[a] ^{1}H NMR: 298 K, 400 MHz. ^{31}P NMR: 298 K, 101,2 MHz. Multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pseudo; m, multiplet; om, overlapped multiplets. Coupling constants are given in Hz and are shown in parentheses after the multiplicity. See figure below for atom numbering. [b] Broad signals for ^{1}H spectrum



spectrometry and ^{13}C, ^{1}H, and ^{31}P NMR spectroscopy. Selected NMR data are shown in Table 1.

The ^{31}P chemical shift values were in the range reported for diamidophosphites[5] and appeared to be mostly influenced by the nature of the amine scaffold. It is worth noting the different chemical shift found for the diastereoisomers of the same ligand (**7a**-(*R,R,R*$_{al}$) and **7a**-(*R,R,S*$_{al}$), **7a**-(*S,S,S*$_{al}$) and **7a**-(*S,S,R*$_{al}$), **7b**-(*R,R*$_{al}$) and **7b**-(*R,S*$_{al}$), **9b**-(*R,R*$_{al}$) and **9b**-(*R,S*$_{al}$)), showing that the different spatial orientation of the substituents on the chiral alkoxy group influenced the ^{31}P chemical shift value.[18d,e] To assign ^{1}H NMR spectra unequivocally, it was necessary to record the two-dimensional experiment HSQC. All the diamidophosphites synthesized showed loss of the C_2 symmetry of the starting substituted diamines. Thus, for ligands **7** the four benzylic protons were unique and exhibited coupling with the geminal proton and the phosphorus atom. Protons bonded to the cyclohexyl chiral carbon always appeared as two multiplets in contrast to one multiplet in the free parent amine. For diazaphospholidines **8** and diazaphosphepine **9** the methyl amino substituents appeared as two different doublets, showing coupling with the phosphorus atom.

Selenide Derivatives. A simple means of evaluating the σ-donor ability of the diamidophosphites is to measure the magnitude of $^{1}J_{SeP}$ in the ^{77}Se isotopomer of the corresponding diamidophosphite selenide. It has been reported that poorly donating phosphine will exhibit values of $^{1}J_{SeP}$ that are larger than those for electron-rich phosphines.[31]

We prepared the corresponding selenides of the new diamidophosphites **Se**(**7**−**9**) and of the structurally related ligands **7f**[14] and **9e**[13a] reported in the literature, by simply reacting the phosphorus compounds with elemental selenium in dichloromethane at room temperature (Scheme 2).

The selenide compounds were characterized *in situ* by ^{31}P NMR spectroscopy. In each case a single new resonance that exhibited coupling to ^{77}Se, at higher fields than free diamidophosphites, was observed (Table 2).

From the magnitude of $^{1}J_{SeP}$ it is possible to draw some interesting conclusions. Within ligands with an identical

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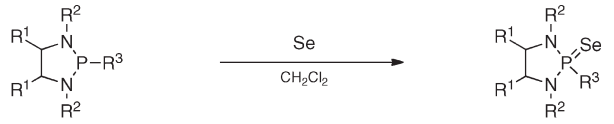
Scheme 2



7a-d, **8b**, **8e**, **9b**, **9e** **Se7a-d**, **Se7f**, **Se8b**, **Se8e**, **Se9b**, **Se9e**

7f-*(R,R)*, R^1= *(R,R)*-Cyclohexyl, R^2= $CH_2C_6H_5$; R^3= Ph
9e-*(R)*, R^1= *(R)*-Binaphtyl, R^2= CH_3; R^3= OCH_3

Table 2. Selected ^{31}P NMR Data[a] for Selenide Derivatives Se(7−9)

SeL	δ^{31}P SeL	J_{SeP} SeL
Se7a-(*R,R,S*$_{al}$)	87.3	884
Se7a-(*S,S,R*$_{al}$)		
Se7a-(*S,S,S*$_{al}$)	86.6	881
Se7a-(*R,R,R*$_{al}$)		
Se7b-(*R,R,S*$_{al}$)	88.8	858
Se7b-(*R,R,R*$_{al}$)	85.8	870
Se7c-(*R,R,S*$_{al}$)	87.4	874
Se7d-(*R,R*)	88.3	888
Se7f-(*R,R*)	87.7	817
Se8b-(*R,R,S*$_{al}$)	85.3	863
Se8e-(*R,R*)	87.6	872
Se9b-(*R,S*$_{al}$)	89.5	866
Se9b-(*R,R*$_{al}$)	91.9	883
Se9e-(*R*)	93.2	891
SeBinepine-(*S*)[b]	49.5	727

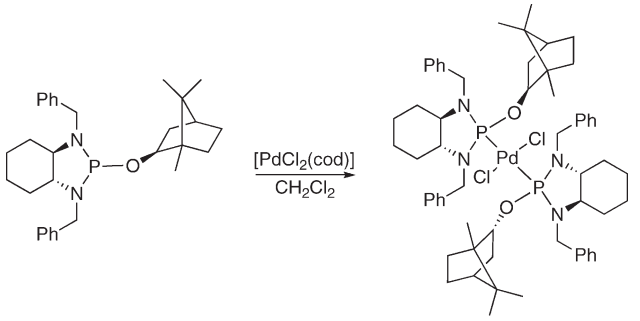
[a] ^{31}P {^{1}H} NMR: 298 K, 101.2 MHz, CH_2Cl_2. δ in ppm. Coupling constants in Hz. [b] Reported value.[32]

substituted diamino backbone and different R^3 group, the lowest $^1J_{SeP}$ value was observed when the more sterically demanding bornyloxy group was bonded to the phosphorus atom. The presence of bulky substituents at phosphorus resulted in a decrease in the s character of the lone pair as a result of the widening of intervalence angles.[31a] Comparing ligands with different backbones (**8b** vs **9b**), a slightly better σ-donor character was seen for those with a cyclohexyl rather than a binaphthyl backbone. The $^1J_{SeP}$ also had interesting stereochemical dependencies; thus, different diastereoisomers showed different values for $^1J_{SeP}$ (see: **Se 7b**-(*R,R,S*$_{al}$) vs **Se7b**-(*S,S,R*$_{al}$); **Se9b**-(*R,S*$_{al}$) vs **Se9b**-(*S,R*$_{al}$)). Higher coupling constant values were registered for diamidophosphite (two P−N bonds and one P−O bond) compared to diamidophosphine ligands **7f** (two P−N bonds and one P−C bond) and Binepine phosphine ligand (three P−C bonds), indicating that the more electronegative substituents bonded to the phosphorus atom, the lower the σ-donor ability of the ligand.

Palladium Complexes. Preparation of [PdCl$_2$L$_2$)] (10). To examine the complexing capacity of the diazaphospholidine ligands and to obtain further structural information, one coordination palladium(II) complex was prepared. The reaction of diazaphospholidine **7b**-(*R,R,S*$_{al}$) with [$PdCl_2$(cod)] in CH_2Cl_2 gave the palladium complex **10** (Scheme 3).

No crystals suitable for X-ray determination were obtained, but we studied the structure of complex **10** in solution. The ^{31}P NMR spectrum showed only one signal (δ = 91.84 ppm), suggesting the presence of a unique complex, and this was assigned as *trans* on the basis of the ^{1}H NMR spectrum: benzylic hydrogen atoms appeared as four doublets of triplets due to coupling with geminal nonequivalent protons and the two phosphorus atoms in *trans* position (4.96 ppm, dt, J_{HH} = 16, J_{HP} = 6.8; 4.85 ppm, dt, J_{HH} = 16, J_{HP} = 6.4; 4.40 ppm, dt, J_{HH} = 16, J_{HP} = 6; 4.08 ppm, dt, J_{HH} = 16.4, J_{HP} = 2.4).

Scheme 3



7b-*(R,R,S*$_{al}$*)* **10**

Preparation of Allylic Palladium(II) Complexes [PdCl(η^3-2-$CH_3C_3H_4$)L)] (11−14). Neutral allylic palladium complexes have been prepared with the new diamodiphosphite **7a**−**d**, **8b**, **8e**, and **9b** ligands and also with the following structurally related ligands reported by other authors, diamidophosphine **7f**-(*R,R*),[14] diamidophosphite **9e**-(*R*),[13] and phosphine Binepine-(*S*),[32a] with the aim of studying the coordination chemistry and dynamic behavior in solution of the new neutral π-allylic complexes. The neutral compounds were used to prepare the corresponding cationic allylic catalytic precursors and to study how the nature of the different substituents in the phosphorus ligands affected activity and selectivity in the hydrovinylation reaction. Very few examples of allylic palladium(II) complexes with diamidophosphite ligands have been reported in the literature.[11a,12]

The allylic complexes **11a**−**d**, **11f**, **12b**, **12e**, **13b**, **13e**, and **14** were prepared by reaction at low temperature of the well-known bridged chloride complex [Pd(μ-Cl)(η^3-2-$CH_3C_3H_4$)]$_2$ with the appropriate stoichiometric amount of the ligand as reported in the literature[30d,f] for similar compounds (Scheme 4).

