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Journal of Organometallic Chemistry 689 (2004) 2382–2394
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Exo- and *endo*-palladacycles derived from (4*R*)-phenyl-2-oxazolines

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Received 11 March 2004; accepted 15 April 2004

Abstract

Two novel oxazoline-derived palladacycles bearing an *endo*- or *exo*-C=N bond were prepared by direct *ortho*-palladation of (*R*)-2,4-diphenyl- or (*R*)-2-methyl-4-phenyl-2-oxazolines, respectively. The structures of the palladacycles' dimeric forms and corresponding mononuclear PPh_3-derivatives were confirmed by IR, ^1H, ^{13}C and 2D NMR spectroscopy. An X-ray diffraction study of the μ-chloro-dimeric cyclopalladated derivative of (*R*)-2,4-diphenyl-2-oxazoline proved the *endo* structure of the palladacycle.

Keywords: Palladacycles; Oxazolines; Chirality transfer; X-ray structural analysis

1. Introduction

During the four decades after the discovery of the first cyclometallated derivatives [1], optically active cyclopalladated compounds have evolved into a powerful tool for solving diverse stereochemical problems. Their efficiency in enantiomer separation of substrates capable of palladium coordination has been widely recognized [2] and the possibility of their application to spectral determination of enantiomeric purity [3] and absolute configuration [4] has been demonstrated as well. These complexes may be successfully used as chiral matrices for stoichiometric asymmetric synthesis [5] and as enantioselective catalysts or precatalysts [6] with very high levels of asymmetric induction in a number of reactions [7]. Development of simple routes to optically active palladacycles from available natural sources is becoming increasingly important. The use of oxazolines as ligands, which are easily available from amino alcohols (derived from natural α-amino acids), seems to be a very attractive direction. Until now, only a limited set of optically active oxazoline-derived cyclopalladated complexes of *CN*- [7–9] and *NCN*-types [10] has been reported; all these compounds have the C=N bond of the oxazoline ring in the *endo* position, with respect to the palladacycle, and all have a 4-alkyl or 4-benzyl substituent on the oxazoline ring.

Following our interest in synthesis and applications of optically active cyclopalladated compounds, we are currently engaged in the study of palladacycles derived from various optically active oxazolines [8]. In this paper, we report synthesis and characterization of two new and structurally different palladacycles prepared from (*R*)-2,4-diphenyl- and (*R*)-2-methyl-4-phenyl-substituted 2-oxazolines, bearing an *endo*- and *exo*-cyclic C=N double bond, respectively.

2. Results and discussion

2.1. Ligand preparation

Two new ligands, (*R*)-2,4-diphenyl-2-oxazoline (**2a**) and (*R*)-2-methyl-4-phenyl-2-oxazoline (**2b**), were

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doi:10.1016/j.jorganchem.2004.04.029

prepared from commercially available (*R*)-(−)-2-amino-2-phenylethanol (**1**) using known procedures [11,12] described for related compounds. Diphenyl-substituted oxazoline (*R*)-**2a** was isolated in a moderate yield from the $ZnCl_2$-catalyzed condensation of the amino alcohol (*R*)-**1** with benzonitrile, while the second ligand (*R*)-**2b** was obtained using the reaction of ethyl acetimidate with the same amino alcohol in a rather high yield (Scheme 1).

2.2. Preparation of cyclopalladated complexes

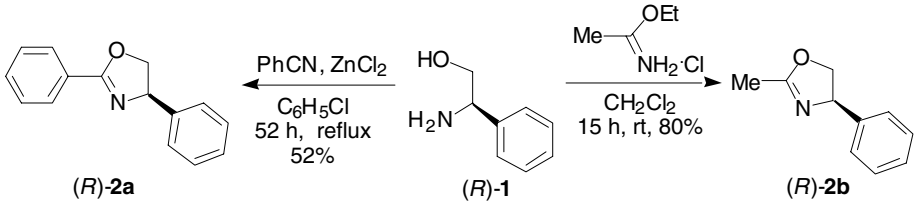
Cyclopalladation of oxazoline (*R*)-**2a** readily occurred using $Pd(OAc)_2$ in acetic acid at 60 °C in the presence of the weak base NaOAc to give nearly quantitative yield of the dimer (*R*,*R*)-**3a** (ca. 95% according to ^{1}H NMR data). Unfortunately, complex (*R*,*R*)-**3a** was unstable, so only limited spectral characterization was performed. The compound was converted to the more stable μ-Cl dimer (*R*,*R*)-**4a** using LiCl in acetone (Scheme 2).

Cyclopalladation of ligand (*R*)-**2b**, using essentially the same method as for oxazoline (*R*)-**2a**, proceeded much more slowly (16 h, 65 °C). Analysis of the ^{1}H NMR spectrum of the reaction mixture revealed that it contained the desired complex (*R*,*R*)-**3b**, along with ca. 20% of the corresponding coordination complex (*R*,*R*)-$[Pd(OAc)_2(\mathbf{2b})_2]$. The reaction mixture was treated with LiCl to afford the μ-Cl analog **4b** and the coordination complex (*R*,*R*)-$[PdCl_2(\mathbf{2b})_2]$ ((*R*,*R*)-**6b** (Scheme 3), which were separated using column chromatography.

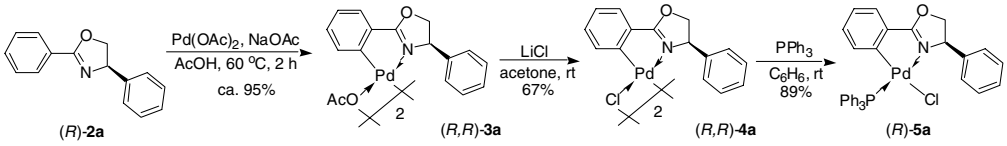
For subsequent spectral studies, dimeric complexes (*R*,*R*)-**4a,b** were transformed into their mononuclear phosphane derivatives (*R*)-**5a,b** by their reaction with PPh_3 in benzene (Schemes 2 and 3).

By comparing the time required to complete the aforementioned cyclometallation reactions and the yields of the products (Schemes 2 and 3), one can conclude that oxazoline (*R*)-**2a** is much more reactive towards cyclopalladation than (*R*)-**2b**. It has been reported that the presence of bulky groups on the ligand facilitates cyclopalladation; therefore, the observed reactivity might be caused by differences in the size of the substituents at C(4) [8a,13,14]. However, the main reason for difficulties in the direct *ortho*-palladation of ligand (*R*)-**2b**, is likely to be the less preferable *exo*-cyclic position of the C=N bond in the palladacycle to be formed. The same factor may also determine the complete regioselectivity in cyclopalladation of (*R*)-**2a** with formation of *endo*-metallacycle (for structure confirmation, see below); no traces of the alternative *exo*-palladacycle (Scheme 4) were detected by TLC and ^{1}H NMR spectroscopy.

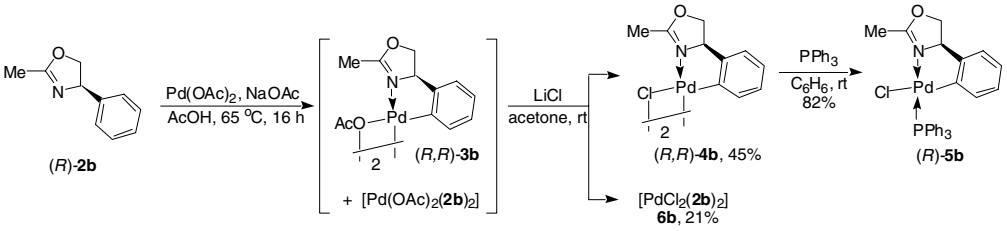
A similar trend in the reactivity was previously described for cyclopalladation of acyclic imines. To the



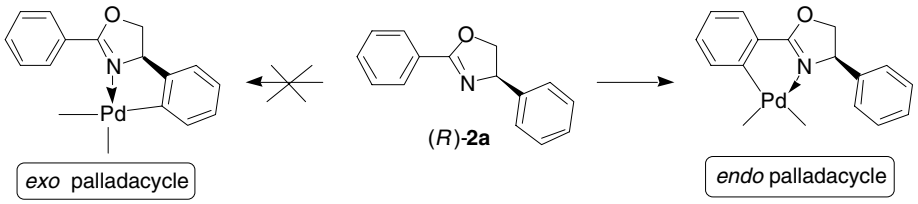
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

best of our knowledge, there have been no reports of *exo*-palladacycle formation if the imine ligand structure offers a possibility of *endo*-palladation under comparable conditions, including identical palladacycle size and hybridization of the carbon atom to be metallated [15–17]. The preference for *endo*-cyclopalladation can be supported by the following reported observations. For example, *endo*-cyclopalladation of the 4-NO_2-substituted benzal ring in N-benzyl-4-nitrobenzaldimine has been achieved in the presence of a benzyl ring more activated for electrophilic attack [17,18]. Formation of a five-membered *endo*-palladacycle with a (sp^3)C–Pd bond has been reported for a ligand which could have given an *exo*-palladacycle of the same size through the more preferable [14] activation of a (sp^2)C–H bond [19,20]. A less favored six-membered *endo*-palladation at an aliphatic C–H bond has also been demonstrated when in competition with formation of a five-membered *exo*-cycle through either aliphatic [21] or aromatic C–H bond activation [22,23]. Isomerization of a five-membered *exo*(sp^2)-palladacycle into a more thermodinamically stable six-membered *endo*(sp^3)-alternative has been reported as well [23]. Preference for the C=N bond inclusion into a palladacycle has also shown to change cyclopalladation chemoselectivity: an *endo*-palladacycle was formed via *ortho*-C–Cl bond oxidative addition to Pd(0) (generated in situ) in lieu of the C–H bond activation at a benzyl ring leading to an *exo*-palladacycle [17,21]. While the strong tendency for such ligands to form *endo*-cyclic compounds has been well documented, the reasons of this preference remain unclear [23].

