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Homochiral cyclopalladated complexes of (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline. X-ray study of (*S*,*S*)-di-μ-chlorobis-{2-[2-(4-*tert*-butyl)oxazolinyl]phenyl-*C*,*N*}dipalladium(II)

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Abstract

Due to steric promotion of C–H bond activation, the direct *ortho*-palladation of (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline using $Pd(OAc)_2$ in AcOH provided (*S*,*S*)-di-μ-acetatobis-[2-(2-(4-*tert*-butyl)oxazolinyl)phenyl-*C*,*N*]dipalladium(II) (**2**) in an excellent yield. This complex was converted into its corresponding μ-chloro analog (**3**) using LiCl in acetone. Dimer **3** reacted with PPh_3 to furnish the phosphane mononuclear derivative **4**. The structure of the dimer complex **3** was confirmed by X-ray diffraction analysis.

Keywords: Homochiral cyclopalladated complexes; Steric promotion of C–H bond activation; (*S*)-4-*tert*-Butyl-2-phenyl-2-oxazoline; X-ray study

1. Introduction

Recently, homochiral cyclopalladated complexes (CPCs) have attracted a great deal of attention due to the variety of their applications. In particular, they have been used for resolution of different substrates possessing ligand properties (e.g. various types of phosphines and amines) [1–6]. Palladacycles have also been utilized as chiral derivatizing agents for enantiomeric purity determination [7–10] and as reference compounds for the evaluation of absolute configuration by X-ray crystallography [3,11], CD [12] or NMR [3,13,14] spectroscopy. Homochiral CPCs are promising enantioselective catalysts [15–19] and chiral matrices in asymmetric synthesis [20]. The majority of known homochiral CPCs are based on α-arylalkylamines [1–9,18,20,21]. It is therefore important to develop new homochiral CPCs (i) with high chiral recognition abilities and (ii) which are easily obtainable from simple precursors. Homochiral oxazolines have attracted our attention because a variety of oxazoline-based metal coordination complexes are known to exhibit high efficiency in stereoselection processes [22]. Also, these ligands can be easily synthesized from commercially available and not very expensive α-amino acid derivatives [23,24]. In contrast to the numerous known coordination complexes of oxazolines [25], the number of their cyclopalladated derivatives remains limited [26,27]. Following our interest in the use of the oxazolinyl group as a chirality inductor in the palladacycle framework, we synthesized and characterized homochiral CPCs of readily available (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline. The results of this study are reported herein.

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2. Results and discussion

2.1. Preparation of cyclopalladated complexes

The ligand, (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline (**1**), was synthesized in a high yield from benzonitrile and commercially available (*S*)-(+)-2-amino-3,3-dimethyl-1-butanol using a known procedure [28] (Scheme 1).

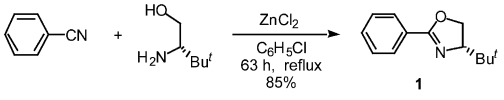
It has been reported that bulky substituents in a ligand facilitate direct cyclopalladation [21,29,30]. In accordance with these reports, the reaction of **1** with $Pd(OAc)_2$ took place much faster than had previously been reported for 2-phenyl-2-oxazoline with no substituents on the heterocycle [26] (Scheme 2). The complex formed (**2**) was unstable and was converted to the corresponding Cl-bridged dimer (**3**) using LiCl in acetone (Scheme 2).

We have also attempted to obtain complex **3** using the ligand exchange reaction [31,32] of **1** with a dimeric *ortho*-palladated complex of *N*,*N*-dimethylbenzylamine. This method was found to be advantageous for the preparation of the dimeric CPC of 2-phenyl-2-oxazoline [26]. Unfortunately, in the case of **1**, this approach was unsuccessful.

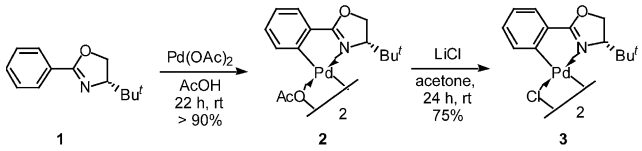
Cyclopalladated dimer **3** was converted into its adduct **4** by reaction with PPh_3 (Scheme 3). Such palladacycle mononuclear derivatives are more suitable for spectral studies.

2.2. Spectral characterization of complexes

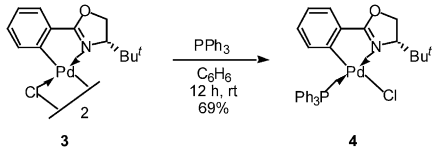
The presence of the Pd–C bond in all the complexes was supported by IR and NMR data. As expected for disubstituted arenes, including *ortho*-palladated compounds, the region of out-of-plane bending vibrations of aromatic C–H bonds in the IR spectra of complexes **2** and **3** contained only one strong absorption band at 734 and 728 cm^{-1}, respectively, compared to two bands at 694 and 779 cm^{-1} for the ligand. In the ^{1}H-NMR spectra of **2** and **3**, the aromatic region had integral intensities corresponding to disubstituted benzene moieties. According to the analysis of ^{13}C-NMR and DEPT data, complexes **2** and **3** have two quaternary aromatic carbons, whereas phosphane adduct **4** has three. The signals at δ 147.7, 145.3, and 151.3 in the spectra of **2**, **3** and **4**, respectively, were assigned to the C atom bonded to the Pd atom based on (i) previously reported data [26] for other oxazoline-derived CPCs and (ii) comparison with the ^{13}C-NMR spectrum of the ligand.



Scheme 1.



Scheme 2.



Scheme 3.

The ^{13}C-NMR spectra of dimeric complexes **2** and **3** contained only one set of signals. These data suggested that the compounds exist in $CDCl_3$ solutions as a single geometrical isomer. The presence of only one signal for OAc groups (δ 2.11 ppm) in the ^{1}H-NMR spectrum of **2** confirmed its *anti* configuration.

Coordination of the oxazoline ring through the imine nitrogen atom was supported by IR spectroscopy. The C=N stretching bands in complexes **2**, **3** and **4** appeared at 1625, 1626 and 1637 cm^{-1}, respectively, compared to 1654 cm^{-1} for the ligand.