The new compounds were characterized, in the solid state, by elemental analysis, and mass spectroscopy where necessary. ^{1}H and ^{31}P NMR spectroscopy allowed us to characterize these complexes in solution. Some relevant NMR spectral data are summarized in Tables S1 and S2. ^{31}P NMR spectra showed two sharp signals, with approximately the same ratio, arising from the two well-known[33] isomers formed due to the different disposition of the chiral ligand and the allylic group around the metal center. For complexes

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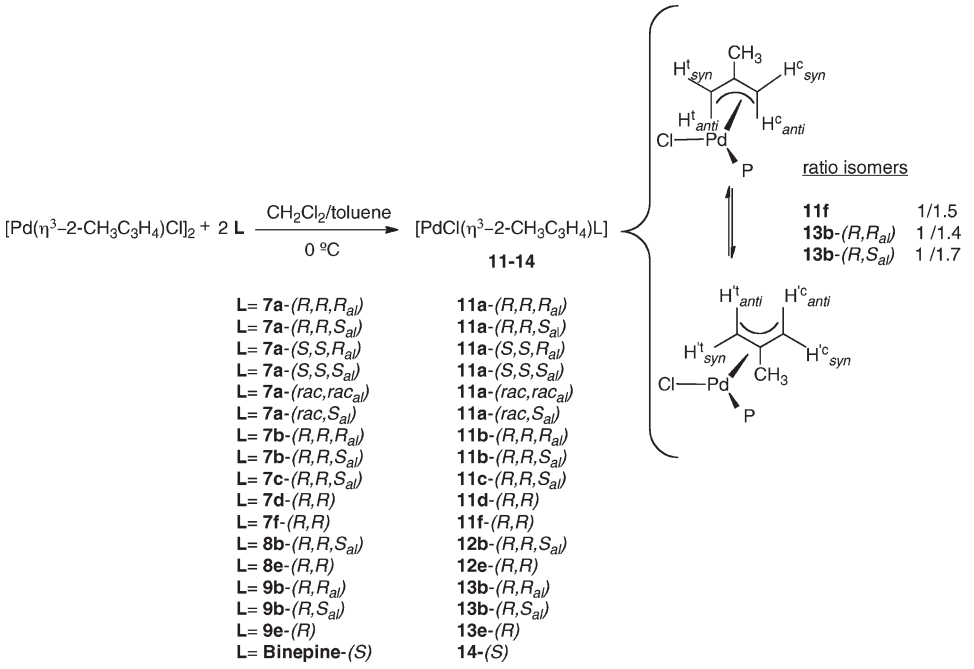
Scheme 4



11f, **13b**-(*R,R*$_{al}$) and **13b**-(*R,S*$_{al}$), the ratio of isomers obtained from the ^{31}P NMR spectra was 1:1.5, 1:1.4, and 1:1.7, respectively. Probably, the Ph substituent of the phosphorus ligand in **11f** and the bulky **b** group (bornyloxy) in **13b** led to some discrimination between the two isomers. The phosphorus chemical shifts of complexes with diamidophosphite ligands lay upfield compared to those of the free ligand, but complexes with diamidophosphine, **11f**, and phosphine, **14**-(*S*), lay downfield. Gavrilov[11a] found the same relation of chemical shifts in complexes with diamidophosphite chiral ligands.

Bidimensional NMR heterocorrelation ^{1}H−^{13}C and NOESY experiments were important for assigning the different signals of the ^{1}H spectra; nevertheless a complete correlation of all the protons of one isomer was not possible in any of the complexes. Relative to the coordinated phosphorus ligand, it is worth noting that all the proton signals of the diamino backbone shifted to lower fields than those of the free ligand. Complexes **11a**−**d**,**f**, with a dibenzylcyclohexyldiamino backbone, showed eight signals for the benzylic protons usually overlapped, both with each other and also with the *trans-syn* allylic hydrogen atoms. The same trend was observed for complex **14**-(*S*) with a Binepine ligand. Complexes **12b**, **12e**, and **13b** showed two signals assigned to methyl substituents in the diamino backbone, but for **13e** four well-defined doublets were detected. Related to the allylic group, ^{1}H NMR spectra showed two sets of signals for each *syn* and *anti* proton and two singlets for the methyl substituent, confirming the presence of the two isomers. Allylic terminal hydrogen atoms located on the carbon atom *trans* to the phosphorus atom appeared at lower field than those in the *cis* position, as has generally been observed for similar compounds.[30d,f,34] Terminal *anti* protons in *trans* position to the P atom appeared as a doublet because of phosphorus coupling.

To elucidate the solution structure of these complexes and their dynamic behavior, 2D NOESY experiments were carried out for complexes **11a**-(*R,R,R*$_{al}$), **11a**-(*R,R,S*$_{al}$), **11b**-(*R,R,S*$_{al}$), **11f**-(*R,R*), **12b**-(*R,R,S*$_{al}$), **13b**-(*R,R*$_{al}$), **13b**-(*R,S*$_{al}$), **13e**-(*R*), and **14**-(*S*). Only NOE contacts between allylic protons and the diamidophosphite ligand were observed for complexes **13b**. Nevertheless, interesting exchange signals between allylic protons were observed. Exchange between *syn*/*anti* allylic protons was observed with the pair in *cis* position to the phosphorus atom for all the complexes studied. The pair that is in *trans* position exchanges only between *syn*/*syn* and *anti*/*anti* protons, in accordance with a selective opening of the palladium carbon bond *trans* to the phosphorus atom. This can be observed in analogous compounds[30d,f,34b] and suggests the well-known $\eta^3-\eta^1-\eta^3$ isomerization process. Cross-peaks that can be assigned to the whole apparent rotation were observed only for complexes **13b**-(*R,R*$_{al}$), **13b**-(*R,S*$_{al}$), and **13e**-(*R*), with ligands containing the binaphthyldiamino backbone, and **14**-(*S*), with the Binepine phosphine ligand. Exchange signals between benzylic hydrogens of different isomers in complexes **11a**-(*R,R,R*$_{al}$), **11a**-(*R,R,S*$_{al}$), **11b**-(*R,R,S*$_{al}$), **11f** (*R,R*), and **14**-(*S*), as well as between methylamino hydrogens in **13b**-(*R,R*$_{al}$), were also detected. For **13b**-(*R,S*$_{al}$) the methylamino signals were too close to clearly detect exchange cross-peaks.

We tested the separation of the stereoisomers of **11a**-(*rac, rac*$_{al}$) species by fractional crystallization. Reaction of [Pd(μ-Cl)(η^3-2-CH$_3$C$_3$H$_4$)]$_2$ with the racemic diazaphospholidine **7a**-(*rac,rac*$_{al}$) led to a solution where a mixture of isomers (**11a**-(*R,R,S*$_{al}$), **11a**-(*R,R,R*$_{al}$), **11a**-(*S,S,R*$_{al}$), **11a**-(*S,S,S*$_{al}$)) was present, confirmed by ^{31}P NMR spectroscopy (signals at 130.7, 129.9, 126.9, 126.4 ppm with a similar ratio). After precipitation with ether, a solid that presented signals at 130.7 and 129.9 ppm was obtained; a second precipitation with pentane enabled the crystallization of a solid with signals at 126.9 and 126.3 ppm, the first of which could be

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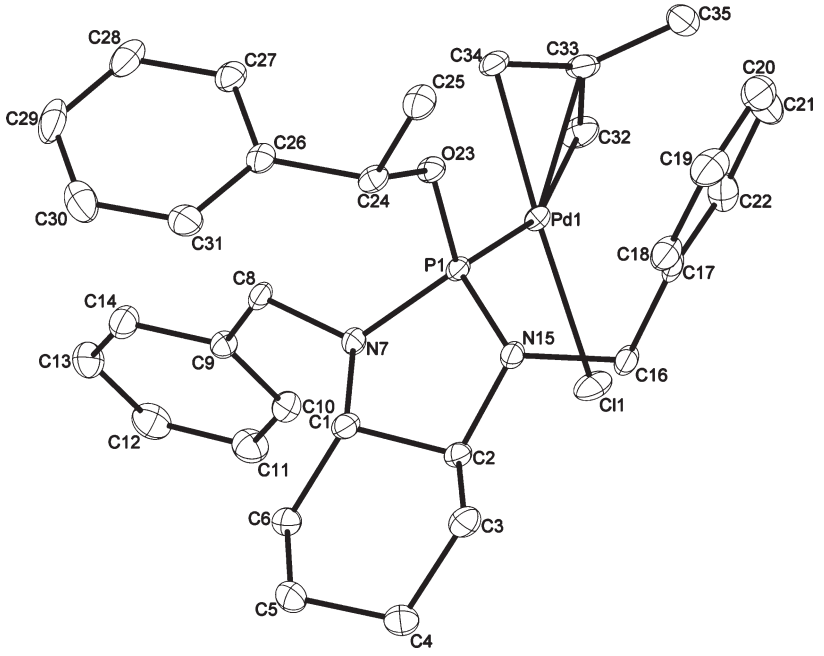

Figure 2. ORTEP drawing of the molecular structure of the compound **11a**-(*S,S,S*$_{al}$) shown at 50% probability. Hydrogen atoms are omitted for clarity.

assigned to the pair of enantiomers **11a**-(*R,R,S*$_{al}$) and **11a**-(*S,S,R*$_{al}$), and the second to the **11a**-(*R,R,R*$_{al}$) and **11a**-(*S,S,S*$_{al}$) pair. We tested the preparation of pure diatereoisomers by reaction of the palladium dimer with the diazaphospholidine **7a**-(*rac,S*$_{al}$) under the same conditions, but the separation by fractional crystallization was not possible, and only a mixture of both diastereoisomers was obtained.

Crystals of sufficient quality for X-ray diffraction measurements were obtained from a mixture of dichloromethane and ether solution of complex **11a**-(*S,S,S*$_{al}$). Figure 2 shows an ORTEP view, and Table 3 gives a list of selected bond lengths and bond angles.

