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A planar chiral non-metallocenic analogue of the most popular *N*,*N*-dimethylbenzylaminate palladacycle

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ABSTRACT

A racemic planar chiral tertiary amine pCp-CH_2NMe_2 (**HL^1**, pCp = [2.2]paracyclophane-4-yl) was prepared by aminomethylation of the bromide pCp-Br with Eschenmoser's salt. Direct cyclopalladation of this new ligand with palladium(II) acetate results in the formation of the racemic *CN*-dimer *rac*-**3** in a moderate yield of 64%. The enantiomerically pure dimer (S_{pl}, S_{pl})-**3** was obtained by the standard procedure of racemic palladacycle resolution using (S_C)-prolinate as a chiral derivatising agent. The *ortho*-palladated structure, absolute configuration of the chiral plane and stereochemical peculiarities of the new *CN*-palladacycle were established by means of NMR spectroscopy and an X-ray diffraction study of its (S_C)-prolinate derivative.

1. Introduction

Excellent efficiency of planar chiral coordination complexes in general [1] and cyclopalladated compounds (CPCs) in particular [2] in diverse processes of chiral recognition is widely recognised. However these promising stereoselectors are mainly derived from ligands with a *metallocenic* framework, possessing undesirable redox-activity. This drawback has stimulated the development of routes to enantiopure planar chiral CPCs of a *non-metallocenic* nature, for example those based on [2.2]paracyclophane (pCp) derived ligands. Until recently, the number of such structures remained to be restricted to several examples of *CN*- and *CP*-palladacycles bearing oxazoline (**I**, **II** [3]), imine (**III** [4]) or phosphinite (**IV** [5]) donor groups (Fig. 1), including palladacycles of only planar chirality (**III**, **IV**) and structures containing elements of planar and central chirality (**I**, **II**).

In this work we report the preparation of an enantiopure *CN*-palladacycle (**1**) with a donor tertiary amino group and a [2.2]paracyclophane framework, which is a planar chiral analogue of the most popular *N*,*N*-dimethylbenzylaminate *CN*-palladacycle.

2. Results and discussion

Taking into account that the boat-like deformation of phenylene rings, typical for sterically compressed pCp-derivatives [6], reduces their aromaticity, we might expect that (sp^2)C–H bond activation may present difficulties. Because of this, we have decided to introduce optical activity at the last stages of the overall process using the strategy of racemic palladacycle resolution.

The starting racemic *N*,*N*-dimethyl([2.2]paracyclophane-4-ylmethyl)amine (*rac*-**HL^1**) was prepared in moderate yield by aminomethylation [7] of the known bromide 4-Br-pCp (*rac*-**2**) [8] using dimethyl(methylene)ammonium iodide (Eschenmoser's salt [9]) as a reagent (Scheme 1).

In spite of a rather wide collection of chiral pCp derived ligands being published [1f,g,j,10], including α-branched 1-([2.2]paracyclophan-4-yl)alkylamines [11] with planar and central chirality, the racemic tertiary amine **HL^1** has not been reported until now.

2.1. Cyclopalladation of the amine *HL^1*

All our experiments on the cyclopalladation of the tertiary amine *rac*-**HL^1** illustrated the reduced ability of the phenylene ring (sp^2)C–H bonds to be activated, which is in drastic contrast with the behaviour of its achiral analogue *N*,*N*-dimethylbenzylamine (**HL^2**). Thus, our initial attempts to use Li_2PdCl_4 as a palladation agent for the amine *rac*-**HL^1** in the presence of sodium acetate as a base failed completely; the target dimer [{Pd(η^2-L^1)(μ-Cl)}$_2$] (*rac*-**3**) was formed only in traces (*Method 1*). To compare, the *ortho*-palladation of the achiral analogue **HL^2** with the same reagent and under milder conditions affords the required dimer [{Pd(η^2-L^2)(μ-Cl)}$_2$] in nearly quantitative yield (95%) [12].

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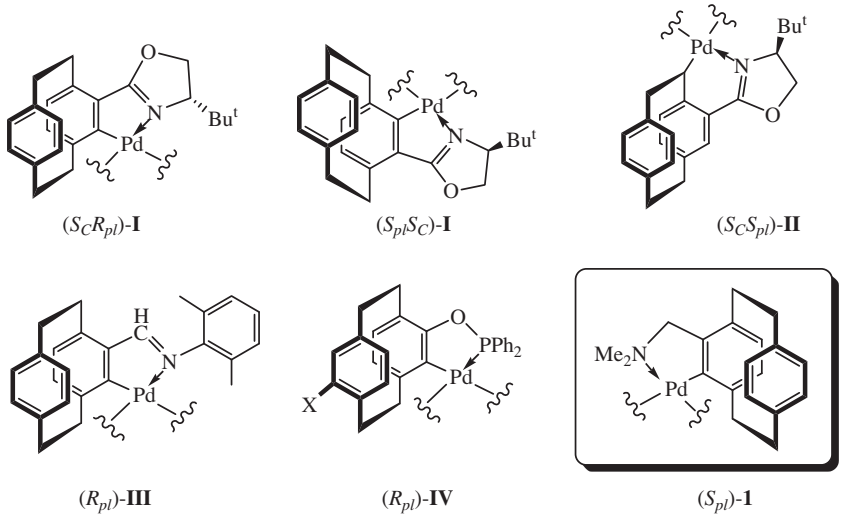
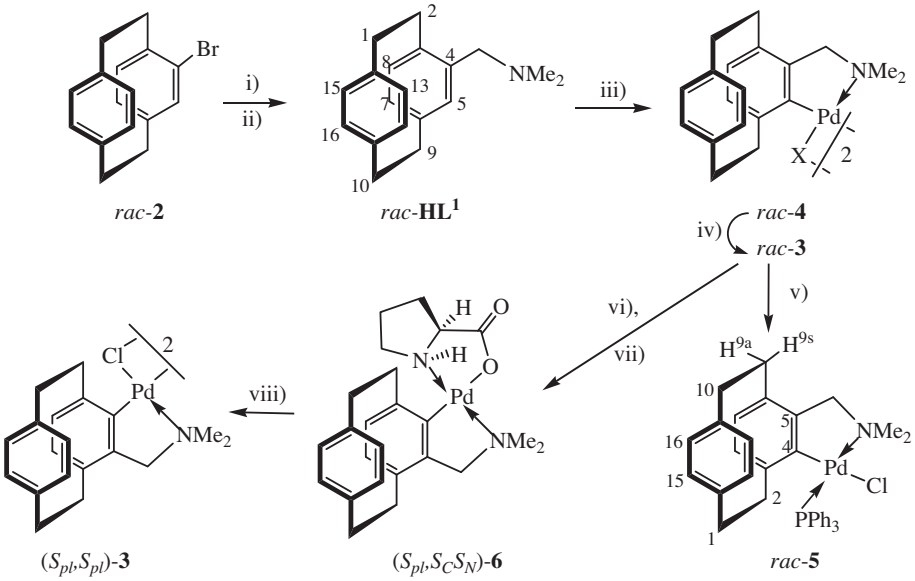


Fig. 1. Reported palladacycles with non-metallocenic planar chirality (**I**–**IV**) and target pCp-derived aminate *CN*-palladacycle (S_{pl})-**1** of the same structural and stereochemical type.



Scheme 1. Syntheses of the ligand $\mathbf{HL^1}$ and its cyclopalladated derivatives, and optical resolution of the dimer *rac*-**3**. Reagents and conditions: (i) BuLi, Et_2O; $[CH_2{=}NMe_2]^+I^-$; HCl, Et_2O; (ii) $NaOH_{aq}$; (iii) $Pd(OAc)_2$, toluene, r.t., 9 days; (iv) LiCl, acetone, r.t., 12 h; (v) PPh_3, toluene, 20 °C, 0.5 h; (vi) potassium (S_C)-prolinate, MeOH, r.t.; (vii) twofold crystallisation of the diastereomer mixture from methanol/diethyl ether; (viii) 0.5 M HCl_{aq}/dichloromethane, r.t.

