First Optically Active Phosphapalladacycle Bearing a Phosphorus Atom in an Axially Chiral Environment

Valery V. Dunina,*,† Pavel A. Zykov,†,‡ Michail V. Livantsov,† Ivan V. Glukhov,‡ Konstantin A. Kochetkov,‡ Igor P. Gloriozov,† and Yuri K. Grishin*,†

Department of Chemistry, M.V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation, and A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciencies, Vavilova Street 28, 119991 Moscow, Russian Federation

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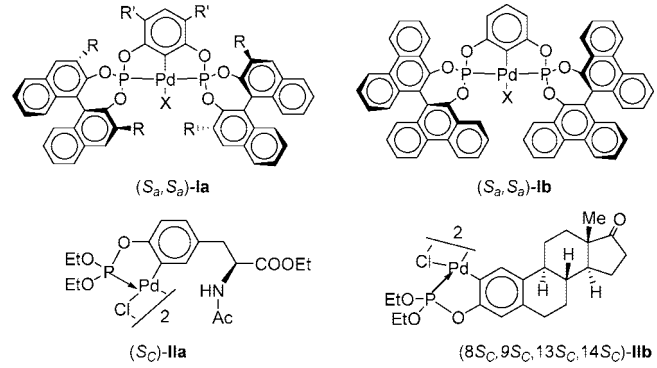
Direct C−H bond activation in the (S_a)-BINOL-derived phosphite (**HL**) afforded the dimeric cyclopalladated complex (S_a,S_a)-{Pd(η^2-L)(μ-Cl)}$_2$ (**1**), which is the first optically active phosphapalladacycle bearing a phosphorus atom in an axially chiral environment. The *ortho*-palladated structure of complex **1** was confirmed by spectral (^{1}H and ^{31}P) investigations of mononuclear derivatives and the X-ray diffraction study of the phosphane adduct (η^2-L)PdCl(PPh$_3$) (**3**). The enantiomeric purity of the starting ligand remained unchanged in the *PC*-palladacycle under the thermal conditions used for the cyclopalladation (∼110 °C); this fact was confirmed by the ^{31}P NMR spectroscopy after chiral derivatization of dimer (S_a,S_a)-**1** with the (R_C)-valinate auxiliary ligand. The *trans*(*N,C*)-configuration of the valinate complex (**4**) was supported by DFT calculations. The chirality transfer in the new system was discussed on the basis of X-ray diffraction data for the phosphane adduct *rac*-**3** and DFT calculations performed for both mononuclear derivatives.

Introduction

Coordination complexes of transition metals with mono-[1] or bidentate[2] *P*-donor ligands bearing elements of axial chirality, including BINOL-derived phosphites[3] and phosphoramidites,[4,5] are well known as very efficient asymmetric catalysts. Participation of the corresponding *PC*-metallacycles in some of the iridium- and palladium-catalyzed processes was established[6a,b] or proposed.[6c] Surprisingly, despite a high catalytic activity of achiral phosphite *PC*-palladacycles[7] and excellent results achieved in asymmetric catalysis with BINOL-derived phosphite ligands, cyclopalladated compounds (CPCs) obtained from the same type of ligands have remained unknown until now. Recently[8] several pincer *PCP*-complexes based on bis(phosphites) derived from binaphthol (**Ia**) or biphenanthrol (**Ib**) were reported. In addition, only two examples of optically active phosphite *PC*-palladacycles (**IIa**,**b**) with rather distant carbon stereocenters[9] have also been described (Chart 1).

Chart 1



The aim of this work was to study the possibility of direct cyclopalladation of BINOL-derived phosphites as a route to

* Corresponding author. Fax: (495) 932 8846. E-mail: dunina@org.chem.msu.ru.
† M.V. Lomonosov Moscow State University.
‡ A.N. Nesmeyanov Institute of Organoelement Compounds.

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enantiopure *PC*-palladacycles and to estimate efficiency of chirality transfer from an axial chiral environment of the phosphorus atom.

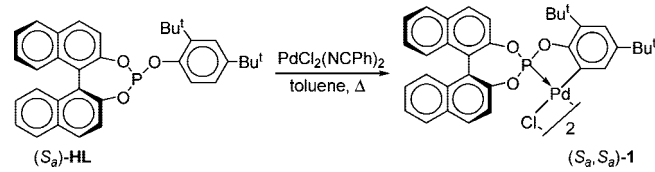
Results and Discussion

Phosphite Cyclopalladation. For steric promotion of an intramolecular C−H bond activation[10] a rather bulky phosphite ligand (S_a)-**HL** was chosen for cyclopalladation. Both racemic and enantiopure phosphites **HL** were prepared by a known route[8d,10c,11] that includes a reaction of the *in situ* obtained BINOL-derived phosphorochloridite[4j] with 2,4-di-*tert*-butylphenol in the presence of a base. Phosphite **HL** possesses moderate oxidative and hydrolytic stability: keeping a pure sample in a chloroform solution in air for a week resulted in 10% decomposition (^{31}P data). To our knowledge, this ligand is a new member[12] of a large group of the BINOL-derived ArO-substituted phosphites.[3g,i,13−15]

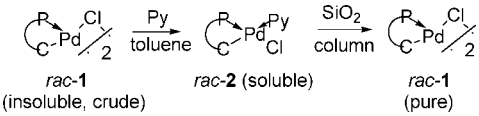
Two protocols were reported for cyclopalladation of achiral phosphite ligands (**HL′**): (i) a two-step procedure through intermediate coordination complex Pd(**HL′**)$_2$Cl$_2$[9a,10b,16,17] and (ii) a one-step synthesis by reaction of $PdCl_2$ with phosphite **HL′** in a 1:1 ratio at heating.[10c,11] Typically, the latter method provides a high yield of CPCs from simple triarylphosphites (up to 98%[10c,18]), which may be decreased to 43−53% in the case of encumbered ligands.[8d,11]

Cyclopalladation of phosphite **HL** appeared to be a rather difficult task. Thus, our attempts to adopt the aforementioned protocols to our system and to use the more electrophilic reagent $Pd(OAc)_2$ resulted in palladium black precipitation and formation of complex mixtures of coordination complexes. However, the reaction of phosphite **HL** with $PdCl_2(NCPh)_2$ in refluxing toluene provided racemic and optically active cyclopalladated dimers, *rac*-**1** and (S_a,S_a)-**1a**, in 40−43% yield after column chromatography (Scheme 1). In a similar reaction carried out in 1,2-dichloroethane (DCE), the yield of *rac*-**1** was slightly lower, 37%. Attempts to promote C−H bond activation with Et_3N as a base in DCE (cf. ref 8d) resulted in palladium(II) reduction.

