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New approach to chiral phosphapalladacycles: first optically active phosphinite PC-palladacycle with non-metallocenic planar chirality

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ABSTRACT

A new proposed methodology for the preparation of phosphapalladacycles in enantiopure form includes the use of the same optically active cyclopalladated CN-reagent for both resolution of a racemic ligand and subsequent direct C–H bond activation of the enantiopure ligand via the cyclopalladated ligand exchange reaction. This protocol was successfully employed for the preparation of the complex, which is both the first PC-palladacycle with a non-metallocenic planar chirality based on the [2.2]paracyclophane framework and the first representative of chiral phosphinite PC-palladacycles.

1. Introduction

Several routes to optically active PC-palladacycles are known: (i) direct cyclopalladation of optically active P-donor ligands,[1–3] including the case when new chirality elements would appear in the resulting complex;[4,5] (ii) resolution of racemic PC-palladacycles using an optically active auxiliary ligand (usually (*S*)-prolinate);[6–8] and (iii) asymmetric cyclopalladation of prochiral P-ligands via transcyclopalladation (also known as the cyclopalladated ligand exchange reaction) using enantiopure cyclopalladated reagents.[9,10] The pronounced oxidative instability of the majority of P-donor ligands has necessitated the search for new routes to enantiopure PC-palladacycles, which would exclude the isolation of the free ligand at the intermediate steps. The aim of this work was the development of a new strategy fitting this requirement. For the targeted cyclopalladated complex (CPC), we chose a phosphinite PC-palladacycle with planar chirality based upon the [2.2]paracyclophane skeleton. To the best of our knowledge, optically active CPCs bearing the *phosphinite* P-donor atom have not been reported, although achiral phosphinite PC-complexes have been widely studied.[11–14] It should be noted that despite a wide application of coordination compounds with [2.2]paracyclophane-derived ligands (e.g., PhanePhos[15]) in asymmetric catalysis,[16] so far only two regioisomeric CN-palladacycles with such a framework have been described[17] while PC-palladacycles of this type have remained unknown.

2. Results and discussion

The starting phosphinite ligand **HL** was prepared by phosphorylation of the corresponding racemic phenol,[11,12,18] and was characterized by ^{1}H and ^{31}P NMR spectroscopy. It should be noted that the (*R*)-enantiomer of this phosphinite has recently been prepared[19] from the corresponding pre-resolved phenol. Cyclopalladation of ligand **HL** was performed using palladium(II) chloride[11,12] to give the cyclopalladated dimer *rac*-**1** in a yield of 37%[20] (Scheme 1).

For subsequent spectroscopic evaluation of regiochemistry of phosphinite **HL** cyclopalladation, dimer *rac*-**1** was transformed into its mononuclear derivative *rac*-**2** via chloride bridge cleavage by the auxiliary triphenylphosphine ligand[21] (Scheme 2).

Unfortunately, coordination of the auxiliary phosphane ligand occurred with a rather low selectivity with the formation of both *trans*-(*P*,*P*)-**2a** and *cis*-(*P*,*P*)-**2b** isomers in ca. 10:1 ratio. The geometry of these isomers was deduced from the $^{2}J_{PP}$ values of 454 and 28 Hz for the major and minor species, respectively.[22] Such an observation is in complete accordance with the known properties of phosphapalladacycles caused by similar structural *trans*-influences of their C- and P-donor atoms.[23] The activation of the (sp^{2})C^{5}–H bond of the [2.2]paracyclophane moiety was established by ^{1}H NMR spectroscopy: the signal of the aromatic C^{5}–H proton disappeared in the spectrum of adduct **2a**, while the (sp^{3})C–H^{2s} signal remained intact.[21]

For the preparation of the enantiopure phosphinite PC-palladacycle, a new strategy was developed based on combining two known approaches, namely the use of a chiral CN-palladacycle as both the resolving and metallating agents. This protocol includes two steps: (i) the in situ monodentate coordination of the racemic

