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New principle for palladacycle resolution: diastereoselective monomer to dimer conversion

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Abstract—A new approach to optically active palladacycles was elaborated based on diastereoselective monomer to dimer transformation on an achiral sorbent. This methodology was illustrated by the preparation of both enantiomers of a cyclopalladated derivative of primary α-*tert*-butylbenzylamine through its (*S*)-prolinate complex. The advantages of the combined using of the new methodology with classical recrystallization of diastereomers and their chromatographic separation are discussed.

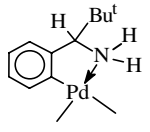
1. Introduction

Two main approaches to enantiomerically pure palladacycles are commonly used: (i) synthesis from optically active ligands (commercially available,[1–8] pre-resolved[9–13] or prepared by asymmetric synthesis[14]); and (ii) resolution of racemic cyclopalladated compounds by recrystallization[15–28] or chromatographic separation[29–33] of their diastereomeric derivatives. The third method based on the asymmetric activation of the C–H bond under control of an optically active base[34–39] or ligand in the palladation agent[40–42] is not so popular and used mainly for prochiral substrates. Except in a few cases,[41] the latter approach does not provide palladacycles in enantiomerically pure form and requires further minor enantiomer removal at the final stages.

In the course of elaboration of the new version of asymmetric cyclopalladation based on the exchange of cyclopalladated ligands[40] we have found that a high level of asymmetric induction (up to 91% ee) may be achieved only with an α-*tert*-Bu-substituted benzylaminate palladacycle bearing the primary amino group. Further development of this method has required large scale preparation of this efficient chirality inductor. However, the routine approach based on the cyclopalladation of the pre-resolved α-*tert*-butylbenzylamine (using known[43] or modified methods[12]) appears to be unacceptable due to a very low reproducibility of the amine resolution step. As the consequence, we were forced to look for alternative approaches to the target palladacycle. Herein we report our results on the elaboration of a new methodology based on the procedure of diastereomer separation via diastereoselective decomplexation of the auxiliary ligand on silica, which is based on our discovery of this effect during studies of *P**-chiral *PC*-palladacycles.[17,44]

2. Results

The stereochemical aspects of diastereomeric palladacycle interactions with sorbents were investigated using *CN*- and *PC*-palladacycles, **1** and **2** respectively, as substrates. As the chiral derivatizing agent for transformation of enantiomers into diastereomers we have chosen (*S*)-prolinate, because this available optically active auxiliary ligand works very efficiently with diverse other *PC*-[16,17] and *CN*-palladacycles.[18,20,22,23,26,33]



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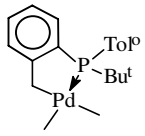

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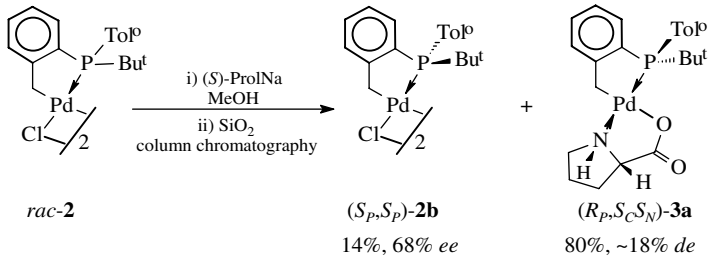
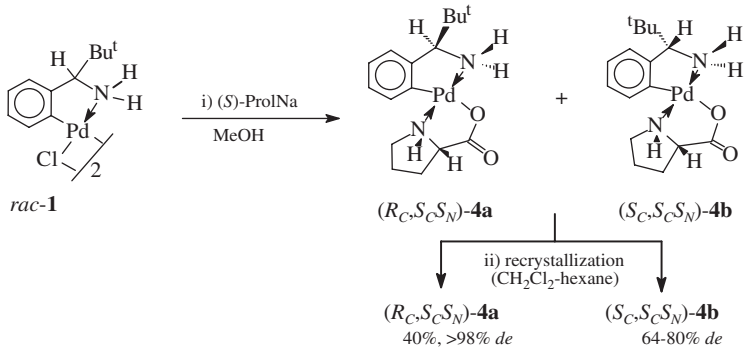


Scheme 1.



Scheme 2.

2.1. Phosphapalladacycle resolution

Some difference in stability of two diastereomers on an achiral sorbent was first discovered during our attempts at the chromatographic isolation of (R_P)-enantiomer of *P**-chiral phosphapalladacycle **2**,[44] which was found to be the less available through recrystallization of its (*S*)-prolinate derivatives.[17] Elution of 1:1 mixture of two diastereomeric (*S*)-prolinate complexes, (R_P,S_CS_N)-**3a** and (S_P,S_CS_N)-**3b**, through a SiO_2-loaded *flash*-column chromatography results in isolation of two compounds: dimer (S_P,S_P)-**2b** (ca. 14% yield,[†] 68% ee) and its (*S*)-prolinate derivative (R_P,S_CS_N)-**3a** enriched with the palladacycle of opposite configuration (<20% de) (Scheme 1).

