# First optically active *PC*-palladacycle bearing a phosphorus atom in an axially chiral environment

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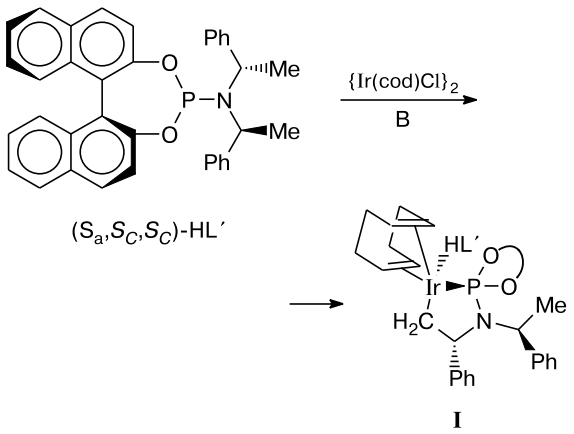
Direct aromatic C—H bond activation in the ($S_a$)-BINOL-derived phosphite ($S_a$)-HL afforded the dimeric cyclopalladated complex ($S_a$,$S_a$)-{Pd($\eta^2$-L)($\mu$-Cl)}$_2$ (**2**) which is the first optically active *PC*-palladacycle bearing a phosphorus atom in an axially chiral environment. *ortho*-Palladated structure of dimer **2** was confirmed by spectral ($^1$H and $^{31}$P NMR) examination of its mononuclear derivatives and by X-ray diffraction analysis of the phosphine adduct ($\eta^2$-L)PdCl(PPh$_3$) (**4**). 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 *in situ* of dimer ($S_a$,$S_a$)-**2** with the ($R_C$)-valinate chiral auxiliary (Val). *trans*(*N*,*C*)-Configuration of the valinate complex ($\eta^2$-L)Pd(Val) (**5**) was established by $^1$H NMR and supported by DFT calculations. The chirality transfer in the new *PC*-palladacycle was discussed on the basis of X-ray diffraction data for the phosphine adduct *rac*-**4** and DFT calculations performed for both phosphine and valinate mononuclear derivatives.

**Key words:** C—H bond activation, cyclopalladated phosphites, optically active *PC*-palladacycles, enantiomeric purity, geometric isomerism, axial chirality, chirality transfer, DFT.

Transition metal coordination complexes with mono-[1] and bidentate[2] P-donor ligands, atropoisomeric or bearing axially chiral moieties, are widely known as highly effective enantioselective catalysts. In particular, phosphites,[3] phosphoramidites[3e,4] and other P-donor ligands[5] derived from commercially available enantiomerically pure diol BINOL[6] or its analogs provide up to 99.9% *ee* selectivity in the asymmetric catalysis of various transformations including palladium catalyzed reactions.[3h,4d,5c,7] Monodentate ligands of the above type often prove more effective than bidentate ones, affording optical yields exceeding 99% *ee*.[3a,b,d,e,k—m,4a,b,5b,7e] A number of processes catalyzed by coordination compounds of iridium and palladium were found[8a,b] or supposed[8c] to be mediated by the appropriate phosphametallacycles. In particular, for the allylic amination involving phosphoramidite HL´, the cyclometalated derivative of the latter, **I** formed *in situ* under catalysis conditions was shown[8a,b] to be a true catalyst (Scheme 1). These results may contribute to the explanation of the high enantioselectivity exhibited by monodentate P-donor ligands of this type.

**Scheme 1**




**I**

B is base, cod is cycloocta-1,5-diene

Despite the high catalytic activity of achiral phosphite palladacycles[9] and the excellent results achieved in asymmetric catalysis with the BINOL-derived transition metal complexes with monodentate phosphites,[3] cyclopalladated derivaives of such chiral ligands remained unknown until this time. Only recently there have emerged the reports[10] on synthesis and application in catalysis of several *PCP*-

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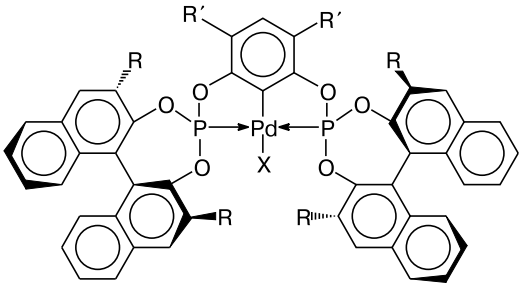
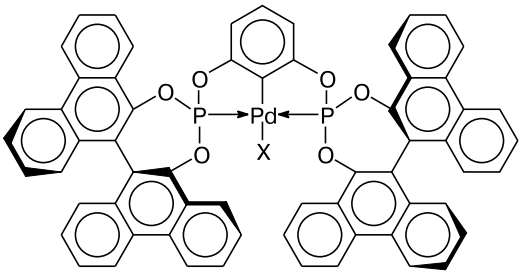
pincer cyclopalladated complexes (CPCs) based on bisphosphites with 1,3-phenylene backbone derived from binaphthol (**II**, R = H, Me, Cl, SMe, SEt, SPh; R′ = H, Bu$^t$) or biphenanthrol (**III**).

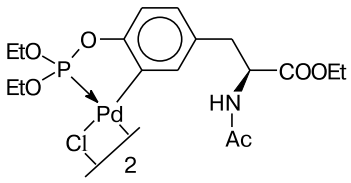


($S_a$,$S_a$)-**II**

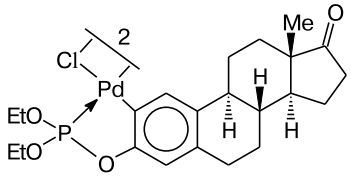


($S_a$,$S_a$)-**III**

Except for these *PCP*-complexes, known are only two optically active phosphite *PC*-palladacycles with the distant stereocenters (**IV** and **V**).[11]



($S_C$)-**IV**



($8S_C$,$9S_C$,$13S_C$,$14S_C$)-**V**

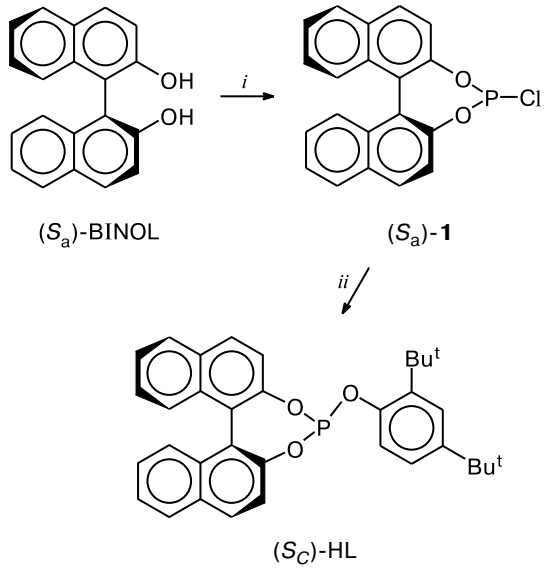
Achiral monophosphites are extremely rarely used in Pd-catalyzed reactions generating C—C and C—heteroatom bonds.[12] It was a fairly new finding that the replacement of σ-donating phosphines by π-acceptor phosphites in such reactions provides high regioselectivity[12b] either maximum efficiency.[12a,c] Involvement of the related *PC*-palladacycles in catalysis is strongly implicated by the structure of the ligands optimal for these systems ($P(OAr)_3$, Ar = Ph, 2,4-$Bu^t_2C_6H_3$) and the reaction conditions. We found attractive an idea of combining high enantioselection potential of BINOL derivatives with high catalytic activity of phosphite *PC*-palladacycles. Our specific target was to develop synthetic routes employing direct phosphite cyclopalladation to yield enantiomerically pure phosphite *PC*-palladacycle bearing a phosphorus atom in an axially chiral environment, as well as to estimate the effectiveness of chirality transfer from its original source to the reaction center. Preliminary results of this work were reported previously.[13]

## Results and Discussion

**Synthesis and cyclopalladation of phosphite HL.** Steric promotion of intramolecular C—H bond activation is widely practiced in cyclopalladation chemistry.[14] Therefore we have chosen for cyclopalladation a rather bulky phosphite ligand, ($S_a$)-HL. The racemic and enantiomerically pure phosphites HL were synthesized by an adaptation of the known procedure[10e,14c,15] based on reacting phosphachloridite **1** formed *in situ* from BINOL (see Ref. 4q) with 2,4-di-*tert*-butylphenol in the presence of a base (Scheme 2).

Phosphite HL is relatively stable to oxidation and hydrolysis: after 1-week storage in air of its chloroform solution, the content of decomposition products did not

**Scheme 2**



*i*. $PCl_3$, $Et_3N$, toluene (35 mL), from −70 to 25 °C, 2 h; *ii*. $Et_3N$, 2,4-$Bu^t_2C_6H_3OH$, toluene (5 mL), from −70 to 25 °C, 13 h.

exceed 10% (by $^{31}$P NMR). Using of HL ligand in catalysis was reported before,[8c] however, since no comment was made on its synthesis and no spectral or other characterization data were provided, HL can be regarded as a new member of an extensive family of ArO-substituted phosphites based on BINOL with Ar = Ph,[3m] 2-Np,[3c] 2-$BrC_6H_4$,[3m] 4-$MeOC_6H_4$,[16] 4-$CF_3C_6H_4$,[17] 2,6-$Me_2C_6H_3$,[3m] 2,6-$Ph_2C_6H_3$,[3m] and 2,6-$Bu^t_2$-4-$MeC_6H_2$.[18]

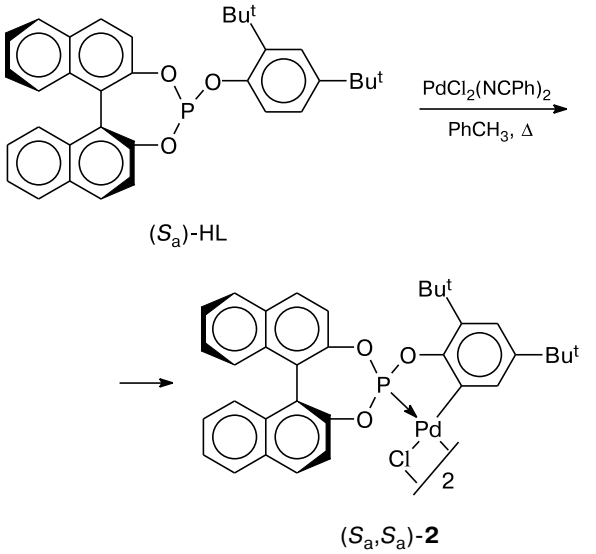
There are two methods for cyclopalladation of achiral phosphites (HL´). For a long time it was effected by a two-stage procedure involving isolation of the intermediate coordination complex $Pd(HL´)_2Cl_2$ with its following thermolysis in the presence of additional molar equivalent of $PdCl_2$.[14b] The yields of thus obtained *PC*-palladacycles vary from moderate[19] to rather high.[11a,20] The more recent one-step route is based on reacting palladium-containing reagents (usually $PdCl_2$) with phosphites HL´ (1 : 1) in 2-methoxyethanol[14c] or toluene[14c,15] under reflux. This method allows obtaining cyclopalladated derivatives of simple triarylphosphites in high yields (up to 98%)[14c,21] yet affording only moderate yields (43—53%) in the case of bulky ligands incorporating seven- or eight-membered heterocycles, [1,3,2]-dioxaphosphepine[10e] or [1,3,2]-dioxaphosphocene.[15]

With the foregoing in view, we expected that cyclopalladation of phosphite HL could be difficult. Indeed, the two-step procedure turned out to be nonproductive as it was accompanied by palladium black precipitation and yielded a multicomponent product mixture even at the stage leading to coordination complex (Pd : HL = 1 : 1, $CH_2Cl_2$, 25 °C). The similar problems were encountered when exploiting the one-step procedure with $PdCl_2$ as a palladating agent (Pd : HL = 1 : 1): the synthesis in the refluxing 2-methoxyethanol proceeded with intense formation of $Pd^0$, yielding the target CPC in only trace amounts.[22] Also unsuccessful was an attempt of using more electrophilic $Pd(OAc)_2$ — reactions in MeCN were dominated by intense palladium black precipitation which occurred already at room temperature.