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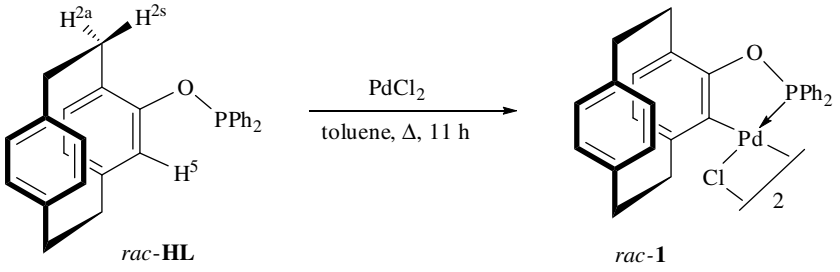
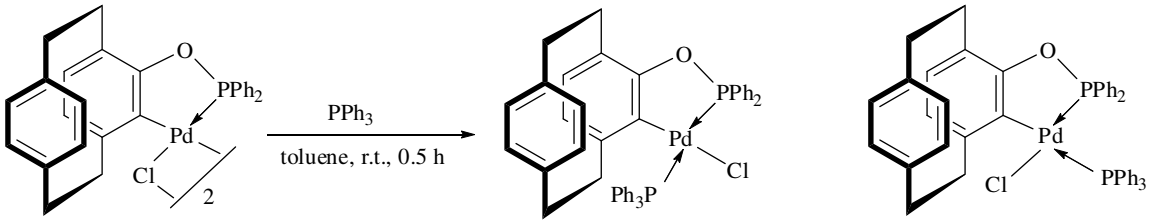


rac-**HL** *rac*-**1**

Scheme 1.



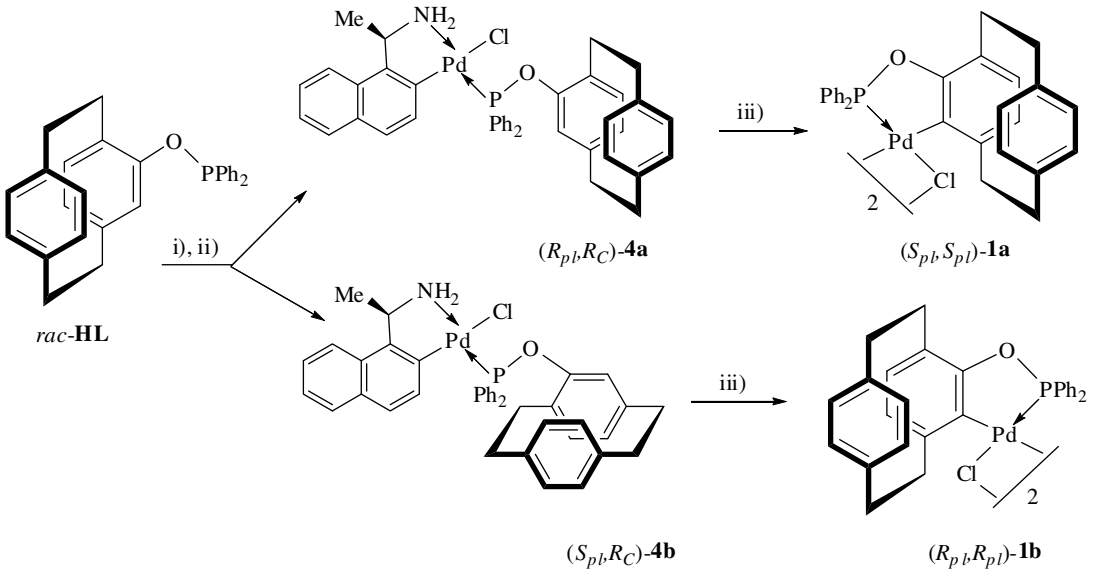
rac-**1** *trans*-(*P*,*P*)-**2a** *cis*-(*P*,*P*)-**2b**

Scheme 2.

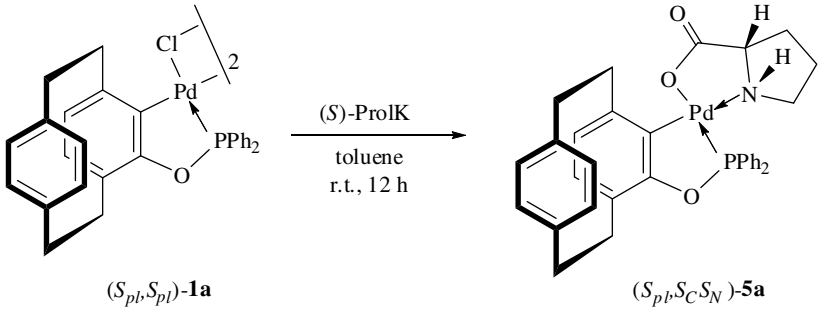
ligand **HL** with an enantiopure CN-matrix with subsequent separation of the two diastereomeric mononuclear adducts formed and (ii) thermal intramolecular C–H bond activation of each of these diastereomers via cyclopalladated ligand exchange. This idea was conceived when we discovered[9,10] that mononuclear CPCs of the general type (η^2-C⌒N)PdX(κ^1-HC⌒P) are intermediates in the transcyclopalladation process. We suggested that thermolysis of such intermediate adducts has to initiate the intramolecular activation of the C–H bond of the monodentate P-coordinated ligand resulting in the formation of the target PC-palladacycle.