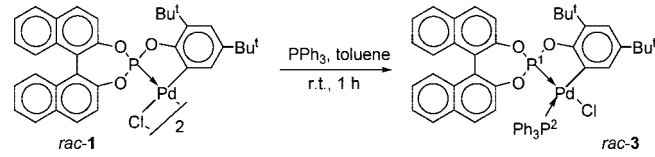
Scheme 1



Scheme 2



Scheme 3



A very low solubility of the racemic dimer **1** complicated its purification. To overcome this obstacle, dimer *rac*-**1** was converted into its more soluble mononuclear pyridine derivative (**2**) followed by its chromatographic purification (cf. ref 19). Strong *trans*-influence of both carbanionic and phosphorus donor atoms of the *PC*-palladacycle facilitated elimination of the auxiliary pyridine ligand from adduct *rac*-**2** with formation of the pure dimer *rac*-**1** (TLC and NMR data; Scheme 2).

Dynamic mobility of dimeric CPCs[20] and their existence as mixtures of *syn*/*anti* and *meso*/*dl* isomers prevent their use for spectral studies; so we converted the dimer *rac*-**1** into its mononuclear phosphane derivative *rac*-**3** by the reaction of chloride bridge cleavage (Scheme 3).

Previously, it was reported that the BINOL-derived bis(phosphites) undergo partial racemization at temperatures above 60 °C.[8a] This report somewhat contradicts the following data: (i) high optical yields in enantioselective transition metal-catalyzed reactions at 45−120 °C with the BINOL-derived ligands;[3a,4a,5a,6c,21] (ii) racemization of BINOL[22] and its monoacylated derivatives[23]

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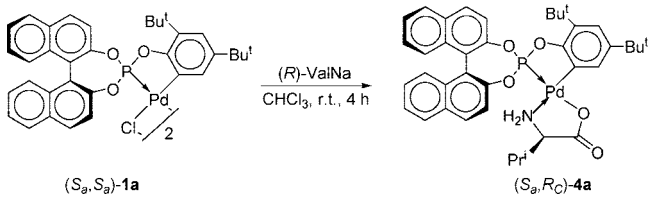
Scheme 4



at much higher temperature (220−280 °C); and (iii) reported mechanistic pathways[24] for racemization are inapplicable in our case. Consequently, we studied whether palladacycle (S_a)-**1a** kept the enantiopurity of the starting diol after C−H bond activation in boiling toluene (∼110 °C).

The enantiopurity of the dimer (S_a,S_a)-**1** was determined by ^{31}P NMR spectroscopy after its chiral derivatization *in situ* with the (R_C)-valinate auxiliary ligand (Scheme 4). The ^{31}P NMR spectrum of (S_a,R_C)-**4a** contains only one singlet at δ 148.03 ppm, while two singlets at δ 148.07 and 147.73 ppm were found in the spectrum of a mixture of two diastereomers, (S_a,R_C/R_a,R_C)-**4a**,**b**, prepared in a similar way from the dimer *rac*-**1**. Thus, the optically active dimer (S_a,S_a)-**1a** completely retained the enantiomeric composition of starting (S_a)-BINOL, confirming the possibility of direct cyclopalladation of chiral BINOL-derived ligands without decrease in their enantiomeric purity.

Spectral Studies of Cyclopalladated Complexes. The signal assignment in the ^{1}H spectra of ligand **HL** and CPCs **1**−**4** was performed using homo- and heteronuclear decoupling, COSY and NOE techniques, DFT structure, and ^{1}H NMR spectra calculations for the complexes **3** and **4a**,**b**.

The chemical shift value in the ^{31}P{^{1}H} NMR spectra of ligand **HL** (δ 145.1 ppm) is typical for the BINOL-derived mono-[13,15] and bis-phosphites.[8c,d,13,25] The ^{31}P{^{1}H} NMR spectra of the dimers *rac*-**1** and (S_a,S_a)-**1a** contain four or two broadened singlets, respectively, which is indicative of their existence as mixtures of *anti* and *syn* isomers. The ^{31}P{^{1}H} NMR spectrum of the mononuclear adduct **3** consists of two doublets at δ 149.9 and 17.66 ppm assigned to the phosphorus atoms of the *PC*-palladacycle (P^1) and auxiliary phosphane PPh_3 (P^2), respectively. The value of the constant $^2J_{PP}$ 45.2 Hz is an unambiguous evidence of its *cis*(*P*,*P*)-geometry,[26] which is typical for phosphite palladacycles.[10c,16b,17,18b,27]

The ^{1}H NMR spectrum of adduct **3** confirms its cyclopalladated structure. The metalation at the *ortho*-C−H bond of the 2,4-di-*tert*-butyl-substituted phenyl ring is supported by the presence of only two one-proton signals at δ 8.57 (ddd) and 7.18 ppm (dd) without a $^3J_{HH}$ coupling constant. Their assignment to H(6″) and H(4″) protons, respectively, was based on the following arguments: (i) the most low-field position of the first signal due to the influence of the adjacent chloride anisotropy [H(6″)···Cl distance is equal to 2.49−2.66 Å, DFT and X-ray data]; (ii) both protons have a spin−spin coupling

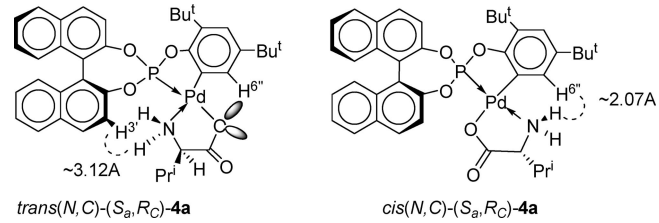


Figure 1. Mutual arrangement of NH and aromatic protons in two geometric isomers of valinate derivative (S_a,R_C)-**4a**.

with the P^1 atom ($^5J_{HP^1}$ 5.6 and 2.6 Hz, respectively), and (iii) only one of the two protons, H(6″), has a rather large $^4J_{HP^2}$ constant (8 Hz) with the P^2 atom of the PPh_3 ligand. The signals of the 1,1′-binaphthyl moiety were identified starting from the $^4J_{HP^1}$ constant values for the H(3)/H(3′) protons (0.9 and 1.2 Hz, respectively).

