Palladium(II) Complexes of Chiral 1,2-Diiminophosphoranes: Synthesis, Structural Characterization, and Catalytic Activity for the Allylic Alkylation

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Chiral 1,2-bis[tris(dimethylamino)phosphinimino]cyclohexane (**7a**, 80% yield), 1,2-bis[tris-(dimethylamino)phosphinimino]-1,2-diphenylethane (**7b**, 74% yield), 1,2-bis[triphenoxyphosphinimino]cyclohexane (**9a**, 85% yield), and 1,2-bis[triphenoxyphosphinimino]-1,2-diphenylethane (**9b**, 70% yield) have been prepared using (1*R*,2*R*)-1,2-diaminocyclohexane or (1*R*,2*R*)-1,2-diphenylethylenediamine and the corresponding phosphine dibromide derivatives (the Kirsanov route). 1,2-Bis[triphenylphosphinimino]cyclohexane (**2**), 1,2-bis[triphenylphosphinimino]-1,2-diphenylethane (**3**), and 1,2-diiminophosphoranes **7b** and **9b** reacted with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in the presence of a silver salt in CH_2Cl_2 at room temperature to afford the cationic complexes **10** (81% yield), **11** (84% yields), **15** (78% yield), and **16** (74% yield), respectively. According to the same general procedure, palladium complexes [(η^3-PhCHCHCHPh)(**2**)Pd]TfO (**13**, 88% yield) and [(η^3-PhCHCHCHPh)(**3**)Pd]TfO (**14**, 86% yield) have been prepared. Single-crystal X-ray diffraction studies of derivatives **10**, **11**, and **13** have been carried out. They revealed that C_2 symmetry was retained for derivative **3** upon coordination, but lost for **2** in the coordination sphere of the metal. ^{13}C NMR chemical shifts for the terminal C atoms of the allyl moiety of these complexes indicate that the donor ability of 1,2-diiminophosphoranes varies with the nature of the P-substituents and is comparable to that of other sp^2-hybridized nitrogen ligands. 1,2-Diiminophosphoranes were evaluated as ligands for the Pd-catalyzed enantioselective allylic substitution reaction of *rac*-1,3-diphenylprop-2-enyl acetate with the anion of dimethyl malonate. Ligands **3** and **7a**,**b** induce good catalytic activities compared with other N,N-ligands but moderate ee's (10−77%) at 36 °C. Higher ee's (85%) were obtained at room temperature with ligand **3** but at the expense of the catalytic activity. This study revealed that 1,2-diimonophosphoranes are able to stabilize Pd(0) species during a catalytic process and to induce notable levels of enantioselectivity.

Introduction

In recent years, optically active bidentate donor species containing sp^2-hybridized nitrogen atoms have attracted much attention as ligands for transition-metal-catalyzed asymmetric transformations.[1] For example, enantiomerically pure C_2-symmetric bis-oxazolines have afforded high levels of enantioselectivity in a number of asymmetric processes such as the Diels−Alder[2a] or the Mukaiayma[2b] reactions and in two important palladium-catalyzed processes, namely allylic alkylation[2c−e] and alternating copolymerization of substituted styrenes with CO.[2f]

Iminophosphoranes (phosphazenes), compounds with the general structure $R_3P{=}N{-}R$, date back to 1919,[3a] but their chemistry has only really been explored in the last three decades. They have found numerous applications, which include their use as ylides in organic synthesis (aza-Wittig reaction) or as building blocks for P−N-backbone polymers (polyphosphazenes).[3] Iminophosphoranes possess a highly polarized P=N bond and have been shown to coordinate to transition metals via the approximately sp^2-hybridized nitrogen atom to give stable complexes.[3,4] In recent years, the most studied ligands incorporating the iminophosphorane moiety have been the homobidentate and heterobidentate derivatives **A**−**D** (Scheme 1). To the best of our knowl-

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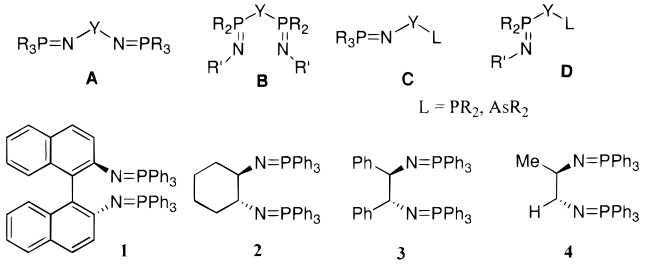
Scheme 1



edge, before 1998,[5] there has been only one report of transition metal complexes of bis-iminophosphoranes **A** (Scheme 1, Y = $-CH_2-CH_2-$).[6a] In contrast, derivatives of type **B** have been studied in depth, with bis(iminophosphoranyl)methane derivatives (Y = CH_2, CHLi, C:) proving to be versatile ligands.[6b−f] Another class of well-studied ligands are difunctional compounds **C** and **D** that contain a second donor site, which, in most cases, is a phosphino group.[6g−q] These heteroatomic donor ligands possess both "hard" nitrogen and "soft" phosphorus(III) centers. Quite surprisingly, iminophosphorane-containing species have received very little attention as ligands for homogeneous catalysis[5a,7] probably because they are believed to be relatively hard donors capable only of stabilizing metals in medium to high oxidation states.

Our research has focused on the synthesis of chiral 1,2-diiminophosphoranes of type **A** possessing a chiral backbone as ligands for asymmetric catalysis. We anticipated that these 1,2-diiminophosphoranes should act as tightly binding chelates and thus would be capable of stabilizing metal centers involved in catalytic cycles, even in rather low oxidation states. Furthermore, chelating ligands are supposed to accomplish higher optical inductions in asymmetric reactions. The ability to access a series of related ligands possessing various steric and electronic properties is often a key factor in their selection for catalytic applications. From a design standpoint, strategic variations of both the steric and electronic properties of derivatives **A** can be envisaged by changing either the substituents at phosphorus or the nature of the carbon backbone.

The first examples of chiral derivatives **A** have recently been reported by Reetz and co-workers[5a] (Scheme 1, compounds **1**, **2**) and by our group[5b] (compounds **2**−**4**). In this paper, the syntheses of new chiral 1,2-diiminophosphoranes containing various P-substituents are described. The coordination behavior of 1,2-diiminophosphoranes toward cationic (allylic)Pd(II) moieties and their first application in palladium-catalyzed allylic alkylation, a classical and useful carbon−carbon bond forming process involving both Pd(II) and Pd(0) complexes,[8] are presented.

Results and Discussion

Synthesis of New Chiral 1,2-Diiminophosphoranes. The steric demand of derivatives **A** should be directly influenced by the nature of the carbon backbone (cyclic versus acyclic, bulkiness of the substituents) and the steric hindrance of the P-substituents. The P-substituents will also concurrently influence the electronic properties of ligands **A** since it is well-known that their nature has a significant influence on the basicity of these ylides.[3b−d] For example, Schwesinger has shown that the basicity of certain P-amino-substituted iminophosphoranes is nearly 10^4 times stronger than DBU [1,8-diazabicyclo[5.4.0]undec-7-ene, pK_a(CH_3CN) = 24],[9a,b] whereas P-alkoxy-substituted iminophosphoranes are weaker bases than Et_3N.[9c] Thus, in the present study, these two types of P-substituents were selected with the goal of obtaining ligands possessing very different electronic properties.

Iminophosphoranes are best prepared through one of two major routes, namely the reaction of azides with phosphines (the Staudinger reaction) and the reaction of phosphine dibromides with amines followed by treatment with a base (the Kirsanov reaction).[3b,c] We selected this second route, which has previously been used to prepare 1,2-diiminophosphoranes **1**−**4**,[5] since it avoids the use of hazardous azides and since optically active 1,2-diamines[10] are now readily accessible.

Optically active diamines **5a**,**b** reacted slowly with 2 equiv of $Br_2P(NMe_2)_3$, in neat triethylamine at room temperature, to give the corresponding diphosphonium salts **6a**,**b** along with 2 equiv of triethylammonium bromide (Scheme 2). Compounds **6a**,**b** were character-

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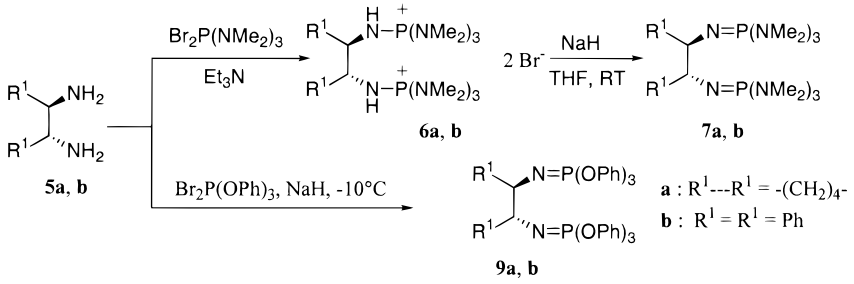
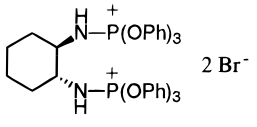
Scheme 2



ized in solution by multinuclear NMR spectroscopy and high-resolution FAB mass spectrometry. Their ^{31}P NMR chemical shifts are typical for tetrakisaminophosphonium salts[11] (**6a**, +38.7; **6b**, +39.7), and according to NMR spectroscopy, they were obtained in almost quantitative yields. Note that these derivatives are air-stable and can be stored for weeks. No purification is needed prior to carrying out the subsequent deprotonation step. Indeed, addition at room temperature of an excess of NaH to THF solutions of crude **6a** and **6b** gave rise to the corresponding 1,2-diiminophosphazenes **7a** and **7b**, which were isolated, after purification, in 80% and 74% overall yields, respectively. As usually observed,[3b,11] their ^{31}P chemical shifts appeared at lower field than those of the corresponding phosphonium salts ($\Delta\delta$: **6a**/**7a**, 24.6 ppm; **6b**/**7b**, 19.8 ppm). The simplicity of the ^{13}C NMR spectra of **7a**,**b** is in favor of symmetric structures; the PN*C*H resonances appear as doublets (**7a**, 58.25, J_{PC} = 18.0 Hz; **7b**, 67.94, J_{PC} = 25.0 Hz) with P−C coupling constants significantly superior to those observed for the corresponding phosphonium salts (**6a**, 55.51, J_{PC} = 11.7 Hz; **6b**, 63.10, J_{PC} = 11.0 Hz). Derivatives **7a**,**b** have been characterized by high-resolution mass spectrometry and gave satisfactory elemental analyses.