In cases where *endo*-metallation is not feasible, five- [17,18,21,23,24] and even six-membered [25] *exo*-palladacycles may be formed. Similar *exo*-structures have been the main products of phenylhydrazone cyclopalladation, presumably due to activation of the phenyl ring by the NH group [26].

2.3. Spectral characterization of complexes

Due to the presence of two phenyl groups, cyclopalladation of oxazoline **2a** could result in the formation of two different complexes with *endo*- or *exo*-palladacycles, respectively (Scheme 4). However, the reported preference of *endo*-cyclometallation for similar ligands allowed us to suggest the *endo* structure for the palladacycle in compounds **3a** and **4a**, which was proven by the X-ray crystallographic analysis of the dimer **3a**. Reaction of oxazoline **2b** with $Pd(OAc)_2$ can provide only *exo*-cyclic metallacycle as the ligand has only one phenyl group and the possibility of cyclopalladation of the 2-methyl substituent is unlikely.

The formation of the Pd–C bond in complexes **3**–**5** was supported by NMR data. Comparison of the ^{13}C NMR and DEPT data obtained for μ-chloride dimers **4a**,**b** and their mononuclear phosphane derivatives **5a**,**b** indicated the appearance of new aromatic quaternary carbon signals at δ 139.7, 147.0, and 141.5, 148.1 ppm, respectively. These chemical shift values are in good agreement with those previously reported for the C atom bonded to Pd in oxazoline- [8] and imine-derived [14] palladacycles. The loss of one hydrogen atom in **4a,b** compared to the corresponding ligands was verified using integral intensities of the signals assigned to the aromatic hydrogens in the ^1H NMR spectra taken in CD_2Cl_2. Pd–C bond formation in **4b** was also supported by the presence of a strong band at 723 cm^{-1} in the IR spectrum. This signal assigned to the out-of-plane bending vibrations of aromatic C–H bonds is characteristic for *ortho*-disubstituted benzene derivatives [27] including those in palladacycles [8a,8b]. For comparison, the IR spectra of the free ligand **2b** and its coordination complex (*R*, *R*)-**6b** exhibited two bands at *v* 700, 762 and 694, 760 cm^{-1}, respectively, which are typical for monosubstituted benzenes [27].

The IR spectroscopy was also helpful to determine the Pd ← N bonding in cyclopalladated complexes **3a**, **4a,b**, **5a,b** and coordination compound (*R*, *R*)-**6b**. The C=N stretching band in the IR spectra of the free ligands **2a,b** appeared at *v* 1657 and 1674 cm^{-1}, respectively. After complex formation, the C=N bond in all these compounds became somewhat weaker with their stretching bands appearing at shorter wavenumbers, Δv C=N 28, 19, 22, 27, 21 and 25 cm^{-1}, respectively.

The ^1H NMR spectrum of dimer **3a** taken in $CDCl_3$ exhibited three signals of expected multiplicity assigned to the oxazoline ring hydrogens and one singlet for the AcO groups; the ^{13}C NMR spectrum of this compound contained one set of signals. These data suggested that the complex in $CDCl_3$ solutions existed as the *anti*-isomer, as has been found for μ-AcO dimeric cyclopalladated complexes of other 2-aryl-substituted oxazolines [8a,9h,9i].

In the case of μ-chloro dimer **4a**, the ^{1}H NMR signals ($CDCl_3$, ambient temperature) of three oxazoline hydrogens appeared as four broad multiplets, and some carbon atoms (e.g., NCH and C=N) were represented as two singlets in the ^{13}C NMR spectrum. When the ^{1}H NMR spectrum was taken at −60 °C, two sets of well-resolved high-field signals were observed (in ca. 4.1:1 ratio). Signal multiplicity of the aromatic protons underwent some changes as well; however, they were unresolved in both spectra. We suggest that the dimeric complex **4a** exists in a solution as a mixture of two geometrical isomers, *anti* and *syn*, as it was found for some of the μ-Cl-dimeric cyclopalladated complexes of 2-aryl-2-oxazolines [8c,9e,9i].

The same conclusion may be made from spectral data for the other μ-chloro dimer **4b**. In its ^{13}C NMR spectrum some carbon signals [CH_3, CHN, C(1)–Pd, C(2) and C(3)] appeared as two singlets (ca. in a 3:2 ratio). The ^{1}H NMR spectrum of dimer **4b** also contained two sets of signals, which were broadened and only partly resolved, with only one oxazoline ring hydrogen (OCH^A) well resolved. This indicated that compound **4b** in $CDCl_3$ solution is likely to be a mixture of geometrical isomers. For comparison, the μ-chloro dimeric cyclopalladated derivative of 4,4-dimethyl-2-(2-naphthyl)oxazoline has been shown to exist as a mixture of *syn* and *anti* isomers in a 2:3 ratio [9e].

The ^{1}H, ^{13}C and ^{31}P NMR spectra of the mononuclear complexes **5a** and **5b** contained one set of signals suggesting that the phosphane adducts were obtained as only one geometrical isomer. The chemical shift values, δ, of the ^{31}P NMR signals for **5a** and **5b**, 27.31 and 27.21, respectively, pointed to their *trans* configuration. For comparison, a similar PPh_3-complex of 2-phenyl-2-oxazoline, whose *trans* geometry was unambiguously proven by the X-ray diffraction analysis [8a], has a ^{31}P NMR signal at 27.92 ppm. Comparison of chemical shift values and multiplicities of the ^{1}H NMR signals assigned to the aromatic hydrogens of the palladated C_6H_4 rings for both complexes with those of reported compounds also supported their *trans*(N,P)-geometry. The multiplets of protons H(6) and H(5) in the spectra of both complexes were shifted upfield significantly, compared to the corresponding signals of the starting ligands. Similar observations were reported for cyclopalladated Ph_3P-adducts of other oxazolines [8] and amines [2e]. In the ^{1}H NMR spectrum of adduct **5a**, the H(6) signal appeared at 6.46 ppm as a doublet of doublets with $J_{HP} = 4.7$ Hz. For comparison, the dd signal of H(6) for two previously reported PPh_3-adducts of 2-phenyl-2-oxazoline-derived CPCs of *trans*(N,P)-geometry was observed at 6.43 ppm and had $J_{HP} = 4.7$ and 5.0 Hz [8a,8b]. The NOESY spectrum of complex **5b** in $CDCl_3$ suggested that the *ortho*-hydrogens of the PPh_3 group are in close proximity to H(6) and H(5) of the C_6H_4-ring, thus confirming the *trans*(N,P)-geometry. In the ^{13}C NMR spectra of **5a** and **5b**, the C(6) and C(5) signals of the C_6H_4 fragment appeared as doublets: $^3J_{PC} = 10.8$, 11.6 and $^4J_{PC} = 4.1$, 5.7 Hz, respectively. These data are in close agreement with those reported for other complexes of *trans*(N,P)-geometry [8a,8b].

It is worth mentioning that in the ^{1}H NMR spectrum of phosphane adduct **5b** the protons of the 2-Me group and H(4) proton of the oxazoline ring display a spin–spin coupling constant $^5J_{HH} = 1.1$ (confirmed by the COSY data). Most surprisingly, this coupling is observed despite the non-coplanarity of these five bonds, which is evident from the absence of a coupling constant $^4J_{HP}$ for the H(4) proton. The occurrence of the spin–spin coupling constant, $^5J_{HH}$, may be explained by the presence of the C=N bond in the chain connecting these interacting protons.

It was reasonable to suggest that the palladacycle's conformation has to be nearly planar in the case of derivatives of 2,4-diphenyl-substituted oxazoline, due to the presence of the *endo*-cyclic C=N bond in addition to the fused C_6H_4 group; the results of the X-ray study of dimer (*R*,*R*)-**4a** (see below) confirmed this assumption. Conformation of the *exo*-palladacycle obtained from 2-methyl-4-phenyl-2-oxazoline was expected to be slightly more puckered, due to the *exo* position of C=N bond in respect to the palladacycle. Molecular models revealed rather high rigidity in the tricyclic system, with a nearly orthogonal orientation of the NCH proton. These assumptions may be confirmed (*i*) by the absence of spin–spin coupling between the NCH proton and the ^{31}P nucleus in the ^{1}H NMR spectra of both phosphane adducts **5a,b** and (*ii*) by the absence of any significant changes in the ^{1}H NMR spectra of the phosphane adduct (*R*)-**5b** taken at different temperatures within a very broad range (from −85 up to +85 °C) in d_8-toluene.