Cyclopalladation of the amine *rac*-$\mathbf{HL^1}$ was realised only in its reactions with the more electrophilic reagent $Pd(OAc)_2$, following anion metathesis of the intermediate acetate-bridged dimer $[\{Pd(\eta^2\text{-}L^1)(\mu\text{-}OAc)\}_2]$ (*rac*-**4**). Careful optimisation of the reaction conditions offered the opportunity to increase the target dimer *rac*-**3** yield from the very low initial yield of 12% with slight heating (50 °C, 1 h; *Method 2*) to 31% with an increased duration (45 °C, 5 h; *Method 3*), and finally to 64% without heating and at a longer reaction time (r.t., 9 days; *Method 4*; Scheme 1).

It is known that usually direct intramolecular activation of aromatic (sp^2)C–H bonds with palladium(II) occurs much more efficiently compared to that of aliphatic (sp^3)C–H bonds; examples of *CN*-palladacycles of the last type are rare [13]. As a consequence, we can propose that some problems in the (sp^2)C–H bond activation in the case of the amine $\mathbf{HL^1}$ may be caused by the decreased aromaticity of the phenylene rings of the [2.2]paracyclophane framework deformed in a boat-like manner. It is important to note that we observed similar difficulties in the course of the cyclopalladation of the pCp-derived phosphinite ligand [5].

2.2. Spectral confirmation of the new CN-palladacycle structure

The structure of the amine $\mathbf{HL^1}$ provides two alternative sites for cyclopalladation: (i) the aromatic (sp^2)C–H bond of the trisubstituted phenylene ring, and (ii) the benzylic (sp^3)C–H bond of the neighbouring methylene group of the pCp-moiety. The sole precedent of high yield isolation of both regioisomeric palladacycles, (S_CR_{pl})-**I** and (S_CS_{pl})-**II**, was reported in the reactions of 2-oxazolinyl-pCp with the same palladation agent, $Pd(OAc)_2$, under comparable conditions [3]. Despite this fact, the first of the two above-mentioned directions of the palladium(II) attack on the pCp-derived ligands in general and on the tertiary amine $\mathbf{HL^1}$ in particular can be considered as much more preferable for the following reasons: (i) more efficient activation of the

(sp^2)C–H bonds with palladium(II) compared to that of the (sp^3)C–H bonds [13]; (ii) the first direction results in the formation of the more preferable five-membered palladacycle compared to the six-membered one in the second case; (iii) the nature of the palladium(II) acetate used as a metallation agent provides optimal conditions for electrophilic aromatic substitution.

Unfortunately, the dimeric complex *rac*-**3** cannot be used for any spectral studies due to its existence as a complicated mixture of *syn*/*anti* and *meso*/*dl* isomers and their dynamic mobility. Because of this, for evaluation of the regiochemistry of the amine *rac*-**HL[1]** cyclopalladation, the dimer *rac*-**3** was transformed into its mononuclear derivative *rac*-**5** via chloride bridge cleavage by the auxiliary triphenylphosphine ligand (Scheme 1). Two main advantages of using a phosphine derivative for this purpose include: (i) facilitation of ^{1}H NMR spectra interpretation due to spin-spin coupling of defined protons with the ^{31}P nucleus, and (ii) regioselective coordination of the auxiliary phosphine ligand in a *trans*(*P*,*N*) configuration, evident from the presence of only one signal in the ^{31}P{^{1}H} NMR spectrum of the adduct *rac*-**5** at δ 30.3 ppm.

The signal assignment in the ^{1}H NMR spectrum of the adduct *rac*-**5** was performed using homo- and heteronuclear decoupling, COSY and NOE experiments. These spectral data unambiguously confirm the activation of the (sp^2)C–H bond in the course of the ligand **HL[1]** cyclopalladation: the ^{1}H NMR spectrum of the phosphine adduct *rac*-**5** contains signals of only six aromatic protons of the pCp-phenylene rings in the range δ 5.46–6.55 ppm, well separated from the signals of the PPh_3 protons (δ 7.25–7.62 ppm), and the signals of all eight methylene protons of the pCp-framework (δ 1.90–3.14 ppm).

As expected, the non-equivalence of the two diastereotopic NMe groups is evident only in the spectrum of the *ortho*-palladated complex *rac*-**5** ($\Delta\delta$ = 0.17 ppm), while in the case of the flexible free amine *rac*-**HL[1]** they are formally equivalent. The difference in the spin-spin coupling efficiency of the diastereotopic α-CH_2 protons and *N*-methyl groups with the ^{31}P nuclei of the auxiliary ligand PPh_3 in the ^{1}H NMR spectrum of the adduct *rac*-**5** has provided a basis for their differentiation: (i) the constants $^4J_{HP}$ = 3.2 and 1.7 Hz were found for the equatorial (*N*-Me^{eq}) and axial (*N*-Me^{ax}) *N*-methyl groups, respectively; (ii) of the two α-methylene proton signals, only one reveals a spin–spin coupling constant, $^4J_{HP}$ = 5.1 Hz, which is indicative of its equatorial orientation (α-CH^{eq}).

As a starting point, in the assignment of the aromatic protons of the pCp moiety we used the signal of the H(8) proton of the metallated phenylene ring, which appears as a doublet with a coupling constant $^5J_{HP} \sim 0.6$ Hz. Proton H(15) of the non-palladated C_6H_4 ring was identified on the basis of a NOE experiment, revealing its dipole–dipole interaction with the *pseudo*-geminal proton H(8) (1.9%, Fig. 2a).

As a reference point for the assignment of the methylene protons of the pCp moiety we used the signal of the H(2a) proton, located due to its dipole–dipole interaction with the aromatic H(8) proton (3.1%), and the high-field position of this signal at δ 1.90 ppm (ddd) caused by the anisotropy influence of the PPh_3 ligand. It should be noted that the same effect was previously observed for the PPh_3 derivative of the imine *CN*-palladacycle *rac*-**III** (δ 1.93 ppm for the H(2a) proton) [4]. The signal at δ 2.78 ppm (dddd) was identified as belonging to the H(2s) proton due to detection of a coupling constant $^5J_{HP} \approx 1.1$ Hz. A rather large value of this constant is indicative of a significant contribution of the through-space ^{1}H···^{31}P interaction of the proton H(2s) with the auxiliary PPh_3 ligand, and may be considered as unambiguous confirmation of a *trans*(*P*,*N*) configuration of the phosphine adduct *rac*-**5**.

The comparative analysis of the ^{1}H NMR spectral data for the triphenylphosphine derivative *rac*-**5** and the corresponding derivatives of other palladacycles bearing a pCp-framework (**III** [4] and **IV** [5,14]), offers the opportunity to determine several trends, which may be useful for signal assignment in the ^{1}H NMR spectra of related structures:

(i) the signal of the methylene H(2a) proton may be identified by its high-field position caused by influence of the auxiliary ligand PPh_3;
(ii) the signal of the methylene H(2s) proton may be located due to the presence of the spin-spin coupling constant ($^5J_{HP}$ 0.7–2.1 Hz) with the phosphorus atom of the auxiliary ligand PPh_3, probably with a contribution of their interaction through space;
(iii) the most low-field position is typical for the signal of the methylene H(9s) proton, which is brought close to the palladacycle side chain (CH_2NMe_2, CH = NAr or $OPPh_2$);
(iv) the signals of the H(7) and H(8) aromatic protons of the metallated phenylene ring are high-field shifted compared to those of other aromatic protons of the pCp-moiety.

2.3. Preparation of enantiomerically pure CN-palladacycle (S_{pl})-**1**

The resolution of the racemic dimeric complex *rac*-**3** was performed using the (S_C)-prolinate ligand for its chiral derivatisation. A high efficiency of this amino acidate for enantiomer separation of *CN*- [15] and *CP*-palladacycles [16] is well documented.