The palladium atom showed a distorted square-planar coordination, bonded to one phosphorus, one chloro, and two terminal allylic carbon atoms. The distances and angles between the atoms of the coordination sphere were in the range expected for this type of allylic complex.[34b,35] The longer Pd−C length *trans* to the phosphorus atom is in agreement with the stronger *trans* influence of the diamidophosphite ligand relative to the chloro ligand. The source of the different environment of the two nitrogen atoms with *R*-configuration in the molecular structure is in the conformation adopted by the phenyl group of the 2-phenylethoxy moiety. This phenyl group is placed over the C8 atom in the base of the N7 pyramid, obliging the two angles with P1 and C1 to reach 120°.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 11a-(*S,S,S*$_{al}$)

Pd−P1	2.2550(6)	P1−O23	1.6132(16)
Pd−Cl1	2.3728(6)	P1−N7	1.6681(19)
Pd−C32	2.219(3)	P1−N15	1.688(2)
Pd−C33	2.182(2)	C32−C33	1.392(3)
Pd−C34	2.089(2)	C33−C34	1.427(3)
Cl1−Pd−P1	95.02(2)	O23−P1−N7	111.28(9)
O23−P1−Pd	109.80(6)	O23−P1−N15	105.73(9)
N7−P1−Pd	113.70(7)	N7−P1−N15	93.70(9)
N15−P1−Pd	121.53(7)	P1−N15−C2	110.27(14)
P1−N7−C1	112.02(14)	P1−N15−C16	116.91(16)
P1−N7−C8	120.58(15)	C2−N15−C16	116.08(18)
C1−N7−C8	120.06(18)	∑angles N15	343.26
∑angles N7	352.66		

It was possible to compare molecules with POON[35−38] (phophoramidites), PNNO[13,18d,39,40] (diamidophosphites), or PNNN[17b] (phosphorus triamides) bonds, free ligands,[17b,36,38] ligands coordinated to a transition metal,[35,39,40] and ligands bonded to borane,[13b,38b] selenium,[37] or sulfur[18d] atoms. It was observed that the P−O and P−N bond lengths were very similar, but the bond length was not always shorter with the more electronegative atom. With POON ligands, coordination reduces bond length, significantly more so in borane or selenium derivatives than in metal complexes. From the limited number of structures containing the PNNO skeleton we conclude that BH_3 or metal coordination led to similar bond lengths. The degree of sp^2 character of the N bonds is a matter for discussion. Free ligands[37,38a] with a POON skeleton show a pronounced planarity of the CCNP plane, but coordination always led to an increase of the pyramidalization around the nitrogen atom. Thus, the nitrogen atom seems to increase the sp^3 contribution of the N−C and N−P bonds on coordination.

Hydrovinylation Reaction. Allylic complexes stabilized with one monodentate phosphine have proved to be very

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useful as catalytic precursors in the hydrovinylation reaction since the metal phosphine ratio is 1:1 and the cleavage of the allyl substituent leads to the actual catalyst that initiates heterodimerization. The model reaction involves codimerization between styrene and ethylene, forming 3-phenyl-1-butene. In addition, variable amounts of dimerization of either styrene or ethylene can be found. The isomerization of the 3-phenyl-1-butene to the more stable 2-phenyl-2-butene could appear as a consecutive process when the active catalyst is a palladium hydride species (Scheme 5).

The excellent regioselectivities obtained were a consequence of the allylic nature of the intermediate. Since only one monodentate ligand may be coordinated to the metal, the factors determining the discrimination capacity of the catalyst remain poorly defined. A concerted effort was made in the preparation of hemilabile ligands to stabilize the active species, thus contributing to improved diatereoselective discrimination and enhancing the selectivity of the process.[21b,23b,25a,28,41]

Solutions of cationic mixed complexes [Pd(η^3-2-$CH_3C_3H_4$)LS]BF_4 obtained "*in situ*", in CH_2Cl_2, from neutral complexes **11**−**14** and $AgBF_4$ in the presence of styrene were used as catalytic precursors in the hydrovinylation reaction. The study of the species present in these solutions is important for evaluating the results obtained in the catalytic process. It has been reported[30f,34a] that similar solutions of cationic allylic palladium(II) complexes with different phosphine and aminophosphine ligands undergo symmetrization, leading to mixtures of three different species. The relative amount of each one seems to be related mainly to steric over electronic parameters of the ligands.

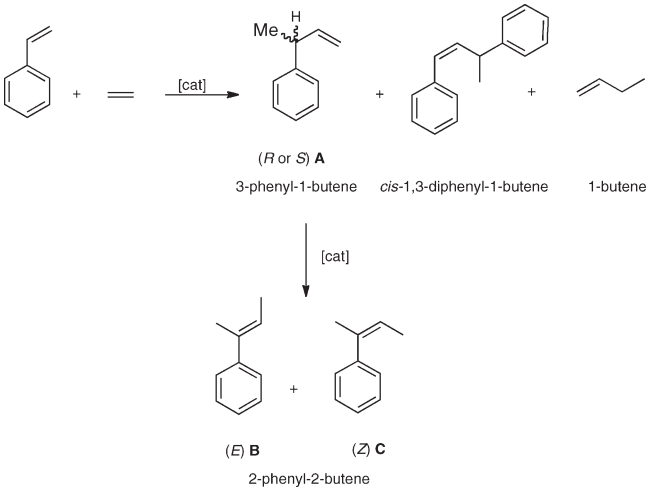
Using ^{31}P NMR spectroscopy, we monitored the solutions of some selected cationic complexes of type [Pd(η^3-2-$CH_3C_3H_4$)LS]BF_4, with the new diamidophosphite ligands prepared in this study. Thus, a CH_2Cl_2 solution of the neutral complex was reacted with a stoichiometric amount of $AgBF_4$ in the presence of a 10-fold excess of styrene or acetonitrile, as shown in Scheme 6.

Testing the symmetrization reaction with acetonitrile or styrene as the labile ligand for complex **11f** (L = **7f-**(*R,R*)), the same results were obtained, showing only the formation of the mixed [Pd(η^3-2-$CH_3C_3H_4$)LS]BF_4 species. Therefore, we used styrene or acetonirile depending on convenience. Solutions of cationic complexes with **7a-**(R,R,R_{al}), **7b-**(R,R,S_{al}), **7d-**(*R,R*), and **7f-**(*R,R*) ligands showed only two singlets in a 1:1 ratio, corresponding to the two isomers of the mixed complex. However, the solution with complex [Pd(η^3-2-$CH_3C_3H_4$)LS]BF_4, L = **8b-**(R,R,S_{al}), showed two separate singlets belonging to the isomers of the mixed cationic complex, and two doublets according to the presence of the bisdiamidophosphite cationic complex [Pd(η^3-2-$CH_3C_3H_4$)-L_2]BF_4. The ratio of the mixed/bisligand cationic complexes was 5:1. These results suggest that cationic complexes containing the diamidophoshite **8b-**(R,R,S_{al}), with the smallest amino substituent (methyl vs benzyl), are the only ones that undergo symmetrization. From these results, we conclude that only cationic complexes with **8b** and **8e** ligands, containing the dimethylcyclohexyl fragment, are prone to present the symmetrization reaction to a significant extent.

The hydrovinylation reaction was carried out using a [Pd]/styrene ratio of 1:1000, CH_2Cl_2 as solvent, 15 bar of starting ethylene pressure, and at 15 °C. The products of the catalytic process were analyzed after 60 or 360 min reaction. The results obtained with the different precursors are shown in Table 4.

Good reproducibility and excellent selectivity toward codimer **A** at low conversions were obtained in accordance

Scheme 5



Scheme 6

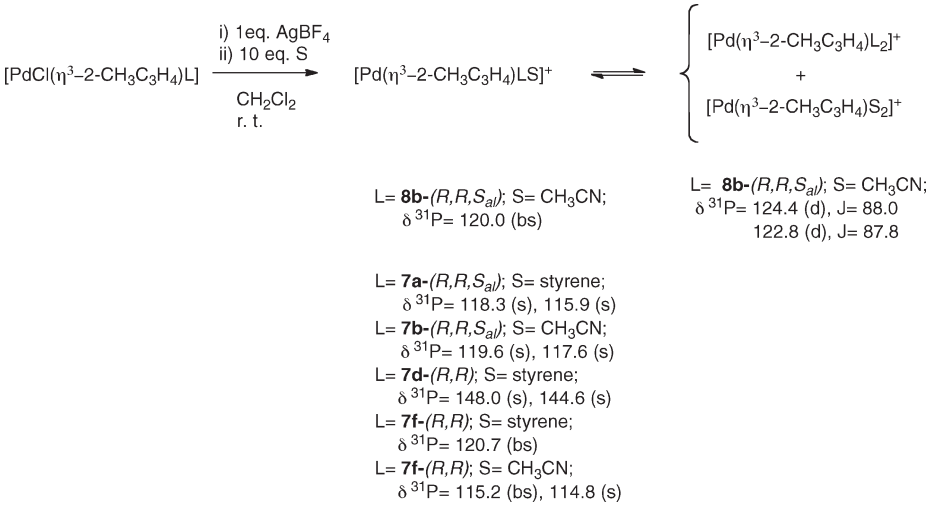


Table 4. Hydrovinylation of Styrene Catalyzed by [Pd(η^3-$CH_3C_3H_4$)LS]BF_4 Precursors[a]

entry	L	time (min)	dimer (%)	codimer[b] (%)	selectivity[c] (%)	TOF[d]	ee (%)
1	**7a**-(*R,R,R*$_{al}$)	60	2.6	7.2	94.9	72	6 (*R*)
2	**7a**-(*R,R,R*$_{al}$)	360	3.1	50.5	77.9	84	11 (*R*)
3	**7a**-(*R,R,S*$_{al}$)	60	0.5	7.4	98.0	74	
4	**7a**-(*R,R,S*$_{al}$)	360	1.8	36.0	89.0	60	2 (*S*)
5	**7a**-(*S,S,S*$_{al}$)	60	0.5	5.2	98.8	52	5 (*S*)
6	**7a**-(*S,S,S*$_{al}$)	360	1.8	54.1	79.0	90	12 (*S*)
7	**7a**-(*S,S,R*$_{al}$)	60	0.6	7.5	98.5	75	2 (*S*)
8	**7a**-(*S,S,R*$_{al}$)	360	1.2	41.8	87.2	70	0
9	**7b**-(*R,R,R*$_{al}$)	60	0.4	11.6	97.7	109	28 (*S*)
10	**7b**-(*R,R,R*$_{al}$)	360	1.1	77.0	74.1	124	32 (*S*)
11	**7b**-(*R,R,S*$_{al}$)	60	0.7	15.3	96,4	156	25 (*R*)
12	**7b**-(*R,R,S*$_{al}$)	180	0.9	44.5	87.7	130	23 (*R*)
13	**7b**-(*R,R,S*$_{al}$)	360	1.1	81.9	67.0	114	19 (*R*)
14	**7c**-(*R,R,S*$_{al}$)	60	0.5	4.3	97.8	40	
15	**7c**-(*R,R,S*$_{al}$)	360	0.6	12.0	93.7	19	4 (*R*)
16[e]	**7c**-(*R,R,S*$_{al}$)	360	0.9	20.2	90.7	29	2 (*R*)
17	**7d**-(*R,R*)	60	0.1				
18	**7d**-(*R,R*)	360	0.2	0.5	100	0.8	
19	**7f**-(*R,R*)	60	5.6	14.9	96.4	149	7 (*S*)
20	**7f**-(*R,R*)	360	5.7	33.2	80.1	55	6 (*S*)
21	**8b**-(*R,R,S*$_{al}$)	60	0.5	2.2	100	19	
22	**8b**-(*R,R,S*$_{al}$)	360	1.4	15.2	94.7	22	23 (*S*)
23	**8e**-(*R,R*)	60	0.2	0.5	100	5	
24	**8e**-(*R,R*)	360	1.5	6.7	91.3	6	7 (*S*)
25	**9b**-(*R,R*$_{al}$)	60	2.0	45.0	95.8	428	80 (*R*)
26	**9b**-(*R,R*$_{al}$)	360	1.1	75.4	88.1	122	80 (*R*)
27	**9b**-(*R,S*$_{al}$)	60	3.0	62.7	92.9	595	90 (*R*)
28	**9b**-(*R,S*$_{al}$)	120	2.4	84.8	84.3	378	90 (*R*)
29	**9b**-(*R,S*$_{al}$)	360	1.6	91.5	76.0	149	90 (*R*)
30	**9e**-(*R*)	60	1.1	9.4	98.9	90	25 (*R*)
31	**9e**-(*R*)	360	3.3	67.7	80.4	114	25 (*R*)
32	Binepine-(*S*)	60	7.8	11.3	96.3	119	25 (*S*)
33	Binepine-(*S*)	360	11.3	48.7	79.7	80	23 (*S*)