These new chiral phosphazenes can be kept under an inert atmosphere at room temperature for weeks. In marked contrast, the related P-phenoxy-substituted derivatives **9a**,**b** prepared according to the same route (Scheme 2) are extremely air- and water-sensitive. They decomposed rapidly in THF or CH_2Cl_2 solutions, giving rise to complicated mixtures of products according to ^{31}P NMR spectroscopy. Only the 1,6-diphosphonium salt **8a** and 1,2-diiminophosphorane **9a** (80% yield) (Scheme 2) possessing the cyclohexyl skeleton are stable enough to be fully characterized by multinuclear NMR spectroscopy in solution; derivative **8a** was also characterized by high-resolution mass spectrometry.



8a

As expected, these P-phenoxy derivatives give ^{31}P NMR signals at rather high field, the 1,2-diiminophosphorane being the most shielded (**8a**, −0.9; **9a**, −36.7). Once again, in the ^{13}C NMR spectra, the PN*C*H resonances appear as doublets with a larger coupling constant for the phosphazene **9a** compared with the phosphonium salt **8a** (**8a**, 57.81, J_{PC} = 10.9 Hz; **9a**, 58.81, J_{PC} = 15.6 Hz). Derivative **9b** is highly unstable, it has been observed only by ^{31}P NMR spectroscopy (−35.2 ppm) in the free state, but has been fully characterized following its coordination to a Pd(II) center (vide infra, complex **16**). The target ligands **9a**,**b** are best prepared in a "one-pot" procedure using NaH with neither isolation nor purification of the intermediate diphosphonium salts (Scheme 2). This method allows derivatives **9a** and **9b** to be obtained in 85% (isolated) and 70% (according to ^{31}P NMR spectroscopy) yields, respectively.

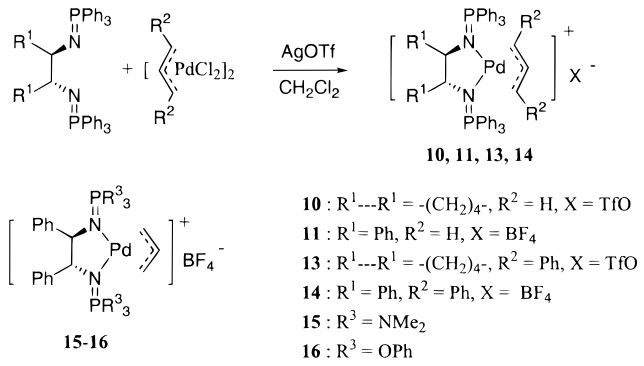
Complex Formation and Crystal Structures. The enantioselective palladium-catalyzed alkylation of allylic acetates is a powerful synthetic tool for the enantioselective construction of carbon−carbon or carbon−heteroatom bonds and has proved to be a useful testing ground for the evaluation and design of new ligands.[2c−d,8] The generally accepted mechanism with "soft" nucleophiles such as stabilized carbanions involves a Pd(0) species which is thought to displace the allylic leaving group to give a cationic [Pd(II)(η^3-allyl)] complex. This species is then subjected to a nucleophilic attack resulting in the formation of the organic substitution product with concomitant regeneration of the catalytically active Pd(0) species.[2c−d,8] As a result, this reaction was selected in order to evaluate the ability of 1,2-diiminophosphoranes to stabilize the reduced transition metal intermediates formed during the catalytic cycle and also to access the efficiency of these ligands at inducing a certain degree of enantioselectivity. Thus, with this in mind, it was first of primary interest to elucidate the coordination behavior of 1,2-diiminophosphoranes toward cationic (allylic)palladium fragments.

The study of the coordination chemistry of 1,2-diiminophosphoranes is practically a virgin area. Solid-state structures are known for only three complexes featuring **2** as a ligand [**2**·Rh(cod)$^+$,[5a] **2**·$CoCl_2$,[5a] and **2**·$PdCl_2$[5b]]. These studies have revealed that derivative **2** always loses its C_2 symmetry upon coordination. It is quite clear that this surprising behavior could strongly influence the chirality transfer during catalytic processes. This poses the important question: to what extent does the nature of the carbon backbone of 1,2-diiminophosphoranes influence the loss of C_2 symmetry in the coordination sphere of a metal? To probe this influence, complexes were prepared using derivatives **2** and **3**, which are the most easily accessible ligands.

Complexes **10** and **11** were obtained using a standard procedure from the corresponding dimeric bridged palladium chloride complex via abstraction of the Cl ligand in CH_2Cl_2 at room temperature by a silver salt in the presence of a slight excess of the 1,2-diiminophospho-

(11) *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; CRC Press Inc.: Boca Raton, 1991.

Scheme 3



rane (Scheme 3). The trifluoromethanesulfonate (TfO^-) and tetrafluoroborate (BF_4^-) salts were isolated in 81% and 84% yields, respectively, after purification by column chromatography on silica gel or by crystallization. It is noteworthy that, in contrast to the free ligands **2** and **3**, these complexes are air- and moisture-stable.

The ^{31}P NMR spectra of complexes **10** and **11** consisted of two sharp lines (**10**, +25.6, +26.5; **11**, +34.0, +35.1) and revealed a large coordination shift effect ($\Delta\delta$ = 25−35 ppm) similar to those observed for other iminophosphoranes.[5,6] According to ^{13}C NMR spectroscopy, all the carbon atoms of the phosphazene skeleton in both complexes are inequivalent. The presence of two phosphorus centers was clearly indicated by the multiplicity of the NCH resonances which appeared as doublets of doublets in the ^{13}C NMR spectra (complex **10**: 67.42, J_{PC} = 14.1 and 3.0 Hz; 68.55, J_{PC} = 14.9 and 3.1 Hz) or in the ^1H NMR spectra (complex **11**: 4.04, J_{PH} = 16.3 and 3.6 Hz; 4.14, J_{PH} = 16.3 and 3.6 Hz). No fluxional behavior of complexes **10** and **11** was observed between room temperature and −80 °C in CD_2Cl_2 solutions, although a rapid apparent rotation of the allyl ligand is very likely.[12] The CH_2 protons from the allylic ligands of complexes **10** and **11** (H_{anti}, 1.12−2.23; H_{syn}, 2.22−2.86) are notably more shielded than in the related cationic η^3-allylic palladium complexes,[12] this effect being more pronounced for the H_{anti} atoms. It is quite likely that these unusual ^1H NMR chemical shifts are due to the anisotropic field provided by the phenyl groups of the $-N{=}PPh_3$ moieties.

The crystal structures of the trifluoromethanesulfonate complex **10** (Figure 1, Table 1) and tetrafluoroborate complex **11** (Figure 2, Table 1) were determined by X-ray crystallographic analyses at room temperature (Table 2). Both structures gave relatively high weighted *R* values (**10**, 0.0802; **11**, 0.0911), and the allyl ligands are disordered, with the central atom occupying two positions. This type of disorder is quite common. For example, it has been observed by high-quality X-ray diffraction studies (weighted *R* values of less than 2%) performed on related cationic palladium complexes featuring bis-oxazoline ligands.[12a]

As expected, these new complexes show a slightly distorted square-planar geometry around the palladium atoms. The maximum deviations from the best plane

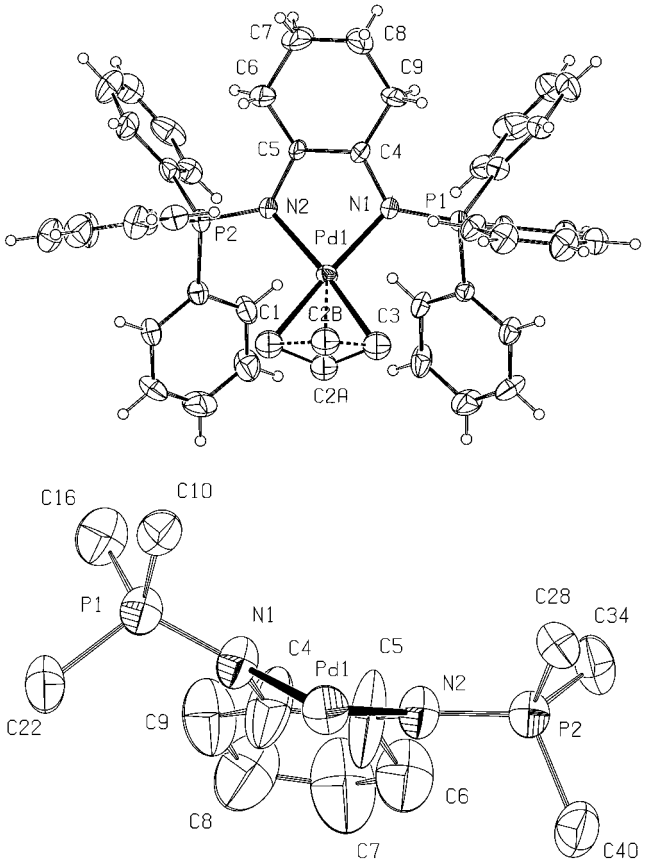


Figure 1. ORTEP drawing (thermal ellipsoid 40% probability) of the cation of complex **10**: (top) general view *a*, (bottom) view *b* along the N(1)−Pd−N(2) axis.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 10, 11, and 13