Diastereoselectivity of chromatographic 'decomposition' of mononuclear (*S*)-prolinate derivatives **3a**,**b** is evident from significant enrichment of the dimer (S_P,S_P)-**2b** thus formed (up to 68% ee). However several characteristics of this process have prevented it from further development: (i) chromatographic mobilities of diastereomeric complexes **3a**,**b** appear to be approximately identical, and column chromatography does not provide any opportunity for their separation; (ii) the low extent of monomer to dimer conversion does not allow the removal of the less stable diastereomer completely: even after additional twofold elution of intermediate mixture of diastereomers **3a**,**b** of composition <20% de(R_P) diastereomeric enrichment of the more stable isomer (R_P,S_CS_N)-**3a** does not exceed 43% de; (iii) dimer (S_P,S_P)-**2b** thus obtained in higher enantiopurity (68% ee) has the same absolute configuration as that available through recrystallization of (*S*)-prolinate derivatives **3a**,**b**. Nevertheless, such chromatographic enrichment of dimer **2** with one of the enantiomers may be useful to facilitate its subsequent resolution via recrystallization of (*S*)-prolinate derivatives.[17]

2.2. Azapalladacycle resolution

For the racemic palladacycle **1** resolution we explored standard procedures of diastereomeric palladacycle separation: recrystallization and chromatography.

2.2.1. Recrystallization. First of all, we have tested crystallization as the simplest technique of diastereomeric complex separation (Method 1). However, recrystallization of the 1:1 mixture of (*S*)-prolinate complexes (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** has allowed us to isolate in diastereomerically pure form only first of them (Scheme 2).

After a single recrystallization of this mixture from dichloromethane–hexane, complex (R_C,S_CS_N)-**4a** was isolated in 40% yield and diastereomeric purity of >98% de (determined from ^{1}H NMR data, see below). Unfortunately, all attempts to separate another isomer (S_C,S_CS_N)-**4b** in diastereopure state from the remaining mother liquid of isomeric composition 74% de by the same technique were unsuccessful due to its higher solubility in all solvents mixtures tested.

2.2.2. Column chromatography. Our search of alternative approaches to the isolation of both diastereomers **4a**,**b** has led us to column chromatography. As might

[†] Hereinafter the values of yield are calculated on the basis of all palladium content.

be expected (see below), we have detected partial formal 'decomposition' (really dimerization) of mononuclear (*S*)-prolinate complexes **4a**,**b** into the starting dimer **1** under the conditions of their TLC-analysis. Relying on our results obtained for *PC*-palladacycles (see Section 2.1) it was reasonable to suppose that in the case of the *CN*-analogue the transformation 'monomer→dimer' can also occur as a diastereoselective process. Taking in mind this opportunity, we have performed chromatographic separation of an equimolar mixture of two diastereomers, (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** (Method 2).

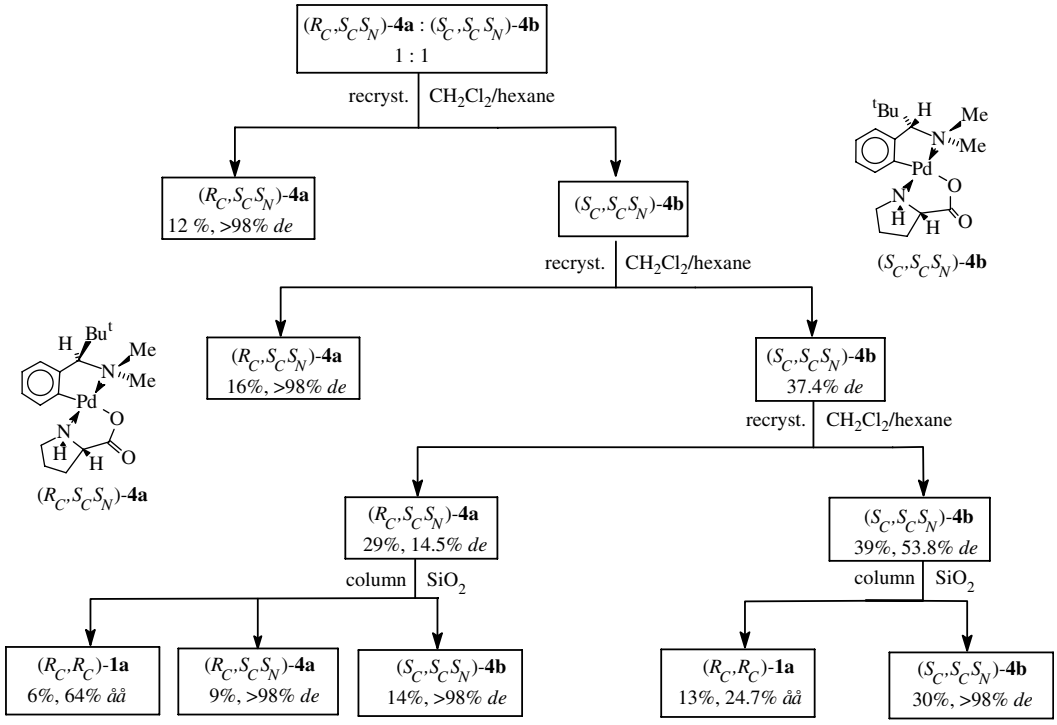
After twofold eluation via a SiO_2-loaded *flash*-column three compounds were isolated: dimer **1** and two diastereomers of its (*S*)-prolinate derivative **4**. Both mononuclear complexes were thus obtained stereochemically pure: (R_C,S_CS_N)-**4a** (32%, >98% de) and (S_C,S_CS_N)-**4b** (43%, >98% de). As a consequence of decreased stability of the first diastereomer **4a** on the sorbent its 'decomposition' appears to be more pronounced, and column chromatography provides dimer (R_C,R_C)-**1a**, enantiomerically enriched up to 63% ee. Both the significant enrichment of dimer **1** thus formed with (R_C)-enantiomer and the ratio of isolated (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** diastereomers (32:43) are indicative of the diastereoselective character of chromatographic 'decomposition' of (*S*)-prolinate complex.