The ^{1}H-NMR spectrum of complex **4** provided the information confirming its *trans*(*N*,*P*)-geometry and *ortho*-palladated structure. As for other known mononuclear phosphane derivatives of *C*,*N*-palladacycles with *trans*(*N*,*P*)-geometry [26], the signal of aromatic H(6) at δ 6.43 ppm appeared as a doublet of doublets due to spin–spin coupling (partially through space) with the ^{31}P nuclei of PPh_3. The H(5) and especially H(6) signals were shifted upfield due to the shielding effect of the phosphane phenyl rings.

The ^{1}H-NMR spectra have also provided valuable data about the oxazoline ring conformations of the ligand as well as complexes **2**–**4** in $CDCl_3$ solutions. One

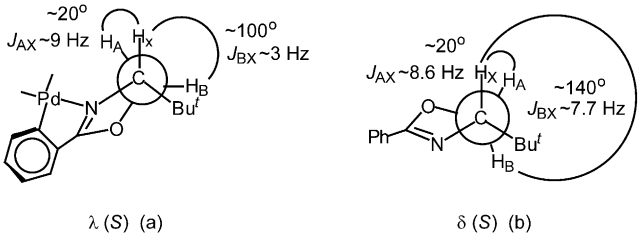


Fig. 1. Newman projections of the (*S*)-oxazoline ring along the C(4)–C(3) bond for two possible twisted conformations $\lambda(S)$ (a) and $\delta(S)$ (b) with the approximate values of dihedral angles H_X–C–C–H_A and H_X–C–C–H_B and their corresponding coupling constants *J*.[11]

[1] The Newman projections were drawn with regard to the flattened conformation of the heterocycle containing a C=N bond.

can expect two principal twisted conformations of the oxazoline ring, $\lambda(S)$ and $\delta(S)$. Analysis of their Newman projections (Fig. 1) and correlations to the Karplus equation [33] predicts: (i) a significant difference in the values of spin–spin coupling constants J_{AX} and J_{BX} for the $\lambda(S)$ conformation and (ii) rather similar values of these constants for the $\delta(S)$ conformation. In ^{1}H-NMR spectra of complexes **2**–**4**, one constant, J_{AX}, is considerably larger (8.8–9.3 Hz) than the other, J_{BX} (2.5–3.5 Hz). Therefore, the heterocycle of the coordinated ligand adopts the $\lambda(S)$ conformation in solutions. The same geometry of the oxazoline ring was determined by the X-ray structure study of complex **3** (vide infra). This suggests that the oxazoline ring conformations of the complexes in solutions and in solid form are practically identical.

The values of coupling constants J_{AX} and J_{BX} found in the ^{1}H-NMR spectrum of the free ligand are not significantly different. This suggests that the oxazoline ring conformation of the free ligand is different from that of the complexes **2**–**4** and must be $\delta(S)$. Therefore, cyclopalladation of (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline results in drastic changes to the heterocycle's conformation.

2.3. X-ray structure study of chloro-bridged dimer 3

The most unambiguous confirmation of η^2-*C*,*N*-bonding of 4-*tert*-butyl-2-phenyl-2-oxazoline was obtained from the X-ray study of chloro-bridged dimer **3**. Single crystals of CPC **3** suitable for the X-ray diffraction study were grown by diffusion crystallization of the compound in a dichloromethane–ether solvent mixture, with hexane as an external solvent. The molecular structure of compound **3** is presented in Figs. 2 and 3;

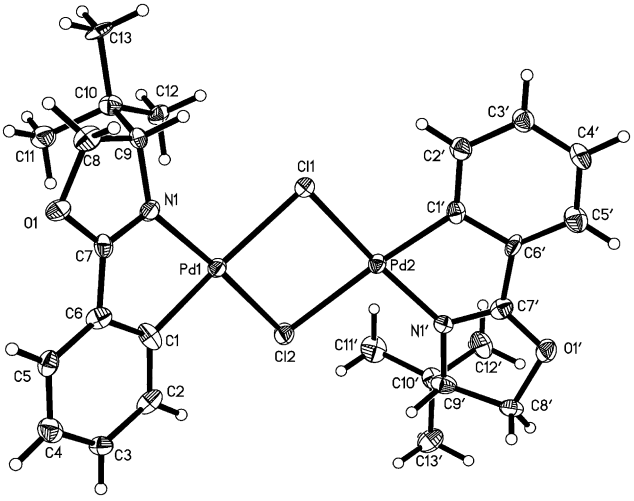


Fig. 2. Molecular structure of chloro-bridged dimer (*S*,*S*)-**3**. Solvent $CHCl_3$ molecule is omitted for clarity. Displacement ellipsoids are shown at 40% probability level.

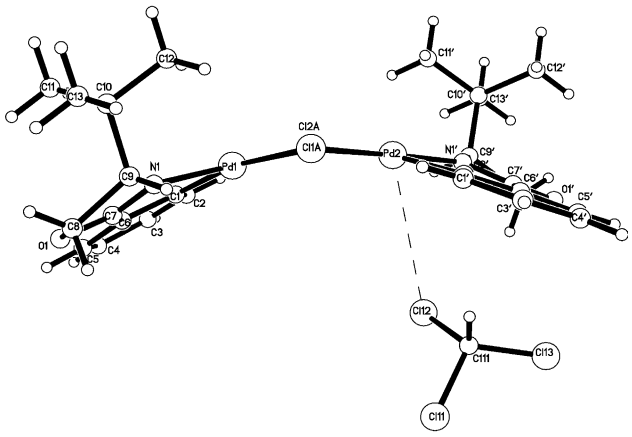


Fig. 3. The projection of molecular structure of chloro-bridged dimer (*S*,*S*)-**3** illustrating the considerable bend of the central $\{Pd_2Cl_2\}$ four-membered ring and efficient screening of the space over the palladium centers by bulky *tert*-butyl substituent.

