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Direct *ortho*-palladation of 2-phenyl-2-oxazoline Crystal structure of $Cl_2Pd(\overline{OCH_2CH_2N{=}C}{-}Ph)_2$ and $Cl(PPh_3)Pd(\overline{OCH_2CH_2N{=}C}{-}C_6H_4)$

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Abstract

Direct *ortho*-palladation of sterically non-hindered 2-phenyl-2-oxazoline (**1**) using $Pd(OAc)_2$ and AcONa in AcOH provided di-μ-acetatobis-[2-(2-oxazolinyl)phenyl,1-C,3-N]dipalladium(II) (**3a**) in a yield of 63%. Dimeric complex **3a** was converted into the corresponding μ-chloro analog (**3b**) by the reaction with LiCl in acetone in quantitative yield. Compound **3b** was also obtained in 90% yield by the ligand exchange reaction of oxazoline (**1**) with dimeric *ortho*-palladated complex of *N*,*N*-dimethylbenzylamine in a AcOH–$CHCl_3$ mixture at 50°C. The same reaction at room temperature provided the coordination complex dichlorobis-(2-phenyl-2-oxazoline)palladium(II) (**2**); the use of toluene in this reaction (50°C) led to the formation of chloro[*N*,*N*-dimethylbenzylamino]-(2-phenyl-2-oxazoline)palladium(II) (**5**). Dimer **3b** reacted with 2,4-pentadionate and PPh_3 to yield the corresponding mononuclear derivatives **6** and **7**, respectively. The structures of coordination complex **2** and phosphane adduct **7** were confirmed by X-ray diffraction analysis. Compound **2** has a centrosymmetric structure with strictly planar coordination environment of the palladium center and a close above-plane approach of the *ortho*-C–H bond to the metal center. In adduct **7**, both the palladium coordination sphere and palladacycle are nearly planar.

Keywords: Cyclopalladated complexes; 2-Phenyl-2-oxazoline; X-ray study

1. Introduction

Recently, optically active oxazoline-derived complexes of Pd(II) [1] and other metals [2] have attracted a great deal of attention due to their high efficiency in enantioselective catalysis [1–5]. The majority of these promising catalysts (or pre-catalysts) are simple coordination compounds of bisoxazolines [3], phosphino–oxazolines [4] or other heteroatom-functionalized bidentate oxazolines [5] containing only metal–heteroatom bonds. The use of homochiral cyclopalladated oxazoline-based complexes in catalysis has also been studied. These organometallic catalysts are of the N,C,N (A, Fig. 1) and C,N types (B, Fig. 1) [6,7]. Analysis of the results achieved using these complexes reveal the greater catalytic efficiency of the latter structural type and a high potential of the oxazolinyl group as a chirality inductor in general. It is also known that optically active palladacycles of the C,N-type derived from amines and imines provide very high stereoselectivity in allylic imidate rearrangements [8,9]. These reports prompted us to initiate a study on preparation

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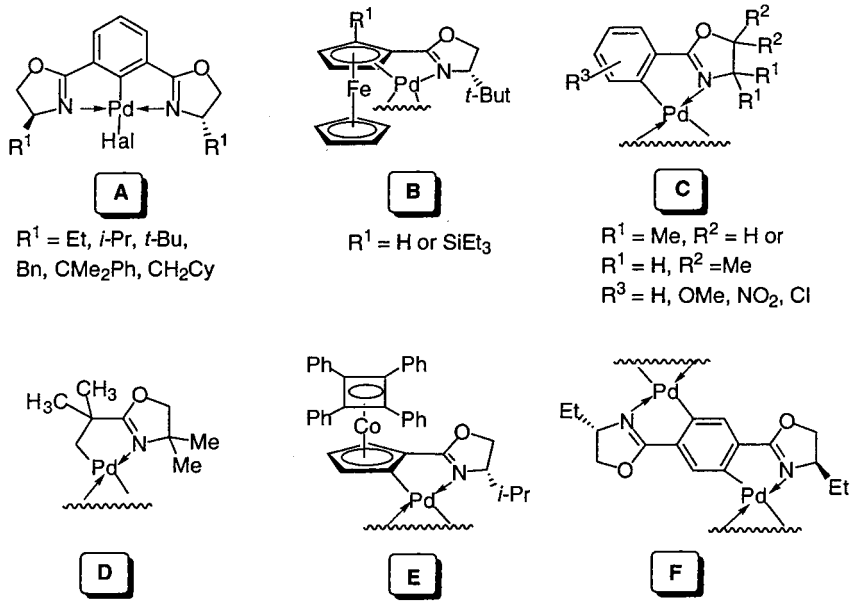


Fig. 1. Types of known cyclopalladated complexes of oxazolines.

and use of C,N-type cyclopalladated complexes of oxazolines including homochiral ones.

Preparation of oxazoline-based palladacycles has not been a simple task. Direct palladation using $Pd(OAc)_2$ was achieved in a moderate (45–60%) [10,11] to high (82–98%) [12,13] yield only for trisubstituted oxazolines furnishing achiral complexes of types C and D (Fig. 1). In the case of disubstituted mono- and bisoxazoline ligands, initial attempts of direct palladation failed. The target complexes of types A and B have been prepared by transmetallation reactions of organolithium [6] and organotin [14] intermediates or by oxidative addition of the corresponding aryl [6] and ferrocenyl [7] halides to a palladium(0) compound. Only two examples of successful direct *ortho*-palladation of disubstituted oxazoline ligands have been reported. In one case, a ligand bearing a metallocene fragment was converted to complex E (Fig. 1) upon treatment with $Pd(OAc)_2$ in AcOH [15]. In the other study, a bisoxazoline derivative reacted with Na_2PdCl_4 in boiling aq. MeOH to yield complex F (Fig. 1) [16].

The observed difference in reactivity of the oxazoline ligands in the *ortho*-palladation reactions points to the importance of steric hindrances in the ligands. Failure of direct cyclopalladation of 2-(2-naphtyl)oxazoline with the 4,5-non-substituted heterocycle may serve as reliable evidence of this effect [17]. Examples of this phenomena have been reported for other ligands as well [18].

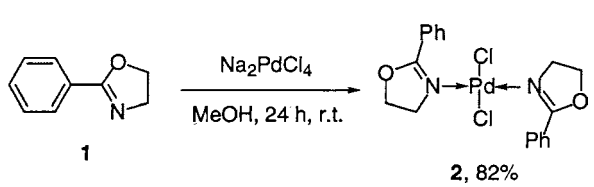
Here we report our results on the preparation of cyclopalladated derivatives of sterically non-hindered 2-phenyl-2-oxazoline.