In attempts to increase the diastereoselectivity of (*S*)-prolinate decomplexation from adducts **4a**,**b** we have increased the duration of their contact with the sorbent. Before starting column chromatography under the same conditions, the solution of an equal mixture of diastereomers (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** in dichloromethane was stored over silica for 23 days. In this case only one of two diastereomers, namely the more stable one—(S_C,S_CS_N)-**4b**, was eluted from column; it was obtained stereochemically pure (>98% de) in 34% yield. As the second product of 'decomposition' we have isolated dimer (R_C,R_C)-**1a** in 63% yield and with enantiomeric composition of 59% ee. These results points to the fact that (R_C,S_CS_N)-diastereomer **4a** was *completely* transformed into dimer (R_C,R_C)-**1a**, however at the same time another (S_C,S_CS_N)-diastereomer **4b** only partly (by 26%) decomposed into dimer (S_C,S_C)-**1b**.

The main advantage of this chromatographic method is the opportunity to isolate diastereomer (S_C,S_CS_N)-**4b** of the (*S*)-prolinate derivative, which was inaccessible via the recrystallization technique.

2.2.3. Combined approach. To optimize this method we have elaborated a combined approach, including isolation of the less soluble diastereomer (R_C,S_CS_N)-**4a** by means of recrystallization, following the column chromatography for isolation of another diastereomer (S_C,S_CS_N)-**4b** from the remaining mother liquor (*Method 3*, Scheme 3).

After twofold recrystallization of the 1:1 mixture of mononuclear complexes **4a**,**b** the pure diastereomer (R_C,S_CS_N)-**4a** (>98% de) was isolated in 28% yield; subsequent twofold column chromatography of the remaining mother liquor isomer mixture permits another diastereopure (>98% de) adduct (S_C,S_CS_N)-**4b** to be obtained in 46% yield, along with a small additional portion of the first isomer (R_C,S_CS_N)-**4a** (9%). As the overall result of this combined procedure we have obtained both isomers of (*S*)-prolinate derivatives,



Scheme 3.

(R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b**, in diastereopure form in total yields of 36% and 44%, respectively (72% and 88% based on each enantiomer content), and have recovered starting dimer (R_C,R_C)-**1a** in enantiomerically enriched state (from 25% to 64% ee) in a total yield of 19%. This scalemic dimer may be further used (after its repeated derivatizing with (*S*)-prolinate ligand) for isolation of enantiopure complex (R_C,R_C)-**1a** by means of recrystallization of the **4a**,**b** mixture.

2.2.4. Control for the resolution course. Diastereomeric purity of (*S*)-prolinate adducts **4a**,**b** were determined by means of ^{1}H NMR spectroscopy; the same method was used for estimation of enantiomeric compositions of isolated samples of scalemic dimer **1** after their in situ conversion into (*S*)-prolinate derivatives **4a**,**b**. Despite the rather complicated character of their ^{1}H NMR spectra (see Experimental), the majority of signals belonging to diastereomeric components are very well resolved. In addition, TLC may be also used for the preliminary (and very rough) estimation of isomeric composition of adducts **4a**,**b**, due to a rather marked difference in chromatographic mobility of diastereomers (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** (R_f 0.28 and 0.16, respectively).

2.2.5. Structure and stereochemistry of (*S*)-prolinate adducts 4a,b. The ^{1}H NMR spectra of diastereomeric (*S*)-prolinate derivatives of α-*tert*-Bu-substituted palladacycles (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** (both isolated individual forms, and their mixtures generated in situ from dimer **1** eluted from column) unambiguously support their structure (see Experimental). Retention of the five-membered *CN*-palladacycle during chromatographic 'decomposition' of complexes **4a**,**b** is evident from the presence of a nine-proton singlet of the α-^{t}Bu-group (δ 1.08 и 1.33 ppm[‡]) and four one-proton signals (partly overlapped) of the *ortho*-palladated phenylene fragment in low fields. *N*-Bonding of the primary amino-group with palladium was confirmed by the diastereotopic nature of NH_2-group protons ($\Delta\delta$ 1.8–2.5 ppm) and their significant lowfield coordination shifts ($\Delta\delta_{coord}$ 1.7–4.2 ppm).

Spectral parameters of α-CH and NH_2 protons of the side chain of the *CN*-palladacycle in diastereomers (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** point to retaining of the λ(S_C)- or δ(R_C)-conformation, respectively, that is typical for other derivatives of α-*tert*-butylbenzylaminate palladacycles.[12,22] From Newman projections of palladacycles along the N–C$^\alpha$ bond (Fig. 1) it becomes clear that in the case of its λ(S_C)- or δ(R_C)-stereochemistry spin–spin coupling of α-methine proton will be possible only with one of two NH-protons, while in the case of alternative λ(R_C)- or δ(S_C)-conformations efficiency of α-CH interaction with both NH_2 protons will be expected as very similar (as the result of equivalence of the corresponding torsion angles ~30° and ~150° in the terms of the Carplus–Konroy equation[45]). Spectral characteristics of complexes **4a**,**b** are in complete accordance with those expected for the λ(S_C)- or δ(R_C)-conformations: α-methine proton is a doublet (at δ 3.92 or 3.82 ppm) due to its spin–spin coupling with only one axial NH proton ($^3J_{H^\alpha CNH}$ 5.5–6.0 Hz). The same λ(S_C)-conformation of the same racemic α-^{t}Bu-substituted *CN*-palladacycle was established previously by NMR data (including NOE experiments) and X-ray study of its triphenylphosphine adduct.[46]