Treatment of the racemic dimer *rac*-**3** with potassium (S_C)-prolinate in a 1:2 ratio affords an equimolar mixture of diastereomeric derivatives, (S_{pl},$S_C$$S_N$)-**6** and ($R_{pl}$,$S_C$$S_N$)-**6**. After its twofold slow crystallisation by the vapour diffusion method using diethyl

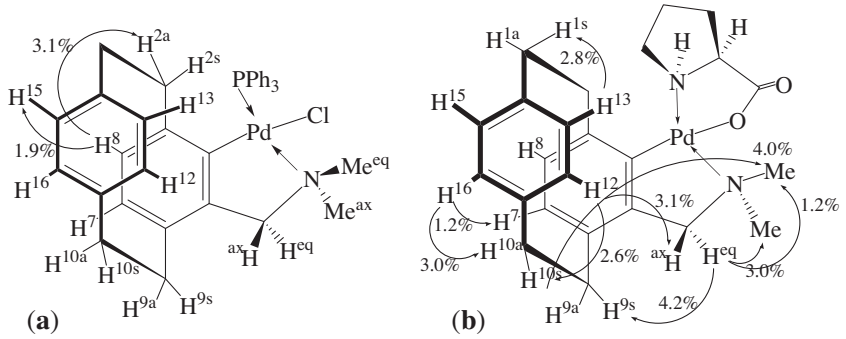


Fig. 2. Numbering schemes and NOE-basis for the assignments of resonances of aromatic and methylene protons of the pCp moiety in the ^{1}H NMR spectra of the phosphine adduct *rac*-**5** (a) and prolinate diastereomer (S_{pl},$S_C$$S_N$)-**6** (b).

ether and methanol, the less soluble diastereomer (S_{pl},$S_C$$S_N$)-**6** was isolated in a diastereomerically pure state (>99% *de*, ^{1}H NMR data) in a moderate yield of 38% (Scheme 1). Unfortunately, the extremely high solubility of the second diastereomer (R_{pl},$S_C$$S_N$)-**6** in all solvents tested has prevented its isolation in the individual state.

The enantiopure dimeric complex (S_{pl},S_{pl})-**3** was obtained with a yield of 86% with $[\alpha]_D$ +360° (*c* 0.12, CH_2Cl_2) using a standard protocol of auxiliary ligand removal by its protonation with dilute HCl in a two-phase solvent system.

2.4. Spectral study of the prolinate derivative (S_{pl},$S_C$$S_N$)-6

The structure of the diastereomer (S_{pl},$S_C$$S_N$)-**6** in solution was confirmed by ^{1}H NMR spectroscopy. Despite rather strong signal overlapping in the high field region, we were able to identify the main signals of the *CN*-palladacycle using homonuclear decoupling, NOE (Fig. 2b) and COSY techniques; in some instances interatomic distances in the crystal structure of the complex (S_{pl},$S_C$$S_N$)-**6** (see Section 2.5) were used for confirmation of the signal assignments. The signal assignments in the spectrum of the prolinate complex (S_{pl},$S_C$$S_N$)-**6** were based on the following arguments:

(i) In the NOE experiment we observed a dipole–dipole interaction (3.1%) between one of the α-methylene protons (represented by the doublet at δ 3.91 ppm) and one of the aromatic protons of the non-metallated phenylene ring (lowfield dd at δ 6.73 ppm), which allows us to identify these signals as belonging to an axial α-methylene proton (α-CH^{ax}) and an aromatic proton H(12), respectively. This assignment may be confirmed additionally by the minimum distance between these protons in the crystal structure (2.505 Å).

(ii) The signals of protons H(13) and H(16) were located using homonuclear ^{1}H{^{1}H} decoupling of proton H(12), which results in the removal of the spin–spin coupling constants $^3J_{HH}$ and $^4J_{HH}$, respectively.

(iii) The assignment of high-field signals at δ 6.07 and 6.11 ppm to protons H(7) and H(8) is evident from their doublet nature; their differentiation was based on the dipole-dipole interaction (1.2%) of the first of these protons with proton H(16).

(iv) Identification of the singlet signals of the diastereotopic *N*-methyl groups, NMe^{ax} and NMe^{eq}, was based on the differences in their dipole–dipole interactions with the axial α-methylene proton, viz., NOE 3.0% and 1.2%, respectively. This difference is in accordance with the differences between the averaged values of the distances α-CH^{eq}···H (Me^{ax}) and α-CH^{eq}···H(Me^{eq}) found in the crystal structure of the prolinate complex (S_{pl},$S_C$$S_N$)-**6** (2.834 and 3.111 Å, respectively).

The signals of the methylene bridges of the pCp moiety are represented by a group of complicated overlapping multiplets with seven of eight signals located in the rather narrow range δ 2.83–3.17 ppm. Nevertheless, several signals were identified using the NOE technique due to the following dipole–dipole interactions (Fig. 2b): α-CH^{eq} → H(9s) (4.2%), H(12) → H(10s) (2.6%), H(16) → H(10a) (3.0%) and H(13) → H(1s) (2.8%).

Signals of the protons of the auxiliary prolinate ligand were separated from all the other signals using the COSY technique. Unfortunately, we were only able to perform unambiguous assignment for the multiplet of the α-C*H* proton at the carbon stereocentre based on its high-field position (at δ 4.15 ppm). Despite using all possible NMR techniques (including temperature variation), our attempts to identify other prolinate proton signals failed due to their complicated form and very strong overlapping.

2.5. X-ray diffraction study of the (S_C)-prolinate diastereomer (S_{pl},$S_C$$S_N$)-6

The *ortho*-palladated structure and the absolute configuration of the new planar chiral *CN*-palladacycle (S_{pl})-**1** and the *trans*(*N*,*N*)-geometry of its (S_C)-prolinate derivative (S_{pl},$S_C$$S_N$)-**6** were established unambiguously by an X-ray diffraction study of the latter complex. The molecular structure of complex (S_{pl},$S_C$$S_N$)-**6**, the numbering scheme and selected bond lengths and angles are presented in Fig. 3.

The (S_{pl})-configuration of the 4,5-disubstituted [2.2]paracyclophane derivative (S_{pl},$S_C$$S_N$)-**6** is confirmed independently using the coordinated ($S_C$$S_N$)-prolinate ligand as a reference point and on the basis of the anomalous X-ray scattering method with the Flack parameter 0.000(17). Taking into account that complex (S_{pl},$S_C$$S_N$)-**6** is a derivative of the first amine *CN*-palladacycle (S_{pl})-**1** with non-metallocenic planar chirality, it was necessary to compare its structural parameters with those of the known achiral *N*,*N*-dimethylbenzylaminate analogues to estimate the influence of the phenylene ring replacement by a pCp-moiety. The set of achiral analogues includes the dimeric compounds **V** and **VI**, and the mononuclear phosphine adducts **VII**, containing a total of 14 non-equivalent palladacycles (Fig. 4).