2. Results and discussion

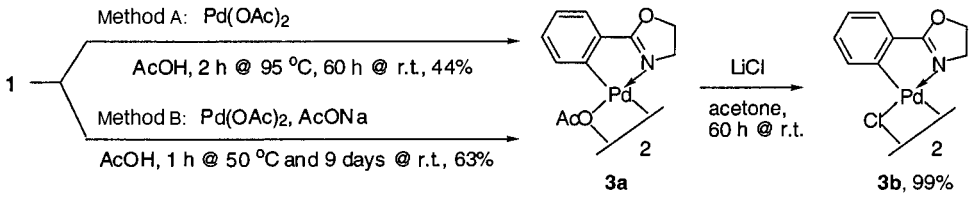
2.1. Cyclopalladation reactions

Many methods for the preparation of cyclopalladated complexes through direct activation of C–H bonds have been reported and reviewed [19–23]. They differ by palladation agent, base, reagents' ratio, solvent polarity, temperature, and reaction time. One of the most common compounds used for palladation is Na_2PdCl_4. We found that the application of an equimolar amount of this rather weak electrophilic reagent in the reaction with 2-phenyl-2-oxazoline (**1**) in MeOH (room temperature (r.t.)) in the presence of AcONa as a base led to the formation of a bis(oxazoline) coordination complex (**2**, 70%) with no traces (^{1}H-NMR data) of the desired cyclopalladated compound (**3a**). The former was also obtained in 82% yield by reacting Na_2PdCl_4 with ligand **1** in a ratio of 1:2 in MeOH at r.t. (Scheme 1). It is noteworthy that pure compound **2** was stable, whereas the crude product decomposed rather quickly to form Pd black.

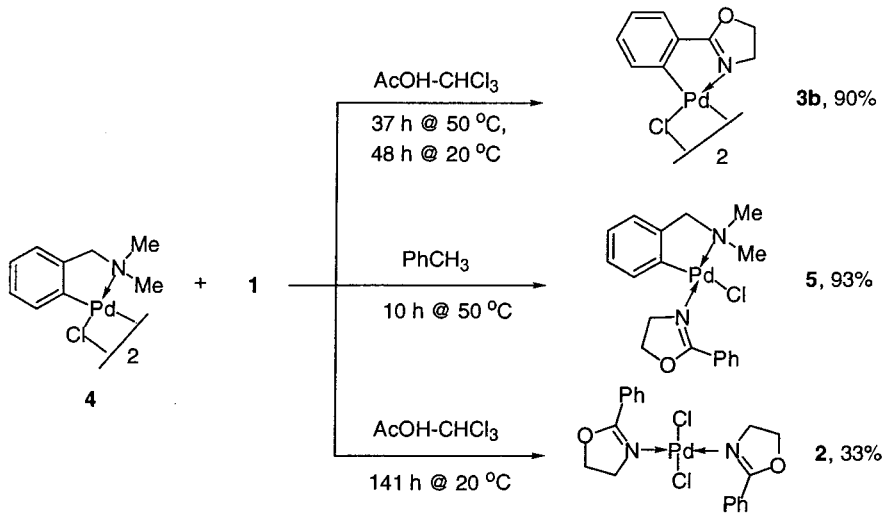
The failure of using Na_2PdCl_4 with AcONa for cyclopalladation was not surprising since this method provided only a trace amount ($< 5\%$) of the corre-



Scheme 1.



Scheme 2.



Scheme 3.

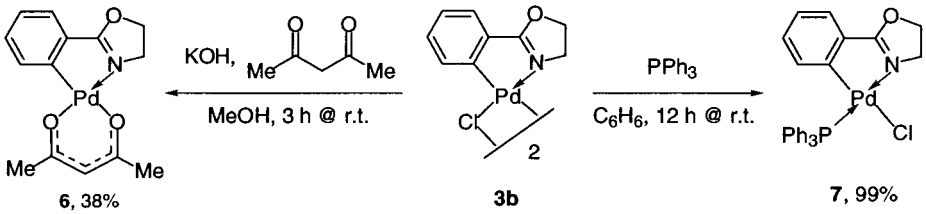
sponding cyclopalladated compound in the reaction with more sterically hindered 4,4-dimethyl-2-(2-naphtyl)-2-oxazoline and no cyclopalladated product at all with a related non-substituted analog [17]. Despite one precedent of *ortho*-palladation of a 4-monosubstituted on the heterocycle 1,4-bis(oxazoline) ligand under similar conditions (Na_2PdCl_4, $MeOH–H_2O$), reliable proof of the proposed cyclopalladated structure has not been provided [16].

One of the most efficient cyclopalladation methods is the use of highly electrophilic $Pd(OAc)_2$ in AcOH. In particular, this approach has been utilized successfully for the synthesis of the known cyclopalladated derivatives of oxazolines [10–13]. Application of this method to the *ortho*-palladation of **1** showed that the reaction was very sensitive to the quality of the reagents and AcOH, as well as to the reaction time and temperature; the yield of the desirable cyclopalladated complex (**3a**) varied from 12 to 44% (cf. Ref. [6]). The best yield of dimer **3a** was achieved when 2-phenyl-2-oxazoline (**1**) reacted with $Pd(OAc)_2$ in AcOH at 95°C for 2 h and then at r.t. for 60 h (Scheme 2, method A). The subsequent anion methathesis using LiCl in acetone led to the quantitative formation of its μ-chloro-bridged analog (**3b**).

It is well known that the use of the weak base AcONa along with $M_2Pd(Hal)_4$ (M = Li, K, Na) promotes cyclopalladation [19,21–23]. We found that the addition of AcONa to the mixture of **1** and $Pd(OAc)_2$ and lowering the reaction temperature (50°C for 1 h and then r.t. for 9 days) increased the yield of **3a** to 63% (Scheme 2, method B). Lowering the temperature without adding AcONa did not improve the yield (24%). Probably, the introduction of AcONa assisted the C–H bond activation and increased to some extent, the polarity of the reaction milieu that, in turn, facilitated the cyclopalladation.

Next we examined a number of other methods of intramolecular C–H bond activation, which have been used successfully for the preparation of cyclopalladated compounds inaccessible by more common means. One method is based on cyclopalladated ligand exchange [24–26]. This methodology worked very well in the case of electron-deficient ligands [27], for the formation of non-optimal six-membered palladacycles [28], and activation of (sp^3) C–H bonds [24,26]. Using this approach, we obtained dimeric *ortho*-palladated complex **3b** by reacting ligand **1** with di-μ-chlorobis-[2-[(dimethylamino)methyl]phenyl-C,N]dipalladium(II) (**4**) at 50°C in a $CHCl_3–AcOH$ mixture in an excellent yield of 90% (Scheme 3).

Previously, it has been suggested that AcOH is a necessary component in the reaction milieu [24,25]. Our data support this hypothesis. Thus, the ligand exchange conducted in toluene at the same temperature resulted in the quantitative formation of compound **5** (Scheme



Scheme 4.

3). Such adducts have been recognized as the first intermediates in cyclopalladated ligand exchange reactions [25,26]. Another necessary condition of a ligand exchange is the thermal activation of this process. When complex **4** reacted with oxazoline **1** at r.t., only coordination complex **2** was formed, probably, due to protonolysis of the Pd–C bond of dimer **4** with subsequent displacement of the tertiary benzylamine by the oxazoline ligand (Scheme 3). Our attempts to convert coordination complex **2** to cyclopalladated dimer **3b** by heating it in an $AcOH–CHCl_3$ mixture (as well as in MeOH, cf. Ref. [28]) failed[4]. This may serve as an indirect indication of the intramolecular activation of a new C–H bond with the assistance of the C–Pd bond in the starting complex; bis(ligand) coordination complexes (related to **2**) may not be intermediates in the cyclopalladated ligand exchange reaction (in contrast to the earlier proposed mechanism [26]).

