New Chiral Tetradentate Oxazolinylphosphine Ligands for Nickel and Palladium. Coordination Behavior and Catalytic Activity in Allylic Alkylations

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Polydentate ***NPPN*** ligands containing nitrogen and chiral phosphorus atoms have been synthesized (**A**−**D**), starting from diphosphines (dppe and dppp) and 2-(3′,4′-dihydro-4′-R-2′-oxazolyl)-1-chlorobenzene (R = ethyl, isopropyl). Their coordination behavior has been studied with nickel and palladium precursors, giving mono- and bimetallic complexes depending on the reaction conditions. For the monometallic compounds, the ***NPPN*** ligands act as tetra- or tricoordinate groups (**Ni-a**−**d** and **Pd-a**,**b**, respectively), while for the bimetallic palladium complexes, the ligand bridges two metallic atoms (**1a**, **3a**−**c**, **4a**−**c**, **5a**−**c**, **6a**−**d**, **7a**, **8d**) in an *N*,*P* bis-bidentate coordination. The X-ray crystal structure of bis(η^3-2-methylallyl)[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinoethane]dipalladium(II) hexafluorophosphate (*RSRR*-**7a**) is described. Acyl complexes **4a**−**c** were obtained from the methyl compounds **3a**−**c** by insertion of carbon monoxide into Pd−CH_3 bond, at high pressure and room temperature. However, these compounds did not undergo insertion of norbornene or norbornadiene into the Pd−$COCH_3$ bonds. Ionic methyl complexes **5a**−**c** reacted faster than the neutral **3a**−**c** toward the insertion of CO, but these ionic acetyl compounds decarbonylated easily, even in the solid state. The activity of the allylic complexes (**6a**−**d**) in palladium-catalyzed allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate was tested, affording enantiomeric excesses up to 90%. The enantioselectivity of these catalytic systems exhibits a strong dependence on the Pd/***NPPN*** ratio, because of the presence of different coordination modes.

Introduction

Ligands containing phosphorus atoms have found important applications in various asymmetric catalytic processes, and a variety of ligands has been developed,[1] in particular chiral diphosphines such as BINAP, CHIRAPHOS, and DuPHOS,[2] whose chiral centers are located on a carbon backbone. Phosphane ligands with chiral phosphorus atoms have been frequently less applied in enantioselective catalysis,[3] with DIPAMP as a notable exception.[3b] Recently, P-chiral phosphanes have been used in hydrogenation[4] and allylic susbtitution reactions.[5] In the past decade, chiral nitrogen ligands have also been applied in many homogeneous catalytic processes.[6] Metal complexes with ligands containing P and N donor atoms (PNNP) have been used in hydrogen transfer[7] and allylic substitution transformations.[8] Among the nitrogen ligands, the versatility of oxazolines is noteworthy.[9] However, C_2-symmetric phosphine−oxazoline hybrid ligands have been less studied.[10] In addition to the ferrocene derivatives, which are active ligands for palladium-catalyzed allylic substitutions,[10a,b] a PNNP ligand containing a rigid chiral bioxazole backbone has been used for rhodium-catalyzed hydrosilylation of ketones.[10c]

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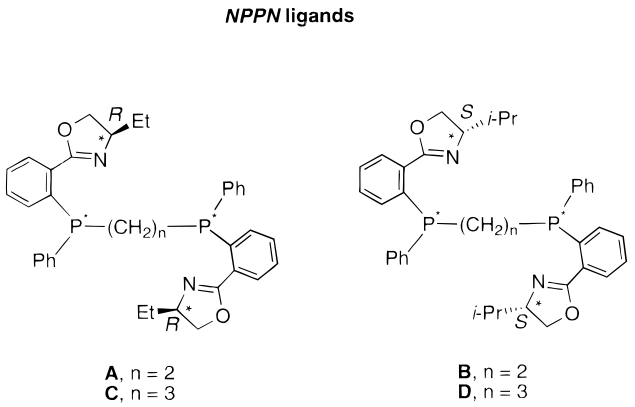

Figure 1. Bis(oxazolinylphosphine) ligands, ***NPPN***.

Heterodonor ligands can give mono- or dinuclear complexes with several coordination modes. In particular, bimetallic systems are of considerable interest. Complexes with two metal centers in relatively close proximity can catalyze the organic processes more efficiently and with different selectivities than analogous monometallic species.[11]

Recently, Togni et al. have described bimetallic palladium complexes with PNNP bis(phosphino)−bis(pyrazole) ligands, which are effective catalysts in allylic substitution reactions.[12] In these complexes, the ligand acts as a bridge between two palladium centers, and an N,P chelate is formed for each metallic atom. Besides allylic subtitutions, monometallic palladium systems containing N,P (oxazolino−phosphine) ligands have been applied in enantioselective Heck reactions[13] and in carbonylation reactions in polyketone or alkoxycarbonylation production.[14]

Here we report the synthesis of chiral ***NPPN*** ligands (**A**−**D**), containing four stereocenters, which were derived from dppe and dppp diphosphines, by substitution of half the phenyl groups by a chiral *o*-oxazolinyl substituent. The presence of four donor centers led to interesting coordination behavior toward nickel and palladium. Moreover, neutral and ionic palladium complexes were tested in carbon monoxide and olefin insertion reactions. Also, ionic allylic compounds were tested in the palladium-catalyzed allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate.

Results and Discussion

Ligands. Ligands **A**−**D** (see Figure 1) were synthesized by reaction of [Li(Ph)P$(CH_2)_n$P(Ph)Li] (n = 2, 3) with the *o*-chlorooxazolylbenzene derivatives, which were prepared by following the literature method[15] with minor modifications (see Scheme 1). The reaction was monitored by ^{31}P NMR, and no side products were found. The lithium diphosphide compounds were prepared by reaction of secondary diphosphines with *n*-BuLi. At once, the secondary diphosphines, [HP(Ph)-$(CH_2)_n$PH(Ph)], were obtained as the diastereomeric mixtures in good yields, by treatment of (diphenylphosphino)ethane (dppe) or (diphenylphosphino)propane (dppp) with lithium metal by ultrasound irradiation, followed by hydrolysis (see Experimental Section).[16,17]

The new ligands ***NPPN*** have four sterocenters: i.e., two chiral carbon atoms in the oxazoline moiety (*R* for **A** and **C**, and *S* for **B** and **D**, because of the optical purity of the amino alcohol used in the synthesis) and two chiral phosphorus atoms. Therefore, the product expected is a mixture of three diastereoisomers: *R*(C)-*R*(P)*R*(P)*R*(C), *RSSR*, and *RSRR* for **A** and **C** (for **B** and **D**, *SRRS*, *SSSS*, *SSRS*). ^{31}P NMR spectra of these compounds consisted of two doublets and two singlets, in a ratio of 1:1:1:1. The doublets are due to the *RRSR* (or *SSRS*) isomer, because the phosphorus atoms are nonequivalent (NMR data are given in the Supporting Information). Column chromatography methods (under several conditions) were unsuccessfully tested in order to separate the diastereomers. Only recrystallizations from nickel derivatives (see below) and further decoordination led to a good purity for the *XRSX* isomers (*X* = *R*, *S*).

Ionic Compounds, [Ni(κ^4-*NPPN*)]$(ClO_4)_2$ (Ni-a−d) and [Pd(OAc)(κ^3-*NPPN*)]PF_6 (Pd-a,b). The nickel derivatives (**Ni-a**−**d**; each of them was a mixture of three diastereomers) were formed as orange products, insoluble in ethanol/THF solvent mixtures, when the free ligands were treated with nickel perchlorate salt (see Scheme 2). After the solids were removed by filtration, the solutions did not show any resonance in the ^{31}P NMR spectra, indicating that the diastereoisomers had identical solubilities under these conditions. Palladium ionic complexes (**Pd-a**,**b**) were also obtained by reaction of palladium acetate and ammonium hexafluorophosphate with the appropriate ligand in dichloromethane solution (see Scheme 2). Their characterization (analytical composition, molar conductivity, mass spectra, NMR data) was consistent with the formation of ionic complexes [Ni(κ^4-***NPPN***)]$(ClO_4)_2$ (***NPPN*** = **A**, **B**, **C**, **D**) and [Pd(OAc)(κ^3-***NPPN***)]PF_6 (***NPPN*** = **A**, **B**). ^{31}P NMR data for **Ni-a**,**c** and **Pd-a** revealed the formation of three isomers, the phosphorus atoms being nonequivalent for *RSRR* and *SSRS* forms; for **Ni-b**,**d** and **Pd-b** only one broad singlet and two doublets were observed (see Experimental Section). P−P coupling constants were larger for nickel complexes than for palladium derivatives, consistent with other series of group 10 compounds described.[18]

RSRR-**Ni-a** and *SSRS*-**Ni-d** were insoluble in acetone, which allows their separation from the starting mixture of diastereoisomers. Their ^{1}H NMR spectra (see Table 1) indicate the nonequivalence of the two oxazoline moieties. The *RRRR*- + *RSSR*-**Ni-a** mixture was recrystallized from ethanol and acetone, yielding an isomeric mixture of composition 9/1. The nickel products