The Pd–C bond in complex (S_{pl},$S_C$$S_N$)-**6**, lying on the diagonal C–Pd–O, is slightly elongated (2.016 Å) compared to the Pd–C bonds in the corresponding achiral compounds, namely, dimers **Vb**–**e** (1.961–1.987 Å) and the phosphine adducts **VIIb**, **c** (1.972–2.012 Å), where it lies on the diagonal C–Pd–Cl. What is more, this bond length also exceeds the Pd–C bond lengths in the complexes

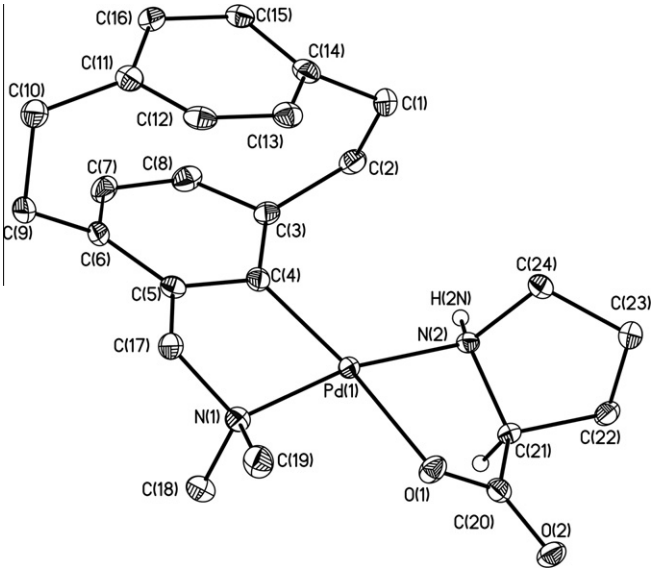


Fig. 3. Molecular structure and numbering scheme for the diastereomer (S_{pl},$S_C$$S_N$)-**6** with thermal ellipsoids at 50%; hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)–C(4) 2.016(2), Pd(1)–N(1) 2.0599(17), Pd(1)–O(1) 2.1096(15), Pd(1)–N(2) 2.0809(17), N(1)–C(17) 1.485(3), N(1)–C(19) 1.480(3), N(1)–C(18) 1.487(3), N(2)–C(21) 1.500(2), N(2)–C(24) 1.504(3), O(1)–C(20) 1.277(2), O(2)–C(20) 1.237(2), C(4)–C(5) 1.421(3), C(5)–C(6) 1.408(3), C(3)–C(4) 1.405(3); selected bond angles (°): C(4)–Pd(1)–N(1) 82.73(8), C(4)–Pd(1)–N(2) 105.76(7), N(1)–Pd(1)–N(2) 168.35(7), C(4)–Pd(1)–O(1) 173.95(7), N(1)–Pd(1)–O(1) 91.72(6), N(2)–Pd(1)–O(1) 79.40(6), C(20)–O(1)–Pd(1) 113.91(12), C(17)–N(1)–Pd(1) 108.71(12), C(18)–N(1)–Pd(1) 105.51(13), C(19)–N(1)–Pd(1) 113.87(13), C(17)–N(1)–C(18) 109.73(17), C(19)–N(1)–C(17) 109.90(16), C(19)–N(1)–C(18) 109.00(17), C(21)–N(2)–Pd(1) 104.86(11), C(24)–N(2)–Pd(1) 119.87(13), C(3)–C(4)–Pd(1) 130.29(15), C(5)–C(4)–Pd(1) 112.30(15), N(1)–C(17)–C(5) 108.17(16), C(21)–N(2)–C(24) 105.26(15), N(2)–C(21)–C(22) 104.28(15), N(2)–C(21)–C(20) 109.65(15), O(2)–C(20)–O(1) 125.35(19), O(1)–C(20)–C(21) 115.95(16), O(2)–C(20)–C(21) 118.60(17), C(4)–C(5)–C(17) 115.83(17), C(6)–C(5)–C(17) 121.09(18).

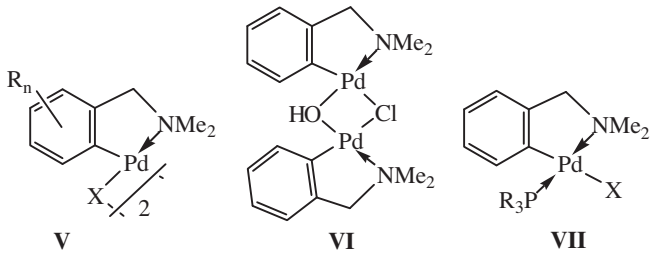


Fig. 4. Structures of achiral *N*,*N*-dimethylbenzylaminate *CN*-palladacycles characterised by the X-ray diffraction method: for **V** R_n = H, X = Tfa (**Va**) [17], Cl (**Vb**) [18]; X = Cl, R_n = 3-MeO (**Vc**) [19], 4-MeO (**Vd**) [19], 5-MeO (**Ve**) [19]; **VI** [20]; for **VII** X = Tfa, R = 4-$CF_3C_6H_4$ (**VIIa**) [21], X = Cl, R = Ph (**VIIb**) [18,21], Cy (**VIIc**) [17].

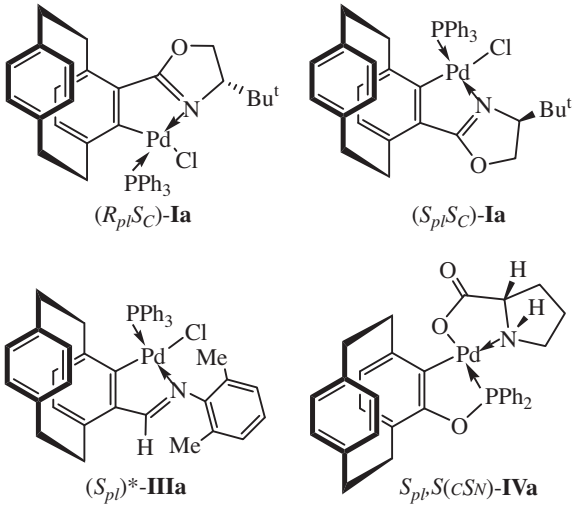


Fig. 5. Planar chiral *CN*- and *CP*-palladacycles based on [2.2]paracyclophane-derived ligands and characterised by the X-ray diffraction method.

Va and **VIIa** where the bonds lies on the same diagonal, C–Pd–O (1.954–1.999 Å). Such weakening of the Pd–C bond in the complex (S_{pl},$S_C S_N$)-**6** may be explained by the repulsive interaction between the pyrrolidine ring of the auxiliary prolinate ligand and the pCp-moiety.

The Pd–N(1) bond length in the complex (S_{pl},$S_C S_N$)-**6** (2.060 Å) is close to the lower end of this parameter range for the dimers **Va–e**, **VI** (2.060–2.094 Å), but is less than the values found for the phosphine adducts **VIIa–c** (2.106–2.159 Å). The last effect is a quite expectable consequence of the much greater Structural Trans-Influence (STI) of the phosphorus atom compared to that of nitrogen [22]. The intrachelate angle ∠CPdN in the structure of the complex (S_{pl},$S_C S_N$)-**6** (82.73°) falls within the range typical for all its achiral analogues **V–VII** (81.44–82.94°).

To follow the chirality transfer in CPCs bearing a pCp-framework, the structure of the complex (S_{pl},$S_C S_N$)-**6** was compared with those of a few known analogues based on the pCp-derived *N*- and *P*-donor ligands. The set of such planar chiral non-metallocenic complexes is restricted to triphenylphosphine derivatives of *CN*-palladacycles with an oxazolinyl donor group (diastereomers ($R_{pl}S_C$)-**Ia** and ($S_{pl}S_C$)-**Ia** [3]) or an imine donor ((S_{pl})*-**IIIa** [4]), and a (S_C)-prolinate derivative (S_{pl},$S_C S_N$)-**IVa** of the phosphinite *CP*-palladacycle (S_{pl})-**IV** [5] (Fig. 5 and Table 1).

The coordination environment of the palladium atom in the complex (S_{pl},$S_C S_N$)-**6** reveals two kinds of deviations from an ideal square-planar configuration. First, a slight pyramidal distortion with the metal atom in the top position was observed, which deviates from the mean coordination plane {$PdC^4N^1O^1N^2$} by +0.076 Å in the direction of the non-metallated phenylene ring of the paracyclophane framework. Such a pyramidal distortion of the coordination sphere has to be recognised as typical for achiral *N*,*N*-dimethylbenzylaminate CPCs **V–VII** since it was found for 12 of the 14 palladacycles of this kind. Second, the palladium coordination environment in the complex (S_{pl},$S_C S_N$)-**6** reveals a marked tetrahedral distortion with an interplanar angle {C^4PdN^1}{N^2PdO^1} (**β_{Pd}**) equal to 7.90°; this value is close to the lower end of this parameter range for all pCp-derived complexes (7.30–30.84°, Table 1), but exceeds the averaged value of this parameter for benzylaminate CPCs **V–VII** (5.63°).