Another possibility for the conversion of dichloro bis(ligand) coordination complexes to cyclopalladated analogs is their consecutive treatment with $AgBF_4$ and *n*-Bu_4NCl [29]. The main driving forces of this reaction are the enhanced electrophilicity of the palladium(II) center (which has acquired the positive charge) and the appearance of the coordination vacancy required for C–H bond activation. Unfortunately, after treatment of complex **4** with $AgBF_4$ in ethyl acetate with the subsequent introduction of *n*-Bu_4NCl, the starting compound **4** was recovered in 12% yield with no traces of cyclopalladated derivative **3b**[5].

Bis(β-diketonate)palladium(II) complexes, e.g. Pd(acac)$_2$, can also serve as palladation agents [30–35]. This method is based on the isomerization of a β-diketonate ligand from the *O,O′*-chelated state to the monodentate γ-C-bonded one [31–35]. As was demonstrated in the case of cyclopalladation of primary benzylamine [30], the γ-C-bonded β-diketonate ligand served as a powerful internal base (similarly to that operating in ligand exchange reactions). To test this approach for cyclopalladation of oxazoline (**1**), we first prepared acetylacetonate derivative **6** by reaction of **3b** with 2,4-pentadione and KOH in MeOH (Scheme 4) [36,37]. Unfortunately, our attempts to synthesize the same complex **6** using the reaction of Pd(acac)$_2$ with **1** failed.

For subsequent structural studies, cyclopalladated dimer **3b** was quantitatively converted into its mononuclear phosphane adduct **7** by reaction with PPh_3 (Scheme 4).

2.2. Spectral characterization of complexes

The proposed structures of the complexes prepared (**2**, **3a**,**b**, **5**–**7**) were supported by IR, ^{1}H- and ^{13}C-NMR spectroscopy. Signal assignment in the routine ^{1}H- and ^{13}C-NMR spectra was done based on the analysis of COSY, DEPT, and HETCOR data.

The presence of the Pd–C bond in the cyclopalladated compounds was confirmed by both IR and NMR spectroscopy. In the IR spectra of cyclopalladated compounds **3a**,**b** and **7**, the region of out-of-plane bending vibrations of aromatic C–H bonds contained only one strong absorption band at 725–729 cm^{-1} as was expected for disubstituted benzene rings [38]. The IR spectra of ligand **1** and coordination complex **2** had two characteristic bands for monosubstituded arenes: 695–697 and 780 cm^{-1}. These frequencies are similar to those found for related cyclopalladated compounds **B** (725–730 cm^{-1}), the corresponding ligands, and coordination compounds (690–695 and 745–750 cm^{-1}) [10]. IR spectroscopy cannot be used for supporting the structures of oxazoline adduct **5** and phosphane complex **7** since their molecules contain both mono- and disubstituted phenyl rings.

The ^{1}H-NMR spectra afforded more reliable evidence of *ortho*-palladated structure of dimer **3a** and mononuclear complexes **6** and **7**[6]. Thus, for these compounds, the total integral intensity of aromatic protons corresponded to the disubstituted aryl ring. In the spectra of dimer **3a,** signals of aromatic protons consisted of a group of unresolved multiplets located in a narrow interval of ca. 0.2 ppm that is typical for other

[4] Complex **2** (100 mg, 0.21 mmol) was refluxed in 3 ml of a 1:1 mixture of $AcOH–CHCl_3$ for 8 h. After solvent evaporation and recrystallization, 86 mg (86%) of **2** was recovered. Another reaction was carried out in CH_3OH under the same conditions; 91% of compound **2** was recovered. In both reactions after solvent evaporation, the residues were analyzed by ^{1}H-NMR spectroscopy. No trace of desired complex **3b** was detected.

[5] The reaction was carried out using *n*-Bu_4NCl under the conditions reported for the preparation of di-μ-iodo-bis{[(2-aminomethyl)phenyl]palladium(II)} in Ref. [29].

[6] NMR spectra of μ-chloro dimer **3b** could not be measured owing its extremely low solubility in common organic solvents.

ortho-palladated 2-aryl-2-oxazolines (δ 6.98–7.10 ppm [12]). These signals were partly resolved in the spectra of acetylacetonate derivative **6**. As was found for related complexes [39], the doublet of aromatic H(6) appeared at lower field compared to other aromatic hydrogens because of the deshielding effect of one of the diketonate carbonyl groups.

In the ^{1}H-NMR spectrum of **7**, the multiplet of aromatic H(6) at δ 6.43 ppm contained splitting by the P atom ($^4J_{PH\text{-}6} = 4.7$ Hz). This is another important proof of the *ortho*-palladated structure of **7** (and, therefore, parent compounds **3a**,**b** as well) and unambiguous evidence of the *trans*(*N*,*P*)-geometry of the mononuclear complex [18a,40]. The H(6) signal was shifted upfield due to the shielding effect of the P–aryl rings. This phenomenon has been observed previously in arylphosphane adducts of some cyclopalladated compounds [18a–d,41,42].

In accordance with the *ortho*-palladated structure of complexes **3a**, **6**, and **7**, their ^{13}C-NMR spectra contained the signal of the quaternary carbon atom (C(1)) directly bonded to the palladium atom: δ 147.6, 150.1, and 151.8 ppm, respectively. These values are within the range of chemical shifts (δ 141–160 ppm) reported for other *ortho*-palladated complexes [43–49].

The structure of μ-acetato complex **3a** was supported by IR and NMR spectroscopy data. The IR spectrum showed two strong bands at 1562 and 1401 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of the O=C–O group, respectively (cf. 1560–1570 and 1400–1420 cm^{-1} for related compounds [10,12,50,51]). The ^{1}H-NMR spectrum contained only one singlet of the μ-AcO groups at δ 2.16 ppm (cf. δ 2.1–2.3 ppm for related dimers [10,12]). This suggests that dimer **3a** exists in $CDCl_3$ solution as a single anti-isomer with the usual open-book-like structure. This conclusion was supported by the presence of only one set of the ^{13}C-NMR signals [11,14]. A strong predominance of this symmetric *ab*–*gh* geometry [10,51] and the dimer's existence in $CDCl_3$ solution as the single isomer [12,52] were found previously for other cyclopalladated oxazoline derivatives [10,12] and related dimeric complexes of aryl substituted heterocycles [51,52].

As a consequence of the open-book structure of dimer **3a**, each of two methylene protons of the oxazoline ring are non-equivalent and gave three unresolved multiplets (δ 2.84, 3.56, and 4.32 ppm) with a relative integration ratio of 1:2:1. According to the HETCOR spectrum of **3a**, two protons giving multiplets at δ 2.84 and 3.56 ppm are attached to the carbon providing the signal at δ 49.5 ppm; two protons attached to the other carbon of the heterocycle (δ 70.1 ppm) gave rise to two multiplets at 3.56 and 4.32. Based on the higher electronegativity of oxygen compared to nitrogen, signals at 70.1, 3.56, and 4.32 ppm in ^{13}C- and ^{1}H-NMR spectra were assigned to the OCH_2 group[7].

The ^{1}H-NMR spectra of phosphane adduct **7** contained three well-separated signals of *ortho*-, *meta*-, and *para*-hydrogens of PPh_3 at δ 7.73, 7.36, and 7.43 ppm, respectively. The multiplets of *ortho*- and *meta*-hydrogens contained spin–spin coupling with the P nuclei ($^3J_{PH} = 11.7$ and $^4J_{PH} = 2$ Hz, respectively). The downfield shift of the signal of the PPh_3 *ortho*-hydrogens might be explained by their close proximity to the palladium anisotropy domain [53,54]. The ^{13}C-NMR spectrum of adduct **7** exhibited six doublets (J_{CP}) of four carbon atoms of the P–phenyl group [55] and C-5 and C-6 of the phenylene ring. Interestingly enough, the PdC(1) signal appeared as a singlet.

