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Synthesis and structural characterization of enantiopure *exo* and *endo* six-membered oxazoline-derived palladacycles

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Abstract

Direct palladation of (*S*)-4-benzyl-2-methyl-2-oxazoline (**1**) and (*S*)-2-benzyl-4-*tert*-butyl-2-oxazoline (**2**) using $Pd(OAc)_2$ in MeCN afforded the corresponding μ-acetato-dimeric complexes with six-membered *exo* and *endo* palladacycles, respectively. The same complexes were obtained by reacting coordination complexes $Pd(\mathbf{1})_2(OAc)_2$ and $Pd(\mathbf{2})_2(OAc)_2$ with $Pd(OAc)_2$ in MeCN. Metalation of (*S*)-2,4-dibenzyl-2-oxazoline (**3**) with $Pd(OAc)_2$ in AcOH, MeCN or CH_2Cl_2 resulted in the regiospecific formation of the six-membered *endo* palladacycle. The obtained μ-acetato-dimeric complexes were converted to the corresponding μ-chloro-dimeric derivatives **7**, **11** and **13** by treatment with LiCl in acetone. The mononuclear PPh_3 adducts **8**, **12** and **14** were obtained by reacting dimers **7**, **11** and **13** with PPh_3 in benzene. NMR spectroscopy data supported the proposed structures of all complexes and suggested that *exo* and *endo* palladacycles in **8** and **12** have rigid boat conformations in $CHCl_3$. The X-ray crystal structures of the μ-acetato dimer **6** with the *exo* palladacycle and the PPh_3 adduct **14** with the *endo* metalacycle revealed boat conformation of both palladacycles and chiral twisted conformations $\delta(S)$ and $\lambda(S)$, respectively, of the oxazoline rings in the solid state.

Keywords: Cyclopalladated complexes; Oxazolines; *endo* and *exo* palladacycles; Six-membered palladacycle

1. Introduction

After the discovery of cyclopalladation by Cope and Siekman in 1965 [1], it was believed that this reaction could afford only five-membered metalacycles. By now, palladacycles of different sizes have been reported, including six-membered cycles [2]. The most common six-membered palladacycles belong to the CN type and are derivatives of the following *N*-containing compounds: amidines (**A**) [3], 2-substituted pyridines (**B** [4–12], **C** [13,14] and **D** [15]), amines (**E** [16–18], **F** [16] and **G** [19]), azo compounds (**H**, X = N) [20], azines (**I** [21]), imines [**H** (X = CH) [22], **I** [23–30], **J** [31,32] and **K** [33–35]) and oxazolines (**L** [36], **M** [37], **N** [38] and **O** [39], Chart 1). CP [40] and CS [19,41] palladacycles of this size have also been obtained. Nevertheless, six-membered palladacycles are still considered uncommon. While compounds with five-membered palladacycles have numerous applications, especially in enantioselective catalysis, cyclopalladated complexes with the larger size metalacycles have found few uses [2]. Complexes with six-membered palladacycles have been tested as achiral [12,30,40,42–45] or chiral [37] catalysts [12,30,37,40,42–45] and as intermediates for the synthesis of biologically active molecules [46]. The limited number of application studies for the palladacycles of this size can be explained by the fact that, to the best of our knowledge, only four of them are chiral [37–39,46].

One of the common ways to introduce chirality to metal complexes is the use of ligands that can be readily synthesized from commercially available enantiopure substrates. Metal complexes of unsymmetrically substituted 2-oxazolines obtained from chiral amino acids and their derivatives have found a variety of applications, particularly in asymmetric synthesis [47]. Recently, a number of C*-chiral enantiopure *exo* [48–50], *endo* [48,50–62] and pincer-type