The signals at δ 1.69 and 2.10 ppm in the ^{1}H NMR spectrum of the valinate derivative (S_a,R_C)-**4a** were assigned to the NH^{eq} and NH^{ax} protons using the correlation of the $^3J_{HNC^{\alpha}H}$ values (4.4 and 7.2 Hz, respectively) with the dihedral angles ∠HNC$^{\alpha}$H (+44.67° and +161.84°, respectively, DFT data). The *trans*-(*N*,*C*)-configuration of complex **4a** can be supported by the following data: (i) the signal of the H(6″) proton was shifted low-field (δ 7.87 ppm) due to anisotropy of the carboxylate oxygen (Figure 1); it was confirmed by DFT calculation of the chemical shifts and the H(6″)···O(CO) distance (2.31 Å, cf. ref 28); (ii) DFT calculations for both isomers predict significant dipole−dipole interactions due to a short H(6″)···NH^{eq} distance (2.22 Å) only for the alternative *cis*(*N*,*C*) isomer (it was not detected); and (iii) the *trans*(*N*,*C*)-configuration seems to be preferable with respect to the "*transphobia*" concept.[27a,29]

DFT calculations were performed for *trans*(*N*,*C*) and *cis*(*N*,*C*) isomers of (S_a,R_C)-**4a** and (R_a,R_C)-**4b** diastereomers of the valinate derivative (Figure 2, Table 1).[30] They provided the following data: (i) for both diastereomers **4a**,**b** the *trans*(*N*,*C*) geometry is more preferable than the *cis*(*N*,*C*) (ΔE^0 2.33 and 2.57 kcal/mol, respectively); (ii) both diastereomers demonstrate preference for the λ(R_C)-conformation of the valinate *N*,*O*-ring;[31]

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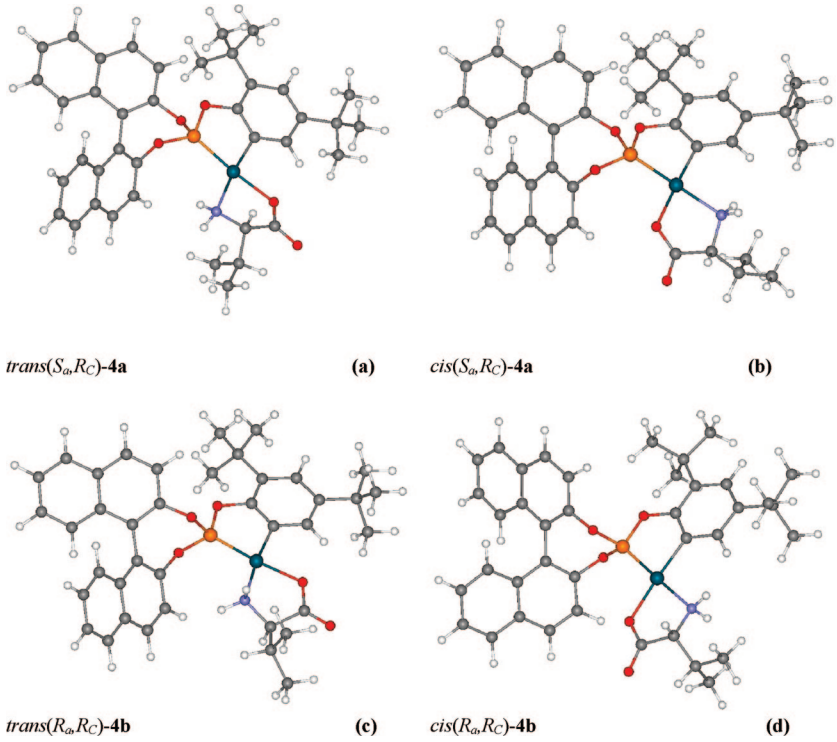

Figure 2. DFT-calculated structures for the more stable conformers of *trans*(*N,C*) (a, c) and *cis*(*N,C*) isomers (b, d) of (S_a,R_C)-**4a** (a, b) and (R_a,R_C)-**4b** diastereomers (c, d) in the gas phase.

Table 1. Selected Parameters of Two Geometric Isomers of Each of Diastereomeric Valinate Derivatives (S_a,R_C)-4a and (R_a,R_C)-4b (DFT data).

		N,O-chelate ring[a]			*PC*-palladacycle		
coordination sphere geometry (*N,C*)	ΔE^0, kcal/mol	ϖ_{av}[b]	∠ONC$^{\alpha}$C(O)	confor-mation	ϖ_{av}[b]	∠C^{1}POC^2	confor-mation
			diastereomer (S_a,R_C)-**4a**				
trans-**4a**	0.10	18.55°	+10.97°	λ	0.71°	+0.60°	–[c]
cis-**4a**	2.43	17.62°	+10.61°	λ	11.93°	+4.64°	λ
			diastereomer (R_a,R_C)-**4b**				
trans-**4b**	0.00	16.87°	+10.03°	λ	2.25°	−1.43°	–[c]
cis-**4b**	2.57	17.30°	+12.83°	λ	9.52°	−3.62°	δ

[a] The *N,O*-chelate ring in all isomers exists in the λ-conformation with equatorial disposition of the *i*-Pr group. [b] The average magnitude of the absolute values of intrachelate torsion angles (ϖ_{av}) was chosen to characterize the nonplanarity extent of the *N,O*-chelate ring or *PC*-palladacycle. [c] The *PC*-palladacycle conformation has to be considered as a nontwisted one.

(iii) the *PC*-palladacycle's nonplanarity is substantial in the complexes *cis*(*N,C*)-**4a**,**b** (ϖ_{av} = 11.93° and 9.52°, respectively), whereas their *trans*(*N,C*) isomers contain a nearly planar metallacycle (ϖ_{av} = 0.71° and 2.25°); (iv) the *PC*-palladacycles in *cis*(*N,C*) isomers of (S_a,R_C)-**4a** and (R_a,R_C)-**4b** exist in opposite envelope-like λ- and δ-conformations, respectively, in accordance with the configuration of the dioxaphosphepine moiety; and (v) the palladium coordination environment is square-planar, with torsion angles ∠P···C^1···O···N < 2.6°.

X-ray Diffraction Study of the Phosphane Adduct *rac*-3. The cyclopalladated structure of dimer **1** and the *cis*(*P,P*)-geometry of its mononuclear phosphane derivative *rac*-**3** were established unambiguously by the X-ray diffraction study of the latter. The molecular structure of complex **3** is presented in Figure 3; selected bond lengths and angles are given in Table 2; its structural and stereochemical peculiarities are discussed using the (S_a)-enantiomer as an example. To follow the chirality transfer and to clarify the influence of the bulky 1,3,2-dioxaphosphepine ring, the structure of complex **3** was compared with those of its pincer *PCP*-analogue **Ia** (R = R′ = H) and known achiral phosphite *PC*-CPCs (Chart 2).