The ^{1}H- and ^{13}C-NMR spectra of compound **6** contained signals of two non-equivalent CH_3 groups (δ 1.99, 2.08, and 27.5, 27.8 ppm, respectively) within the range of chemical shifts reported for other acetylacetonate derivatives of cyclopalladated complexes (δ 1.8–2.2 ppm [35,39] and 27–29 ppm [39,43]). In the IR spectrum of **6**, three characteristic bands at 1576, 1563, and 1515 cm^{-1} resulted from the coupled symmetric C=O stretching vibrations, out-of-plane C–H bending vibrations, and asymmetric stretches of the C⋯C⋯C fragment [35].

Coordination of the oxazoline ring through the imine nitrogen atom in complexes **2**, **3a**,**b**, **6**, and **7** was evident enough from a low-frequency shift of the strong band of C=N stretching vibration. This band moved from 1649 cm^{-1} in the IR spectrum of ligand **1** down to 1630–1638 cm^{-1} in the spectra of dimers **3a**,**b**. The coordination shift was somewhat smaller ($\Delta\nu$C=N = −7 cm^{-1}) in the case of phosphane adduct **7** due to the large *trans*-influence of the phosphorus atom weakening this bond. The rather weak N → Pd coordination of the oxazoline in complex **2** ($\Delta\nu$C=N = −6 cm^{-1}) might be caused by steric effects.

Comparative analysis of the ^{1}H-NMR spectra of cyclopalladated compounds **3a**,**b**, **6**, and **7** with those of coordination complex **2** and adduct **5** revealed additional spectral differences of these two groups of complexes. The signals of oxazoline aromatic hydrogens were presented in the spectra of complexes **2** and **5** by two multiplets at δ 8.98–8.94 and 7.55–7.45 ppm with a relative integration intensity ratio of 2:3, respectively. Based on the COSY spectra of **2** and **5**, the signals were assigned to *ortho*- and *meta*-, and *para*-protons of the aromatic ring, respectively. The observed downfield

[7] In Ref. [12], ^{13}C-NMR signals of OCH_2 and $NCMe_2$ groups for the related compound di-μ-acetatobis-[2-(4′,4′-dimethyl-2-oxazolinyl)phenyl-C,N]dipalladium (Fig. 1, structure B, R^1 = Me, R^2 = H) were assigned incorrectly. We synthesized this compound, and its DEPT spectrum indicated that the higher field signal at 64.8 ppm belonged to the quaternary carbon of the $NCMe_2$ group, whereas the lower field signal at 81.8 ppm resulted from the resonance of the secondary carbon of the OCH_2 fragment.

shift of the *ortho*-proton signals may be indicative of the orthogonal orientation of the oxazoline ring in respect to the palladium coordination plane [48,51]. Magnetic non-equivalence of the NCH_2 protons in complex **5** due to the asymmetric environment of the N-donor atom may serve as additional evidence in favor of the proposed configuration. The orthogonal orientation of the oxazoline ligand led to the preferable position of the *ortho*-protons of ligand **1** in close proximity to the anisotropy domain of the palladium center in axial position (cf. [48,51]). A large downfield shift of the *ortho*-H signal observed in the spectra of complexes **2** and **5** compared to free ligand **1** ($\Delta\delta = 1.08$ and 1.03 ppm, respectively) suggests some C–H bond interaction with the metal center which is considered now as a necessary stage in the C–H bond activation processes [52].

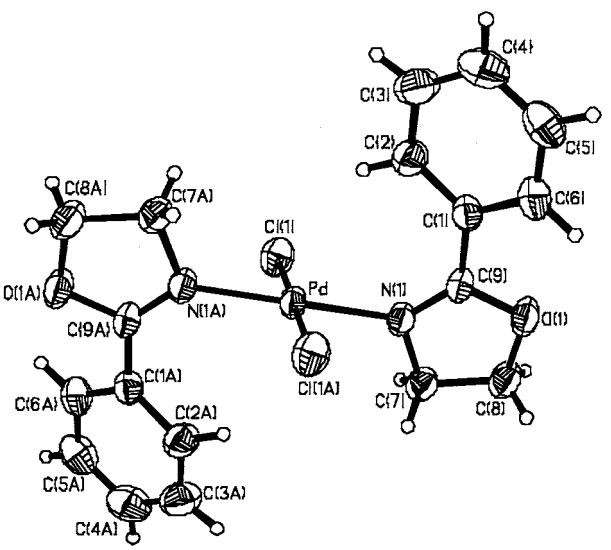


Fig. 2. Molecular structure and numbering scheme of the coordination complex **2**. Displacement ellipsoids are shown 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for coordination complex **2**

Bond lengths			
Pd–N(1A)	2.0072(14)	O(1)–C(8)	1.459(2)
Pd–N(1)	2.0072(14)	N(1)–C(9)	1.271(2)
Pd–Cl(1)	2.300(2)	N(1)–C(7)	1.475(2)
Pd–Cl(1A)	2.300(2)	C(1)–C(9)	1.468(2)
O(1)–C(9)	1.344(2)	C(7)–C(8)	1.524(2)
Bond angles			
N(1A)–Pd–N(1)	180.0	C(9)–N(1)–Pd	130.02(11)
N(1A)–Pd–Cl(1)	89.13(5)	C(7)–N(1)–Pd	119.89(10)
N(1)–Pd–Cl(1)	90.87(5)	C(2)–C(1)–C(9)	121.17(14)
N(1A)–Pd–Cl(1A)	90.87(5)	C(6)–C(1)–C(9)	118.82(14)
N(1)–Pd–Cl(1A)	89.13(5)	N(1)–C(7)–C(8)	102.95(13)
Cl(1)–Pd–Cl(1A)	180.0	O(1)–C(8)–C(7)	104.37(13)
C(9)–O(1)–C(8)	107.08(12)	N(1)–C(9)–O(1)	116.10(14)
C(9)–N(1)–C(7)	109.30(13)	N(1)–C(9)–C(1)	127.98(13)
		O(1)–C(9)–C(1)	115.92(13)

2.3. X-ray structure study of coordination complex **2** and phosphane adduct **7**

The most unambiguous confirmation of η^2-C,N-bonding of 2-phenyl-2-oxazoline ligand in phosphane adduct **7** and its monodentate η^1-N-coordination in the case of complex **2** was obtained from their X-ray diffraction study.

2.3.1. Coordination complex **2**

The crystals of coordination complex **2** suitable for the X-ray diffraction study were grown from a dichloromethane–hexane mixture. The molecular structure of compound **2** is presented in Fig. 2; selected bond lengths and angles are given in Table 1.

Despite a number of palladium(II) coordination complexes with bi- [1c,56,57] and tridentate [58] oxazoline ligands structurally characterized, the X-ray study of only one palladium(II) complex bearing a monodentate oxazoline ligand [$PdCl_2$ complex with 4,4-dimethyl-2-(2-naphthyl)oxazoline (**8**)] has been reported thus far [17]. The data for compound **8** were used here for comparison purposes.