	10	**11**	**13**
Pd(1)−N(1)	2.127(7)	2.112(12)	2.133(3)
Pd(1)−N(2)	2.119(7)	2.097(12)	2.161(3)
Pd(1)−C(1)	2.146(11)	2.17(3)	2.136(4)
Pd(1)−C(2a)	2.117(15)	2.09(3)	2.109(4)
Pd(1)−C(2b)	2.12(4)	2.02(5)	-
Pd(1)−C(3)	2.129(11)	2.14(2)	2.203(4)
N(1)−C(4)	1.446(11)	1.452(19)	1.480(5)
C(5)−N(2)	1.465(11)	1.50(2)	1.472(5)
N(1)−P(1)	1.593(7)	1.584(13)	1.593(3)
N(2)−P(2)	1.595(7)	1.585(13)	1.582(3)
N(1)−Pd(1)−C(3)	107.3(4)	108.0(7)	103.05(14)
C(3)−Pd(1)−C(1)	68.2(4)	67.4(9)	68.41(17)
C(1)−Pd(1)−N(2)	105.4(3)	103.8(8)	112.56(15)
N(2)−Pd(1)−N(1)	79.0(3)	81.0(4)	76.97(12)
Pd(1)−N(1)−C(4)	106.7(6)	111.4(9)	110.4(2)
N(1)−C(4)−C(5)	115.9(8)	109.7(13)	108.2(3)
C(4)−C(5)−N(2)	114.9(8)	108.1(14)	108.1(3)
C(5)−N(2)−Pd(1)	110.4(5)	111.1(9)	96.9(2)
P(1)−N(1)−Pd(1)	123.0(4)	126.7(7)	125.58(17)
P(1)−N(1)−C(4)	128.3(6)	121.7(10)	119.6(2)
P(2)−N(2)−Pd(1)	123.0(4)	125.4(6)	132.1(2)
P(2)−N(2)−C(5)	126.5(6)	122.6(10)	130.4(3)

defined by Pd, the two N-atoms of the phosphazene moieties, and the two terminal allylic C atoms are 0.027 Å for **10** and 0.055 Å for **11**. The bond lengths and bond angles of the (η^3-C_3H_5)Pd cores are consistent with known literature values for palladium complexes involving π-allyl ligands.[12a,13] The Pd−C allylic terminal bond length differences are not significant (Δ = 0.03 Å), given the rather large experimental uncertainties characteristic of these values in the present study (0.011 Å).

(12) (a) von Matt, P.; Lloyd-Jones G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (b) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067. (c) Sprinz, J.; Kiefer, M.; Helmchem, H.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523.

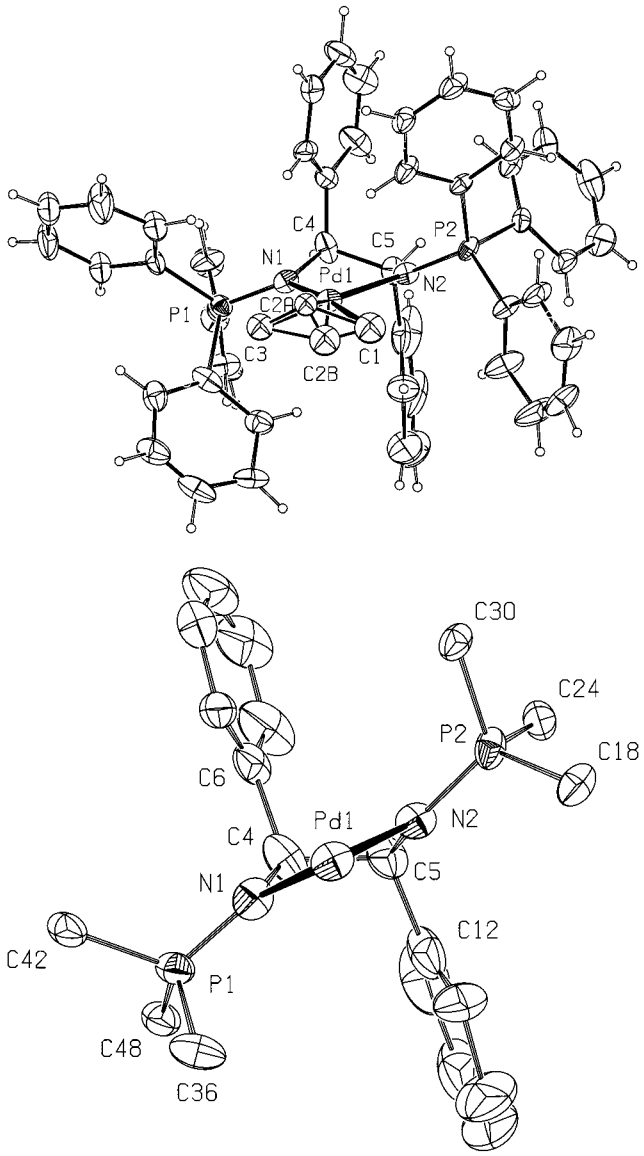
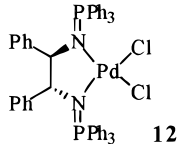


Figure 2. ORTEP drawing (thermal ellipsoid 40% probability) of the cation of complex **11**: (top) general view *a*, (bottom) view *b* along the N(1)−Pd−N(2) axis.

In both cases, the Pd-coordinated nitrogen atoms are almost planar (sum of angles around N atoms > 358°) and the P−N distances [1.595(7)−1.584(13) Å] are short but normal values for coordinated iminophosphoranes.[6b−r] The N(1)−Pd-N(2) angles [**10**, 79.0(3)°; **11**, 81.0(4)°] and the N−Pd bond lengths [2.097(12)−2.127(7) Å] are very similar for both derivatives and are consistent with those recorded for other chelating nitrogen donor ligands forming five- or six-membered metallacycles such as alkaloid-sparteine [86.1(5)°; 2.14(1)−2.16(1) Å],[14] bipyridine [78.67(10)°; 2.085(2)−2.089(3) Å],[13a] and bisoxazolines [84−87°; 2.075(3), 2.099(3) Å],[12a] respectively. The C−N bond lengths [1.44−1.50 Å] are also typical. These data as a whole clearly indicate that the five-membered metallacycles of complexes **10** and **11** are strain-free. The only dramatic difference between the two structures is the conformation of the five-membered metallacycles and the relative positions of the two phosphorus moieties. For complex **10**, the C(4), C(5), N(2), and Pd atoms lie almost in the same plane [maximum deviation, 0.04 Å], with the N(1) atom being out of this plane [Pd−N(1)−C(4)−C(5), 37.2(13)°; N(2)−Pd−N(1)−C(4), −31.4(7)°]. As already observed for other complexes of **2**,[5a,b] the five-membered metallacycle of complex **10** adopts a slightly distorted envelope conformation, with the two phosphino groups in a mutually cis configuration (Figure 1, view b). These structural features induce a loss of the C_2 symmetry for ligand **2**. In marked contrast, the five-membered metallacycle of complex **11** adopts a half-chair conformation [C(4)−C(5)−N(2)−Pd, 35.7(16)°; C(5)−C(4)−N(1)−Pd, 37.4(18)°], with the two phosphino groups in a mutually trans configuration (Figure 2, view b); ligand **3** retains its C_2 symmetry in the coordination sphere of the metal.

The loss of C_2 symmetry for 1,2-diiminophosphorane **2** upon coordination is now quite well established. It has been observed in the solid state with various transition metals (Co,[5a] Rh,[5a] Pd[5b]) and in solution for the complex **2**−$PdCl_2$ (^{31}P NMR: +29.5 and +32.5; according to ^{13}C NMR spectroscopy, all the C atoms are inequivalent).[5b] The NMR spectra of complex **11** are not temperature-dependent between −80 and +50 °C, suggesting that no dynamic behavior of the five-membered metallacycle occurs over this temperature range. Furthermore, complex **12**, which is easily obtained in 91% yield by reacting 1,2-diiminophosphorane **3** with $(CH_3CN)_2PdCl_2$ at room temperature, possesses a C_2 symmetry in solution. It showed only one resonance by ^{31}P NMR spectroscopy (+36.6), and the NCHPh moieties gave only one set of signals in the ^{1}H (3.45, dd, J_{H-P} = 13.6 and 6.9 Hz, 2 H, NCH) and the ^{13}C NMR (76.42, d, J_{C-P} = 12.0 Hz, NCH; 127.03, C_p; 127.79, 128.57, $C_{o,m}$; 144.59, C_i) spectrum. It is thus very likely that the retention of C_2 symmetry by **3** in the coordination sphere of a metal is also quite general. This result nicely illustrates the considerable influence of the carbon skeleton (cyclic versus acyclic) on the coordination behavior of 1,2-diiminophosphoranes.