The cyclopalladated CN-dimer (*R*,*R*)-**3**[24,25] derived from commercially available primary 1-(1-naphthyl)ethylamine was selected as the reagent for two major reasons. Firstly, the conformational stability of this CN-palladacycle assured its high efficiency in the chiral recognition required in the first step. Secondly, the presence of the primary amino group was expected to increase the reagent's activity in the transcyclopalladation step.[9,10] A mixture of two diastereomeric derivatives **4a** and **4b** generated in situ by reacting the racemic phosphinite **HL** with dimer (*R*,*R*)-**3** was separated efficiently using column chromatography to give both isomers, (R_{pl},R_C)-**4a** and (S_{pl},R_C)-**4b**, in diastereomerically pure form (>98% *de*, ^{31}P NMR data) in yields of 77% and 85%, respectively[26] (Scheme 3).

The final step of transcyclopalladation was performed in toluene in the presence of glacial acetic acid, promoting this process.[27,28] Heating of each of the diastereomers, (R_{pl},R_C)-**4a** and (S_{pl},R_C)-**4b**, under these conditions afforded two enantiomers of the target dimeric CPC, (S_{pl},S_{pl})-**1a** and (R_{pl},R_{pl})-**1b**, in yields of ca. 50%.[29] The enantiomeric purity of the obtained CPCs was evident from the presence of only two ^{31}P NMR signals, δ 151.8 and



Scheme 3. Reagents and conditions: (i) (R_C,R_C)-**3**, toluene, 2 h; (ii) column chromatography on SiO_2; (iii) toluene/AcOH 10:1, Δ, 1.5 h.



(S_{pl},S_{pl})-**1a** $(S_{pl},S_C S_N)$-**5a**

Scheme 4.

153.7 ppm, corresponding to the *syn*- and *anti*-forms of the dimeric complexes, compared to four signals in the ^{31}P NMR spectrum of the racemic dimer **1**.[20] These data allowed us to assign two other signals, δ 151.3 and 152.6 ppm, in the spectrum of the racemic dimer **1** to the *syn*- and *anti*-isomers of the *meso* form of the dimer, (R_{pl},S_{pl})-**1**.

Unfortunately, our attempts to estimate the absolute configuration of phosphinite **HL** in the complexes (R_{pl},R_C)-**4a** and (S_{pl},R_C)-**4b** using the NOE technique with the CN-palladacycle (*R*,*R*)-**3** as a reference point were unsuccessful, probably due to the high rotameric mobility of the monodentate coordinated ligand **HL**. Attempts to prepare crystalline samples of enantiopure dimers (S_{pl},S_{pl})-**1a** and (R_{pl},R_{pl})-**1b** have also failed. To determine the absolute configuration of the new palladacycle, dimer (S_{pl},S_{pl})-**1a** was converted into its (*S*)-prolinate derivative $(S_{pl},S_C S_N)$-**5a** via chloride bridge cleavage[30] (Scheme 4).

The presence of one singlet in the ^{31}P NMR spectrum of $(S_{pl},S_C S_N)$-**5a** provided one more piece of evidence in favour of the complete enantiomeric purity of the starting dimer (S_{pl},S_{pl})-**1a** (within the accuracy of the NMR spectroscopy). It is intriguing that, according to the ^{31}P NMR data,[31] the other diastereomer of (*S*)-prolinate derivative $(R_{pl},S_C S_N)$-**5b** exists in solution as a mixture of two geometric isomers of *trans*(*N*,*C*) and *cis*(*N*,*C*) configurations.

The most conclusive evidence for the *ortho*-palladated structure of the new *PC*-palladacycle was obtained from the X-ray diffraction study of the (*S*)-prolinate derivative $(S_{pl},S_C S_N)$-**5a**[32] (Fig. 1). Both the (S_{pl})-configuration of the 4,5-disubstituted [2.2]paracyclophane moiety and the *trans*(*N*,*C*)-geometry of the coordination sphere are unambiguous. The palladium atom exhibits the square planar coordination environment with a slight distortion; the palladacycle's conformation can be described as a slightly distorted envelope with the palladium atom displaced from the plane of the remaining four atoms by 0.345(6) Å.