Both complexes **2** and **8** have a centrosymmetric structure with strictly planar coordination environment of the palladium center. The deviation from the square geometry is also small, with the N–Pd–Cl angles of 90.87–91.1°[8].Two monodentate N-bonded oxazoline ligands are *trans*-disposed with nearly identical lengths of Pd–N and Pd–Cl bonds equal to 2.007–2.036 and 2.300–2.303 Å, respectively. The heterocycle in both complexes may be described as nearly planar with the ring having a negligible twisting extent: the average *endo*-cyclic torsion angle is equal to 2.9–2.5°, and maximal displacement from the mean oxazoline plane (observed for the carbon of the OCH_2 group) is equal to 0.026–0.022 Å.

In full accordance with our predictions from the ^{1}H-NMR data (see Section 2.2), in both complexes **2** and **8** the oxazoline ligands are oriented nearly orthogonal to the mean coordination plane, with interplanar angles taken for oxazoline ring equal to 101.9 and 93.7°, respectively. The difference between the two related complexes becomes more pronounced when the tilting of the azomethine C=N bond with respect to the mean coordination plane is considered: the torsion angle C=N–Pd–Cl equals 107.9 and 97.9° for complexes **2** and **8**, respectively.

Two non-symmetric organic ligands are *anti*-arranged with respect to the mean coordination plane

[8] Here and below, the first and second values are parameters of complexes **2** and **8**, respectively.

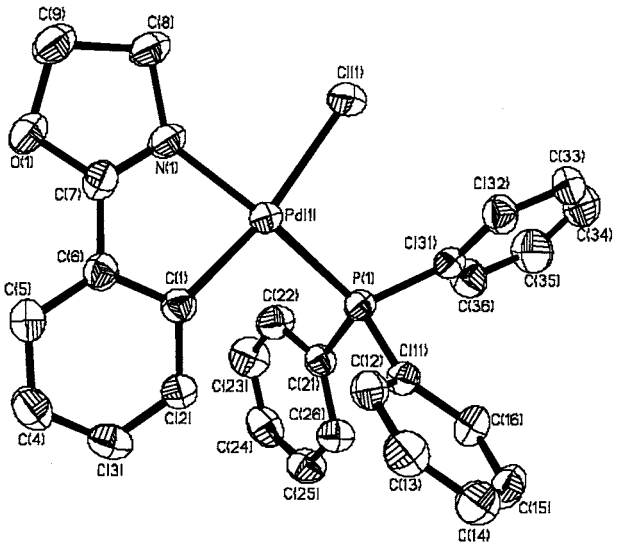


Fig. 3. Molecular structure and numbering scheme of the phosphine adduct **7**. Displacement ellipsoids are shown 50% probability level. Hydrogen atoms and solvent CH_3Cl_2 molecule are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for phosphane adduct **7**·CH_2Cl_2

Bond lengths			
Pd(1)–C(1)	2.030(4)	N(1)–C(8)	1.471(6)
Pd(1)–N(1)	2.062(3)	C(1)–C(2)	1.395(6)
Pd(1)–P(1)	2.256(1)	C(1)–C(6)	1.414(5)
Pd(1)–Cl(1)	2.368(2)	C(2)–C(3)	1.378(6)
P(1)–C(11)	1.818(4)	C(3)–C(4)	1.389(7)
P(1)–C(21)	1.827(4)	C(4)–C(5)	1.380(7)
P(1)–C(31)	1.832(4)	C(5)–C(6)	1.387(6)
O(1)–C(7)	1.335(5)	C(6)–C(7)	1.440(6)
O(1)–C(9)	1.457(6)	C(8)–C(9)	1.530(7)
N(1)–C(7)	1.266(6)		
Bond angles			
C(1)–Pd(1)–N(1)	80.7(2)	C(3)–C(2)–C(1)	122.0(4)
C(1)–Pd(1)–P(1)	94.8(1)	C(2)–C(3)–C(4)	121.9(4)
N(1)–Pd(1)–P(1)	174.1(1)	C(5)–C(4)–C(3)	118.3(4)
C(1)–Pd(1)–Cl(1)	169.0(1)	C(4)–C(5)–C(6)	119.2(4)
N(1)–Pd(1)–Cl(1)	88.6(1)	C(5)–C(6)–C(1)	124.0(4)
P(1)–Pd(1)–Cl(1)	96.07(4)	C(5)–C(6)–C(7)	122.2(4)
C(11)–P(1)–C(21)	107.4(2)	C(1)–C(6)–C(7)	113.8(4)
C(11)–P(1)–C(31)	101.0(2)	N(1)–C(7)–O(1)	117.4(4)
C(21)–P(1)–C(31)	103.6(2)	N(1)–C(7)–C(6)	119.9(4)
C(11)–P(1)–Pd(1)	116.1(1)	O(1)–C(7)–C(6)	122.6(4)
C(21)–P(1)–Pd(1)	110.5(1)	N(1)–C(8)–C(9)	101.5(4)
C(31)–P(1)–Pd(1)	117.0(1)	O(1)–C(9)–C(8)	105.8(4)
C(7)–O(1)–C(9)	105.6(3)	C(12)–C(11)–P(1)	120.9(3)
C(7)–N(1)–C(8)	109.7(4)	C(16)–C(11)–P(1)	120.9(3)
C(7)–N(1)–Pd(1)	113.4(3)	C(22)–C(21)–P(1)	116.6(3)
C(8)–N(1)–Pd(1)	136.9(3)	C(26)–C(21)–P(1)	124.5(3)
C(2)–C(1)–C(6)	114.5(4)	C(36)–C(31)–P(1)	122.5(3)
C(2)–C(1)–Pd(1)	133.5(3)	C(32)–C(31)–P(1)	118.3(3)
C(6)–C(1)–Pd(1)	112.0(3)		

with their 2-aryl substituents disposed above and below it, resulting in the creation of a prochiral structure [59]. The 2-aryl ring is markedly twisted regarding the oxazoline ring, with interplanar angles of 29.6–27.6°. Their orientation to the mean coordination plane remains close to the orthogonal, with interplanar angles of 105.4–93°.

The most interesting structural feature of the coordination complex **2** is a rather short contact of one of the *ortho*-hydrogens of the 2-phenyl substituent with the palladium atom with a $H^2\cdots Pd$ distance of 2.679 Å. The similar contact between the C^1H of naphthalene ring and metal at the distance of 2.734 Å was found also for the related complex **8**. These distances are markedly less than the sum of van der Waals radii of Pd and H atoms (3.1 Å [60]) and may be considered as evidence of some kind of secondary interaction [54c,h]. This structural peculiarity is in full accordance with the ^{1}H-NMR data for complex **2** (see Section 2.2) which point to the retaining of the same configuration in solution.

Such interactions are often considered as a step preceding the C–H bond activation [54c,h] Thus, in the case of coordination complex **2**, a close above-plane approach of the *ortho*-C–H bond to the metal center may be recognized as the optimal orientation for subsequent *ortho*-palladation of 2-phenyl-2-oxazoline.

2.3.2. X-ray structure investigation of phosphane adduct **7**

Suitable crystals of this complex were grown from a dichloromethane–hexane mixture in the presence of trace amounts of ether. The molecular structure of the complex and its packing in the crystal are presented in Fig. 3 and 4; selected bond lengths and angles are given in Table 2. The crystal contains wide channels passing along the *b*-axis, which are occupied by disordered molecules of dichloromethane.