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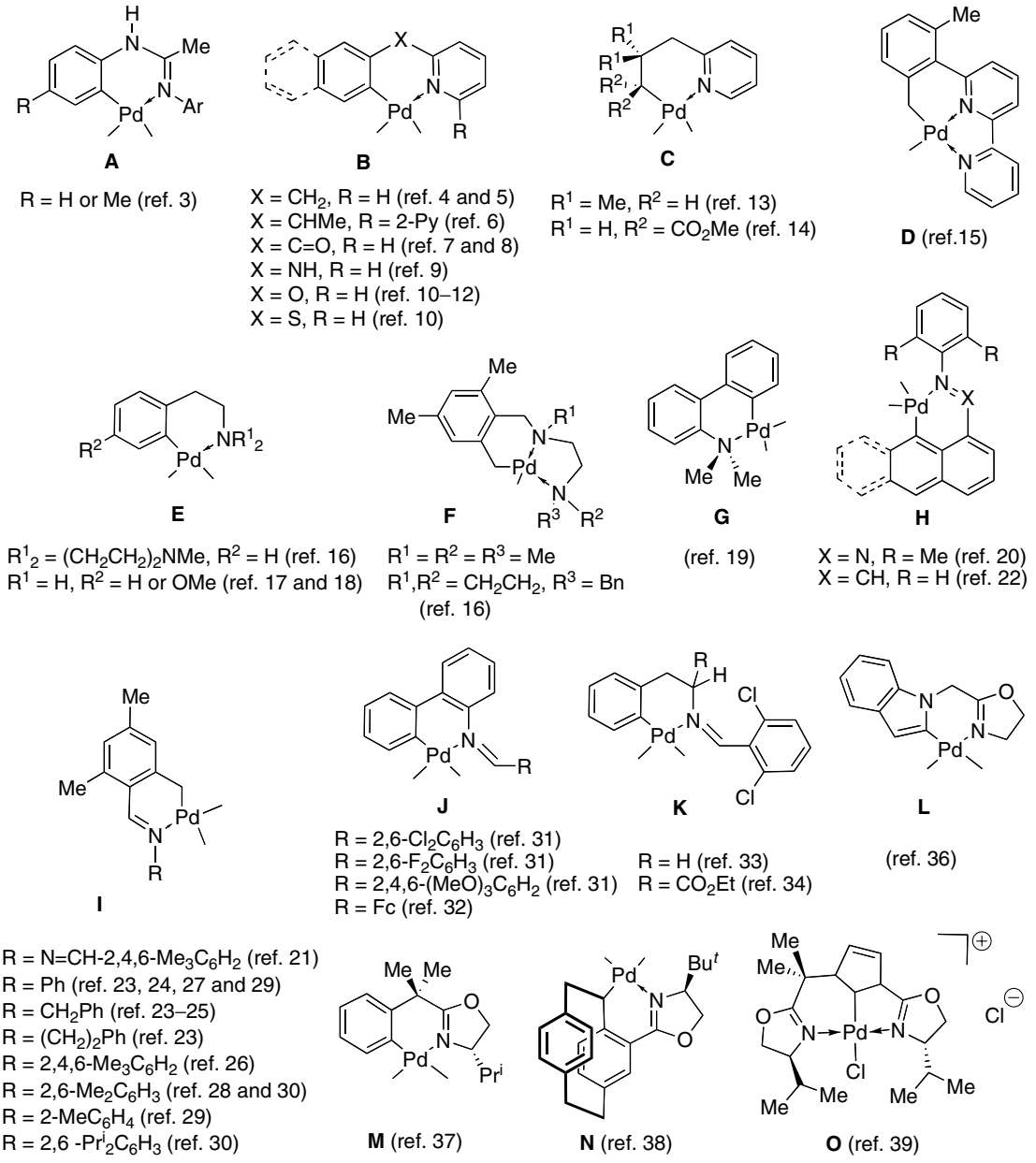


Chart 1. Examples of known six-membered palladacycles.

