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First enantiopure imine *CN*-palladacycle of non-metallocenic planar chirality with the [2.2]paracyclophane backbone

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ABSTRACT

Herein the preparation of a planar chiral imine *CN*-palladacycle free of redox activity is reported. The direct cyclopalladation of a [2.2]paracyclophane-derived imine (HL) afforded the racemic dimer $\{Pd(\eta^2\text{-L})(\text{-Cl})\}_2$ **1**; its *ortho*-palladated structure was confirmed by spectroscopic (^{1}H and ^{31}P NMR) data for mononuclear derivatives and the X-ray study of the phosphane adduct $(\eta^2\text{-L})PdCl(PPh_3)$ **4**. Both the (S_{pl},S_{pl})- and (R_{pl},R_{pl})-enantiomers of dimer **1** were isolated by the diastereoselective decoordination of the (R_C)-valinate auxiliary ligand (Val) from the adduct $(\eta^2\text{-L})Pd(\kappa^2\text{-Val})$ **5** using column chromatography on silica gel. The absolute configuration of these new *CN*-palladacycles was established by the independent synthesis of the (R_{pl},R_{pl})-enantiomer of dimer **1** from the pre-resolved (S_{pl})-4-formyl[2.2]paracyclophane.

1. Introduction

The high efficiency of planar chiral palladacycles in the processes of chiral recognition is well known;[1] some of them provide enantioselectivities up to 99% ee in asymmetric catalysis. However, the majority of the described cyclopalladated complexes (CPCs) of this stereochemical type are derived from redox-active ferrocene-,[1a–c,2] ruthenocene,[2k,3] or cobalticene-based ligands[1h,i,k–m,4] or contain the (tricarbonyl)chromium moiety.[5] Examples of non-metallocenic CPCs with planar chirality are limited to diastereo- (**I**) and regioisomeric (**II**) derivatives of cyclopalladated oxazolinyl[2.2]paracyclophane[6] (Chart 1).

The collection of optically active imine-derived palladacycles is rather rich, including metallocenic compounds with planar chirality[2c,f,i–n,p,5a] and C*-chiral palladacycles,[7] mainly benzylideneimine derivatives bearing a carbon stereocenter in the N-substituent. Some of them possess mesomorphic properties[7f] or anticancer activity,[7d] or may be used as resolving agents.[7g,k] Achiral and racemic cyclopalladated imines have also been investigated[8] and have found application as (pre)catalysts in diverse processes[9] and liquid-crystalline materials.[10] Starting our program of preparation of non-metallocenic planar chiral CPCs free of redox activity, we recently reported the synthesis of the first enantiopure phosphapalladacycle with a [2.2]paracyclophane (pCp) skeleton.[11] The aim of this research was to prepare a planar chiral palladacycle of the *CN*-type bearing an imine nitrogen donor atom and estimate its stereochemical peculiarities.

2. Results and discussion

2.1. *CN*-Palladacycle preparation

Racemic *N*-(2,6-dimethylphenyl)-[2.2]paracyclophane-4-carbaldimine (**HL**) was prepared by a reported method;[12] several conditions for its direct cyclopalladation were tested. For imine substrates it is common to employ palladium(II) acetate in glacial acetic acid with heating;[13] this approach was reported as a 'high-yield method'[13d] providing yields up to quantitative.[13a,d,h] However, in the cyclopalladation of imine **HL** under these conditions (Method 1), racemic dimer **1** was obtained in a rather low yield of 41%. The same reaction when conducted in toluene, afforded dimer **1** with an increased yield of 85% (Method 2, Scheme 1).

The next method of the cyclopalladation of imine **HL** was based on solid-phase C–H bond activation on silica (Method 3). This approach was recently developed in detail for the cyclopalladation of diverse N- and P-donor ligands.[14a] Previously reported examples of solid-phase[14b] or silica-assisted cyclometallation[14c,d] are rare.

The solid-state heating of a mixture of palladium(II) acetate and ligand **HL** loaded on silica under rather mild conditions (85 °C, 14 h) resulted in efficient C–H bond activation. The four-step procedure includes (Scheme 2): (i) C–H bond activation to give acetate-bridged dimer *rac*-**2**, (ii) imine palladacycle elution by pyridine solution as the mononuclear derivative $(\eta^2\text{-L})Pd(OAc)(Py)$, followed by (iii) acetate/chloride anion exchange to give adduct

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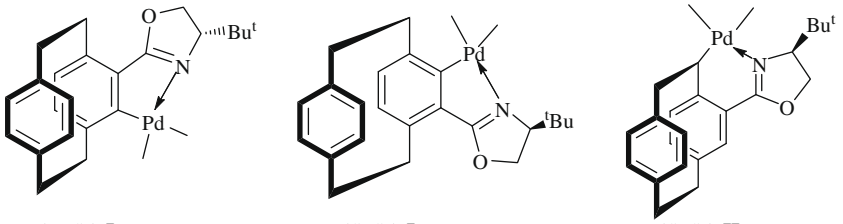
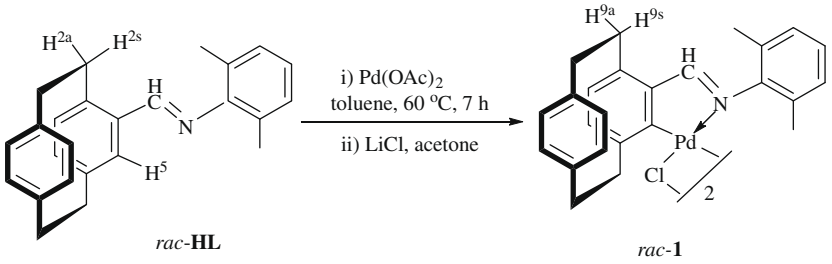


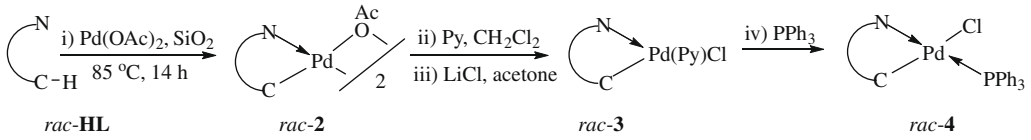
($R_{pl}S_C$)-**I** ($S_{pl}S_C$)-**I** ($S_{pl}S_C$)-**II**

Chart 1.



rac-**HL** *rac*-**1**

Scheme 1.



rac-**HL** *rac*-**2** *rac*-**3** *rac*-**4**

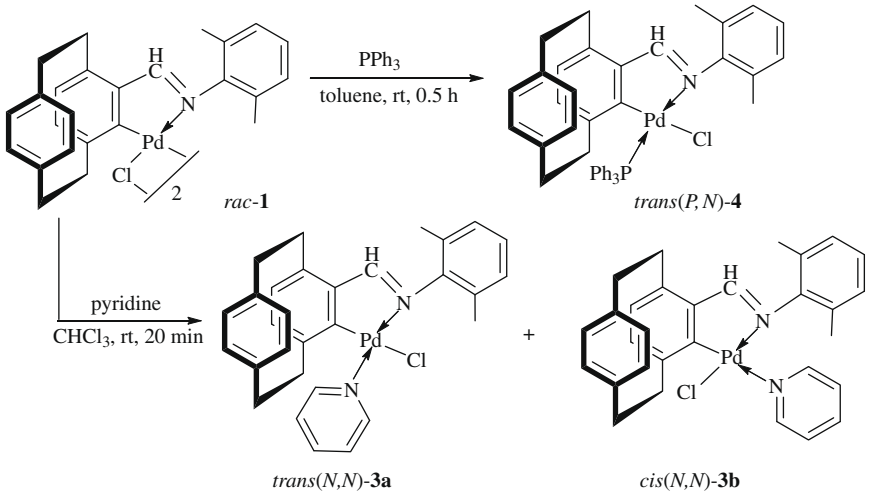
Scheme 2.

rac-**3**, and finally (iv) labile auxiliary pyridine ligand replacement by a more tightly bound triphenylphosphine ligand affording the phosphane derivative *rac*-**4**. Despite this multi-step protocol, the final product was isolated in a high yield of 70%. This method may be useful for preparation of diverse mononuclear derivatives of the new *CN*-palladacycle.

For further spectroscopic studies, both mononuclear derivatives, *rac*-**3** and *rac*-**4** were prepared independently by the reaction of the chloride bridge cleavage in dimer *rac*-**1** (Scheme 3).

2.2. *CN*-Palladacycle resolution

Initially, we undertook an attempt to perform the resolution of the racemic imine *CN*-palladacycle via kinetic separation of its enantiomers at the stage of dimer *rac*-**1** complexation with (*R*)-valinate (Val) as chiral auxiliary ligand. However, this attempt was not successful. In the reaction of dimer *rac*-**1** with (*R*)-valinate in the Pd:Val ratio of 2:1 in MeOH at room temperature, the unreacted dimer remained racemic ($[\alpha]_D^{24} \sim 0$), while the (*R*)-valinate



rac-**1** *trans*(*P*,*N*)-**4**

trans(*N*,*N*)-**3a** *cis*(*N*,*N*)-**3b**

Scheme 3.

derivative appears to be a nearly equal mixture of two diastereomers (^{1}H NMR data).