We could synthesize CPC in a moderate yield only by reaction of HL with $PdCl_2(NCPh)_2$ in the refluxing toluene (Scheme 3). The racemic and optically active dimers, *rac*-**2** and ($S_a$,$S_a$)-**2** were obtained in 53 and 40% isolated yields, respectively (after chromatograpihc purification). In the similar reaction conducted in 1,2-dichloroethane, the yield of dimer *rac*-**2** has dropped to 37%, while the attempts to induce C—H bond activation by introduction of $Et_3N$ as a base[10e] failed because of the rapid palladium(II) reduction under these conditions.

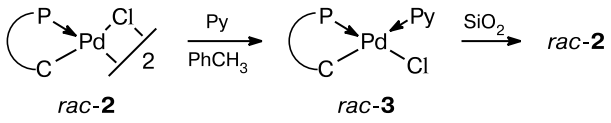
A slightly higher yield of a racemic dimer *rac*-**2** (53%) compared with enantiomerically pure dimer ($S_a$,$S_a$)-**2** (40%) is probably due to the extremely low solubility of the former, owing to which the equilibrium is shifted towards palladacycle formation. This feature of *rac*-**2** useful as it was at the synthesis stage, complicated its

**Scheme 3**




purification considerably. The problem has been solved by *in situ* converting insoluble dimer *rac*-**2** into its well soluble mononuclear pyridine derivative, $PdCl(\eta^2\text{-L})(Py)$ (**3**), which was further purified chromatographically. Previously[23] we have already demonstrated the possibility of regenerating dimeric CPCs from their mononuclear derivatives on silica. In the present case, strong *trans* influence of the carbanion and electron-donating phosporus atom of *PC*-palladacycle facilitated the elimination of the auxiliary pyridine ligand from adduct *rac*-**3** appreciably, which allowed isolation of the purified dimer *rac*-**2** under conditions of column chromatography (Scheme 4).

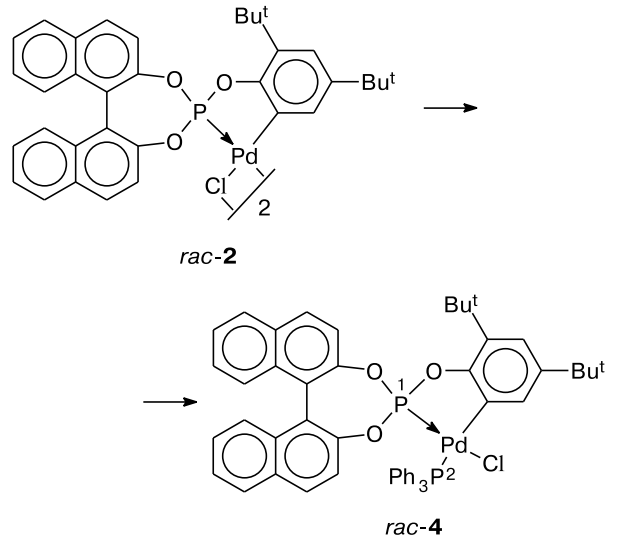
**Scheme 4**




Spectral study of dimeric CPC cannot provide the full information, being restricted by dynamic mobility of these species[24] and their occurrence as a mixture of *syn*/*anti* and *meso*/*dl* isomers (in case of racemic compounds). Thus dimer *rac*-**2** was converted to its mononuclear phosphine derivative *rac*-**4** *via* the chloride bridge splitting reaction (Scheme 5).

Another problem was associated with the possible 1,1´-binaphthyl moiety racemization upon thermal activation of the C—H bond in HL ligand. The BINOL-derived bis-phosphites were demonstrated[10b] to racemize partially at temperatures exceeding 60 °C. Therefore, most pincer *PCP*-complexes of **II** and **III** types were synthe-

**Scheme 5**




**Reaction conditions:** $PPh_3$, $PhCH_3$, 25 °C, 1 h.

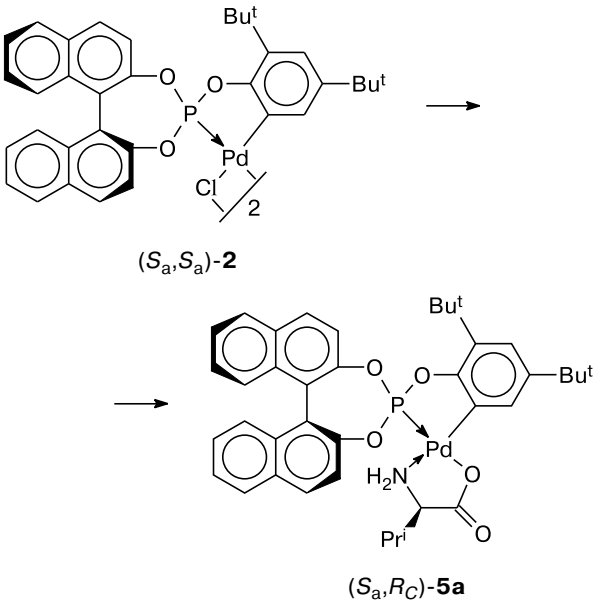
sized using a rather long and tedious route, *i.e.*, through the functionalization of the ligands followed by their oxidative addition to zerovalent palladium.[10a—d]

*A priori* the possibility of 1,1′-binaphthyl moiety racemization under so mild conditions can be excluded on the basis of the following arguments. First, this is inconsistent with the high optical yields (up to 99.8% *ee*) observed in enantioselective reactions catalyzed by transition metal complexes with BINOL-derived phosphites[3f] and phosphoramidites[4c,f,g,7d,25] under the same or more severe temperature conditions (up to 120 °C). Second, it is known that a partial racemization of parent BINOL through rotation about C(1)—C(1′) bond requires more severe conditions ($\tau^{1/2}_{rac}$ = 60 min at 220 °C),[26] whereas its monoacylated derivatives racemize only at 275—280 °C.[27] Third, the quantum chemical estimation yielded rather high racemization barriers for diol BINOL[26] and its monoacylated derivatives[27] ($\Delta G^{\#}_{rac}$ = 158 kJ mol$^{-1}$ and $E_a$ = 159—165 kJ mol$^{-1}$, respectively). Lastly, a mechanistically alternative route to binaphthyl moiety racemization that was discussed in the literature is the interaction between the 2,2′-derivatives resulting in a five-membered ring formation. For example, this type of racemization proceeding *via* the five-membered *CC*-pallada(IV)cycle was suggested as the mechanism accounting for the loss of enantiomeric purity by 2,2′-diiodo-1,1′-binaphthyl under conditions of Suzuki reaction.[28] The similar racemization mechanism can be supposed for monoacylated BINOL derivatives undergoing Newman—Quote rearrangement,[27] in which case quite probable is the formation of an intermediate bearing dinaphthofuran or dinaphthothiophene five-membered cycle closed through C(2) and C(2′) atoms. However, under relatively mild conditions such processes are obviously unfeasible for the HL related BINOL derivatives with the seven-membered dioxaphosphepine ring.

Anyhow it was necessary to check if enantiomeric purity of ($S_a$)-BINOL is retained in the palladacycle ($S_a$)-**2** formed under thermal conditions applied for C—H bond activation in HL ligand (toluene, 110 °C). It should be noted that much more severe conditions were used for direct C—H bond activation in the synthesis of one of the pincer complexes of type **II** (150 °C, microwave activation).[10e] However, the cited communication gives no data on the enantiomeric composition of reaction products, hence, the question about applicability of direct C—H bond activation for producing optically active *PCP*-complexes of that type remained unanswered.

Enantiomeric purity of dimer ($S_a$,$S_a$)-**2** was determined by $^{31}$P NMR after its chiral derivatization *in situ* with the ($R_C$)-valinate auxiliary ligand (Scheme 6).

**Scheme 6**




**Reaction onditions:** (*R*)-ValNa, $CHCl_3$, 25 °C, 4 h.

The similar reaction with the racemic dimer **2** was used to yield the mixture of two diastereomers of the mononuclear ($R_C$)-valinate derivative, ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b**. The $^{31}$P NMR spectra of an individual ($R_C$)-valinate derivative, ($S_a$,$R_C$)-**5a**, as well as the mixture of diastereomers ($S_a$,$R_C$)-**5a**/($R_a$,$R_C$)-**5b** prepared from dimers ($S_a$,$S_a$)-**2** and *rac*-**2**, respectively were measured *in situ*, prior to any purification procedures. The spectrum of ($S_a$,$R_C$)-**5a** shows only one singlet at δ 147.96. In the spectrum of the mixture of diastereomers ($S_a$,$R_C$/$R_a$,$R_C$)-**5a**,**b** there are two closely located singlets at δ 147.73 and 148.05 (Δδ 0.32). However, such resolution is quite sufficient to

confirm completely retained enantiomeric composition of the starting ($S_a$)-BINOL in dimer ($S_a$,$S_a$)-**2**. Thus we have proved the possibility of direct cyclopalladation of chiral ligands based on BINOL without loss of enantiomeric purity.

**Spectral studies of cyclopalladated complexes.** Signal assignments in the $^1$H NMR spectra of HL ligand and CPCs **2**—**5** were based on homo- and heteronuclear decoupling experiments, COSY and NOE techniques, and also quantum chemical calculations of the structure and $^1$H NMR spectra for complexes *rac*-**4** (Table 1), ($S_a$,$R_C$)-**5a** (Table 2), and ($R_a$,$R_C$)-**5b**.

The chemical shift of HL ligand in $^{31}P\{^1H\}$ NMR spectrum (δ 145.1) lies in the range δ 143.5—148.4 typical of the known mono-[16,18] and bis-phosphites with 1,1′-binaphthyl fragment.[10d,e,16,29] The relatively large $\delta_P$ values produced by these ligands are most probably attributable to their cyclic dioxaphosphepine structure. For comparison, this shift value increases from δ ~127 for the simplest phosphite $P(OPh)_3$ (see Ref. 30) to δ 132.9—134.0 when we move to the analogs containing eight-membered dioxaphosphocane ring.[14c,15] The $^1$H NMR spectrum of HL ligand is in full agreement with its presumed structure.

The $^{31}P\{^1H\}$ NMR spectrum of a racemic dimer **2** contains four broadened singlets in the narrow range at δ 138.45 and 138.54 (86%), 140.75 and 140.81 (14%). The two of them, found in the spectrum of optically active dimer ($S_a$,$S_a$)-**2** (δ 138.43 and 140.68) must be assigned to its *anti* and *sin* isomers, respectively. The chemical shift for dimer **2** in the $^{31}P\{^1H\}$ spectrum falls out from the δ range 115—125 characteristic for its analogs with an acyclic moiety $P(OAr)_2$[14c,20,21b] or with a less sterically strained eight-membered dioxaphosphocane *P*-donor.[14c,15] It is possible that the significantly larger chemical shift in the $^{31}P\{^1H\}$ NMR spectrum of dimer **2** results from strongly distorted bond angles in the molecule. As the chemical shifts $\delta_P$ for monodentate phosphites $P(OAr)_3$ in the spectra of their coordination complexes of $Pd(HL')_2Cl_2$ type are typically found at the much lower field (δ 81—87)[14c,20,31] as compared with the signals from free ligands, the shift produced by dimer **2** can be indicative of its cyclopalladated structure.