The Pd−C bond length (2.072 Å) in complex **3** is close to those of known analogues **V** and **VII** with *trans*(P^2,*C*)-configuration (2.084−2.064 Å). The length of the *endo*-cyclic Pd−P^1 bond in adduct **3** (2.152 Å) falls in the range 2.142−2.177 Å, typical for other triarylphosphite complexes bearing bridged (**IIIa**−**d**) or terminal (**V**, **VII**) chloride on the P^1−Pd−Cl diagonal. The Pd−Cl bond in complex **3** (2.381 Å) is weakened to some extent compared to that in mononuclear analogues **V** and **VII** (2.349−2.319 Å); however, it is stronger than the (μ)Cl−Pd bond *trans*-disposed to the phosphite *P*-donor atom in dimers **IIIa**−**d** and **IIb** (2.390−2.419 Å). The *exo*-cyclic Pd−P^2 bond length in adduct **3** (2.357Å) falls in the range of

(40) Mononuclear pyridine adduct **2** partially decomposed on the silica to give the dimer **1** (R_f 0.98).
(41) Signal is overlapped with that of the *ortho*-PPh protons.
(42) Partial decomposition of valinate complexes **4a**,**b** on silica was observed, resulting in formation of dimer **1** (R_f 0.90).
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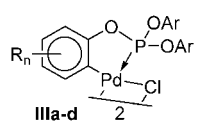
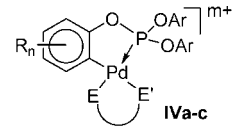
Chart 2



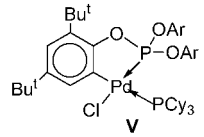
IIIa-d

Ar = Ph, R_n = H (**IIIa**);[18b]
Ar = 2-Bu^{t}C$_6$H$_4$, R_n = 2-Bu^t (**IIIb**);[18b]
Ar = 2,4-Bu$^t_2$C$_6$H$_3$, R_n = 2,4-Bu$^t_2$ (**IIIc**);[7g]
Ar_2 = (2-Bu^t-4-MeC$_6$H$_2$-6)$_2$CH$_2$, R_n = 2,4-Me$_2$ (**IIId**)[10c]



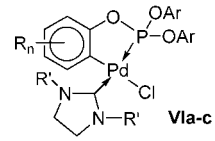
IVa-c

Ar = 2,4-Bu$^t_2$C$_6$H$_3$, R_n = 2,4-Bu$^t_2$; E⌒E′ = Et$_2$NCSS$^-$ (**IVa**),[10c] Ph$_2$P(O)CH$_2$C(Me)(CH$_2$PPh$_2$)$_2$ (**IVb**);[32]
Ar = Ph, R_n = H, E⌒E′ = η^5-Cp$^-$ (**IVc**)[17]



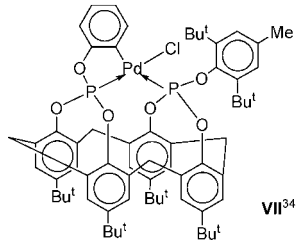
V

Ar = 2,4-Bu$^t_2$C$_6$H$_3$ (**V**)[33]

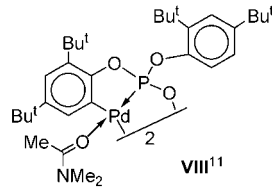


VIa-c

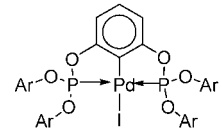
Ar = Ph, R_n = H, R′ = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**VIa**);
Ar = 2,4-Bu$^t_2$C$_6$H$_3$, R_n = 2,4-Bu$^t_2$, R′ = Mes (**VIb**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**VIc**)[7a]



VII[34]



VIII[11]



Ar = 4-MeOC$_6$H$_4$ (**IX**)[35]

this parameter's values (2.340−2.405 Å) found for analogues **IVb**, **V**, and **VII** with the P^2−Pd−C diagonal.

The square-planar coordination environment of the palladium atom in complex **3** reveals a marked tetrahedral distortion (C^{1}Pd^{1}P^1/Cl^{1}Pd^{1}P^2 14.83°), which exceeds that for the majority of phosphite *PC*-CPCs (0.81−5.76°), including those reported for the sterically congested compounds **IIIb**,**d**, **VIc**, and **VII** (8.36−13.45°). According to the "skew-line convention"[36] the configuration of the pseudo-tetrahedron in adduct **3** may be defined as Λ on the basis of the positive sign of the torsion angle ∠P$^1\cdots$C$\cdots$Cl$\cdots$P^2 (+15.48°) connecting four metal-bonded donor atoms (Figure 4).

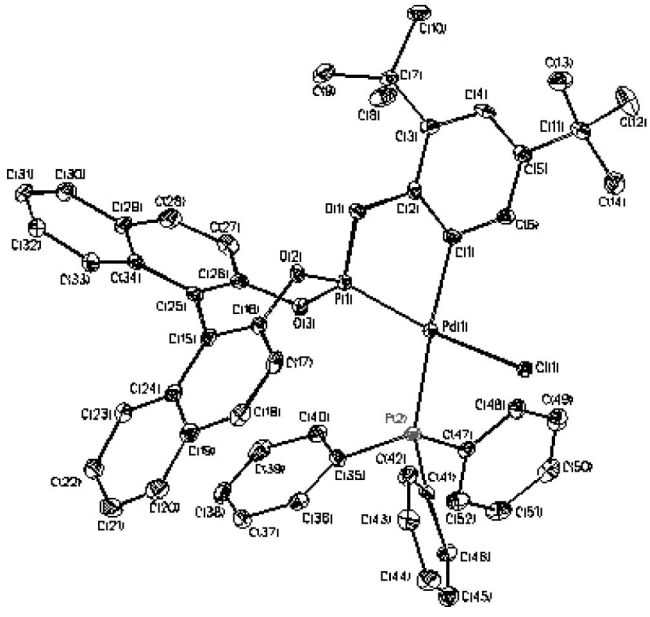


Figure 3. Molecular structure and numbering scheme of the (S_a)-enantiomer of the phosphane derivative *rac*-**3**. The dichloroethane solvate molecules are omitted for clarity; thermal ellipsoids are given for 50% probability.

The *PC*-palladacycle in complex **3** has an envelope-like conformation[37] with P^{1}O^{1}C^{2}C^1 atoms coplanar within 0.0344 Å and the palladium atom deviating from their plane by 0.587 Å. The nonplanarity of the *PC*-palladacycle is rather high, with average absolute values of intrachelate torsion angles (ϖ_{av}) equal to 16.80°. Only three sterically encumbered analogues possess a palladacycle of comparable (**V**) or more pronounced (**IIId** and **VIb**) puckering extent (ϖ_{av} = 15.19−21.08°), while in other CPCs the palladacycle is rather flattened (ϖ_{av} = 1.16−10.29°). The envelope-like conformation of the palladacycle in adduct **3** is twisted, with the negative torsion angle ∠C$^1\cdots$P^1−O^1−C^2 (−5.48°) determining its $\delta(S_a)$-stereochemistry.[36]

The (S_a)-BINOL-derived dioxaphosphepine ring in complex **3** is highly puckered (ϖ_{av} 42.35°); it adopts the $\delta(S_a)$ conformation (∠O$^2\cdots$O^3−C$^{26}\cdots$C^{16} = −28.59°). These characteristics are similar to those reported for phosphepine rings of the *PCP*-analogue (R_a)-**Ia** (ϖ_{av} = 44.12° and 46.03°) with the same $\lambda(R_a)$ relationship between axial and conformational chirality.