Table 1
Bond lengths (Å) for the chloro-bridged dimeric cyclopalladated complex (*S*,*S*)-**3** (mono-chloroform solvate)

Pd(1)–C(1)	1.997(8)	C(3)–C(4)	1.379(11)
Pd(1)–N(1)	2.033(6)	C(4)–C(5)	1.396(11)
Pd(1)–Cl(2)	2.323(2)	C(5)–C(6)	1.387(11)
Pd(1)–Cl(1)	2.455(2)	C(6)–C(7)	1.449(10)
Pd(2)–C(1′)	1.987(8)	C(8)–C(9)	1.542(11)
Pd(2)–N(1′)	2.028(7)	C(9)–C(10)	1.559(11)
Pd(2)–Cl(1)	2.320(2)	C(10)–C(12)	1.509(10)
Pd(2)–Cl(2)	2.470(2)	C(10)–C(13)	1.541(11)
Cl(11)–C(111)	1.762(11)	C(10)–C(11)	1.558(11)
Cl(12)–C(111)	1.760(11)	C(1′)–C(2′)	1.392(10)
Cl(13)–C(111)	1.750(11)	C(1′)–C(6′)	1.392(10)
N(1)–C(7)	1.295(10)	C(2′)–C(3′)	1.394(10)
N(1)–C(9)	1.474(10)	C(3′)–C(4′)	1.385(12)
N(1′)–C(7′)	1.293(10)	C(4′)–C(5′)	1.375(11)
N(1′)–C(9′)	1.475(9)	C(5′)–C(6′)	1.394(12)
O(1)–C(7)	1.351(9)	C(6′)–C(7′)	1.470(11)
O(1)–C(8)	1.471(11)	C(8′)–C(9′)	1.562(11)
O(1′)–C(7′)	1.319(9)	C(9′)–C(10′)	1.540(11)
O(1′)–C(8′)	1.484(9)	C(10′)–C(11′)	1.516(12)
C(1)–C(6)	1.380(11)	C(10′)–C(12′)	1.524(11)
C(1)–C(2)	1.414(11)	C(10′)–C(13′)	1.545(11)
C(2)–C(3)	1.367(11)		

selected bond lengths and angles are given in Tables 1 and 2, respectively.

Several chiral cyclopalladated derivatives of 2-substituted oxazolines have previously been structurally characterized: two ferrocene-based μ-iodo *C*,*N*-dimers **5a**,**b** bearing a bulky 4-substituent [34], and two pincer *N*,*C*,*N*-complexes **6a**,**b** (Fig. 4) [35,36]. Several achiral complexes of *C*,*N*-type have also been reported, including the mononuclear phosphane adduct of 4-nonsubstituted ligand **7** [26], and the *ortho*-palladated μ-acetato dimers **8a**,**b** [37] and **9a**,**b** [38,39] derived from 2-phenyl-2-oxazolines and two benzoxazolines, respectively (Fig. 4).

Table 2
Bond angles (°) for the chloro-bridged dimeric cyclopalladated complex (*S*,*S*)-**3** (mono-chloroform solvate)

C(1)–Pd(1)–N(1)	80.3(3)	N(1)–C(9)–C(8)	100.7(6)
C(1)–Pd(1)–Cl(2)	96.2(2)	N(1)–C(9)–C(10)	111.8(6)
N(1)–Pd(1)–Cl(2)	176.4(2)	C(8)–C(9)–C(10)	116.3(7)
C(1)–Pd(1)–Cl(1)	169.0(2)	C(12)–C(10)–C(13)	110.3(7)
N(1)–Pd(1)–Cl(1)	97.0(2)	C(12)–C(10)–C(11)	110.2(7)
Cl(2)–Pd(1)–Cl(1)	86.56(7)	C(13)–C(10)–C(11)	109.4(7)
C(1′)–Pd(2)–N(1′)	81.2(3)	C(12)–C(10)–C(9)	110.5(6)
C(1′)–Pd(2)–Cl(1)	94.8(2)	C(13)–C(10)–C(9)	107.9(6)
N(1′)–Pd(2)–Cl(1)	176.0(2)	C(11)–C(10)–C(9)	108.5(6)
C(1′)–Pd(2)–Cl(2)	172.4(2)	C(2′)–C(1′)–C(6′)	117.7(7)
N(1′)–Pd(2)–Cl(2)	97.6(2)	C(2′)–C(1′)–Pd(2)	128.2(6)
Cl(1)–Pd(2)–Cl(2)	86.29(7)	C(6′)–C(1′)–Pd(2)	114.0(6)
Pd(2)–Cl(1)–Pd(1)	92.15(7)	C(1′)–C(2′)–C(3′)	119.9(8)
Pd(1)–Cl(2)–Pd(2)	91.71(7)	C(4′)–C(3′)–C(2′)	120.8(8)
C(7)–N(1)–C(9)	109.7(6)	C(5′)–C(4′)–C(3′)	120.7(8)
C(7)–N(1)–Pd(1)	112.0(5)	C(4′)–C(5′)–C(6′)	117.8(8)
C(9)–N(1)–Pd(1)	138.1(5)	C(1′)–C(6′)–C(5′)	123.2(8)
C(7′)–N(1′)–C(9′)	108.9(7)	C(1′)–C(6′)–C(7′)	112.4(7)
C(7′)–N(1′)–Pd(2)	113.2(5)	C(5′)–C(6′)–C(7′)	124.4(7)
C(9′)–N(1′)–Pd(2)	137.5(5)	N(1′)–C(7′)–O(1′)	117.2(7)
C(7)–O(1)–C(8)	105.5(6)	N(1′)–C(7′)–C(6′)	117.9(7)
C(7′)–O(1′)–C(8′)	105.5(6)	O(1′)–C(7′)–C(6′)	124.9(7)
C(6)–C(1)–C(2)	117.3(7)	O(1′)–C(8′)–C(9′)	103.3(6)
C(6)–C(1)–Pd(1)	114.9(6)	N(1′)–C(9′)–C(10′)	113.5(6)
C(2)–C(1)–Pd(1)	127.6(6)	N(1′)–C(9′)–C(8′)	100.4(6)
C(3)–C(2)–C(1)	119.0(7)	C(10′)–C(9′)–C(8′)	113.9(7)
C(2)–C(3)–C(4)	122.9(8)	C(11′)–C(10′)–C(12′)	109.8(7)
C(3)–C(4)–C(5)	119.3(8)	C(11′)–C(10′)–C(9′)	109.9(6)
C(6)–C(5)–C(4)	117.4(8)	C(12′)–C(10′)–C(9′)	111.4(7)
C(1)–C(6)–C(5)	124.0(8)	C(11′)–C(10′)–C(13′)	108.7(7)
C(1)–C(6)–C(7)	111.2(7)	C(12′)–C(10′)–C(13′)	109.9(7)
C(5)–C(6)–C(7)	124.8(7)	C(9′)–C(10′)–C(13′)	107.0(7)
N(1)–C(7)–O(1)	115.5(7)	Cl(13)–C(111)–Cl(12)	110.8(6)
N(1)–C(7)–C(6)	119.8(7)	Cl(13)–C(111)–Cl(11)	110.7(6)
O(1)–C(7)–C(6)	124.6(7)	Cl(12)–C(111)–Cl(11)	110.1(6)
O(1)–C(8)–C(9)	104.6(6)		