**Table 1.** The DFT calculated and experimental values of chemical shifts (δ) in the $^1$H NMR spectrum of phosphine adduct *rac*-**4**

| Proton | PBE/TZ2P | Experiment |
|---|---|---|
| *ortho*-H ($PPh_3$) | 7.68 | 7.35—7.41 |
| *meta*-H ($PPh_3$) | 7.17 | 7.01—7.08 |
| *para*-H ($PPh_3$) | 7.14 | 7.10—7.15 |
| H(6″) | 9.27 | 8.47 |
| H(4″) | 7.37 | 7.17 |
| H(3/3′) | 7.80 | 7.38 |
| H(4/4′) | 8.16 | 7.58 |
| H(5/5′) | 8.13 | 7.84 |
| H(6/6′) | 7.65 | 7.48—7.52 |
| H(7/7′) | 7.40 | 7.22—7.28 |
| H(8/8‘) | 7.41 | 7.21 |
| H(3′/3) | 7.81 | 7.46 |
| H(4′/4) | 7.92 | 8.03 |
| H(5′/5) | 7.97 | 7.98 |
| H(6′/6) | 7.61 | 7.50—7.54 |
| H(7′/7) | 7.38 | 7.33 |
| H(8′/8) | 7.31 | 7.22—7.28 |
| $Bu^t$ | 1.18 | 1.14 |
| $Bu^t$ | 1.35 | 1.40 |

**Table 2.** The DFT calculated and experimental values of chemical shifts (δ) in the $^1$H NMR spectrum of valinate derivative ($S_a$,$R_C$)-**5a**

| Proton | PBE/TZ2P | Experiment |
|---|---|---|
| $NH^{ax}$ | 1.57 | 2.10 |
| $NH^{eq}$ | 1.27 | 1.69 |
| Me | 0.53 | 0.94 |
| Me | 0.78 | 1.16 |
| H(6″) | 8.73 | 7.83 |
| H(4″) | 7.26 | 7.23 |
| H(3/3′) | 7.81 | 7.48 |
| H(4/4′) | 8.24 | 8.09 |
| H(8/8′) | 7.65 | 7.38— |
| H(7/7′) | 7.56 | —7.43 |
| H(5/5′) | 8.22 | 8.04 |
| H(6/6′) | 7.75 | 7.57 |
| H(3′/3) | 7.83 | 7.72 |
| H(4′/4) | 8.23 | 8.17 |
| H(5′/5) | 8.22 | 8.06 |
| H(6′/6) | 7.77 | 7.63 |
| H(7′/7) | 7.60 | 7.46 |
| H(8′/8) | 7.77 | 7.53 |
| $Bu^t$ | 1.32 | 1.27 |
| $Bu^t$ | 1.37 | 1.33 |
| $C\underline{H}Me_2$ | 2.72 | 2.47 |
| α-CH | 3.22 | 3.40 |

As the $^1$H NMR spectrum of dimer **2** is unsuitable for structural characterization (see above), to identify the structures of the new complexes, we examined spectrally mononuclear derivatives of **2**.

The $^{31}P\{^1H\}$ NMR spectrum of a mononuclear adduct *rac*-**4** displays two doublets at δ 149.9 and 17.66, corresponding to the phosphorus atoms of *PC*-palladacycle (P(1)) and of an auxiliary phosphine ligand, $PPh_3$ (P(2)). The coupling constant $^2J_{P,P}$ = 45.2 Hz unequivocally indicates the *cis*-(*P*,*P*) geometry of the complex.[32] *cis*-(*P*,*P*)-Coordination of P-donor ligands is typical of the most phosphite palladacycles;[14c,19b,20,21b,33] examples of *cis*/*trans* isomer mixture formation are extremely rare.[9c,14c]

The $^1$H NMR spectra of phosphine adduct *rac*-**4** are consistent with its *ortho*-palladated structure completely.

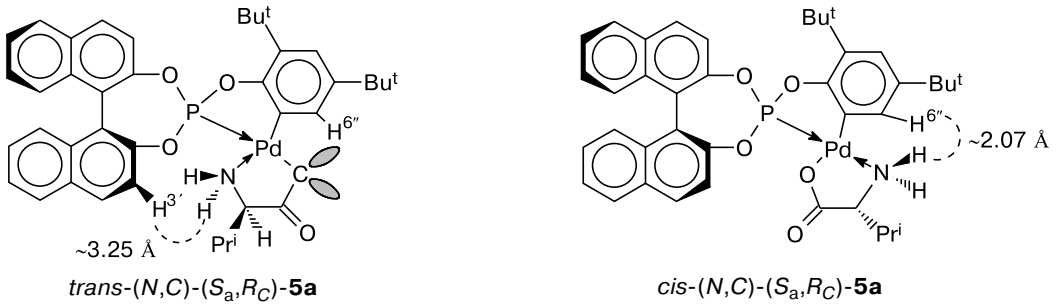
The metalation at the *ortho*-C—H bond of 2,4-di-*tert*-butyl-substituted phenyl ring of HL ligand follows from the presence of only two 1H signals at δ 8.57 (ddd) and 7.18 (dd) without $^3J_{H,H}$ coupling. The correspondence of these signals to H(6″) and H(4″) protons, respectively, was concluded on the following grounds. First, the low-field shift of the first signal (see Table 1) is indicative of the chloride anisotropy influence: the DFT and X-ray diffraction yielded the H(6″)···Cl separation of 2.49 and 2.66 Å, respectively. Second, a useful information is provided by the difference in the spin-spin coupling constants of these protons with two phosphorus atoms: both protons show coupling with the *PC*-palladacycle phosphorus P(1) with $^5J_{H,P(1)}$ of 5.6 and 2.6 Hz, respectively, but only the H(6″) proton has a rather strong coupling with the P(2) atom of auxiliary ligand $PPh_3$ ($^4J_{H,P(2)} = 8$ Hz). The $J_{H,P}$ constants were assigned by the $^1H$ $\{^{31}P\}$ selective double resonance technique.

The assignment of signals from 1,1′-binaphthyl moiety was based on H(3)/H(3′) resonances (δ 7.38 and 7.46) with the coupling constants $^4J_{H,P(1)}$ 0.9 and 1.2 Hz, respectively. To assign H(5)/H(5′) (δ 7.84) and H(4)/H(4′) (δ 7.59) proton signals we have conducted the NOE experiments where irradiation at H(5)/H(5′) resonance frequency resulted in the responses from H(4)/H(4′) protons and *vice versa*, with 4.8 и 3.9% efficiency, respectively. Note that the DFT estimate of the H(5)···H(4) distance was 2.44 Å.

The similar procedure was used for assigning the signals in the $^1H$ NMR spectrum of valinate derivative ($S_a$,$R_C$)-**5a**. To distinguish between two diastereotopic protons of the valinate $NH_2$ group we correlated the coupling constants $^3J_{HNC_\alpha H}$ (4.4 and 7.2 Hz, respectively) to dihedral angles H—N—$C_\alpha$—H (+44.67 and +161.84°, respectively) for $NH^{eq}$ and $NH^{ax}$ protons. The dihedral angles were taken from the DFT calculated structural data for the *trans*-(*N*,*C*)-isomer of adduct ($S_a$,$R_C$)-**5a**. The additional evidence for the signals at δ 1.69 and 2.10 generated by $NH^{eq}$ and $NH^{ax}$ protons, respectively, comes from the similarity of their spectral pattern with that obtained by the quantum chemical simulation of the $^1H$ NMR spectrum of the *trans*-(*N*,*C*)-isomer of adduct ($S_a$,$R_C$)-**5a**: $\delta_H$ 1.27 and 1.57 for $NH^{eq}$ and $NH^{ax}$ protons, respectively (see Table 2).

Identification of the geometric configuration of a valinate complex ($S_a$,$R_C$)-**5a** presented a difficult problem. The spectral data only provide an indirect indication in favor of the *trans*-(*N*,*C*) configuration. First, the low-field shift of the H(6″) proton signal compared to that of the H(4″) proton (δ 7.87 and 7.23, respectively) points toward the influence of the carboxylate oxygen anisotropy (Fig. 1). The DFT calculated H(6″)···O(CO) distance is 2.31 Å (the sum of van de Waals radii of these atoms being ~2.6 Å).[34] The $^1H$ NMR spectral parameters calculated for *trans*-(*N*,*C*)-($S_a$,$R_C$)-**5a** isomer predict even more pronounced carboxylate group anisotropy influence on the H(6″) proton and a larger low-field shift of its signal from the signal of H(4″) proton ($\delta_H$ (DFT) 8.73 and 7.26, respectively). Second, since the DFT calculated H(6″)···$NH^{eq}$ distance for alternative *cis*-(*N*,*C*) configuration is only 2.22 Å, it was reasonable to expect significant dipole-dipole interaction between the H(6″) proton of the palladated phenyl ring and the equatorial valinate NH proton (see Fig. 1). However, the NOE experiments have not shown any interaction between $NH^{eq}$ and H(6″) protons. It is noteworthy that in the case of *trans*-(*N*,*C*)-isomer, the shortest inter-ligand contact between the amino group and 1,1′-binaphthyl moiety is H(3′)···$NH^{ax}$ with a separation of 3.25 Å (DFT) which is too large for observing dipole-dipole interaction.

The *trans*-(*N*,*C*) configuration of adduct ($S_a$,$R_C$)-**5a** is preferred also due to the "transphobia" effect.[33a,35] Structural *trans* influence (STI) of the primary amino group is somewhat stronger than that of the carboxylate oxygen,[33a] while STI of the phosphite *P*-donor atom is comparable or even surpassing STI of the aromatic carbanion center.[33a] As a result, the *trans* position of the two softer donor atoms (N and P) must destabilize the molecule to some extent. Besides that, *trans*-(*N*,*C*) coordination of the aminoacidate ligands is consistent with the abnormal




*trans*-(*N*,*C*)-($S_a$,$R_C$)-**5a** *cis*-(*N*,*C*)-($S_a$,$R_C$)-**5a**

**Fig. 1.** Mutual disposition of valinate NH protons and aromatic protons of *PC*-palladacycle in the two geometric isomers of valinate derivative ($S_a$,$R_C$)-**5a**.