According to the "skew-line convention" [23] the absolute configuration (AC) of the *pseudo*-tetrahedral coordination environment of the metal in the complex (S_{pl},$S_C S_N$)-**6** may be defined as **Δ**(S_{pl}) on the basis of the negative value of the *pseudo*-torsion angle ∠$C^4N^1O^1N^2$ connecting the four palladium-bonded atoms (**τ_{Pd}**), which is equal to −4.00°. It is important that the same **Δ**(S_{pl}) stereochemistry was found for the palladium environment in the complexes ($S_{pl}S_C$)-**Ia** and (S_{pl})*-**IIIa**, that may be deduced from the negative sign of the corresponding angles, equal to −12.35 and −16.48°, respectively. In contrast, the direction of tetrahedral distortion is inverted to the **Λ**(R_{pl}) configuration in the case of the diastereomer ($R_{pl}S_C$)-**Ia** of the opposite planar chirality (the angle **τ_{Pd}** is equal to +29.02°, see Table 1).

The conformation of the *CN*-palladacycle in the complex (S_{pl},$S_C S_N$)-**6** may be described as a distorted envelope with the nitrogen atom in the top position, which deviates from the plane of four remaining atoms by 0.542 Å. Such a conformation is typical for achiral *N*,*N*-dimethylbenzylaminate CPCs, since it was found for 13 of the 14 palladacycles in complexes **V–VII**. The palladacycle non-planarity in complex (S_{pl},$S_C S_N$)-**6** is rather high, with the

Table 1
Stereochemical characteristics of *CN*- and *CP*-palladacycles with a pCp-framework from X-ray data for complexes of the general type *trans*(E,E′)-[{η^2-C(4)^E)Pd(E′)X].

Complex	Palladacycle conformation		Palladium environment		pCp-framework[a]	
	ω_{av}[b] (°)	∠E-Y-C^5-C^4[c] (°)	**β_{Pd}**[d] (°)	**τ_{Pd}**[e] (°)/AC	**β_{Ar}**[f] (°)	**τ_{Ar}**[g] (°)/AC
(S_{pl},$S_C S_N$)-**6**	23.03	−31.8 (λ)	7.90	−4.00/**Δ**	14.11–15.45	−1.7/**σ**
(S_{pl},S_C)-**Ia**	16.21	+10(3) (δ)	16.02	−12.35/**Δ**	13.77–16.12	−3.08/**σ**
(R_{pl},S_C)-**Ia**	4.44	+6.0(8) (δ)	30.84	+29.02/**Λ**	14.26–16.19	+6.52/**ρ**
(S_{pl})*-**IIIa**	6.19	+1.80(3)	16.9	−16.48/**Δ**	13.18–16.56	−3.01/**σ**
(S_{pl},$S_C S_N$)-**IVa**	9.41	+2.1(5)	7.30	−4.81/**Δ**	12.97–14.30	−3.9/**σ**

[a] Parameter **ω_{av}** denotes the average intrachelate torsion angle.
[b] There are only parameters of the metallated phenylene ring of pCp moiety presented.
[c] Here E is the palladium-bonded heterodonor atom, and Y is the adjacent α-disposed atom of the palladacycle.
[d] Parameter **β_{Pd}** denotes the interplanar angle {C^4PdE}{E′PdX}.
[e] Parameter **τ_{Pd}** denotes the *pseudo*-torsion angle ∠C^4···E···X···E′.
[f] Parameter **β_{Ar}** denotes the averaged value of the two dihedral angles between the mean plane of four central atoms of the metallated phenylene ring {$C^4C^5C^7C^8$}, forming the "boat basis", and the planes including the methylene-bonded *ipso*-carbon atoms, viz., {$C^3C^4C^8$} and {$C^5C^6C^7$}.
[g] Parameter **τ_{Ar}** denotes the *pseudo*-torsion angle between the four central atoms of the metallated phenylene ring, forming the "boat basis", viz., ∠C^4–C^5···C^7–C^8.

average magnitude of the absolute values of intrachelate torsion angles (ω_{av}) equal to 23.03°. This parameter falls within the range of values 19.89–25.39° found for all its achiral α-non-substituted analogues **V**–**VII**. In addition, the *CN*-palladacycle in the prolinate derivative (S_{pl},$S_C S_N$)-**6** reveals a pronounced twisting, with the torsion angle ∠N^1–C^{17}–C^5–C^4 equal to −31.8(2)°. The absolute value of this parameter also falls in the range of values 23.66–37.90°, found for the achiral α-non-substituted analogues **V**–**VII**, and its sign is indicative of a *CN*-palladacycle λ(**S_{pl}**) conformation (Fig. 6).

The torsion angles, related to ∠N^1–C^{17}–C^5–C^4 in the structure of complex (S_{pl},$S_C S_N$)-**6**, are positive in the case of both diastereomers of Bolm's complex of opposite planar chirality, ($S_{pl}S_C$)-**Ia** and ($R_{pl}S_C$)-**Ia** (see Table 1), which is indicative of the dependence of these palladacycle conformations upon the oxazoline carbon (S_C)-stereocentre rather than upon the chiral plane of the pCp-moiety. Unfortunately, the twisting extent of two other palladacycles in the complexes (S_{pl})*-**IIIa** and (S_{pl},$S_C S_N$)-**IVa** is too low (with torsion angles of ca. 2°) for any discussion of their stereochemistry.

It is known [6,24] that the phenylene rings of the pCp-moiety adopt a boat-like form due to steric compression. Their non-planarity extent may be characterised by angles between the plane of four central atoms (forming the "boat basis") and planes including the methylene-bonded *ipso*-carbon atoms (β_{Ar}). In the case of complex (S_{pl},$S_C S_N$)-**6**, this parameter varies in the range 14.11–15.45° for the metallated phenylene ring, which is comparable with this parameter range found for other CPCs with a pCp-backbone (12.97–16.56°, see Table 1). In all the pCp-derived CPCs, this kind of deformation is more pronounced for the palladated phenylene ring. More importantly, the latter possesses an additional puckering: the "boat base" of this phenylene ring is twisted according to the torsion angles ∠C^4–C^5···C^7–C^8 equal to −1.70° for complex (S_{pl},$S_C S_N$)-**6**, and varying from −3.01° to −3.9° for complexes (S_{pl},S_C)-**Ia**, (S_{pl})*-**IIIa** and (S_{pl},$S_C S_N$)-**IVa**, but inverting to +6.52° for complex (R_{pl},S_C)-**Ia**. The signs of these angles are indicative of the dependence of this twist direction upon the configuration of the chiral plane: it may be described as an σ(S_{pl})-twist for the complexes with an (S_{pl})-configuration, but as an ρ(R_{pl})-twist for the complex with an (R_{pl})-configuration.

The analysis of CCDC data has shown that a similar dependence is also applicable for more general cases of organic 4-X-5-Y-disubstituted derivatives of [2.2]paracyclophane: all the compounds with an (S_{pl})-configuration are characterised by a negative torsion angle ∠C^4–C^5···C^7–C^8 corresponding to σ(S_{pl})-twist, while the positive angles are typical for compounds with an (R_{pl})-configuration, which is indicative of ρ(R_{pl})-twist [4,14]. Thus, the directed twist of the tetrasubstituted phenylene ring of the pCp moiety cannot be considered as a fortuitous phenomenon.

The geometric parameters of the prolinate moiety of the diastereomer (S_{pl},$S_C S_N$)-**6** are mainly in the range of values typical for the other known ($S_C S_N$)-prolinate derivatives of *CN*- [15b–d,16a,25] and *CP*-palladacycles [15a,16b,c] of a *trans*(*O*,*C*)-configuration.