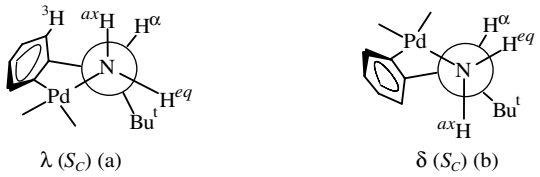
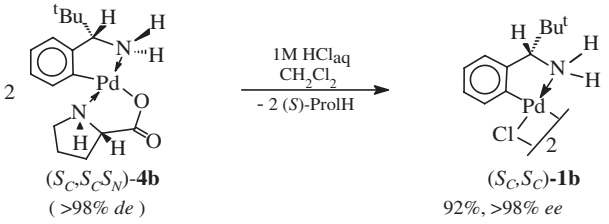


Figure 1. Newman projections of *N*-unsubstituted α-*tert*-butylbenzylaminate palladacycle along the N–C$^\alpha$ bond for λ(S_C) (a) and δ(S_C) (b) conformations.

2.2.6. Enantiopure dimer isolation. The isolation of both enantiomers of the target dimer, (R_C,R_C)-**1a** and (S_C,S_C)-**1b**, from the corresponding diastereomerically pure (*S*)-prolinate complexes, (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b**, respectively, was performed in high yield using a standard procedure of the auxiliary ligand protonolysis (Scheme 4).



Scheme 4.

Whilst one of these enantiopure dimers, (R_C,R_C)-**1a**, was prepared previously[40] by direct cyclopalladation of the pre-resolved (R_C)-amine, the second enantiomer (S_C,S_C)-**1b** is prepared at the first time.

3. Discussion

To the best of our knowledge, only two properties of diastereomeric derivatives of palladacycles have been used to date for the separation of their enantiomers: a difference in the solubility of two diastereomers[15–28,47] or in their chromatographic mobility.[29–33] The new methodology described here is based on the difference in stability of two diastereomeric palladacycles relative to the achiral sorbent (here it is silica). In order for this technique to be put to practical use, we have to estimate the conditions of its applicability.

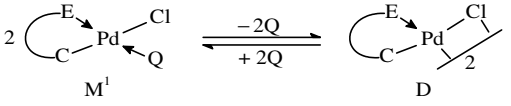
An evident pre-requisite to this new methodology application is a *decreased stability* of the auxiliary ligand bonding with palladacycle. Two main properties of the auxiliary ligand used for chiral derivatizing of a pallada-

[‡]Here and later on the two numbers are parameters of diastereomers (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b**, respectively.

cycle may be important to fulfil this requirement: (i) it has to contain hard donor atom(s)—for example nitrogen or oxygen, and/or (ii) increased steric hindrances stemming from its coordination with the palladacycle may be considered as a desirable condition. To gain a significant difference in stability between two diastereomers the auxiliary ligand structure should provide its *efficient steric interaction* with the palladacycle to be resolved. Perhaps, the presence in an intermediate complex of any groups capable of interaction with the sorbent may also assist the implementation of this new methodology.

In addition to our own results certain published data may be presented in support of these ideas. Thus it has been reported previously[48] that *monodentate N*-bonded pyridine ligands may be completely displaced from their adducts with *CN*-palladacycles under the conditions of column chromatography resulting in the corresponding μ-chloro-bridged dimer isolation. The same process of chromatographic decomplexation of the monodentate auxiliary (*S*)-α-methylbenzylamine ligand was employed practically for diastereopure monomer conversion to enantiopure dimer at the final stage of *CS*-palladacycle resolution.[24,25] Furthermore, partial decomposition of *bidentate* auxiliary ligands under the conditions of chromatography on silica (TLC) was also detected in the case of *O*,*O*′-bonded acetylacetonate derivatives of *CN*-palladacycles,[49] and for *N*,*O*-chelated α-amino acidate derivatives of *PC*-palladacycle.[17] In the light of these data it is not surprising that prolinate complexes **3a**,**b**, and **4a**,**b** reveal the tendency to lose the auxiliary ligand on the sorbent. As for the reason of such instability, it could arise from a rather weak bonding of hard donor atom(s) of auxiliary ligands of this kind with the very soft metal centre of the palladacycle with assistance of known palladium(II) metal lability.[50–52]

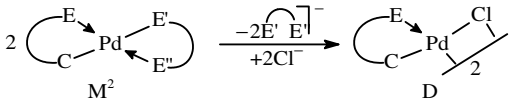
Decomplexation of monodentate ligand Q from its adduct with palladacycle on the sorbent is reduced to the shift of the equilibrium between mononuclear (M^1) and dimeric species (D) to the latter (Scheme 5).



Scheme 5.

In contrast, in the case of mononuclear derivatives of palladacycles bearing a bidentate auxiliary ligand (M^2), the similar monomer to dimer transformation requires halide-ion introduction (Scheme 6). It seems reasonable to suppose that the source of chloride-ions may be their admixture in the silica used.

Considering that available homochiral amines and α-amino carboxylates are the most popular auxiliary ligands for palladacycle resolutions, in a combination with a likely instability on the sorbent of such products of chiral derivatizing, it is not surprising that precedents of chromatography using for resolution of palladacycles are rather scarce. The published examples include routes via diastereomeric derivatives with (*S*)-α-methylbenzylamine[32] (monodentate *N*-donor) and (*R*)-phenylglycinate,[30] (*S*)-leucinate[31] or (*S*)-prolinate[33,44] (bidentate *N*,*O*-donors) as auxiliary ligands. To our knowledge, before our first report on this subject[44] neither decomposition of such complexes on sorbent nor stereochemistry of this process had been discussed.