[58,63–70] cyclopalladated oxazolines with a five-membered metalacycle have been reported (Chart 2). Other cyclopalladated oxazolines with planar and central chirality have also been studied [38,71–80]. It has also been shown that the formation of five-membered oxazoline-derived metalacycles complies with the *endo* rule: the preference of *endo* palladation over *exo* [48,50]. Two of the four known oxazoline-based six-membered palladacycles (Chart 1, **L** and **N**) were obtained by activation of either the indol's or benzylic C–H bond using $Pd(OAc)_2$. The metalacycle **M** was obtained by oxidative addition of the corresponding bromine-containing preligand to $Pd_2(dba)_3$. The fourth known six-membered palladacycle bearing the oxazolinyl moiety, **O**, is a part of the carbene-derived asymmetrical pincer complex and was synthesized by transmetalation [39]. These four palladacycles belong to the *endo* type. The goals of the present study were preparation of the first example of an oxazoline-derived six-membered *exo* palladacycle and expanding the number of known enantiopure six-membered *endo* metalacycles by using direct palladation of oxazolines. We have also investigated whether the *endo* rule holds for the formation of six-membered palladacycles.

2. Results and discussion

Oxazoline **1** was prepared from commercially available (*S*)-phenylalaninol and ethylacetimidate hydrochloride in 65% yield using a known procedure (Scheme 1) [81]. Ligands **2** and **3** were synthesized in 79% and 84% yield,

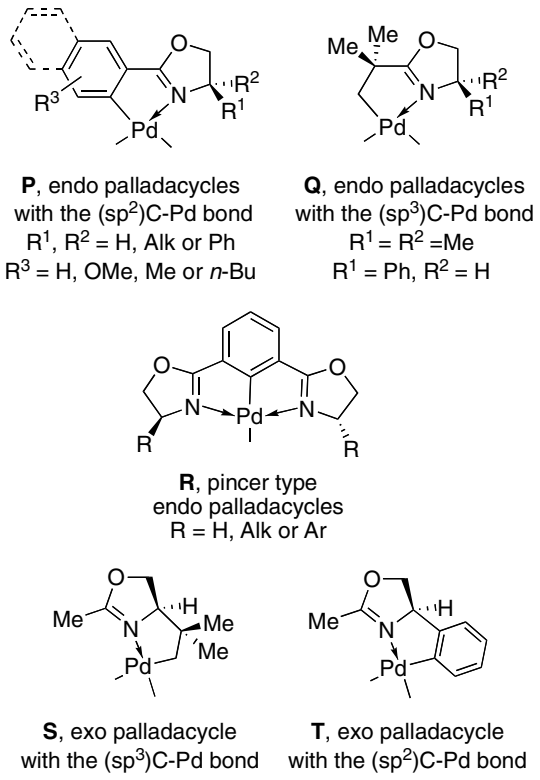
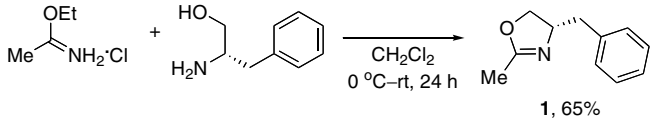


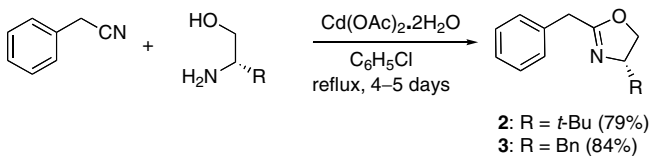
Chart 2. Known oxazoline-derived *exo* and *endo* five-membered palladacycles with C*-central chirality.



Scheme 1.

respectively, by refluxing a chlorobenzene solution of phenylacetonitrile with the corresponding amino alcohol according to a modified protocol reported for the synthesis of bis(oxazolines) (Scheme 2) [82].