The ^{1}H NMR spectra provided valuable information about the oxazoline ring conformation in the ligands and their complexes. The signals of the oxazoline ring hydrogens in the spectra of free ligands **2a,b** are well-resolved with the values of coupling constants J_{AX} and J_{BX} identical for both compounds and equal to 8.3 and 10.1 Hz, respectively. Based on the original Karplus equation for analyzing vicinal couplings in rigid aliphatic systems [27], one can predict that the dihedral angles H_ACCH_X and H_BCCH_X are approximately equal to 145° and 25°, respectively. These angle values are expected for the $\lambda(R)$ conformation of the oxazoline ring (Fig. 1(a)). For comparison, the other possible twisted conformation of the oxazoline ring, $\delta(R)$, should provide one large and one small coupling constant (see Fig. 1(b)). Therefore, it can be concluded that, in $CDCl_3$ solutions, the heterocycle in the ligands has one predominant chiral conformation and that being $\lambda(R)$.

In the case of cyclopalladated derivatives of 2-methyl-4-phenyl-2-oxazoline **4b** and **5b**, both constants J_{AX} and J_{BX} have rather high values (10.4–9.8 and 10.4–10.0 Hz,

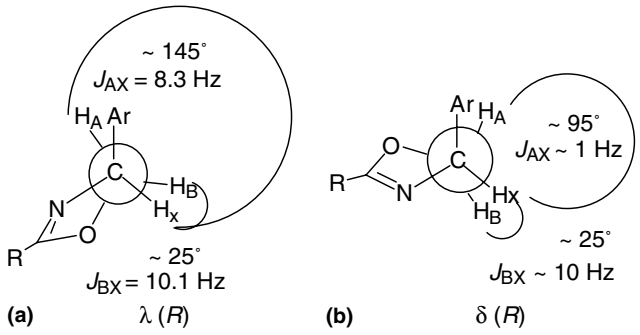


Fig. 1. Newman projections of the ligands' oxazoline ring along the C(4)–C(3) bond for two possible twisted conformations (a) $\lambda(R)$ and (b) $\delta(R)$ with the approximate values of dihedral angles H_XCCH_A and H_XCCH_B and their corresponding expected coupling constants J.

respectively). This may be considered an indication of the $\lambda(R)$-conformation of the oxazoline ring in these two complexes. In contrast, for cyclopalladated derivatives of 2,4-diphenyl-2-oxazoline **3a** and **5a**, the values of constant J_{AX} decreased to 7.6 and 4.9 Hz, respectively, while retaining a high value of constant J_{BX} (10.1 and 9.7 Hz). These data point to greater flexibility of the oxazoline ring, with a possible equilibrium between two conformations, $\lambda(R)$ and $\delta(R)$ (probably, with a greater contribution of the former). The contribution of the $\lambda(R)$ conformation increased in an aromatic solvent: in the ^{1}H NMR spectra measured in d_8-toluene both constants J_{AX} and J_{BX} become nearly identical with the average value of 9.7–10.1 Hz in the temperature interval from +85 to −40 °C. These data are in agreement with the results of the X-ray study of dimer (*R*)-**4a** (see below).

2.4. X-ray diffraction studies: crystal structures of dimers (R,R)-4a and 7a

The spectroscopic data obtained for the cyclopalladated complexes of (*R*)-2,4-diphenyl-2-oxazoline **3a**, **4a** and **5a** were insufficient to select between 2-Ph and 4-Ph ring as the palladation site. In order to determine the regiochemistry of (*R*)-2,4-diphenyl-2-oxazoline *ortho*-palladation, an X-ray diffraction study of chloro-bridged dimer (*R*,*R*)-**4a** was performed. The data obtained from this study unambiguously confirmed the *endo*-structure of the palladacycle derived from (*R*)-2,4-diphenyl-2-oxazoline. The molecular structure and numbering scheme are presented in Fig. 2, with selected bond lengths and angles given in Tables 1 and 2, respectively. The asymmetric unit in the structure of complex (*R*,*R*)-**4a** contains two independent dimeric molecules and two dichloromethane solvate molecules.

To estimate the steric influence of the phenyl group at position 4 of the oxazoline ring, an X-ray diffraction study was done on the acetate-bridged dimer **7a**, which was synthesized previously [8c] from 2-phenyl-2-oxazoline. Its

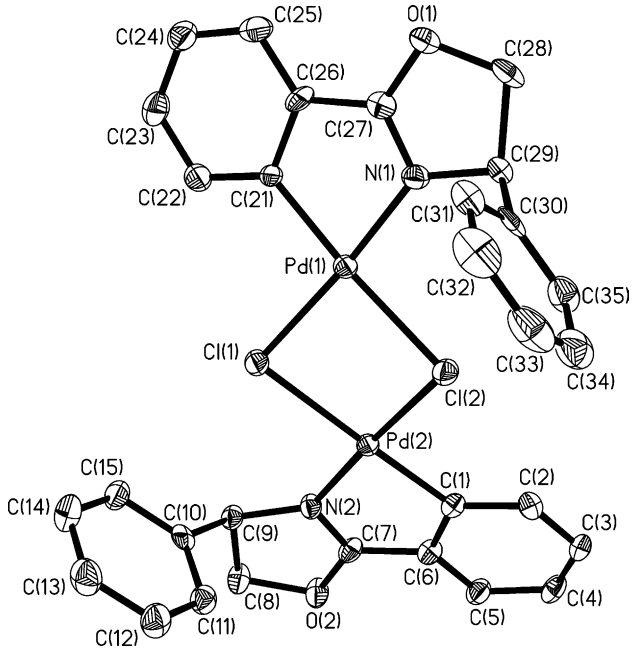


Fig. 2. Molecular structure and numbering scheme of one of the two crystallographically independent molecules of (*R*,*R*)-di-μ-chlorobis{2-[2-(4-phenyl)oxazolinyl]phenyl-C,N}dipalladium(II) (**4a**); solvate molecules are omitted for clarity.

molecular structure and numbering scheme are presented in Fig. 3 and selected bond lengths and angles are given in Tables 3 and 4, respectively. Complex **7a** crystallizes in the space group *Cmcm* with the unit cell containing two crystallographically independent dimeric molecules. [1] Both molecules have the same complicated type of disorder and are located at the two orthogonal mirror planes. One of these planes orthogonally bisects the Pd···Pd line. The second plane includes both palladium atoms and a plane that bisects the acetato-bridges. The symmetry of this position (*mm*) appears to be higher than the symmetry of the dimer molecule itself; as a result, the phenylene ring and oxazoline heterocycle lie in the same position with an occupancy ratio of 0.5/0.5.

To our knowledge, all previously reported and crystallographically characterized oxazoline-derived *CN*-palladacycles have contained only 4-alkyl-substituted oxazoline fragments (Fig. 4). This collection includes dimeric *CN*-cyclopalladated derivatives of 2-phenyl- (**7b–d**) [8b,9a,9i] and 2-ferrocenyl oxazolines (**8a,b**) [7e], and PPh_3-adduct of 2-phenyl-2-oxazoline-derived μ-Cl-dimer (**9**) [8c]. X-ray diffraction studies for several neutral and cationic "pincer" complexes of *NCN*-type (**10a–d**) have been performed as well [10a,10b,10e,10f].

[1] The structure was also solved and refined in the space group *Cmc21*; however, the same disorder remained. Thus, the space group *Cmcm* was chosen.

Table 1
Selected bond lengths (Å) for a dichloromethane solvate of (*R*, *R*)-**4a**

Pd(1)–C(21)	1.991(6)	Pd(3)–C(41)	1.997(6)
Pd(1)–N(1)	2.010(5)	Pd(3)–N(3)	2.016(5)
Pd(1)–Cl(1)	2.3287(15)	Pd(3)–Cl(4)	2.3122(14)
Pd(1)–Cl(2)	2.4340(15)	Pd(3)–Cl(3)	2.4719(14)
Pd(2)–C(1)	1.989(6)	Pd(4)–C(61)	1.996(6)
Pd(2)–N(2)	2.007(5)	Pd(4)–N(4)	2.014(5)
Pd(2)–Cl(2)	2.3227(15)	Pd(4)–Cl(3)	2.3409(13)
Pd(2)–Cl(1)	2.4656(14)	Pd(4)–Cl(4)	2.4331(15)
O(1)–C(27)	1.326(7)	O(3)–C(47)	1.334(7)
O(1)–C(28)	1.464(8)	O(3)–C(48)	1.486(7)
O(2)–C(7)	1.324(7)	O(4)–C(67)	1.349(7)
O(2)–C(8)	1.482(7)	O(4)–C(68)	1.474(8)
N(1)–C(27)	1.298(8)	N(3)–C(47)	1.285(7)
N(1)–C(29)	1.487(8)	N(3)–C(49)	1.475(7)
N(2)–C(7)	1.288(7)	N(4)–C(67)	1.287(7)
N(2)–C(9)	1.476(7)	N(4)–C(69)	1.479(8)
C(1)–C(6)	1.421(8)	C(41)–C(46)	1.425(8)
C(6)–C(7)	1.458(8)	C(46)–C(47)	1.454(8)
C(8)–C(9)	1.564(8)	C(48)–C(49)	1.560(8)
C(9)–C(10)	1.510(8)	C(49)–C(50)	1.522(8)
C(21)–C(26)	1.424(8)	C(61)–C(66)	1.422(8)
C(26)–C(27)	1.459(9)	C(66)–C(67)	1.457(8)
C(28)–C(29)	1.561(9)	C(68)–C(69)	1.566(8)
C(29)–C(30)	1.511(9)	C(69)–C(70)	1.525(9)