Three cyclopalladated derivatives of aryl substituted oxazolines have been previously characterized structurally: the μ-acetato dimer containing a palladacycle of C,N-type, **C**[1] (Fig. 1, complex type **C**, $R^1 = Me$, $R^2 = R^3 = H$) [13] and two related cyclopalladated derivatives of bis(oxazoline)benzenes of N,C,N-pincher type, **A**[1] (Fig. 1, complex type **A**, Hal = Cl, R = *i*-Pr) [15] and **A**[2] (Fig. 1, complex type **A**, Hal = I, R = CMe_2Ph) [6b]. Unfortunately, only two X-ray structural data sets of compounds **A**[1] and **C**[1] are available from the CCDC; they are used here for comparison purposes.

The unit cell contains four molecules of the mononuclear complex **7** and four solvate molecules of dichloromethane (Fig. 4). The latter molecules are disordered and are inserted into the cages in the unit cell without any bonding with the complex atoms. The *ortho*-palladated structure of this phosphane adduct (and, therefore, that of the starting dimers **3a**,**b**) is quite evident. In accordance with the spectral data (see above, Section 2.2), complex **7** has *trans*(P,N) geometry. The Pd–C and Pd–N bond lengths equal 2.030(4) and 2.062(3) Å, respectively, and are longer to

some extent compared to the μ-AcO-dimer **C**[1] (1.968 and 2.030 Å, respectively), probably, due to the *cis*- and *trans*-influence of phosphane instead of the μ-acetato ligand.

The palladium atom in complex **7** has a nearly square-planar coordination environment with a rather slight tetrahedral distortion. The dihedral angle between the planes $\{C^1Pd^1N^1\}$ and $\{P^1Pd^1Cl^1\}$ is equal to 4.3° and the displacement of the main atoms from the mean coordination plane does not exceed 0.064 Å.

The palladacycle conformation in the phosphane adduct **7** may be described as nearly planar, with the averaged absolute value of intrachelate torsion angle ca. 3.4°. It shows good consistency with the corresponding values for palladacycles in complexes **A**[1] and **C**[1] (1.3 and 1.7°, respectively) and may be recognized as their general property. This characteristic is in drastic contrast with the pronounced twisting of the benzylamine-derived palladacycles where the range of average intrachelate torsion angles is expanded up to the 32° in the case of adducts with the sterically crowded diphosphine ligands [61].

The oxazoline heterocycle in **7** may be described as ideally planar with the displacement of its main atoms from the mean plane $\{N^1C^7O^1C^9C^8\}$ not exceeding 0.0032 Å (found for the nitrogen atom). The same holds true for two other oxazoline-derived *ortho*-palladated complexes, **A**[1] and **C**[1] (0.0025 and 0.0041 Å, respectively).

As may be expected for such a strongly conjugated tricyclic system, all three rings in molecule **7** are nearly coplanar, with the interplanar angles between the phenylene or oxazoline ring on one hand, and the palladacycle on the other, being equal to 3.4 and 3.8°, respectively. The same parameters for the related complexes **A**[1] and **C**[1] are decreased down to values of 1.5–2.0 and 2.4–2.2°, respectively. It is noteworthy that only in the case of the **A**[2] complex which bears a very bulky CMe_2Ph group, a more pronounced twisting of two oxazoline rings out of the plane of the aromatic ring (6.8 and 8.8°, respectively) was reported [6b].

In accordance with the ^{1}H-NMR data for the phosphane adduct **7** (where the signal of phosphane *ortho*-hydrogens is shifted downfield to δ 7.75 ppm), the distance between one of the *ortho*-Ph protons and the palladium atom ($C^{22}H\cdots Pd^1$) is decreased to 2.93 Å, which is smaller than the sum of van der Waals radii of these atoms (3.1 Å) [62]. In the cases of other arylphosphane adducts of *ortho*-palladated complexes, the similar H···Pd distances were found to be shorter (2.66–2.78 Å) with the corresponding larger downfield shifts of the phosphane *ortho*-H signal (δ 8.38–8.47 ppm) [53].

3. Conclusions

Direct *ortho*-palladation of a 2-phenyl-2-oxazoline ligand non-substituted on the heterocyclic ring was achieved in a moderate yield of 63% through its reaction with $Pd(OAc)_2$ in the presence of AcONa. A high efficiency of the cyclopalladated ligand exchange method was demonstrated: the target μ-chloro dimer was prepared in a high yield of 90% by the reaction of the oxazoline ligand with *ortho*-palladated complex of *N*,*N*-dimethylbenzylamine in a $AcOH–CHCl_3$ mixture at 50°C. The complexes obtained were characterized by IR, ^{1}H- and ^{13}C-NMR data. The structures of coordination complex **2** and cyclopalladated mononuclear complex **7** were unambiguously established by their X-ray diffraction study.

Currently we are working on synthesis and applications of chiral oxazoline-based cyclopalladated complexes.

4. Experimental

4.1. General

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 as Nujol mulls. Analytical TLC was performed on Merck precoated 0.2 mm plates of silica gel 60 F_{254}. Melting points were measured on a Laboratory Device Mel-Temp apparatus and were not corrected.

All chemicals, including complex **4**, were purchased from Aldrich Chem. Co. $Pd(OAc)_2$ was purified by refluxing in benzene for 5 min, filtering the solution, and removing the solvent. AcOH was refluxed over $KMnO_4$ for 3 h and then distilled. Other solvents were distilled over CaH_2 prior to use.

4.2. Dichlorobis-(2-phenyl-2-oxazoline)palladium(II) (2)

4.2.1. Method A

A solution of Na_2PdCl_4 (100 mg, 0.34 mmol) in abs. MeOH (3 ml) was added to 2-phenyl-2-oxazoline (110 mg, 0.75 mmol). A yellow precipitate was formed immediately. After stirring the mixture for 24 h at r.t., the yellow solid was filtered out, washed with MeOH, and recrystallized from $CHCl_3$–hexane. Yield, 132 mg (82%). R_f 0.57 (1:9 ethyl acetate–toluene); m.p. (dec.) 226–227°C; IR (ν, cm^{-1}): 1643 s (C=N); 780 s and 697 m (arom. CH); ^{1}H-NMR (δ, ppm): 4.33 (t, 2H, $J = 9$, NCH_2), 4.60 (t, $J = 9$, OCH_2), 7.56 (t, 2H, $^3J = 7.7$, *meta*-CH), 7.63 (t, 1H, $^3J = 7.7$, *para*-CH), 8.98 (d, 2H,

$^3J = 7.7$, *ortho*-CH); ^{13}C-NMR (δ, ppm): 55.5 (NCH_2), 68.1 (OCH_2), 124.9 (arom. quat. C), 128.5, 130.1, 133.1 (arom. CH), 167.9 (OCN). Anal. Calc. For $C_{18}H_{18}N_2O_2Cl_2Pd$: C, 45.84; H, 3.85; N, 5.94. Found: C, 45.67; H, 3.75; N, 5.71%.