To solve this problem we turned our attention to a new methodology of racemic palladacycle resolution elaborated recently.[15] This is based on the diastereoselective decomplexation of the auxiliary ligand in diastereomeric derivatives on silica. As the chiral derivatizing agent for the transformation of enantiomers of the racemic dimer **1** into diastereomers we chose the (*R*)-valinate ligand (Val) instead of the (*S*)-prolinate ligand in the reported system.[15] We assumed that the primary amino group of the valinate may make for a more efficient CPC interaction with the sorbent. The decreased stability of mononuclear derivatives of *PC*-[16a,b] and *CN*-palladacycles[16c] containing bidentate auxiliary ligands bearing hard donor atoms (including α-amino acidate ones[16a,b]) on silica is well known. As might be expected, we detected the partial formal 'decomposition' (really decomplexation) of the mononuclear (*R*)-valinate complex **5** into the starting dimer **1** on TLC plates. From our preceding results,[15] it was reasonable to suppose that in this case, the 'monomer→dimer' transformation can also occur as a diastereoselective process. Thus, we performed the chromatographic separation of an equimolar mixture of two diastereomers, (R_{pl},R_C)-**5** and (S_{pl},R_C)-**5** (Scheme 4).

After elution via a SiO_2-loaded *flash*-column only two compounds were isolated: the optically active dimer (+)$_b$-**1** and one of the two diastereomers of its (*R*)-valinate derivative **5** in the yields of 40% and 68%, respectively. Both these complexes were thus obtained in a stereochemically pure state. The comparison of the ^{1}H NMR spectra of chromatographically isolated diastereomer (S_{pl},R_C)-**5** and the starting mixture of diastereomers (R_{pl},R_C)-**5**/(S_{pl},R_C)-**5** confirms the absence of any admixture of another (R_{pl},R_C)-**5** diastereomer in the first sample, which corresponds to a diastereomeric purity of >98% de. The complete enantiomeric purity (>98% ee) of the chromatographically isolated dimer (R_{pl},R_{pl})-**1** was confirmed by comparison of its specific rotation with that of the sample of the other enantiomer, (S_{pl},S_{pl})-**1**, obtained by protolytic removal of the auxiliary valinate ligand from the pure diastereomer (S_{pl},R_C)-**5**: $[\alpha]_D^{22} = +551$ (*c* 0.247, CH_2Cl_2) and −549 (*c* 0.253, CH_2Cl_2), respectively.

The absolute configuration of the imine palladacycles obtained was established by the independent synthesis of the (R_{pl},R_{pl})-enantiomer of dimer **1**. The starting (S_{pl})-4-formyl[2.2]paracyclophane with an enantiomeric purity of 96.3% ee was obtained by resolution of the racemic aldehyde via its diastereomeric Schiff bases with (R_C)-α-methylbenzylamine,[17] and then converted into optically active imine (S_{pl})-**HL** by the method described for the racemate.[12] The cyclopalladation of imine (S_{pl})-**HL** was performed by Method 2, described for the racemate. The positive sign of the specific rotation determined for the dimer (R_{pl},R_{pl})-**1**, $[\alpha]_D^{22} = +559$ (*c* 0.247, CH_2Cl_2), is indicative of the same (R_{pl},R_{pl})-configuration of dimer (+)$_b$-**1**, which was chromatographically isolated during racemate resolution. The large value of the specific rotation of the dimer (R_{pl},R_{pl})-**1** prepared from the scalemic aldehyde is indicative of its enantiomeric purity being close to complete in the stages of the imine (S_{pl})-**HL** synthesis or isolation of its cyclopalladation product (R_{pl},R_{pl})-**1**.

2.3. Spectroscopic studies of imine *CN*-palladacycle derivatives

Taking into account Bolm et al.'s research results,[6] we considered two possible sites for the C–H bond activation in the pCp-derived imine ligand **HL**: the aromatic (sp^2)C–H bond of the functionalized phenylene ring (regioisomer **A**) and the aliphatic (sp^3)C–H bond of the closest methylene group (regioisomer **B**, Fig. 1). This forced us to conduct detailed spectroscopic studies of the mononuclear derivatives **3**–**5** of the new *CN*-palladacycle. The signal assignment in their ^{1}H NMR spectra was performed using diverse NMR techniques and invoking parameters from the X-ray diffraction study of adduct **4**.

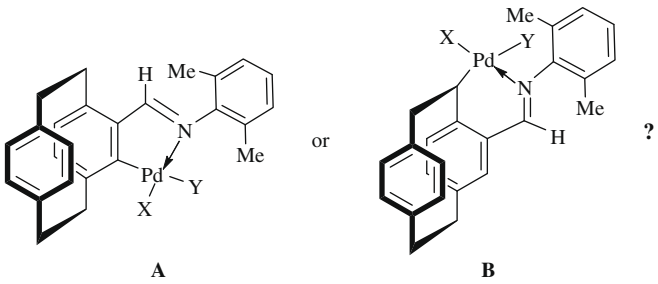
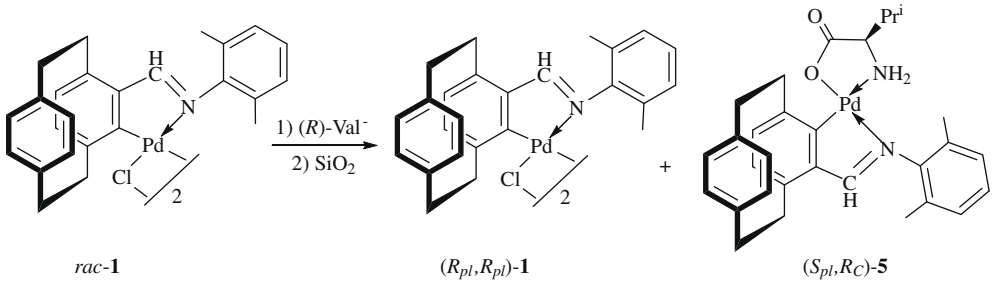


Figure 1. Alternative directions of C–H bond activation.

2.3.1. Phosphane adduct *rac*-4

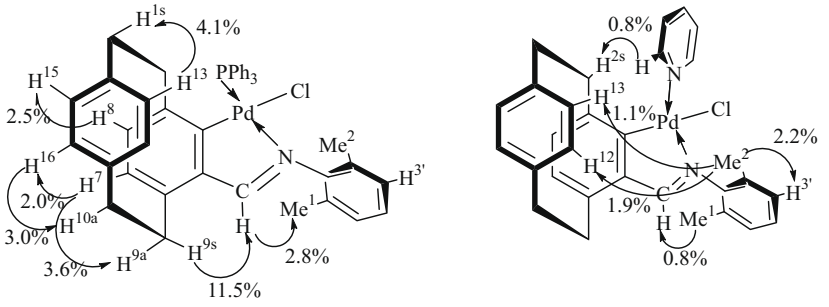
The ^{1}H NMR spectrum of the phosphane derivative *rac*-**4** is in complete accordance with its *ortho*-palladated structure. The aromatic protons of the pCp-framework provided only six well resolved signals in the range of δ 5.72–6.78 ppm, separated from signals of other aromatic protons (δ 7.11–7.64 ppm). As a starting point in the assignment of the aromatic protons of the pCp moiety, we used the H(8) proton signal, which appears as a doublet with the constant $^5J_{HP} \sim 0.8$. Protons H(15) and H(16) of the non-palladated C_6H_4 ring were identified on the basis of NOE experiments revealing their dipole–dipole interaction with the corresponding *pseudo*-geminal protons, H(8) and H(7) (Fig. 2a).

The methylene proton signals appear as four groups of overlapped multiplets in the range of δ 2.74–3.30 ppm and one separated signal at δ 1.93 ppm. The latter was identified as belonging to the H(2a) proton due to its NOE enhancement (4.0%) from the irradiation of the aromatic H(8) proton: the H(8)···H(2a) distance is equal to 2.540 Å in the crystal. The methylene protons H(10a), H(1s), and H(9a) were identified due to their dipole–dipole interactions with aromatic H(16), H(13), and H(7) protons, respectively (Fig. 2a). The assignment of the signal at δ 3.27 ppm to the H(9s)



rac-**1** (R_{pl},R_{pl})-**1** (S_{pl},R_C)-**5**

Scheme 4.



(a) *trans*(*P,N*)-**4** (b) *trans*(*N,N*)-**3a**

Figure 2. NOE data for signal assignment in the ^{1}H NMR spectra of phosphane adduct **4** (a) and major isomer of pyridine derivative **3** (b).

proton was based on an intense response of the imine α-CH proton on irradiation at this frequency: the α-CH···H(9s) distance is equal to 2.218 Å in the crystal. These data exclude the regioisomeric structure **B** (Fig. 1).