The unit cell of complex **3** contains four dimeric complex molecules and four chloroform solvate molecules. Two projections of the complex are shown in Figs. 2 and 3. The solvent molecule is situated near an apical position of the Pd(2) atom (see the side projection, Fig. 3), with the Pd···Cl distance equaling 3.819 Å. This arrangement is favorable for a weak secondary interaction.

The *ortho*-palladated structure of this μ-chloro dimer (and, therefore, that of the starting μ-acetato dimer **2**) is quite evident. In common with most structurally characterized CPCs of *C*,*N*-type [40], including ferrocenyloxazoline derivatives **5a**,**b** [34], dimer **3** displays an *anti*-arrangement of identical donor atoms. The dimeric molecule consists of two crystallographically independent halves, with differences in their structural parameters. The main geometric peculiarity of this dimer is a marked bend in the central four-membered cycle {$Pd_2(\mu\text{-}Cl)_2$} of 161.1° along the Cl(1)–Cl(2) axis, compared to 163.7–180° for dimeric *anti*-configured cyclopalladated derivatives of benzylamines [40–42]. With this bend of the central four-membered cycle, the dihedral angle between the two mean coordination planes (mcpl) is equal to 155.2°. It is of interest that μ-iodo dimers **5a**,**b** with very bulky ferrocenyloxazoline ligands have a greater bend in the central ring {$Pd_2(\mu\text{-}I)_2$}, 115.5–113.3°, with the dihedral angle between the mcpls equal to 108.2 and 106.1°, respectively [34].

The Pd–C bond lengths in dimer **3**, 1.997–1.987(8) Å,[2] fall within the range of the values reported for other cyclopalladated derivatives of oxazoline ligands (1.928–2.038 Å) and close to the mean value (1.981 Å) [26,34,35,37–39]. The Pd–N bond lengths (2.033–2.029(6) Å) are also close to the mean value of 2.029 Å. However, they are shorter than those found in the μ-iodo bridged ferrocenyl analogues **5a**,**b** (2.084–2.085 Å). This is apparently due to a combination of two factors: (i) a difference in the *trans* influence of μ-chloro and μ-iodo ligands and (ii) the geometric differences associated with the palladacycle being fused with the phenyl ring in **3** and the five-membered cyclopentadienyl rings in **5a**,**b**. The difference between the Pd–Cl bond distances in the *trans* position to the carbon (2.455–2.470 Å) and the nitrogen (2.323–2.320 Å) atoms of the palladacycle in dimer **3**, is in accordance with the *trans* influences of

[2] Here and later on, the two values cited correspond to Pd(1) and Pd(2) containing halves of dimeric molecule, respectively.

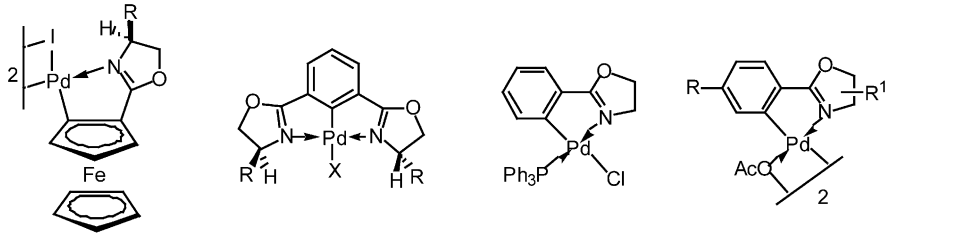


Fig. 4. Oxazoline-based CPCs with reported X-ray diffraction data.

these donor atoms; their values are close to the lower limit of the values reported previously for chloro-bridged cyclopalladated benzylaminate dimers (2.464–2.493 and 2.330–2.347 Å) [40–42].

The coordination environment of the palladium atom in dimer **3** may be described as nearly square–planar with a moderate tetrahedral distortion: the dihedral angles between the planes {CPdN} and {Cl^1PdCl^2} equal 10.8–7.5°, with maximum displacement of the C(1) [C(1′)] atom equaling 0.1397–0.0898 Å. Similar tetrahedral distortions were also found for the sterically crowded ferrocenyl analogues **5a**,**b** (8.5–8.2°) [34] and for the 4,4-dimethyl substituted dimer **8b** (7.7°) [37]; this is in contrast to the much more flattened derivatives of 4-non-substituted complexes **7** [26] and **9a**,**b** [38,39] (1.7–5.3°).

The conformation of the palladacycle in dimeric complex **3** may be described as a flattened envelope. Its puckering is somewhat more pronounced compared to that in the related mono- (**7**) [26] and binuclear derivatives (**8a**) [43] of the non-substituted 2-phenyl-2-oxazoline ligand: the averaged absolute values of intrachelate torsion angle are equal to 8.88–7.94 and 3.4–4.52°, respectively; their further increase was observed in the case of the derivatives of bulky ferrocenyloxazoline ligands **5a**,**b** (10.42–11.34°) [34]. Whereas pincer complex **6a**, bearing rather bulky isopropyl groups attached to the oxazoline rings, contains two nearly planar two fused palladacycles, with an intrachelate torsion angle equal to 1.28° [35].