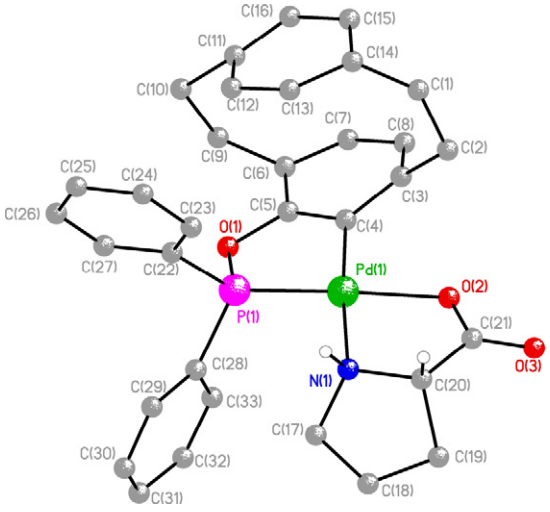


Figure 1. Molecular structure and numbering scheme for the complex $(S_{pl},S_C S_N)$-**5a**.

3. Conclusions

A new protocol for the preparation of enantiopure PC-palladacycles has been developed. The use of the optically active CN-matrix as both resolving and metallating agents allowed us to avoid the isolation of the intermediate, a readily oxidizable P-ligand. This approach was demonstrated by the preparation of the first enantiopure PC-palladacycle with non-metallocenic planar chirality based on the [2.2]paracyclophane framework; this complex is also the first representative of chiral phosphinite PC-palladacycles. Its absolute configuration was determined by the X-ray diffraction study of the (*S*)-prolinate derivative of the (S_{pl},S_{pl})-dimer.