Scheme 6.

Chromatographic methods have gained more widespread acceptance in the related (but inverted) processes of diverse substrate resolutions on homochiral palladacyclic templates at the stage of diastereomeric derivative separation. However, except in one case,[53] this methodology has been used only for the resolution of substrates (Q) with a soft donor atom(s)—mainly of monodentate phosphines—via *neutral* mononuclear intermediates of type [(C^N)Pd(κ^1-Q)Cl].[54–62] There are known also several instances of application of this approach to bidentate diphosphine ligands[63–65] (P^P) with *neutral* binuclear complexes of type [{(C^N)PdCl}$_2$(μ-P^P)] as intermediates. Taking into account a rather tight bonding of soft phosphorus donor atom(s) with a soft palladium centre of a palladacycle, it would be hard to expect for these systems any decomplexation processes in the absence of serious steric hindrances.

Among the reports of processes of this latter kind only one example of diastereoselective decomposition on silica of cyclopalladated complex, namely, *CN*-palladacycle adduct with *Sb*,*Sb*-donor ligand *BINASb* resulting in isolation of enantiomerically enriched free distibine has been reported.[66] Such behaviour of the intermediate complex therewith formed may be attributed to both significant bulkiness of the distibine ligand based on the 1,1′-binaphthyl framework and weakened Sb→Pd bonding.[67,68] Unfortunately, the fate of chiral *CN*-palladacycle in the latter transformation has remained unknown, as well as the true structure of intermediate diastereomeric complexes (mono- or binuclear).

As evidence of the significant influence of steric hindrance on the stability of palladacycle derivatives, mention may be made of one more instance of diastereoselective decomposition of mononuclear adduct of *CN*-palladacycle with bulky diphosphine *Binap*.[69] However, this reaction occurs in solution (during very long storage of this complex in $CDCl_3$) without any sorbent participation, and results in *complete degradation* of chiral *CN*-palladacycle in one of two diastereomers to give the simple coordination compound [$PdCl_2${(S_{pl})-*Binap*}] as the final product.

Difference *in the thermodynamic stability* of two diastereomers in solution forms the basis for a valuable version of the processes of ligand resolution through the cyclopalladated intermediates, which may be named as

'method of half-equivalents'[70] in accordance with its requirement for using at least twofold excess of the substrate to be resolved. After the pioneering report of Otsuka et al.[71] this methodology of chiral recognition has found wide application for resolution of monodentate phosphines,[20,72–75] stibine,[61] and of diverse bidentate ligands of *P,N*-,[70] *N,N*-,[76] and *N,O*-type;[77] it also works efficiently in systems with configurationally labile *P*-,[78] *P,N*-[79] and *N,N*-donor substrates.[80–82]

However, it is noteworthy that the success in resolution by this method is really dependent on the combination of two factors: efficiency in chiral recognition and solubility difference between two diastereomeric intermediates at the final stage of reaction mixture treatment. In spite of excellent results achieved in this field,[61,70,72,83] several instances are known, when strong thermodynamic preference for one diastereomer found in solution cannot guarantee it being maintained on crystallization.[76,79] Perhaps, chromatographic separation of diastereoselective reaction products may be a more promising method taking into account the opportunity for preferential decomposition of the minor (less stable) diastereomer of intermediate complex.

4. Conclusion

Thus, we have elaborated a new approach to the palladacycle resolution based on diastereoselective removing of the auxiliary (*S*)-prolinate ligand from the intermediate mononuclear adduct resulting in the formation of the starting chloro-bridged dimer in enantiomerically enriched state. Complete conversion of one of two diastereomers of the (*S*)-prolinate derivative into dimeric complex may be achieved in the regime of its prolonged contact with the sorbent.

Several advantages of this methodology have to be mentioned: (i) chromatography does not lead to any significant loss of the total palladacycle amount (<4% under optimal conditions); (ii) this method offers an opportunity to isolate both diastereomers in pure form (including the isomer which may be inaccessible through their recrystallization); (iii) the best results may be achieved by means of this methodology combined with classical techniques commonly used for the separation of diastereomers of cyclopalladated compounds, namely recrystallization and chromatography; in this case the procedure of the separation of two diastereomers may be facilitated providing the optimal relation between their properties: solubility, chromatographic mobility and stability on the sorbent.

The new principle proposed here is of general practical significance for diastereomeric palladacycle separation in diverse processes. For example, it may be useful not only (i) for resolution of the racemic palladacycles, but also (ii) for removing of the minor diastereomer remaining after resolution of racemic substrates (capable to palladium coordination) by other methods, (iii) for enantiomeric purity increasing of the products of asymmetric C–H bond activation and (iv) for separation of complexes formed in diastereoselective cyclopalladation reactions connected with appearance of additional chirality elements.

5. Experimental

5.1. General

The ^{1}H and ^{31}P NMR spectra were recorded with a Varian VXR-400 spectrometer operating at the frequencies 400 and 161.9 MHz for ^{1}H and ^{31}P nuclei, respectively, using TMS as internal standard for protons and H_3PO_4 as an external reference for the ^{31}P nuclei. The assignment of signals was based on the homonuclear decoupling. Optical rotations were measured with a VNIEKI-Prodmush AI-EPO polarimeter in 0.25 and 1.0-dm cells at 20 °C in dichloromethane (*C* 0.4, CH_2Cl_2). Solvents and starting reagents were purified as described previously.[46] Racemic dimers di-μ-chlorobis[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*]dipalladium(II) **1**[46] and di-μ-chlorobis[2-(*tert*-butyl-*ortho*-tolylphosphine)- benzyl-*C*,*P*]dipalladium(II) **2**[17] were prepared by the known methods.