Table 2
Selected bond angles (°) for a dichloromethane solvate of (*R*, *R*)-**4a**

C(21)–Pd(1)–N(1)	80.7(2)	C(41)–Pd(3)–N(3)	81.1(2)
N(1)–Pd(1)–Cl(1)	173.61(15)	N(3)–Pd(3)–Cl(4)	175.39(16)
C(21)–Pd(1)–Cl(2)	174.59(17)	C(41)–Pd(3)–Cl(3)	178.06(19)
C(1)–Pd(2)–N(2)	81.1(2)	C(61)–Pd(4)–N(4)	80.6(2)
N(2)–Pd(2)–Cl(2)	176.52(14)	N(4)–Pd(4)–Cl(3)	176.82(15)
C(1)–Pd(2)–Cl(1)	175.15(17)	C(61)–Pd(4)–Cl(4)	174.71(17)
C(27)–O(1)–C(28)	105.6(5)	C(47)–O(3)–C(48)	105.9(4)
C(7)–O(2)–C(8)	105.8(4)	C(67)–O(4)–C(68)	106.1(4)
C(27)–N(1)–C(29)	109.1(5)	C(47)–N(3)–C(49)	110.1(5)
C(27)–N(1)–Pd(1)	115.0(4)	C(47)–N(3)–Pd(3)	114.3(4)
C(7)–N(2)–C(9)	109.5(5)	C(67)–N(4)–C(69)	110.7(5)
C(7)–N(2)–Pd(2)	115.6(4)	C(67)–N(4)–Pd(4)	114.6(4)
C(6)–C(1)–Pd(2)	113.5(4)	C(46)–C(41)–Pd(3)	113.8(4)
C(1)–C(6)–C(7)	112.5(5)	C(41)–C(46)–C(47)	111.3(5)
N(2)–C(7)–O(2)	118.2(5)	N(3)–C(47)–O(3)	116.7(5)
N(2)–C(7)–C(6)	117.2(5)	N(3)–C(47)–C(46)	119.3(5)
O(2)–C(8)–C(9)	105.0(5)	O(3)–C(48)–C(49)	104.0(4)
N(2)–C(9)–C(8)	101.5(4)	N(3)–C(49)–C(48)	100.9(4)
C(26)–C(21)–Pd(1)	114.9(4)	C(66)–C(61)–Pd(4)	114.9(4)
C(21)–C(26)–C(27)	110.8(5)	C(61)–C(66)–C(67)	110.4(5)
N(1)–C(27)–O(1)	118.0(6)	N(4)–C(67)–O(4)	116.6(5)
N(1)–C(27)–C(26)	118.5(5)	N(4)–C(67)–C(66)	119.5(5)
O(1)–C(28)–C(29)	106.2(5)	O(4)–C(68)–C(69)	105.5(5)
N(1)–C(29)–C(28)	100.5(5)	N(4)–C(69)–C(68)	100.9(5)

In common with most of the structurally characterized dimeric halide-bridged cyclopalladated complexes of *CN*-type [3d], including known oxazoline-derived representatives **7b–d** and **8a,b**, dimer (*R*, *R*)-**4a** reveals an *anti*-arrangement of the two nitrogen and two carbon donor atoms. Each of the two independent dimeric molecules consists of two crystallographically independent halves

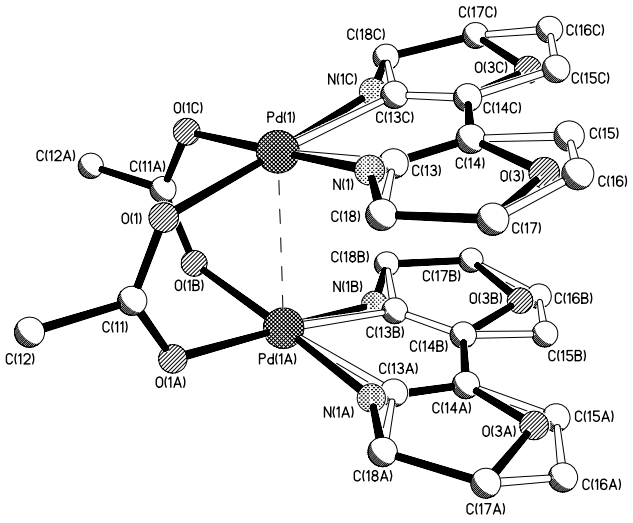


Fig. 3. Molecular structure and numbering scheme of *di-μ-acetato-bis{2-(2-oxazolinyl) phenyl-C,N}dipalladium(II)* (**7a**); hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) for dimer **7a**

Pd(1)–N(1)#1	1.93(4)	Pd(2)–N(2)	1.89(3)
Pd(1)–N(1)	1.93(4)	Pd(2)–N(2)#2	1.89(3)
Pd(1)–C(13)#1	2.06(5)	Pd(2)–O(2)#2	2.085(3)
Pd(1)–C(13)	2.06(5)	Pd(2)–O(2)	2.085(3)
Pd(1)–O(1)	2.079(3)	Pd(2)–C(23)#2	2.16(3)
Pd(1)–O(1)#1	2.079(3)	Pd(2)–C(23)	2.16(3)
Pd(1)–Pd(1)#2	2.851(2)	Pd(2)–Pd(2)#3	2.8502(13)
O(1)–C(11)	1.239(4)	O(2)–C(21)	1.235(4)
C(11)–O(1)#2	1.239(4)	C(21)–O(2)#1	1.235(4)
N(1)–C(18)	1.37(4)	N(2)–C(28)	1.588(14)
N(1)–C(14)	1.51(2)	N(2)–C(24)	1.31(3)
C(13)–C(14)	1.15(3)	C(23)–C(24)	1.46(4)
O(3)–C(14)	1.415(11)	O(4)–C(24)	1.428(12)
O(3)–C(17)	1.572(10)	O(4)–C(27)	1.592(11)
C(14)–C(14)#1	1.447(12)	C(24)–C(24)#2	1.440(13)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, z$; #2 $x, y, -z+1/2$; #3 $-x+1, y, -z+1/2$.

differing to some extent in their structural parameters (see below).

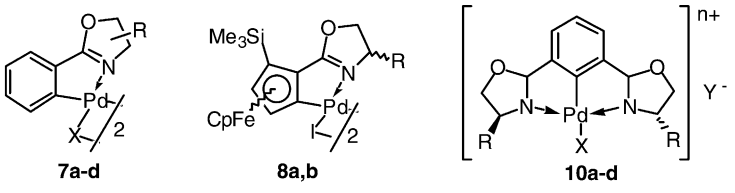
The most interesting peculiarity of the dimer (*R*, *R*)-**4a** structure is the rather considerable bend (152.4–151.1°) in the central four-membered ring $\{Pd_2(\mu\text{-}Cl)_2\}$ along the Cl(1)···Cl(2) axis (deviation from co-planarity of 27.6–28.9°) [2] (see Fig. 5) with decreased values (151.1–151.2°) of the angles between the mean coordination planes (*mcpl*) of the two palladacycles. Such bending is in drastic contrast to the nearly planar configuration of this fragment in most of the reported halide-bridged dimeric complexes of *CN*-type with an *anti*-arrangement

[2] Here, and later on, two values cited correspond to interval of four values for two halves of two independent dimeric molecule **4a**.

Table 4
Selected bond angles (°) for dimer **7a**

N(1)–Pd(1)–O(1)	90.8(7)	N(2)–Pd(2)–O(2)	98.9(8)
N(1)#1–Pd(1)–O(1)	177.9(10)	N(2)#2–Pd(2)–O(2)	174.0(7)
C(13)–Pd(1)–O(1)	100.3(9)	C(23)–Pd(2)–O(2)	91.8(9)
C(13)#1–Pd(1)–O(1)	171.6(9)	C(23)#2–Pd(2)–O(2)	177.6(8)
O(1)–Pd(1)–O(1)#1	88.0(2)	O(2)–Pd(2)–O(2)#2	86.5(2)
N(1)–Pd(1)–Pd(1)#2	100.3(13)	N(2)–Pd(2)–Pd(2)#3	97.1(8)
C(13)–Pd(1)–Pd(1)#2	100(2)	C(23)–Pd(2)–Pd(2)#3	100.4(9)
O(1)–Pd(1)–Pd(1)#2	81.13(10)	O(2)–Pd(2)–Pd(2)#3	81.05(11)
C(11)–O(1)–Pd(1)	125.4(3)	C(21)–O(2)–Pd(2)	125.6(3)
O(1)–C(11)–O(1)#2	126.1(6)	O(2)–C(21)–O(2)#1	126.1(6)
O(1)–C(11)–C(12)	116.9(3)	O(2)–C(21)–C(22)	116.9(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, z$; #2 $x, y, -z+1/2$; #3 $-x+1, y, -z+1/2$.