The *P*-configuration of the PPh$_3$ propeller in adduct (S_a)-**3** was determined by a known method[38] (ω_{av} 38.6°). The calculated ω_i values for three PPh groups reveal dependence on their disposition regarding the BINOL-derived phosphepine ring: ω_A, ω_B and ω_C values are equal to 66.8°, 33.7°, and 15.4°, respectively.

The comparative analysis of X-ray data for complex **3** and its analogues has shown that the introduction of bulky substituents, including a dioxaphosphepine ring, to the structure of phosphite CPCs results in an increase in the tetrahedral distortion of the coordination sphere and palladacycle's puckering.

DFT Investigation of the Phosphane Adduct (S_a)-3. To estimate the influence of the crystal packing on the structure and stereochemistry of complex **3**, we have performed a DFT study of its (S_a)-enantiomer (Figure 5). The DFT data confirmed the tetrahedral distortion of the metal coordination sphere

Table 2. Comparison of the Experimental and DFT-Calculated Values of the Selected Bond Lengths (Å) and Bond Angles (deg) for Phosphane Adduct *rac*-3

bond lengths (l)				bond angles (ϕ)			
bond	X-ray	DFT	Δl	angle	X-ray	DFT	$\Delta\phi$
Pd(1)−C(1)	2.072(3)	2.097	0.025	C(1)−Pd(1)−P(1)	76.28(9)	77.40	1.12
Pd(1)−P(1)	2.1517(9)	2.180	0.028	C(1)−Pd(1)−P(2)	169.84(9)	173.25	3.41
Pd(1)−P(2)	2.3567(9)	2.409	0.052	P(1)−Pd(1)−P(2)	104.31(3)	105.94	1.63
Pd(1)−Cl(1)	2.3813(8)	2.360	−0.022	C(1)−Pd(1)−Cl(1)	95.22(9)	92.94	−2.28
P(1)−O(3)	1.588(2)	1.635	0.047	P(1)−Pd(1)−Cl(1)	167.02(3)	169.12	2.10
P(1)−O(1)	1.588(2)	1.654	0.066	P(2)−Pd(1)−Cl(1)	85.81(3)	84.20	−1.61
P(1)−O(2)	1.609(2)	1.628	0.019	O(3)−P(1)−O(1)	103.47(12)	103.00	−0.47
O(1)−C(2)	1.421(3)	1.416	−0.005	O(3)−P(1)−O(2)	104.03(11)	101.56	−2.47
O(2)−C(16)	1.406(4)	1.391	−0.015	O(1)−P(1)−O(2)	100.20(12)	98.07	−2.13
O(3)−C(26)	1.414(3)	1.402	0.012	O(3)−P(1)−Pd(1)	120.97(9)	121.93	0.96
C(1)−C(2)	1.387(4)	1.399	0.022	O(1)−P(1)−Pd(1)	111.13(9)	109.67	−1.46
C(1)−C(6)	1.395(4)	1.398	0.003	O(2)−P(1)−Pd(1)	114.56(9)	119.06	4.50
C(2)−C(3)	1.398(4)	1.407	0.009	C(2)−O(1)−P(1)	110.33(18)	110.95	0.62
C(3)−C(4)	1.392(4)	1.401	0.009	C(16)−O(2)−P(1)	115.84(19)	119.32	3.48
C(4)−C(5)	1.391(4)	1.402	0.011	C(26)−O(3)−P(1)	120.15(19)	119.68	−0.47
C(5)−C(6)	1.384(4)	1.400	0.016	C(2)−C(1)−Pd(1)	119.6(2)	118.99	−0.61
				C(6)−C(1)−Pd(1)	123.1(2)	122.96	−0.14

($\angle P^1\cdots C\cdots Cl\cdots P^2 = +8.69°$) and the same Λ-configuration of the pseudo-tetrahedron (Figure 6a). The calculated nonplanarity extent of the *PC*-palladacycle ($\varpi_{av} = 15.41°$) is very close to that found for the crystal with the same δ-conformation ($\angle C^1\cdots P^1-O^1-C^2 = -6.15°$, Figure 6b). The ($S_a$)-dioxaphosphepine ring possesses a similar puckering extent (ϖ_{av} 41.58°) and the same δ(S_a)-conformation ($\angle O^2\cdots O^3-C^{26}\cdots C^{16} = -27.89°$, Figure 6c). The calculated rotameric state of the PPh_3 ligand corresponds to that found for the crystal, with the same

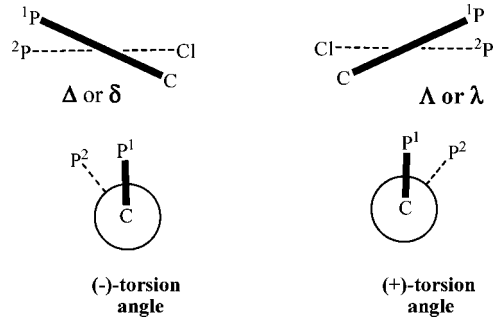


Figure 4. Correlation of the skew-line disposition with torsion angle sign.

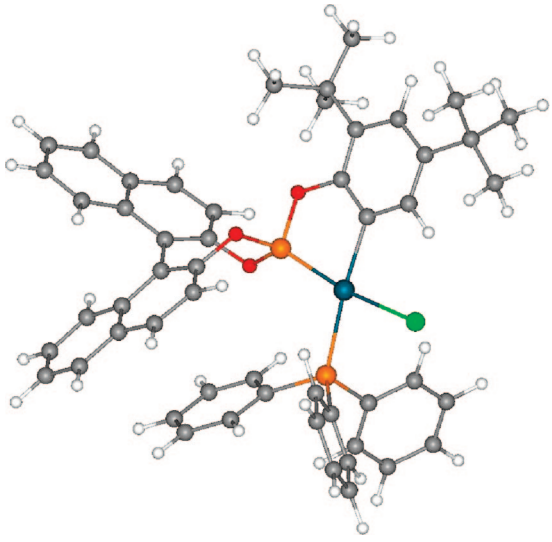


Figure 5. DFT-calculated structure for the phosphane derivative *rac*-**3** in the gas phase.

P-configuration of the PPh_3 propeller ($\omega_{av} = 41.20°$) and similar dependence of PPh group orientation on their disposition regarding the phosphepine ring (ω_A, ω_B, and ω_C values are equal to 68.74°, 35.14°, and 19.73°, respectively, Figure 6d).