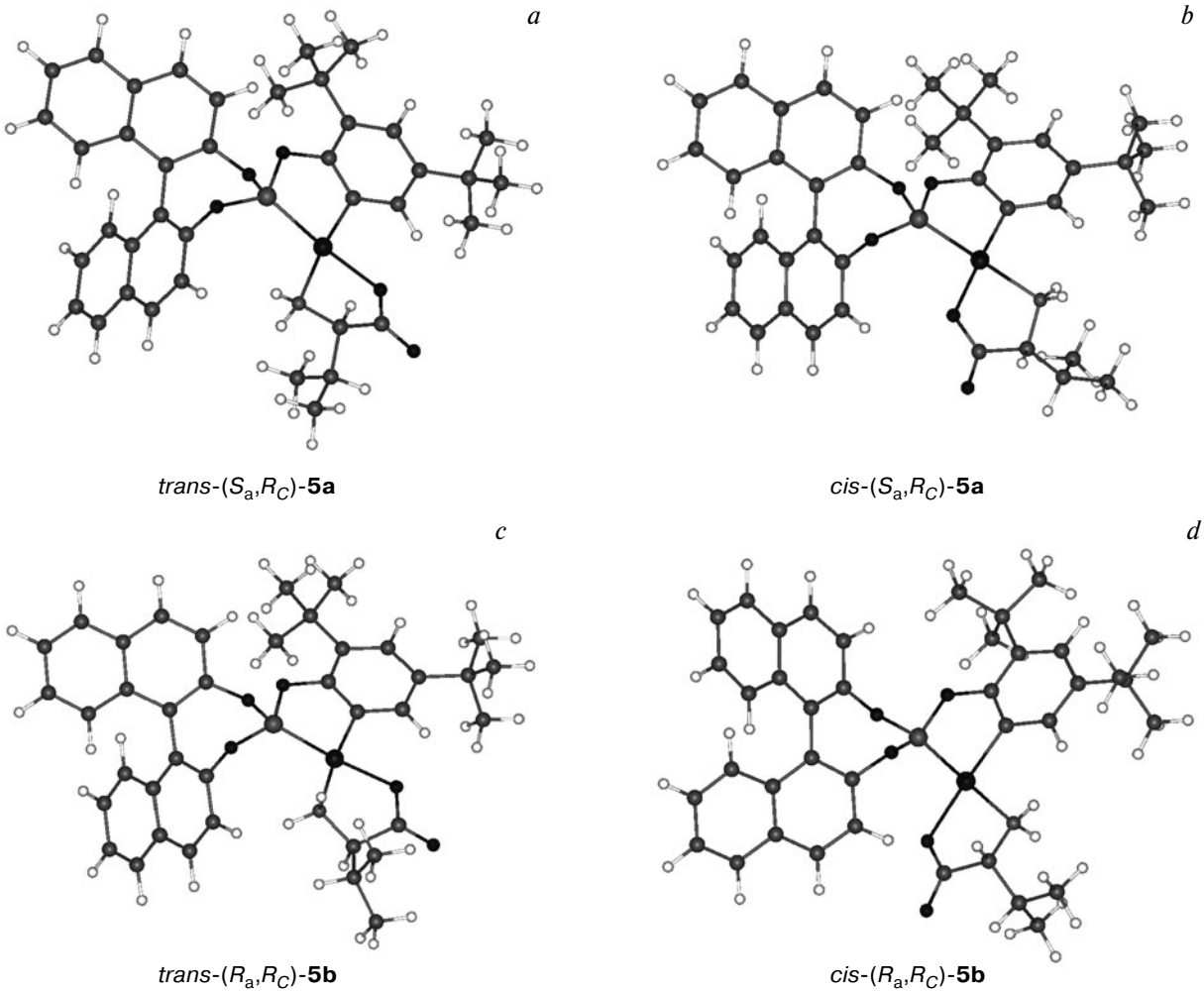



**Fig. 2.** The PBE/TZ2P optimized structures of most stable conformers of *trans*-(*N*,*C*)- (*a*, *c*) and *cis*-(*N*,*C*)-isomers (*b*, *d*) for two diastereomers of valinate derivative **5**, ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b**.

(compared to *CN*-systems) *trans*-(P(2),C) regiochemistry of the coordination of auxiliary phosphine ligands with the phosphite *PC*-palladacycles.[33a]

**Quantum chemical calculation of the structure of valinate adducts 5a,b.** To verify the conclusions based on the spectral data, we performed quantum chemical calculations of the structures of *trans*-(*N*,*C*) and *cis*-(*N*,*C*) isomers for each of valinate adduct diastereomers, ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b**, for the gas phase conditions and without account for the solvation effect. Fully optimized geometries of these structures are presented in Fig. 2 and their selected parameters* are collected in Table 3.

The comparison of the parameters for the four isomers has led to the following conclusions.

(i) For both diastereomers, ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b**, the *trans*-(*N*,*C*) configuration is more energetically favorable than *cis*-(*N*,*C*) configuration, $\Delta E^\circ$ = 2.43 and 2.57 kcal mol$^{-1}$, respectively.

(ii) The valinate chelate ring in both ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** diastereomers shows preference for $\lambda(R_C)$ conformation with equatorial orientation of the isopropyl group at carbon stereocenter.[36]

(iii) Nonplanarity of *PC*-palladacycle is strongly dependent on the metal coordination sphere geometry: in ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** complexes with *cis*-(*N*,*C*) configuration, *PC*-palladacycle is markedly distorted ($\varpi_{av}$ = 11.93 and 9.52°, respectively), whereas in *trans*-(*N*,*C*) isomers it retains an essentially planar structure ($\varpi_{av}$ = 0.71 and 2.25°, respectively).

(iv) Only *cis*-(*N*,*C*) isomers of diastereomers ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** show considerable distortions of *PC*-palladacycles. The latter adopt the conformation which can be described as an envelope with the apical phosphorus atom. The envelopes are slightly twisted with regard to

* Definitions for the parameters used in the discussion of conformation of *N*,*O*-chelate valinate cycle and *PC*-palladacycle are given below in the section describing X-ray characterization of *rac*-**4**.

**Table 3.** Selected parameters of the geometric isomers of two diastereoisomers of valinate derivative **5**, ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** (DFT)

| Isomer | $\Delta E°$ /kcal mol$^{-1}$ | *N*,*O*-Chelate ring[a] | | *PC*-Palladacycle | | |
|---|---|---|---|---|---|---|
| | | $\varpi_{av}$[b] | O—N—$C_\alpha$—C(O) angle/deg | $\varpi_{av}$[b] | C(1)—P—O—C(2) angle/deg | Conformation |
| | | | Diastereomer ($S_a$,$R_C$)-**5a** | | | |
| *trans*-**5a** | 0.10 | 18.55 | +10.97 | 0.71 | +0.60 | —[c] |
| *cis*-**5a** | 2.43 | 17.62 | +10.61 | 11.93 | +4.64 | λ |
| | | | Diastereomer ($R_a$,$R_C$)-**5b** | | | |
| *trans*-**5b** | 0.00 | 16.87 | +10.03 | 2.25 | −1.43 | —[c] |
| *cis*-**5b** | 2.57 | 17.30 | +12.83 | 9.52 | −3.62 | δ |

[a] *N*,*O*-Chelate ring in all isomers exists in the λ-configuration with $Pr^i$ group positioned equatorially.
[b] Nonplanarity of *N*,*O*-chelate ring and *PC*-palladacycle is characterized by the average of the absolute value of the intra-chelate torsion angles ($\varpi_{av}$/deg).
[c] Non-twisted *PC*-palladacycle conformation is assumed.

basal planes with C(1)—P—O—C(2) torsion angles of +4.64 and −3.62° for ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b**, respectively. The opposite signs of the angles can be interpreted to mean that stereochemistry of *PC*-palladacycles depends on dioxaphosphepine fragment configuration: diastereomer ($S_a$,$R_C$)-**5a** bears *PC*-palladacycle in the λ conformation, and ($R_a$,$R_C$)-**5b** — in δ conformation.

(v) Coordination environment of palladium atom is also dependent on the geometry of the complexes. The both *trans*-(*N*,*C*) isomers of diastereomers ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** can be described as square-planar as indicated by the nearly zero torsion angles formed by the four donor atoms (P···C(1)···O···N angle is +0.97 and −0.03°, respectively). For *cis*-(*N*,*C*) isomers ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** it is only slightly larger (+1.21 and +2.57°, respectively).

Thus, the DFT calculations confirm the *trans*-(*N*,*C*) configuration of diastereomer ($S_a$,$R_C$)-**5a** suspected on the basis of $^1$H NMR data. The lower thermodynamic stability of *cis*-(*N*,*C*) isomers compared to *trans*-(*N*,*C*) structures for both diastereomers ($S_a$,$R_C$)-**5a** and ($R_a$,$R_C$)-**5b** can be ascribed to the stronger distortion of the palladium coordination sphere from square-planar geometry most

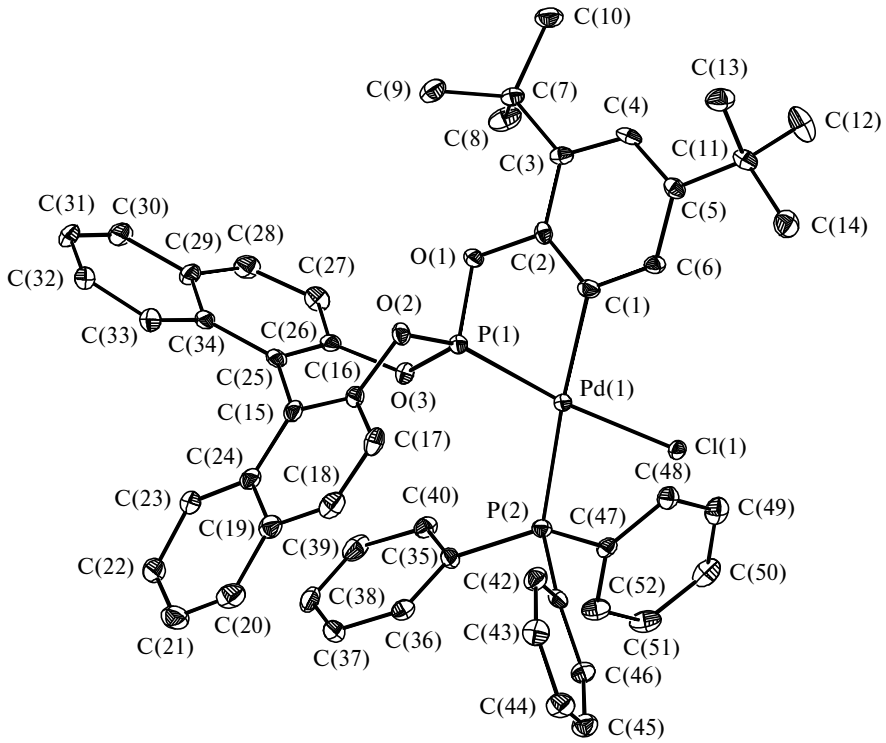



**Fig. 3.** Molecular structure of ($S_a$)-enantiomer of phosphine adduct *rac*-**4**. 1,2-Dichloroethane solvate molecule is omitted, thermal ellipsoids are scaled to the 50% probability level.

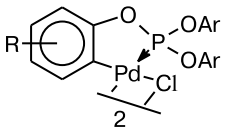
typical of palladium(II), as well as to conformation of *PC*-palladacycle distorted from planar, which is usually adopted by sterically non-hindered palladacycles (see below). The lack of these two important elements of chirality in *trans*-(*N*,*C*) valinate adduct isomers may reduce the chiral information transfer efficiency for such systems considerably; however, this is amendable by introducing more sterically demanding auxiliary ligands.

**X-ray diffraction analysis of phosphine adduct *rac*-4.** The cyclopalladated structure and *ortho*-metallation site in dimer *rac*-**2** are established unambiguously by X-ray examination of its mononuclear phosphine derivative *rac*-**4**; the X-ray data have also confirmed the *cis*-(*P*,*P*) configuration of the metal coordination sphere. Racemic complex **4** crystallizes in the triclinic space group $P\bar{1}$ with two enantiomeric molecules in the unit cell. The molecular structure of the complex is shown in Fig. 3. Selected bond lengths and angles are summarized in Table 4. Structural and stereochemical features of complex **4** are discussed for the ($S_a$)-enantiomer.