A further consequence of the bulky substituent presence is the considerable puckering of the oxazoline ring in **3**. By contrast to the ideally planar heterocycle in achiral *C*,*N*-complexes **7** [26], **8b** [37], and chiral pincer *N*,*C*,*N*-compound **6a** [35] (with the displacement of the framework atoms from the mean heterocycle plane below 0.004 Å), chiral dimers **3** and **5a**,**b** [34] exhibit marked twist-like non-planarity of the oxazoline rings with displacement of two carbon atoms of the dicarbon chain (at 0.111–0.126 and 0.121–0.131 Å, respectively) in opposite directions (Fig. 5). This corresponds to the chiral $\lambda(S)$-conformation of the oxazoline ring predicted based on the analysis of ^{1}H-NMR data (Fig. 1, vide supra). It seems reasonable to suppose that this chiral conformation of the heterocycle can contribute, to some extent, to the optical activity of these complexes.

In accordance with this conformation, the bulky *tert*-butyl substituents in the oxazoline rings of dimer **3** assume a position that is nearly axial: the (ox)C–C(Bu^t) bonds form angles of 166.6–160.4° (adjacent angles 13.4–19.6°) with the normal to the corresponding mean coordination planes. It is probable that a weak secondary interaction between one of the methyl groups of the *tert*-butyl substituent and the palladium center contributes to the stability of this chiral conformation: the $H^{12a}\cdots Pd^1$ distance is 2.885 Å, which is less than the sum of the van der Waals radii for these atoms (3.1 Å) [44]. As a result, the bulky *tert*-butyl groups can efficiently screen the space over the metal center (as is evident from the side projection presented in Fig. 3). This geometry may enable the new palladacycle to display highly effective chiral recognition properties.

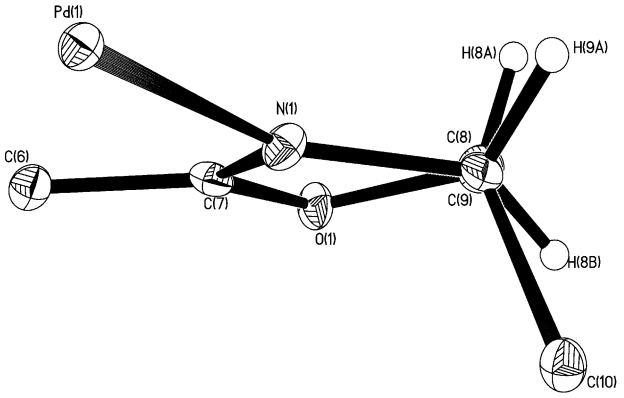


Fig. 5. Twisted conformation of the oxazoline ring in the dimer **3** found by the X-ray study and projected along the C–C bond of the heterocycle. All atoms except those directly bonded to the oxazoline ring are omitted for clarity.

3. Conclusions

Due to steric promotion, readily available (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline easily underwent direct cyclopalladation using $Pd(OAc)_2$ in acetic acid in a high yield. The structure of the obtained cyclopalladated complex **2**, as well as its two stable derivatives **3** and **4**, were confirmed by spectroscopic methods. The X-ray crystal study of Cl-bridged dimeric CPC **3** supported the proposed structure and revealed pronounced puckering of the oxazoline ring and the palladacycle. The oxazoline ring in the CPCs adopts the $\lambda(S)$ conformation in the crystal form and in $CDCl_3$ solutions. This allows the use of X-ray study data for predicting behavior of the complex in stereocontrol processes. Currently, our groups are engaged in the application of homochiral CPCs, including oxazoline derivatives, in different stereoselection processes.

4. Experimental

All chemicals were purchased from Aldrich Chemical Company, Inc., USA. Palladium acetate was purified by refluxing in benzene for 5 min, filtering the solution, and removing the solvent. Acetic acid was refluxed over $KMnO_4$ for 3 h and then distilled. Other solvents were distilled over CaH_2 prior to use.

4.1. Physical measurements

Routine ^{1}H- and ^{13}C-NMR (500 and 125 MHz, respectively), DEPT, COSY, and HETCOR spectra were recorded in $CDCl_3$ using TMS as an internal standard on an Avance 500 Bruker spectrometer. Spin–spin coupling constants, J, are given in Hz. IR spectra were recorded on an ATI Mattson Genesis Series FTIR. Optical rotations were measured on a Rudolph Autopol III automatic polarimeter using a 1 dm tube. Analytical TLC was performed on Merck precoated 0.2 mm plates of silica gel 60 F_{254}. Column chromatography was carried out using Natland Silica Gel 60 (230–400 mesh). Melting points were measured on a Laboratory Devices Mel-Temp apparatus and were not corrected.

4.2. Ligand synthesis

4.2.1. (*S*)-4-tert-Butyl-2-phenyl-2-oxazoline (**1**)

The compound was prepared from benzonitrile and (*S*)-(+)-leucinol in 84% yield using a slightly modified procedure described for other oxazolines (the reaction time was increased from 50 to 63 h) [28]. M.p. 31–33 °C; R_f 0.64 (1:3 ether–hexane); $[\alpha]_{633}^{22}$ −57.5°, $[\alpha]_{589}^{22}$ −64.8°, $[\alpha]_{546}^{22}$ −82.9°, $[\alpha]_{405}^{22}$ −197.2° (*c* 0.29, CH_2Cl_2); IR (neat, ν, cm^{-1}): 1654 s (C=N), 694 and 779 s (CH-arom.); ^{1}H-NMR (δ, ppm): 0.95 s (9H, $C(CH_3)_3$); 4.05 dd (1H, $J_{BX} = 7.7$, $J_{AB} = 10.1$; OCH^A); 4.24 dd (1H, $J_{AX} = 8.6$, NCH^X); 4.34 dd (1H, OCH^B); 7.32, 7.46 and 7.94 three m (2H, 1H, and 2H, respectively, H-arom.); ^{13}C-NMR (δ, ppm): 24.8 (CH_3), 33.0 ($C(CH_3)_3$), 67.7 (NCH), 75.1 (OCH_2), 126.9 (C-arom.), 127.20, 127.22, 130.1 (CH-arom.), 162.2 (OCN). Anal. Calc. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.63, H 8.62, N 6.89%.