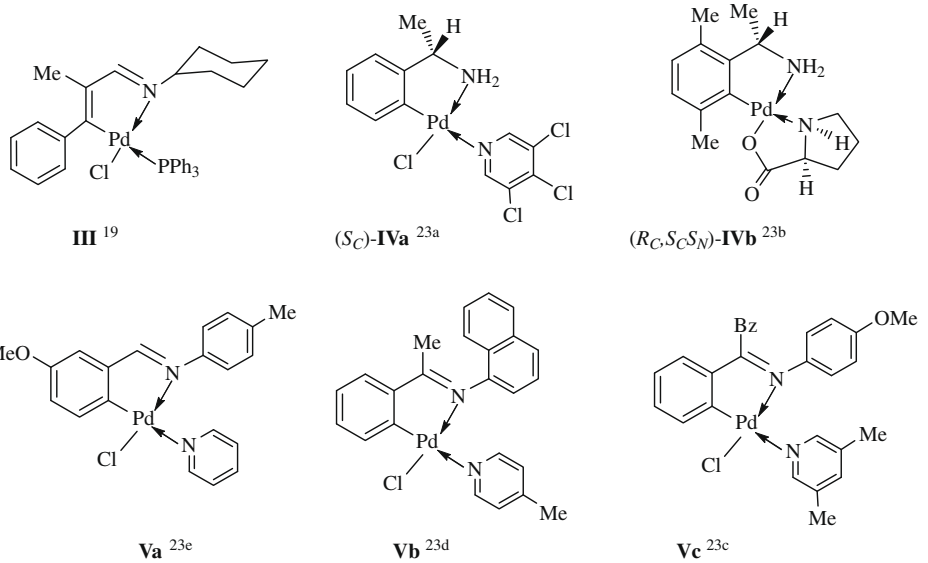
The *trans*(*P,N*)-geometry of the phosphane derivative **4** in solution is evident from the following data. (i) The high-field position of the H(2a) proton signal (δ 1.93 ppm) is indicative of the anisotropy influence of the aromatic rings of auxiliary PPh_3 ligand: in the crystal the distance between the H(2a) atom and centroid of the closest PPh-ring is significantly shorter (2.81 Å) than that found for the H(2s) atom (3.34 Å). (ii) A slight dipole–dipole interaction (0.8%) was observed between the H(2s)-proton and *ortho*-protons of the PPh_3 ligand; these data may also be considered as additional support for the methylene signal assignment. The *trans*(*P,N*)-geometry of the coordination sphere is quite typical for the phosphane derivatives of benzylidene imine palladacycles.[13c–e,g,18] The only known exception from this rule (**III**, Chart 2) was explained by steric hindrance for standard *trans*(*P,N*)-configuration.[19]

The value of the constant $^4J_{HP}$ = 7.3 Hz for the aldimine C*H*=N proton in the spectrum of the complex **4** may be used for estimation of the palladacycle conformation, taking into account that the efficiency of two nuclei coupling is dependent on the extent of coplanarity of the linking bonds.[20] For its benzaldimine analogues this parameter varies in the range of 7.8–10.0 Hz,[13c–e,g,18a–e,g] with an averaged value of 8.45 Hz and record value of 10.0 Hz reported for the palladacycle of very high planarity.[13e] The decreased value of the constant $^4J_{HP}$ in the case of the phosphane adduct **4** is indicative of some deviation of the α-H–C=N–Pd–P nuclei from planar disposition. This means that the palladacycle conformation or the metal coordination environment in the pCp-derived systems may not be so ideally planar as is typical for the benzaldimine analogues.

The rather significant difference between the chemical shifts of diastereotopic methyl groups of imine *N*-aryl substituent in the ^{1}H NMR spectrum of the adduct **4** is worth noting: δ 2.35 and 2.68 ppm for Me^1 and Me^2, respectively, while in the free imine HL both Me-groups are equivalent (δ 2.29 ppm). The low-field shift of the signal of the Me^2 group in the NMR spectrum of adduct **4** can be caused by a pronounced deshielding influence of the palladium-bonded chloride ligand in the case of the preferred nearly planar orientation of the *N*-aryl ring regarding *mcpl*. NOE data confirm this assumption: irradiation of the imine C*H*=N proton resulted in the rather intense response (2.8%) of only one of the two Me groups (Me^1) giving the signal at δ 2.35 ppm, whereas the other Me-group provided only a low response (0.7%).

2.3.2. Pyridine derivative *rac*-3

The ^{1}H NMR spectrum of the pyridine derivative *rac*-**3** consists of two sets of signals in ca. 5:1 ratio. Strong signal overlapping hampers the complete signal assignment for both isomers (see Section 4). NOE experiments (Fig. 2b) allow us to differentiate between the H(12) and H(13) proton signals of the major isomer.



III [19] (S_C)-**IVa** [23a] (R_C,S_CS_N)-**IVb** [23b]

Va [23e] **Vb** [23d] **Vc** [23c]

Chart 2.

Irradiation at the frequency of the Me^2 group of the *N*-Ar substituent results in responses of signals at δ 6.49 and 6.94 ppm (1.9% and 1.1%, respectively). Taking into account a difference between averaged distances (Me^2)H···H(12) and (Me^2)H···H(13) found for adduct **4** in the crystal (2.821 and 4.033 Å, respectively) we can assign these signals to the H(12) and H(13) protons, respectively.

The C_2-symmetry of the *N*-aryl substituent (2,6-$Me_2C_6H_3$) excludes the possibility of atropoisomerism caused by the hindered rotation about the N–C(Ar) bond, which was described for some ferrocenyl ketimine CPCs bearing a non-symmetric *N*-aryl substituent.[9d,21] Consequently, we can propose the existence of *trans*(*N,N*) and *cis*(*N,N*) isomers in solution.

This seems to be an unexpected result, since regioselective bonding of auxiliary N-donor ligands in a *trans*-position regarding the nitrogen atom of a palladacycle is typical for the *CN*-CPCs in general and for imine CPCs in particular. This trend is based on the difference between structural *trans*-influences (STI) of mild carbanionic and hard nitrogen atoms of the palladacycle.[22] Despite this general trend observed for hundreds of complexes of this kind, several exceptions to this rule were reported,[23] including examples of amine- (**IVa,b**[23a,b]) and imine-derived CPCs (**Va-c**,[23c–e] Chart 2) of *cis*(*N,N*)-configuration, mainly with pyridines as auxiliary ligands.[23a,c–e] In several cases their anomalous *cis*(*N,N*)-geometry was confirmed by X-ray diffraction studies.[23a,b,d] This configuration may be retained in solutions as the sole form,[23a] or *cis*/*trans* isomer mixtures may be detected by ^{1}H NMR data.[23c–e]

The *trans*(*N,N*) geometry of the major isomer of adduct **3** (**3a**) was deduced from the ^{1}H NMR data and NOE experiments. The high-field shift of the H(2s) proton signal (δ 1.77 ppm) compared to those of other methylene protons (δ 2.32–3.28 ppm) is indicative of the shielding effect of the pyridine ring. The dipole–dipole interaction between the H(2s) proton and α-H atoms of the pyridine ligand (0.8%, Fig. 2b) confirms their adjacent disposition. In support of the *cis*(*N,N*) configuration of the minor isomer of adduct **3** (**3b**), we can mention the high-field shift of all pyridine proton signals compared to those of the major isomer ($\Delta\delta$ −0.63 ppm for the α-protons). This effect may be explained by anisotropy influence of the neighboring *N*-aryl ring of the imine palladacycle.

Numerous manifestations of ^{1}H magnetization transfer observed in our NOE experiments are indicative of dynamic behavior of the pyridine adduct **3** in solution, which includes equilibrium between its *cis*-**3a** and *trans*-**3b** isomers, and slow (in the NMR timescale) rotation about the N–C(Ar) bond. Thus, magnetization 'leaks' from the α-proton of the pyridine ligand in major isomer **3a** to the same proton of minor isomer **3b** (−18.7%) to give further a response of the β-proton of the latter isomer (+1.4%). Irradiation of the Me^1 group of the *N*-aryl substituent of the isomer **3a** results in magnetization transfer to the other Me group of the same isomer (−11.0%) due to rotation of the N–Ar group, and to both these groups in minor isomer **3b** (−11.9% and −6.7% for Me^1 and Me^2 groups, respectively) due to *trans*→*cis* isomerization. Similar effects were observed during irradiation of the Me^2 group of the major isomer **3a**, namely magnetization transfer to Me^1 group of **3a** and both Me^1 and Me^2 groups of minor isomer **3b** (−10.4%, −6.9% and −11.4%, respectively).

2.3.3. Valinate derivative (S_{pl},R_C)-5

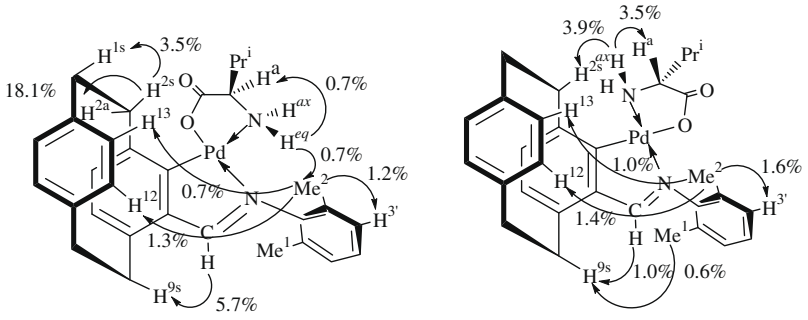
After spectroscopic studies of pyridine adduct **3**, it seems less surprising, that valinate derivative **5** also exists in solution as a mixture of *cis*(*N,N*)-**5a** and *trans*(*N,N*)-**5b** geometric isomers with predominance of the former, anomalous isomer. The ^{1}H NMR spectrum of the individual (S_{pl},R_C)-**5** diastereomer consists of two sets of signals, while four sets of signals were found in the spectrum of the diastereomeric mixture (R_{pl},R_C)-**5**/(S_{pl},R_C)-**5**. The *cis*(*N,N*)/*trans*(*N,N*) isomer ratio was equal to ca. 2:1 and was estimated from integral intensities of pairs of isolated singlets of imine C*H* protons.