**Table 4.** Comparison of experimental (X-ray) and DFT calculated values of selected bond lengths (*d*) and angles (φ) for phosphine adduct *rac*-**4**

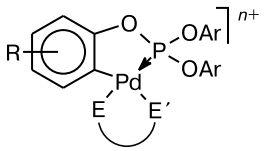
| Parameter | X-ray | DFT | Δ |
|---|---|---|---|
| Bond length | | *d*/Å | |
| Pd(1)—C(1) | 2.072(3) | 2.097 | 0.025 |
| Pd(1)—P(1) | 2.1517(9) | 2.180 | 0.028 |
| Pd(1)—P(2) | 2.3567(9) | 2.409 | 0.052 |
| Pd(1)—Cl(1) | 2.3813(8) | 2.360 | −0.022 |
| P(1)—O(3) | 1.588(2) | 1.635 | 0.047 |
| P(1)—O(1)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

To estimate the efficiency of chirality transfer in CPCs of this type (in particular, in the presence of a bulky 1,3,2-dioxaphosphepine ring) we compared the structures of adduct ($S_a$)*-**4**, the analogous *PCP*-pincer complex of type **II** (R = R′ = H, X = I, **IIa**)[8c] and a series of achiral phosphite CPCs (**VI**—**XII**) characterized previously by



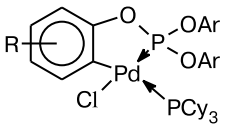

**VIa—d**

| **VI** | Ar | R |
|---|---|---|
| **a**[21b] | Ph | H |
| **b**[21b] | 2-Bu$^t$C$_6$H$_4$ | 2-Bu$^t$ |
| **c**[9i] | 2,4-Bu$^t_2$C$_6$H$_3$ | 2,4-Bu$^t_2$ |
| **d**[14c] | (2-Bu$^t$-4-MeC$_6$H$_2$-6)$_2$CH$_2$ | 2,4-Me$_2$ |



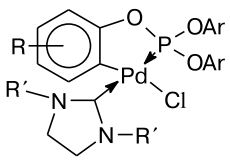

**VIIa—c**

| **VII** | Ar | R | E⌒E′ |
|---|---|---|---|
| **a**[14c] | 2,4-Bu$^t_2$C$_6$H$_3$ | 2,4-Bu$^t_2$ | $Et_2NCSS^-$ |
| **b**[39] | 2,4-Bu$^t_2$C$_6$H$_3$ | 2,4-Bu$^t_2$ | $Ph_2P(O)CH_2C(Me)(CH_2PPh_2)_2$ |
| **c**[20] | Ph | H | $\eta^5$-Cp$^-$ |



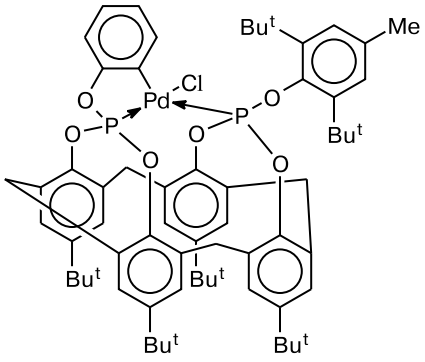

**VIII**

Ar = 2,4-Bu$^t_2$C$_6$H$_3$, R = 2,4-Bu$^t_2$ (see Ref. 37)

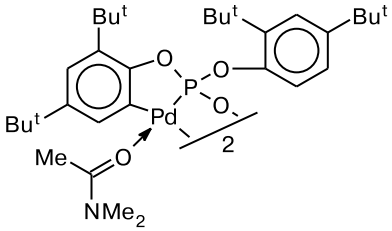



**IXa—c**

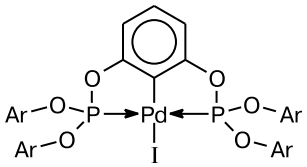
| **IX** | Ar | R | R′ |
|---|---|---|---|
| **a** | Ph | H | 2,6-Pr$^i_2$C$_6$H$_3$ |
| **b** | 2,4-Bu$^t_2$C$_6$H$_3$ | 2,4-Bu$^t_2$ | 2,6-Pr$^i_2$C$_6$H$_3$ |
| **c**[9b] | 2,4-Bu$^t_2$C$_6$H$_3$ | 2,4-Bu$^t_2$ | Mes |



**X** (see Ref. 38)



**XI** (see Ref. 15)



**XII**

Ar = 4-$MeOC_6H_4$ (see Ref. 40)

X-ray diffraction. The latter included several dimeric *PC*-complexes (**VI**,[9i,14c,21b] **XI** (see Ref. 15), and their mononuclear derivatives with mono- (**VIII**,[37] **IX**,[9b] **X** (see Ref. 38)) and bidentate auxiliary ligands (**VII**),[14c,20,39] and *PCP*-pincer complex **XII**.[40]

The Pd—C bond length (2.072 Å) in complex **4** is close to those of *trans*-(*P*(*2*),*C*)-configured CPCs **VIII** and **X** (2.084 and 2.064 Å, respectively), but less than in a cationic diphosphine derivative **VIIb** (2.118 Å). The endocyclic Pd—P(1) bond length in adduct **4** (2.152 Å) falls in the range 2.142—2.177 Å characteristic of triarylphosphite CPCs containing bridging (**VI**) or terminal (**VIII**, **X**) chloride on the P(1)—Pd—Cl diagonal. The Pd—Cl bond in adduct **4** (2.381 Å) is slightly lengthened compared to that in mononuclear analogs **VIII** and **X** (2.349 and 2.319 Å, respectively), but is expectedly stronger than the (μ)Cl—Pd bonds positioned *trans* to phosphite P-donor atom in dimers **VI** (2.390—2.419 Å). The exocyclic Pd—P(2) bond length in adduct **4** (2.357 Å) is within the range established for phosphine derivatives **VIIb**, **VIII**, and **X** with P(2)—Pd—C diagonal (2.340—2.405 Å). The C—Pd—P(1) angle in the palladacycle of **4** (76.27°) is smaller compared with the values typical of all phosphite *PC*-palladacycles (77.83—81.47° for **V**—**XI**). It is most likely due to steric strain in adduct **4**, as the minimal angles were found in the structures bearing bulky substituents (78.08 and 77.83° for **VId** and **VIII**, respectively).

The formally square-planar metal coordination environment in complex $(S_a)$*-**4** displays a significant tetrahedral distortion with a {C(1)Pd(1)P(1)}/{Cl(1)Pd(1)P(2)} dihedral angle of 14.83° that is larger than that observed in all known phosphite *PC*-palladacycles (0.81—13.45°). Most phosphite CPCs show characteristic tendency for the square-planar coordination (0.81—5.76°), which acquires tetrahedral distortion only on the introduction of bulky substituents (8.36—8.97° for **VIb**,**d**, **X**), maximum distortion (13.45°) being found for the sterically strained adduct **IXb**. To describe stereochemistry of palladium pseudotetrahedral coordination environment and palladacycle conformation in complex $(S_a)$*-**4** we applied the skew line convention.[41] The pseudotetrahedral configuration is controlled by a sign of the torsion angle formed by four metal-bound donor atoms, preferably starting from the *PC*-palladacycle P(1) and C atoms (Fig. 4). In adduct $(S_a)$*-**4**, the P(1)···C···Cl···P(2) torsion angle has a positive sign (+15.48°), accordingly, pseudotetrahedral configuration is Λ. It should be noted that in the formally achiral dimeric CPCs **VIb**,**d** with the pronounced tetrahedral distortion, pseudotetrahedral configurations in their two halves are opposite (Δ and Λ), thus, these molecules can be regarded as configurational racemates.[42]

The five-membered *PC*-palladacycle in complex $(S_a)$-**4** has been found in envelope conformation with a base P(1)O(1)C(2)C(1) (average displacement 0.0344 Å)* with palladium atom shifted 0.587 Å out of the basal plane and a twist with regard to C(1)···P(1) line of 20.62°. An alternative description for this conformation is the envelope with a base Pd(1)C(1)C(2)O(1) (average displacement from the basal plane 0.039 Å), P(1) atom

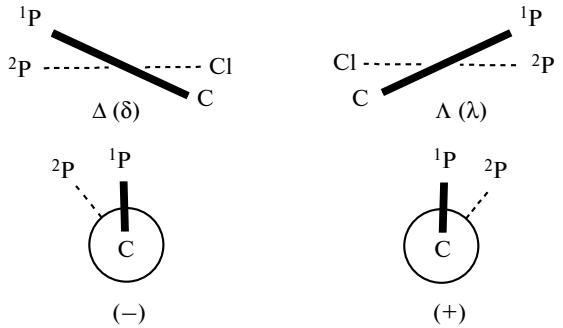



**Fig. 4.** Correlations between the skew-line projections and the sign of torsion angle for phosphine adduct **4** coordination sphere.

* Hereafter, the choice of four envelope basal atoms was based on the minimum values of appropriate intra-chelate torsion angles.

0.464 Å out-of-plane, a twist with regard to O(1)···Pd(1) line 26.23°. This duality results from the presence of two nearly equal intra-chelate torsion angles (8.97 and 10.85° compared to 19.10—23.32° for the three other angles).

Nonplanarity of *PC*-palladacycle ($S_a$)-**4** is substantial: the average of the absolute value of the torsion angles ($\varpi_{av}$) is 16.80°. Among the known analogs only three complexes were found to contain palladacycles with a comparable (**VIII**) or even stronger (**VId**, **IXc**) distortion ($\varpi_{av}$ 15.19, 21.08, and 17.81°, respectively). Not surprisingly, these falling out structures are those in which steric strain is induced either by the bulky *P*-substituents (**VId**) or auxiliary carbene ligand (**IXc**), or by the *cis*-coordinated and rather bulky phosphine $PCy_3$ (the Tolman cone angle θ is 179°)[43] adjacent to a cumbersome $P(OAr)_2$ group (**VIII**). By contrast, CPCs **VIa**, **VIIc**, **IXa** based on nonsubstituted phosphites $P(OPh)_3$ have the essentially planar palladacycle as evidenced by minimal $\varpi_{av}$ varying in the range 1.16—4.20°. In most of other complexes with relatively low steric demands, palladacycle adopts the flattened envelope conformation ($\varpi_{av}$ 5.89—10.29°). Thus it is safe to state that in the absence of considerable steric hindrance, phosphite palladacycles show clear tendency to adopting a virtually planar conformation.

The conformation of the palladacycle in adduct ($S_a$)*-**4** can be described as twisted-envelope. The average displacement of the basal atoms from the basal least-squares plane is 0.039 Å that is comparable with distortions exhibited by sterically strained analogs (0.020—0.036 Å for **VId**, **VIIb**, **VIII**) but exceeds those observed for other complexes (0.001—0.010 Å). In accordance with the skew-line convention,[41] configuration of this new element of chirality in the structure of adduct ($S_a$)*-**4** must be defined as δ-conformation as being characterized by negative C(1)···P(1)—O(1)—C(2) torsion angle (−5.48°). Hence configuration of palladacycle in ($S_a$)*-**4** (δ) is opposite to that of the coordination polyhedron (Λ). The same relation between palladacycle and coordination polyhedron configurations is found for the formally achiral sterically strained dimer **VId** whose two halves have enantiomeric configurations Λδ and Δλ.

The primary source of stereochemical information in complex ($S_a$)*-**4** is axial chirality of ($S_a$)-1,1′-binaphthyl fragment in 1,3,2-dioxaphosphepine heterocycle. This ring is strongly twisted ($\varpi_{av}$ 42.35°), and applying the skew-line convention to seven-membered rings, its conformation will be δ($S_a$) based on the negative O(2)···O(3)—C(26)···C(16) torsion angle (−28.59°). The both results compare well with the conformations of two dioxaphosphepine rings of the *PCP*-analog, ($R_a$)-**IIa** characterized by a slightly higher distortion ($\varpi_{av}$ 44.12 and 46.03°) at identical λ($R_a$)-relations between the axial and conformational chirality.

The metal-coordinated triarylphosphines are known[44] to exist in chiral propeller-type rotamer forms. While exploring the stereochemistry of $PPh_3$ chiral auxiliary in adduct ($S_a$)*-**4**, we have evaluated the orientation ($\omega_i$) of three *P*-phenyl rings (*A*—*C*) on the basis of three pairs of $C_o$—$C_i$—P—Pd torsion angles ($\omega_{i_1}$ and $\omega_{i_2}$) using the known formula $\omega_i = 0.5(\omega_{i_1} + \omega_{i_2} + 180°)$.[44g] The $\omega_i$ values obtained for PPh rings demonstrate the pronounced dependence upon the ring arrangement with regard to dioxaphosphepine heterocycle containing the fragment of BINOL: angles $\omega_A$, $\omega_B$, and $\omega_C$ are 66.8, 33.7, and 15.4°, respectively. The average value of the torsion angle ($\omega_{av} = (1/3)(\omega_A + \omega_B + \omega_C) = 38.6°$) corresponds to the *P*-configuration of phosphine propeller in ($S_a$)*-**4**.

From comparison of the X-ray diffraction data for ($S_a$)*-**4** and its analogs it is seen that the introduction of bulky substituents (including dioxaphosphepine ring formed by BINOL) into phosphite CPC structure increases the tetrahedral distortion of coordination sphere and the twist of palladacycle, also resulting in Pd—Cl bond weakening and in the reduction of intra-chelate C—Pd—P(1) angle.