4.3. Preparation of the cyclopalladated complexes

4.3.1. (*S,S*)-Di-μ-acetatobis-[2-(2-(4-tert-butyl)oxazolinyl)phenyl-*C,N*]dipalladium(II) (**2**)

A suspension of $Pd(OAc)_2$ (0.0505 g, 0.225 mmol) in glacial AcOH (2 ml) was added to a solution of (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline (0.0457 g, 0.225 mmol) in AcOH (1 ml). After stirring at room temperature (r.t.) for 22 h, the mixture was diluted with H_2O and extracted with $CHCl_3$ (3 × 10 ml). The organic layers were combined, washed with an aqueous saturated $NaHCO_3$ solution, and run through a layer of Celite ($h = 1.5$ cm). After solvent removal in vacuo (r.t.), the crude product was obtained as a dark-orange oil. According to the ^{1}H-NMR spectrum, it contained at least 95% product. Attempts to obtain the complex in solid state were unsuccessful because of its rather fast decomposition. The yield of the crude oily product was 0.0820 g (99%). IR (Nujol, ν, cm^{-1}): 1625 s (C=N), 734 s (CH-arom.), 1585 s and 1410 s (COO); ^{1}H-NMR (δ, ppm): 0.86 s (9H, $C(CH_3)_3$), 2.11 s (3H, CH_3), 2.84 dd (1H, $J_{AX} = 9.3$, $J_{BX} = 3.5$, NCH^X); 3.08 t (1H, $J_{AB} = 8.8$, OCH^A), 4.13 dd (1H, OCH^B), 7.04, 7.09, and 7.19 three m (2H, 1H and 1H, respectively, CH-arom.); ^{13}C-NMR (δ, ppm): 24.2 (CH_3), 25.7 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 70.5 (NCH), 71.3 (OCH_2), 123.6, 125.4, 130.0 and 131.12 (CH-arom.), 131.10 (C(2)-arom.), 147.7 (PdC(1)), 173.8 (OCN), 180.4 (COO).

4.3.2. (*S,S*)-Di-μ-chlorobis-{2-[2-(4-tert-butyl)oxazolinyl]phenyl-*C,N*}dipalladium(II) (**3**)

LiCl (0.0104 g, 0.245 mmol) was added to a solution of freshly prepared crude complex **2** (0.082 g, 0.112 mmol) in abs. acetone (5 ml). The solution was stirred for 24 h at r.t. Then the solvent was removed in vacuo and the yellow solid was purified using column chromatography (1:1 $CHCl_3$–hexane, $h = 8$ cm, $d = 2$ cm). Yield 0.0577 g (75%). M.p. 212–212.5 °C (dec.); R_f 0.46 (1:1 $CHCl_3$–hexane); $[\alpha]_{589}^{21}$ +262.5°, $[\alpha]_{546}^{21}$ +336.9°, $[\alpha]_{633}^{21}$ +211.8° (*c* 0.54, CH_2Cl_2); IR (Nujol, ν, cm^{-1}): 1626 s (C=N), 728 s (CH-arom.); ^{1}H-NMR (δ, ppm): 1.05 s (9H, $C(CH_3)_3$), 3.9 dd (1H, $J_{AX} = 8.9$, $J_{BX} = 2.9$, NCH^X), 3.08 t (1H, $J_{AB} = 9.1$, OCH^A), 4.13 dd (1H, OCH^B), 7.04 br. t (1H, $J \approx 7.1$, CH(5)-arom.), 7.10 br. dt (1H, $J_1 \approx 7.1$, $J_1 \approx 1.3$, CH(4)-arom.), 7.14 br. dd (1H, $J_1 \approx 7.2$, $J_1 \approx 1.3$, CH(6)-arom.), 7.41 br. d (1H, $J_1 \approx 7.7$, CH(3)-arom.); ^{13}C-NMR (δ, ppm): 26.1 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 70.7 (NCH), 72.2 (OCH_2), 124.5, 126.1, 131.0 and 133.2 (CH-arom.), 130.4 (arom. C(2)), 145.3 (PdC(1)), 175.0 (OCN). Anal. Calc. for $C_{26}H_{32}Cl_2N_2O_2Pd_2 \cdot CHCl_3$:[3] C, 40.15; H, 4.12; N, 3.47. Found: C, 40.20; H, 4.15; N, 3.50%.

4.3.3. (*S*)-Chloro-{2-[2-(4-tert-butyl)oxazolinyl]phenyl-*C,N*}(triphenylphosphine)-palladium(II) (**4**)

Triphenylphosphine (0.0545 g, 0.207 mmol) was added to a suspension of complex **3** (0.0715 g, 0.103 mmol) in benzene. The mixture was stirred at r.t. for 12 h, then the solvent was removed in vacuo. A pale yellow solid was recrystallized from $CHCl_3$ and hexane. Yield 0.0839 g (69%). R_f 0.78 (1:9 ethyl acetate–$CHCl_3$); m.p. 120 °C (dec.); IR (Nujol, ν, cm^{-1}): 1637 s (C=N); $[\alpha]_{633}^{22}$ +83.2° $[\alpha]_{589}^{22}$ +94.6°, $[\alpha]_{546}^{22}$ +121.6°, $[\alpha]_{435}^{22}$ +309.6°, $[\alpha]_{405}^{22}$ +544.4° (*c* 0.17, CH_2Cl_2); ^{1}H-NMR (δ, ppm): 1.05 s (9H, $C(CH_3)_3$), 4.40 dd (1H, $J_{AX} = 8.8$, $J_{BX} = 2.5$, NCH^X), 4.54 t (1H, $J_{AB} = 8.9$, OCH^A), 4.75 dd (1H, OCH^B), 6.43 dd (1H, $^3J_{HH} = 7.7$, $J_{HP} = 5.0$, H(6)-arom.), 6.59 dt (1H, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.3$, H(5)-arom.), 6.92 t (1H, $^3J_{HH} = 7.7$, H(4)-arom.), 7.30 dd (1H, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.3$, H(3)-arom.), 7.35 dt (6H,

[3] The presence of one molecule of $CHCl_3$ per one molecule of the complex is proven by integrating signals in the ^{1}H-NMR spectrum of the sample in acetone-d_6.