Despite a strong signal overlapping in the spectrum of diastereomer (S_{pl},R_C)-**5**, we succeeded in the assignment of the most important protons using the aforementioned techniques and solvent varying (see Section 4). For example, signals of aromatic H(12) and H(13) protons were located due to difference in their responses on irradiation of Me^2 protons of *N*-aryl substituent; the signal of methylene H(9s) proton was identified leaning upon its response to irradiation of the aldimine CH═N proton (Fig. 3).

The *cis*(*N,N*)-configuration of the major isomer (S_{pl},R_C)-**5a** was confirmed by following data: (i) an irradiation at the frequency of the NH^{eq} proton results in the response of the Me^2 protons of *N*-Ar substituent (Fig. 3a); (ii) a rather marked low-field shift of the signal of the methylene H(2s) proton is indicative of the anisotropy influence of oxygen atoms of the nearby valinate carboxylate group: it was detected at δ 4.40 ppm compared to its position at the δ 3.34 ppm in the spectrum of minor *trans*(*N,N*)-isomer. The *trans*(*N,N*)-geometry of the minor isomer (S_{pl},R_C)-**5b** was deduced from (i) intensive response of the methylene H(2s) proton on the irradiation at the frequency of the NH^{ax} proton (Fig. 3b), and (ii) the increased difference between the chemical shifts of the two diastereotopic methyl groups of the *N*-aryl substituent (from $\Delta\delta$ 0.3 ppm for the major isomer **5a** to $\Delta\delta$ 0.5 ppm in the case of its minor counterpart **5b**) due to the anisotropy influence of the oxygen atoms of the valinate carboxylate group.

Spectroscopic parameters of auxiliary valinate ligand are indicative of the preferred *N,O*-chelate existence in the unusual δ(R_C)-conformation with an axial position of a ^{i}Pr group at the carbon stereocenter in both *cis*(*N,N*)- and *trans*(*N,N*)-isomers of diastereomer (S_{pl},R_C)-**5**. The following arguments may be presented in support of this conclusion.

(i) The multiplicity of the two NH proton signals, br dd and br d, is in accordance with δ(R_C) stereochemistry. From Newman



(a) *cis*(*N,N*)-(S_{pl},R_C)-**5**(**5a**) (b) *trans*(*N,N*)-(S_{pl},R_C)-**5**(**5b**)

Figure 3. NOE data for *cis*(*N,N*)- (a) and *trans*(*N,N*)- (b) isomers of valinate derivative (S_{pl},R_C)-**5b**: basis for signal assignment in the ^{1}H NMR spectra and support for their geometry.

projections along the N–C(α) bond, it is clear that only in $\delta(R_C)$-conformation of the *N,O*-chelate ring an observable spin–spin coupling with the α-CH proton can be expected for only one of the two NH protons, namely NH^{ax} (Fig. 4a), while in the case of the alternative $\lambda(R_C)$-conformation conditions for spin–spin coupling are very similar for NH^{ax} and NH^{eq} protons (Fig. 4b, cf.[24]).

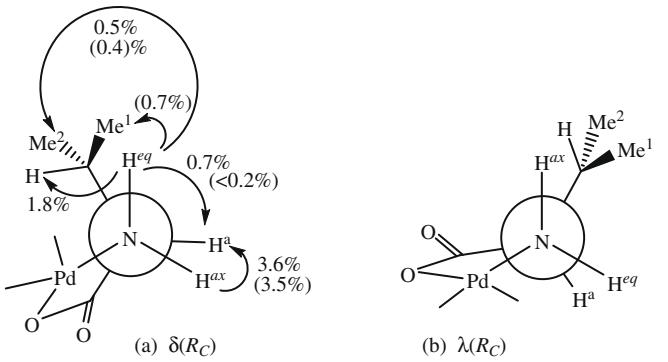


Figure 4. Newman projections of (R_C)-valinate chelate ring along the N–C(α) bond for two possible conformations, δ(R_C) (a) and λ(R_C) (b) of complex (S_{pl},R_C)-**5**; NOE data for major *cis*(*N,N*) isomer **5a** and for minor *trans*(*N,N*)-isomer **5b** are presented directly and in brackets, respectively.

(ii) NOE experiments provided evidence of the closer proximity of the α-CH to the NH^{ax} proton compared to the α-CH···NH^{eq} distance: the observed intensities of α-CH responses on the NH^{ax} and NH^{eq} irradiation are equal to 3.6% and 0.7% for major isomer **5a**, and 3.5% and <0.2% for minor form **5b** (Fig. 4a).

(iii) The difference in the dipole–dipole interaction of the two protons of NH_2 group with the protons of the *iso*-propyl substituent at the C*-stereocenter is also in agreement with the $\delta(R_C)$ conformation of the chelate ring. The responses of methine (1.8%) and methyl group protons (0.4–0.7%) were detected only upon irradiation at the frequency of the NH^{eq} proton (Fig. 4a), while any similar effects were not observed upon irradiation of the NH^{ax} proton.

Thus, we can mention two peculiarities of the structure of the valinate derivative (S_{pl},R_C)-**5**: (i) it exists as an equilibrium mixture of two geometric isomers, unusual *cis*(*N,N*) and standard *trans*(*N,N*) forms, with twofold predominance of the former, and (ii) the valinate chelate ring exists in solution in the $\delta(R_C)$ conformation with an axial disposition of the *iso*-propyl substituent at the carbon stereocenter, that is unusual for amino acidate complexes.[25]

2.4. X-ray diffraction study of the phosphane adduct *rac*-4

The *ortho*-palladated structure of dimer *rac*-**1** was unambiguously established by X-ray diffraction study of its mononuclear phosphane derivative *rac*-**4**; the *trans*(*P,N*)-geometry of the coordination sphere of the metal in the latter was also confirmed. The molecular structure of the complex **4** is presented in Figure 5; selected bond lengths and angles are given in Table 1; its structural and stereochemical peculiarities are discussed using the (S_{pl})-enantiomer as an example.

Taking into account that complex **4** is the first representative of imine *CN*-palladacycles with planar chirality of a non-metallocenic nature, it was necessary to compare its structural peculiarities with those of known achiral analogues derived from *N*-aryl benzaldimines to estimate the influence of phenylene ring replacement by a pCp-moiety. The model compounds are represented by seven dimers (**VI**–**VIII**) and two mononuclear phosphane derivatives (**IX**, Chart 3).[9,26]

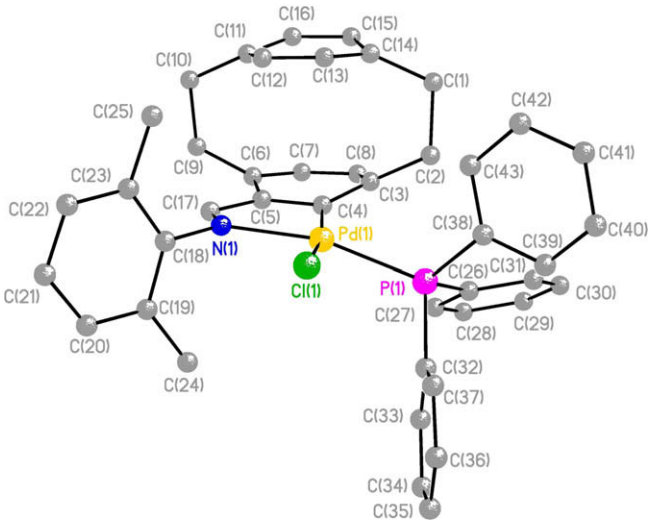


Figure 5. Molecular structure and numbering scheme for the phosphane derivative *rac*-**4**.

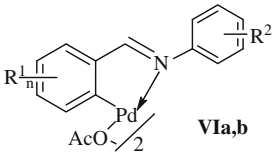
The Pd–C bond length in complex **4** (2.033 Å) is slightly increased compared to those in its achiral analogues (1.951–2.016 Å for **VI**–**IX**); the Pd–N bond length (2.097 Å) is almost the same as that found for known phosphane derivatives **IXa,b** (2.109–2.122 Å). The Pd–P bond length in complex **4** (2.270 Å) lies in the range from 2.249 to 2.305 Å, found for its analogues **IXa** and **IXb**, respectively. Its weakening in the sequence **IXa** > **4** > **IXb** may be explained by the following factors: (i) difference in steric requirements of phosphane ligands (Tolman angles θ for PPh_3 and PCy_3 are equal to 145° and 170°, respectively.[27]), (ii) increasing of steric encumbrance due to the volume of *N*-aryl substituent (Ph < 2,6-$Me_2C_6H_3$ < 2,6-$Pr^i_2C_6H_3$), and (iii) repulsion of the phosphane ligand from the pCp-moiety in adduct **4**.