**Quantum chemical study of phosphine adduct ($S_a$)-4.** In order to estimate the effect of crystal packing on the structure and stereochemistry of complex **4**, we have carried out quantum chemical modeling of its ($S_a$)-enantiomer (Fig. 5). The structural parameters of ($S_a$)-**4** calculated and optimized for the gas phase appeared to be rather close to those obtained crystallographically with the discrepancy between the calculated and X-ray determined bond lengths and angles not exceeding 2% (see Table 4). More important, however, is the fact that stereochemical parameters of the complex in the gas and crystalline phases also differ insignificantly.

In particular, DFT theory also predicts the tetrahedral distortion of the metal coordination sphere, although

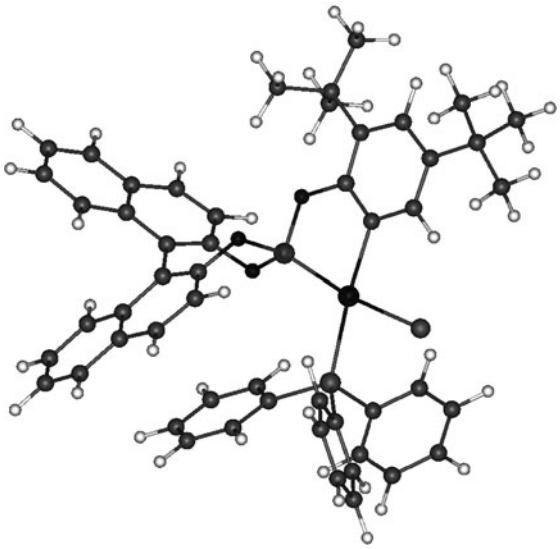


**Fig. 5.** The PBE/TZ2P optimized structure of phosphine adduct ($S_a$)-**4** (gas phase).

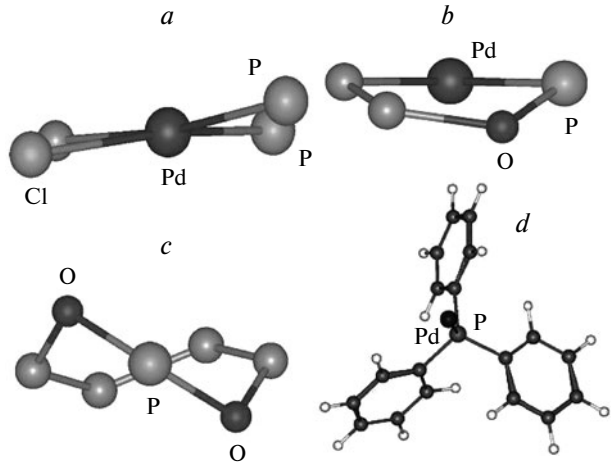



**Fig. 6.** Elements of chirality in phosphine adduct ($S_a$)-**4**.

weaker than that found for the crystal: P(1)···C···Cl···P(2) angles for the two phases are +8.68 and +15.48°, respectively. The positive sign of this angle is indicative of the retained pseudotetrahedral Λ-configuration in the gas phase (Fig. 6, *a*).

The calculated degree of nonplanarity of *PC*-palladacycle is close to the X-ray result for the crystal ($\varpi_{av}$ = 15.41 and 16.80°, respectively). The envelope geometry of palladacycle with apical phosphorus is more pronounced in the gas phase: only one of the five intra-chelate angles, O—C(2)—C(1)—Pd is characterized by the considerably smaller value (+6.29°) compared to others (11.84—23.22°). Phosphapalladacycle in the gas phase retains its δ-conformation identified in the crystal as follows from the negative sign of both calculated and experimental C(1)···P(1)—O(1)—C(2) torsion angle values, −6.15 and −5.48°, respectively (Fig. 6, *b*).

The calculated parameters of 1,3,2-dioxaphosphepine ring bearing ($S_a$)-binaphthyl fragment agreed with the experimental geometry derived from the X-ray data. The twist of the seven-membered ring is nearly the same in both cases, with angles $\varpi_{av}$ = 41.58 and 42.35°, respectively. The conformation of the seven-membered ring was also found to be the same (δ($S_a$)) for the crystal and gas phase as determined from the sign and value of O(2)···O(3)—C(26)···C(16) torsion angle: −27.89 and −28.59°, respectively (Fig. 6, *c*).

Finally, the rotameric state of $PPh_3$ ligand coordinated to palladium in a phosphine adduct ($S_a$)-**4** was estimated almost identically by X-ray and gas-phase model DFT calculation, with $\omega_A$, $\omega_B$, and $\omega_C$ angles of 68.74, 35.14, and 19.73°, respectively for the gas phase and 66.8, 33.7, and 15.4° for crystal. The average torsion angles ($\omega_{av}$) for the gas phase and crystal are 41.20 and 38.6°, indicating *P*-configured $PPh_3$ propeller in both cases (Fig. 6, *d*).

From comparison of the calculated parameters for two phosphite *PC*-palladacycle derivatives, the phosphine adduct ($S_a$)-**4** and valinate complex ($S_a$,$R_C$)-**5a** it is obvious that steric demands of auxiliary ligands affect the complex stereochemistry considerably. In particular, in a phosphine adduct ($S_a$)-**4**, the square-planar palladium environment is distorted stronger than in a less strained valinate derivative ($S_a$,$R_C$)-**5a**, P(1)···C(1)···Cl···P(2) angles being +8.68 and +0.97°, respectively. This also holds for *PC*-palladacycle conformation which is much more twisted in ($S_a$)-**4** compared to ($S_a$,$R_C$)-**5a**, $\varpi_{av}$ = 15.41 and 0.60°, respectively. It is most likely that chirality transfer in the phosphite CPCs of this type will be more effective in the presence of sterically demanding auxiliary ligands due to involvement of two additional elements of chirality, the pseudotetrahedral coordination sphere and twisted palladacycle conformation.

**The calculation of conformational equilibria in adduct ($S_a$)-4.** An important factor of effective chirality transfer is the conformational stability of the complex. To estimate the conformational rigidity of adduct ($S_a$)-**4** and reveal possible conformational equilibria, we have examined the complex structure with the aid of additional DFT calculations with the modified configurational or conformational parameters. The previously optimized structure of complex ($S_a$)-**4** was taken as a starting point. The calculation was run in three series, each characterized by a preset iteration step of variation of the torsion angles controlling i) palladacycle conformation, ii) pseudotetrahedral configuration or iii) $PPh_3$ propeller configuration. At each step one of parameters was kept fixed to fully optimize the CPC geometry with respect to all other parameters, then the CPC energy was determined.

In the first series, *PC* palladacycle conformation was changed by varying C(1)···P(1)—O(1)—C(2) angle value. All calculated structures had the higher energy than the starting one (Fig. 7). The energy curve showed no addi-

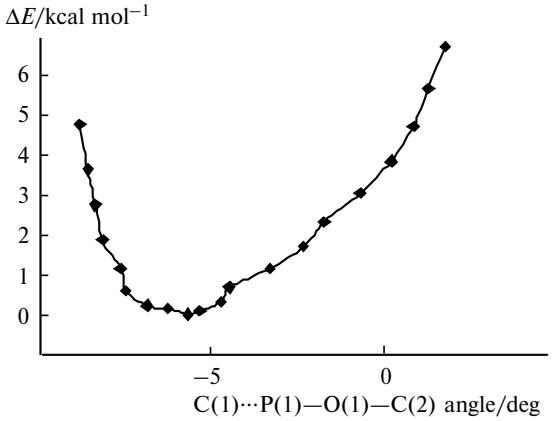



**Fig. 7.** Dependence of the energy of complex ($S_a$)-**4** on *PC*-palladacycle conformation.

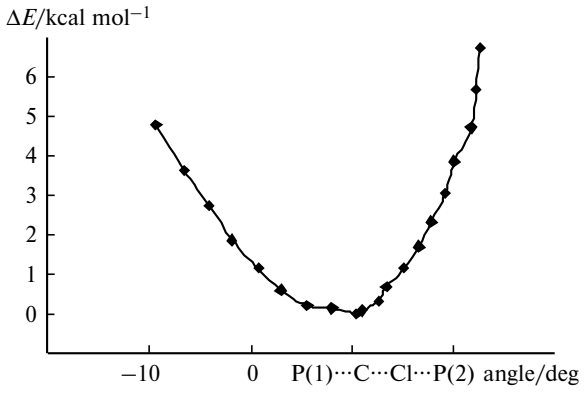



**Fig. 8.** Dependence of the energy of complex ($S_a$)-**4** on configuration of pseudotetrahedral metal environment.

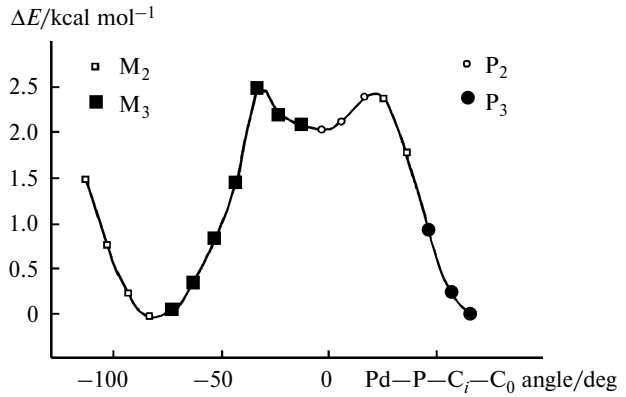



**Fig. 9.** Dependence of the energy of complex ($S_a$)-**4** on the rotameric state of $PPh_3$ propeller as determined by *A* ring (*P*-phenyl ring oriented toward binaphthyl moiety) rotation. $M_2$ and $P_2$ are two-bladed propellers, $M_3$ and $P_3$ are three-bladed propellers.

tional minima corresponding to the different, more stable conformation. So it can be concluded that 1,1′-binaphthyl fragment hinders any conformational alterations of *PC*-palladacycle in complex ($S_a$)-**4**, hence strictly dictating its δ-stereochemistry.

The second series of calculations was performed to check for palladium in complex ($S_a$)-**4** the possibility of adopting an alternative pseudotetrahedral coordination environment. For this purpose we calculated a set of structures having different P(1)···C···Cl···P(2) torsion angles. As in the first series, the energy curve showed no additional minima corresponding to configurations different from the starting point; all modified structures are characterized by a higher energy (Fig. 8). These results conclusively indicate that in adduct ($S_a$)-**4**, the BINOL fragment determines the Λ-configuration of palladium coordination environment; ($S_a$)-axially chiral structure does not admit the possibility of the opposite pseudotetrahedral Δ-configuration

The last calculation series was aimed at energy estimation for various rotameric states of $PPh_3$ propeller. Since the energy calculation for all probable structures would require enormous computation time, we have restricted their number to those with only one *P*-phenyl ring position varied, *i.e.*, the one proximate to binaphthyl moiety and thus most sensitive to the primary chirality inducer (hereafter, *A* ring). Despite the identical positions of *A* ring in the structures of the starting and final (yielded by a 180° rotation) points in the energy curve (Fig. 9), these states differ in energy because of the different orientations of the two other *P*-phenyl rings. The calculation results demonstrate the absence of any hindrance for the concerted rotation of PPh rings about the P—$C_{ipso}$ axes at room temperature: the obtained barrier for two propeller configurations, *P* and *M*, is not higher than 2.5 kcal $mol^{-1}$ that is only slightly exceeding the rotation barrier for free $PPh_3$ group (~1.5 kcal $mol^{-1}$).[44f,h] Our estimate for the barrier to concerted rotation of the propeller *P*-phenyl rings is typical of the transition metal complexes with triphenylphosphine.[44a,e,f]

Thus, the quantum chemical calculations of the conformational equilibria in complex ($S_a$)-**4** demonstrated that axially chiral 1,1′-binaphthyl moiety strictly dictates the δ-conformation for the *PC*-palladacycle and Λ-configuration for the metal pseudotetrahedral environment. The alternative λΔ($S_a$)-stereochemistry of these structural units cannot be realized. The stereochemical information transfer from axially chiral ($S_a$)-1,1′-binaphthyl moiety to the reaction center in complex ($S_a$)-**4** is anticipated to be rather effective due to involvement of additional induced elements of chirality in the process.