5.2. Racemic dimer 1 resolution

5.2.1. Chiral derivatizing. (R_C,S_CS_N/S_C,S_CS_N)-[2-{1-Amino-2,2-dimethylpropyl}phenyl-2*C*,*N*](prolinato-*N*,*O*)-palladium(II) 4a,b. A solution of a slight excess of potassium (*S*)-prolinate (0.2198 g, 1.578 mmol) in anhydrous MeOH (4 mL) was added to a suspension of racemic dimer **1** (0.4363 g, 0.7173 mmol) in the same solvent (8 mL) and the reaction mixture was stirred for 4 h at rt. The homogeneous solution was evaporated to dryness in vacuo, the residue was treated with water (25 mL) and extracted with dichloromethane (4 × 20 mL); the combined organic layers were dried over Na_2SO_4 and evaporated to dryness in vacuo, to give diastereomeric complexes **4a**,**b** mixture as a colourless amorphous powder in the yield of 92% (0.5052 g, 1.320 mmol). For (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** diastereomers R_f 0.28 and 0.16 (Silufol, dichloromethane/methanol mixture in 10:1 ratio), respectively; mp (dec) 200–202 °C; $[\alpha]_D^{20} = +122.5$. Anal. Calcd for $C_{16}H_{24}N_2PdO_2 \cdot 0.5CH_2Cl_2$: C, 46.6; H, 5.93; N, 6.59%. Found: C, 46.70; H, 5.93; N, 6.52%.

^{1}H NMR ($CDCl_3$, δ, ppm, Hz): for (R_C,S_CS_N)-**4a**: 1.086 (s, 9H, ^{t}Bu), 3.896 (d, 1H, $^3J_{H^{\alpha}CNH}$ 6.0, α-CH), 3.210 (m, 1H, NH^1), 5.407 (dd, 1H, $^2J_{HNH}$ 10.5, $^3J_{HN^{\alpha}CH}$ 6.0, NH^2), 6.753 (d, 1H, $^3J_{HH}$ 7.5, C^{6}H), 6.874 (dt, 1H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 2.2, C^{5}H), 6.880–7.05 (m, 2H, C^{3}H and C^{4}H); signals of (*S*)-prolinate ligand: 1.280 (m, 1H, β′-H), 1.490 (m, 1H, β′-H), 1.880–2.14 (m, 5H,[§] 2β-H), 3.669 (m, 1H, NH), 2.975 (m, 1H, α′-H), 3.287 (m, 1H, α′-H), 3.990 (m, 1H, α-CH): for (S_C,S_CS_N)-**4b**: 1.120 (s, 9H, ^{t}Bu), 3.721 (d, 1H, $^3J_{H^{\alpha}CNH}$ 5.5, α-CH), 3.423 (br d, 1H, $^2J_{HNH}$ 10.6, NH^1), 4.942 (br m, 1H,

[§] Signals of β-CH_2-protons of both diastereomers and β′-CH proton of diastereomer (S_C,S_CS_N)-**4b** are overlapped.

NH^2), protons of palladated Ph-ring are present by series of overlapped multiplets at 6.89–7.1; signals of (*S*)-prolinate ligand: 1.608 (m, 1H, β′-H), 1.880–2.14 (m, 5H,§ β′-H and 2β-H), 2.581 (m, 1H, α′-H); signals of α′-H, NH and α-CH protons are hidden under other signals.

5.2.2. Diastereomeric (*S*)-prolinate complexes 4a,b separation

5.2.2.1. Method 1—recrystallization. The mixture of diastereomeric complexes **4a**,**b** in 1:1 ratio (0.1080 g, 0.282 mmol, $[\alpha]_D^{20} = +122.5$) was dissolved in dichloromethane (5 mL) and treated with hexane up to the dimness. After storage at the temperature −13 °C during 4 days the precipitate formed was filtered and washed with hexane to give diastereomer (R_C,S_CS_N)-**4a** in a yield of 39.5% (0.0427 g, 0.1115 mmol) and isomeric purity of >98% de (^{1}H NMR data). The mother liquor remained was evaporated to dryness, the residue was dissolved in benzene (5 mL) and treated with hexane up to the slight cloudiness; after storage at the temperature +8 °C during 2 days the precipitate formed was filtered to give isomer mixture enriched with diastereomer (S_C,S_CS_N)-**4b** in a yield of 17.4% (0.0188 g, 0.0491 mmol) and isomeric composition of 64% de (estimated from the specific rotation value, $[\alpha]_D = +160$). The second mother liquor remained (0.0385 g, 0.1005 mmol, 35.6%) was enriched with the same diastereomer **4b** at more high extent (79.7% de(S_c) according to the specific rotation value, $[\alpha]_D = +169$); however, attempts to further recrystallization of this mixture have failed.