The coordination environment around palladium in adduct **4** displays significant tetrahedral distortion, with the interplanar angle {$C^4Pd^1N^1$}/{P^1Pd^1Cl} equal to 16.9° essentially exceeding the range for all other achiral analogues (1.7–9.9°). According to the convention of skew lines,[28] the configuration of a *pseudo*-tetrahedron may be defined as Δ, on the basis of the negative value of the torsion angle ∠$C^4N^1Cl^1P^1$ connecting the four palladium-bonded atoms (−16.48°). From comparison of these data with related parameters for the diastereomeric 4-oxazolinyl-pCp-derived analogues (R_{pl},S_C)-**I** and (S_{pl},S_C)-**I** one may conclude that both the extent of tetrahedral distortion and its direction are dependent on both chirality elements: (i) the interplanar angle {CPdN}/{PPdCl} increases from 16(2)° for (S_{pl},S_C)-**I** up to 30.84° in (R_{pl},S_C)-**I**, and (ii) the configuration of *pseudo*-tetrahedron inverts from Δ to Λ after passing from (S_{pl},S_C)-**I** to (R_{pl},S_C)-**I** (∠CNClP −12.35 и +29.02°, respectively).

The palladacycle in complex (S_{pl})*-**4** may be described as a slightly distorted envelope with the metal in the top position

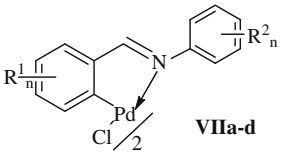
Table 1
Selected bond lengths (Å) and angles (°) for phosphane adduct *rac*-**4**

Bond	Length (Å)	Angles	Value (°)
Pd(1)–C(4)	2.033(2)	C(5)–C(4)–Pd(1)	111.62(17)
Pd(1)–N(1)	2.097(2)	C(4)–Pd(1)–N(1)	80.82(9)
Pd(1)–P(1)	2.2704(7)	C(17)–N(1)–Pd(1)	112.56(17)
Pd(1)–Cl(1)	2.3712(7)	N(1)–C(17)–C(5)	119.1(2)
N(1)–C(17)	1.285(3)	C(4)–C(5)–C(17)	115.0(2)
N(1)–C(18)	1.437(3)	C(4)–Pd(1)–P(1)	101.35(7)
P(1)–C(38)	1.819(2)	N(1)–Pd(1)–Cl(1)	92.13(6)
P(1)–C(32)	1.835(3)	P(1)–Pd(1)–Cl(1)	87.56(2)
P(1)–C(26)	1.837(3)	C(18)–N(1)–Pd(1)	127.59(16)



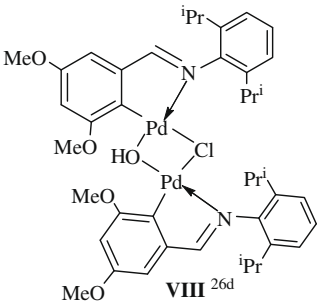
VIa,b

VIa: $R^1{}_n$ = 4-MeO, R^2 = 4′-Me;[26a]
VIb: $R^1{}_n$ = 3,4,5-$(MeO)_3$, R^2 = H;[26b]

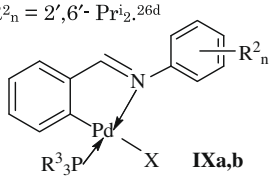


VIIa-d

VIIa: $R^1{}_n$ = H, $R^2{}_n$ = 2′,6′-Me_2;[26c]
VIIb: $R^1{}_n$ = H, $R^2{}_n$ = 2′,6′-$Pr^i{}_2$;[26d]
VIIc: $R^1{}_n$ = 4,6-$(MeO)_2$, $R^2{}_n$ = 2′,6′-$Pr^i{}_2$;[26d]
VIId: $R^1{}_n$ = 4,6-{2,6-$(MeO)_2C_6H_3$}$_2$, $R^2{}_n$ = 2′,6′- $Pr^i{}_2$.[26d]



VIII [26d]



IXa,b

IXa: $R^2{}_n$ = H, R^3 = Ph, X = CF_3COO;[9l]
IXb: $R^2{}_n$ = 2′,6′-$Pr^i{}_2$, R^3 = Cy, X = Cl.[26e]

Chart 3.

which deviates from the plane of four remaining atoms by −0.22 Å. Such palladacycle distortion has to be recognized as typical for imine *CN*-complexes since it was found for 13 of the 17 palladacycles. The high extent of palladacycle planarity is typical for imine CPCs: the average magnitude of the absolute values of intrachelate torsion angles (ϖ_{av})[16b,29] varies in the range 0.25–3.50° for dimers **VIa,b**, **VIIa,b,d**, increasing to some extent with the appearance of the MeO-substituent in the proximity of metallation site in dimers **VIIc**, **VIII** (ϖ_{av} 6.27–6.70°) or due to introduction of the bulky phosphine ligand in adducts **IXa,b** (ϖ_{av} 10.68–10.96°). In the case of complex $(S_{pl})^*$-**4**, the palladacycle puckering is only moderate (ϖ_{av} 6.19°) with a negligible extent of twisting (∠CNCC −0.93°).

It is known[30] that the phenylene rings of pCp-moiety adopt a boat-like form due to steric reasons. Their non-planarity extent may be characterized by angles between the plane of the four central atoms (forming the boat basis) and planes including the methylene-bonded *ipso*-carbon atoms. In the case of complex $(S_{pl})^*$-**4**, this parameter varies in the range of 11.89–16.56°, which is comparable with the related parameters of Bolm's complexes **I** (10.84–16.19°). In all these structures, this kind of deformation is more pronounced for the palladated phenylene ring, possessing additional puckering: the boat base is twisted according to the torsion angles equal to −3.01, −3.08, and +6.52° for complexes $(S_{pl})^*$-**4**, (S_{pl},S_C)-**I**, and (R_{pl},S_C)-**I**, respectively. The signs of these angles are indicative of the dependence of this twist direction from the configuration of the chiral plane: for complexes $(S_{pl})^*$-**4** and (S_{pl},S_C)-**I** this angle is negative, while for (R_{pl},S_C)-**I** diastereomer, it is positive. To confirm the validity of such a correlation, we should note that the same dependence was found in a series of organic 4-X-5-Y-disubstituted derivatives of [2.2]paracyclophane, which exhibited a marked twist of the tetrasubstituted phenylene ring ($\angle C^8C^7C^5C^4$ >2.0°): in eleven compounds with an (S_{pl})-configuration, the torsion angle is negative, while it is positive in the case of 18 compounds with an (R_{pl})-configuration (CCDC data). Thus, the twist of the tetrasubstituted phenylene ring cannot be considered as a fortuitous phenomenon.

The rotameric state of the PPh_3 ligand in the phosphane adduct $(S_{pl})^*$-**4** was estimated using a known approach.[31] The average value (ω_{av}) of torsion angles, ω_A, ω_B, and ω_C (characterizing disposition of three PPh-groups), is equal to 130.54° that is an indication of the ***M*** configuration of the PPh_3 propeller. The PPh_3 propeller has the same ***M*** configuration in diastereomer (S_{pl},S_C)-**I** (ω_{av} 130.62°), but the opposite ***P*** configuration in diastereomer (R_{pl},S_C)-**I** (ω_{av} 48.83°). It allows to suggest that the rotameric state of the PPh_3 propeller in the crystal is governed by the configuration of the chiral plane.

3. Conclusion

In conclusion, we have prepared the first planar chiral imine *CN*-palladacycle based on the [2.2]paracyclophane backbone and free of redox activity. Three versions of a direct cyclopalladation of a pCp-derived imine were developed, including a solid-phase reaction, to afford the racemic dimer **1** in the yields up to 85%, despite decreased sp^2-character of the aromatic C–H bond to be activated. The *ortho*-palladated structure of dimer **1** was confirmed by spectroscopic (^1H and ^{31}P NMR) studies of its mononuclear derivatives **3**–**5** and the X-ray diffraction study of the phosphane adduct **4**. Resolution of the racemic dimer **1** was performed by diastereoselective decoordination of the (R_C)-valinate auxiliary ligand from the corresponding adduct **5** under the conditions of column chromatography on silica gel. Both (S_{pl},S_{pl})- and (R_{pl},R_{pl})-enantiomers of dimer **1** were isolated in a stereochemically pure state in moderate yields. The enhanced efficiency of this new methodology compared to the previously reported system[15] based on the use of (S_C)-prolinate ligand may be attributed to a more efficient interaction with SiO_2 of the primary amino groups of the chelated (R_C)-valinate compared to the secondary ones of the (S_C)-prolinate ligand. The absolute configuration of this new *CN*-palladacycle was established by independent synthesis of the (R_{pl},R_{pl})-enantiomer of dimer **1** starting from the (S_{pl})-4-formyl[2.2]paracyclophane resolved by the standard method.

With regard to the reactivity of the new imine *CN*-palladacycle, we have disclosed a disadvantageous peculiarity: it appears to be unable to regioselectively bond mono- and bidentate auxiliary ligands bearing a rather hard O- and/or N-donor atom. The corresponding mononuclear derivatives exist as mixtures of geometric *trans*(*N*,*N*)- and *cis*(*N*,*N*)-isomers. However, coordination of P-donor ligands occurs with complete regioselectivity in the *trans*(*P*,*N*)-configuration. This circumstance imposes certain restrictions on the new *CN*-palladacycle application for chiral recognition.