$^3J_{HH} = 7.8$, $^4J_{HP} = 1.8$, *meta*-H of PPh_3), 7.43 br. dt (3H, $^3J_{HH} \approx 7.6$, $^4J_{HH} = 1.9$, *para*-H of PPh_3), 7.74 m (6H, *ortho*-H of PPh_3); ^{13}C-NMR (δ, ppm): 25.3 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 68.6 (NCH), 71.6 (OCH_2), 122.6 (HC(4) of C_6H_4), 125.3 (HC(3) of C_6H_4), 127.0 d ($^3J_{PC} = 11.0$, *meta*-CH of PPh_3), 129.4 d ($^5J_{PC} = 4.8$, HC(5) of C_6H_4), 129.7 d ($^4J_{PC} = 2$, *para*-CH of PPh_3), 130.0 d ($^1J_{PC} = 51.6$, quat. C of PPh_3), 132.3 (quat. C(2) of C_6H_4), 134.3 d ($^2J_{PC} = 13$, *ortho*-CH of PPh_3), 136.5 d ($^3J_{PC} = 13.8$, HC(6) of C_6H_4), 151.3 (PdC(1)), 173.7 (NCO). Anal. Calc. for $C_{31}H_{31}ClNOPPd$: C, 53.43; H, 4.48; N, 4.44. Found: C, 53.20; H, 4.47; N, 4.39%.

4.4. X-ray diffraction study of complex 3

Single crystals of compound **3** were grown by diffusion crystallization of the complex in a chloroform–ether solvent mixture, with hexane as an external solvent. A colorless crystal was covered with perfluorated oil and mounted on a Bruker SMART CCD diffractometer. Crystal data, data collection and structure solution and refinement parameters are given in Table 3.

The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 for all data using SHELX software [45,46]. Hydrogen atoms were located objectively. All non-hydrogen atoms were refined with anisotropic displacement parameters; H atoms were refined with isotropic displacement parameters.

Table 3
Crystal data, data collection, structure solution and refinement parameters for the chloro-bridged dimeric cyclopalladated complex (*S*,*S*)-**3** (chloroform solvate)

Empirical formula	$C_{27}H_{33}Cl_5N_2O_2Pd_2$
Formula weight	807.60
Color, habit	light-yellow
Crystal size (mm)	0.24 × 0.12 × 0.08
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	9.2840(8)
b (Å)	13.5525(12)
c (Å)	24.448(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3076.1(5)
Z	4
D_{calc} (g cm^3)	1.744
Absorption coefficient (mm^{-1})	1.631
$F(000)$	1608
Diffractometer	Bruker SMART
Temperature (K)	150.0(2)
Radiation (λ, Å)	Graphite monochromatized Mo–K_α (0.71073)
Scan mode	ω
Scan step (in ω) (°)	0.3
Time per step (s)	15
θ range (°)	1.67–28.00
Index ranges	$-12 \le h \le 12$, $-19 \le k \le 16$, $-34 \le l \le 31$
Reflections collected	28 519
Independent reflections	7420 [$R_{int} = 0.1428$]
Absorption correction	Not applied
Data/restraints/parameters	6990/0/344
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0597$, $wR_2 = 0.0989$
R indices (all data)	$R_1 = 0.0926$, $wR_2 = 0.1121$
Absolute structure parameter	−0.07(5)
Extinction coefficient	0.00000(14)
Largest difference peak and hole (e Å^{-3})	0.991 and −0.919

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 176328 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] J. Albert, J.M. Cadena, J. Granell, G. Muller, D. Panyella, C. Sañudo, Eur. J. Inorg. Chem. (2000) 1283 (and references cited therein).
[2] V.V. Dunina, L.G. Kuz'mina, A.G. Parfyonov, Y.K. Grishin, Tetrahedron: Asymm. 9 (1998) 1917 (and references cited therein).
[3] V.V. Dunina, L.G. Kuz'mina, M.Y. Rubina, Y.K. Grishin, Y.A. Veits, E.I. Kazakova, Tetrahedron: Asymm. 10 (1999) 1483 (and references cited therein).
[4] A. Marinetti, P. Hubert, J.-P. Genet, Eur. J. Org. Chem. (2000) 1815 (and references cited therein).
[5] J. Kurita, F. Usuda, S. Yasuike, T. Tsuchiya, Y. Tsuda, F. Kiuchi, S. Hosoi, J. Chem. Soc. Chem. Commun. (2000) 191 (and references cited therein).
[6] S.B. Wild, Coord. Chem. Rev. 166 (1997) 291.
[7] A. Böhm, D. Seebach, Helv. Chim. Acta 83 (2000) 3262.