X = OAc, R = H (**7a**)
X = OAc, R = 4,4-Me_2 (**7b**) [9i]
X = OAc, R = (4*S*)-Pr^i (**7c**) [9a]
X = Cl, R = (4*R*)-Bu^t (**7d**) [8b]

R = (4*S*)-Bu^t [($S_C R_{pl}$)-**8a**] [7e]
R = (4*R*)-CEt_2OMe [($R_C S_{pl}$)-**8b**] [7e]

n = 0, R = (4*S*)-CMe_2Ph, X = I (**10a**) [10e]
n = 0, R = (4*S*)-Pr^i, X = Cl (**10b**) [10a,f]
n = 1, R = (4*S*)-Pr^i, X = H_2O, Y = OTf (**10c**) [10b]
n = 1, R = (4*S*)-Pr^i, X = H_2O, Y = BF_4 (**10d**) [10a]

Fig. 4. Structures of complexes **7a–d**, **8a,b** and **10a–d**.

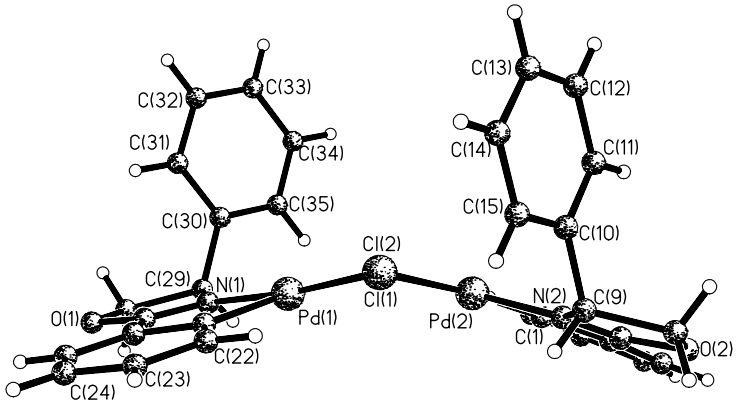


Fig. 5. Illustration of the central four-membered ring {Pd_2Cl_2} bending for dimer (*R*, *R*)-di-μ-chlorobis{2-[2-(4-phenyl)oxazolinyl]phenyl-C,N}-dipalladium(II) (**4a**).

of the two palladacycles [28]. Moreover, these values are far beyond the upper limit for angles ($\geqslant$163.7°) displayed in rare examples of bended cyclopalladated μ-Cl-*anti*-dimers of the *CN*-type described previously [3d]. The bending is somewhat more pronounced in the case of dimer (*R*, *R*)-**4a** when compared to that found previously for its more bulky 4-*tert*-butyl-substituted analog (*S*, *S*)-**7d** (161.1°) [8b]. The reason of such strong distortion in the structure of (*R*, *R*)-**4a** remains unclear, given the distance between the bulky 4-phenyl groups in the *anti*-configurated dimeric molecule (Fig. 5). Probably, distortion is caused by crystal packing effects; however steric hindrance may also make some contribution. For example, in the case of the dimers **8a,b**, bearing very bulky 4-substituents (*tert*-Bu or CEt_2OMe) and the sterically demanding ferrocenyl backbone, deviation from co-planarity increases to 64.5–66.7° (in the terms of the bend along the I···I axis).

The length of the Pd–N bond [2.007(5)–2.016(5) Å] in dimer (*R*,*R*)-**4a** falls in the normal range of values reported for related chloro- and acetato-bridged oxazoline-derived cyclopalladated dimers **7a–d** (1.886–2.029 Å) [8b,9a,9i]. It is slightly shortened, however, compared to the Pd–N bonds in iodo-bridged dimeric ferrocenyloxazoline complexes **8a,b** (2.084–2.085 Å) [7e] and elongated compared to the 4-nonsubstituted μ-acetato-dimer **7a** [1.89(3)–1.93(4) Å]. The Pd–C bond in dimer (*R*,*R*)-**4a** has a normal value [1.989(6)–1.997(6) Å] typical for all other oxazoline-based dimeric CPCs (1.926–1.997 Å) [7e,8b,9a,9i]. In the case of 4-nonsubstituted dimer **7a**, this bond length is increased to 2.06(5)–2.16(3) Å. The difference between the lengths of the Pd–Cl bonds *trans* to the *C*-[2.4331(15)–2.4719(14) Å] and *N*-donor atoms of the palladacycle (2.3122(14)–2.3409(13) Å) in the structure of dimer (*R*,*R*)-**4a** structure is in accordance with the *trans*-influences of these atoms and their values are close to those reported previously for the related 4-*tert*-Bu-substituted μ-Cl-dimer [2.455(2)–2.470(2) and 2.320(2)–2.323(2) Å, respectively] [8b].

Both palladium atoms in complex (*R*,*R*)-**4a** are nearly in square-planar coordination with a slight tetrahedral distortion. The dihedral angles between the planes {CPdN) and (ClPdCl′} are equal to 3.0–7.3°, which is inside the range (1.7–10.8°) reported previously for mono- and binuclear derivatives of oxazoline-derived *CN*-palladacycles, which is somewhat decreased compared to that found for the 4-*tert*-butyl-substituted analog (8.7–10.8°) [8b]. To note, the low limit of this parameter (0.0°) may be found in the case of the *NCN*-pincer complexes **10b–d** bearing palladium atoms in ideally planar coordination environments.

As a consequence of the rather low extent of tetrahedral distortion, its direction [3] in the structures of chiral complexes (*R*,*R*)-**4a** and **7b–d** does not reveal strict dependence on the configuration of the C*-stereocenter in the oxazoline ring. Only in the structures of the more twisted complexes (*S*,*S*)-**7d** and (*R*,*R*)-**4a** does tetrahedral distortion result in the Λ(S_C) and Δ(R_C) chirality, respectively; while among the eight independent palladacycles of the more flattened dimer (*S*,*S*)-**7c**, both the Δ(S_C) and Λ(S_C) configurations of tetrahedral distortion may be found. It must also be noted that ferrocenyl-oxazoline complexes bear other peculiarities, such as the square-pyramidal configuration of the palladium environment (with the apical metal displaced from the base by ca. 0.1 Å) and pronounced twisting in the polyhedron base (8.2–8.5°).

[3] For description of the tetrahedron stereochemistry we have proposed [28] to use the sign of the *pseudo*-torsion angle formed by four palladium-bonded atoms (for example, $Cl^1\cdots C\cdots N\cdots Cl^2$ in the case of μ-Cl-dimers): its positive sign indicates the Λ-configuration, and the negative sign refers to Δ-stereochemistry.

In dimer (*R*,*R*)-**4a**, the five-membered *CN*-palladacycles have a rather flattened envelope-like conformation with average intrachelate torsion angles (τ) [3d] of 1.8–2.4°, which are near the lower limit of the range (1.7–11.3°) for previously reported *ortho*-palladated 2-aryl- and 2-ferrocenyl-oxazolines **7–10** (with the sterically crowded complexes **8a,b** at the upper limit). This feature should be considered rather typical for palladacycles bearing oxazoline donor groups with the C=N double bond in the *endo*-position, in contrast with the much more puckered benzylaminate *CN*-palladacycles, with τ values increased to 20–32° for ca. 90% of known palladacycles of this kind [28].

As a consequence of the nearly planar palladacycle conformation, the orientation of the 4-phenyl substituent on the oxazoline ring appears to be intermediate between axial and equatorial, with the torsion angles between the (ox)C^4–C^{ipso}(Ph) bond and the normal to the *mcpl* equal to 28.3–34.2°. A similar orientation was found for the 4-isopropyl substituent in the complex **7c** (17.7–33.3°), while in the case of dimer **7d** the more bulky 4-*tert*-butyl group is located in the vicinity of the axial position (13.4–19.6°). The plane of the 4-phenyl ring in the structure of dimer (*R*,*R*)-**4a** takes a position nearly orthogonal with respect to the *mcpl* (78.6–92.5°), the mean plane of the palladacycle (78.0–89.6°), and the plane of the oxazoline ring (84.3–90.0°).

A second consequence of the rather flattened palladacycle conformation in dimer (*R*,*R*)-**4a** is the absence of strict correlation between its chirality and the absolute configuration of the C*-stereocenter. Among the four palladacycles of the two independent molecules in the unit cell, only one is of the λ(R_C)-chirality, while the other three are twisted in the δ(R_C) conformation. For comparison, all other known chiral oxazoline-derived complexes (**7c,d** and **8a,b**; 7 dimeric molecules, 14 palladacycles) contain their more puckered palladacycles (τ 4.7–11.3°) only in the λ(R_C)- or δ(S_C)-conformation, with strict dependence on the configuration of the C*-stereocenter, (*R*) or (*S*), respectively.