[a] Reaction carried out at 15 °C, 15 bar of initial pressure of ethylene in 10 mL of CH_2Cl_2, ratio styrene/Pd = 1000:1. [b] Codimer: Total amount of codimers (A + B + C): see Scheme 5. [c] Selectivity: % of 3-phenyl-1-butene with respect to the codimers. [d] TOF = (mol codimer)(mol neutral complex)$^{-1}$ (h)$^{-1}$. [e] 30 bar of initial pressure of ethylene.

with previous research.[29,30b−30d] Dimerization of styrene is low and does not increase with reaction time, suggesting that the dimer is produced in the preparation of the precursor. To confirm the origin of the styrene dimer, we reproduced a hydrovinylation experiment but without the pressurization of ethylene using precursors containing the ligands **7a**-(*R,R,S*$_{al}$) and **7f**-(*R,R*). Monitoring the reaction by GC showed that dimerization increases with time and that the initial value of the dimer obtained at 30 min reaction was similar to that obtained in the hydrovinylation reaction (3.8% for **7f**-(*R,R*) and 0.9% for **7a**-(*R,R,S*$_{al}$)).

Data in Table 4 show a decrease for all the precursors of the selectivity toward 3-phenyl-1-butene (**A**) with reaction time. The coordination of the hydrovinylation product **A** to the active species allows the isomerization with subsequent increase of the 2-phenyl-2-butene isomers (**B** and **C**). The consecutive isomerization reaction may take place with a kinetic resolution modifying the ee value as already reported.[29]

In Table 4, the activity of the catalysts is expressed in terms of TOF values, which also allow an evaluation of the stability of the active species, whereby a decrease in TOF values over a long reaction time (60 vs 360 min) indicates the decomposition of the active species. All the precursors with actual monodentate ligands were active to a different extent, but those with ligands (**7c**, **7d**) that can act as hemilabile present very low activity (entry 14, TOF = 40 and entry 17, TOF = 0 at 60 min reaction). As has been reported, for Ni[22b,43] and Pd[21b] systems the use of a monophosphine that carries a hemilabile group might have an advantage, since such a group could stabilize the putative cationic intermediate by internal coordination, yielding better activities and selectivities of the process. However, the double bond of the allyloxy substituent in **7c** and the oxygen atoms of the oxylactate group in **7d** ligands presumably compete strongly with the substrates for the vacant coordination site in the active species, thus blocking the catalytic process, as described by Rajanbabu.[42]

The cationic precursors with a dimethylcyclohexyldiamino backbone, **8b** and **8e**, yielded low activity (entries 21−24). These complexes undergo the symmetrization process mentioned above, lowering the concentration of the active species and leading to low TOF values. Moreover, the bisphosphorous-donor cationic complexes formed are not active in the hydrovinylation reaction, as reported.[30f]

Table 4 shows that precursors containing ligands with a dimethylbinaphthyldiamino backbone (**9b**, **9e**) are more active and selective toward 3-phenyl-1-butene (**A**) than those with a dibenzylcyclohexyldiamino one (**7a**, **7b**) (entries 1−13 vs 25−30), and the best activities were always achieved when the third substituent was bornyloxy (**b**).

Related to enantioselectivity, once again, very good results were obtained with diazaphosphepine ligands **9b**-(*R,S*$_{al}$) (ee = 90% (*R*)) and **9b**-(*R,R*$_{al}$) (ee = 80% (*R*)), and as the ee

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values show, a *mismatch* effect was observed depending on the chirality of the third bornyloxy group substituent. The enantioselectivity of the process is determined by the amine backbone chirality in diazaphosphepine ligands (entries 25−31), while the third alkoxy substituent chirality determines the configuration of the major enantiomer when the ligand contains the cyclohexyl backbone. For the **7b-**(R,R,S_{al}) ligand, ee = 25% (*R*), whereas for **7b-**(R,R,R_{al}) ee = 28% (*S*) (entries 9 vs 12). A decrease in the selectivity toward codimer **A** was observed because of the secondary isomerization process when the reaction time was 360 min, but with only diazaphospholidine ligands a kinetic resolution controlled by the backbone chirality was observed (entries 9−13 with **7b** ligands). Moreover, less isomerization was observed with **9** ligands, presumably because the bulky dimethylbinaphthyldiamino fragment hinders the coordination of the 3-phenyl-1-butene product. In order to compare the activity of precursors containing similar backbones but with different phosphorus substituent groups, we ran a hydrovinylation reaction with a cationic complex containing the Binepine ligand (three P−C bonds). Moderate activities and enantioselectivities were achieved, suggesting that the best catalytic precursors are obtained when the ligand contains P−O/P−N bonds (entries 32 and 33).

The results obtained with the palladium(II) precursor containing the **9b-**(R,S_{al}) diamidophosphite ligand, with a dimethylbinaphthyldiamino backbone and chiral bornyloxy as a third substituent, are the best that have been reported to date in the literature for the asymmetric codimerization of styrene and ethylene at moderate conditions (15 °C and 15 bar ethylene pressure). It can be argued that the good enantioselectivity comes from a secondary interaction between the metal center and the arene electrons from the atropisomeric chiral auxiliary, as reported by Pregosin.[43] This interaction might lead to an active species with better discrimination in the coordination step of the prochiral faces of the styrene, improving the enantiosectivity of the reaction.

Conclusions

We have developed a new family (12 members) of chiral phosphorus ligands of general structure **I** (Figure 1) for use in enantioselective catalysis. The new diamidophosphite ligands with substituted diaminobinaphthyl and diaminocyclohexyl backbones possess a highly modular structure that is well suited to the synthesis of a library. The preparation of the selenide derivatives and examination of the $^1J_{PSe}$ coupling constants provide a simple technique for a rough estimation of the σ-donor ability of these ligands.

We have prepared neutral allyl palladium complexes of general formula [PdCl(η^3-2-$CH_3C_4H_4$)L]. Through NMR spectroscopy of their solutions we have detected the presence of two isomers, while with 2D NOESY experiments we have observed their dynamic behavior; complexes with a cyclohexyl scaffold showed the $\pi-\sigma-\pi$ exchange, but those with the binaphthyl backbone showed the two well-known movements, namely, apparent π-allyl rotation and $\pi-\sigma-\pi$ exchange, under the same conditions. The determination of the X-ray structure of one complex, **11a-**(S,S,S_{al}), confirmed the expected configuration for all the stereogenic carbon atoms of the ligand after the synthesis.

The cationic derivatives [Pd(η^3-2-$CH_3C_4H_4$)LS]BF_4 were prepared and monitored by NMR spectroscopy, in order to evaluate a possible symmetrization process. The cationic compounds were used as catalyst precursors in the hydrovinylation of styrene. Those without hemilabile ligands were active and selective toward the codimerization of styrene and ethylene. Very good activity (TOF = 595) and enantioselectivity (ee = 90%) were obtained with the precursor that contained the **9b-**(R,S_{al}) ligand, with the dimethylbinaphthyldiamino backbone and the bornyloxy group as a third substituent in the phosphorus atom. Thus, as stated by Leitner,[28a] it seems that an efficient ligand for asymmetric hydrovinylation should possess a P−N bond and contain more than one element of chirality, one of them preferably being an atropoisomeric unit.

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; the reagents were obtained from commercial sources and used without further purification. The diamines (*R*,*R*)-1,2-diaminocyclohexane, *N*,*N*′-dimethyl-1,2-diaminocyclohexane (**2-**(*R*,*R*)), and (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine (**3-**(*R*)) were used as supplied from Aldrich. *N*,*N*′-Dibenzyl-1,2-diaminocyclohexane (**1-**(*S*,*S*), **1-**(*R*,*R*)),[44] the diamidophosphites **7f-**(*RR*)[14a] and **9e-**(*R*),[13] and the dimeric palladium complex [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$[45] were prepared as previously described. The ^{1}H, ^{13}C (^{1}H, ^{13}C, standard $SiMe_4$), and ^{31}P (^{31}P, standard H_3PO_4) NMR spectra were recorded on either a Bruker DRX 250 (^{31}P, 101 MHz), Varian Mercury 400 MHz (^{13}C, 100 MHz), or Varian Mercury 500 MHz (^{13}C, 125 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Chemical shifts in ppm were reported downfield from standards. The two-dimensional experiments were carried out in a Varian Mercury 400 MHz or a Varian Mercury 500 MHz instrument at 298 K with mixing time of 500 ms for NOESY experiments. FAB mass chromatograms were obtained on a LC7MSD-TOF (Agilent Technologies) instrument. The GC analyses were performed on an Agilent Technologies 6890N gas chromatograph (30 m HP-5 column) with a FID detector. 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. Optical rotations were measured on a Perkin-Elmer 241 MC spectropolarimeter at 25 °C.