As shown by the gas phase calculations, the state of the $PPh_3$ propeller which was determined for the ($S_a$)*-**4** crystal is not the only possibility. There are no significant energetic barriers for the propeller phenyl ring rotation at room temperature.

In summary, in this work we described the synthesis of the first optically active *PC*-palladacycle with the phosphorus atom in axially chiral environment. The feasibility of direct thermal (at ~110 °C) C—H bond activation in ($S_a$)-BINOL-derived phosphites without loss of enantiomeric purity was proved spectrally ($^{31}$P NMR) with using ($R_C$)-valinate auxiliary in the step of chiral derivatization of dimer ($S_a$,$S_a$)-**2a**. The *ortho*-palladated structure of a new palladacycle was confirmed by the single-crystal X-ray diffraction analysis of the mononuclear phosphine derivative of dimer *rac*-**2**. Chirality transfer in the novel CPCs is discussed on the basis of comparing the results from DFT studies and X-ray data for ($R_C$)-valinate derivative ($S_a$)-**5** and phosphine adduct ($S_a$)-**4**. It is shown that axial chirality of ($S_a$)-1,1′-binaphthyl moiety determines the δ-conformation of the seven-membered 1,3,2-dioxaphosphepine ring and five-membered *PC*-pal-

ladacycle, as well as the Λ-configuration of pseudo-tetrahedral palladium coordination environment that is confirmed by DFT calculations of the conformational transition energy in the complex ($S_a$)-**4**.

## Experimental

$^1$H and $^{31}$P{$^1$H} NMR spectra were recorded on Varian VXR-400 and Bruker DPX-400 spectrometers with operating frequency of 400 and 169 MHz, respectively, in $CDCl_3$ at room temperature (unless otherwise stated). Chemical shifts in $^1$H and $^{31}$P NMR spectra were referenced internally to $Me_4Si$ and externally to $H_3PO_4$, respectively. Signal assignments were based on homo- and heteronuclear decouplings, and also on COSY and NOE techniques. Optical rotation was measured using a Perkin—Elmer 341 polarimeter in 0.5-dm cuvettes at 25 °C. Melting points were measured in vacuum-sealed capillary tube with an Electrothermal IA 9000 digital melting point apparatus. TLC (on Silufol UV-254 plates) was used to follow the course of the reaction and control product purity. All manipulations with the free phosphite HL were performed under purified Ar in absolute deaerated solvents using Schlenk techniques. The products were isolated by preparative flash-chromatography or dry column chromatography[45] on Fluka 60 silica.

The solvents were purified by standard procedures: benzene and toluene were dried over $CaCl_2$, refluxed over Na and then distilled under argon; anhydrous MeOH was obtained by distillation over MeONa; chloroform and methylene chloride were passed through the column of neutral $Al_2O_3$ (Brockmann activity grade II) (L 40/250) and distilled under argon; 1,2-dichloroethane was passed through the column of neutral $Al_2O_3$ (Brockmann activity II) (L 40/250) and distilled over $P_2O_5$; chloroform-$d_1$ and methylene chloride-$d_2$ (Aldrich) were distilled over $CaH_2$ under argon directly before use; hexane and light petroleum were distilled over Na under argon.

The reagents, $PdCl_2$, $Pd(OAc)_2$, (*R*)-valine (Aldrich), $Pd(PhCN)_2Cl_2$ (Merck), and ($S_a$)-1,1′-binaphthyl-2,2′-diol (BINOL) (Fluka) were used without additional purification. Racemic BINOL (Aldrich) and $PPh_3$ were purified by twofold recrystallizations from benzene—hexane mixture and acetone, respectively; 2,4-di-*tert*-butylphenol (Aldrich) was recrystallized twice from light petroleum and dried over $P_2O_5$ and paraffin *in vacuo*.

**Racemic (1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)-phosphite (*rac*-HL).** The solution of racemic BINOL (860 mg, 3.0 mmol) in anhydrous toluene (25 mL) heated to 60 °C was added dropwise at vigorous stirring over 10 min to the solution of $PCl_3$ (0.26 mL, 410 mg, 3.0 mmol) and $Et_3N$ (0.83 mL, 606 mg, 6.0 mmol) in the same solvent (10 mL) cooled to −70 °C. After stirring at −70 °C (2 h) and more stirring at ~20 °C (1 h), formation of 4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxaphosphepine **1** was confirmed by $^{31}$P NMR examination of an aliquote of the reaction mixture: $\delta_P$ 179.51 (*cf.* Ref. 29: $\delta_P$ 179.0). Immediately after that, the reaction mixture was treated with additional $Et_3N$ (302 mg, 3.0 mmol) under vigorous stirring and then dropwise by the solution of 2,4-di-*tert*-butylphenol (600 mg, 2.9 mmol) in anhydrous toluene (5 mL). The reaction mixture was stirred for 12 h at ~20 °C, the precipitate formed was filtered off, mother liquor was evaporated *in vacuo*. The residue was purified by dry column chromatography[45] on deaerated Silpearl silica ($h$ = 6.5 cm, $d$ = 2.5 cm, eluting with toluene—hexane mixtures (50 : 50—100 : 0)) under argon to yield 1.17 g (78%) of phosphite *rac*-HL as colorless amorphous powder. M.p. (decomp.) 182 °C, $R_f$ 0.40 (toluene—hexane (1 : 5)). Found (%): C, 78.25; H, 6.58. $C_{34}H_{33}O_3P$. Calculated (%): C, 78.43; H, 6.40. $^{31}$P{$^1$H} NMR, δ: 145.11 (s). $^1$H NMR, δ: 1.34 (s, 9 H, Bu$^t$); 1.39 (s, 9 H, Bu$^t$); 7.20 (dd, 1 H, H(5″), $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.5 Hz); 7.24 (d, 1 H, H(6″), $^3J_{H,H}$ = 8.3 Hz); 7.27 (ddd, 1 H, H(7)/H(7′), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.29 (ddd, 1 H, H(7′)/H(7), $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.5 Hz); 7.39 (d, 1 H, H(3″), $^4J_{H,H}$ = 2.5 Hz); 7.40 (d, 1 H, H(8)/H(8′), $^3J_{H,H}$ = 8.2 Hz); 7.42 (d, 1 H, H(8′)/H(8), $^3J_{H,H}$ = 8.2 Hz); 7.43 (ddd, 1 H, H(6)/H(6′), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.46 (ddd, 1 H, H(6′)/H(6), $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.5 Hz); 7.49 (dd, 1 H, H(3)/H(3′), $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,P}$ = 0.8 Hz); 7.59 (d, 1 H, H(3′)/H(3), $^3J_{H,H}$ = 8.8 Hz); 7.90 (d, 1 H, H(4)/H(4′), $^3J_{H,H}$ = 8.8 Hz); 7.91 (d, 1 H, H(5)/H(5′), $^3J_{H,H}$ = 8.2 Hz); 7.95 (d, 1 H, H(5′)/H(5), $^3J_{H,H}$ = 8.2 Hz); 8.01 (d, 1 H, H(4′)/H(4), $^3J_{H,H}$ = 8.3 Hz).

**($S_a$)-(1,1′-Binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)-phosphite (($S_a$)-HL)** was synthesized and purified as described in the previous step, from ($S_a$)-BINOL (1040 mg, 3.63 mmol), $PCl_3$ (0.32 mL, 500 mg, 3.63 mmol), 2,4-di-*tert*-butylphenol (749 mg, 3.63 mmol), and $Et_3N$ (1.50 mL, 1100 mg, 10.89 mmol) in anhydrous toluene (40 mL) in a yield of 1.34 g (71%) as colorless amorphous powder. M.p. (decomp.) 187 °C, $R_f$ 0.40 (toluene—hexane (1 : 5)), $[\alpha]_D^{25}$ +103.5 (*c* 1.31, $CH_2Cl_2$). Found (%): C, 78.60; H, 6.48. $C_{34}H_{33}O_3P$. Calculated (%): C, 78.43; H, 6.40. $^{31}$P{$^1$H} NMR, δ: 145.07 (s). $^1$H NMR, δ: 1.32 (s, 9 H, Bu$^t$); 1.37 (s, 9 H, Bu$^t$); 7.19 (dd, 1 H, H(5″), $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.5 Hz); 7.24 (d, 1 H, H(6″), $^3J_{H,H}$ = 8.3 Hz); 7.27 (ddd, 1 H, H(7)/H(7′), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.29 (ddd, 1 H, H(7′)/H(7), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.5 Hz); 7.39 (d, 1 H, H(3″), $^4J_{H,H}$ = 2.5 Hz); 7.40 (d, 1 H, H(8)/H(8′), $^3J_{H,H}$ = 8.3 Hz); 7.42 (d, 1 H, H(8′)/H(8), $^3J_{H,H}$ = 8.3 Hz); 7.43 (ddd, 1 H, H(6)/H(6′), $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.46 (ddd, 1 H, H(6′)/H(6), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.48 (dd, 1 H, H(3)/H(3′), $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,P}$ = 0.8 Hz); 7.58 (d, 1 H, H(3′)/H(3), $^3J_{H,H}$ = 8.8 Hz); 7.90 (d, 1 H, H(4)/H(4′), $^3J_{H,H}$ = 8.8 Hz); 7.91 (d, 1 H, H(5)/H(5′), $^3J_{H,H}$ = 8.3 Hz); 7.95 (d, 1 H, H(5′)/H(5), $^3J_{H,H}$ = 8.3 Hz); 8.01 (d, 1 H, H(4′)/H(4), $^3J_{H,H}$ = 8.8 Hz).

**Racemic di-μ-chloro-bis[(1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C,P*]dipalladium(II) (*rac*-2).** To the solution of $Pd(PhCN)_2Cl_2$ (71.5 mg, 0.186 mmol) in 1,2-dichloroethane (3 mL) was added phosphite HL (97.0 mg, 0.186 mmol), the homogeneous reaction mixture was heated to reflux with stirring for 9 h. The precipitate formed was filtered off and dried *in vacuo* to yield 0.0707 g (57%, 0.0534 mmol) of impure dimer **2** as absolutely insoluble powder. The suspension of dimer *rac*-**2** in methylene chloride (3 mL) was further treated with pyridine (8.5 mg, 0.107 mmol), this followed by stirring of the reaction mixture for 15 min. The homogeneous solution of pyridine adduct **3** ($R_f$ 0.30, toluene—acetone (1 : 1))* was evaporated and passed through the flash-column ($h$ = 13 cm,

* Pyridine adduct **3** is completely decomposed on silica with formation of dimer **2** ($R_f$ 0.98).

$d$ = 2 cm) eluting with toluene—hexane (2 : 1) → toluene → toluene—acetone (5 : 1) to isolate pure dimer *rac*-**2** (a product of complete decomposition of adduct **3** in the column) as a colorless amorphous powder (yield 53.3 mg, 43%). M.p. (decomp.) 247 °C, $R_f$ 0.5 (toluene—hexane (1 : 1)). Found (%): C, 61.44; H, 5.05. $C_{68}H_{64}Cl_2O_6P_2Pd_2$. Calculated (%): C, 61.73; H, 4.89. $^{31}P\{^1H\}$ NMR, δ: 138.45 (s), 138.54 (s) (86%); 140.75 (s), 140.81 (s) (14%).