[8] V.V. Dunina, O.N. Gorunova, M.V. Livantsov, Y.K. Grishin, Tetrahedron Lett. 11 (2000) 2907.
[9] W. McFarlane, J.D. Swarbrick, J.L. Bookham, J. Chem. Soc. Dalton Trans. (1998) 3233 (and references cited therein).
[10] B. Staubach, J. Buddrus, Angew. Chem. Int. Ed. Engl. 35 (1996) 1344 (and references cited therein).
[11] S. Selvaratnam, P.-H. Leung, A.J.P. White, D.J. Williams, J. Organomet. Chem. 552 (1998) 187.
[12] O. Cantin, C. Cativiela, M.D. Diaz-de-Villegas, R. Navarro, E.P. Urriolabeitia, Tetrahedron: Asymm. 7 (1996) 2695.
[13] P.-H. Leung, G.H. Quek, H. Lang, A.M. Liu, K.F. Mok, A.J.P. White, D.J. Williams, N.H. Rees, W. McFarlane, J. Chem. Soc. Dalton Trans. (1998) 1639.
[14] B.-H. Aw, S. Selvaratnam, P.-H. Leung, N.H. Rees, W. McFarlane, Tetrahedron: Asymm. 7 (1996) 1753.
[15] J.M. Longmire, X. Zhang, M. Shang, Organometallics 17 (1998) 4374.
[16] M.A. Stark, C.J. Richards, Tetrahedron Lett. 38 (1997) 5881.
[17] T.K. Hollis, L.E. Overman, J. Organomet. Chem. 576 (1999) 290 (and references cited therein).
[18] A.D. Ryabov, G.M. Kazankov, S.A. Kurzeev, P.V. Samuleev, V.A. Polyakov, Inorg. Chim. Acta 280 (1998) 57.
[19] A.L. Seligson, W.C. Trogler, Organometallics 12 (1993) 744.
[20] P.-H. Leung, Y. Qin, G. He, K.F. Mok, J.J. Vittal, J. Chem. Soc. Dalton Trans. (2001) 309 (and references cited therein).
[21] V.V. Dunina, M.Y. Kazakova, Y.K. Grishin, O.R. Malyshev, E.I. Kazakova, Russ. Chem. Bull. 46 (1997) 1321 (and references cited therein).
[22] Some recent examples of the use of oxazoline-derived complexes in asymmetric catalysis: (a) N. Østergaard, J.F. Jensen, D. Tanner, Tetrahedron 57 (2001) 6083;
(b) M. Ogasawara, K. Yoshida, T. Hayashi, Heterocycles 52 (2000) 195;
(c) Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, J. Org. Chem. 65 (2000) 3326;
(d) T. Kambara, K. Tomioka, Chem. Pharm. Bull. 48 (2000) 1577;
(e) M. Glos, O. Reiser, Org. Lett. 2 (2000) 2045.
[23] D.J. Ager, I. Prakash, D.R. Schaad, Chem. Rev. 96 (1996) 835–875.
[24] T.G. Gant, A.I. Meyers, Tetrahedron 50 (1994) 2297–2360.
[25] Some recent examples of oxazoline-based coordination complexes: (a) P. Braunstein, F. Naud, A. Dedieu, M. Rohmer, A. DeCian, S.J. Rettig, Organometallics 20 (2001) 2966;
(b) Y. Peng, X. Feng, K. Yu, Z. Li, Y. Jiang, C. Yeung, J. Organomet. Chem. 619 (2001) 204;
(c) P. Braunstein, M.D. Fryzuk, M.L. Dall, F. Naud, S.J. Rettig, F. Speiser, J. Chem. Soc. Dalton Trans. (2000) 1067;
(d) J.M. Canal, M. Gómez, F. Jiménez, M. Rocamora, G. Muller, E. Dunach, D. Franco, A. Jiménez, F.H. Cano, Organometallics 19 (2000) 966.
[26] I.P. Smoliakova, K.J. Keuseman, D.C. Haagenson, D.M. Wellmann, P.B. Colligan, N.A. Kataeva, A.V. Churakov, L.G. Kuz'mina, V.V. Dunina, J. Organomet. Chem. 603 (2000) 86 (and references cited therein).
[27] M. Ohff, A. Ohff, D. Milstein, J. Chem. Soc. Chem. Commun. (1999) 357.
[28] J.V. Allen, G.J. Dawson, C.G. Frost, M.J. Williams, S.J. Coote, Tetrahedron 50 (1994) 799.
[29] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 57 (1988) 434.
[30] V.V. Dunina, L.G. Kuz'mina, M.Y. Kazakova, O.N. Gorunova, Y.K. Grishin, E.I. Kazakova, Eur. J. Inorg. Chem. (1999) 1029.
[31] A.D. Ryabov, A.K. Yatsimirsky, Inorg. Chem. 23 (1984) 789.
[32] A.D. Ryabov, G.M. Kazankov, J. Organomet. Chem. 268 (1984) 85.
[33] R.S. Macomber, A Complete Introduction to Modern NMR Spectroscopy, Wiley, New York, 1998, p. 139.
[34] Y. Donde, L.E. Overman, J. Am. Chem. Soc. 121 (1999) 2933.
[35] Y. Motoyama, N. Makihara, Y. Mikami, K. Aoki, H. Nishiyama, Chem. Lett. (1997) 951.
[36] S.E. Denmark, R.A. Stavenger, A.-M. Faucher, J.P. Edwards, J. Org. Chem. 62 (1997) 3375.
[37] G. Balavoine, J.C. Clinet, P. Zerbib, K. Boubekeur, J. Organomet. Chem. 389 (1990) 259.
[38] M.R. Churchill, H.J. Wasserman, G.L. Young, Inorg. Chem. 19 (1980) 762.
[39] C. Navarro-Ranninger, F. Zamora, L.A. Martinez-Cruz, R. Isea, J.R. Masaguer, J. Organomet. Chem. 518 (1996) 29.
[40] V.V. Dunina, L.G. Kuz'mina, M.Y. Kazakova, Y.K. Grishin, Y.A. Veits, E.I. Kazakova, Tetrahedron: Asymm. 8 (1997) 2537.
[41] L.G. Kuz'mina, O.Y. Burtseva, M.A. Porai-Koshits, V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Zh. Obshch. Khim. (Russ.) 59 (1989) 2525.
[42] E.C. Alyea, S.A. Dias, A.J. McAlees, G. Ferguson, R. McGrindle, P.J. Roberts, J. Am. Chem. Soc. 99 (1977) 4985.
[43] N.A. Kataeva, K.J. Keuseman, L.G. Kuz'mina, V.V. Dunina, I.P. Smoliakova, unpublished data.
[44] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[45] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[46] G.M. Sheldrick, SHELXL-93—Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1993.