These new imine *CN*-CPCs may be considered as compound of pure planar chirality only from a formal point of view. Detailed analysis of structural parameters of phosphane adduct (S_{pl})*-**4** has shown, that it acquires at least two additional chirality elements: a *pseudo*-tetrahedral **Δ**-configurated metal environment, and a twisted metallated phenylene ring of the pCp-framework.

4. Experimental

4.1. General

The ^{1}H and ^{31}P NMR spectra were recorded with a Bruker Avance-400 spectrometers operating at the frequencies 400 and 161.9 MHz for ^{1}H 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 on the δ-scale in parts per million relative to TMS as internal standard for protons and relative to H_3PO_4 as an external reference for the ^{31}P nuclei. The assignment of signals was based on the homo- and heteronuclear decoupling—^{1}H{^{1}H} and ^{1}H{^{31}P} COSY, and NOE experiments. Optical rotations were measured with a VNIEKI-Prodmush AI-EPO polarimeters in a 0.25 dm cell at 22 °C. The melting points were measured with a Electrothermal IA 9000 series device in a sealed capillary. All reactions were conducted under an argon atmosphere using TLC control on Silufol UV-254. The purification of the compounds was performed by means of short dry column[32] or flash-chromatography on Silica Gel 60 (from Fluka) (unless otherwise indicated). Enantiomeric analysis of (S_{pl})-4-formyl[2.2]paracyclophane was performed by HPLC (Varian 5000 LC) on Chiracel OD (250 × 4.6 mm) with hexane/isopropanol 9/1 as eluent, flow rate 1 mL/min, temperature 20 °C, detector UV 254 nm, the retention times were 11.8 (*S*) and 15.8 min (*R*), respectively.

4.2. Solvents and starting reagents

Toluene was dried over $CaCl_2$, refluxed over Na, and then distilled from Na; dichloromethane and chloroform were passed through a short Al_2O_3 column and distilled over P_2O_5; chloroform-d_1 was distilled from CaH_2; hexane and petroleum ether were distilled from Na; methanol and pyridine were distilled from MeONa and Na, respectively. Acetone of high purity (from Reachim) was used without additional purification. Glacial acetic acid was prepared by twofold low-temperature recrystallization. (*R*)-Valine and $Pd(OAc)_2$ (from Aldrich), and Et_2SnCl_2 (from Alfa Aesar), were used as received. Triphenylphosphine was purified by twofold recrystallization from a benzene/hexane mixture and acetone; 2,6-dimethylaniline (from Aldrich) was distilled in vacuo just before use (bp 102–104°/20 mmHg). (R_C)-α-Methylbenzylamine of 97% ee was purchased from Merck and used without purification. Racemic 4-formyl[2.2]paracyclophane was prepared by reported method[33] and purified using column chromatography on silica (*h* 23 cm, *d* 2.7 cm; eluents toluene/hexane 5:1 mixture); R_f 0.5 ($CHCl_3$). The (S_{pl})-enantiomer of the 4-formyl[2.2]paracyclophane was obtained by resolution of the racemic aldehyde via its diastereomeric imine derivatives with (R_C)-α-phenylethylamine:[17] $[\alpha]_D^{25} = -173$ (*c* 0.42, $CHCl_3$), 96.3% ee. Racemic *N*-(2,6-dimethylphenyl)-[2.2]paracyclophane-4-carbaldimine (**HL**) and its (S_{pl})-enantiomer were prepared by a reported method;[12] for (S_{pl})-**HL** $[\alpha]_D^{22} = +443$ (*c* 0.492, CH_2Cl_2).

4.3. Cyclopalladation of the imine HL

4.3.1. Racemic di-μ-chlorobis{4-(*N*-2,6-dimethylphenyl) iminomethyl[2.2]paracyclophan-5-yl-*C,N*}dipalladium(II), *rac*-1

Method 1. A suspension of the racemic imine **HL** (0.0580 g, 0.1709 mmol) and $Pd(OAc)_2$ (0.0384 g, 0.171 mmol) in glacial acetic acid (4 mL) was heated at 60 °C for 8 h. The reaction mixture was evaporated in vacuo to dryness, the solution of the residue in dichloromethane (10 mL) was treated with a solution of LiCl (0.0149 g, 0.351 mmol) in acetone (5 mL). After stirring at rt for 2 h the solvent was removed, the residue treated with water (15 mL), and the dimer formed was extracted with dichloromethane (3 × 5 mL). The combined organic solutions were dried over $MgSO_4$, evaporated in vacuo to dryness, and the crude product was purified using flash column chromatography on silica (*h* 14 cm, *d* 1.9 cm) with toluene and toluene/acetone 10:1 mixture as eluents. After precipitation from dichloromethane by hexane and drying in vacuo, dimer *rac*-**1** was obtained in the yield of 41% (0.0335 g, 0.0350 mmol) as a yellow amorphous powder: mp (dec) 240–245 °C, R_f 0.66 (10:1 toluene/acetone). Anal. Calcd for $C_{50}H_{48}Cl_2N_2Pd_2$: C, 62.51; H, 5.04; N, 2.92. Found: C, 62.25; H, 4.81; N, 3.18.

Method 2. A suspension of the imine **HL** (0.0580 g, 0.1709 mmol) and $Pd(OAc)_2$ (0.0384 g, 0.171 mmol) in toluene (10 mL) was heated at 60 °C for 7 h. The reaction mixture was evaporated in vacuo to dryness, the residue was treated with the solution of LiCl (0.0149 g, 0.351 mmol) in acetone (5 mL). After stirring at rt for 1 h the solvent was removed, the residue was treated with water (15 mL), and after additional stirring for 0.5 h the precipitate formed was filtered, washed with water, and dried in vacuo over $CaCl_2$ to afford chromatographically pure (TLC data) dimer *rac*-**1** in the yield of 85% (0.0697 g, 0.0726 mmol) as yellow amorphous powder: R_f 0.66 (10:1 toluene/acetone).

Method 3. Racemic chloro{4-(*N*-2,6-dimethylphenyl)iminomethyl[2.2]paracyclophan-5-yl-*C,N*}(triphenylphosphine-*P*)palladium(II), *rac*-**4**. A solution of the imine **HL** (0.0500 g, 0.1473 mmol) in the minimum volume of dichloromethane (1 mL) was mixed with SiO_2 (0.0552 g), evaporated to dryness, and heated at 85 °C for 14 h. The dimer *rac*-**2** formed was eluted from silica by a solution of pyridine (0.0835 g) in dichloromethane (20 mL) as its pyridine adduct, which was then treated with a solution of LiCl (0.0125 MΓ, 0.295 mmol) in acetone (5 mL) and stirred at rt for 1 h. After addition of PPh_3 (0.0425 g, 0.162 mmol) to the pyridine derivative **2** formed and stirring at rt for 0.5 h, the reaction mixture was evaporated. The residue was dissolved in dichloromethane, filtered from admixtures, and recrystallized from chloroform/hexane to afford phosphane adduct *rac*-**4** in a yield of 70% (0.0762 g, 0.1026 mmol): mp (dec) 228–229 °C, R_f 0.68 (3:1 toluene/acetone). ^{1}H and ^{31}P NMR data are identical to those presented below (see Section 4.4.1).

4.3.2. Enantiopure dimer (R_{pl},R_{pl})-di-μ-chlorobis{4-(*N*-2,6-dimethylphenyl)iminomethyl[2.2]paracyclophan-5-yl-*C,N*}dipalladium(II), (R_{pl},R_{pl})-1 (independent synthesis)

A suspension of the imine (S_{pl})-**HL** (0.1012 g, 0.2981 mmol) and $Pd(OAc)_2$ (0.0669 g, 0.2981 mmol) in toluene (15 mL) was heated at 60 °C for 7 h. The reaction mixture was evaporated in vacuo to dryness, the residue was treated with a solution of LiCl (0.0255 g, 0.6015 mmol) in acetone (10 mL), and stirred at rt for 1 h. Then the solvent was removed, the residue was treated with water (20 mL), stirred for 0.5 h, and the precipitate formed was filtered, washed with water, and dried in vacuo over $CaCl_2$. After the additional chromatographic purification on dry column (Silica gel, *h* 7 cm, *d* 4.5 cm; eluents are toluene/hexane mixtures of increasing polarity, in ratios from 1:5 to 10:1) and precipitation from toluene by petroleum ether dimer (R_{pl},R_{pl})-**1** was obtained in a yield of 72% (0.1029 g, 0.1071 mmol) as a yellow amorphous powder: mp (dec) 284–285 °C, R_f 0.66 (10:1 toluene/acetone), $[\alpha]_D^{24} = +559$ (*c* 0.247, CH_2Cl_2). Anal. Calcd for $C_{50}H_{48}Cl_2N_2Pd_2$: C, 62.51; H, 5.04; N, 2.92; Found: C, 62.61; H, 4.88; N, 2.83.