Synthesis of Diamidophospite Ligands. 7a-(R,R,R_{al}), **7a-**(S,S,S_{al}), **7a-**(R,R,S_{al}), and **7a-**(S,S,R_{al}) were prepared following the method described in the literature for similar ligands[14a] with some modifications. (*R*,*R*)-*N*,*N*′-Dibenzyl-1,2-diaminecyclohexane or (*S*,*S*)-*N*,*N*′-dibenzyl-1,2-diaminecyclohexane (1.17 g, 3.98 mmol) and NEt_3 (1.66 mL, 11.95 mmol) were dissolved in 8 mL of toluene. PCl_3 (0.35 mL, 3.98 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C. The mixture was stirred for 3 h at 0 °C, and (*S*)-1-phenylethanol or (*R*)-1-phenylethanol (1.01 mL, 3.98 mmol) was added at the same temperature. After 2 h stirring hexane (5 mL) was added and the white precipitate of triethylamine hydrochloride was filtered off. The solvent was removed under vacuum, and a colorless oil was obtained and used without purification. MS/ESI (+) (*m*/*z*): 445.2403 [(MH)]$^+$. **7a-**(R,R,R_{al}): yield 1.35 g (76%); $[\alpha]^{298}$ (*c* 1.04, CH_2Cl_2) = −18.98. **7a-**(S,S,S_{al}): yield: 1.05 g (60%); $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = +4.11. **7a-**(R,R,R_{al}) and **7a-**(S,S,S_{al}): ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 135.2 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.30−7.09 (om, 15H, Ar), 4.95 (dq,

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J_{HP} = 8.8, J_{HH} = 6.4, 1H, OC*H*), 4.17−4.04 (om, 2H, CH_2), 3.96 (dd, J_{HH} = 15.6, J_{HP} = 12, 1H, CH_2), 3.48 (dd, J_{HH} = 15.2, J_{HP} = 9.6, 1H, CH_2), 2.91 (m, C*H*), 2.44 (m, C*H*), 1.77−1.50 (om, 4H, CH_2), 1.36 (d, J_{HH} = 6.4, 3H, CH_3), 1.21−0.91 (om, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 128.74−125.48 (Ar), 71.74 (O*C*H), 67.33 (*C*H), 66.44 (*C*H), 50.23 (*C*H_2), 48.27 (*C*H_2), 30.45 (*C*H_2), 30.22 (*C*H_2), 26.61 (*C*H_2), 26.06 (*C*H_2), 24.29 (*C*H_3). **7a**-(*R,R,S*$_{al}$): yield 0.95 g (60%); $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −36.7. **7a**-(*S,S,R*$_{al}$): yield 1.43 g (81%); $[\alpha]^{298}$ (*c* 1.29, CH_2Cl_2) = +21.88. **7a**-(*R,R,S*$_{al}$) and **7a**-(*S,S,R*$_{al}$): ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 140.7 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.31−7.09 (om, 15H, Ar), 4.86 (m, 1H, OC*H*), 4.23 (pt, J_{HH} = J_{HP} = 13.5, 1H, CH_2), 4.17 (pt, J_{HH} = J_{HP} = 13.5, 1H, CH_2), 3.82 (pt, J_{HH} = J_{HP} = 14.8, 1H, CH_2), 3.52 (dd, J_{HH} = 15.2, J_{HP} = 10.4, 1H, CH_2), 2.99 (m, C*H*), 2.46 (m, C*H*), 1.31 (d, J_{HH} = 6.4, 3H, CH_3), 1.77−0.81 (om, 8H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 129.15−125.31 (15H Ar), 72.55 (O*C*H), 67.55 (*C*H), 66.23 (*C*H), 50.37 (*C*H_2), 48.25 (*C*H_2), 30.45 (*C*H_2), 30.29 (*C*H_2), 26.19 (*C*H_3), 24.60 (*C*H_2), 24.38 (*C*H_2).

7b-(*R,R,R*$_{al}$) and **7b**-(*R,R,S*$_{al}$) were synthesized in a similar way to that described for the preparation of **7a**. Starting materials: diamine **1**-(*R,R*) (2.5 g, 8.5 mmol), NEt_3 (3.54 mL, 25.5 mmol), PCl_3 (0.73 mL, 8.5 mmol), (*R*)-1-borneol or (*S*)-1-borneol (1.31 mmol, 8.5 mmol). MS/ESI (*m*/*z*): 477.3025 $[(MH)]^+$. **7b**-(*R,R,R*$_{al}$): yield 2.85 g (70%); $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −30.45; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 135.9 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.41−7.08 (om, 10H, Ar), 4.28 (dd, J_{HH} = 15.3, J_{HP} = 11.7, 1H, CH_2), 4.20 (t, J_{HH} = J_{HP} = 14.1, 2H, CH_2), 4.09 (m, 1H, OC*H*), 3.73 (dd, J_{HH} = 15.3, J_{HP} = 8.4, 1H, CH_2), 2.92 (m, 1H, C*H*), 2.46 (m, C*H*), 2.07−1.90 (m, 2H, CH_2), 1.75−1.50 (om, 6H, 5 CH_2, 1 C*H*), 1.24−0.92 (om, 6H, CH_2), 0.83−0.73 (om, 10H, 1 CH_2, 9 CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 128.72−126.87 (Ar), 77.60 (O*C*H), 67.22 (*C*H), 66.56 (*C*H), 50.05 (*C*H_2), 48.77 (*C*H_2), 45.25 (*C*H), 38.24 (*C*H_2), 30.67 (*C*H_2), 30.29 (*C*H_2), 30.25 (*C*H_2), 28.36 (*C*H_2), 26.78 (*C*H_2), 24.47 (*C*H_2), 20.17 (*C*H_3), 19.00 (*C*H_3), 13.82 (*C*H_3). **7b**-(*R,R,S*$_{al}$): yield 3.36 g (83%); $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −22.29; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 142.4 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.36−7.13 (m, 10H, Ar), 4.34 (dd, J_{HH} = 16, J_{HP} = 13.6, 1H, CH_2), 4.11 (dd, J_{HH} = 15, J_{HP} = 12, 2H, CH_2), 3.98 (m, 1H, OC*H*), 3.76 (dd, J_{HH} = 15.2, J_{HP} = 10.8, 1H, CH_2), 2.95 (m, 1H, C*H*), 2.47 (m, 1H, C*H*), 2.1 (m, 1H, CH_2), 2.0 (m, 1H, CH_2), 1.72−1.48 (om, 6H, 5CH_2, 1C*H*), 1.24−0.77 (om, 7H, CH_2), 0.75 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 0.65 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 128,5−125.0 (Ar), 79.0 (O*C*H), 67.72 (*C*H), 66.62 (*C*H), 50.82 (*C*H_2), 48.75 (*C*H_2), 45.0 (*C*H), 38.87 (*C*H_2), 30.92 (*C*H_2), 30.24 (*C*H_2), 28.44 (*C*H_2), 26.77 (*C*H_2), 24.42 (2 *C*H_2), 20.14 (*C*H_3), 18.90 (*C*H_3), 13.63 (*C*H_3).

7c-(*R,R,S*$_{al}$) was synthesized in a similar way to that described for the preparation of **7a**. Starting materials: diamine **1**-(*R,R*) (1 g, 3.4 mmol), NEt_3 (2.42 mL, 10.2 mmol), PCl_3 (0.20 mL, 3.4 mmol), methyl-(*S*)-lactate (0.32 mL, 3.4 mmol). Yield: 1.02 g (70%). MS/ESI (+) (*m*/*z*): 427.2151 $[(MH)]^+$; $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −46.55; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 140.4 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.38−7.18 (om, 10H, Ar), 4.40−4.15 (om, 3H, 2CH_2, 1C*H*), 4.0−3.80 (om, 2H, CH_2), 3.72 (s, 3H, CH_3), 3.07 (m, 1H, C*H*), 2.51 (m, 1H, C*H*), 1.90−1.54 (om, 4H, CH_2), 1.30 (d, J_{HH} = 7.2, 3H, CH_3), 1.22−0.85 (om, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 129.03−126.77 (Ar), 68.80 (*C*H), 66.88 (*C*H), 66.17 (*C*H), 52.59 (*C*H_3), 49.91 (*C*H_2), 47.97 (*C*H_2), 29.88 (*C*H_2), 29.18 (*C*H_2), 24.38 (*C*H_2), 24.20 (*C*H_2), 20.45 (*C*H_3).

7d-(*R,R*) was synthesized in a similar way to that described for the preparation of **7a**. Starting materials: diamine **1**-(*R,R*) (1.2 g, 4.15 mmol), NEt_3 (1.73 mL, 12.46 mmol), PCl_3 (0.36 mL, 4.15 mmol), allylic alcohol (0.35 mL, 4.15 mmol). Yield: 1.11 g (78%); MS/ESI (+) (*m*/*z*) 381.2098 $[(MH)]^+$; $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −46.14; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 137.1 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.30−7.18 (om, 10H, Ar), 5.80 (m, 1H, C*H*), 5.17 (d, J_{trans} = 17.9, 1H, CH_2), 5.04 (d, J_{cis} = 10.4, 1H, CH_2), 4.35−3.82 (om, 6H, 4CH_2, 2OCH_2), 3.07 (m, C*H*), 2.51 (m, C*H*), 1.78−1.54 (om, 4H, CH_2), 1.14−0.84 (om, 4H, CH_2). No ^{13}C NMR data because of fast oxidation.