From the comparison between the calculated parameters for two derivatives of phosphite *PC*-palladacycle, **3** and **4a**, one can see that bulkiness of the auxiliary ligand has a considerable impact on the overall stereochemistry of the complexes. Thus, phosphane adduct **3** reveals a more pronounced tetrahedral distortion and a more puckered *PC*-palladacycle conformation compared to the less sterically congested valinate adduct **4a**. Such a difference allows one to assume that chirality transfer from the phosphite palladacycle to sterically encumbered auxiliary ligands may be rather efficient due to participation of two additional chirality elements (pseudo-tetrahedron and twisted conformation) in this process.

Conclusions

We have described the preparation of the first optically active *PC*-palladacycle with a phosphorus atom in an axially chiral environment. The possibility of direct C−H bond activation in the (S_a)-BINOL-derived phosphite under thermal conditions (~110 °C) without decrease its enantiopurity was confirmed by ^{31}P NMR spectroscopy after chiral derivatization of dimer (S_a,S_a)-**1** with the (R_C)-valinate auxiliary ligand. The X-ray diffraction data and DFT calculations performed for the phosphane derivative (S_a)-**3** showed that axial chirality of the (S_a)-

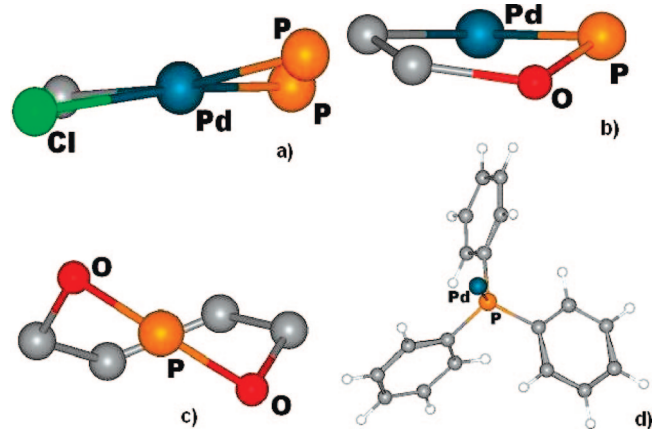


Figure 6. Chirality elements in the phosphane derivative *rac*-**3**.

BINOL fragment causes both the seven-membered 1,3,2-dioxaphosphepine ring and the five-membered *PC*-palladacycle to adopt the δ-conformation. The (S_a)-BINOL moiety in complex (S_a)-**3** also triggers both the Λ-configuration of the pseudo-tetrahedral palladium coordination environment and the *P*-rotameric state of the PPh_3 propeller.

Experimental Section

General Procedures. The ^1H and ^{31}P NMR spectra were recorded on Varian VXR-400 and Bruker DPX-400 spectrometers operating at the frequencies 400 and 161.9 MHz for ^1H and ^{31}P nuclei, respectively. The measurements were carried out at ambient temperature in $CDCl_3$ solutions (unless otherwise indicated). The chemical shifts are reported in δ-scale in parts per million relative to TMS as an internal standard for ^1H NMR and relative to H_3PO_4 as an external reference for the ^{31}P NMR spectra. The signal assignment was based on homo- and heteronuclear decoupling, COSY, and NOE experiments. Optical rotations were measured on a Perkin-Elmer (model 341) polarimeter in 0.5 dm cells at 25 °C. Melting points were measured on an Electrothermal IA 9000 series device in sealed capillaries. All reactions were conducted under argon using TLC control on Silufol. All manipulations with the free phosphite were carried out under dry purified argon in deoxygenated and dried solvents using Schlenk techniques. Compound purification was performed using a short, dry column[39] or flash chromatography on silica gel (60, Fluka).

Toluene was dried over $CaCl_2$, refluxed over Na, and then distilled under argon. Anhydrous MeOH was prepared by distillation from MeONa. Chloroform and dichloromethane were passed through a short Al_2O_3 column and distilled under argon. Hexane and light petroleum ether were distilled from Na under argon. $CDCl_3$ and CD_2Cl_2 (from Aldrich) were distilled from CaH_2 under argon just before using. Palladium(II) chloride and acetate and (R_C)-valine (from Aldrich), $Pd(PhCN)_2Cl_2$ (from Merck), and (S_a)-1,1′-binaphthyl-2,2′-diol (from Fluka) were used as received. PPh_3 and racemic BINOL (from Aldrich) were purified by 2-fold recrystallization from benzene/hexane and acetone, respectively. PCl_3 was distilled under argon. Et_3N was distilled from Na under argon before using. 2,4-Di-*tert*-buthylphenol (from Aldrich) was recrystallized two times from light petroleum ether and dried under P_2O_5 and paraffin *in vacuo*.

(S_a)-(1,1′-Binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite, (S_a)-HL. (S_a)-**HL** was prepared by a slightly modified known method[8d,10c,11] and chromatographically purified. $[\alpha]_D^{25}$ +103.5 (*c* 1.31, CH_2Cl_2). Anal. Calcd for $C_{34}H_{33}PO_3$: C, 78.43; H, 6.40. Found: C, 78.60; H, 6.48. $^{31}P\{^1H\}$ NMR: δ 145.07 (s). ^1H NMR: δ 1.32 (s, 9H, Bu^t), 1.37 (s, 9H, Bu^t), 7.19 (dd, $^3J_{HH}$ 8.3, $^4J_{HH}$ 2.5, 1H, H$^{5''}$), 7.24 (d, $^3J_{HH}$ 8.3, 1H, H$^{6''}$), 7.27 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.3, 1H, H^7/H$^{7'}$), 7.29 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.5, 1H, H$^{7'}$/H^7), 7.39 (d, $^4J_{HH}$ 2.5, 1H, H$^{3''}$), 7.40 (d, $^3J_{HH}$ 8.3, 1H, H^8/H$^{8'}$), 7.42 (d, $^3J_{HH}$ 8.3, 1H, H$^{8'}$/H^8), 7.43 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.3, 1H, H^6/H$^{6'}$), 7.46 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.3, 1H, H$^{6'}$/H^6), 7.48 (dd, $^3J_{HH}$ 8.8, $^4J_{HP}$ 0.8, 1H, H^3/H$^{3'}$), 7.58 (d, $^3J_{HH}$ 8.8, 1H, H$^{3'}$/H^3), 7.90 (d, $^3J_{HH}$ 8.8, 1H, H^4/H$^{4'}$), 7.91 (d, $^3J_{HH}$ 8.3, 1H, H^5/H$^{5'}$), 7.95 (d, $^3J_{HH}$ 8.3, 1H, H$^{5'}$/H^5), 8.01 (d, $^3J_{HH}$ 8.8, 1H, H$^{4'}$/H^4).

Racemic (1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphate. was obtained similarly.