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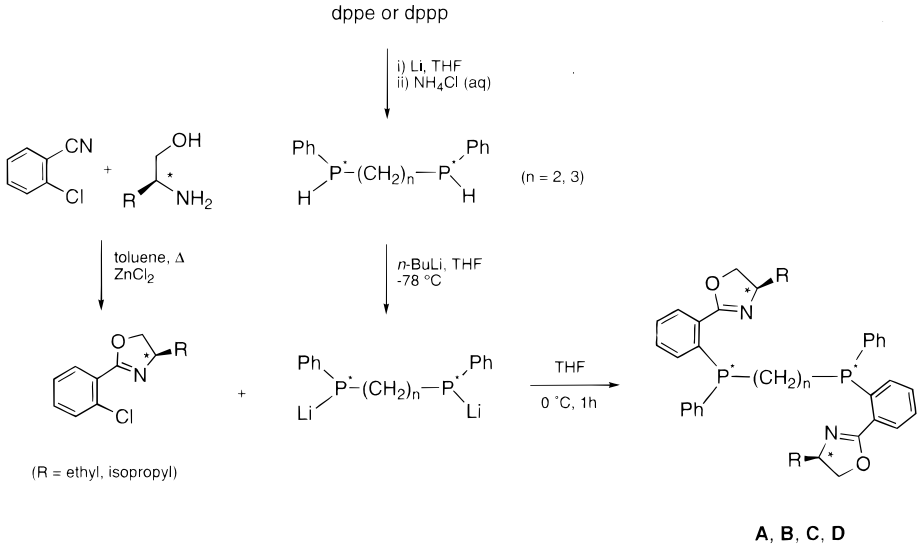
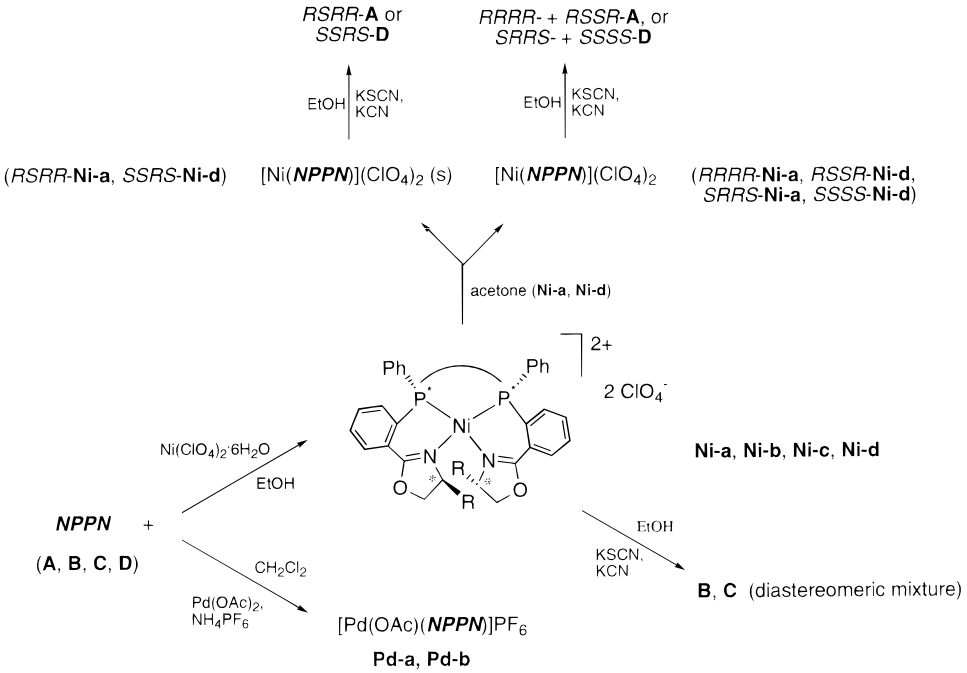
Scheme 1



Scheme 2



were treated with potassium thiocyanate and potassium cyanide in order to obtain the free ligands.[19]

Neutral Palladium Compounds, [PdClMe(κ^2-*NPPN*)] (2a−c) and [$Pd_2Cl_2R_2$(μ-*NPPN*)] (3a−c, R = Me; 4a−c, R = COMe). To establish the coordination behavior in solution of ***NPPN*** ligands with the starting neutral complexes, the reaction of [$PdCl_2$(cod)] with *RSRR*-**A** was monitored by ^{31}P NMR spectroscopy. For a 1/5 ratio of Pd to ligand, two doublets (AB system) at 65.8 and 66.0 ppm (27.0 Hz) were observed. When the ratio of palladium to ligand was 1/1, the number of the signals in the same region of the spectrum (70−60 ppm) increased. For a large excess of palladium (5/1), however, only two doublets (AB system) at 23.2 and 21.2 ppm (71.0 Hz) appeared, indicating that another palladium species had formed. The former chemical shifts are consistent with a P,P-bidentate coordination, yielding a five-membered ring,[20] and the high-field shifts, with an N,P-chelating bimetallic complex, containing two six-membered palladium rings, *RSRR*-**1a** (see Scheme 3).[18b]

When the reaction was performed with [PdClMe(cod)] and *RSRR*-**A**, a similar pattern was observed. For low ratio of Pd to ligand, two doublets at 62.2 and 40.3 ppm (20.5 Hz) appeared, analogously to [PdClMe(dppe)].[21] When the Pd/ligand ratio was increased, two new doublets (AB system) at 27.8 and 24.9 ppm (58.7 Hz) were observed. The ^{31}P chemical shifts showed the absence of a *trans* P−Me bond, which confirms N,P coordination. Moreover, the ^1H NMR spectrum was also useful, especially in the methyl proton region (0−1.4

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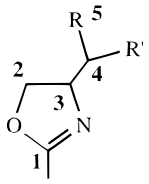
Table 1. Selected ^{1}H NMR Data[a] (δ in ppm) for the Complexes *RSRR*-Ni-a and *SSRS*-Ni-d (500 MHz, CD_3CN) and for *RSRR*-3a and *SSRS*-3b (300 MHz, $CDCl_3$)

compd	H2[b]	H3	H4	H5	Pd−Me
RSRR-**Ni-a**	4.70 (1H, pt, 9.0)	4.34 (1H, m)	1.53 (1H, m)	0.79 (3H, t, 7.5)	
	4.46 (1H, dd, 9.5, 4.5)	4.02 (1H, m)	0.63 (1H, m)	0.71 (3H, t, 7.5)	
	4.57 (2H, m)		1.25 (1H, m)		
			1.12 (1H, m)		
SSRS-**Ni-d**	4.81 (1H, pt, 9.5)	4.30 (1H, m)	2.36 (1H, m)	1.11 (3H, d, 7.0)	
	4.73 (1H, pt, 9.5)	3.85 (1H, dt, 8.5, 3.0)	2.13 (1H, m)	0.82 (3H, d, 7.0)	
	4.69 (2H, m)			0.74 (3H, d, 6.5)	
				0.12 (3H, d, 6.5)	
RSRR-**3a**	4.28 (1H, dd, 9.3, 4.8)	5.40 (1H, m)	nd[c]	0.73 (3H, t, 7.5)	0.14 (3H, d, 5.2)
	4.36 (1H, dd, 9.3, 4.8)	5.30 (1H, m)	nd[c]	0.61 (3H, t, 7.5)	0.12 (3H, d, 5.2)
	4.47 (2H, pq, 10)				
SSRS-**3b**	4.41 (2H, bd)	5.35 (1H, m)	2.35 (1H, m)	0.92 (3H, d, 6.9)	0.38 (3H, d, 4.0)
	4.32 (2H, bd)	5.28 (1H, m)	1.88 (1H, m)	0.86 (3H, d, 6.9)	0.34 (3H, d, 3.8)
				0.27 (3H, d, 6.9)	
				0.25 (3H, d, 6.9)	

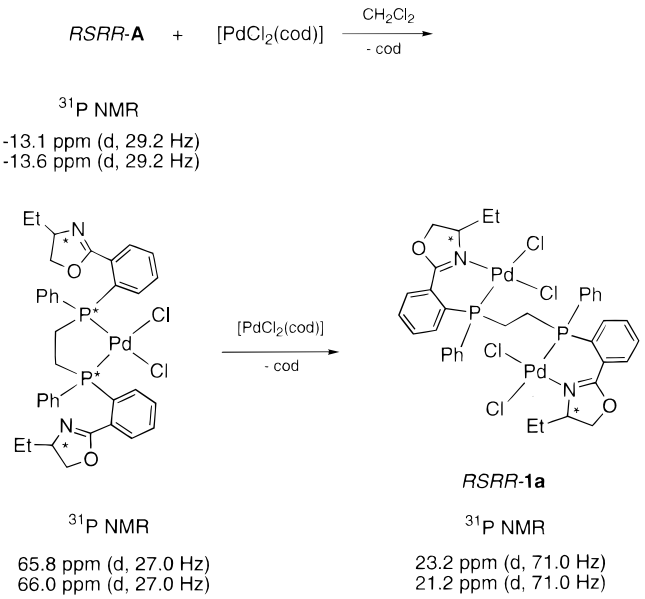
[a] Relative integration, multiplicity (b, broad; d, doublet; m, multiplet; p, pseudo; q, quadruplet; t, triplet), and coupling constants (in Hz) in parentheses. [b] Atom labeling:



R = Me, R' = H for **A** and **C**
R = R' = Me for **B** and **D**

[c] Not distinguished; overlapped with other methylenic groups (P−CH_2).

Scheme 3



ppm; see Figure 2). In this zone, two types of methyl groups are expected: the methyl groups of oxazoline moieties (0.8−0.3 ppm zone) and the methyl group bonded to palladium (0−0.2 ppm zone). The low value of the P−H coupling constant shows a *cis* relationship between phosphorus and the methyl group.[22] This NMR analysis is consistent with formation of monometallic species (Pd/L < 1), where the ligand coordinates in a P,P-chelate fashion (**2a**−**c**), and bimetallic species (Pd/L = 2), where the ligand acts as a bridge between two "PdClMe" moieties (**3a**−**c**; see Scheme 4). This latter coordination behavior has been recently observed for PNNP ligands.[23]

Bimetallic neutral complexes (**3a**−**c**) were precipitated and fully characterized by means of NMR and IR spectroscopy and FAB mass spectrometry. For **B**, *SSRS*-**3b** was separated from the mixture of isomers, due to its lower solubility in toluene (see Table 1). In positive FAB mass spectra for **3a**−**c**, four signals were observed in the highest *m/z* region corresponding to $[M - CH_4]^+$, $[M - HCl]^+$, $[M - HCl - CH_3]^+$, and $[M - HCl - 2\,CH_3]^+$, in agreement with theoretical ion distributions. In all cases, attempts to obtain pure monometallic species (**2a**−**c**) in the solid state from the reaction mixtures were unsuccessful.