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It was of interest to prepare the related cationic palladium complexes possessing the η^3-1,3-diphenylallyl moieties since the asymmetric allylic alkylation tests were carried out using 1,3-diphenylprop-2-enyl acetate as the electrophile. These palladium complexes are the key intermediates that are subject to the attack of the soft malonate nucleophile in the well-accepted catalytic cycle.[2c−d,8] Complexes **13** (88% yield) and **14** (86% yield) were obtained by standard methods as air-stable crystalline TfO^- and BF_4^- salts, respectively (Scheme 3). Their spectroscopic data compare well with those of the related complexes **10** and **11** (Table 3). In the ^{31}P NMR spectra, two sharp lines were observed (**13**, +24.7, +33.6 ppm; **14**, + 35.1, +37.6 ppm). One NCH moiety of complex **13** appeared as doublet of doublets in the ^{13}C NMR spectrum (69.50, J_{C-P} = 17.0 and 3.1 Hz), while

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(14) Togni, A.; Rihs, G.; Pregosin, P. S.; Ammam, C. *Helv. Chim. Acta* **1990**, *38*, 723.

Table 2. Crystallographic Data for Compounds 10, 11, and 13

	10	11	13
formula	$PdC_{46}H_{43}N_2P_2F_3SO_3$	$PdC_{53}H_{47}N_2P_2BF_4$	$PdC_{58}H_{53}N_2P_2F_3SO_3$
solvent	$1/2C_4H_{10}O$	-	-
fw, g·mol^{-1}	966.28	967.08	1083.42
cryst syst	tetragonal	monoclinic	triclinic
space group	$P4_2/n$	$P2_1$	$P\bar{1}$
temp, °C	20	20	20
a, Å	22.825(4)	12.075(5)	11.436(2)
b, Å		14.809(12)	13.142(3)
c, Å	18.598(12)	14.401(9)	18.580(3)
α, deg			104.025(10)
β, deg		112.22(5)	100.37(2)
γ, deg			99.39(2)
V, Å^3	9689(7)	2384(3)	2601.7(9)
F(000)	3976	992	1116
Z	8	2	2
λ(Mo Kα), Å	0.71073	0.71073	0.71073
ρ(calcd), g·cm^{-3}	1.325	1.347	1.383
μ(Mo Kα), cm^{-1}	5.45	5.09	5.15
2θ range, deg	4−54	4−54	4−54
no. of data collected	10 492	5393	10 077
no. of unique data	10 027	5164	9284
no. of params varied	479	542	575
S	1.023	0.998	1.052
R^a	0.0802	0.0911	0.0548
$R_w{}^b$	0.1628	0.1611	0.0697
$(\Delta/\rho)_{max}$	3.611	1.227	1.848
$(\Delta/\rho)_{min}$,e·Å^{-3}	−1.450	−2.016	−1.769

^{a} $R = \sum||F_o| - |F_o||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.186P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 3. Selected NMR Data for the η^3-Allylic Complexes 10, 11, and 13−16[a]

	δ ^{31}P NMR	δ ^{1}H NMR			δ ^{13}C NMR		
		$H_{1a,3a}$	$H_{1s,3s}$	H_2	C_1	C_2	C_3
10	+25.6; +26.5	1.12; 1.18	2.22; 2.25	4.33	58.69	109.02	58.69
11	+34.0; +35.1	1.47; 2.23	2.56; 2.86	5.15	59.19	109.98	59.94
13	+24.7; +33.6	2.38; 3.38		5.64	72.97	106.16	74.51
14	+35.1; +37.6	3.59; 4.92		5.06	72.63	99.97	78.07
15	+42.8; +42.9	2.76; 2.91	3.70; 3.85		57.18	109.87	58.09
16	−5.6; −5.3	2.70; 2.90	3.98	5.27	59.76	111.88	61.33

[a] Measured in $CDCl_3$ at room temperature.

in complex **14** both gave a doublet of doublets in the ^{1}H NMR spectrum (4.03, J_{H-P} = 19.5 and 2.2 Hz; 4.10, J_{H-P} = 19.5 and 3.3 Hz). Considering that derivative **2** is supposed to lose its C_2 symmetry upon coordination, it was quite surprising that only one of the possible diastereomeric complexes **13** was formed, according to ^{31}P NMR spectroscopy of the crude reaction mixture recorded at room and low (−80 °C) temperatures. This observation led us to characterize complex **13** by a single-crystal X-ray diffraction study (Figure 3, Tables 1 and 2). Complex **13** has a typical π-allyl palladium structure with a distorted square-planar arrangement. The geometric data for derivative **13** compare well with those observed for complex **10** (Table 1). For example, the two Pd−N [2.133(3), 2.161(3) Å] and the P−N [1.593(3), 1.583(3) Å] bond lengths are very close to those recorded for compound **10** [Pd−N, 2.127(7)−2.119(7) Å; P−N, 1.593(7)−1.593(7) Å]. The five-membered metallacycle of complex **13** adopts an envelope conformation with the two phosphino groups in a mutually cis configuration. Once again, derivative **2** loses its C_2 symmetry upon coordination to a transition metal center (Figure 3, view b).

A crucial step in determining the degree of enantioselectivity of the allylic alkylation reaction is the regioselectivity of the attack of the soft nucleophile at the coordinated allylic moiety. Chiral homobidentate ligands

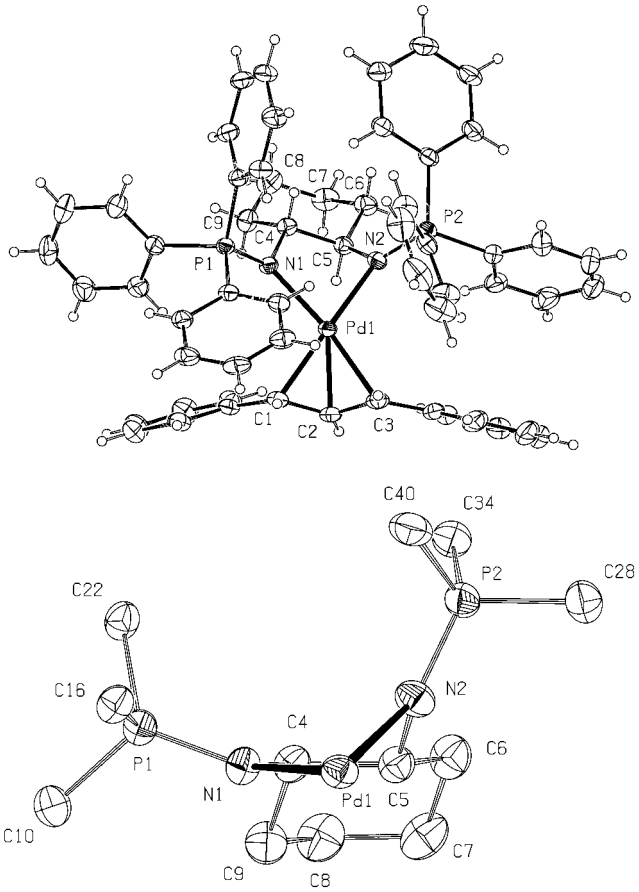


Figure 3. ORTEP drawing (thermal ellipsoid 40% probability) of the cation of complex **13**: (top) general view *a*, (bottom) view *b* along the N(1)−Pd−N(2) axis.

generally induce a discrimination of the two enantiotopic termini of the coordinated allyl ligand. In the solid state, the allyl fragment of complex **13** is not symmetrically bonded to the palladium atom. The allyl

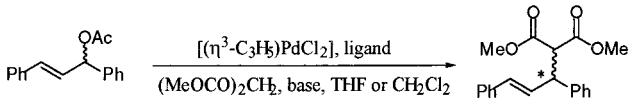
ligand is only slightly tilted [12°] from the perpendicular to the N(1)−Pd−N(2) plane; however the Pd−C(1) and Pd−C(3) bond lengths are significantly different [2.203(4), 2.136(4) Å]. In solution, the degree of discrimination between the two allyl carbon atoms can be evaluated from their ^{13}C chemical shifts, which give an empirical indication of their electrophilicity.[15] As expected from the solid-state structure, the two terminal allyl C atoms in complex **13** are inequivalent, but the difference between their ^{13}C chemical shifts is not large ($\Delta\delta$ = 1.5 ppm). Interestingly, this difference is more significant in complex **14** ($\Delta\delta$ = 5.4 ppm) (Table 3).

The next structural parameter that was examined was the nature of the P-substituents. Dialkylamino and phenoxy P-substituents were investigated in conjunction with the 1,2-diphenylethyl backbone. Complexes **15** (78% yield) and **16** (74% yield) were obtained as air- and moisture-stable solids (Scheme 3). The stability of complex **16** is particularly noteworthy since the corresponding free ligand **9b** decomposes within minutes in solution under an inert atmosphere.