**($S_a$,$S_a$)-Di-μ-chloro-bis[(1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C,P*]dipalladium(II) (($S_a$,$S_a$)-2).** The solution of $Pd(PhCN)_2Cl_2$ (46.5 mg, 0.1212 mmol) and phosphite ($S_a$)-HL (63.1 mg, 0.1212 mmol) in toluene (2 mL) was refluxed for 7 h with stirring. Palladium black was filtered off, the mother liquor was evaporated. The residue was purified by flash-chromatography ($h$ = 13 cm, $d$ = 2 cm; elution with toluene—hexane (1 : 1) → toluene → toluene—acetone (10 : 1)) to yield 32.0 mg (40%) of dimer ($S_a$,$S_a$)-**2** as colorless amorphous powder. M.p. (decomp.) 230 °C, $R_f$ 0.5 (toluene—hexane (1 : 1)). Found (%): C, 61.49; H, 4.88. $C_{68}H_{64}Cl_2O_6P_2Pd_2$. Calculated (%): C, 61.73; H, 4.89. $^{31}P\{^1H\}$ 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 (br.m); 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 (br.d); 8.06 (br.d).

**Racemic chloro[(1,1′-binaphthyl-2,2′-diyl)(2,4-di-*tert*-butylphenyl)phosphite-*C,P*](triphenylphosphine-*P*)palladium(II) (*rac*-4).** To the suspension of racemic dimer **2** (18.2 mg, 0.0138 mmol) in toluene (1.5 mL) was added triphenylphosphine (7.2 mg, 0.0275 mmol). The reaction mixture was stirred for 30 min at ~20 °C and evaporated *in vacuo*. The residue was purified by dry column chromatography[45] ($h$ = 5 cm, $d$ = 4 cm; eluting with toluene → toluene—acetone (5 : 1)). Two crystallizations from methylene chloride—hexane mixture afforded 20.0 mg (60% yield) of adduct *rac*-**4** as light-orange crystals. M.p. (decomp.) 225 °C, $R_f$ 0.73 (toluene—acetone (10 : 1)). Found (%): C, 67.43; H, 5.25. $C_{52}H_{47}ClO_3P_2Pd$. Calculated (%): C, 67.60; H, 5.14. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$), δ: 17.66 (d, $^2J_{P,P}$ = 45.2 Hz); 149.91 (d, $^2J_{P,P}$ = 45.2 Hz). $^1H$ NMR ($CD_2Cl_2$), δ: 1.14 (s, 9 H, $Bu^t$); 1.40 (s, 9 H, $Bu^t$); 7.01—7.08 (m, 6 H, *m*-PPh, $^4J_{H,P(2)}$ = 2.0 Hz); 7.10—7.15 (m, 3 H, *p*-PPh, $^5J_{H,P(2)}$ = 2.0 Hz); 7.17 (dd, 1 H, H(4″), $^5J_{H,P(1)}$ = 2.6 Hz, $^4J_{H,H}$ = 2.1 Hz); 7.21 (d, 1 H, H(8)/H(8′), $^3J_{H,H}$ = 8.6 Hz); 7.22—7.28 (m, 2 H, H(7)/H(7′), H(8′)/H(8)); 7.33 (m, 1 H, H(7′)/H(7))*; 7.35—7.41 (m, 6 H, *o*-PPh, $^3J_{H,P(2)}$ = 10.9 Hz); 7.38 (dd, 1 H, H(3)/H(3′), $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,P(1)}$ = 0.9 Hz); 7.46 (dd, 1 H, H(3′)/H(3), $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,P(1)}$ = 1.2 Hz); 7.48—7.52 (m, 1 H, H(6)/H(6′)); 7.50—7.54 (m, 1 H, H(6′)/H(6)); 7.58 (d, 1 H, H(4)/H(4′), $^3J_{H,H}$ = 8.8 Hz); 7.84 (d, 1 H, H(5)/H(5′), $^3J_{H,H}$ = 8.2 Hz); 7.98 (d, 1 H, H(5′)/H(5), $^3J_{H,H}$ = 8.2 Hz); 8.03 (d, 1 H, H(4′)/H(4), $^3J_{H,H}$ = 8.9 Hz); 8.47 (ddd, 1 H, H(6″), $^4J_{HP(1)}$ = 5.6 Hz, $^4J_{HP(2)}$ = 8.0 Hz, $^4J_{H,H}$ = 2.2 Hz).

**The mixture of diastereomers [(1,1′-binaphthyl-2,2′-diyl)-(2,4-di-*tert*-butylphenyl)phosphite-*C,P*][($R_C$)-valinato-*N,O*]-palladium(II) (($S_a$,$R_C$)-5a and ($R_a$,$R_C$)-5b).** Dimer *rac*-**2** (15.7 mg, 0.0118 mol) was added to the solution of sodium (*R*)-valinate (2.9 mg, 0.0237 mmol) in chloroform (2 mL). The reaction mixture was stirred for 3 h at ~20 °C, filtered and evaporated. At this step, the $^{31}P\{^1H\}$ NMR spectrum shows two equal intensity signals at δ 147.73 (s) and 148.07 (s). The residue was recrystallized from methylene chloride—hexane mixture at low temperature to yield 14.1 mg (84%) of the mixture of diastereomers **5a**,**b** as colorless fine crystals. M.p. (decomp.) 235—237 °C, $R_f$ 0.53 (toluene—acetone (1 : 1))*, $[\alpha]_D^{25}$ ~0.00, $[\alpha]_{436}^{25}$ +17.0 ($c$ 0.19, $CHCl_3$). Found (%): C, 63.07; H, 5.74; N, 1.93. $C_{39}H_{42}NO_5PPd$. Calculated (%): C, 63.11; H, 5.72; N, 1.89. $^{31}P\{^1H\}$ NMR, δ: 147.73 (s); 148.07 (s).

**[{($S_a$)-1,1′-Binaphthyl-2,2′-diyl}(2,4-di-*tert*-biphenyl)phosphite-*C,P*][($R_C$)-valinato-*N,O*]palladium(II) (($S_a$,$R_C$)-5a).** Dimer ($S_a$,$S_a$)-**2** (8.2 mg, 0.0062 mmol) was introduced into the solution of sodium (*R*)-valinate excess (2.8 mg, 0.0248 mmol) in chloroform (2 mL). The reaction mixture was stirred for 4 h, then filtered and evaporated. Recrystallization from chloroform—hexane mixture at low temperature gave 8.3 mg (93% yield) of diastereomer ($S_a$,$R_C$)-**5a** as fine colorless crystals. M.p. (decomp.) 228—230 °C, $R_f$ 0.48 (toluene—acetone (1 : 1))*, $[\alpha]_D^{25}$ +155.6 ($c$ 0.25, $CHCl_3$). Found (%): C, 63.09; H, 5.70; N, 1.94. $C_{39}H_{42}NO_5PPd$. Calculated (%): C, 63.11; H, 5.72; N, 1.89. $^{31}P\{^1H\}$ NMR, δ: 148.12 (s). $^1H$ NMR, δ: 0.94 (d, 3 H, Me, $^3J_{H,H}$ = 7.1 Hz); 1.16 (d, 3 H, Me, $^3J_{H,H}$ = 7.0 Hz); 1.27 (s, 9 H, $Bu^t$); 1.33 (s, 9 H, $Bu^t$); 1.69 (br.dd, 1 H, $NH^{eq}$, $^2J_{H,H}$ = 11.0 Hz, $^3J_{HNC\alpha H}$ = 4.4 Hz); 2.10 (br.dd, 1 H, $NH^{ax}$, $^2J_{H,H}$ = 11.0 Hz, $^3J_{HNC\alpha H}$ = 7.2 Hz); 2.47 (m, 1 H, C<u>H</u>$Me_2$); 3.40 (ddd, 1 H, α-CH, $^3J_{HCNH}$ = 7.2 Hz, $^3J_{HCNH}$ = 4.4 Hz, $^3J_{HCCH}$ = 6.9 Hz); 7.23 (dd, 1 H, H(4″), $^5J_{H,P}$ = 3.5 Hz, $^4J_{H,H}$ = 2.1 Hz); 7.38—7.43 (m, 2 H, H(7)/H(7′), H(8)/H(8′)); 7.46 (ddd, 1 H, H(7′)/H(7), $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.48 (br.d, 1 H, H(3)/H(3′), $^3J_{H,H}$ = 8.8 Hz); 7.53 (d, 1 H, H(8′)/H(8), $^3J_{H,H}$ = 8.7 Hz); 7.57 (m, 1 H, H(6)/H(6′)); 7.63 (ddd, 1 H, H(6′)/H(6), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.3 Hz); 7.72 (br.d, 1 H, H(3′)/H(3), $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,P}$ = 0.4 Hz); 7.87 (dd, 1 H, H(6′), H(5)/H(5′), $^4J_{H,P}$ = 7.1 Hz, $^4J_{H,H}$ = 2.1 Hz); 8.04 (d, 1 H, $^3J_{H,H}$ = 8.3 Hz); 8.06 (d, 1 H, H(5′)/H(5), $^3J_{H,H}$ = 8.3 Hz); 8.09 (d, 1 H, H(4)/H(4′), $^3J_{H,H}$ = 8.8 Hz); 8.17 (d, 1 H, H(4′)/H(4), $^3J_{H,H}$ = 8.8 Hz).

**Quantum chemical calculations.** All DFT calculations were performed for the gas phase using the nonempirical PBE functional within the Generalized gradient approximation[46] (PRIRODA-6 program package[47]). For expansion of one-electron wave functions we used more extensive TZ2P basis set constructed from Gaussian functions: {311/1} for H atoms, {51111/51111/5111} for Pd atoms, and {6,11111/411/11} for other (C, N, O, and P) atoms. Relativistic SBK pseudopotential was used as implemented in Ref. 48. The energy $E^0$ was calculated taking into account the zero-point vibration in the harmonic approximation. All structures were fully optimized. Zero-point energy corrections were included within the harmonic approximation. $^1H$ NMR spectra were simulated by GIAO (gauge-including-atomic-orbital)[49] technique using PBE functional with TZ2P all-electron basis set. Calculated chemical shifts are presented as the difference in shielding between the standard ($Me_4Si$) and the protons in the complex in question. All computation was run on a MVS 15000BM cluster at the Joint Supercomputer Center (JSCC, Moscow).

**X-ray diffraction analysis of phosphine adduct *rac*-4.** Crystals of *rac*-**4** suitable for X-ray examination were grown by the slow

* The signal overlaps with signals of $PPh_3$ *ortho*-protons.

* Valinate complexes **5a**,**b** are partially decomposed on silica with formation of dimer **2** ($R_f$ 0.90).

diffusion of pentane vapor into a dichloroethane solution. Crystals of *rac*-**4** ($C_{56}H_{55}Cl_5O_3P_2Pd$, $M = 1121.59$) are triclinic, space group $P\bar{1}$, at 100 K $a = 12.9201(7)$ Å, $b = 14.3239(8)$ Å, $s = 16.3593(14)$ Å, $\alpha = 111.534(2)°$, $\beta = 106.222(2)°$, $\gamma = 98.2940(10)°$, $V = 2598.8(3)$ Å$^3$, $Z = 2$, $F(000) = 1152$, $d_{calc} = 1.433$ g cm$^{-3}$, $\mu = 0.719$ mm$^{-1}$. The lattice parameters and intensities of 32453 reflections were measured on a Bruker SMART APEX2 CCD Area Detector diffractometer ($\lambda$(Mo-K$\alpha$) = 0.71072 Å, graphite monochromator, 100 K, $\omega$-scans, $\theta_{max} = 29°$). The reflection intensities were integrated using SAINT program,[50] SADABS v2.03 program[51] was used to apply semiempirical absorption correction. The structure was solved by the direct method and refined using the full-matrix least-squares on $F^2$ in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed in the geometrically calculated positions and then refined isotropically, "riding" on their parent atoms. A crystal of *rac*-**4** contains two 1,2-dichloroethane solvate molecules, with one having carbon atoms disordered about two positions with a 3 : 7 population ratio. All calculations were performed using SHELXTL program package.[52] Final *R*-factors: $R_1 = 0.0517$ for 9366 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0749$ for all 14061 independent reflections. Crystallographic data for the structure of complex *rac*-**4** have been deposited with the Cambridge Crystallographic Data Center (CCDC-677989); X-ray data are available at www.ccdc.cam.ac.uk/data_request/cif.

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