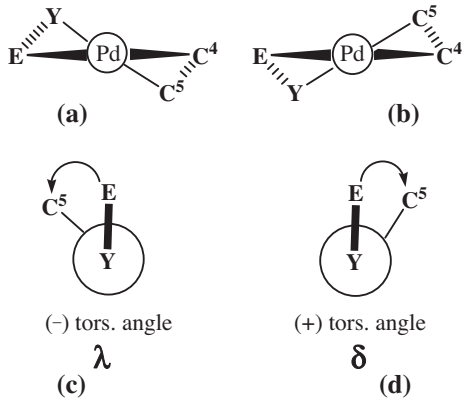


Fig. 6. Chiral λ (a) and δ (b) conformations of five-membered palladacycles and Newmen's projections along the bond Y–C^4 (c and d), illustrating the correlation between the sign of the torsion angle ∠E–Y–C^5–C^4 and the palladacycle conformation.

3. Conclusions

We have synthesised the previously unknown tertiary amine pCp-CH$_2$NMe$_2$ with a [2.2]paracyclophane framework as a racemate. Its direct cyclopalladation was possible only with palladium(II) acetate due to the decreased (sp^2)-character of the deformed phenylene rings of the pCp-moiety; it occurs in a regioselective mode with the formation of an (sp^2)C–Pd bond. Enantiomerically pure dimer (S_{pl},S_{pl})-**3** was obtained by the standard procedure of racemic palladacycle resolution using (S_C)-prolinate as the chiral derivatising agent. The *ortho*-palladated structure of the new *CN*-dimer *rac*-**3** and the absolute configuration of the chiral plane in enantiopure dimer (S_{pl},S_{pl})-**3** were established by means of spectral studies of their mononuclear phosphine (*rac*-**5**) or (S_C)-prolinate derivative ((S_{pl},$S_C S_N$)-**6**), respectively, and an X-ray diffraction study of the latter.

Important conclusions regarding chirality transfer in CPCs with a [2.2]paracyclophane framework were deduced from a comparison of the stereochemical peculiarity of the new *CN*-palladacycle in the (S_C)-prolinate complex (S_{pl},$S_C S_N$)-**6** with those of phosphine or (S_C)-prolinate derivatives of known structurally characterised *CN*- (**I**, **III**) and *CP*-palladacycles (**IV**). First, the configuration of the chiral plane determines the twist direction of the metallated phenylene ring of the pCp-framework, namely it becomes **σ**-twisted in the complexes with an (S_{pl})-configuration, but it reveals a **ρ**-twist in the case of the complex with an (R_{pl})-configuration. Second, the tetrahedral distortion of the metal coordination environment in pCp-derived CPCs also reveals a clear dependence upon the absolute configuration of the chiral plane: a *quasi*-tetrahedron of **Δ**-configuration was found in structures of all known complexes of the (S_{pl}) chiral plane, in contrast with the **Λ**-*quasi*-tetrahedron in the case of a sole complex containing a chiral plane of the (R_{pl})-configuration. The routes of chirality transfer for all pCp-derived CPCs may be represented as following:

(S_{pl})-chiral plane → **σ**-pCp-twist → **Δ**-tetrahedron, or
(R_{pl})-chiral plane → **ρ**-pCp-twist → **Λ**-tetrahedron.

The chirality transfer from the pCp-framework to the palladacycle conformation is not so universal. In the case of the amine-derived complex (S_{pl},$S_C S_N$)-**6**, the (S_{pl}) chiral plane induces a twist of the strongly puckered palladacycle in the λ conformation. In this case the total scheme of the chirality transfer may be presented as follows:

(S_{pl})-chiral plane → **σ**-pCp-twist → **Δ**-tetrahedron
→ **λ**-conformation.

In contrast, in the complexes of mixed stereochemistry, ($R_{pl}S_C$)-**Ia** and ($S_{pl}S_C$)-**Ia**, the (S_C)-carbon stereocentre in the side chain dictates the opposite **δ** conformation of the palladacycles in both these diastereomers:

($S_C S_{pl}$)-configuration → **σ**-pCp-twist → **Δ**-tetrahedron →
δ-conformation.

The extent of the versatility of these conclusions may be estimated only after further investigation of other pCp-derived CPCs

bearing diverse donor atoms and belonging to diverse stereochemical types.

4. Experimental

4.1. General remarks

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with Varian VXR-400 and Bruker DPX-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. The proton chemical shifts are reported in parts per million relative to TMS as an internal standard; the ^{31}P chemical shifts are given relative to H_3PO_4 as an external reference. The assignment of the 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 at 25 °C. Melting points were measured with an Electrothermal IA 9000 series device in a sealed capillary. Elemental analyses were performed with an automatic analyser VarioMicroCOBE of the firm Elementar.

All reactions were conducted under argon using TLC control on Silufol UV-254. The purification of the compounds was performed by means of short dry column [26] or flash-chromatography on Silica Gel 60 (from Fluka).

Benzene, toluene, hexane and ether were dried with the appropriate drying agents and then distilled from sodium; CH_2Cl_2 and $CHCl_3$ were purified chromatographically on a column of Al_2O_3 and then distilled from CaH_2; MeOH was refluxed over magnesium methoxide for 3 h and then distilled; $CDCl_3$ (from Aldrich) was distilled from CaH_2 just before use. Acetone of high purity (from Reachim) was used without additional purification.

4.2. Reagents and starting compounds

Palladium(II) chloride and acetate, BuLi (from Aldrich) and (*S*)-proline (high purity grade) were used as received; triphenylphosphine (from Chemapol) was purified by twofold recrystallization from a benzene/hexane mixture. Racemic 4-bromo[2.2]paracyclophane [8] and dimethyl(methylene)ammonium iodide (Eschenmoser's salt) [9] were synthesized by known methods. Potassium (*S*)-prolinate was prepared by treatment of (*S*)-proline with an equimolar amount of KOH in methanol at r.t.; after removal of the solvent, the residue was thoroughly dried in vacuo.

4.3. Synthesis of the racemic amine ***HL*^{1}**

4.3.1. Preparation of racemic N,N-dimethyl([2.2]paracyclophane-4-ylmethyl)ammonium chloride (rac-***HL*^{1}*HCl)*

A 2.5 M solution of ^{n}BuLi in hexane (14 mL, 34.8 mmol) was added drop-by-drop to a solution of 4-bromo[2.2]paracyclophane (5.00 g, 17.4 mmol) in ether (200 mL) under argon, with stirring. The reaction mixture was stirred at r.t. for 2 h, Eschenmoser's salt (6.50 g, 35.1 mmol) was added and stirring was continued for additional 1 h. After washing with water (200 mL) and drying over Na_2SO_4, the organic solvents were removed in vacuo, and the residue was dissolved in ether (50 mL) and ammonium salt was treated with a saturated solution of HCl gas in ether. The precipitate formed was filtered, washed by ether and thoroughly dried in vacuo (1 mm Hg). After its precipitation from chloroform (50 mL) by benzene, the salt *rac*-**HL^1**·HCl was isolated in 55% yield (2.95 g, 9.78 mmol). M.p. 244.5–246 °C. *Anal.* Calc. for $C_{19}H_{24}NCl$: C, 75.45; H. 8.15; N, 4.61. Found: C, 75.60; H, 8.01; N, 4.64%. ^{1}H NMR (d_6-DMSO; δ, ppm, *J*, Hz): 2.57 (br s, 6H, N*Me*$_2$), 2.78–3.18 (m, 7H, C*H*$_2$–C*H*$_2$), 3.48–3.62 (m, 1H, C*H*H–CH$_2$), 3.99 (d, ^2J(HH) = 13.0, 1H, α-C*H*), 4.24 (d, ^2J(HH) = 13.0, 1H, α-C*H*), 6.36–6.69 (m, 7H, aromatic protons), 10.6 (br s, 1H, N*H*).