Multinuclear NMR spectroscopy clearly identifies complexes **15** and **16** (Table 3). As expected, the ^{31}P NMR spectra show a large coordination shift effect ($\Delta\delta$ = 20−30 ppm) similar to that observed for complexes **10**−**14**. For both complexes, the NCH moieties appeared as doublets of doublets in the ^1H NMR spectra [**15**, 4.29, J_{H-P} = 14.0 and 3.6 Hz; 4.37, J_{H-P} = 14.0 and 3.6 Hz; **16**, 4.92, J_{H-P} = 14.3 and 7.1 Hz; 5.02, J_{H-P} = 14.3 and 7.1 Hz]. ^{13}C NMR spectroscopy can be used to assess the "trans-influence" of donor ligands, which includes not only an electronic but also a steric contribution, through examination of the chemical shifts for the terminal C atoms of the allyl fragment.[15a,b] These chemical shifts vary from 57.18 to 61.33 ppm (Table 3), values that are in the range found for other nitrogen-donor ligands such as bis-oxazolines[12a] or pyridine.[15a] The donor ability of 1,2-diiminophosphoranes featuring polarized ylide functions is clearly reflected in these data and, most importantly, is comparable to that of other sp^2-hybridized nitrogen ligands which are widely used in homogeneous catalysis.[1] As expected from the known influence of these substituents on the pK_a's of iminophosphoranes,[3b,c] the donor ability of 1,2-diiminophosphoranes decreases along the series Me_2N > Ph > OPh. However, the influence of these substituents on the donor ability of these ligands is relatively small (57.18 < δ < 61.33) and contrasts with the correspondingly large effect on the basicity of iminophosphoranes.

Enantioselective Pd-Catalyzed Allylic Alkylation. The ability of 1,2-diiminophosphoranes to stabilize intermediate Pd(0) species and to induce enantioselectivity was evaluated using the standard test reaction in the palladium-catalyzed allylic substitution, namely the reaction of *rac*-1,3-diphenylprop-2-enyl acetate with the soft nucleophile derived from dimethyl malonate and KH. The catalytic runs were carried out in THF at 36 °C using [Pd(η^3-C_3H_5)Cl]$_2$ as precatalyst and 4 equiv of the chiral ligand to prevent decomposition of the catalytic species. Ligands **3** and **7a**,**b** induced good catalytic activities (Table 4, entries 2−4), bearing in mind that

Table 4. Palladium-Catalyzed Enantioselective Allylic Alkylation with Chiral 1,2-Diiminophosphoranes



entry	ligand	*t* (h)	*T* (°C)	solvent	base	yield (%)	ee (%)[a]
1	**2**	1.5	36	THF	KH	38	10
2	**3**	1.5	36	THF	KH	61	77
3	**7a**	1.5	36	THF	KH	73	15
4	**7b**	1.5	36	THF	KH	75	15
5	**9a**	36	36	THF	KH	11	
6	**9b**	36	36	THF	KH	8	
7	**3**	1.5	36	CH_2Cl_2	KH	99	73
8	**3**	1.5	36	THF	NaH	99	70
9	**3**	1.5	36	THF	BSA-AcOK	50	76
10	**3**	1.5	36	CH_2Cl_2	BSA-AcOK	99	68
11	**3**	1.5	20	THF	NaH	45	81
12	**3**	1.5	20	THF	KH	15	85
13	**3**	1.5	20	CH_2Cl_2	KH	53	75
14	**3**	18	0	CH_2Cl_2	KH	48	77

[a] The % ee's were determined, after purification of the product by flash chromatography, by ^1H NMR using Eu(hfc)$_3$ as chiral shift agent and by gas chromatography on a CHIRALCEL OD column (99:1hexane/butanol; 0,7 mL/mn).

long reaction times (1−3 days for completion) are usually needed with N,N-ligands.[2c−d,8,16] The low yields observed with ligands **9a**,**b** (entries 5, 6) is certainly due to their low stability, "black palladium" precipitating during the course of the reaction. Comparison of the results obtained with P-phenyl-substituted 1,2-diiminophosphoranes (entries 1−2) reveals the dramatic influence imparted by the carbon skeleton in this series. The enantioselectivity and the catalytic activity are notably higher with the 1,2-diphenylethenyl ligands **3** (61% yield, ee = 77%) than with the 1,2-cyclohexyl derivative **2** (38% yield, ee = 10%).[17] It is interesting to note that ligand **3**, which gives the highest enantioselectivity, also induces the largest ^{13}C chemical shift difference between the carbon termini of the coordinated η^3-1,3-diphenylallyl moiety (Table 3, complex **13** and **14**). The nature of the P-substituents also has a considerable influence on the catalytic performances. The highest catalytic activities were obtained using P-dimethylamino-substituted iminophosphoranes (entries 3 and 4); however only ligand **3** bearing P-phenyl groups gave an interesting ee (entry 2).

Among the various 1,2-diiminophosphoranes, derivative **3** is the most efficient, and an optimization of the reaction parameters (solvent, base, and temperature) was undertaken with this ligand. Quantitative yields were obtained within 1.5 h when CH_2Cl_2 with KH or THF with NaH was employed (entries 7 and 8). However, in both cases the observed ee's (73% and 70%, respectively) were slightly lower than those obtained with KH in THF (77%). The same trend was observed using *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and KOAc; the reaction is more rapid in CH_2Cl_2 but the highest ee is achieved in THF (entries 9 and 10). As usually

(15) (a) Akermark, B.; Krakenberger, B.; Hansonn, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620. (b) Sakate, A.; Nakata, T. *J. Am. Chem. Soc.* **1998**, *120*, 10391.

(16) Bremberg, U.; Larhed, M.; Moberg, C.; Hallberg, A. *J. Org. Chem.* **1999**, *64*, 1082.

(17) No racemization of the product dimethyl 1,3-diphenylprop-2-enylmalonate occurred in the presence of an excess of **2** or **3** at 36 °C nor under the catalytic reaction conditions.

observed, the enantioselectivity increased by lowering the temperature but at the expense of the catalytic activity (entries 11−14). The best ee's were obtained in THF at room temperature with NaH (ee = 81%) or KH (85%).

The catalytic activities observed with 1,2-diiminophosphoranes **3** and **7a**,**b** are comparatively high for nitrogen-donors ligands. Of particular importance, this study has revealed that 1,2-diiminophosphoranes are able to stabilize Pd(0) species during a catalytic process and to induce notable levels of enantioselectivity.

Conclusion

1,2-Diiminophosphoranes have recently emerged as new chelating, chiral sp^2-nitrogen donors.[5a,b] These derivatives are readily prepared from commercially available diamines and present good stability when the phosphorus atoms feature phenyl or amino substituents. These chelating ligands give very stable cationic (allyl)-Pd(II) complexes, and their coordination behavior is considerably influenced by the nature of their carbon skeleton. 1,2-Diiminophosphoranes appear to possess a relative "hardness" comparable to other classical sp^2-nitrogen donors and are able to stabilize reduced metal centers in catalytic processes. Although relatively modest ee's have been obtained for Pd-catalyzed allylic alkylation reactions, these results encourage further investigation of the use of these ligands in metal-catalyzed processes and for the preparation of new chiral ligands possessing the iminophosphoranes moiety.

Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). Et_3N was freshly distilled under argon from KOH. Ph_3PBr_2, $(Me_2N)_3PBr_2$, $(PhO)_3PBr_2$, (*E*)-3-acetoxy-1,3-diphenyl-1-propene, $[PdCl(\eta^3\text{-}(C_3H_5)]_2$, and $[PdCl(\eta^3\text{-}(PhCHCH_2CHPh)]_2$[18] were prepared by standard procedures. Melting points are uncorrected. Chiral diamines were obtained from the Aldrich Chemical Co. and were used as received. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM300 or DPX200 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass at CRMPO, University of Rennes. Conventional glassware was used.

Crystallography. The unit cell constant, space group determination, and the data collection were carried out on an automatic CAD4 NONIUS diffractometer with graphite-monochromatized Mo Kα radiation.[19a] The cell parameters were obtained by fitting a set of 25 high-θ reflections. After Lorentz and polarization corrections, absorption corrections were done with ψ scans,[19b] and the structures were solved with SIR-97,[19c] which reveals non-hydrogen atoms of the structure. The remaining non-hydrogen atoms were found after some Fourier difference calculations, which revealed disordered allylic ligands (complexes **10** and **11**) and BF_4^- anion (complex **11**). All the hydrogen atoms are set in theoretical positions. All the structures were refined with SHELXL97[19d] by full-matrix least-squares techniques (use of *F* magnitude; *x*, *y*, *z*, β_{ij} for Pd, P, C, and N atoms (including allylic ligand and anion for **12**), *x*, *y*, *z*, for allylic ligands and anions, riding mode for H atoms (solvent an anion fixed in **10**). Atomic scattering factors were obtained from International Tables for X-ray Crystallography.[18e] ORTEP views were prepared with PLATON98.[19f] All calculations were performed on a Silicon Graphics Indy computer. Selected crystallographic and other relevant data are listed in Tables 1 and 2.