8b-(*R,R,S*$_{al}$) was synthesized in a similar way to that described for the preparation of **7a**. Starting materials: diamine **2**-(*R,R*) (1 g, 7.0 mmol), NEt_3 (7.82 mL, 56.3 mmol), PCl_3 (0.61 mL, 7.0 mmol), (*S*)-1-borneol (1.08 g, 7.0 mmol). Yield: 1.78 g (78%); MS/ESI (+) (*m*/*z*) 325.2407 $[(MH)]^+$; $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −141.45; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 144.0 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 4.02 (m, 1H, OC*H*), 2.63 (m, 1H, C*H*), 2.60 (d, J_{HP} = 13.2, 3H, NCH_3), 2.42 (d, J_{HP} = 14, 3H, NCH_3), 2.29 (m, 1H, C*H*), 2.11 (m, 1H, CH_2), 2.01−1.85 (om, 3H, CH_2), 1.75−1.70 (om, 2H, CH_2), 1.60 (m, 1H, CH_2), 1.50 (t, J_{HH} = 4.8, 1H, C*H*), 1.2−0.95 (om, 6H, 4CH_2 (Cy), 2CH_2), 0.89 (dd, J_{HH} = 13.2, J_{HP} = 3.2, 1H, CH_2), 0.78 (bs, 3H, CH_3) 0.77 (bs, 3H, CH_3), 0.74 (bs, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 79.86 (O*C*H), 69.55 (*C*H), 66.83 (*C*H), 45.07 (*C*H), 38.85 (*C*H_2), 33.29 (N*C*H_3), 30.45 (N*C*H_3), 29.88 (*C*H_2), 29.25 (*C*H_2), 28.19 (*C*H_2), 29.25 (*C*H_2), 24.28 (2*C*H_2), 20.28 (*C*H_3), 19.95 (*C*H_3), 13.61 (*C*H_3).

8e-(*R,R*) was synthesized in a similar way to that described for the preparation of **7a**. Starting materials: diamine **2**-(*R,R*) (1 g, 7.0 mmol), NEt_3 (7.83 mL, 56.3 mmol), PCl_3 (0.61 mL, 7 mmol), methanol (0.37 mL, 9.2 mmol). Yield: 0.73 g (52%); MS/ESI (+) (*m*/*z*) 203.0882 $[(MH)]^+$; $[\alpha]^{298}$ (*c* 1.00, CH_2Cl_2) = −126.70; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 136.0 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.36 (d, J_{HP} = 9.6, 3H, OCH_3), 2.65 (m, 1H, C*H*), 2.61 (d, J_{HP} = 14, 3H, NCH_3), 2.48 (d, J_{HP} = 14, 3H, NCH_3), 2.24 (m, 1H, C*H*), 2.00−1.82 (om, 2H, CH_2), 1.80−1.64 (om, 2H, CH_2), 1.22−0.5 (om, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 68.65 (*C*H), 65.58 (*C*H), 50.75 (OCH_3), 32.55 (N*C*H_3), 29.55 (N*C*H_3), 28.56 (2*C*H_2), 23.53 (2*C*H_2).

9b-(*R,S*$_{al}$). (*R*)-*N,N*′-Dimethyl-1,1′-binaphthyl-2,2′-diamine (**3**-(*R*)) (0.5 g, 1.6 mmol) and freshly dried and distilled NEt_3 (1.78 mL, 12.8 mmol) were dissolved in 20 mL of toluene. PCl_3 (0.14 mL, 1.6 mmol) dissolved in 10 mL of toluene was added dropwise at 0 °C and stirred for 2 h. (*S*)-1-Borneol (0.25 g, 1.6 mmol) was added and stirred for 10 h at 0 °C. The white precipitate of triethylamine hydrochloride was filtered off after hexane addition (5 mL). The solvent was removed under reduced pressure, and a yellow solid was obtained. Yield: 0.65 g (83%); MS/ESI (+) (*m*/*z*) 495.2558 $[(MH)]^+$; $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −51.5; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 177.6 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.86−6.68 (om, 12H, Ar), 4.27 (m, 1H, *H*CO), 2.91 (d, J_{HP} = 13.6, 3H, NCH_3), 2.89 (d, J_{HP} = 9.6, 3H, NCH_3), 2.21 (m, 1H, CH_2), 1.82 (m, 1H, CH_2), 1.71−1.54 (om, 2H, 1CH_2, 1C*H*), 1.22−1.12 (om, 2H, CH_2), 0.81−0.77 (om, 10H, 1CH_2, 9CH_3); ^{13}C NMR, no data because of fast oxidation.

9b-(*R,R*$_{al}$). (*R*)-*N,N*′-Dimethyl-1,1′-binaphthyl-2,2′-diamine (**3**-(*R*)) (0.5 g, 1.6 mmol) and freshly dried and distilled NEt_3 (1.78 mL, 12.8 mmol) were dissolved in 10 mL of toluene. PCl_3 (0.28 mL, 3.2 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C and stirred for 2 h. The mixture was allowed to warm to room temperature and stirred overnight. After evaporation to dryness the solid was dissolved in 10 mL of toluene, and NEt_3 (24 mmol) and (*R*)-1-borneol (1.6 mmol) were added. The mixture was stirred for 2 h at 0 °C and 20 h at room temperature. After 20 min at 4 °C the formation of a white precipitate was observed and filtered off. The evaporation of the solvent under reduced pressure led to the formation of a yellow solid. Yield: 0.65 g (83%); MS/ESI (+) (*m*/*z*) 495.2554 $[(MH)]^+$; $[\alpha]^{298}$ (*c* 1.0, CH_2Cl_2) = −37.37; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 178.6 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.84−6.99 (om, 12H, Ar), 4.32 (m, 1H, *H*CO), 2.88 (d, J_{HP} = 12, 3H, NCH_3), 2.81 (d, J_{HP} = 8, 3H, NCH_3), 2.17 (m, 1H,

CH_2), 1.86 (m, 1H, CH_2), 1.63−1.49 (om, 2H, 1CH_2, 1CH), 1.20−1.00 (om, 3H, CH_2), 0.91 (s, 3H, CH_3), 0.82 (s, 3H, CH_3), 0.80 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) [δ/ppm] 128.24−121.54 (Ar), 81.78 (HCO), 44.91 (CH), 38.36 (NCH_3), 35.20 (NCH_3), 37.56 (CH_2), 28.12 (CH_2), 26.68 (CH_2), 20.12 (CH_3), 18.93 (CH_3), 13.68 (CH_3).

Selenides. General procedure: 0.15 mmol of ligand dissolved in 2 mL of toluene in the presence of 1.2 mmol of selenium powder was stirred for 2 h. Then the reaction mixture was filtered through Celite. The compounds were characterized by ^{31}P NMR (101 MHz) in toluene solution.

Synthesis of Palladium(II) Complexes. [$PdCl_2L_2$] (10). $PdCl_2$(cod) (0.29 g, 1.05 mmol) and 1 g (2.1 mmol) of ligand **7b-**(*R,R,S*$_{al}$) were dissolved in 20 mL of CH_2Cl_2 at room temperature. After 2 h stirring, the resulting yellow solution was concentrated under vacuum and 10 mL of ether was added. The yellow precipitate was filtered and dried. Yield: 0.98 g (83%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 91.84 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.63−7.09 (om, 20H, Ar), 4.96 (dt, J_{HH} = 16, J_{HP} = 6.8, 2H, CH_2), 4.85 (dt, J_{HH} = 16, J_{HP} = 6.4, 2H, CH_2), 4.58−4.81 (m, 2H, OCH), 4.40 (dt, J_{HH} = 16, J_{HP} = 6, 2H, CH_2), 4.08 (dt, J_{HH} = 16.4, J_{HP} = 2.4, 2H, CH_2), 3.20 (m, 2H, CH), 2.98 (m, 2H, CH), 2.27 (m, 1H, CH_2), 2.08 (m, 1H, CH_2), 1.76−0.86 (om, 28H, 26CH_2, 2CH), 0.85 (s, 6H, CH_3), 0.80 (s, 6H, CH_3), 0.79 (s, 6H, CH_3). Anal. Calcd for $C_{60}H_{82}Cl_2N_4O_2P_2Pd$ (%): C, 63.74; H, 7.31; N, 4.96. Found: C, 63.53; H, 7.59; N, 4.95.

[PdCl(η^3-2-$CH_3C_3H_4$)L] (11−14). The complexes were obtained by similar procedures described in the literature.[30]

For **11a-**(*R,R,R*$_{al}$), **11a-**(*S,S,S*$_{al}$), **11a-**(*R,R,S*$_{al}$), and **11a-**(*S,S,R*$_{al}$), 0.22 g (0.6 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ was dissolved in 5 mL of toluene and 0.5 g (1.1 mmol) of ligand **7a** dissolved in 5 mL of CH_2Cl_2 was added. The mixture was stirred at 0 °C for 2 h, and the solvent removed under reduced pressure. Addition of ether (10 mL) led to a brown solid. **11a-**(*R,R,R*$_{al}$): yield 0.48 g (67%). **11a-**(*S,S,S*$_{al}$): yield 0.43 g (60%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 126.7 (s), 126.2 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.50−7.03 (m, 30H, Ar), 5.27 (m, 1H, OCH), 5.21 (m, 1H, OCH), 4.95 (dd, J_{HH} = 15.2, J_{HP} = 12, 1H, CH_2), 4.83 (dd, J_{HH} = 15.2, J_{HP} = 12.4, 1H, CH_2), 4.34−4.21 (om, 3H, CH_2), 4.13 (pt, J_{HH} = J_{HP} = 16, 1H, CH_2), 3.80 (m, 1H, CH_2), 3.54 (dd, J_{HH} = 16 J_{HP} = 12, 1H, CH_2), 3.42 (d, J_{HP} = 14.4, 1H, CH_2), 3.37 (bs, 1H, CH_2), 3.25 (bs, 1H, CH_2), 3.09 (m, 2H, CH), 2.94 (d, J_{HP} = 14.4, 1H, CH_2), 2.92 (m, 1H, CH_2), 2.77 (m, 2H, CH), 2.52 (dd, J_{HH} = 16.4 J_{HP} = 6.4, 1H, CH_2), 2.43 (bs, 1H, CH_2), 2.08 (bs, 1H, CH_2), 1.86 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.14 (d, J_{HH} = 6.4, 3H, CH_3), 1.01 (d, J_{HH} = 6.4, 3H, CH_3), 1.63−0.71 (om, 16H, CH_2). Anal. Calcd for $C_{32}H_{40}ClN_2OPPd$ (%): C, 59.91; H, 6.28; N, 4.37. Found: C, 59.63; H, 6.71; N, 4.02. **11a-**(*R,R,S*$_{al}$): yield 0.24 g (34%). **11a-**(*S,S,R*$_{al}$): yield 0.17 g (24%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 130.7 (s), 130.0 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.44−6.96 (m, 30H, Ar), 5.64 (m, 1H, CH), 5.52 (m, 1H, CH), 4.65−4.55 (om, 2H, CH_2), 4.42−4.20 (om, 6H, CH_2), 3.79 (dd, J_{HH} = 16.0 J_{HP} = 8, 1H, CH_2), 3.70 (dd, J_{HH} = 16.8 J_{HP} = 5.6, 1H, CH_2), 3.32 (d, J_{HP} = 14.0, 1H, CH_2), 3.32 (bs, 1H, CH_2), 3.24 (bs, 1H, CH_2), 3.17 (d, J_{HP} = 14.0, 1H, CH_2), 3.08−2.94 (om, 4H, CH), 2.21 (bs, 2H, CH_2), 1.72 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.63−1.45 (om, 8H, CH_2), 1.45 (d, J_{HH} = 6.4, 6H, CH_3), 1.18−0.94 (om, 8H, CH_2). Anal. Calcd for $C_{32}H_{40}ClN_2OPPd$ (%): C, 59.91; H, 6.28; N, 4.37. Found: C, 59.63; H, 6.71; N, 4.02.