Carbonylation products (**4a**−**c**) were obtained from complexes **3a**−**c** by reaction with CO (23−25 bar) in dichloromethane (see Scheme 4). These reactions were monitored by NMR spectroscopy (^{1}H and ^{31}P) using a high-pressure NMR tube.[24] The insertion process was slow, and complete conversion of methylpalladium complexes was reached after 22−26 h at room temperature. After the system was depressurized and the solvent removed, yellow products were separated, corresponding to acyl derivatives. At 1 bar of CO pressure and room temperature, no insertion was observed. Complexes **3a**−**c** reacted more slowly than N,P monometallic complexes (where N is an amino group).[14a]

The formation of the acetyl groups was shown by ^{1}H NMR spectroscopy by the disappearance of the Pd−CH_3 resonances (0.1−0.7 ppm for **3a**−**c**) and appearance of

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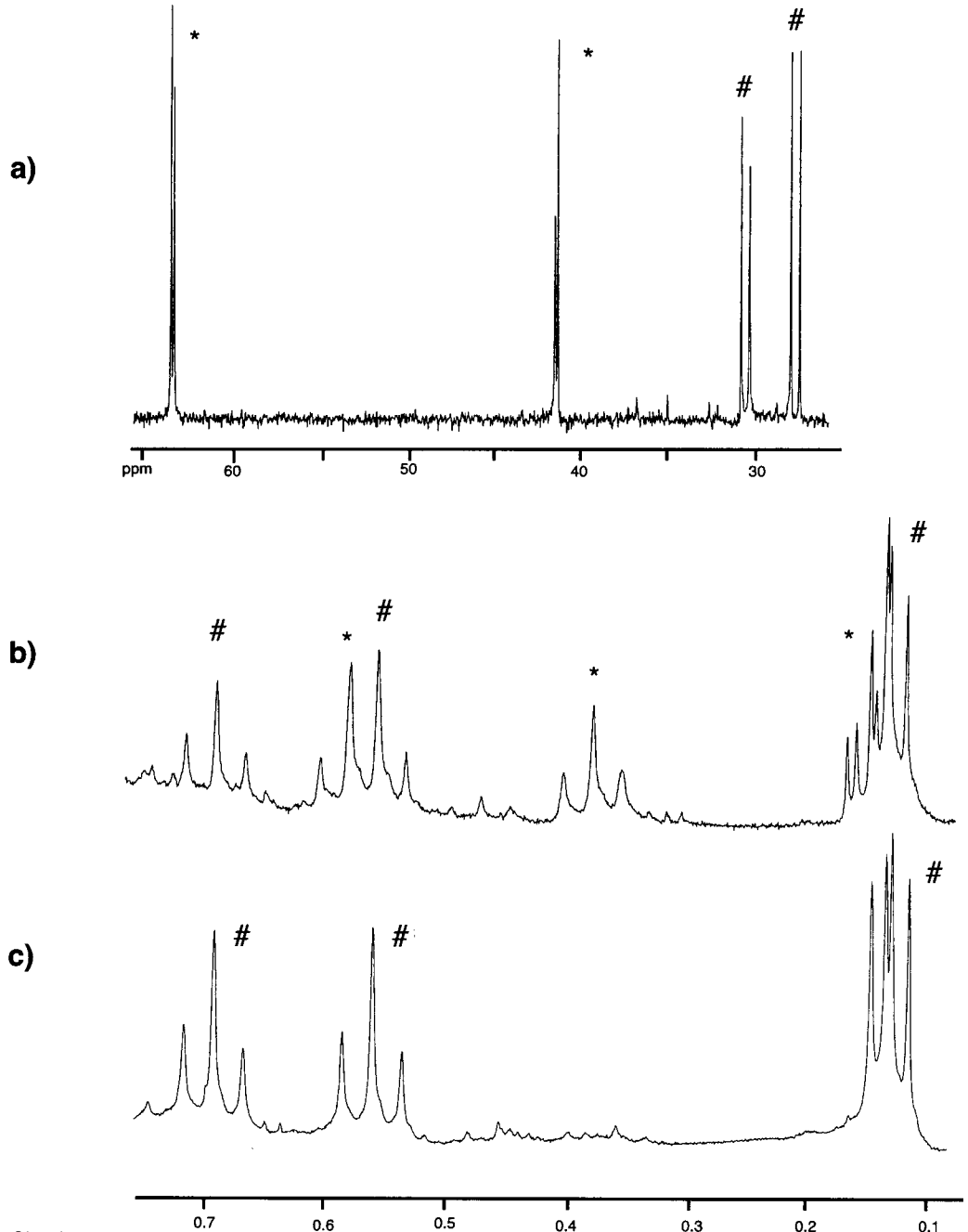

Figure 2. (a) $^{31}P\{^1H\}$ NMR spectrum for a mixture of monometallic *RSRR*-**2a** (*) and bimetallic *RSRR*-**3a** (#) complexes. (b) ^1H NMR spectrum (methyl region) for a mixture of monometallic *RSRR*-**2a** (*) and bimetallic *RSRR*-**3a** (#) complexes. (c) ^1H NMR spectrum (methyl region) for *RSRR*-**3a** (#).

new, narrow singlets at 1.8−2.3 ppm. In addition, upon carbonylation, the phosphorus resonances shifted to higher fields (16−19 ppm for **4a**−**c**) relative to methylpalladium complexes (22−30 ppm). These NMR results are consistent with a *cis* arrangement between the phosphorus atom and the acetyl group.[14a,25] Also, CO stretching vibrations at 1684−1686 cm^{-1} were observed in IR spectra (KBr pellets) corresponding to an acetyl group.[26] It is noteworthy that no carbonylation in neutral monometallic species (**2a**−**c**) was observed under the same conditions.

Olefin insertion reactions were tested with acyl compounds (**4a**−**c**) with norbornene and norbornadiene. No change was observed after 8−10 days in dichloromethane at room temperature, and the starting acyl complexes were recovered quantitatively.

Ionic Methyl Palladium Compounds, $[Pd_2Me_2(CH_3CN)_2(\mu\text{-}NPPN)]Y_2$ (5a−c). Ionic complexes (**5a**−**c**) were synthesized from the analogous neutral chlorides (**3a**−**c**) by reaction with silver *p*-toluenesulfonate or ammonium hexafluorophosphate salts, in the presence of acetonitrile (see Scheme 4).

Carbonylation reactions with ionic complexes (**5a**−**c**) were tested. At 1 bar of CO, dichloromethane solutions decomposed quickly at room temperature. In the range of −10 to 0 °C insertion was observed and ionic acetyl

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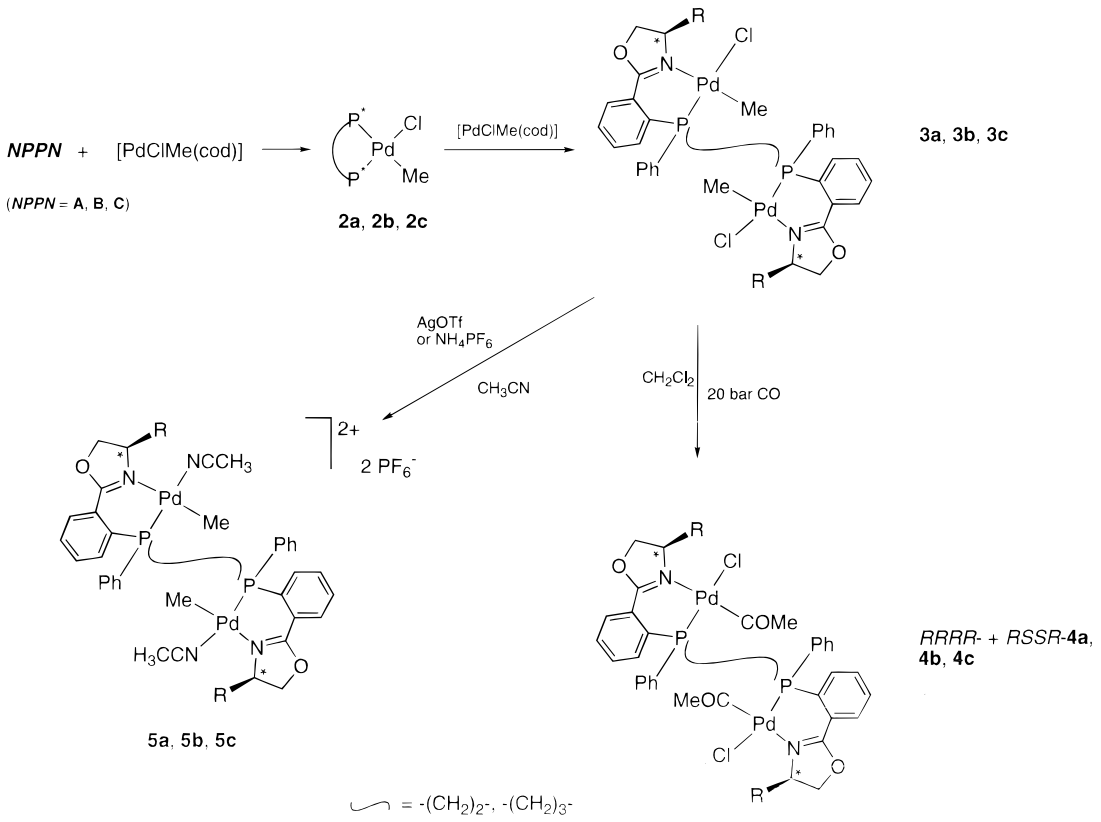
Scheme 4

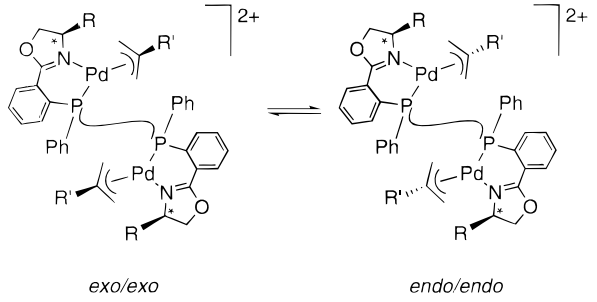


complexes precipitated following additon of diethyl ether. However, these products decarbonylated at room temperature in the solid state, as shown by the absence of CO-acetyl stretching vibrations in the IR spectra.

Ionic monometallic species were generated in situ at −10 °C, by addition of AgOTf to a solution of **2a** (in the presence of free ligand), to study the insertion process. After CO was bubbled for 30 min in a dichloromethane solution, ether was added and a dark solid precipitated. The IR spectrum of the solid showed an absorption at 1642 cm^{-1}. When the solid was dissolved at −10 °C in deuterated chloroform, it decomposed, yielding palladium black. Reaction of **2c** with AgOTf, at −20 °C and 20 bar of CO in CD_2Cl_2, was monitored by NMR spectroscopy. NMR spectra showed the formation of the acetyl complex, but decarbonylation took place after depressurizing the system.

Ionic Allyl Palladium Compounds, [Pd$_2$(η^3-allyl)$_2$(μ-*NPPN*)](PF$_6$)$_2$ (6a−d, 7a, 8d). Ionic allyl complexes [$Pd_2(\eta^3$-allyl$)_2(\mu$-*NPPN*)](PF$_6$)$_2$ (**6a**−**d**, *RSRR*-**7a**, **8d**) were prepared by reaction of [Pd(η^3-allyl)(μ-Cl)]$_2$ (allyl = C_3H_5 for **6a**−**d**; 2-Me-C_3H_4 for *RSRR*-**7a**; 1,3-Ph_2-C_3H_3 for **8d**) with the appropriate ***NPPN*** ligand, in the presence of ammonium hexafluorophosphate (see Scheme 5), following the procedure described by Baltzer and co-workers, with minor modifications.[27] ^{1}H NMR spectra for allyl complexes at room temperature showed broad signals due to their dynamic behavior.