Synthesis of 1,2-Bis[tris(dimethylamino)phosphinimino]cyclohexane, 7a. Neat (1*R*,2*R*)-1,2-diaminocyclohexane (**5a**) (0.09 g, 0.7 mmol) was added dropwise to a Et_3N solution (10 mL) of $(Me_2N)_3PBr_2$ (0.50 g, 1.5 mmol) at room temperature. After warming at 36 °C for 12 h, the solvent was removed under vacuum. The residue was washed with diethyl ether (2 × 10 mL) and pentane (2 × 10 mL) to give a white solid containing derivative **6a** and Et_3NHBr. NaH (0.50 g, 20.8 mmol) was added in portions, at room temperature, to a suspension of this solid in THF (10 mL). The mixture was stirred for 1 h at 40 °C and then filtered. The solvent and Et_3N were removed in vacuo, and the residue was extracted with pentane. Compound **7a** was obtained as a moisture-sensitive white solid (0.24 g, 80% yield): mp 138 °C. **6a**: ^1H NMR ($CDCl_3$, 200 MHz): δ 1.10 (m, 2H, CH_2), 1.48−1.90 (m, 6H, CH_2), 2.77 (d, J_{H-P} = 9.7 Hz, 36H, NCH_3), 3.36 (s broad, 2H, NCH), the NH are not observed. ^{13}C NMR ($CDCl_3$, 50.323 MHz): δ 24.70 (s, $NCHCH_2CH_2$), 34.63 (s, $NCHCH_2$), 37.52 (d, J_{C-P} = 3.9 Hz, NCH_3), 55.51 (d, J_{C-P} = 11.7 Hz, NCH). ^{31}P NMR ($CDCl_3$; 81.019 MHz): δ +38.7. HR-MS (FAB-mNBA) *m*/*z* 519.2666 (calculated: 519.2642, $M^{2+} + Br^-$). **7a**: ^1H NMR (C_6D_6, 200 MHz): δ 1.55−1.82 (m, 4H, CH_2), 2.31−2.50 (m, 4H, CH_2), 2.61 (d, J_{H-P} = 9.1 Hz, 36H, NCH_3), 3.58 (m, 2H, NCH). ^{13}C NMR (C_6D_6, 50.323 MHz): δ 22.76 (s, $NCHCH_2CH_2$), 33.37 (s, $NCHCH_2$), 37.52 (s, NCH_3), 58.25 (d, J_{C-P} = 18.0 Hz, NCH). ^{31}P NMR (C_6D_6; 81.019 MHz): δ +14.1. HR-MS (FAB-mNBA) *m*/*z* 436.3341 (calculated: 436.3220, M^+). Anal. Calcd for $C_{18}H_{46}N_8P_2$: C, 49.52; H, 10.62; N, 25.67. Found: C, 49.78; H, 10.74; N, 25.55.

Synthesis of 1,2-Bis[tris(dimethylamino)phosphinimino]-1,2-diphenylethane, 7b. Using the above procedure, (1*R*,2*R*)-1,2-diphenylethylenediamine (**5b**) (0.23 g, 1.1 mmol) and $(Me_2N)_3PBr_2$ (0.77 g, 2.4 mmol) were reacted, giving rise to derivative **7b** (0.43 g, 74% yield) as a colorless oily product via the diphosphonium **6b**. **6b**: ^1H ($CDCl_3$; 200.130 MHz): δ 2.45 (d, J_{H-P} = 9.8 Hz, 36H, NCH_3), 4.84 (m, 2H, NCH), 7.11−7.35 (m, 6H, $CH_{arom.}$), 7.85−8.00 (m, 4H, $CH_{arom.}$), the NH's are not observed. ^{13}C NMR ($CDCl_3$, 50.323 MHz): δ 37.50 (d, J_{C-P} = 4.7 Hz, NCH_3), 63.10 (d, J_{C-P} = 11.0 Hz, NCH), 128.00 (s, C_p), 128.50, 128.70 (s, $C_{o,m}$), 140.21 (s, C_i). ^{31}P NMR ($CDCl_3$; 81.019 MHz): δ +39.7. HR-MS (FAB-mNBA) 617.2790 (calculated: 617.2817, $M^{2+} + Br^-$). **7b**: ^1H NMR (C_6D_6, 200 MHz): δ 2.44 (d, J_{H-P} = 9.3 Hz, 36H, NCH_3), 4.69 (d, J_{H-P} = 4.7 Hz, 2H, NCH), 7.11−7.22 (m, 6H, CH_{arom}), 7.52−7.56 (m, 4 H, CH_{arom}). ^{13}C NMR (C_6D_6, 50.323 MHz): δ 37.31 (s, NCH_3), 67.94 (d, J_{C-P} = 25.0 Hz, NCH), 124.90 (s, C_p), 125.75, 130.00 (s, $C_{o,m}$), 149.72 (s, C_i). ^{31}P NMR (C_6D_6; 81.019 MHz): δ +19.9. HR-MS (FAB-mNBA) 267.1748 (calculated: 267.1738, $M^+/2$).

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Anal. Calcd for $C_{26}H_{48}N_8P_2$: C, 58.39; H, 9.05; N, 20.96. Found: C, 58.48; H, 9.04; N, 20.85.

Synthesis of 1,2-Bis[triphenoxyphosphinimino]cyclohexane, 9a. Neat (1*R*,2*R*)-1,2-diaminocyclohexane (**5a**) (0.20 g, 1.75 mmol) was added dropwise to a CH_2Cl_2 solution (10 mL) of Et_3N (0,58 mL, 4.20 mmol) and $(PhO)_3PBr_2$ (1.70 g, 3.61 mmol) at −10 °C. The mixture was allowed to warm to room temperature. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with diethyl ether (3 × 15 mL) and extracted with THF (10 mL) to eliminate the triethylammonium salt. **8a** was obtained as an air- and moisture-sensitive pale orange solid. NaH (0.17 g, 7.0 mmol) was added in portions, at room temperature, to a THF solution (10 mL) of **8a**. The solution was stirred for 1 h at room temperature and then filtered. The solvent was removed in vacuo, and the residue extracted with pentane. Compound **9a** was obtained as an extremely air- and moisture-sensitive colorless viscous oil (1.02 g, 80% yield). Derivative **9a** can be obtained in a one-pot procedure using (1*R*,2*R*)-1,2-diaminocyclohexane **5a**, $(PhO)_3PBr_2$, and an excess of NaH in THF at −10 °C (85% yield). **8a**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.97−1.95 (m, 8H, CH_2), 4.02 (m, 2H, NCH), 7.02−7.51 (m, 30H, CH_{arom}), the NH are not observed. ^{13}C NMR ($CDCl_3$, 50.323 MHz): δ 24.21 (s, NCHCH$_2$*C*H$_2$), 33.72 (s, NCH*C*H$_2$), 57.81 (d, J_{C-P} = 10.9 Hz, NCH), 120.62 (d, J_{C-P} = 4.7 Hz, C_o), 127.44 (s, C_p), 130.51 (s, C_m), 149.47 (d, J_{C-P} = 10.2 Hz, C_i). ^{31}P NMR ($CDCl_3$; 81.019 MHz): δ −0.9. HR-MS (FAB-mNBA) *m*/*z* 731.2443 (calculated: 731.2440, $M^{2+} - H^+$). **9a**: ^{1}H NMR (C_6D_6, 200 MHz): δ 0.97−1.95 (m, 8H, CH_2), 4.02 (m, 2H, NCH), 7.01−7.42 (m, 30H, CH_{arom}). ^{13}C NMR (C_6D_6, 50.323 MHz): δ 23.42 (s, NCHCH$_2$*C*H$_2$), 34.23 (s, NCH*C*H$_2$), 58.81 (d, J_{C-P} = 15.6 Hz, NCH), 120.65 (d, J_{C-P} = 5.5 Hz, C_o), 124.45 (s, C_p), 129.41 (s, C_m), 151.77 (d, J_{C-P} = 9.4 Hz, C_i). ^{31}P NMR (C_6D_6; 81.019 MHz): δ −36.7.

Synthesis of 1,2-Bis[triphenoxyphosphinimino]-1,2-diphenylethane, **9b**. Neat (1*R*,2*R*)-1,2-diphenylethylenediamine (**5b**) (0.38 g, 1.8 mmol) was added dropwise to CH_2Cl_2 solution (10 mL) of $(PhO)_3PBr_2$ (1.70 g, 3.6 mmol) at −10 °C. After 10 min, an excess of NaH (0.22 g, 9 mmol) was added at this temperature. The solution was allowed to warm to room temperature and filtered. Compound **9b**, obtained in 70% yield according to ^{31}P NMR spectroscopy, rapidly decomposed in solution (THF, toluene, pentane), which prevents any purification. As a free ligand, **9b** has been observed only by ^{31}P NMR spectroscopy but fully characterized when coordinated to a (allyl)Pd(II) fragment (complex **16**). ^{31}P NMR (CH_2Cl_2; 81.019 MHz): δ −35.2.