4.4. Synthesis of mononuclear derivatives of dimer *rac*-1

4.4.1. Racemic chloro{*N*-4-(2,6-dimethylphenyl)iminomethyl [2.2]paracyclophan-5-yl-*C,N*}(triphenylphosphine-*P*) palladium(II), *rac*-4

A slight excess of PPh_3 (0.0787 g, 0.0301 mmol) was added to a suspension of racemic dimer **1** (0.0130 g, 0.0135 mmol) in toluene (5 mL). The homogeneous reaction mixture was stirred at rt for 0.5 h, concentrated in vacuo to a minimum volume, and target complex was precipitated by hexane to afford after drying in vacuo over $CaCl_2$ adduct *rac*-**4** in a yield of 76% (0.0152 g, 0.0205 mmol) as a yellow amorphous powder: mp (dec) 228–229 °C, R_f 0.68 (3:1 toluene/acetone). Monocrystals of this complex were obtained by slow evaporation of its solution in chloroform. Anal. Calcd for $C_{43}H_{39}ClNPPd$: C, 69.55; H, 5.29; N, 1.89. Found: C, 69.68; H, 5.27; N, 1.94.

^{31}P NMR ($CDCl_3$): δ 30.31 ppm (s). ^1H NMR ($CDCl_3$): aromatic protons of the [2.2]paracyclophane moiety: δ 5.72 (br dd, 1H, $^3J_{HH}$ 7.6, $^5J_{HP}$ 0.8, H^8), 6.03 (d, 1H, $^3J_{HH}$ 7.6, H^7), 6.46 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{15}), 6.49 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{12}), 6.58 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{16}), 6.78 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{13}); methylene protons of [2.2]paracyclophane moiety: δ 1.93 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.4, $^3J_{HH}$ 3.9, H^{2a}), 2.76 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.4, $^3J_{HH}$ 4.3, H^{1a}), 2.79 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.5, $^3J_{HH}$ 4.3, H^{2s}), 2.92 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.4, $^3J_{HH}$ 4.9, H^{10s}), 2.95 (ddd, 1H, $^2J_{HH}$ 13.7, $^3J_{HH}$ 10.9, $^3J_{HH}$ 4.9, H^{9a}), 3.09 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.9, $^3J_{HH}$ 3.1, H^{10a}), 3.08 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.5, $^3J_{HH}$ 3.9, H^{1s}), 3.27 (ddd, 1H, $^2J_{HH}$ 13.7, $^3J_{HH}$ 10.4, $^3J_{HH}$ 3.1, H^{9s}); side chain protons: δ 2.35 (s, 3H, Me), 2.68 (s, 3H, Me), 7.12–7.15 (m, 3H, C_6H_3), 8.19 (d, 1H, $^4J_{HP}$ 7.3, C*H*=N); PPh_3 protons: δ 7.26–7.28 (m, 6H, *meta*-H), 7.35–7.38 (m, 3H, *para*-H), 7.61 (ddd, 6H, $^4J_{HH}$ 1.3, $^3J_{HH}$ 7.5, $^3J_{HP}$ 11.0, *ortho*-H).

4.4.2. Racemic chloro{4-(*N*-2,6-dimethylphenyl) iminomethyl[2.2]-paracyclophan-5-yl-*C,N*}(pyridine-*N*)palladium(II), *rac*-3

A suspension of dimer *rac*-**1** (0.600 g, 0.0625 mmol) in chloroform (5 mL) was treated with a slight excess of pyridine (0.0110 g, 0.1395 mmol; 1.2 mL of 0.1163 M solution). The homogeneous reaction mixture was stirred at rt for 20 min, and evaporated to dryness. The residue was dissolved in minimum volume of toluene and the target complex was precipitated by hexane containing trace quantity of pyridine (1 drop per 3 mL). The precipitate formed was filtered, washed with hexane, dried in vacuo over $CaCl_2$ to afford adduct *rac*-**3** as a yellow amorphous powder in a yield of 78% (0.0548 g, 0.0980 mmol): mp (dec) 174–175 °C, R_f 0.4 (1:1 toluene/acetone).[†] Anal. Calcd for $C_{30}H_{29}ClN_2Pd$: C, 64.41; H, 5.22; N, 5.01. Found: C, 64.54; H, 5.32; N, 4.92.

^1H NMR ($CDCl_3$; two sets of signals in 5:1 ratio). For major *trans*(*N,N*)-isomer **3a**: aromatic protons of the [2.2]paracyclophane moiety: δ 6.21 (d, 1H, $^3J_{HH}$ 7.8, $H^{7/8}$), 6.22 (d, 1H, $^3J_{HH}$ 7.8, $H^{8/7}$), 6.49 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{12}), 6.57 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{15}), 6.64 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{16}), 6.94 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, H^{13}); methylene protons of [2.2]paracyclophane moiety: δ 1.77 (ddd, 1H, $^2J_{HH}$ 13.8, $^3J_{HH}$ 9.4, $^3J_{HH}$ 4.4, H^{2s}), 2.32 (ddd, 1H, $^2J_{HH}$ 13.8, $^3J_{HH}$ 9.5, $^3J_{HH}$ 5.3, H^{2a}), 2.85 (ddd, 1H, $^2J_{HH}$ 13.3, $^3J_{HH}$ 9.5, $^3J_{HH}$ 4.4, H^{1a}), 3.03 (m, 1H, H^{1s}), 3.28, 3.15, 3.06, 2.99 (group of m, each 1H, H^{9s}, H^{9a}, H^{10s}, H^{10a}); side chain protons: δ 2.39 (s, 3H, Me), 2.78 (s, 3H, Me), 7.13 (m, 1H, $H^{4'}$ of C_6H_3), 7.18 (m, 2H, $H^{3'}$, $H^{5'}$ of C_6H_3), 7.94 (s, 1H, C*H*=N); pyridine protons: 7.34 (m, 2H, β-H), 7.82 (m, 1H, γ-H), 8.91 (m, 2H, α-H). For minor *cis*(*N,N*)-isomer **3b**: aromatic protons of [2.2]paracyclophane moiety: δ 6.20 (d, 1H, $^3J_{HH}$ 7.8, $H^{7/8}$), 6.30 (d, 1H, $^3J_{HH}$ 7.8, $H^{8/7}$); other palladacycle protons: 7.97 (s, 1H, C*H*=N), 2.26 (s, 3H, Me), 2.64 (s, 3H, Me); pyridine protons: 7.00 (m, 2H, β-H), 7.48 (m, 1H, γ-H), 8.28 (m, 2H, α-H); signals of remaining protons are hidden under those of the major isomer.

4.5. Racemic dimer 1 resolution

4.5.1. Chiral derivatization: ($R_{pl}R_C/S_{pl}R_C$)-{4-(*N*-2,6-dimethylphenyl) iminomethyl[2.2]paracyclophan-5-yl-*C,N*}(valinato-*N,O*)-palladium(II), 5

A suspension of dimer *rac*-**1** (0.0903 g, 0.094 mmol) in methanol (10 mL) was consecutively treated with (*R*)-valine (0.0221 g, 0.188 mmol) and sodium bicarbonate (0.0158 g, 0.188 mmol). The reaction mixture was stirred at rt for 4 h, evaporated in vacuo; the residue was dissolved in dichloromethane, filtered from inorganic admixtures, and evaporated to give a mixture of diastereomeric complexes **5** as a yellow amorphous powder, and used without further additional purification: R_f 0.44 (20:1 CH_2Cl_2/MeOH).[‡]

4.5.2. Diastereoselective (*R*)-valinate decoordination from complex ($R_{pl}R_C/S_{pl}R_C$)-5

The equimolar mixture of two diastereomers, ($R_{pl}R_C$)-**5** and ($S_{pl}R_C$)-**5** (105.50 g, 0.1880 mmol), was eluted through a *flash*-column (Silpearl, *h* 19 cm, *d* 2.5 cm; eluents are mixtures of dichloromethane and methanol of increasing polarity, in ratios from 100:1, via 80:1, 50:1, 30:1, and 20:1 to 10:1). The following complexes were isolated: dimer ($R_{pl}R_{pl}$)-**1** and (*R*)-valinate derivative ($S_{pl}R_C$)-**5**.

For dimer ($R_{pl}R_{pl}$)-**1**: a yield of 40% (0.0179 g, 0.0186 mmol) was obtained after precipitation from dichloromethane by petroleum ether; mp (dec) 280–283 °C, R_f 0.66 (10:1 toluene/acetone), $[\alpha]_D^{22} = +551$ (*c* 0.247, CH_2Cl_2). Anal. Calcd for $C_{50}H_{48}Cl_2N_2Pd_2$: C, 62.51; H, 5.04; N, 2.92. Found: C, 62.56; H, 5.18; N, 2.82. ^1H NMR ($CDCl_3$, series of broad signals): δ 7.78 (s, 1H, C*H*=N), 7.17 (m, 2H, *meta*-NC_6H_3), 7.03 (m, 1H, *para*-NC_6H_3), 7.03 (br s, 1H, pCp), 6.60 (m, 2H, pCp), 6.49 (m, 1H, pCp), 6.14 (m, 2H, pCp), 3.76 (m, 1H, CH_2 from pCp), 3.30 (m, 1H, CH_2 from pCp), 2.98–3.17 (m, 4H, CH_2 from pCp), 2.52 (m, 2H, CH_2 from pCp), 2.21 (s, 3H, MeC_6H_3), 2.85 (s, 3H, MeC_6H_3).