4.3.2. Isolation of free racemic N,N-dimethyl([2.2]paracyclophane-4-yl)methylamine (rac-***HL*^{1}*)*

A suspension of the ammonium salt *rac*-**HL**·HCl (0.3890 g, 1.290 mmol) in toluene (15 mL) was treated with an excess of a 1 M aqueous solution of NaOH (0.150 g, 3.75 mmol) and stirred at r.t. for 2 h. The organic phase was washed with water (5 × 10 mL) up to pH 7, dried over Na_2SO_4, evaporated to dryness and the residue was dried in vacuo (1 mm Hg) over paraffin and $CaCl_2$. The amine *rac*-**HL^1** was obtained in a yield of 90.3% (0.3157 g, 1.189 mmol) as a colourless oil which became solid after cooling. M.p. 52 °C, R_f 0.48 (toluene/acetone, 10:1). ^{1}H NMR ($CDCl_3$; δ, ppm, *J*, Hz): 2.24 (c, 6H, N*Me*$_2$), 2.90 (ddd, ^2J(HH) = 13.1, ^3J(HH) = 10.7, ^3J(HH) = 5.8, 1H, C*H*H–CH$_2$), 3.02–3.23 (m, 6H, C*H*$_2$–CH$_2$), 3.05 (d, ^2J(HH) = 12.6, 1H, α-C*H*), 3.55 (d, ^2J(HH) = 12.6, 1H, α-C*H*), 3.56 (m, 1H, H(2*s*)), 6.35 (br s, 1H, H(5)), 6.54 (br d, ^3J(HH) = 7.7, 1H, H(7)), 6.51 (d, ^3J(HH) = 7.7, 1H, H(8)), 6.47 (d, ^3J(HH) = 7.9, 1H, H(12) or H(13)), 6.69 (d, ^3J(HH) = 7.9, 1H, H(13) or H(12)), 6.56 (d, ^3J(HH) = 7.9, 1H, H(15) or H(16)), 6.62 (d, ^3J(HH) = 7.9, 1H, H(16) or H(15)).

4.4. Syntheses of the cyclopalladated complexes

4.4.1. Preparation of racemic dimer di-μ-chlorobis{5-(N,N-dimethylaminomethyl)[2.2]paracyclophane-4-yl-C,N}dipalladium(II) (rac-***3*)**

Method 1. A solution of a mixture of the ammonium salt *rac*-**HL^1**·HCl (0.1222 g, 0.4053 mmol), Li_2PdCl_4 (0.1063 g, 0.4053 mmol) and sodium acetate (0.0997 g, 1.216 mmol) in methanol (10 mL) was stirred at 50 °C for 1 h. Intensive formation of palladium black prevented the isolation of the target dimer **3**, which was detected in only trace quantities (TLC data).

Method 2. A solution of $Pd(OAc)_2$ (0.0457 g, 0.2037 mmol) and amine *rac*-**HL^1** (0.0541 g, 0.2038 mmol) in toluene (10 mL) was stirred for 1 h at 50 °C, then the solvent was evaporated and the residue was treated with a solution of LiCl (0.01730 g, 0.4081 mmol) in acetone (10 mL). The reaction mixture was stirred for 1 h at r.t., treated with water (15 mL) and additionally stirred for 1 h. The precipitate formed was filtered, washed with water and dried in vacuo (1 mm Hg). After purification using dry column chromatography (*h* = 6 cm, *d* = 3.7 cm; eluents: toluene/acetone mixtures in ratios from 50:1 to 20:1), the target dimer was crystallized from a dichloromethane/hexane mixture, washed with hexane and dried in vacuo (1 mm Hg) over paraffin and $CaCl_2$ to afford the target dimer *rac*-**3** as a yellow amorphous powder. Yield: 12% (0.0108 g, 0.0132 mmol). M.p. (dec.) 222–223 °C; R_f 0.66 (benzene/acetone, 10:1). *Anal.* Calc. for $C_{38}H_{44}Cl_2N_2Pd_2$: C, 56.17; H, 5.34; N, 3.45. Found: C, 56.40; H, 5.34; N, 3.32%.

Method 3. The reaction of $Pd(OAc)_2$ (0.0489 g, 0.2177 mmol) with the amine *rac*-**HL^1** (0.0578 g, 0.2177 mmol) in toluene (10 mL) was conducted in a similar manner, but in the more mild temperature regime: for 3 h at 34 °C, then 5 h at 45 °C, and finally for 16 h at r.t. After purification using flash-column chromatography (*h* = 14 cm, *d* = 2.5 cm; eluents: benzene/acetone mixtures in ratios from 80:1 to 30:1) and crystallization, the dimer *rac*-**3** was obtained in a 31% yield (0.0276 g, 0.0339 mmol).

Method 4. The same reaction of $Pd(OAc)_2$ (0.1488 g, 0.6627 mmol) with the amine *rac*-**HL^1** (0.1759 g, 0.6627 mmol) was conducted in toluene (15 mL) at r.t. for 9 days. After purification using flash-column chromatography (*h* = 14.5 cm, *d* = 1.5 cm; eluents: toluene, then toluene/acetone mixtures in ratios from 80:1 to 30:1) and crystallization from a toluene/hexane mixture, dimer *rac*-**3** was obtained in a yield of 64% (0.1713 g, 0.2108 mmol).

*4.4.2. Preparation of the racemic mononuclear adduct chloro{5-(N,N-dimethylaminomethyl)[2.2]paracyclophane-4-yl-C,N}(triphenylphosphine-P)palladium(II) (rac-**5**)*

A solution of the dimer *rac*-**3** (0.0210 g, 0.0258 mmol) and a slight excess of PPh_3 (0.0149 g, 0.0570 mmol) in toluene (15 mL) was stirred for 30 min at r.t. Then the reaction mixture was concentrated and treated with hexane. The precipitate formed was washed with hexane and dried in vacuo (1 mm Hg) over paraffin and $CaCl_2$ to afford the target adduct *rac*-**5** as a light-yellow amorphous powder. Yield: 92% (0.0317 g, 0.0474 mmol). M.p. (dec.) 166–167 °C; R_f 0.68 (toluene/acetone, 3:1). *Anal.* Calc. for $C_{37}H_{37}ClNPPd$: C, 66.47; H, 5.58; N, 2.10. Found: C, 66.45; H, 5.36; N, 1.97%.

$^{31}P\{^1H\}$ NMR ($CDCl_3$; δ, ppm): 30.31 (s). ^1H NMR ($CDCl_3$; δ, ppm, *J*, Hz): palladacycle signals: 1.90 (ddd, $^2J(HH) = 13.2$, $^3J(HH) = 10.6$, $^3J(HH) = 3.3$, 1H, H(2a)), 2.68 (ddd, $^2J(HH) = 13.3$, $^3J(HH) = 10.6$, $^3J(HH) = 4.7$, 1H, H(1a)), 2.78 (dddd, $^2J(HH) = 13.2$, $^3J(HH) = 10.3$, $^3J(HH) = 4.7$, $^5J(HP) = 1.1$, 1H, H(2s)), 2.89–2.97 (m, 3H, H(9a), H(10s), H(10a)), 3.04 (ddd, $^2J(HH) = 13.3$, $^3J(HH) = 10.3$, $^3J(HH) = 3.3$, 1H, H(1s)), 3.10 (d, $^4J(HP) = 3.2$, 3H, NMe^{eq}), 3.14 (m, 1H, H(9s)), 3.27 (d, $^4J(HP) = 1.7$, 3H, NMe^{ax}), 3.83 (dd, $^2J(HH) = 15.4$, $^4J(HP) = 5.1$, 1H, α-CH^{eq}), 4.34 (d, $^2J(HH) = 15.4$, 1H, α-CH^{ax}), 5.46 (dd, $^3J(HH) = 7.5$, $^5J(HP) = 0.6$, 1H, H(8)), 5.83 (d, $^3J(HH) = 7.5$, 1H, H(7)), 6.47 (br s, 2H, H(12), H(13)), 6.54 (dd, $^3J(HH) = 7.7$, $^4J(HH) = 1.5$, 1H, H(16)), 6.55 (dd, $^3J(HH) = 7.7$, $^4J(HH) = 1.5$, 1H, H(15)); PPh_3 ligand signals: 7.25–7.30 (m, 6H, *meta*-H), 7.36–7.40 (m, 3H, *para*-H), 7.62 (ddd, $^4J(HH) = 1.3$, $^3J(HH) = 7.7$, $^3J(HP) = 11.1$, 6H, *ortho*-H).