Synthesis of [Pd(η^3-C_3H_5)(2)]TfO, 10. Solid AgTfO (0.081 g, 0.31 mmol) was added to a CH_2Cl_2 solution (10 mL) of [Pd(η^3-C_3H_5)Cl]$_2$ (0.058 g, 0.16 mmol) and derivative (*R*,*R*)-**2**[5a,b] (0.22 g, 0.35 mmol) at room temperature. The mixture was stirred for 1 h in the dark, and the precipitate of AgCl was filtered off using a plug of Celite. The solvent was removed under vacuum, and the residue was subjected to column chromatography on silica gel (CH_2Cl_2 then MeOH). Complex **10** was isolated as an air-stable pale yellow solid (0.234 g, 81% yield). Single crystals suitable for X-ray diffraction were grown from a CH_2Cl_2−Et_2O solution at room temperature using racemic **2**. ^{1}H NMR ($CDCl_3$; 300.133 MHz): δ 0.65−0.92 (m, 6H, CH_2), 1.12 (d, J_{H-H} = 12.0, 1H, CH_{anti}), 1.18 (d, J_{H-H} = 12.0, 1H, CH_{anti}), 1.45 (m, 2H, CH_2), 2.22 (dd, J_{H-H} = 6.5 and 1.8 Hz, 1H, H_{syn}), 2.25 (dd, J_{H-H} = 6.5 and 1.8 Hz, 1H, H_{syn}), 3.24 (s broad, J_{PH} < 1 Hz, 2H, NCH), 4.33 (sept-like, J_{H-H} = 12.0 and 6.5 Hz, 1H, C*H*CH$_2$), 7.30−7.70 (m, 20H, CH_{arom}), 7.85−7.90 (m, 10H, CH_{arom}). ^{13}C NMR ($CDCl_3$; 50.332 MHz): δ 25.21, 25.42 (s, NCHCH$_2$*C*H$_2$), 36.03, 36.07 (s broad, NCH*C*H$_2$), 58.69 (s, CH*C*H$_2$), 67.42 (dd, J_{C-P} = 14.1 and 3.0 Hz, NCH), 68.55 (dd, J_{C-P} = 14.9 and 3.1 Hz, NCH), 109.02 (s, *C*HCH$_2$), 129.01 (d, J_{C-P} = 12.2 Hz, $C_{o,m}$), 129.91 (d, J_{C-P} = 98.9 Hz, C_i), 129.93 (d, J_{C-P} = 98.9 Hz, C_i), 130.02 (d, J_{C-P} = 13.4 Hz, $C_{o,m}$), 132.94 (s, C_p), 133.09 (d, J_{C-P} = 9.8 Hz, $C_{o,m}$), 133.17(s, C_p), 133.98 (d, J_{C-P} = 11.0 Hz, $C_{o,m}$), the *C*F_3SO_3 is not observed. ^{31}P NMR ($CDCl_3$; 81.019 MHz): δ +25.6, +26.5. Anal. Calcd for $C_{46}H_{45}N_2P_2PdSF_3O_3\cdot 0.5Et_2O$: C, 59.54; H, 5.17; N, 2.89. Found: C, 59.68; H, 5.22; N, 2.81.

Synthesis of [Pd(η^3-C_3H_5)(3)]BF_4, 11. Using the standard procedure above, (*R*,*R*)-**3**[5b] (0.095 g, 0.13 mmol), $AgBF_4$ (0.022 g, 0.11 mmol), and [Pd(η^3-C_3H_5)Cl]$_2$ (0.020 g, 0.054 mmol) were reacted, giving rise to complex **11**, which was obtained as an air-stable pale yellow solid after crystallization from a CH_2Cl_2−Et_2O solution (0.09 g, 84% yield). Single crystals suitable for X-ray diffraction were grown from a CH_2Cl_2−Et_2O solution at room temperature. ^{1}H NMR ($CDCl_3$, 300.133 MHz): δ 1.47 (d, J_{H-H} = 12.0 Hz, 1H, CH_{anti}), 2.23 (d, J_{H-H} = 12.0 Hz, 1H, CH_{anti}), 2.56 (dd, J_{H-H} = 6.5 and 1.9 Hz, 1H, CH_{syn}), 2.86 (dd, J_{H-H} = 6.5 and 1.9 Hz, 1H, CH_{syn}), 4.04 (dd, J_{H-P} = 16.3 and 3.6 Hz, 1H, NCH), 4.14 (dd, J_{H-P} = 16.3 and 3.6 Hz, 1H, NCH), 5.15 (sept-like, J_{H-H} = 12.0 and 6.5 Hz, 1H, C*H*CH$_2$), 7.10−7.60 (m, 40H, CH_{arom}). ^{13}C NMR ($CDCl_3$; 75.469 MHz): δ 59.19, 59.94 (s, CH*C*H$_2$), 73.37 (d, J_{C-P} = 12.2 Hz, NCH), 74.12 (d, J_{C-P} = 13.4 Hz, NCH), 109.98 (s, *C*HCH$_2$), 127.12 (s broad, C_p CH*Ph*), 127.43 (d, J_{C-P} = 100.1 Hz, C_i P*Ph*), 127.52 (d, J_{C-P} = 100.1 Hz, C_i P*Ph*), 127.71, 127.78, 127.81, 127.88 (s, $C_{o,m}$ CH*Ph*), 128.69 (d, J_{C-P} = 12.0 Hz, $C_{o,m}$ P*Ph*), 128.75 (d, J_{C-P} = 12.2 Hz, $C_{o,m}$ P*Ph*), 132.83 (d, J_{C-P} = 3.0 Hz, C_p P*Ph*), 132.95 (d, J_{C-P} = 3.0 Hz, C_p P*Ph*), 133.26 (d, J_{C-P} = 9.8 Hz, $C_{o,m}$ P*Ph*), 133.43 (d, J_{PC} = 10.7 Hz, $C_{o,m}$ P*Ph*), 144.61, 144.88 (C_i CH*Ph*). ^{31}P NMR ($CDCl_3$; 121.496 MHz): δ +34.0, +35.1. Anal. Calcd for $C_{53}H_{47}N_2P_2PdBF_4$: C, 65.82; H, 4.90; N, 2.90. Found: C, 65.84; H, 4.96; N, 2.85.

Synthesis of (3)$PdCl_2$, 12. A CH_2Cl_2 solution (10 mL) of derivative **3** (0.184 g; 0.25 mmol) was added at room temperature to a CH_2Cl_2 solution of $(CH_3CN)_2PdCl_2$ (0.059 g; 0.23 mmol). After 1 h, the solvent was removed under vacuum. The residue was washed with pentane (3 × 10 mL) and with ether (3 × 10 mL). Complex **12** was obtained as an orange solid from a CH_2Cl_2 solution at room temperature (0.19 g, 91% yield). ^{1}H NMR (CD_2Cl_2, 200.133 MHz): δ 3.45 (dd, J_{H-P} = 13.6 and 6.9 Hz, 2H, NCH), 7.10−7.61 (m, 40H, CH_{arom}). ^{13}C NMR (CD_2Cl_2; 50.323 MHz): δ 76.42 (d, J_{C-P} = 12.0 Hz, NCH), 127.03 (s, C_p CH*Ph*), 127.63 (d, J_{C-P} = 11.0 Hz, $C_{o,m}$ P*Ph*), 127.79, 128.57 (s, $C_{o,m}$ CH*Ph*), 131.83 (d, J_{C-P} = 3.1 Hz, C_p P*Ph*), 134.24 (d, J_{C-P} = 9.4 Hz, $C_{o,m}$ P*Ph*), 144.59 (C_i CH*Ph*), the C_iP*Ph* is not observed. ^{31}P NMR (CD_2Cl_2; 121.496 MHz): δ +36.6. Anal. Calcd for $C_{48}H_{42}N_2P_2PdCl_2$: C, 65.06; H, 4.78; N, 3.16. Found: C, 65.12; H, 4.82; N, 3.25.

Synthesis of [Pd(η^3-PhCHCHCHPh)(2)]TfO, 13. Using the standard procedure, (*R*,*R*)-**2** (0.22 g, 0,35 mmol), AgTfO (0.079 g, 0.30 mmol), and [Pd(η^3-PhCHCHCHPh)Cl]$_2$ (0.1 g, 0.15 mmol) were reacted, giving rise to complex **13**, which was obtained as an air-stable orange solid after crystallization from a CH_2Cl_2−Et_2O solution at room temperature (0.29 g, 88% yield). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.32 (m, 1H, CH_2), 0.63 (m, 1H, CH_2), 0.95−1.65 (m, 6H, CH_2), 2.38 (d, J_{H-H} = 11.2 Hz, 1H, CHC*H*Ph), 2.64 (m, 1H, NCH), 3.38 (d, J_{H-H} = 11.2 Hz, 1H, CHC*H*Ph), 3.78 (m, 1H, NCH), 5.64 (dd, J_{H-H} = 11.2 and 11.2 Hz, 1H, C*H*CHPh), 6.70−7.82 (m, 40H, CH_{arom}). ^{13}C NMR ($CDCl_3$; 50.332 MHz): δ 25.24, 26.19 (s, NCHCH$_2$*C*H$_2$), 33.88 (d, J_{C-P} = 10.2 Hz, NCH*C*H$_2$), 37.07 (s, NCH*C*H$_2$), 65.57 (s broad, NCH), 69.50 (dd, J_{C-P} = 17.0 and 3.1 Hz, NCH), 72.97 (s, CH*C*HPh), 74.51 (s, CH*C*HPh), 106.16 (s, *C*HCHPh), 121.07 (qua., J_{C-F} = 323.2 Hz, CF_3), 127.53, 127.86, 127.92, 128.23 (s, C_{arom} CH*Ph*), 128.36 (d, J_{C-P} = 98.6 Hz, C_i P*Ph*), 128.68 (d, J_{C-P} = 12.2 Hz, $C_{o,m}$ P*Ph*), 128.75 (d, J_{C-P} = 11.7 Hz, $C_{o,m}$ P*Ph*), 132.50 (s, C_{arom}), 132.95 (d, J_{C-P} = 10.2 Hz, $C_{o,m}$ P*Ph*), 133.04 (broad s, C_pP*Ph*), 133.59 (d, J_{C-P} = 9.4 Hz, $C_{o,m}$ P*Ph*), 138.82, 139.72 (C_i CH*Ph*). ^{31}P NMR ($CDCl_3$; 81.019 MHz): δ +24.7, +33.6. Anal. Calcd for $C_{58}H_{53}N_2P_2PdSF_3O_3$: C, 64.30; H, 4.89; N, 2.58. Found: C, 64.38; H, 4.86; N, 2.51.