Acknowledgements

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20. Cyclopalladation of phosphinite **HL**: A suspension of $PdCl_2$ (0.110 mmol) in a solution of the ligand **HL** (0.110 mmol) in anhydrous toluene (5 mL) was refluxed for 9 h. After removing Pd-black, the reaction mixture was concentrated in vacuo and the residue was purified using flash column chromatography (*h* 15 cm, *d* 1.1 cm, eluent $CHCl_3$), and was recrystallized to afford dimer *rac*-**1** in a yield of 37% as a yellow amorphous powder: mp (dec.) 227–230 °C, R_f 0.54 (Silufol, $CHCl_3$). Anal. Calcd for $C_{56}H_{48}Cl_2O_2P_2Pd_2$: C, 61.22; H, 4.40. Found: C, 60.88; H, 4.22. ^{31}P NMR ($CDCl_3$): δ 151.3 (s), 151.9 (s), 152.6 (s), 153.5 (s).
21. Preparation of phosphine adduct **2**: A solution of PPh_3 (0.0178 mmol) and dimer *rac*-**1** (0.0089 mmol) in toluene (8 mL) was stirred at rt for 50 min and concentrated in vacuo. The addition of hexane afforded complex *rac*-**2** in a yield of 71% as a yellow amorphous powder: mp (dec.) 213–214 °C, R_f 0.13 ($CHCl_3$). Anal. Calcd for $C_{46}H_{39}ClOP_2Pd$: C, 68.07; H, 4.84. Found: C, 68.39; H, 4.69. ^{31}P NMR ($CDCl_3$): for *trans*(*P*,*P*)-**2a**: δ149.5 (d) and 21.5 (d), $^2J_{PP}$ 453.8; for *cis*(*P*,*P*)-**2b**: δ 155.4 (d) and 16.7 (d), $^2J_{PP}$ 27.7. ^{1}H NMR ($CDCl_3$) for major isomer *trans*(*P*,*P*)-**2a**: aromatic protons of [2.2]paracyclophane framework: δ 5.53 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.6, H^{13}), 5.67 (d, 1H, $^3J_{HH}$ 7.6, H^7), 6.01 (dd, 1H, $^3J_{HH}$ 7.6, $^5J_{HP}$ 1.2, H^8), 6.33 (dd, 1H, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.6, H^{12}), 6.37 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.6, H^{15}), 6.43 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.6, H^{16}); methylene protons of [2.2]paracyclophane framework: δ 2.03 (ddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.5, $^3J_{HH}$ 4.5, H^{9a}), 2.69 (ddd, 1H, $^2J_{HH}$ 13.3, $^3J_{HH}$ 11.7, $^3J_{HH}$ 3.0, H^{2a}), 2.80–2.87 (m, 3H, H^{1a}, H^{1s}, H^{10a}), 2.93 (dddd, 1H, $^2J_{HH}$ 13.2, $^3J_{HH}$ 10.2, $^3J_{HH}$ 3.5, H^{9s}, $^5J_{HP}$ 2.1), 3.06 (ddd, 1H, $^2J_{HH}$ 12.8, $^3J_{HH}$ 10.2, $^3J_{HH}$ 4.5, H^{10s}), 3.35 (ddd, 1H, $^2J_{HH}$ 13.3, $^3J_{HH}$ 12.0, $^3J_{HH}$ 2.3, H^{2s}); protons of the $OPPh_2$ group and PPh_3 ligand: δ 7.16–7.19 (m, 6H, *m*-PPh_3), 7.31–7.35 (m, 3H, *p*-PPh_3), 7.40–7.44 (m, 8H, *o*-PPh_3, *m*′-$OPPh_2$), 7.49–7.51 (m, 1H, *p*′-$OPPh_2$), 7.63 (m, 3H, H_m, H_p $OPPh_2$-group), 7.80–7.85 (m, 2H, $^3J_{HP}$ 11.7,$H_{o'}$ of $OPPh_2$-group), 8.44–8.49 (m, 2H, $^3J_{HP}$ 12.2, H_o $OPPh_2$).
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26. For diastereomer $(-)_D$-(R_{pl}, R_C)-**4a**: mp (dec.) 160–162 °C, R_f 0.4 (diethyl ether), $[\alpha]_D^{24} = -36.7$ (*c* 1.2, CH_2Cl_2); ^{31}P NMR ($CDCl_3$): δ 121.5 (s). For diastereomer $(+)_D$-(S_{pl},R_C)-**4b**: mp (dec.) 165–167 °C; R_f 0.33 (diethyl ether); $[\alpha]_D^{24} = +21.7$ (*c* 1.2, CH_2Cl_2); ^{31}P NMR ($CDCl_3$): δ 125.1 (s).
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29. For (S_{pl},S_{pl})-**1a**: mp (dec.) 225–228 °C, R_f 0.62 (toluene), $[\alpha]_D^{25} = +166$ (*c* 0.676, CH_2Cl_2). Anal. Calcd for $C_{56}H_{48}Cl_2O_2P_2Pd_2$: C, 61.22; H, 4.40. Found: C, 61.38; H, 4.28. ^{31}P NMR ($CDCl_3$): δ 151.8 (s), 153.5 (s). For (R_{pl},R_{pl})-**1b**: mp (dec.) 245–250 °C, R_f 0.62 (toluene), $[\alpha]_D^{25} = -163$ (*c* 0.65, CH_2Cl_2). Anal. Calcd for $C_{56}H_{48}Cl_2O_2P_2Pd_2{\cdot}0.5CH_2Cl_2$: C, 58.94; H, 4.21. Found: C, 58.97; H, 4.17. ^{31}P NMR ($CDCl_3$): δ 151.8 (s), 153.5 (s).
30. Prolinate derivative (S_{pl},S_C,S_N)-**5a** preparation: A suspension of dimer (S_{pl},S_{pl})-**1a** (0.0248 mmol) and potassium (*S*)-prolinate (0.0497 mmol) in toluene (10 mL) was stirred for 12 h at rt, evaporated to dryness, dissolved in CH_2Cl_2 and washed with water. After recrystallization from dichloromethane–hexane, adduct **5a** was obtained in a yield of 72% as colourless crystals: mp (dec) 215–216 °C; $[\alpha]_D^{20} = +245$ (*c* 0.47, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 151.58 ppm (s).
31. Diastereomer (R_{pl},S_C,S_N)-**5b** was generated in situ in a similar way;[30] ^{31}P NMR ($CDCl_3$): δ 149.0 (s) and 150.2 (s) in ca. 62:38 ratio, respectively.
32. Crystals of (S_{pl},S_C,S_N)-**5a** ($C_{33}H_{32}NO_3PPd$, FW = 627.97) are orthorhombic, space group $P2_12_12_1$ at 298 K, a = 8.8866(11), b = 16.926(2), c = 18.882(2) Å, V = 2840.2(6) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.469 g cm^{-3}, μ(MoKα) = 7.45 cm^{-1}. Intensities of 34,589 reflection were measured with SMART APEX II CCD (λ(MoKα) = 0.71072 Å, $2\theta < 58°$) and 7553 independent reflections (R_{int} = 0.0254) 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 analysis of Fourier density synthesis has revealed that C(10) atom of ethylene bridge and C(17)–C(19) atoms of the five-membered ring are disordered by two positions with equal occupancies. These disordered fragments were refined in the isotropic approximation. The positions of the hydrogen atom were calculated from geometrical point of view. The refinement converged to wR_2 = 0.1068 and GOF = 1.020 for all independent reflections (R_1 = 0.0441 was calculated against F for 5914 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0. 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 687646. 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).