4.2.2. Method B

2-Phenyl-2-oxazoline (30.9 mg, 0.210 mmol) was added to a solution of complex **4** (52.5 mg, 0.095 mmol) in 1.5 ml AcOH and 1.5 ml $CHCl_3$. The mixture was stirred at r.t. for 141 h. The yellow precipitate formed was filtered out, washed with AcOH and hexane, and recrystallized from $CHCl_3$–hexane. Yield, 15 mg (33%).

4.3. Di-μ-acetatobis-[2-(2-oxazolinyl)phenyl-C,N]dipalladium(II) (3a)

4.3.1. Method A

AcOH (1 ml) was added to $Pd(OAc)_2$ (224 mg, 1 mmol) and the mixture was heated at 95°C for a few minutes. Then 2-phenyl-2-oxazoline (0.13 ml, 1 mmol) was added. After stirring at 95°C for 2 h and then at r.t. for 60 h, the mixture was diluted with H_2O and extracted with $CHCl_3$ (3×10 ml). Organic layers were combined, washed with aqueous saturated solution of $NaHCO_3$, and run through a layer of SiO_2 (H = 1 cm). After solvent removal, the yellow solid was recrystallized from $CHCl_3$–hexane. Yield, 137 mg (44%). R_f 0.46[9] (1:9 ethyl acetate–toluene); m.p. (dec) 218–220°C; IR (ν, cm^{-1}): 1630 s (C=N), 727 s (arom. CH), 1562 s and 1401 s (COO); ^{1}H-NMR (δ, ppm): 2.16 (s, 3H, CH_3), 2.84 (m, 1H, NCH), 3.56 (m, 2H, NCH and OCH), 4.31 (m, 1H, OCH), 6.98–7.18 (m, 4H, arom. CH); ^{13}C-NMR (δ, ppm): 24.5 (CH_3), 49.7 (NCH_2), 70.3 (OCH_2), 123.9, 125.6, 130.5 and 131.6 (arom. CH), 131.3 (arom. C(2)), 147.6 (PdC(1)), 174.6 (OCN), 181.6 (COO); Anal. Calc. for $C_{22}H_{22}N_2O_6Pd_2$: C, 42.39; H, 3.56; N, 4.49. Found: C, 42.29, H 3.57, N 4.51%.

4.3.2. Method B

A mixture of $Pd(OAc)_2$ (73.6 mg, 0.328 mmol) and AcONa (27.0 mg, 0.329 mmol) was partially dissolved in AcOH (1 ml). 2-Phenyl-2-oxazoline (57.6 mg, 0.357 mmol) was dissolved in AcOH (1 ml). The two solutions were combined and allowed to stir at r.t. overnight. The reaction mixture was stirred at 50°C for 1 h and then at r.t. for 9 days. The yellow precipitate started forming after 3 days. The mixture was diluted with H_2O and extracted with $CHCl_3$ (3×10 ml). Organic layers were combined, washed with aqueous saturated solution of $NaHCO_3$, and run through a layer of SiO_2 (H = 2 cm). After solvent removal, the yellow solid was recrystallized from $CHCl_3$–hexane. Yield, 58.3 mg (63%).

[9] The compound streaks on a TLC plate. R_f value is given for the top of the streak.

4.4. Di-μ-chlorobis-[2-(2-oxazolinyl)phenyl-C,N]dipalladium(II) (3b)

4.4.1. Method A

LiCl (9.3 mg, 2.2 mmol) was added to a solution of **3a** (62.3 mg, 1 mmol) in abs. acetone (5 ml). After stirring for 60 h at r.t., the pale-yellow solid formed was washed with H_2O, MeOH, and Et_2O. The compound was insoluble in a variety of solvents, so no purification was attempted. Yield, 57.4 mg (99%). m.p. (dec.) 208°C; IR (ν, cm^{-1}): 1638 s (C=N); 725 s (arom. CH); Anal. Calc. for $C_{18}H_{16}N_2O_2Cl_2Pd_2$: C, 37.53; H, 2.80; N, 4.86. Found: C, 36.84; H, 2.89; N, 4.60%.

4.4.2. Method B

2-Phenyl-2-oxazoline (28.3 mg, 0.192 mmol) was added to a solution of **4** (53.7 mg, 0.097 mmol) in 1.5 ml AcOH and 1.5 ml $CHCl_3$. The mixture was stirred at 50°C for 37 h and then at r.t. for 48 h. The yellow precipitate was filtered off, washed with AcOH and H_2O. The solid was insoluble in a variety of solvents, so no recrystallization was attempted. Yield of the crude product was 48.9 mg (90%).

4.5. Chloro[N,N-dimethylbenzylamino]-(2-phenyl-2-oxazoline)palladium(II) (5)

2-Phenyl-2-oxazoline (265 mg, 1.8 mmol) was added to a solution of **4** (50.3 mg, 0.091 mmol) in toluene (3 ml). The mixture was stirred at 50°C for 10 h. The pale yellow precipitate was filtered off, washed with hexane, and recrystallized from $CHCl_3$–hexane. Yield, 26.8 mg (93%). R_f 0.43 (1:9 ethyl acetate–toluene); m.p. (dec.) 164°C; IR (ν, cm^{-1}): 1649 s (C=N); ^{1}H-NMR (δ, ppm): 2.95, 2.98 (two s, 6H, $N(CH_3)_2$), 3.80, 4.10 (two d, $^2J = 14$, $PhCH_2$), 4.20 (m, 1H, NCH), 4.60 (m, 3H, OCH_2CHN), 6.44 (d, 1H, $^3J = 7.6$, H(6) of C_6H_4), 6.78 (m, 1H, H(5) of C_6H_4), 6.94 (m, 2H, H(3) and H(4) of C_6H_4), 7.43 (br. t, 2H, $^3J \approx 8$, *meta*-H of C_6H_5), 7.51 (br. t, 1H, $^3J \approx 8$, *para*-H of C_6H_4), 8.93 (br. d, 1H, $^3J \approx 8$, *ortho*-H of C_6H_5); ^{13}C-NMR (δ, ppm): 52.5 and 52.9 ($N(CH_3)_2$), 56.7 (NCH_2), 68.4 (OCH_2), 74.0 (NCH_2Ph), 121.6 (HC-3 of C_6H_4), 124.4 (HC(4) of C_6H_4), 125.2 (quat. C of C_6H_5), 125.4 (HC(5) of C_6H_4), 128.2 (*meta*-CH of C_6H_5), 130.0 (*ortho*-CH of C_6H_5), 131.4 (HC(6) of C_6H_4), 132.8 (*para*-CH of C_6H_5), 146.1 and 147.5 (PdC(1) and C(2) of C_6H_4), 166.8 (OCN); Anal. Calc. for $C_{18}H_{21}N_2OClPd$: C, 51.07; H, 5.01; N, 6.62. Found: C, 50.59; H, 4.96; N, 6.53%.