For **11b-**(*R,R,R*$_{al}$) and **11b-**(*R,R,S*$_{al}$), 1.90 g (4.0 mmol) of ligand **7b** dissolved in toluene (5 mL) was added to a solution of 0.78 g (2.0 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ in 5 mL of CH_2Cl_2. The mixture was stirred at 0 °C for 2 h, and the solution was dried under reduced pressure. The resulting orange residue was washed with pentane (3 × 20 mL), giving the desired product as an orange solid. **11b-**(*R,R,R*$_{al}$): yield 1.86 g (70%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 130.0 (s), 129.9 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.73−7.13 (m, 20H, Ar), 4.87 (dd, J_{HH} = 16 J_{HP} = 14, 1H, CH_2), 4.79 (dd, J_{HH} = 16, J_{HP} = 14, 1H, CH_2), 4.70 (m, 1H, HCO) 4.60−4.30 (om, 7H, 6CH_2, 1HCO), 4.04 (dd, J_{HH} = 15.6 J_{HP} = 10, 1H, CH_2), 3.87 (dd, J_{HH} = 16.4, J_{HP} = 5.6, 1H, CH_2), 3.48 (bs, 1H, CH_2), 3.48 (d, J_{HP} = 14, 1H, CH_2), 3.35 (bs, 1H, CH_2), 3.14 (d, J_{HP} = 14.8, 1H, CH_2), 3.18−2.94 (om, 4H, CH), 2.56 (m, 1H, CH_2), 2.24−2.18 (om, 3H, CH_2), 1.98−1.54 (om, 21H, 2CH, 13CH_2, 6CH_3), 1.3−0.98 (om, 31H, 13CH_2, 18CH_3). Anal. Calcd for $C_{34}H_{48}ClN_2OPPd$ (%): C, 60.63; H, 7.18; N, 4.16. Found: C, 60.92; H, 7.36; N, 4.38. **11b-**(*R,R,S*$_{al}$): 2.00 g, yield 75%; ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 133.5 (s), 131.2 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.62−7.18 (m, 20H, Ar), 4.98 (m, 1H, HCO), 4.82 (m, 2H, CH_2), 4.6−4.3 (om, 7H, 6CH_2, 1HCO), 4.05 (dd, J_{HH} = 16, J_{HP} = 8.4, 1H, CH_2), 3.70 (dd, J_{HH} = 16.4, J_{HP} = 5.4, 1H, CH_2), 3.44 (d, J_{HP} = 14, 1H, CH_2), 3.41 (bs, 1H, CH_2), 3.37 (bs, 1H, CH_2), 3.19 (d, J_{HP} = 14, 1H, CH_2), 3.10 (m, 2H, CH), 2.99 (m, 2H, CH), 2.39 (bs, 1H, CH_2), 2.28 (bs, 1H, CH_2), 2.25−1.41 (om, 22H, 14CH_2, 2CH, 6CH_3), 1.38−0.90 (om, 13H, CH_2), 0.91−0.82 (om, 19H, 1CH_2, 18CH_3). Anal. Calcd for $C_{34}H_{48}ClN_2OPPd$ (%): C, 60.63; H, 7.18; N, 4.16. Found: C, 59.58; H, 7.23; N, 3.89.

11c-(*R,R,S*$_{al}$) was synthesized in a similar way to that used for **11b**. Starting materials: 0.48 g (1.2 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$and 1.02 g (2.38 mmol) of ligand **7c-**(*R,R,S*$_{al}$). Yield: 1.07 g (72%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 134.3 (s), 133.9 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.55−7.15 (m, 20H, Ar), 5.09 (dq, J_{HP} = 12.4 J_{HH} = 6.4, 1H, CH), 4.94 (dq, J_{HP} = 12.4, J_{HH} = 6.4, 1H, CH), 4.74 (pt, J_{HP} = J_{HH} = 16.4, 2H, CH_2), 4.61−4.31 (om, 6H, CH_2), 4.19 (dd, J_{HP} = 16, J_{HH} = 9.6, 1H, CH_2), 4.04 (dd, J_{HP} = 16.4, J_{HH} = 6, 1H, CH_2), 3.63 (s, 3H, CH_3), 3.59 (s, 3H, CH_3), 3.52 (bs, 2H, CH_2), 3.44 (d, J_{HP} = 14, 1H, CH_2), 3.25 (d, J_{HP} = 14.4, 1H, CH_2), 3.11−3.03 (m, 4H, CH), 2.52 (bs, 1H, CH_2), 2.31 (bs, CH_2), 1.83−1.50 (om, 14H, 6CH_3, 8CH_2), 1.38 (d, J_{HH} = 6.8, 6H, CH_3), 1.25−1.04 (om, 8H, CH_2). Anal. Calcd for $C_{28}H_{38}ClN_2O_3PPd$ (%): C, 55.36; H, 6.31; N, 4.61. Found: C, 53.11; H, 6.44; N, 4.57.

11d-(*R,R*) was synthesized in a similar way to that used for **11b**. Starting materials: 0.42 g (1.05 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ and 0.82 g (2.16 mmol) of ligand **7d-**(*R,R*). Yield: 0.27 g (44%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 129.0 (s), 128.6 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.48−7.13 (om, 20H, Ar), 5.13−5.05 (om, 4H, CH_2), 4.81−4.66 (om, 2H, CH_2), 4.44−4.38 (om, 8H, CH_2), 3.32 (m, 1H, CH_2), 3.17−3.14 (om, 3H, 2CH, 1CH_2), 3.01−2.98 (om, 4H, 2CH, 2CH_2), 2.18 (bs, 2H, CH_2), 2.04 (bs, 2H, CH_2), 1.76 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.86−1.08 (om, 16H, CH_2); MS/ESI (+) (m/z) 541.1601 [(M − Cl)]$^+$. Anal. Calcd for $C_{27}H_{36}ClN_2OPPd$ (%): C, 56.16; H, 6.28; N, 4.86. Found: C, 56.35; H, 6.69; N, 5.10.

11f-(*R,R*) was synthesized in a similar way to that used for **11b** and precipitated in ether. Starting materials: 0.41 g (1.05 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ and 0.84 g (2.09 mmol) of ligand **7f-**(*R,R*). Yield: 0.31 g (51%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 120.0 (s), 118.2 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.66−7.13 (om, 30H, Ar), 4.80 (pq, J_{HP} = J_{HH} = 15.6, 2H, CH_2), 4.52−5.37 (om, 4H, CH_2), 4.29 (pt, J_{HP} = J_{HH} = 14, 1H, CH_2), 4.19 (pt, J_{HP} = J_{HH} = 14, 1H, CH_2), 3.71 (dd, J_{HH} = 15.2 J_{HH} = 9.6, 1H, CH_2), 3.47 (m, 1H, CH_2), 3.35 (d, J_{HP} = 11.6, 1H, CH_2), 3.31 (d, J_{HP} = 12, 1H, CH_2), 3.19 (m, 1H, CH), 3.06 (m, 1H, CH), 2.94 (bs, 1H, CH_2), 2.86 (bs, 1H, CH_2), 2.81 (m, 1H, CH), 2.72 (m, 1H, CH), 2.10 (bs, 1H, CH_2), 2.00 (bs, 1H, CH_2), 1.78 (bs, 6H, CH_3), 1.73−1.08 (om, 16H, CH_2); MS/ESI (+) (m/z) 561.1726 [(M − Cl)]$^+$. Anal. Calcd for $C_{30}H_{36}ClN_2PPd$ (%): C, 60.31; H, 6.07; N, 4.69. Found: C, 57.26; H, 5.77; N, 4.12.

12b-(*R,R,S*$_{al}$) was synthesized in a similar way to that used for **11b** Starting materials: 0.75 g (1.9 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ and 1.24 g (3.8 mmol) of ligand **8b-**(*R,R,S*$_{al}$). Yield: 1.39 g (70%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm]

128.5(s), 127.6(s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 4.36 (m, 2H, CH_2), 4.11 (m, 2H, OCH), 3.54 (bs, 1H, CH_2), 3.51 (bs, 1H, CH_2), 3.49 (d, J_{HP} = 14.8, 1H, CH_2), 3.38 (d, J_{HP} = 14.8, 1H, CH_2), 2.81−2.59 (om, 18H, 12NCH_3, 4CH, 2CH_2), 2.24 (m, 2H, CH_2), 2.05−1.57 (om, 20H, 12CH_2, 2CH, 6CH_3), 1.35−0.95 (om, 14H, CH_2), 0.89−0.86 (om, 18H, CH_3). Anal. Calcd for $C_{22}H_{40}ClN_2OPPd$ (%): C, 50.58; H, 7.73; N, 5.37. Found: C, 50.35; H, 7.74; N, 5.18.