To elucidate the structure of these complexes in solution, NMR spectra in different solvents and at variable temperature were recorded for *RSRR*-**7a**. The analysis of the signals indicated two isomers (probably *endo*/*endo* and *exo*/*exo*; see eq 1), which are in equilib-



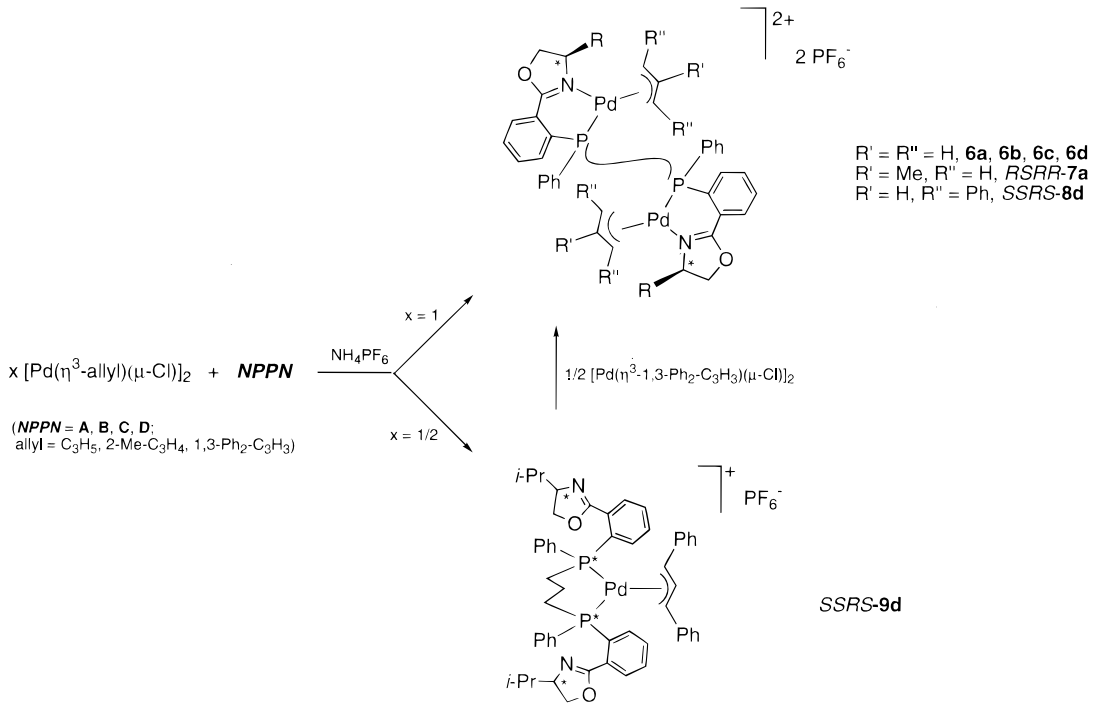
(1)

rium and differ in the relative position of the substituent on the central allylic carbon and the substituent on the stereocenter of the oxazoline group. The complex was soluble in coordinating solvents (acetone, acetonitrile, pyridine) and in chloroform with the addition of one drop of pyridine. The relative ratio of isomers was independent of temperature but strongly dependent on the solvent: for chloroform with pyridine, the isomeric composition was 9/1, while for coordinating solvents (acetone, acetonitrile, or pyridine) the ratio was 7/3.

^{31}P NMR spectra exhibited broad signals at room temperature in all solvents used. Signals were more clearly defined below 273 K, yielding a double system of two doublets (due to the nonequivalence of phosphorus atoms for each isomer). For instance, at 250 K, in acetone, four doublets were observed: 20.70 and 19.60 (65.4 Hz, major species) ppm and 20.80 and 19.30 (63.4 Hz, minor species) ppm. The methyl−oxazoline region in the ^{1}H NMR spectra also distinguished the isomers in solution. At room temperature, the acetonitrile solu-

(27) Baltzer, N.; Macko, L.; Schaffner, S.; Zehnder, M. *Helv. Chim. Acta* **1996**, *79*, 803.

Scheme 5



tion showed two well-defined triplets (0.84 and 0.68 ppm), but in acetone, one of them was broad, and below 283 K, the signal was resolved into two triplets; the other one broadened between 250 and 240 K, also showing two close triplets at 230 K. Hence, the two sets of signals have different coalescence temperatures. Moreover, at low temperatures, two triplets were seen for each. This behavior was also observed for other solvents (pyridine, chloroform with 5% of pyridine), albeit at different coalescence temperatures. When the movement was fast, as in a solution of pyridine at 323 K, four well-defined triplets were observed (major isomer, 0.75 and 0.72 ppm; minor isomer, 0.93 and 0.61 ppm). In addition, four singlets were seen for the methyl−allyl moiety (major, 2.18 and 1.78 ppm; minor, 1.96 and 1.94 ppm).

Crystals of *RSRR*-**7a** were obtained by slow diffusion of diethyl ether over an acetone solution of the complex (see Figure 3). Crystallographic data are summarized in Table 2. Selected bond lengths and angles are listed in Table 3. No metallic interaction between the palladium atoms was observed (Pd(1)−Pd(2) is ca. 7.0 Å).

The Pd−$C_{\text{allyl terminus}}$ bond lengths *trans* to phosphorus are longer than those *trans* to nitrogen for both palladium fragments (2.22−2.19 Å vs 2.12−2.00 Å, respectively), indicating that the phosphorus atom has a greater *trans* influence than does the nitrogen atom.

Due to the nonplanarity of the chelate ring, one of the substituents at the P atom adopts a pseudoequatorial position and the other a pseudoaxial one relative to the Pd−N−P plane. Therefore, for the *S*-phosphorus (P(1)) the phenyl group is equatorially positioned and the alkyl group ("CH_2−CH_2−P") is axially arranged, while for the *R*-phosphorus (P(2)) the relative position of the two substituents is inverted.

In contrast to the main *exo* palladium allyl structures with oxazoline−phosphine ligands,[27,28] the allyl groups in both palladium fragments adopt the *endo* configura-

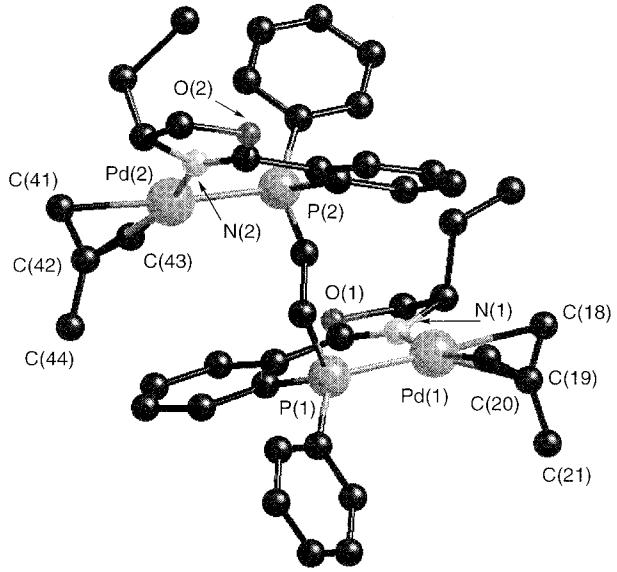


Figure 3. View of the molecular structure of *RSRR*-**7a**. Hydrogen atoms and the hexafluorophosphate anion have been omitted for clarity.

tion; i.e., the methyl group at the central allylic carbon (C(21) and C(44)) points away from the isopropyl at the stereocenter of the oxazoline moiety.

In addition to the bimetallic allylic compounds, the P,P-monometallic complex [Pd(η^3-1,3-Ph_2-C_3H_3)(κ^2-**D**)]-PF_6 (**9d**) was prepared and characterized both in solution and in the solid state. This complex gave the complex **8d** by treatment with excess of starting allyl compound (see Scheme 5).

Allylic Alkylations. Ionic palladium allyl complexes are catalytic precursors in asymmetric allylic substitutions. Therefore, we tested the catalytic activity of Pd/

(28) (a) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523. (b) Wiese, B.; Helmchen, G. *Tetrahedron Lett.* **1998**, *39*, 5727.

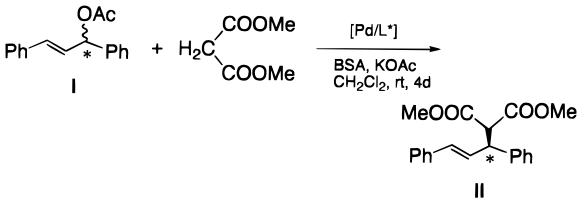
Table 2. Crystal Data for *RSRR*-7a

formula	$C_{44}H_{52}F_{12}N_2O_2P_4Pd_2 \cdot 2C_3H_6O$
mol wt	1205.6
data collecn *T*, K	293
cryst syst	monoclinic
space group	$P2_1$
a, Å	9.208(2)
b, Å	27.031(4)
c, Å	11.610(2)
α, deg	90
β, deg	109.637(9)
γ, deg	90
V, Å^3	2877(1)
Z	2
density (calcd), g cm^{-3}	1.49
F(000)	1308
R index (no. of obsd rflns)	0.075 (5667)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for *RSRR*-7a (with Esd's in Parentheses)

Pd(1)−P(1)	2.255(9)	Pd(1)−C(19)	2.19(2)
Pd(2)−P(2)	2.258(9)	Pd(1)−C(20)	2.12(2)
Pd(1)−N(1)	2.09(1)	Pd(2)−C(41)	2.19(2)
Pd(2)−N(2)	1.96(2)	Pd(2)−C(42)	2.15(2)
Pd(1)−C(18)	2.22(2)	Pd(2)−C(43)	2.00(2)
N(1)−Pd(1)−P(1)	92.5(5)	C(18)−Pd(1)−C(20)	65.2(5)
N(2)−Pd(2)−P(2)	90.6(5)	C(41)−Pd(2)−C(43)	70.5(7)

NPPN systems in the allylic alkylation of the model substrate *rac*-3-acetoxy-1,3-diphenyl-1-propene, using dimethyl malonate as nucleophile, under basic Trost conditions (see eq 2).[29] No important differences in the



(2)

organic process were observed between the use of catalytic precursors **6a**−**d** and the generation of catalytic species under in situ conditions with the same Pd/ligand ratio. The catalytic results are collected in Table 4.