Synthesis of Pd(η^3-PhCHCHCHPh)(3)]BF_4, 14. Using the standard procedure, (*R*,*R*)-**3** (0.19 g, 0.26 mmol), $AgBF_4$ (0.047 g, 0.24 mmol), and [Pd(η^3-PhCHCHCHPh)Cl]$_2$ (0.082

g, 0.12 mmol) were reacted, giving rise to complex **14**, which was obtained as an air-stable orange solid after crystallization from a $CH_2Cl_2-Et_2O$ solution at room temperature (0.23 g, 86% yield). Single crystals suitable for X-ray diffraction were grown from a $CH_2Cl_2-Et_2O$ solution at room temperature. ^{1}H NMR ($CDCl_3$, 300.133 MHz): δ 3.59 (d, J_{H-H} = 11.8 Hz, 1H, CHC*H*Ph), 4.03 (dd, J_{H-P} = 19.5 and 2.2 Hz, 1H, NCH), 4.10 (dd, J_{H-P} = 19.5 and 3.3 Hz, 1H, NCH), 4.92 (d, J_{H-H} = 7.8 Hz, 1H, CHC*H*Ph), 5.06 (dd, J_{H-H} = 11.8 and 7.8 Hz, 1H, C*H*CHPh), 6.70−7.73 (m, 50H, CH_{arom}). ^{13}C NMR ($CDCl_3$; 75.469 MHz): δ 70.95 (d, J_{C-P} = 12.2 Hz, NCH), 71.52 (d, J_{C-P} = 13.4 Hz, NCH), 72.63 (s, CH*C*HPh), 78.07 (s, CH*C*HPh), 99.97 (s, *C*HCHPh), 126.65 (d broad, J_{C-P} = 101.9 Hz, C_i P*Ph*), 127.24 (s, C_{arom}), 127.31 (d, J_{C-P} = 100.7 Hz, C_i P*Ph*), 127.37, 127.54, 127.80, 128.09, 128.13, 128.33, 128.48, 129.17, 131.83, 131.98, 132.05, 132.18, 132.19, 132.23 (C_{arom}), 132.99 (d, J_{C-P} = 3.0 Hz, C_p P*Ph*), 133.18 (d, J_{C-P} = 9.8 Hz, $C_{o,m}$ P*Ph*), 133.67 (d, J_{PC} = 9.8 Hz, $C_{o,m}$ P*Ph*), 136.90, 139.28 (s, C_i CH*Ph*), 143.27 (d, J_{C-P} = 1.8 Hz, C_i NCH*Ph*), 144.15 (d, J_{C-P} = 2.4 Hz, C_i NCH*Ph*). ^{31}P NMR ($CDCl_3$; 121.496 MHz): δ +35.1, +37.6. Anal. Calcd for $C_{65}H_{55}N_2P_2PdBF_4$: C, 69.75; H, 4.91; N, 2.50. Found: C, 69.68; H, 4.98; N, 2.54.

Synthesis of Pd(η^3-C_3H_5)(7b)]BF_4, 15. Using the standard procedure, ligand **7b** (0.15 g, 0.28 mmol), $AgBF_4$ (0.05 g, 0.26 mmol), and [Pd(η^3-C_3H_5)Cl]$_2$ (0.05 g, 0.13 mmol) were reacted, giving rise to complex **15**, which was obtained as an air-stable pale yellow solid after crystallization from a $CH_2Cl_2-Et_2O$ solution at room temperature (0.16 g, 78% yield). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.45 (d, J_{H-P} = 8.9 Hz, 18H, NCH_3), 2.48 (d, J_{H-P} = 9.0 Hz, 18H, NCH_3), 2.76 (d, J_{H-H} = 11.9 Hz, 1H, CH_{anti}), 2.91 (d, J_{H-H} = 11.9 Hz, 1H, CH_{anti}), 3.70 (dd, J_{H-H} = 6.3 and 2.0 Hz, 1H, CH_{syn}), 3.85 (dd, J_{H-H} = 6.3 and 2.0 Hz, 1H, CH_{syn}), 4.29 (dd, J_{H-P} = 14.0 and 3.6 Hz, 1H, NCH), 4.37 (dd, J_{H-P} = 14.0 and 3.6 Hz, 1H, NCH), 5.55 (sept-like, J_{H-H} = 11.9 and 6.3 Hz, 1H, C*H*CH_2), 7.10−7.90 (m, 10H, CH_{arom}). ^{13}C NMR ($CDCl_3$; 50.323 MHz): δ 38.02 (d, J_{C-P} = 4.0 Hz, NCH_3), 38.12 (d, J_{C-P} = 4.3 Hz, NCH_3), 57.18, 58.09 (s, CH*C*H_2), 72.91 (dd, J_{C-P} = 11.0 and 3.1 Hz, NCH), 73.20 (dd, J_{C-P} = 11.0 and 3.1 Hz, NCH), 109.87 (s, *C*HCH_2), 126.94, 127.02 (s, C_p CH*Ph*), 127.32, 127.55, 127.73, 127.81 (s, $C_{o,m}$ CH*Ph*), 146.16, 146.32 (C_i CH*Ph*). ^{31}P NMR ($CDCl_3$; 81.019 MHz): δ +42.8, +42.9. Anal. Calcd for $C_{29}H_{53}N_8P_2PdBF_4$: C, 45.30; H, 6.95; N, 14.58. Found: C, 45.38; H, 6.98; N, 14.50.

Synthesis of Pd(η^3-C_3H_5)(9b)]BF_4, 16. Using the standard procedure, ligand **9b** (0.260 g, 0.31 mmol), $AgBF_4$ (0.057 g, 0.29 mmol), and [Pd(η^3-C_3H_5)Cl]$_2$ (0.053 g, 0.14 mmol) were reacted, giving rise to complex **16**, which was obtained as a pale yellow solid after crystallization from a $CH_2Cl_2-Et_2O$ solution at room temperature (0.228 g, 74% yield). ^{1}H NMR ($CDCl_3$, 300.133 MHz): δ 2.70 (d, J_{H-H} = 12.2 Hz, 1H, CH_{anti}), 2.90 (d, J_{H-H} = 12.2 Hz, 1H, CH_{anti}), 3.98 (d, J_{H-H} = 6.8, 2H, CH_{syn}), 4.92 (dd, J_{H-P} = 14.3 and 7.1 Hz, 1H, NCH), 5.02 (dd, J_{H-P} = 14.3 and 7.1 Hz, 1H, NCH), 5.27 (sept-like, J_{H-H} = 12.2 and 6.8 Hz, 1H, C*H*CH_2), 6.65−7.50 (m, 30 H, CH_{arom}). ^{13}C NMR ($CDCl_3$; 75.469 MHz): δ 59.76, 61.33 (s, CH*C*H_2), 71.14 (d, J_{C-P} = 15.6 Hz, NCH), 111.88 (s, *C*HCH_2), 119.33 (d, J_{C-P} = 6.1 Hz, C_o O*Ph*), 119.41 (d, J_{C-P} = 6.1 Hz, C_o O*Ph*), 126.40 (s, C_p O*Ph*), 127.07, 127.23 (s, $C_{o,m}$ *Ph*), 127.78, 127.88 (C_p *Ph*), 128.44, 128.59 (s, $C_{o,m}$ *Ph*), 130.25 (s, C_m O*Ph*), 142.48 (d, J_{C-P} = 3.7 Hz, C_i *Ph*), 142.71 (d, J_{C-P} = 3.7 Hz, C_i *Ph*), 149.80 (d, J_{C-P} = 11.0 Hz, C_i O*Ph*). ^{31}P ($CDCl_3$; 121.496 MHz): δ −5.3, −5.6. Anal. Calcd for $C_{53}H_{47}N_2P_2O_6PdBF_4$: C, 59.87; H, 4.42; N, 2.63. Found: C, 59.81; H, 4.48; N, 2.58.

General Procedure for the Allylic Alkylation. Dimethylmalonate (0.14 g; 1.1 mmol) and potassium hydride (0.040 g; 1.0 mmol) were stirred under argon in CH_2Cl_2 (5 mL) at room temperature. When gas evolution had ceased after 10 min, the catalyst *prepared in situ* by mixing [Pd(η^3-C_3H_2)Cl]$_2$ (3.6 mg; 0.01 mmol) and ligand (*R*,*R*)-**3** (29 mg; 0.04 mmol) in CH_2Cl_2 (5 mL) was added followed by *rac*-1,3-diphenylprop-2-enyl acetate (0.125; 0.50 mmol). The reaction mixture was heated at 36 °C for 1.5 h. The solution was diluted with a saturated aqueous solution of NH_4Cl. Dichloromethane was added (10 mL), and the organic layer was dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (20% ethyl acetate in heptane). Yield: 160 mg, 99%. The % ee's were determined by ^{1}H NMR using Eu(hfc)$_3$ as chiral shift agent and by HPLC on a CHIRALCEL OD column (99:1 hexane/butanol; 0.7 mL/mn).

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Supporting Information Available: Tables of crystal and intensity collection data, position and thermal parameters, and interatomic distances and angles for derivatives **10**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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