5.2.2.2. Method 2a—chromatography. (i) Equimolar mixture of two diastereomers, (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** (0.1080 g, 0.282 mmol), was eluted through *flash*-column (*d* 1.3 cm, *h* 13 cm, eluents are mixtures of dichloromethane and methanol of increasing polarity, in ratios from 100:1 to 5:1). Following complexes were isolated: dimer (R_C,R_C)-**1a** (0.0096 g, 0.0314 mmol) of enantiomeric purity of 56% ee and two diastereomers of (*S*)-prolinate complex, (R_C,S_CS_N)-**4a** (0.0237 g, 0.0619 mmol, yield of 21.9%, diastereomeric purity >98% de) and (S_C,S_CS_N)-**4b** (0.0667 g, 0.1742 mmol, yield of 61.8%, diastereomeric composition of 48.7% de). After additional chromatographic separation of the latter diastereomer (S_C,S_CS_N)-**4b** on the *flash*-column (*d* 0.7 cm, *h* 13 cm, eluents are the same), following complexes were isolated: dimer (R_C,R_C)-**1a** (0.0033 g, 0.0108 mmol) of enantiomeric purity 63.4% ee (from the optical rotation value $[\alpha]_D = -92.6$) and two diastereomers of (*S*)-prolinate complex, (R_C,S_CS_N)-**4a** (0.0113 g, 0.0295 mmol, yield of 10.4%) and (S_C,S_CS_N)-**4b** (0.0461 g, 0.1204 mmol, yield of 42.6%) possessing complete diastereomeric purity (>98% de, ^{1}H NMR data). Total yield of individual diastereomers (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** was 32.3 and 42.6%, respectively.

5.2.2.3. Method 2b—time-modified version. The suspension of SiO_2 (1.23 g) in the solution of equimolar mixture of two diastereomers of (*S*)-prolinate complex, (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** (0.0603 g, 0.1575 mmol) in dichloromethane (2 mL) was stored during 23 days. Then solvent was evaporated in vacuo, and silica containing complexes absorbed was placed on the top part of the *flash*-column (*h* 10 cm, *d* 1.2 cm) and chromatographic separation was performed according method 2a. Only two complexes were isolated: dimer (R_C,R_C)-**1a** (0.0301 g, 0.0990 mmol; yield of 63%, enantiomeric purity of 59% ee according ^{1}H NMR data), and one individual diastereomer of the (*S*)-prolinate derivative, (S_C,S_CS_N)-**4b** (0.0205 g, 0.0535 mmol, yield of 34%; diastereomeric purity of >98% de according ^{1}H NMR data).

5.2.2.4. Method 3—combined approach. Equimolar mixture of two diastereomers of (*S*)-prolinate complex, (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** (0.3000 g, 0.7836 mmol) was dissolved in minimum volume of dichloromethane and treated with hexane up to the slight cloudiness. After 2 days at +8 °C the precipitation containing pure diastereomer (R_C,S_CS_N)-**4a** (0.0351 g, 0.0916 mmol) was filtered; an additional portion of the same diastereomer (0.0474 g, 0.1238 mmol) of the same purity was isolated from recrystallization of the mother liquor. After twofold recrystallization isomer (R_C,S_CS_N)-**4a** was isolated in a total yield of 27.5% (0.0825 g, 0.2155 mmol) and diastereomeric purity of >98% de (1H NMR data); The diastereomer mixture from the mother liquor was divided into two fractions by means of an additional recrystallization: (i) a precipitation obtained in a yield of 29.3% (0.0880 g, 0.2298 mmol) of the composition nearly close to the pseudo-racemate—14.5% de (*SC*,*SCSN*), and (ii) a mother liquor containing 39.2% of (*S*)-prolinate complex **4b** (0.1176 g, 0.3072 mmol) of more high enrichment extent—53.8% de (S_C,S_CS_N). These two fractions were separately subjected to the chromatographic separation under the conditions of method 2. Column chromatography (*h* 13 cm, *d* 1.2 cm) of the first fraction gives dimer (R_C,R_C)-**1a** of enantiomeric composition of 64% ee in a yield of 3.1% (0.0146 g, 0.024 mmol), and both isomers of (*S*)-prolinate complex, (R_C,S_CS_N)-**4a** (0.0266 g, 0.0694 mmol) and (S_C,S_CS_N)-**4b** (0.0424 g, 0.1107 mmol) in diastereomerically pure state (>98% de) in the yields of 8.9% and 14.1%, respectively. Similar treatment of the second fraction (for column *h* 16 cm, *d* 1.2 cm) results in the isolation of the dimer (R_C,R_C)-**1a** (0.039 g, 0.102 mmol) of low enrichment extent (24.7% ee) in a yield of 13% and only one diastereomer of (*S*)-prolinate complex, (S_C,S_CS_N)-**4b** (0.0887 g, 0.2317 mmol) in diastereomerically pure form (>98% de). Total yields of dimer (R_C,R_C)-**1a** (of enantiomeric composition from 25% to 64%) and diastereomerically pure (*S*)-prolinate complexes, (R_C,S_CS_N)-**4a** and (S_C,S_CS_N)-**4b** were equal 16.1%, 36.4% and 43.7%, respectively; the loss of palladacycle did not exceed 1%.

(R_C,S_CS_N)-[2-{1-Amino-2,2-dimethylpropyl} phenyl-2*C*,*N*](prolinato-*N*,*O*)palladium(II), (R_C,S_CS_N)-**4a**. Mp (dec) 196–198 °C; R_f 0.28 (dichloromethane/methanol 10:1); $[\alpha]_D^{20} = +64$. Anal. Calcd for $C_{16}H_{24}N_2PdO_2 \cdot 1.5CH_2Cl_2$: C, 41.2; H, 5.33; N, 5.49. Found: C, 40.79; H, 5.71; N, 5.60.