Bulky groups at the oxazoline stereocenter (ligands **B** and **D**; entries 6, 9, 11, and 17) induce higher enantiomeric excesses, due to the lability increase of the allylic terminal carbon *trans* to the phosphorus atom; both steric and electronic factors are well-known for the *N*,*P*-palladium catalytic systems in allylic substitutions.[11]

The configuration of the stereogenic phosphorus atom does not seem to affect the enantioselectivity of the process, because under analogous experimental conditions the use of one of the ligand diastereoisomers gives the same enantioselectivity as a mixture of them (entries 2 vs 4; 9 vs 11), as Helmchen et al. concluded from their studies with monooxazolines containing chiral phosphorus atoms, for acyclic allylic acetates.[28a] Moreover, no important differences concerning in enantioselectivity were observed between N,P-monometallic systems and our N,P-bimetallic precursors (for a 2/1 Pd/ligand ratio),[28,30] although Pd/***NPPN*** systems are less

(29) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

Table 4. Results of Asymmetric Alkylation of *rac*-3-Acetoxy-1,3-diphenyl-1-propene with Dimethyl Malonate (See Eq 2)[a]

entry	ligand	Pd/***NPPN***	% Pd	conversn (%)[b]	ee (%)[c]	config[d]
		Complex[e]				
1	*RRRR*-**A** + *RSSR*-**A**[f]	2/1	1	12	34.0	*R*
2	*RRRR*-**A** + *RSSR*-**A**[f]	2/1	2	40	38.5	*R*
3	*RRSR*-**A**	2/1	1	10	36.5	*R*
4	*RRSR*-**A**	2/1	2	50	39.0	*R*
5	**B**	2/1	1	25	30.0	*S*
6	**B**	2/1	2	100 (98)[g]	81.0	*S*
7	**C**	2/1	1	60	44.0	*R*
8	**C**	2/1	2	100 (94)[g]	80.0	*R*
9	*SSRS*-**D**	2/1	2	80	89.0	*S*
10	*SRRS*-**D** + *SSSS*-**D**	2/1	1	50	34.0	*S*
11	*SRRS*-**D** + *SSSS*-**D**	2/1	2	70	90.0	*S*
		In Situ[h]				
12	**C**	1/1	1	50	51.5	*R*
13	**C**	1/1	2	100 (95)[g]	48.0	*R*
14	**C**	2/1	1	60	37.0	*R*
15	**C**	2/1	2	100 (93)[g]	85.5	*R*
16	**C**	1/2	2	98	70.0	*R*
17	**D**	2/1	2	100 (98)[g]	87	*S*
18	**D**	2/1	4	100 (97)[g]	85	*S*
19	*SSRS*-**D**	1/1	2	70	48.0	*S*
20	*SRRS*-**D** + *SSSS*-**D**	1/1	2	65	49.0	*S*

[a] Results determined from duplicate experiments. [b] Conversion based on the substrate. [c] Determined by HPLC on a Chiralcel-OD column. [d] Determined by optical rotation: Leutenegger, U.; Umbricht, G.; Fahrni, C.; Matt, P. V.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. [e] **6a**−**d** complexes used as catalytic precursors. [f] The ratio of both diastereomers was 9/1. [g] In parentheses, isolated product after column chromatography. [h] Catalytic precursor generated in situ from $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (1 mol % unless stated otherwise) and the appropriate ligand (1 mol %).

active, especially ligand **A**, which also shows a low enantioselectivity (entries 1−4).

The effect of the Pd/***NPPN*** ratio on the enantioselectivity, for 2 mol % of palladium (entries 13 vs 15 and 9 vs 19), suggests different catalytic species for 1/1 and 2/1 Pd/***NPPN*** ratios. As shown above, P,P-monometallic species are formed for low palladium/ligand ratios (**2a**−**c**), which evolve to the bimetallic complexes when the ratio increases (**3a**−**c**). Analogously, we monitored the reaction of $[Pd(\eta^3\text{-}C_3H_5)(cod)]BF_4$ with **D** (*SRRS* + *SSSS*), in $CDCl_3$, by ^{31}P NMR spectroscopy. For the Pd/**D** ratios 1/4, 1/2, and 1/1, besides the free ligand, only one singlet was observed at 12.2 ppm. For the ratio 2/1, several singlets were seen in the 14−16 ppm region, due to the different *endo* and *exo* N,P-bimetallic conformations (see above the NMR discussion for *RSRR*-**7a**). The P,P-monometallic species may thus be the catalytically active species for a 1/1 ratio. These catalytic systems induce lower asymmetry (entries 13, 19, and 20) than the analogous systems with a 2/1 Pd/ligand ratio (entries 8, 9, 11, 15, and 17). The former moderate selectivity observed (ca. 50%) is consistent with that for other published palladium chiral diphosphine systems.[20,31] An excess of ligand (1/2 Pd/***NPPN*** ratio) enhances the enantioselectivity up to 70% (entry 16),

(30) (a) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (b) Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149.

(31) Longmire, J. M.; Zhu, G.; Zhang, X. *Tetrahedron Lett.* **1997**, *38*, 375.

but it remains lower than for 2/1 palladium/ligand systems (80%, entry 8). For monometallic species, an excess of ligand may favor the N-coordination.

The palladium concentration (1 or 2 mol % based on the substrate) affects not only the conversion rate but also the enantioselectivity. This behavior concerns the 2/1 palladium/ligand ratios (1 mol %, entries 5, 7, 10, and 14; 2 mol %, entries 6, 8, 9, 11, 15, and 17), but not the 1/1 ratios (entry 12 vs 13). Higher mole percentages of palladium (4 mol %) had no effect on the enantiomeric excess (entry 17 vs 18). Similar behavior was detected for other PNNP ligands, which can also stabilize bimetallic palladium species, suggesting the formation of monometallic complexes for low palladium concentrations.[12] The dissociation of a bimetallic allylic complex (as **6**, **7**, or **8**; see Scheme 5) toward the formation of monometallic species may be favored at relatively low concentrations of starting palladium compound. Under these conditions, nitrogen decoordination seems probable.

Conclusions

New chiral polydentate ligands were synthesized (**A**−**D**), containing four stereocenters: two carbon and two phosphorus atoms. Among the different ways of coordination for these ligands (κ^2-*PP*; κ^4-*NPPN*, affording monometallic species; μ-*NPPN*, bimetallic species), the bis-N,P-bidentate fashion (μ-*NPPN*) is preferred by palladium compounds (**3a**−**c**, **4a**−**c**, **5a**−**c**, **6a**−**d**, *RSRR*-**7a**, **8d**), although for Ni(II) and Pd(II) salts (metallic centers bonded to very weak Lewis bases) tetra- and tri-coordination was exhibited (**Ni-a**−**d**, **Pd-a**,**b**). An excess of ligand led to P,P coordination both in solution (**2a**−**c**) and in the solid state (**9d**).

For the neutral complexes **3a**−**c**, slow carbonylation took place at high pressure of CO (23−25 bar), affording the quantitatively neutral acyl complexes **4a**−**c**. No insertion was observed for monometallic neutral species (**2a**−**c**). Further reaction of acyl complexes (**4a**−**c**) with olefins, such as norbornadiene or norbornene, did not occur. Fast CO insertion processes were observed for ionic species (both in monometallic and in bimetallic species), but acyl ionic complexes were not isolated as stable solids.

Allylic palladium species were tested in allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate as the nucleophile. The Pd/***NPPN*** catalytic systems induced high enantioselectivity (up to 90% of enantiomeric excess), but they were only moderately active. As generally accepted for oxazoline−phosphine ligands, the higher *trans* influence of the phosphorus atom leads preferentially to nucleophilic attack at one of the terminal allylic carbon atoms. The absolute configuration of the organic product **II** points to a fast substitution for the *exo* allyl palladium conformation. In addition, the enantioselectivity was enhanced by bulky substituents on the oxazoline moiety. However, these catalytic systems were strongly dependent on the Pd/***NPPN*** ratio. For 2/1 ratios, the ee values were higher than for the 1/1 ratios. This behavior indicates different catalytic species in the solution: bimetallic vs monometallic compounds. Moreover, palladium concentration based on the substrate **I** influenced the enantioselectivity for the 2/1 systems. For low palladium contents, lower enantiomeric excesses were obtained. This can be explained by partial ligand dissociation, probably by nitrogen decoordination of the oxazoline moiety.

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. L-(−)-2-Aminobutanol and L-valinol (Fluka) were used without previous purification. $ZnCl_2$ (Merck) was purified as described elsewhere.[32] [PdClMe(cod)] was prepared as previously described.[33] NMR spectra were recorded on Varian XL-500 (^{1}H, standard $SiMe_4$), Varian Gemini (^{13}C, 50 MHz, standard $SiMe_4$), Bruker DRX 250 (^{31}P, 101.25 MHz, standard H_3PO_4), and Bruker 300 (^{31}P, 121.5 MHz, standard H_3PO_4) spectrometers. Chemical shifts were reported downfield from standards. IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. The GC/MS analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column) interfaced to a Hewlett-Packard 5971 mass selective detector. Enantiomeric excesses were determined by HPLC on a Hewlettt-Packard Series 1050 chromatograph (Chiralcel-OD chiral column) with a UV detector. Optical rotations were measured on a Perkin-Elmer 241MC spectropolarimeter (*c* 0.1, $CHCl_3$). Conductivities were obtained on a Radiometer CDM3 conductimeter. Elemental analyses were carried out by the Serveis Científico-Tècnics de la Universitat de Barcelona in an Eager 1108 microanalyzer.