Racemic Di-μ-chlorobis[(1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C*,*P*]dipalladium(II), *rac*-1. A solution of $Pd(PhCN)_2Cl_2$ (0.0715 g, 0.186 mmol) in 1,2-dichloroethane (3 mL) was added to a phosphite **HL** (0.097 g, 0.186 mmol) and the homogeneous reaction mixture was refluxed for 9 h under stirring. The precipitate formed was filtered and dried *in vacuo* to give the crude dimer **1** in a yield of 57% (0.0707 g, 0.0534 mmol) as a highly insoluble powder. The suspension of the crude dimer *rac*-**1** in dichloromethane (3 mL) was treated with pyridine (0.0085 g, 0.107 mmol) and stirred for 15 min to give the homogeneous solution of the pyridine adduct **2** (R_f 0.30; toluene/acetone, 1:1),[40] which was evaporated. In the course of the complex *rac*-**2** eluation through the flash column loaded with silica (h = 13 cm, d = 2 cm; eluents: toluene/light ligroin, 2:1, then toluene and toluene/acetone, 5:1) the complete decomplexation of auxiliary pyridine ligand took place to afford purified dimer *rac*-**1** in a yield of 43% (0.0533 g, 0.0402 mmol) as a colorless, amorphous powder: mp (dec) 247 °C; R_f 0.5 (toluene/hexane, 1:1). Anal. Calcd for $C_{68}H_{64}P_2O_6Pd_2Cl_2$: C, 61.73; H, 4.89. Found: C, 61.44; H, 5.05. $^{31}P\{^1H\}$ NMR: δ 138.45 (s) and 138.54 (s) (86%); 140.75 (s) and 140.81 (s) (14%).

(S_a,S_a)-Di-μ-chlorobis[(1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C*,*P*]dipalladium(II), (S_a,S_a)-1a. A solution of $Pd(PhCN)_2Cl_2$ (0.0465 g, 0.1212 mmol) and phosphite (S_a)-**HL** (0.0631 g, 0.1212 mmol) in toluene (2 mL) was refluxed for 7 h under stirring. The palladium black formed was removed by filtration, and mother liquid was evaporated. The residue was purified using flash-column chromatography (h = 13 cm, d = 2 cm; eluents: toluene/petroleum ether, 1:1, then toluene, and toluene/acetone, 10:1) to give dimer (S_a,S_a)-**1a** in a yield of 40% (0.0320 g, 0.0242 mmol) as a colorless, amorphous powder: mp (dec) 230 °C; R_f 0.5 (toluene/hexane, 1:1). Anal. Calcd for $C_{68}H_{64}P_2O_6Pd_2Cl_2$: C, 61.73; H, 4.89. Found: C, 61.49; H, 4.88. $^{31}P\{^1H\}$ NMR: δ 140.68 (s, 16%), 138.43 (s, 84%). ^1H NMR: δ 1.12 (s, Bu^t), 1.20 (s, Bu^t), 7.10 (app. br s), 7.14−7.19 (m), 7.24−7.26 (m), 7.28−7.29 (m), 7.31−7.35 (m), 7.37−7.42 (m), 7.49−7.53 (m), 7.81 (br d), 7.97 (app. br d), 8.06 (br d).

Racemic Chloro[(1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C*,*P*](triphenylphosphane)palladium(II), *rac*-3. A suspension of the racemic dimer **1** (0.0182 g, 0.0138 mmol) in toluene (1.5 mL) was treated with triphenylphosphane (0.0072 g, 0.0275 mmol). The reaction mixture was stirred for 30 min at rt under TLC control and evaporated, and the residue was purified using dry column chromatography[39] (h = 5 cm, d = 4 cm; eluents: toluene and then toluene/acetone, 5:1). After 2-fold recrystallization from dichloromethane/hexane mononuclear derivative *rac*-**3** was obtained in a yield of 60% (0.020 g, 0.0216 mmol) as a light-yellow crystalline solid: mp (dec) 225 °C; R_f 0.73 (toluene/acetone, 10:1). Anal. Calcd for $C_{52}H_{47}P_2O_3PdCl$: C, 67.60; H, 5.14. Found: C, 67.43; H, 5.25. The monocrystals for X-ray investigation were grown from 1,2-dichloroethane/pentane using vapor diffusion technique. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.66 (d, $^2J_{PP}$ 45.2), 149.91 (d, $^2J_{PP}$ 45.2). ^1H NMR (CD_2Cl_2): δ 1.14 (s, 9H, Bu^t), 1.40 (s, 9H, Bu^t), 7.01−7.08 (m, $^4J_{HP^2}$ 2.0, 6H, *meta*-PPh), 7.10−7.15 (m, $^5J_{HP^2}$ 2.0, 3H, *para*-PPh), 7.17 (dd, $^5J_{HP^1}$ 2.6, $^4J_{HH}$ 2.1, 1H, H$^{4''}$), 7.21 (d, $^3J_{HH}$ 8.6, 1H, H^8/H$^{8'}$), 7.22−7.28 (m, 2H, H^7/H$^{7'}$ and H$^{8'}$/H^8), 7.33 (m, 1H, H$^{7'}$/H^7),[41] 7.35−7.41 (m, $^3J_{HP^2}$ 10.9, 6H, *ortho*-PPh), 7.38 (dd, $^3J_{HH}$ 8.8, $^4J_{HP^1}$ 0.9, 1H, H^3/H$^{3'}$), 7.46 (dd, $^3J_{HH}$ 8.9, $^4J_{HP^1}$ 1.2, 1H, H$^{3'}$/H^3), 7.48−7.52 (m, 1H, H^6/H$^{6'}$), 7.50−7.54 (m, 1H, H$^{6'}$/H^6), 7.58 (d, $^3J_{HH}$ 8.8, 1H, H^4/H$^{4'}$), 7.84 (d, $^3J_{HH}$ 8.2, 1H, H^5/H$^{5'}$), 7.98 (d, $^3J_{HH}$ 8.2, 1H, H$^{5'}$/H^5), 8.03 (d, $^3J_{HH}$ 8.9, 1H, H$^{4'}$/H^4), 8.47 (ddd, $^4J_{HP^1}$ 5.6, $^4J_{HP^2}$ 8.0, $^4J_{HH}$ 2.2, 1H, H$^{6''}$).