The geometric parameters of oxazoline rings in all known cyclopalladated compounds (**4a** and **7–10**) demonstrate the pronounced flexibility of the heterocycle and dependence of its twisting extent on the presence of 4-position substituents and their bulkiness. For example, the values of the average intracyclic torsion angles for the oxazoline ring (τ′) in the independent palladacycles of complexes **4a**, **7b** and **7c** have a rather wide range of values 0.4–7.3°, 1.1–10.3° and 3.3–14.0°, respectively. For compounds **7d** and **8a,b**, bearing a very bulky substituent at the C(4)-atom of the heterocycle (Bu^t or CEt_2OMe), this parameter (τ′) is retained at a rather high level (13.2–14.7°), in contrast with ca. 0.5° found for the PPh_3-adduct of the 4-nonsubstituted complex.

The chiral nature of oxazoline ring distortion is evident from the displacement of the carbon atoms of the (N)C*HR–CH_2(O) fragment in opposite directions with reference to the mean plane of this heterocycle. Thus, the chirality of oxazoline ring conformation may be estimated from the sign of the torsion angle O···C^5···C^4···N: with a positive sign corresponding to the δ-twist, while a negative sign indicating the λ-conformation. All previously reported oxazoline-derived CPCs (**7c,d** and **8a,b**; 7 dimeric molecules, 14 palladacycles) contain oxazoline rings in the $\delta(R)$- or $\lambda(S)$-conformation, with strict dependence on the configuration of the C*-stereocenter, (*R*) or (*S*), respectively. The same tendency is retained in three palladacycles of the two molecules of 4-phenyl-substituted complex (*R*,*R*)-**4a** in the unit cell, which contain the oxazoline cycle in the $\delta(R_C)$-conformation; however, in the case of the fourth molecule, the oxazoline ring exists in the opposite $\lambda(R_C)$-conformation. This and other deviations from the general stereochemical rules typical for the more sterically hindered analogues (**7c,d** and **8a,b**) may be connected with the more flattened structure of this complex.

In conclusion, in the oxazoline derived CPCs bearing a bulky substituent at position 4, the chirality of the carbon stereocenter may be successfully transferred to the other types of chirality, namely, oxazoline ring and palladacycle conformation, and tetrahedral distortion of the metal coordination sphere. Unfortunately, the 4-phenyl substituent is not bulky enough (for example, compared to *tert*-butyl) to guarantee the same level of chirality transfer.

3. Conclusions

Direct palladation of (*R*)-2,4-diphenyl-2-oxazoline using $Pd(OAc)_2$ and AcONa in acetic acid resulted in the regiospecific formation of a complex with a C=N bond *endo* with respect to the palladacycle. Using the same conditions but much longer reaction time, the reaction with (*R*)-2-methyl-4-phenyl-2-oxazoline provided a complex with an *exo* palladacycle. These data confirmed that 4-phenyl-substituted oxazolines, similar to benzaldimines, prefer to form a palladacycle with the C=N bond in the *endo* position. In the absence of a suitable substituent (at position 2 of the heterocycle) to form an *endo* metallacycle, cyclopalladation of 4-substituted 2-oxazolines may lead to a less preferable *exo* palladacycle. Spectroscopic data obtained for cyclopalladated complexes **3a,b–5a,b** proved cyclometallation; however, these data were insufficient to determine the regiochemistry of the direct palladation for (*R*)-2,4-diphenyl-2-oxazoline. The *endo*-structure of cyclopalladated complexes based on this ligand was proven by the X-ray crystallographic analysis of compound **4a**. Comparison of the structural parameters for this complex to those for a series of known analogs has shown that, in the oxazoline derived CPC's bearing a bulky substituent at position 4, the chirality of the carbon stereocenter may be successfully transferred to the other types of chirality, such as the oxazoline ring and palladacycle conformation, and tetrahedral distortion of the metal coordination sphere. The 4-phenyl substituent is not bulky enough to induce the same level of chirality transfer in comparison to the 4-*tert*-butyl group.

4. Experimental

4.1. General

Routine ^{1}H and ^{13}C NMR (500 and 125 MHz, respectively), DEPT, COSY, and HSQC (or HETCOR) spectra were recorded at ambient temperature (unless otherwise noted) in $CDCl_3$, using TMS as an internal standard on an Avance 500 Bruker spectrometer. ^{31}P NMR spectra were recorded at 202 MHz using triethyl phosphite as an external reference. Spin–spin coupling constants, *J*, are given in Hz. IR spectra were recorded on an ATI Mattson Genesis Series FTIR as Nujol mulls or neat liquids. Analytical TLC was performed on Merck pre-coated 0.2 mm plates of silica gel 60 F_{254}. Melting points were measured on a Laboratory Device Mel-Temp-II apparatus and were not corrected.

All chemicals were purchased from Aldrich Chemical Company, USA. Palladium acetate was treated prior to use by dissolving in hot benzene, followed by filtration and solvent removal in vacuo. Acetic acid was distilled over $KMnO_4$. Other solvents were distilled over CaH_2 prior to use.

4.2. Ligand synthesis

4.2.1. (*R*)-2,4-Diphenyl-2-oxazoline (*2a*)

Zinc chloride (0.099 g, 0.73 mmol) was sublimed onto the inside surface of a 100 ml Schlenk flask. Benzonitrile (1.9 ml, 0.019 mol), (*R*)-(−)-2-phenylglycinol (2.00 g, 0.0146 mol) and chlorobenzene (42 ml) were added to the flask. The mixture was refluxed for 52 h, during which time it changed from cloudy-white to clear-yellowish in color. The solvent was removed in vacuo. Column chromatography (SiO_2, $h = 14$ cm, $d = 3$ cm, gradient elution from pure hexane to 1:1 hexane–CH_2Cl_2) of the crude product afforded 1.71 g (52%) of pure (*R*)-**2a** as a colorless liquid. R_f 0.64 (20:1 CH_2Cl_2–ethyl acetate); $[\alpha]^{20}_{365}$ +256°, $[\alpha]^{20}_{405}$ +153°, $[\alpha]^{20}_{435}$ +115°, $[\alpha]^{20}_{546}$ +52.0°, $[\alpha]^{20}_{589}$ +41.0°, $[\alpha]^{20}_{633}$ +33.3°, (*c* 0.40, CH_2Cl_2); IR (neat, ν, cm^{-1}): 1657 s (C=N); ^{1}H NMR (δ, ppm): 4.26 t (1H, $^2J_{AB} = {}^3J_{AX} = 8.3$, OCH^A), 4.77 dd, (1H, $^3J_{BX} = 10.1$, OCH^B), 5.37 br. t (1H, NCH^X), 7.35 and 8.05 two m (8H and 2H, CH arom.); ^{13}C NMR (δ, ppm): 70.1 (NCH), 74.9 (OCH_2), 126.7 (CH arom.),

127.6 (C arom.), 127.6 (CH arom.), 128.4 (CH arom.), 128.5 (CH arom.), 128.7 (CH arom.), 131.7 (CH arom.), 142.4 (C arom.), 164.7 (OCN). Anal. Calc. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.23; H, 5.85; N, 6.21%.

4.2.2. (*R*)-2-methyl-4-phenyl-2-oxazoline (**2b**)

A solution of (*R*)-2-phenylglycinol (1.50 g, 0.0109 mol) in 5 ml CH_2Cl_2 was added drop-wise to a stirred suspension of ethyl acetimidate hydrochloride (1.76 g, 0.0142 mol) in CH_2Cl_2 (25 ml) at 0 °C. After stirring at RT overnight, the reaction mixture was poured into H_2O (80 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The combined organic layers were dried over Na_2SO_4, and the solvent was removed by distillation at atmospheric pressure. Vacuum distillation of the crude product afforded pure (*R*)-2-methyl-4-phenyl-2-oxazoline (1.40 g, 80%) as a colorless liquid, b.p. 78–80 °C/4 mmHg; R_f 0.45 (1:20 hexane–CH_2Cl_2); $[\alpha]_{589}^{20}$ +108°, $[\alpha]_{546}^{20}$ +132°, $[\alpha]_{435}^{20}$ +243° (*c* 0.20, CH_2Cl_2), IR (neat, *v*, cm^{-1}): 1674 s (C═N); ^1H NMR (δ, ppm): 2.08 d (3H, $^5J = 1.3$, CH_3), 4.08 t (1H, $^3J_{AX} = {}^2J_{AB} = 8.3$, OCH^A), 4.59 dd (1H, $^3J_{BX} = 10.1$, OCH^B), 5.16 br. t (1H, NCH^X), 7.25 m (3H, *meta*- and *para*-H of Ph), 7.34 m (2H, *ortho*-H of Ph); ^{13}C NMR (δ, ppm): 14.3 (CH_3), 70.2 (NCH_2), 75.0 (OCH_2), 126.9 (*meta*-C of Ph), 127.9 (*para*-C of Ph), 129.8 (*ortho*-C of Ph), 142.8 (*ipso*-C of Ph), 166.1 (OCN). Anal. Calc. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.44; H, 6.80; N, 8.68%.