Preparation of (+)-(4′*R*)-2-(3′,4′-Dihydro-4′-ethyl-2′-oxazolyl)-1-chlorobenzene and (−)-(4′*S*)-2-(3′,4′-Dihydro-4′-isopropyl-2′-oxazolyl)-1-chlorobenzene. The oxazolines were synthesized by following published procedures with minor modifications.[15] The amino alcohol (37 mmol: 3.31 g for L-2-aminobutanol; 3.81 g for L-valinol), 2-chlorobenzonitrile (2.75 g, 20 mmol), and $ZnCl_2$ (90 mg, 0.66 mmol) were dissolved in 25 cm^3 of toluene and refluxed under nitrogen (5 days for *ethyl* oxazoline, 3 days for *isopropyl*), until no more nitrile was observed (reaction monitored by gas chromatography). The reaction mixture was filtered off and the solvent was removed under reduced pressure. The residue was dissolved in 20 cm^3 of dichloromethane and washed in degassed water (5 × 10 cm^3). The organic phase was dried over Na_2SO_4 and filtered, and solvent was removed under reduced pressure, affording a yellow oil. Yields: *ethyl*, 3.60 g, 85%; *isopropyl*, 4.0 g, 90%. $[\alpha]_D^{25}$ = +32.3° (*ethyl*), −41.6° (*isopropyl*). ^{1}H NMR data ($CDCl_3$; see footnote *b* of Table 1 for atom labeling): *ethyl* (500 MHz), 0.98 (H5, 3H, t, 7.5 Hz), 1.63 (H4, 1H, m), 1.75 (H4, 1H, m), 4.27 (H3, 1H, m), 4.05 (H2, 1H, dd, 8.0, 1.5 Hz), 4.49 (H2, 1H, dd, 8.0, 1.5 Hz), 7.32 (1H, dd, 8.0, 1.5 Hz), 7.40 (1H, dd, 8.0, 1.5 Hz), 7.25 (1H, dd, 7.5, 1.5 Hz), 7.69 (1H, dd, 7.5, 1.5 Hz); *isopropyl* (250 MHz), 1.05 (H5, 3H, d, 6.8 Hz), 0.97 (H5, 3H, d, 6.8 Hz), 1.90 (H4, 1H, m), 4.10 (H2 + H3, 2H, m), 4.43 (H2, 1H, m), 7.60 (2H, m), 7.45 (2H, m) ppm. ^{13}C NMR data ($CDCl_3$, 50 MHz; see footnote *b* of Table 1 for atom labeling): *ethyl*, 10.3 (C5), 28.9 (C4), 68.7 (C3), 72.6 (C2), 163.5 (C1); *isopropyl*, 18.3, 17.7 (C5), 32.2 (C4), 69.7 (C3), 76.0 (C2), 162.3 (C1) ppm.

Preparation of 1,2-Bis(phenylphosphino)ethane. 1,2-Bis(diphenylphosphino)ethane (1.0 g, 2.51 mmol) was dissolved in 25 cm^3 of THF, and finely cut lithium metal (3.50 mg, 5.0 mmol) was then added. The mixture was sonicated for 15 min and then stirred overnight. To eliminate the phenyl anion

(32) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.
(33) Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M. *Inorg. Chem.* **1993**, *32*, 5769.

formed together with the dilithium diphosphide compound, the lithium mixture was hydrolyzed by an aqueous ammonium chloride solution (10%). The organic phase was dried over Na_2SO_4 and the solvent evaporated under reduced pressure, affording a colorless oil. Yield: 0.50 g, 80%. ^{31}P NMR data (CD_3COCD_3): −47.70 (J(P−H) = 56.8 Hz), −48.90 (J(P−H) = 56.8 Hz) ppm.

Preparation of 1,3-Bis(phenylphosphino)propane. This diphosphine was synthesized in a way similar to that used above for 1,2-bis(phenylphosphino)ethane. Yield: 0.60 g, 90%. ^{31}P{^{1}H} NMR data (CD_3COCD_3): −53.07 (s), −53.18 (s) ppm.

Preparation of 1,2-Bis[(4′*R*)-phenyl[2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl)]phenylphosphino]ethane (A), 1,2-Bis-[(4′*S*)-phenyl[2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl)]-phenylphosphino]ethane (B), 1,3-Bis[(4′*R*)-phenyl[2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl)]phenylphosphino]propane (C), and 1,3-Bis[(4′*S*)-phenyl[2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl)]phenylphosphino]propane (D). A 2 mmol portion of chlorooxazoline (0.42 g for (+)-(4′*R*)-2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl)-1-chlorobenzene; 0.44 g for (−)-(4′*S*)-2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl)-1-chlorobenzene) and 1 mmol of secondary diphosphine (0.25 g for 1,2-bis(phenylphosphino)ethane; 0.26 g for 1,3-bis(phenylphosphino)propane) were dissolved in 15 cm^3 of THF, and the solution was cooled to −78 °C. Then, 1.6 cm^3 of *n*-BuLi (ca. 1.6 M in hexane) was slowly added. The cooling bath was removed, and the mixture was stirred for ca. 1 h at room temperature. The reaction was monitored by ^{31}P NMR: when signals of the starting diphosphine had disappeared, the solution was hydrolyzed with water (5 × 10 cm^3) to eliminate any salts. Organic extracts were dried over anhydrous Na_2SO_4 and filtered off, and the solvent was removed under reduced pressure, affording a yellow oil. Yield: **A**, 0.41 g, 70%; **B**, 0.40 g, 65%; **C**, 0.48 g, 80%; **D**, 0.44 g, 70%.

Preparation of [(4′*R*)-Phenyl[2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl)]phenylphosphinoethane]nickel(II) Perchlorate (Ni-a), [(4′*S*)-Phenyl[2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl)]phenylphosphinoethane]nickel(II) Perchlorate (Ni-b),[(4′*R*)-Phenyl[2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl)]-phenylphosphinopropane]nickel(II) Perchlorate (Ni-c), and [(4′*S*)-Phenyl[2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl)]-phenylphosphinopropane]nickel(II) Perchlorate (Ni-d). The ligand (1 mmol: 0.59 g for **A**, 0.62 g for **B**, 0.61 g for **C**, 0.63 g for **D**) was dissolved in 5 cm^3 of THF, and a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.37 g, 1 mmol), dissolved in 25 cm^3 of ethanol, was added. The reaction mixture immediately became dark red, and, after it was stirred for ca. 30 min, an orange solid was formed. The mixture was kept in the freezer overnight. Then the solid was separated by filtration (the absence of phosphine—free or coordinated—in the solution was verified by ^{31}P NMR spectroscopy), washed successively in ethanol and diethyl ether, and dried under reduced pressure. Yields: **Ni-a**, 0.64 g, 75%; **Ni-b**, 0.70 g, 80%; **Ni-c**, 0.69 g, 80%; **Ni-d**: 0.76 g, 85%. Data for **Ni-a** are as follows. Mp: 125 °C dec. Anal. Calcd for $C_{36}H_{38}Cl_2N_2O_{10}P_2Ni$: C, 50.85; H, 4.50; N, 3.29. Found: C, 50.20; H, 4.65; N, 3.05. MS (FAB positive): *m*/*z* 749 (M − ClO_4). Molar conductivity (*c* 10^{-3} M, CH_3CN): 206.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C=N) 1613 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 58.40 (d, 72.0 Hz), 57.10 (d, 72.0 Hz), 63.67 (s), 61.90 (s) ppm. Data for **Ni-b** are as follows. Mp: 120 °C dec. Anal. Calcd for $C_{38}H_{42}Cl_2N_2O_{10}P_2Ni$: C, 52.00; H, 4.82; N, 3.19. Found: C, 51.85; H, 4.60; N, 3.00. MS (FAB positive): *m*/*z* 779 (M − ClO_4). Molar conductivity (*c* 10^{-3} M, CH_3CN): 210.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C=N) 1615 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 61.33 (d, 74.5 Hz), 55.50 (d, 74.5 Hz), 62.65 (bs) ppm. Data for **Ni-c** are as follows. Mp: 150 °C dec. Anal. Calcd for $C_{37}H_{40}Cl_2N_2O_{10}P_2Ni$: C, 51.41; H, 4.66; N, 3.24. Found: C, 51.10; H, 4.30; N, 3.10. MS (FAB positive): *m*/*z* 765 (M − ClO_4). Molar conductivity (*c* 10^{-3} M, CH_3CN): 208.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C=N) 1618 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 3.37 (d, 119.4 Hz), 6.67 (d, 119.4 Hz), 6.64 (s), 4.69 (s) ppm. Data for **Ni-d** are as follows. Mp: 143 °C dec. Anal. Calcd for $C_{39}H_{44}Cl_2N_2O_{10}P_2Ni$: C, 52.40; H, 4.93; N, 3.14. Found: C, 52.55; H, 5.10; N, 2.95. MS (FAB positive): *m*/*z* 792 (M − ClO_4). Molar conductivity (*c* 10^{-3} M, CH_3CN): 210 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C=N) 1611 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 9.50 (d, 110.0 Hz); 5.52 (d, 110.0 Hz); 8.90 (bs) ppm.

Separation of *RSRR*-A and *SSRS*-D from Diastereomeric Mixtures of Ni-a and Ni-d. The diastereomeric mixture of complexes **Ni-a** and **Ni-d** (0.5 g; 0.59 and 0.56 mmol, respectively) were stirred in 20 cm^3 of acetone for 1 h at room temperature. Then, the mixtures were filtered and the orange solids obtained were washed with acetone (4 × 5 cm^3), corresponding to *RSRR*-**Ni-a** and *SSRS*-**Ni-d**, respectively. These solids (0.20 mmol; 0.17 g for *RSRR*-**Ni-a** and 0.18 g for *SSRS*-**Ni-d**) were treated with KSCN (0.030 g, 0.31 mmol) and a large excess of KCN (0.40 g, 6 mmol) in 20 cm^3 of ethanol. The mixtures were stirred at room temperature until colorless solutions were obtained. The solvent was then removed under reduced pressure, and 25 cm^3 of dichloromethane was added. The mixtures were washed with water until no free cyanide was observed in the aqueous phase. The organic phases were dried over anhydrous Na_2SO_4, filtered off, and the solvent removed under reduced pressure, affording white oils. Yields: *RSRR*-**A**, 0.10 g, 83%; *SSRS*-**D**, 0.11 g, 85%.

Preparation of (Acetato)[(4′*R*)-phenyl[2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl)]phenylphosphinoethane]palladium-(II) Hexafluorophosphate (Pd-a) and (Acetato)[(4′*S*)-phenyl[2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl)]phenylphosphino-ethane]palladium(II) Hexafluorophosphate (Pd-b). A 0.12 mmol portion of ligand (0.071 g for **A**; 0.074 g for **B**), 0.027 g (0.12 mmol) of palladium acetate, and 0.029 g (0.24 mmol) of ammonium hexafluorophosphate were dissolved in 4 cm^3 of dichloromethane. The reaction mixture was stirred overnight at room temperature. The solution was then washed in water (until neutral pH). The organic phase was dried over $MgSO_4$ and filtered off, and the solvent was removed under reduced pressure, affording an orange solid, which was then recrystallized from dichloromethane/diethyl ether. Yields: **Pd-a**, 0.08 g, 73%; **Pd-b**, 0.09 g, 82%. Data for **Pd-a** are as follows. Mp: 105 °C dec. Anal. Calcd for $C_{38}H_{41}F_6N_2O_4P_3Pd$: C, 50.60; H, 4.58; N, 3.11. Found: C, 50.20; H, 4.70; N, 3.35. MS (FAB positive): *m*/*z* 757 (M − PF_6). Molar conductivity (*c* 10^{-3} M, CH_3CN): 135.1 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C=N + CH_3COO) 1610−1630 (bs) cm^{-1}. ^{31}P NMR data (121.25 MHz, CD_3COCD_3): 72.71 (d, 13.1 Hz), 68.19 (d, 13.1 Hz), 66.02 (s), 64.90 (s) ppm. Data for **Pd-b** are as follows. Mp: 20 °C dec. Anal. Calcd for $C_{40}H_{45}F_6N_2O_4P_3Pd$: C, 51.60; H, 4.87; N, 3.01. Found: C, 51.82; H, 4.50; N, 2.80. MS (FAB positive): *m*/*z* 786 (M − PF_6). Molar conductivity (*c* 10^{-3} M, CH_3CN): 114.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C=N + CH_3COO) 1610−1630 (bs) cm^{-1}. ^{31}P NMR data (121.25 MHz, CD_3COCD_3): 63.65 (d, 9.0 Hz), 63.03 (d, 9.0 Hz), 65.08 (bs) ppm.