4.6. [2-(2-Oxazolinyl)phenyl-C,N](acetylacetonato-O,O′)palladium(II) (6)

A solution of 2,4-pentanedione (20 mg, 0.169 mmol) in MeOH (5 ml) and a solution of KOH (9 mg, 0.161 mmol) in MeOH (1 ml) were added to a suspension of **3b** (50 mg, 0.081 mmol) in MeOH (6 ml). The mixture was stirred at r.t. for 3 h. After filtration, MeOH was removed from the solution and the crude complex was recrystallized from MeOH–H_2O. Yield, 23 mg (38%). R_f 0.56 (1:9 ethyl acetate–toluene); m.p. (dec.) 158°C; IR (ν, cm^{-1}): 1631 s (C=N); 725 s and 729 s (arom. CH); 1576 s, 1563 s, and 1515 s (C=O, C–H, and C=C); ^{1}H-NMR (δ, ppm): 1.99 and 2.08 (two s, 6H, two CH_3 groups), 3.99 (t, 2H, $J = 9$, NCH_2), 4.75 (t, 2H, $J = 9$, OCH_2), 5.38 (s, 1H, γ-CH of acac), 7.06 (t, 1H, $J = 7.3$, arom. H-4), 7.23 (m, 2H, arom. H(3) and H(5)), 7.57 (broad d, 1H, $J = 7.8$, arom. H(6)); ^{13}C-NMR (δ, ppm): 27.5 and 27.8 (two CH_3 groups), 49.6 (OCH_2), 70.3 (NCH_2), 100.4 (γ-CH of acac), 124.1, 125.2, 130.4, and 130.8 (four arom. CH), 131.3 (arom. C(2)), 150.1 (PdC(1)), 176.2 (OC=N), 186.1 and 188.0 (two C=O). Anal. Calc. for $C_{14}H_{15}NO_3Pd$: C, 47.82; H, 4.30; N, 3.92. Found: C, 47.42; H, 4.12; N, 4.03%.

4.7. Chloro[2-(2-oxazolinyl)phenyl,1-C,3-N](triphenylphosphine)palladium(II) (7)

Triphenylphosphine (27.3 mg, 0.104 mmol) was added to a suspension of **3b** (30.0 mg, 0.052 mmol) in benzene. The mixture was stirred at r.t. for 12 h, then the solvent was removed in vacuum. A pale yellow solid was purified by column chromatography (1:9 ethyl acetate–$CHCl_3$). Yield, 57.0 mg (99%). R_f 0.67 (ethyl acetate–toluene, 1:9); m.p. (dec.) 150–152°C; IR (ν, cm^{-1}): 1642 s (C=N), 720 s (arom. CH); ^{1}H-NMR (δ, ppm): 4.25 (t, 2H, $J = 9.5$, NCH_2), 4.74 (t, 2H, $J = 9.5$, OCH_2), 6.43 (dd, 1H, $^3J_{HH} = 7.5$, $J_{HP} = 4.7$, arom. H(6)), 6.63 (dt, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.4$, arom. H(5)), 6.92 (t, 1H, $^3J_{HH} = 7.5$, arom. H(4)), 7.30 (dd, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.4$, arom. H(3)), 7.36 (dt, 6H, $^3J_{HH} = 7.2$, $^3J_{HH} = 7.4$ Hz, $^4J_{HP} = 2$, *meta*-H of PPh_3), 7.43 (dt, 3H, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$, *para*-H of PPh_3), 7.74 (ddd, 6H, $^3J_{HP} = 11.7$, $^3J_{HH} = 7.2$, $^4J_{HH} = 1.2$, *ortho*-H of PPh_3); ^{13}C-NMR (δ, ppm): 51.0 (NCH_2), 70.8 (OCH_2); 123.8 (HC(4) of C_6H_4), 126.3 (HC(3) of C_6H_4), 128.1 (d, $^3J_{PC} = 11$, *meta*-CH of PPh_3), 130.8 (d, $^4J_{PC} = 2$, *para*-CH of PPh_3), 130.8 (d, $^1J_{PC} = 45$, quat. C of PPh_3), 131.0 (d, $^4J_{PC} = 6.5$, HC(5) of C_6H_4), 133.4 (quat. C(2) of C_6H_4), 138.1 (d, $^3J_{PC} = 11$, HC(6) of C_6H_4); Anal. Calc. for $C_{27}H_{23}NOClPPd$: C, 58.93; H, 4.21; N, 2.55. Found: C, 59.18; H, 4.57; N, 2.81%.

4.8. X-ray structure determinations of 2 and 7

Crystal data, data collection, structure solution and refinement parameters are listed in Table 3. Unit-cell dimensions for **7** were calculated from the setting angles

Table 3
Crystal data, data collection, structure solution and refinement parameters for complexes **2** and **7**·CH_2Cl_2

	2	7·CH_2Cl_2
Empirical formula	$C_{18}H_{18}Cl_2N_2O_2Pd$	$C_{28}H_{25}Cl_3N_1O_1P_1Pd_1$
Formula weight	471.64	635.21
Color, habit	Orange block	Light-green block
Crystal size (mm)	$0.50 \times 0.40 \times 0.40$	$0.5 \times 0.4 \times 0.2$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	7.848(5)	11.578(5)
b (Å)	11.170(4)	10.786(8)
c (Å)	11.479(4)	22.069(8)
β (°)	108.41(4)	93.32(3)
V (Å^3)	954.8(8)	2751(3)
Z	2	4
$D_{calc.}$ (g cm^{-3})	1.641	1.533
Absorption coefficient (mm^{-1})	1.265	1.046
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD4
Temperature (K)	293	295
Radiation λ (Å)	Graphite-monochromated Mo–K_α (0.71073)	Graphite-monochromated Mo–K_α (0.71073)
θ range (°)		2.04–26.97
Index ranges	$-10 \le h \le 10$ $0 \le k \le 14$ $-15 \le l \le 15$	$-14 \le h \le 0$ $-4 \le k \le 13$ $-28 \le l \le 28$
Reflections collected	4562	6492
Independent reflections	2295 [$R_{int} = 0.0160$]	5883 [$R_{int} = 0.0223$]
Data reduction		XCAD4 [63]
Absorption correction	Empirical (Ψ scan)	Empirical (Ψ scan)
Min./max. transmission	0.4280 and 0.5269	0.6788 and 0.7755
Solution method	Direct methods (SHELX-86) [64]	Direct methods (SHELX-86) [64]
Refinement method	Full-matrix least-squares on F^2 (SHELXL-93) [65]	Full-matrix least-squares on F^2 (SHELXL-93) [65]
Data/restraints/parameters	2295/0/152	5418/6/406
Goodness-of-fit on F^2	1.088	1.036
Final R indices [$I > 2\sigma(I)$]	$R^1 = 0.0203$, $wR^2 = 0.0536$	$R^1 = 0.0397$, $wR^2 = 0.1098$
R indices (all data)	$R^1 = 0.0234$, $wR^2 = 0.0553$	$R^1 = 0.0686$, $wR^2 = 0.1267$
Largest difference peak and hole (e Å^{-3})	0.487/−0.621	0.704/−0.795

of 25 accurately centered reflections. Two reflections were chosen as intensity standards and were measured every 120 min. Three orientation controls were checked every 300 reflections. The experimental intensities for both complexes were corrected for Lorentz and polarization effects [63]. All non-hydrogen atoms (except solvent CH_2Cl_2 molecule) in both structures were refined in the anisotropic approximation. The solvent molecule in the crystal of **7** was found disordered over two positions with occupancy ratio 0.5/0.5. All hydrogen atoms were placed in calculated positions. Both coordinates and isotropic thermal parameters for the hydrogens of the main molecule were refined. A riding model was applied for the H atoms of CH_2Cl_2 molecule [63–65].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138520 (complex **2**) and 138519 (compound **7**). Copies of the data can be obtained free of charge on application to 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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