4.3. Synthesis of complexes

4.3.1. (*R,R*)-di-μ-acetatobis{2-[2-(4-phenyl)oxazolinyl]phenyl-*C,N*}dipalladium(II) (**3a**)

$Pd(OAc)_2$ (0.0751 g, 0.335 mmol) and NaOAc (0.0274 g, 0.334 mmol) were added to a solution of (*R*)-2,4-diphenyl-2-oxazoline (0.0747 g, 0.335 mmol) in AcOH (6 ml). The solution was stirred at 60 °C for 2 h. The mixture was diluted with H_2O (25 ml) and extracted with $CHCl_3$ (3 × 10 ml). The organic layers were combined, washed with a saturated aqueous solution of $NaHCO_3$, and run through a layer of Celite® (*h* = 1.5 cm). After solvent removal in vacuo (RT), the dark red-brown oily residue was analyzed by ^1H NMR spectroscopy. According to the NMR data, it contained at least 95% product. Due to the fairly rapid decomposition of (*R,R*)-**3a**, only minimal characterization was performed. $[\alpha]_{589}^{20}$ −240° (*c* 0.20, CH_2Cl_2); IR (Nujol, *v*, cm^{-1}): 1571, 1415 (COO), 1629 (C═N); ^1H NMR (δ, ppm): 1.78 s (3H, CH_3), 3.94 dd (1H, $^2J_{AB} = 8.6$, $^3J_{BX} = 10.1$, OCH^B), 4.14 br. t (1H, OCH^A), 4.27 dd (1H, $^3J_{AX} = 7.6$, NCH^X), 7.5 m (9H, CH arom.); ^{13}C NMR (δ, ppm): 23.6 (CH_3), 64.9 (NCH), 77.3 (OCH_2), 123.9 (CH arom.), 125.8 (CH arom.), 126.6 (CH arom.), 128.2 (CH arom.), 128.7 (CH arom.), 130.6 (CH arom.), 131.0 (C arom.), 131.6 (CH arom.), 139.4 (C arom.), 148.4 (C arom.), 174.6 (OCN), 180.9 (COO).

4.3.2. (*R,R*)-di-μ-chlorobis{2-[2-(4-phenyl)oxazolinyl]phenyl-*C,N*}dipalladium(II) (**4a**)

Freshly prepared crude **3a** (260 mg, 0.335 mmol) was dissolved in acetone (5 ml) and treated with LiCl (28 mg, 0.66 mmol). The mixture was stirred at RT for 40 min. After solvent removal in vacuo, the solid residue was dissolved in CH_2Cl_2 (5 ml) and washed with H_2O (3 × 5 ml). Dry column vacuum chromatography [29] (SiO_2, $h = 2.5$ cm, $d = 4$ cm; eluents: hexane, 1:1 hexane-dichloromethane, dichloromethane, and 10:1 dichloromethane-ethyl acetate) afforded 105 mg of the crude product. After recrystallization (CH_2Cl_2/hexane), 82 mg (67%) of the pure (*R,R*)-**4a** as a yellow powder was obtained, m.p. 202 °C (decomp); R_f 0.44 (2:1 CH_2Cl_2–hexane); $[\alpha]_{435}^{20}$ −1190°, $[\alpha]_{546}^{20}$ −504°, $[\alpha]_{589}^{20}$ −394° (*c* 0.20, CH_2Cl_2); IR (Nujol, *v*, cm^{-1}): 1638 s (C═N); ^1H NMR (δ, ppm): 4.53 and 5.02 two m (2H, CH_2O), 4.95 and 5.28 two m (1H, CHN), 7.40 m (9H, CH arom.); ^{13}C NMR (δ, ppm): 65.8 (NCH), 78.0 (OCH_2), 124.5, 126.3, 127.0, 128.9, 130.1, 131.3, 133.3 (CH arom.), 139.7 (C–Pd), 146.2 (*ipso*-C–Ph), 146.7 (*ipso*-C–Ph), 175.7 (OCN). Anal. Calc. for $C_{30}H_{24}Cl_2N_2O_2Pd$: C, 49.48; H, 3.32; N, 3.85. Found: C, 49.63; H, 3.45; N, 3.84%.

4.3.3. (*R,R*)-di-μ-chlorobis{2-[4-(2-methyl)oxazolinyl]-phenyl-*C,N*}dipalladium(II) (**4b**)

$Pd(OAc)_2$ (165 mg, 0.735 mmol) and NaOAc (60.1 mg, 0.732 mmol) were added to a solution of (*R*)-2-methyl-4-phenyl-2-oxazoline (0.118 g, 0.732 mmol) in AcOH (6 ml). The solution was stirred at 65 °C for 16 h. After removal of acetic acid in vacuo, the residue was dissolved in acetone (5 ml) and LiCl (61.9 mg, 1.46 mmol) was added. After stirring the solution at RT for 1 h, the solvent was removed in vacuo. Dry column vacuum chromatography [29] (SiO_2, $h = 2.5$ cm, $d = 4$ cm; eluents: hexane, 1:1 hexane–CH_2Cl_2, CH_2Cl_2, and 10:1 CH_2Cl_2–EtOAc) afforded 98 mg (45%) of the pure dimer (*R,R*)-**4b** as a yellow powder; another fraction contained pure coordination complex (*R,R*)-**6b** (21%, see Section 4.3.6). Data for (*R,R*)-**4b**, m.p. 154 °C (decomp.); R_f 0.54 (1:10 hexane–CH_2Cl_2); $[\alpha]_{435}^{20}$ +495°, $[\alpha]_{546}^{20}$ +182°, $[\alpha]_{589}^{20}$ +140°, $[\alpha]_{633}^{20}$ +114° (*c* 0.050, CH_2Cl_2); IR (Nujol, *v*, cm^{-1}): 1652 s (C═N); ^1H NMR (δ, ppm): 2.31–2.36 (overlapping singlets, 3H, CH_3), 4.23 (dd, 1H, $J_{AX} = 10.4$, $J_{AB} = 8.5$, OCH^A), 4.88 (m, 1H, OCH^B), 5.60 (br t, 1H, $J_{AX} \approx J_{BX}$, NCH), 6.63, 6.92, 7.02 and 7.25 (four m, 1H each, CH arom.); ^{13}C NMR (δ, ppm): 14.56 and 14.60 (CH_3), 74.27 (OCH_2), 75.03 and 75.08 (NCH), 120.3 (C(6)H arom.), 125.8 (C(5)H arom.), 126.4 (C(4)H arom.), 134.0 and 134.2 (C(3)H arom.), 140.15 and 140.32 (C(2) arom.), 147.0 (PdC(1) arom.), 171.81 (OCN arom.). Anal. Calc. for $C_{20}H_{20}Cl_2$

$N_2O_2Pd_2$: C, 39.76; H, 3.34; N, 4.64. Found: C, 39.44; H, 3.46; N, 4.33%.

4.3.4. (*R*)-chloro-{2-[2-(4-phenyl)oxazolinyl]phenyl-C,N}(triphenylphosphane)palladium(II) (**5a**)

Compound (*R*,*R*)-**4a** (18.5 mg, 0.0239 mmol) was combined with 13.9 mg (0.0530 mmol) of triphenyl phosphane in benzene (15 ml) and the mixture was stirred at RT for 1 h. Then the solvent was removed in vacuo and the crude product was purified using dry column chromatography [29] (SiO_2, $h = 4$ cm, $d = 2$ cm; eluents: hexane, 1:1 benzene–hexane, 20:1 benzene–acetone, 10:1 benzene–acetone). Yield 14.2 mg (89%), m.p. 125 °C (decomp.); R_f 0.63 (1:20 CH_2Cl_2–EtOAc); $[\alpha]^{20}_{435}$ −369.7°, $[\alpha]^{20}_{546}$ −144.2°, $[\alpha]^{20}_{589}$ −116.4°, $[\alpha]^{20}_{633}$ −94.5 (*c* 0.165, CH_2Cl_2); IR (Nujol, *v*, cm^{-1}) 1630 s (C═N); ^1H NMR (δ, ppm): 4.69 dd (1H, $^2J_{AB} = 8.7$, $^3J_{AX} = 4.9$, OCH^A), 5.00 dd, (1H, $^3J_{BX} = 9.7$, OCH^B), 5.67 dd (1H, NCH), 6.46 dd (1H, $J_{PH} = 4.7$, $^3J_{HH} = 7.6$, CH(6) arom.), 6.66 dt (1H, $^5J_{PH} = 1.6$, $^3J_{HH} \approx 7.6$, CH(5) arom.), 6.96 dt (1H, CH(4) arom.), 7.25, 7.33 and 7.39 three m (15H, 4-Ph, CH(3) arom., *meta*- and *para*-CH of PPh_3), 7.69 m (6H, *ortho*-CH of PPh_3); ^{13}C NMR (δ, ppm): 65.8 (HCN), 78.6 (OCH_2), 123.8 (C(4)H), 126.7 (C(3)H), 127.2 and 128.7 (*ortho*- and *meta*-CH of 4-Ph), 127.8 (*para*-CH of 4-Ph), 128.0 d ($^3J_{CP} = 10.8$, *meta*-CH of PPh_3), 130.7 br. s (*para*-CH of PPh_3), 130.8 d ($^1J_{CP} = 50.9$, *ipso*-C of PPh_3), 131.2 d ($^4J_{CP} = 4.1$, C(5)H), 133.1 (C(2)), 135.4 d ($^2J_{CP} = 11.9$, *ortho*-H of PPh_3), 138.1 d ($^3J_{CP} = 10.8$, C(6)H), 141.5 (PdC(1)), 152.6 (*ipso*-C of 4-Ph), 176.3 (OCN). Anal. Calc. for $C_{33}H_{29}ClNOPPd \cdot 2CHCl_3$: C, 48.59; H, 3.38; N, 1.62. Found: C, 48.08; H, 3.48; N, 1.82%.