*4.5. Optical resolution of the racemic dimer rac-**3***

*4.5.1. Preparation of the diastereomer {(S_{pl})-5-(N,N-dimethylaminomethyl)[2.2]paracyclophane-4-yl-C,N}{($S_C S_N$)-prolinate-N,O}palladium(II) ((S_{pl},$S_C S_N$)-**6**)*

A suspension of the dimer *rac*-**3** (0.1513 g, 0.1862 mmol) and potassium (S_C)-prolinate (0.0571 g, 0.3729 mmol) in methanol (15 mL) was stirred at r.t. for 9 h, and evaporated to dryness. The residue was dissolved in dichloromethane, washed with water (3 × 15 mL), dried over Na_2SO_4 and evaporated to dryness. After twofold recrystallization from methanol/ether (under conditions of ether diffusion into a concentrated solution of the complex in MeOH), washing with ether and drying in vacuo (1 mm Hg) over paraffin and $CaCl_2$, the diastereomer (S_{pl},$S_C S_N$)-**6** was obtained in a yield of 38% (0.0342 g, 0.0705 mmol) as a light-yellow crystalline solid. M.p. (dec.) 184–185 °C, R_f 0.35 (CH_2Cl_2/MeOH, 10:1), $[\alpha]_D^{25}$ +244.6° (*c* 0.39, CH_2Cl_2). *Anal.* Calc. for $C_{24}H_{30}N_2O_2Pd$: C, 59.44; H, 6.24; N, 5.78. Found: C, 59.46; H, 6.25; N, 5.71%. ^1H NMR ($CDCl_3$; δ, ppm, *J*, Hz): palladacycle signals: 2.53–2.63 (m, 1H, C*H*HCH$_2$), 2.64 (s, 3H, NMe^{ax}), 2.83–2.89 (m, 2H, CHHC*H*H), 2.85 (m, 1H, H(9s)), 2.93 (m, 1H, H(10s)), 3.03 (s, 3H, NMe^{eq}), 3.06 (m, 1H, H(1s)), 3.07 (m, 1H, H(10a)), 3.10–3.17 (m, 1H, C*H*HCH$_2$), 3.72 (d, $^2J(HH) = 14.2$, 1H, α-CH^{eq}), 3.91 (d, $^2J(HH) = 14.2$, 1H, α-CH^{ax}), 6.07 (d, $^3J(HH) = 7.7$, 1H, H(7)), 6.11 (d, $^3J(HH) = 7.7$, 1H, H(8)), 6.53 (dd, $^3J(HH) = 7.8$, $^4J(HH) = 1.7$, 1H, H(13)), 6.59 (dd, $^3J(HH) = 7.8$, $^4J(HH) = 1.7$, 1H, H(16)), 6.67 (dd, $^3J(HH) = 7.8$, $^4J(HH) = 1.7$, 1H, H(15)), 6.73 (dd, $^3J(HH) = 7.8$, $^4J(HH) = 1.7$, 1H, H(12)); (S_C)-prolinate ligand signals: 1.79–1.88 (m, 2H, β-C*H*H), 1.95–2.01 (m, 1H, β-C*H*H), 2.37–2.44 (m, 1H, β-C*H*H), 3.41–3.49 (m, 1H, α′-C*H*H), 3.51–3.63 (m, 2H, N*H*, α′-C*H*H), 4.15 (m, 1H, α-C*H*).

*4.5.2. Isolation of the enantiopure dimer (S_{pl},S_{pl})-di-μ-chlorobis{5-(N,N-dimethylaminomethyl)[2.2]paracyclophane-4-yl-C,N}dipalladium(II) ((S_{pl},S_{pl})-**3**)*

A solution of the individual diastereomer (S_{pl},$S_C S_N$)-**6** (0.0109 g, 0.0230 mmol) in dichloromethane (8 mL) was treated with aqueous 0.5 M HCl (2 × 5 mL). Then the combined organic layers were washed with water (3 × 5 mL), dried over Na_2SO_4, evaporated to dryness and precipitated from toluene by hexane to obtain the dimer (S_{pl},S_{pl})-**3** as a yellow amorphous powder. Yield: 86% (0.0080 g, 0.0984 mmol). M.p. (dec.) 178–180 °C, R_f 0.66 (benzene/acetone, 10:1), $[\alpha]_D^{25}$ +360° (*c* 0.12, CH_2Cl_2). *Anal.* Calc. for $C_{38}H_{44}Cl_2N_2Pd_2$: C, 56.17; H, 5.34; N, 3.45. Found: C, 56.40; H, 5.34; N, 3.32%. ^1H NMR ($CDCl_3$; δ, ppm, *J*, Hz; two sets of signals of *anti*- and *syn*-isomers in ca. 4:3 ratio): 2.56, 2.63 (s, 3H, N*Me*), 2.89, 3.01 (s, 3H, N*Me*), 3.65, 3.67 (d, $^2J(HH) = 13.4$, 1H, α-CH), 4.12, 4.17 (d, $^2J(HH) = 13.4$, 1H, α-CH), 3.84–3.96 (m, 1H, H(2s)), 2.75–3.22 (group of m, 7H, CH_2CH_2), aromatic protons: 6.0–6.10 (m, 2H), 6.51, 6.52 (d, $^3J(HH) = 7.7$, 1H, H(7) or H(8)), 6.07, 6.08 (d, $^3J(HH) = 7.7$, 1H, H(8) or H(7)), 6.61–6.67 (m, 1H), 6.82 (br t, $^3J(HH) = 7.8$, 1H, H(12)), 6.91 (br t, $^3J(HH) = 7.8$, 1H, H(13)).

*4.6. X-ray crystallographic data for the diastereomer {(S_{pl})-5-(N,N-dimethylaminomethyl)[2.2]paracyclophane-4-yl-C,N}{($S_C S_N$)-prolinate-N,O}palladium(II) ((S_{pl},$S_C S_N$)-**6**)*

Crystals of complex **6** ($C_{24}H_{30}N_2O_2Pd$, FW = 484.90) are orthorhombic, space group $P2_12_12_1$ at 100 K, $a = 10.3221(4)$, $b = 12.1660(4)$, $c = 16.5131(6)$ Å, $V = 2073.7(1)$ Å^3, $Z = 4$ ($Z' = 1$), $D_{calc} = 1.553$ g cm^{-3}, μ(Mo Kα) = 9.18 cm^{-1}, $F(000) = 1000$. Intensities of 26399 reflections were measured with a Bruker APEX II CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans, $2\theta < 58°$] and 5773 independent reflections [$R_{int} = 0.0423$] were used in further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The absolute configuration was additionally proved by Flack parameter whose value in the case of the (S_{pl},$S_C S_N$) configuration was equal to 0.000(17). Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the riding model. The refinement converged to $wR_2 = 0.0533$ and GOF = 1.017 for all the independent reflections ($R_1 = 0.0223$ was calculated against *F* for 5561 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0 software.

Appendix A. Supplementary data

CCDC 838753 contains the supplementary crystallographic data for the complex (S_{pl},$S_C S_N$)-**6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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