12e-(*R,R*) was synthesized in a similar way to that used for **11b**. Starting materials: 1.04 g (2.7 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ and 1.04 g (2.7 mmol) of ligand **8e**-(*R,R*). The complex was obtained as an orange oil. Yield: 0.78 g (30%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 131.7(s), 131.3(s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 4.41 (s, 1H, CH_2), 4.39 (s, 1H, CH_2), 3.51−3.43 (om, 10H, 4CH_2, 6OCH_3), 2.90−2.50 (om, 18H, 2CH_2, 4CH, 12NCH_3), 2.07−1.73 (om, 14H, 6CH_3, 8CH_2), 1.39−0.90 (om, 8H, CH_2); MS/ESI (+) (*m*/*z*) 363.0817 [(M − Cl)]$^+$.

13b-(*R,R*$_{al}$) and **13b-**(*R,S*$_{al}$) were obtained in a similar way to that used for **11b** and precipitated in toluene/hexane. Starting materials: 0.31 g (0.8 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ and 0.79 g (1.6 mmol) of ligand **8b**. **13b**-(*R,R*$_{al}$): yield 0.72 g (65%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 151.8 (s), 150.7 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.96−7.11 (om, 24H, Ar), 5.22 (m, 1H, OCH), 5.13 (m, 1H, OCH), 4.54 (dd, J_{HH} = 9.2 J_{HP} = 3.3, 1H, CH_2), 4.45 (dd, J_{HH} = 9.6 J_{HP} = 3.2, 1H, CH_2), 3.60 (d, J_{HP} = 12.4, 1H, CH_2), 3.59 (d, J_{HP} = 12.4, 1H, CH_2), 3.47 (bs, CH_2), 3.37 (bs, CH_2), 3.17 (d, J_{HP} = 13.2, 3H, NCH_3), 3.10 (d, J_{HP} = 13.6, 3H, NCH_3), 3.08 (d, J_{HP} = 9.2, 3H, NCH_3), 3.07 (d, J_{HP} = 8.8, 3H, NCH_3), 2.65 (m, 1H, CH_2), 2.54 (1H, CH_2), 2.46 (bs, 1H, CH_2), 2.38 (bs, 1H, CH_2), 1.92 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.81−1.60 (om, 5H, 2CH, 3CH_2), 1.30−1.09 (om, 7H, 7CH_2), 0.98 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 0.85 (s, 3H, CH_3); MS/ESI (+) (*m*/*z*) 655.2068 [(M − Cl)]$^+$. Anal. Calcd for $C_{36}H_{42}ClN_2OPPd$ (%): C, 62.52; H, 6.12; N, 4.05. Found: C, 63.31; H, 7.23; N, 3.92. **13b-**(*R,S*$_{al}$): yield 0.39 g (36%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 152.1 (s), 151.9 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.9−7.0 (om, 24H, Ar), 5.32 (m, 2H, OCH), 4.45 (d, J_{HP} = 10.8, 1H, CH_2), 4.39 (d, J_{HP} = 9.2, 1H, CH_2), 3.53 (d, J_{HP} = 10.0, 1H, CH_2), 3.51 (d, J_{HP} = 13.2, 1H, CH_2), 3.36 (s, CH_2), 3.20 (s, CH_2), 3.11 (d, J_{HP} = 13.6, 3H, NCH_3), 3.05 (d, J_{HP} = 9.6, 3H, NCH_3), 3.03 (d, J_{HP} = 14.4, 3H, NCH_3), 3.02 (d, J_{HP} = 8.8, 3H, NCH_3), 2.39 (s, 1H, CH_2), 2.31 (s, 1H, CH_2), 2.34−2.30 (om, 2H, CH_2), 1.85 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.74−1.55 (om, 6H, 2CH, 4CH_2), 1.23−1.02 (om, 6H, CH_2), 0.89−0.76 (om, 18H, CH_3). Anal. Calcd for $C_{36}H_{42}ClN_2OPPd$ (%): C, 62.52; H, 6.12; N, 4.05. Found: C, 62.56; H, 6.79; N, 4.15.

13e-(*R*) was synthesized in a similar way to that used for **11b**. Starting materials: 0.11 g (0.3 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)(μ-Cl)]$_2$ and 0.2 g (0.6 mmol) of ligand **9e**-(*R*). Yield: 0.09 g (31%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 152.6 (s), 152.2 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 7.91−6.98 (om, 24H, Ar), 4.42 (m, 2H, CH_2), 3.51−3.49 (om, 8H, 6OCH_3, 2CH_2), 3.16 (d, J_{HP} = 13.5, 6H, NCH_3), 3.07−3.02 (om, 7H, 6NCH_3, 1CH_2), 2.92 (s, 1H, CH_2), 2.31 (s, 1H, CH_2), 2.26 (s, 1H, CH_2), 1.87 (s, 3H, CH_3), 1.77(s, 3H, CH_3). Anal. Calcd for $C_{27}H_{28}ClN_2OPPd$ (%): C, 56.96; H, 5.68; N, 4.15. Found: C, 56.22; H, 5.68; N, 4.15.

14-(*S*) was synthesized in a similar way to that used for **11b**. Starting materials: 0.10 g (0.25 mmol) of [Pd(η^3-2-$CH_3C_3H_4$)-(μ-Cl)]$_2$ and 0.18 g (0.5 mmol) of ligand Binepine-(*S*). Yield: 0.1 g (38%); ^{31}P NMR (toluene, 101 MHz) [δ/ppm] 40.32 (s), 39.79 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) [δ/ppm] 8.07−7.01 (om, 34H, Ar), 4.48 (m, 2H, CH_2), 3.82 (d, J_{HH} = 12.5, 1H, CH_2), 3.70 (d, J_{HH} = 12, 1H, CH_2), 3.57 (bs, 1H, CH_2), 3.48 (d, J_{HH} = 10, 1H, CH_2), 3.47 (d, J_{HH} = 10.5, 1H, CH_2), 3.39−3.19 (om, 6H, CH_2), 3.32 (bs, 1H, CH_2), 2.83 (s, 1H, CH_2), 2.46 (s, 1H, CH_2), 2.01 (s, 3H, CH_3), 1.78 (s, 3H, CH_3); MS/ESI (+) (*m*/*z*) 590.1229 [(M − Cl + (CH_3CN)]$^+$. Anal. Calcd for $C_{32}H_{28}ClPPd$ (%): C, 65.66; H, 4.82. Found: C, 67.32; H, 5.18.

Table 5. Crystal Data and Structure Refinement for 11a-(*S,S,S*$_{al}$)

empirical formula	$C_{32}H_{40}ClN_2OPPd$	
fw	641.48	
temperature	100(2) K	
wavelength	0.71073 Å	
cryst syst	monoclinic	
space group	$P2_1$	
unit cell dimens	a = 9.9272(2) Å	α = 90°
	b = 14.8544(5) Å	β = 104.707(2)°
	c = 10.7168(3) Å	γ = 90°
volume	1528.55(7) Å^3	
Z	2	
density (calcd)	1.394 Mg/m^3	
absorp coeff	0.774 mm^{-1}	
F(000)	664	
cryst size	0.37 × 0.17 × 0.07 mm	
θ range for data collection	1.96 to 30.03°	
reflns collected	33 806	
indep reflns	8899 [R(int) = 0.0399]	
completeness to θ = 30.03°	100.0%	
absorp correction	semiempirical from equivalents	
max. and min transmn	1.0000 and 0.8487	
refinement method	full-matrix least-squares on F^2	
data/restraints/params	8899/1/358	
goodness-of-fit on F^2	1.032	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0293, wR2 = 0.0609	
R indices (all data)	R1 = 0.0333, wR2 = 0.0629	
abs struct param	0.000(15)	
largest diff peak and hole	0.731 and −0.615 e Å^{-3}	

Structural Characterization. Suitable crystals of [PdCl(η^3-2-$CH_3C_3H_4$)**7a**-(*S,S,S*$_{al}$)] (**11a**-(*S,S,S*$_{al}$)) for X-ray characterization were mounted on a Bruker X8 Kappa APEXII diffractometer. The data were collected at 100 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). SHELXTL software was used for solution and refinement.[46] Absortion corrections were made with the SADABS program.[47] The structure was refined by full-matrix least-squares on F^2. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 795003.

Hydrovinylation Reaction. General Procedure. 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 was controlled with a thermocouple, and pressure was controlled with a transductor. The catalyst precursor solution was placed in the autoclave, which had previously been purged by succesive vacuum/nitrogen cycles and thermostated at 15 °C. 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 mL) was added. The mixture was stirred 30 min in order to quench the catalyst. The CH_2Cl_2 layer was decanted off, filtered through Celite and dried with Na_2SO_4. The quantitative distribution of products and their enantiomeric excess were determined by GC analysis.

(46) Sheldrick, G. M. *SHELXS 97: A Computer Program for Crystal Structure Determination*; University of Göttingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXS 97: A Computer Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997

(47) Sheldrick, G. M. *SADABS: A Program for Empirical Absortion Correction of Area Detector Data*; University of Göttingen: Geramny, 1996. Based on the method of Robert Blessing: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

Preparation of Catalyst Precursor Solutions. To 0.03 mmol of the appropiate neutral palladium complex (**11**−**14**) dissolved in 10 mL of CH_2Cl_2 were added 3.45 mL (30 mmol) of styrene and 35.1 mg (0.18 mmol) of $AgBF_4$. After stirring in the dark at room temprature for 30 min and filtering off the AgCl formed, the resulting solution was introduced in the reactor.

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Supporting Information Available: NMR data for complexes **11**−**14**. CIF file of complex **11a-**(S,S,S_{al}). This material is available free of charge via the Internet at http://pubs.acs.org.