4.3.5. (*R*)-chloro-{2-[4-(2-methyl)oxazolinyl]phenyl-C,N}(triphenylphosphine)palladium(II) (**5b**)

The compound was prepared by the method described for (*R*)-**5a** in 82% yield, m.p. 118 °C (decomp.); R_f 0.84 (1:1 EtOAc–$CHCl_3$); $[\alpha]^{20}_{435}$ +246°, $[\alpha]^{20}_{546}$ +120°, $[\alpha]^{20}_{589}$ +93° (*c* 0.10, CH_2Cl_2); IR (Nujol, *v*, cm^{-1}) 1653 s (C═N); ^1H NMR (δ, ppm): 2.41 d (3H, $^5J_{HH} = 1.1$, CH_3), 4.28 dd (1H, $^2J_{AB} = 8.5$, $^3J_{AX} = 9.8$, OCH^A), 4.81 dd (1H, $J_{BX} = 10.0$, OCH^B), 5.77 br. t (1H, NCH), 6.32 m (2H, C(6)H and C(5)H arom.), 6.65 d (1H, $^3J_{HH} = 7.6$, C(3)H arom.), 6.80 m (1H, C(4)H arom.), 7.27 m (6H, *meta*-H of PPh_3), 7.34 m (3H, *para*-H of PPh_3), 7.66 m (6H, *ortho*-H of PPh_3); ^{13}C NMR (δ, ppm): 14.5 (CH_3), 73.9 (OCH_2), 74.66 d ($^3J_{CP} = 15.7$,

Table 5
Crystal data, data collection, structure solution and refinement parameters for a dichloromethane solvate of (*R*,*R*)-**4a** and **7a**

	(*R*,*R*)-**4a**	**7a**
Empirical formula	$C_{31}H_{26}Cl_4N_2O_2Pd_2$	$C_{22}H_{22}N_2O_6Pd_2$
Formula weight	813.14	623.20
Color, habit	Light-yellow needle	Light-yellow block
Crystal size (mm)	$0.40 \times 0.10 \times 0.10$	$0.5 \times 0.3 \times 0.2$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	*Cmcm*
Unit cell dimensions		
a (Å)	14.1393(5)	15.325(5)
b (Å)	10.0108(3)	18.690(5)
c (Å)	21.7675(7)	15.507(11)
β (°)	97.388(1)	
V (Å^3)	3055.52(17)	4442(4)
Z	4	8
D_{calc} (g cm^{-3})	1.768	1.864
Absorption coefficient (mm^{-1})	1.559	1.661
F (000)	1608	2464
Diffractometer	Bruker SMART	Enraf-Nonius CAD4
Temperature (K)	120(2)	293
Radiation (λ, Å)	Graphite monochromatized Mo K_α (0.71073)	
θ range (°)	0.94 to 27.50	2.16 to 24.97
Index ranges	$-18 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 12$, $-28 \leqslant l \leqslant 26$	$-3 \leqslant h \leqslant 18$, $-4 \leqslant k \leqslant 22$, $-3 \leqslant l \leqslant 18$
Reflections collected	18118	3990
Independent reflections	12947 [$R_{int} = 0.0319$]	2118 [$R_{int} = 0.0219$]
Absorption correction	Semi-empirical from equivalents	Empirical (psi scan)
Max. and min. transmission	0.8597 and 0.5744	0.3628 and 0.2905
Data/restraints/parameters	12947/1/739	2004/0/190
Goodness-of-fit on F^2	1.024	1.086
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0412$, $wR_2 = 0.0970$	$R_1 = 0.0302$, $wR_2 = 0.0835$
R indices (all data)	$R_1 = 0.0471$, $wR_2 = 0.1002$	$R_1 = 0.0473$, $wR_2 = 0.0918$
Absolute structure parameter	0.01(3)	–
Extinction coefficient	–	0.00021(7)
Largest difference peak and hole (e Å^{-3})	1.945 and −1.027	0.459 and −0.420

NCH), 120.8 (C(3)H arom.), 124.9 (C(4)H arom.), 125.9 d ($^4J_{CP} = 5.7$, CH arom.), 128.4 d ($^3J_{CP} = 10.7$, *m*-C of PPh_3), 131.0 d ($^4J_{CP} = 2.5$, *para*-C of PPh_3), 131.4 ($^2J_{CP} = 51.3$, *ipso*-C of PPh_3), 135.8 d ($^2J_{CP} = 11.7$, *ortho*-C of PPh_3), 138.6 d ($^3J_{CP} = 11.6$, C(6)H arom.,), 148.1 (PdC(1)), 149.6 d ($^4J_{CP} = 1.5$, C(2) arom.), 171.5 d ($^3J_{CP} = 6.8$, OCN); ^{31}P NMR (δ, ppm): 27.21 (PPh_3). Anal. Calc. for $C_{28}H_{25}ClNOPPd$: C, 59.59; H, 4.47; N, 2.48. Found: C, 59.52; H, 4.76; N, 2.50%.

4.3.6. (*R,R*)-dichlorobis-(2-methyl-4-phenyl-2-oxazoline)palladium(II) (**6b**)

The complex was isolated in 21% yield along with complex **4b** (see Section 4.3.3), m.p. 212–214 °C; R_f 0.61 (1:20 hexane–EtOAc); $[\alpha]^{20}_{435}$ −1847°, $[\alpha]^{20}_{546}$ −575°, $[\alpha]^{20}_{589}$ −469° (*c* 0.022, CH_2Cl_2); IR (Nujol, *v*, cm^{-1}) 1648 s (C=N); ^{1}H NMR (δ, ppm): 2.27 s (3H, CH_3), 4.20 t (1H, $^2J_{AB} \approx {}^3J_{AX} = 9.2$, OCH^A), 4.66 dd (1H, $J_{BX} = 10.5$, OCH^B), 5.22 br. t (1H, NCH), 7.20 m (5H, CH arom.); ^{13}C NMR (δ, ppm): 15.9 (CH_3), 69.2 (NCH), 75.7 (OCH_2), 128.5, 128.68 and 128.71 (3 CH arom.), 138.3 (C arom.), 170.7 (OCN). Anal. Calc. for $C_{20}H_{22}Cl_2N_2O_2Pd$ C, 48.07; H, 4.44; N, 5.61. Found: C, 48.27; H, 4.43; N, 5.71%.

4.4. X-ray diffraction study of complexes (*R,R*)-**4a** and **7a**

Single crystals of dimers (*R*,*R*)-**4a** and **7a** suitable for X-ray structural analysis were grown from dichloromethane–hexane and $CDCl_3$ solution, respectively. Details of the crystal data, data collection and structure refinement are given in Table 5. The structures were solved by direct methods [30] (SHELXS-86) and refined by full matrix least squares based on F^2 using SHELXL-97 software [31]. For both structures, all non-hydrogen atoms were refined with anisotropic displacement parameters. In the structure of **7a**, both independent molecules were found to be arranged on two crystallographic mirror planes. Thus, phenyl and oxazolinyl rings are disposed on the same position with occupancy ratio 0.5/0.5. In the structure of (*R*,*R*)-**4a**, H atoms were placed in the calculated positions and refined using a riding model. As for the structure **7a**, methyl hydrogen atoms were placed in calculated positions and refined using a riding model; other H atoms were not included in the model.

Crystallographic data (excluding structure factors) for the structures (*R*,*R*)-**4a** and **7a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-191537 (XOZNOP) and CCDC-191535 (XOZNEF). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We would like to acknowledge North Dakota EPSCoR (“Network in Catalysis”, Grant No. NSF EPS-0132289), the Russian Foundation of Basic Research (Grant No. 04-03-32986a), and NATO (Collaborative Linkage Grant, No. PST.CLG.979757) for support. We are grateful to Professor J.A.K. Howard for help. K.J.K. thanks the GAAANN Fellowship program (Grant No. P200A00205). O.N.G. is grateful to the Russian Science Support Foundation. A.V.C. and L.G.K. would like to acknowledge The Royal Society for financial support. A.V.C. is grateful to the Royal Society of Chemistry for the RSC Journal Grants for International Authors.

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