^{1}H NMR ($CDCl_3$, δ, ppm, Hz): 1.080 (s, 9H, ^{t}Bu), 3.921 (d, 1H, $^3J_{H^{\alpha}CNH}$ 6.0, α-CH), 3.117 (d, 1H, $^2J_{HNH}$ 10.6, NH^1), 5.587 (dd, 1H, $^2J_{HNH}$ 10.6, $^3J_{HN^{\alpha}CH}$ 6.0, NH^2), 6.722 (d, 1H, $^3J_{HH}$ 7.5, C^6H), 6.864 (dt, 1H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 2.2, C^5H), 6.880–6.970 (m, 2H, C^3H and C^4H); signals of (*S*)-prolinate ligand: 1.247 (m, 1H, β′-H), 1.357 (m, 1H, β′-H), 1.850 (m, 1H, β-H), 1.930 (m, 1H, β-H), 3.469 (m, 1H, NH), 2.948 (m, 1H, α′-H), 3.256 (m, 1H, α′-H), 3.974 (m, 1H, α-CH).

(S_C,$S_C S_N$)-[2-{1-Amino-2,2-dimethylpropyl}phenyl-2*C*,*N*]-(prolinato-*N*,*O*)palladium(II), (S_C,$S_C S_N$)-**4b**. Mp (dec) 205–207 °C, R_f 0.16 (dichloromethane/methanol 10:1); $[\alpha]_D^{20} = +181$. Anal. Calcd for $C_{16}H_{24}N_2PdO_2 \cdot 0.25CH_2Cl_2$: C, 48.31; H, 6.11; N, 6.93. Found: C, 48.08; H, 6.27; N, 6.51.

^{1}H NMR ($CDCl_3$, δ, ppm, Hz): 1.133 (s, 9H, ^{t}Bu), 3.819 (d, 1H, $^3J_{H^{\alpha}CNH}$ 5.5, α-CH), 3.343 (d, 1H, $^2J_{HH}$ 10.6, NH^1), 5.182 (dd, 1H, $^2J_{HNH}$ 10.6, $^3J_{HN^{\alpha}CH}$ 5.5, NH^2), protons of palladated Ph-ring are present by series of overlapped multiplets at 6.9–7.1; signals of (*S*)-prolinate ligand: 1.602 (m, 1H, β′-H), 1.880–2.120 (m, 3H, β′-H and 2β-H), 2.670 (m, 1H, α′-H), 3.000-3.190 (m, 2H, α′-H and NH), 3.242 (m, 1H, α-CH).

5.2.3. Isolation of enantiopure dimeric complexes ($R_C R_C$)-1a and ($S_C S_C$)-1b. ($R_C R_C$)-Di-μ-chlorobis[2-{1-amino-2,2-dimethylpropyl} phenyl-2*C*,*N*]dipalladium(II), ($R_C R_C$)-**1a**. The solution of diastereomerically pure (*S*)-prolinate complex (R_C,$S_C S_N$)-**2a** (0.150 g, 0.3918 mmol) in dichloromethane (10 mL) was treated with diluted (1 M) aqueous solution of HCl (2 × 10 mL) under vigorous shaking under TLC-control. The combined organic layers were washed with water (2 × 5 mL), dried over Na_2SO_4 and concentrated in vacuo to dryness. The residue was dried in vacuo (10^{-2} mmHg) over P_2O_5 to give dimer ($R_C R_C$)-**1a** as amorphous light-yellow powder in a yield of 89% (0.1061 g, 0.1743 mmol) and of >98% ee. Mp (dec) 217–219 °C; $[\alpha]_D^{20} = -146$ (*c* 0.4, dichloromethane/pyridine); R_f 0.44 (benzene/acetone 7:1).

($S_C S_C$)-Di-μ-chlorobis[2-{1-amino-2,2-dimethylpropyl} phenyl-2*C*,*N*]dipalladium(II), ($S_C S_C$)-**1b** was isolated by the same way from the individual diastereomer (S_C,$S_C S_N$)-**2b** (0.1500 g, 0.3918 mmol) in a yield of 92% (0.1096 g, 0.1802 mmol) and of >98% ee. Mp (dec) 217–219 °C; $[\alpha]_D^{20} = +146$ (0.4, dichloromethane/pyridine); R_f 0.44 (benzene/acetone 7:1).

5.2.4. Partial resolution of racemic dimer 2. Equimolar mixture of two diastereomers, (R_P,$S_C S_N$)-**3a** and (S_P,$S_C S_N$)-**3b**[17] (0.1850 g, 0.3776 mmol), was eluted through *flash*-column (*d* 1.5 cm, *h* 20 cm, eluents are mixtures of dichloromethane and ethanol of increasing polarity, in ratios from 30:1 to 5:1). Following complexes were isolated: dimer (S_P,S_P)-**2b** (0.0201 g, 0.0488 mmol, yield 12.9%) of enantiomeric purity of 68% ee and its (*S*)-prolinate derivative (R_P,$S_C S_N$)-**3a** (0.1503 g, 0.3068 mmol, yield 81.3%). After additional twofold chromatography of the latter complex (R_P,$S_C S_N$)-**3a** on the *flash*-column (*d* 2.5 cm, *h* 15 cm, eluents are the same), following complexes were isolated: dimer (S_P,S_P)-**2b** (0.0550 g, 0.1337 mmol, yield 35.4%) of enantiomeric purity 37–45% ee and diastereomer (R_P,$S_C S_N$)-**3a** (0.0682 g, 0.1392 mmol, yield 36.9%) of diastereomeric purity 43% de.

Enantiomeric purity of dimer **2** and diastereomeric composition of intermediate (*S*)-prolinate derivative **3a**,**b** were determined by means of ^{31}P NMR spectroscopy (for dimer after its chiral derivatizing with (*S*)-prolinate in situ) as described previously.[84]

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