[{(S_a)-1,1′-Binaphthyl-2,2′-diyl}(2,4-di-*tert*-butylphenyl)phosphite-*C*,*P*][(R_C)-valinato-*N*,*O*)palladium(II), (S_a,R_C)-4a. The dimer (S_a)-**1a** (0.0062 g, 0.0062 mmol) was added to a solution of excess sodium (*R*)-valinate (0.0028 g, 0.0248 mmol) in chloroform (2 mL), and the reaction mixture was stirred at rt for 4 h, filtered, and evaporated. At this stage $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 148.03 (s). After recrystallization of the residue from chloroform/hexane at low temperature diastereomer (S_a,R_C)-**4a** was obtainned in a yield of 93% (0.0083 g, 0.0115 mmol) as a colorless, finely crystalline solid: mp (dec) 228−230 °C, R_f 0.48 (toluene/acetone, 1:1).[42] $[\alpha]_D^{25}$ +155.6 (*c* 0.25, $CHCl_3$). Anal. Calcd for $C_{39}H_{42}PO_5NPd$: C, 63.11; H, 5.72; N 1.89. Found: C, 63.09; H, 5.70; N 1.94. $^{31}P\{^1H\}$ NMR: δ 148.12 (s). ^1H NMR: δ 0.94 (d, $^3J_{HH}$ 7.1, 3H, Me), 1.16 (d, $^3J_{HH}$ 7.0, 3H, Me), 1.69 (br dd, $^2J_{HH}$ 11.0, $^3J_{HNC^{\alpha}H}$ 4.4, 1H, NH^{eq}), 2.10 (br dd, $^2J_{HH}$ 11.0, $^3J_{HNC^{\alpha}H}$ 7.2, 1H, NH^{ax}), 2.47 (m, 1H, C*H*Me$_2$),

3.40 (ddd, $^3J_{HCNH}$ 7.2, $^3J_{HCNH}$ 4.4, $^3J_{HCCH}$ 6.9, 1H, α-CH), 1.27 (s, 9H, Bu^t), 1.33 (s, 9H, Bu^t), 7.23 (dd, $^5J_{HP}$ 3.5, $^4J_{HH}$ 2.1, 1H, H$^{4''}$), 7.38−7.43 (m, 2H, H^7/H$^{7'}$ and H^8/H$^{8'}$), 7.46 (ddd, $^3J_{HH}$ 8.7, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.3, 1H, H$^{7'}$/H^7), 7.48 (br d, $^3J_{HH}$ 8.8, 1H, H^3/H$^{3'}$), 7.53 (d, $^3J_{HH}$ 8.7, 1H, H$^{8'}$/H^8), 7.57 (m, 1H, H^6/H$^{6'}$), 7.63 (ddd, $^3J_{HH}$ 8.3, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.3, 1H, H$^{6'}$/H^6), 7.72 (app. d, $^3J_{HH}$ 8.8, $^4J_{HP}$ 0.4, 1H, H$^{3'}$/H^3), 7.87 (dd, $^4J_{HP}$ 7.1, $^4J_{HH}$ 2.1, 1H, H$^{6''}$), 8.04 (d, $^3J_{HH}$ 8.3, 1H, H^5/H$^{5'}$), 8.06 (d, $^3J_{HH}$ 8.3, 1H, H$^{5'}$/H^5), 8.09 (d, $^3J_{HH}$ 8.8, 1H, H^4/H$^{4'}$), 8.17 (d, $^3J_{HH}$ 8.8, 1H, H$^{4'}$/H^4).

Diastereomer Mixture of [(1,1′-Binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C,P*][(*R*$_C$)-valinato-*N,O*)palladium(II), (*S*$_a$*R*$_C$)-4a and (*R*$_a$*R*$_C$)-4b. Dimer *rac*-**1** (0.0157 g, 0.0118 mmol) was added to a solution of sodium (*R*)-valinate (0.0029 g, 0.0237 mmol) in chloroform (2 mL), and the reaction mixture was stirred at rt for 3 h, filtered, and evaporated. At this stage $^{31}P\{^1H\}$ NMR: δ 147.73 (s), 148.07 (s). After recrystallization of the residue from dichloromethane/hexane at low temperature diastereomer mixture **4a**,**b** was obtained in a yield of 84% (0.0141 g, 0.0197 mmol) as a colorless, finely crystalline solid: mp (dec) 235−237 °C, R_f 0.53 (toluene/acetone, 1:1).[42] $[\alpha]_D^{25}$ 0.00, $[\alpha]_{436}^{25}$ 17.0 (*c* 0.19, $CHCl_3$). Anal. Calcd for $C_{39}H_{42}PO_5NPd$: C, 63.11; H, 5.72; N 1.89. Found: C, 63.07; H, 5.74; N 1.93. $^{31}P\{^1H\}$ NMR: δ 147.73 (s), 148.05 (s).

Computational Details. All DFT calculations were performed for the gas phase at the generalized gradient approximation for the nonempirically constructed PBE functional,[43] using the program package in version PRIRODA-6.[44] The one-electron wave functions were expanded into the extended TZ2P basis sets[44] including the contracted Gauss functions {311/1} for the hydrogen atoms, {51111/51111/5111} for palladium atom, and {6,11111/411/11} for all other atoms (carbon, nitrogen, oxygen, and phosphorus). The relativistic pseudopotential SBK was used in the known version.[45] The energy E^0 was calculated taking into account the zero-point vibration energy in harmonic approximation. All structures were fully optimized. Corrections for zero-point energies were calculated in the harmonic approximation. The ^1H NMR spectra were calculated using gauge-including atomic orbitals (GIAO)[46] in the complete electronic TZ2P basis. The calculated chemical shifts were expressed as the difference between the shielding of the reference (TMS) and the complex to be studied. All calculations were performed on the MVS 15000BM computer cluster at the Joint Supercomputer Center (JSCC, Moscow).

X-ray Diffraction Study of Phosphane Derivative *rac*-3. Crystal of adduct **3** ($C_{56}H_{55}Cl_5O_3P_2Pd$, M = 1121.59), triclinic, space group $P\bar{1}$, at 100 K, a = 12.9201(7) Å, b = 14.3239(8) Å, c = 16.3593(14) Å, α = 111.534(2)°, β = 106.222(2)°, γ = 98.2940(10)°, V = 2598.8(3) Å^3, Z = 2, $F(000)$ = 1152, d_{calc} = 1.433 g·cm^{-3}, μ = 0.719 mm^{-1}. Unit cell parameters and intensities of 32 453 reflections were measured with a Bruker SMART APEX2 CCD area detector diffractometer, using graphite-monochromated Mo Kα radiation at 100 K, φ- and ω-scan, θ_{max} = 29°. Reflection intensities were integrated using SAINT software,[47] and absorption correction was applied semiempirically using the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions, and their positions were refined in isotropic approximation in a riding model. The crystal of **3** contains two solvate molecules of 1,2-dichloroethane; in one of them the carbon atoms are disordered over two sites with 3:7 occupancies. All calculations were performed using the SHELXTL software.[48] Final R-factors are equal to R_1 = 0.0517 for 9366 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0749 for all 14 061 independent reflections. CCDC-677989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Full crystallographic data for complex **3** are available as a cif file. Synthesis of phosphites *rac*-**HL** and (*S*$_a$)-**HL**, experimental ^1H and ^{31}P NMR spectra, DFT-calculated ^1H chemical shifts, and structures of complexes **4a**,**b** (in Decart coordinates) are given. These materials are available free of charge via the Internet at http://pubs.acs.org.

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