Preparation of Tetrachloro[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinoethane]-dipalladium(II) (*RSRR*-1a). A 0.30 g (0.5 mmol) portion of *RSRR*-**A** was dissolved in 5 cm^3 of benzene, and 0.29 g (1 mmol) of [$PdCl_2$(cod)] was added. The reaction mixture was stirred for 1 h at room temperature, until no more free ligand was observed (reaction monitored by ^{31}P NMR spectroscopy). The solvent was then removed under reduced pressure, and the residue was crystallized from dichloromethane and diethyl ether. This solid was separated by filtration, washed in diethyl ether, and dried under reduced pressure. Yield: 0.38 g, 85%. Mp: 120 °C dec. Anal. Calcd for $C_{36}H_{38}Cl_4N_2O_2P_2Pd_2$: C, 45.65; H, 4.04; N, 2.96. Found: C, 45.90; H, 4.00; N, 3.05. MS (FAB positive): *m*/*z* 947 (M). IR data: ν(C=N) 1625 cm^{-1}. ^{31}P NMR data (101.25 MHz, CD_3COCD_3): 23.20 (d, 71.0 Hz), 21.20 (d, 71.0 Hz) ppm.

Preparation of Dichlorodimethyl[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinoet-

hane]dipalladium(II) (3a), Dichlorodimethyl[μ-(4′*S*)-phenyl(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))phenylphosphinoethane]-dipalladium(II) (3b), and Dichlorodimethyl[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinopropane]dipalladium(II) (3c). The ligand (0.5 mmol: 0.30 g for **A**, 0.31 g for **B**, 0.32 g for **C**) was dissolved in 5 cm^3 of benzene, and 0.27 g (1 mmol) of [PdClMe(cod)] was added. The reaction mixture was stirred for 1−2 h at room temperature, until no more free ligand was observed (reaction monitored by ^{31}P NMR spectroscopy). The solvent was then removed under reduced pressure, and the residue was crystallized from dichloromethane and diethyl ether. The solid was then separated by filtration, washed in diethyl ether, and dried under reduced pressure. Yields: **3a**, 0.38 g, 85%; **3b**, 0.37 g, 80%; **3c**, 0.32 g, 70%. Data for **3a** are as follows. Mp: 200 °C dec. Anal. Calcd for $C_{38}H_{44}Cl_2N_2O_2P_2Pd_2$: C, 50.35; H, 4.89; N, 3.09. Found: C, 50.00; H, 5.00; N, 3.25. MS (FAB positive): *m*/*z* 890.4 (M − CH_4), 870.0 (M − HCl), 855.0 (M − HCl − CH_3), 840.0 (M − HCl − $2CH_3$). IR data: ν(C═N) 1630 cm^{-1}. ^{31}P NMR data (101.25 MHz, CD_3COCD_3): 29.90 (d, 58.5 Hz), 26.90 (d, 58.5 Hz), 28.02 (s), 27.75 (s) ppm. Data for **3b** are as follows. Mp: 172 °C dec. Anal. Calcd for $C_{40}H_{48}Cl_2N_2O_2P_2Pd_2$: C, 51.41; H, 5.18; N, 3.00. Found: C, 51.80; H, 5.00; N, 3.20. IR data: ν(C═N) 1628 cm^{-1}. ^{31}P NMR data (101.25 MHz, CD_3CN): 29.70 (d, 60.0 Hz), 26.95 (d, 60.0 Hz), 29.97 (s), 27.91 (s) ppm. Data for **3c** are as follows. Mp: 90 °C dec. Anal. Calcd for $C_{39}H_{46}Cl_2N_2O_2P_2Pd_2$: C, 50.89; H, 5.04; N, 3.04. Found: C, 50.60; H, 4.90; N, 2.80. MS (FAB positive): *m*/*z* 904.5 (M − CH_4), 884.0 (M − HCl), 869.0 (M − HCl − CH_3), 855.0 (M − HCl − $2CH_3$). IR data: ν(C═N) 1635 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 25.71 (s), 24.06 (s), 23.74 (s), 22.70 (s) ppm.

Preparation of Diacetyldichloro[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinoethane]-dipalladium(II) (*RRRR*- and *RSSR*-4a), Diacetyldichloro-[μ-(4′*S*)-phenyl(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))-phenylphosphinoethane]dipalladium(II) (4b), and Diacetyldichloro[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))-phenylphosphinopropane]dipalladium(II) (4c). A 0.065 mmol portion of **3x** (0.059 g for *RRRR*- + *RSSR*-**3a**; 0.061 g for **3b**; 0.060 g for **3c**) was dissolved in 1.5 cm^3 of dichloromethane-d_2. The solution was transferred into a high-pressure NMR tube, and a pressure of 23−25 bar of CO was applied at room temperature. The reaction was monitored by NMR, and it was completed after ca. 24 h. After depressurizing the system, the solution was filtered over Celite and the solvent was removed under reduced pressure, affording a yellow solid. Yields: *RRRR*- + *RSSR*-**4a**, 0.042 g, 65%; **4b**, 0.051 g, 80%; **4c**, 0.047 g, 75%. Data for *RRRR*- + *RSSR*-**4a** are as follows. Anal. Calcd for $C_{40}H_{44}Cl_2N_2O_4P_2Pd_2$: C, 49.92; H, 4.61; N, 2.91. Found: C, 50.15; H, 4.70; N, 2.60. IR data: ν($COCH_3$) 1686, ν(C═N) 1627 cm^{-1}. ^{31}P NMR data (121.5 MHz, CD_2Cl_2): 16.60 (s), 17.60 (s) ppm. Data for **4b** are as follows. Anal. Calcd for $C_{42}H_{48}Cl_2N_2O_4P_2Pd_2$: C, 50.93; H, 4.88; N, 2.83. Found: C, 51.05; H, 4.60; N. 2.60. IR data: ν($COCH_3$) 1687, ν(C═N) 1620 cm^{-1}. ^{31}P NMR data (121.5 MHz, CD_2Cl_2): 19.03 (d, 57.0 Hz), 16.14 (d, 57.0 Hz), 16.05 (bs) ppm. Data for **4c** are as follows. Anal. Calcd for $C_{41}H_{46}Cl_2N_2O_4P_2Pd_2$: C, 50.43; H, 4.75; N, 2.87. Found: C, 50.10; H, 4.85; N, 2.60. IR data: ν($COCH_3$) 1684, ν(C═N) 1628 cm^{-1}. ^{31}P NMR data (121.5 MHz, CD_2Cl_2): 14.60 (d, 51.0 Hz), 13.50 (d, 51.0 Hz), 13.90 (s), 12.04 (s) ppm.

Preparation of Bis(acetonitrile)dimethyl[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphino-ethane]dipalladium(II) Hexafluorophosphate (*RRRR*- and *RSSR*-5a), Bis(acetonitrile)dimethyl[μ-(4′*S*)-phenyl-(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))phenylphosphinoethane]dipalladium(II) Hexafluorophosphate (5b), and Bis(acetonitrile)dimethyl[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinopropane]-dipalladium(II) Hexafluorophosphate (5c). A 0.1 mmol portion of **4x** (0.091 g for *RRRR*- + *RSSR*-**4a**, 0.093 g for **4b**, 0.092 g for **4c**) and 0.033 g (0.2 mmol) of NH_4PF_6, dissolved in 4 cm^3 of dichloromethane and 1 cm^3 of acetonitrile, was stirred overnight. Solvent was then removed under reduced pressure, the residue was dissolved in 5 cm^3 of dichloromethane, and washings with water (until pH 7) were performed. The organic phase was dried over $MgSO_4$ and filtered off, and the solvent was removed under vacuum. Addition of diethyl ether afforded yellow solid precipitates. Yields: **5a**, 0.06 g, 50%; **5b**, 0.08 g, 65%; **5c**, 0.055 g, 45%. Data for *RRRR*- + *RSSR*-**5a** are as follows. Anal. Calcd for $C_{42}H_{50}F_{12}N_4O_2P_4Pd_2$: C, 41.77; H, 4.17; N, 4.64. Found: C, 41.50; H, 4.25; N, 4.43. IR data: ν(C═N) 1627 cm^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 28.00 (s), 27.77 (s) ppm. Data for **5b** are as follows. Anal. Calcd for $C_{44}H_{54}F_{12}N_4O_2P_4Pd_2$: C, 42.77; H, 4.41; N, 4.53. Found: C, 42.50; H, 4.65; N, 4.80. IR data: ν(C═N) 1625 cm^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 36.78 (d, 67.5 Hz), 34.40 (d, 67.5 Hz), 36.70 (s), 35.90 (s) ppm. Data for **5c** are as follows. Anal. Calcd for $C_{44}H_{52}F_{12}N_4O_2P_4Pd_2$: C, 43.26; H, 4.29; N, 4.59. Found: C, 43.60; H, 4.00; N, 4.35. IR data: ν(C═N) 1630 cm^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 38.00 (d, 58.0 Hz), 35.50 (d, 58.0 Hz), 36.40 (s), 34.00 (s) ppm.