For (*R*)-valinate derivative ($S_{pl}R_C$)-**5**: a yield of 68% (0.0356 g, 0.0635 mmol), a yellow crystalline solid after recrystallization from dichloromethane/hexane; mp (dec) 238–242 °C, R_f 0.57 (10:1 CH_2Cl_2/MeOH); $[\alpha]_D^{24} = -589$ (*c* 0.367, CH_2Cl_2). Anal. Calcd for $C_{30}H_{34}N_2O_2Pd$: C, 64.23; H, 6.11; N, 4.99. Found: C, 64.01; H, 6.26; N, 4.88.

^1H NMR ($CDCl_3$, two sets of signals in 2:1 ratio). For major *cis*(*N,N*)-isomer **5a**: aromatic protons of the [2.2]paracyclophane moiety: δ 6.24 (d, 1H, $^3J_{HH}$ 7.8, H^7), 6.30 (d, 1H, $^3J_{HH}$ 7.8, H^8), 6.50 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{12}), 6.59 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{16}), 6.62 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{15}), 7.03 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{13}); methylene protons of the [2.2]paracyclophane moiety: δ 2.78 (m, 1H, H^{2a}), 3.15 (m, 1H, H^{1s}), 3.23 (m, 1H, H^{9s}), 2.95-3.45 (group of m, 4H, H^{1a}, H^{9a}, H^{10s}, H^{10a}), 4.37 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 9.2, $^3J_{HH}$ 2.8, H^{2s}); side chain protons: δ 2.27 (s, 3H, Me^1), 2.75 (s, 3H, Me^2), 7.15 (br d, 1H, $^3J_{HH}$ 7.4, $H^{3'}$ of C_6H_3), 7.19 (t, 1H, $^3J_{HH}$ 7.4, $H^{4'}$ of C_6H_3), 7.25 (br d, 1H, $^3J_{HH}$ 7.4, $H^{5'}$ of C_6H_3), 7.89 (s, 1H, C*H*=N); for Val^- ligand: 0.99 (br d, 1H, $^2J_{HH}$ 10.6, NH^{eq}), 1.06 (d, 3H, $^3J_{HH}$ 6.9, Me^1), 1.18 (d, 3H, $^3J_{HH}$ 6.9, Me^2), 2.19 (br dd, 1H, $^2J_{HH}$ 10.6, $^3J_{HH}$ 6.7, NH^{ax}), 2.46 (m, 1H, C*H*Me_2), 3.18 (m, 1H, α-CH).

For minor *trans*(*N,N*)-isomer **5b**: aromatic protons of the [2.2]paracyclophane moiety: δ 6.21 (d, 1H, $^3J_{HH}$ 7.8, $H^{7/8}$), 6.24 (d,

[†] Partial decomposition of the pyridine adduct on silica was observed resulting in the formation of dimer **1** (R_f >0.99).

[‡] Partial decomposition of the valinate derivatives on silica results in the formation of dimer **1** (R_f >0.99).

1H, $^3J_{HH}$ 7.8, $H^{8/7}$), 6.39 (br d, 1H, $^3J_{HH}$ 7.8, H^{12}), 6.64 (m, 2H, H^{15}, H^{16}), 6.90 (br d, 1H, $^3J_{HH}$ 7.8, H^{13}); methylene protons of the [2.2]paracyclophane moiety: δ 2.59 (m, 1H, H^{2s}), 2.85 (m, 1H), 3.10 (m, 1H, H^{9s}), 3.34 (m, 1H), 3.00–3.20 (group of m, 4H); side chain protons: δ 2.23 (s, 3H, Me^1), 2.54 (s, 3H, Me^2), 7.04 (m, 1H, $H^{3'}$ of C_6H_3), 7.06 (m, 1H, $H^{5'}$ of C_6H_3), 7.10 (t, 1H, $^3J_{HH}$ 7.4, $H^{4'}$ of C_6H_3), 7.88 (s, 1H, C*H*=N); for Val^- ligand: 1.04 (d, 3H, $^3J_{HH}$ 6.9, Me^1), 1.07 (d, 3H, $^3J_{HH}$ 6.9, Me^2), 2.34 (m, 1H, C*H*Me_2), 2.84 (br d, 1H, $^2J_{HH}$ 10.6, NH^{eq}), 3.43 (m, 1H, α-CH), 4.31 (br dd, 1H, $^2J_{HH}$ 10.6, $^3J_{HH}$ 0.6, NH^{ax}).

^{1}H NMR ($CDCl_3$ + C_6D_6, two sets of signals in 2:1 ratio). For major *cis*(*N,N*)-isomer **5a**: aromatic protons of the [2.2]paracyclophane moiety: δ 5.98 (d, 1H, $^3J_{HH}$ 7.8, $H^{7/8}$), 6.06 (d, 1H, $^3J_{HH}$ 7.8, $H^{8/7}$), 6.30 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{12}), 6.36 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, $H^{16/15}$), 6.39 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, $H^{15/16}$), 6.88 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{13}); methylene protons of the [2.2]paracyclophane moiety: δ 2.55–2.63 (m, 2H), 2.77–2.90 (m, 3H), 2.97–3.01 (m, 2H), 4.39 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 9.2, $^3J_{HH}$ 2.8, H^{2s}); side chain protons: δ 2.02 (s, 3H, Me^1), 2.09 (s, 3H, Me^2), 6.81–7.00 (m, 3H, C_6H_3), 7.48 (s, 1H, C*H*=N); for Val^- ligand: 0.61 (br d, 1H, $^2J_{HH}$ 10.6, NH^{eq}), 0.86 (d, 3H, $^3J_{HH}$ 6.9, Me^1), 0.96 (d, 3H, $^3J_{HH}$ 6.9, Me^2), 1.95 (br dd, 1H, $^2J_{HH}$ 10.6, $^3J_{HH}$ 6.7, NH^{ax}), 2.22 (m, 1H, C*H*Me_2), 2.89 (m, 1H, α-CH).

For minor *trans*(*N,N*)-isomer **5b**: aromatic protons of the [2.2]paracyclophane moiety: δ 5.94 (d, 1H, $^3J_{HH}$ 7.8, $H^{7/8}$), 6.00 (d, 1H, $^3J_{HH}$ 7.8, $H^{8/7}$), 6.17 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{12}), 6.40 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, $H^{16/15}$), 6.44 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, $H^{15/16}$), 6.77 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8, H^{13}); methylene protons of the [2.2]paracyclophane moiety: δ 2.59 (m, 1H, H^{2s}), 2.65–2.96 (group of m, 5H), 3.15 (m, 1H, H^{9s}), 3.23 (m, 1H); side chain protons: δ 2.03 (s, 3H, Me^1), 2.31 (s, 3H, Me^2), 6.85–6.98 (m, 3H, C_6H_3), 7.55 (s, 1H, C*H*=N); for Val^- ligand: 0.82 (d, 3H, $^3J_{HH}$ 6.9, Me^1), 0.86 (d, 3H, $^3J_{HH}$ 6.9, Me^2), 2.07 (m, 1H, C*H*Me_2), 2.46 (br d, 1H, $^2J_{HH}$ 10.6, NH^{eq}), 3.14 (m, 1H, α-CH), 4.09 (br m, 1H, NH^{ax}).

4.5.3. Isolation of enantiopure dimeric complex (S_{pl},S_{pl})-di-μ-chlorobis{4-(*N*-2,6-dimethylphenyl)iminomethyl[2.2]paracyclophan-5-yl-*C*,*N*}-dipalladium(II), (S_{pl},S_{pl})-1

A solution of diastereomerically pure (*R*)-valinate derivative (S_{pl},R_C)-**5** (0.0118 g, 0.021 mmol) in dichloromethane (8 mL) was treated with diluted 0.5 M aqueous solution of HCl (2 × 5 mL) with vigorous shaking under TLC control. The combined organic layers were washed with water (3 × 5 mL), dried over Na_2SO_4, concentrated to dryness, and precipitated from dichloromethane by hexane to give dimer (S_{pl},S_{pl})-**1** in ca. 100% yield (0.0101 g, 0.0105 mmol): mp (dec) 253–256 °C, R_f 0.66 (10:1 toluene/acetone), $[\alpha]_D^{22} = -548.6$ (*c* 0.253, CH_2Cl_2). Anal. Calcd for $C_{50}H_{48}Cl_2N_2Pd_2$: C, 62.51; H, 5.04; N, 2.92. Found: C, 62.80; H, 5.10; N, 2.86.

4.5.4. X-ray diffraction study of phosphane adduct *rac*-4

Crystals of the complex **4** ($C_{43}H_{39}ClNPPd$, FW = 742.57) are orthorhombic, space group *Pbca* at 100 K; a = 15.2614(5), b = 19.1961(6), c = 23.2667(8) Å, V = 6816.2(4) Å^3, Z = 8 (Z' = 1), d_{calcd} = 1.447 g cm^{-3}, μ(Mo Kα) = 7.03 cm^{-1}. Intensities of 45,244 reflections were measured with SMART APEX II CCD (λ(Mo Kα) = 0.71072 Å, 2θ <58° and 9057 independent reflections (R_{int} = 0.0651) were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The positions of the hydrogen atom were calculated from geometrical point of view. The refinement converged to wR_2 = 0.0904 and GOF = 1.022 for all independent reflections (R_1 = 0.0355 was calculated against F for 5914 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.10.[34]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary no. CCDC 688360. Copies of the data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ UK; fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk).

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