Preparation of Bis(η^3-allyl)[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinoethane]-dipalladium(II) Hexafluorophosphate (6a), Bis(η^3-allyl)-[μ-(4′*S*)-phenyl(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))phenylphosphinoethane]dipalladium(II) Hexafluorophosphate (6b), Bis(η^3-allyl)[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinopropane]dipalladium(II) Hexafluorophosphate (6c), and Bis(η^3-allyl)[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))phenylphosphinopropane]dipalladium(II) Hexafluorophosphate (6d). A 0.06 g portion of [Pd(η^3-C_3H_5)-(μ-Cl)]$_2$ (0.17 mmol) and 0.17 mmol of ligand (0.10 g for **A** and **C**; 0.11 for **B** and **D**) were dissolved in 10 cm^3 of ethanol. The reaction mixture was stirred at room temperature for 20 min. A 0.04 g amount of NH_4PF_6 (0.25 mmol) was then added, affording a white solid. The mixture was stirred overnight, and then the solvent was filtered off. The solid was dissolved in chloroform, and extractions with water were perfomed (until pH 7). Organic extracts were dried over $MgSO_4$ and filtered off, and the solvent was removed under reduced pressure, affording a pale yellow solid. The product was recrystallized from ethanol/dichloromethane (1/1). Yields: **6a**, 0.17 g, 85%; **6b**, 0.14 g, 70%; **6c**, 0.18 g, 90%; **6d**, 0.17 g, 80%. Data for **6a** are as follows. Anal. Calcd for $C_{42}H_{48}F_{12}N_2O_2P_4Pd_2$: C, 42.84; H, 4.10; N, 2.38. Found: C, 42.50; H, 3.95; N, 2.42. MS (FAB positive): *m*/*z* 1033 (M − PF_6). Molar conductivity (acetonitrile): 230.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C═N) 1615 cm^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 20.0 (broad signal) ppm. Data for **6b** are as follows. Anal. Calcd for $C_{44}H_{52}F_{12}N_2O_2P_4Pd_2$: C, 43.84; H, 4.35; N, 2.32. Found: C, 44.73; H, 4.94; N, 2.16. MS (FAB positive): *m*/*z* 1061 (M − PF_6). Molar conductivity (acetonitrile): 235.0 Ω^{-1} cm^2 mol^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 18.0 (broad signal) ppm. Data for **6c** are as follows. Anal. Calcd for $C_{43}H_{50}F_{12}N_2O_2P_4Pd_2$: C, 43.34; H, 4.23; N, 2.35. Found: C, 43.10; H, 4.10; N, 4.20. MS (FAB positive): *m*/*z* 1047 (M − PF_6). Molar conductivity (acetonitrile): 195.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C═N) 1620 cm^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 23.0 (broad signal) ppm. Data for **6d** are as follows. Anal. Calcd for $C_{45}H_{54}F_{12}N_2O_2P_4Pd_2$: C, 44.32; H, 4.46; N, 2.29. Found: C, 44.40; H, 4.70; N, 2.35. MS (FAB positive): *m*/*z* 1075 (M − PF_6). Molar conductivity (acetonitrile): 200 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C═N) 1612 cm^{-1}. ^{31}P NMR data (121.5 MHz, $CDCl_3$): 14.0 (broad signal) ppm.

Preparation of Bis(η^3-2-methylallyl)[μ-(4′*R*)-phenyl(2-(3′,4′-dihydro-4′-ethyl-2′-oxazolyl))phenylphosphinoeth-ane]dipalladium(II) Hexafluorophosphate (*RSRR*-7a). This compound was synthesized in the same way as for **6a**−**d**. Starting materials: 0.07 g (0.17 mmol) of [Pd(η^3-2-Me-C_3H_4)-(μ-Cl)]$_2$, 0.10 g (0.17 mmol) of *RSRR*-**A**, and 0.04 g (0.25 mmol)

of NH_4PF_6. Yield: 0.15 g, 75%. Anal. Calcd for $C_{44}H_{52}F_{12}N_2O_2P_4Pd_2$: C, 43.84; H, 4.35; N, 2.32. Found: C, 43.50; H, 4.55; N, 2.10. MS (FAB positive): *m/z* 1061 (M − PF_6). Molar conductivity (acetonitrile): 233.4 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C═N) 1620 cm^{-1}. ^{31}P NMR data (121.5 MHz, CD_3COCD_3, 250 K): major isomer, 20.70 (d, 65.4 Hz), 19.60 (d, 65.4 Hz), 20.80 (d, 63.4 Hz), 19.30 (d, 63.4 Hz) ppm.

Preparation of (η^3-1,3-Diphenylallyl)[(4′*S*)-phenyl(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))phenylphosphinopropane-*P,P*]palladium(II) Hexafluorophosphate (*SSRS*-9d). A 0.014 g portion of [Pd(η^3-1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$ (0.02 mmol), 0.03 g of **D** (0.04 mmol), and 0.014 g of NH_4PF_6 (0.06 mmol) were dissolved in 15 cm^3 of ethanol, 15 cm^3 of dichloromethane, and 15 cm^3 of chloroform. The reaction mixture was stirred at room temperature for 2 days. Then, it was filtered off and solvent was removed under reduced pressure. The product was dissolved in dichloromethane (15 cm^3) and washed in water (3 × 10 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and filtered and the solvent removed under reduced pressure, affording a yellow solid. Yield: 0.020 g (41%). Anal. Calcd for $C_{54}H_{57}F_6N_2O_2P_3Pd$: C, 60.09; H, 5.32; N, 2.60. Found: C, 60.50; H, 5.30; N, 2.85. MS (FAB positive): *m/z* 934 (M − PF_6). Molar conductivity (acetonitrile): 125.0 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C═N) 1618 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 15.0 (broad signal) ppm.

Preparation of Bis(η^3-1,3-diphenylallyl)[μ-(4′*S*)-phenyl-(2-(3′,4′-dihydro-4′-isopropyl-2′-oxazolyl))phenylphosphinopropane]dipalladium(II) Hexafluorophosphate (8d). This compound can be prepared in the same way as **6a**−**d** and can also be synthesized from **9d**. A 0.020 g portion of **9d** (0.019 mmol), 6 mg of Pd(η^3-1,3-Ph_2-C_3H_3)(μ-Cl)]$_2$ (0.009 mmol), and 0.007 of NH_4PF_6 (0.03 mmol) were dissolved in 10 cm^3 of ethanol, 15 cm^3 of dichloromethane, and 20 cm^3 of chloroform. The reaction mixture was stirred at room temperature for 2 days. Then, it was filtered and solvent was removed under reduced pressure. The product was dissolved in dichloromethane (15 cm^3) and washed in water (3 × 10 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and filtered and the solvent removed under reduced pressure, affording a yellow solid. Yield: 0.010 g (74%). Anal. Calcd for $C_{69}H_{70}F_{12}N_2O_2P_4Pd_2$: C, 54.38; H, 4.63; N, 1.84. Found: C, 54.50; H, 4.30; N, 1.70. MS (FAB positive): *m/z* 1379 (M − PF_6). Molar conductivity (acetonitrile): 220 Ω^{-1} cm^2 mol^{-1}. IR data: ν(C═N) 1615 cm^{-1}. ^{31}P NMR data (101.25 MHz, $CDCl_3$): 10.0 (broad signal) ppm.

General Procedure for Palladium-Catalyzed Allylic Alkylation. In Situ Reactions. [$Pd_2(\eta^3$-$C_3H_5)_2Cl_2$] (2 mol % Pd, unless stated otherwise) and the appropriate ***NPPN*** ligand (1 mol %, unless stated otherwise) were dissolved in 1 cm^3 of CH_2Cl_2. The solution was stirred at room temperature for 30 min. *rac*-1,3-Diphenyl-2-propenyl acetate (1 equiv), dissolved in 1 cm^3 of CH_2Cl_2, was added followed by dimethyl malonate (3 equiv), BSA (3 equiv), and a catalytic amount of KOAc. The mixture was stirred at room temperature for 4 days. The solution was then diluted with 15 cm^3 of diethyl ether and washed with saturated aqueous ammonium chloride solution (3 × 10 cm^3) and water (3 × 10 cm^3). The organic phase was dried over anhydrous $MgSO_4$ and filtered off, and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO_2; ethyl acetate). The enantiomeric excesses were determined by HPLC on a Chiralcel OD column, using 2% *i*-PrOH in heptane, as eluent, in a flow of 0.5 cm^3/min.

Precursor Complex Reactions. The method was similar to that described above for in situ conditions, but the palladium complex used was [$Pd_2(\eta^3$-$C_3H_5)_2(\mu$-***NPPN***)](PF$_6$)$_2$ (**6a**−**d**) (2 mol % unless stated otherwise).

Crystallography. A crystal of **7a** with dimensions approximately 0.33 × 0.35 × 0.40 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation (λ(Cu Kα) = 1.5418 Å, μ(Cu Kα) = 58.57 cm^{-1}) and $\omega-2\theta$ scan. A total of 7751 unique reflections was measured within the range $-13 < h < 12$, $0 < k < 33$, $0 < l < 17$. Of these, 6480 were above the significance level of $2.5\sigma(I)$. The range of (sin θ)/λ was 0.037−0.626 Å ($3.3 < \theta < 74.9°$). Two reference reflections ([232], [−1,5,3]) were measured hourly and showed 5% decrease during 91 h collecting time, which was corrected for. In addition, 875 "Friedel" reflections were measured, which were used in the determination of the absolute configuration. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 84°$. Corrections for Lorentz and polarization effects were applied. Absorption correction was performed with the ABSCAL program[34] using Ψ-scans of the [−2,2,5] reflection, with coefficients in the range 1.0−1.75. The structure was solved by the PATTY option of the DIRDIF96 program system.[35] After isotropic refinement a ΔF synthesis revealed eight peaks which were interpreted as two molecules of one of the solvents used during the crystallization. The hydrogen atoms were calculated. Full-matrix least-squares refinement on *F*, anisotropic for the non-hydrogen atoms and isotopic for the hydrogen atoms keeping the latter fixed at their calculated positions with $U = 0.15$ Å^2, converged to $R = 0.075$, $R_w = 0.088$, $(\Delta/\sigma)_{max} = 0.53$, $S = 1.05$. The weighting scheme $w = [15 + 0.01(\sigma(F_o))^2 + 0.0001/(\sigma(F_o))]^{-1}$ was used. The secondary isotropic extinction coefficient was refined to Ext = 0.062(8).[36] The absolute structure parameter was refined to $X_{abs} = -0.04(3)$, thus confirming the correct enantiomer.[37] A final difference Fourier map revealed a residual electron density between −3.3 and 2.2 e Å^{-3} in the vicinity of the Pd atoms. Scattering factors were taken from Cromer and Mann and ref 38. The anomalous scattering of Pd and P was taken into account.[39] All calculations were performed with XTAL, unless stated otherwise.[40]

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Supporting Information Available: Tables giving NMR data for the compounds prepared in this paper and X-ray crystal data for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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