Coordination complexes $Pd(\mathbf{1})_2(OAc)_2$ (**4**) and $Pd(\mathbf{2})_2(OAc)_2$ (**9**) were obtained quantitatively by the reaction of $Pd(OAc)_2$ with 2 equiv. of ligands **1** and **2**, respectively, in acetone (Schemes 3 and 4). Coordination complexes $Pd(\mathbf{1})_2Cl_2$ (**5**) and $Pd(\mathbf{2})_2Cl_2$ (**10**) were prepared in good yields by reacting Na_2PdCl_4 with oxazolines **1** and **2** in acetone (Schemes 3 and 4). Compound **10** was also synthesized in 87% yield by treating complex **9** with LiCl in acetone (Scheme 4).



Scheme 2.

Acetic acid is the most common solvent for direct cyclopalladation of different substrates, including oxazolines, using $Pd(OAc)_2$ [50,83]. Surprisingly, our attempts of the direct cyclopalladation of **1** with $Pd(OAc)_2$ in glacial acetic acid at 76 °C for 2–24 h were not successful. Under these conditions, only traces of the desirable cyclopalladated complex (**6**) were detected and the corresponding coordination complex (**4**) was isolated in a high yield. However, the reaction proceeded efficiently in acetonitrile to provide the μ-acetato dimer **6** in 89% yield (Scheme 3). Compound **6** was also obtained in 86% yield from the coordination complex **4** by reacting with 1 equiv. of $Pd(OAc)_2$ in acetonitrile at 76–82 °C for 1 h. Conversions of coordination complexes $Pd(HL)_2X_2$ to the corresponding cyclopalladated derivatives $(PdLX)_2$ either by using $Pd(OAc)_2$ in MeCN [17,18] or by dissolving the complex in a polar solvent [84] have been known previously. However, such transformations have never been reported for other oxazolines, and our attempts to carry out the same reactions for 2-phenyloxazoline, 2,4-diphenyl-2-oxazoline and other similar preligands to form five-membered palladacycles failed.

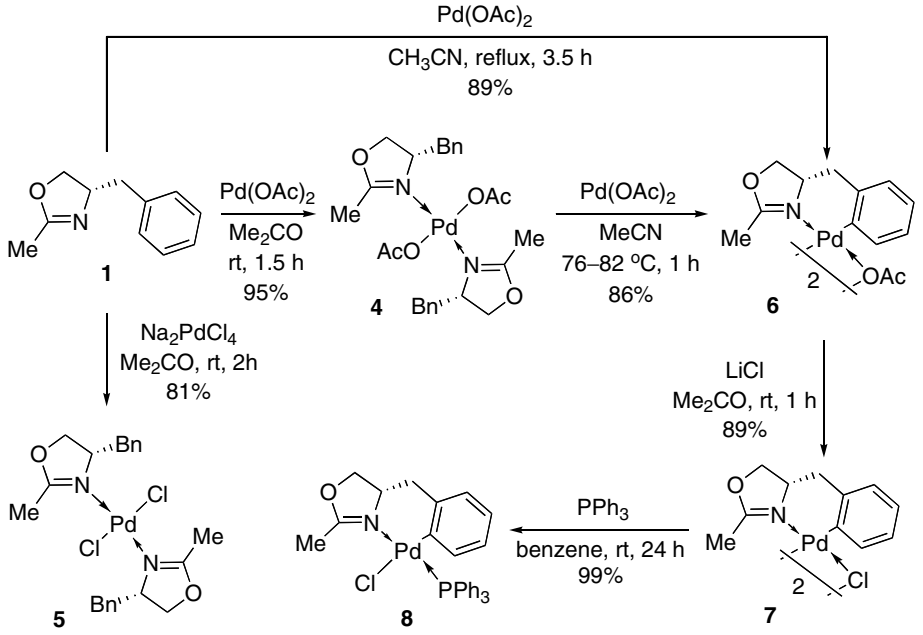
Ligand metathesis of **6** with 2 equiv. of LiCl in acetone afforded the μ-chloro dimer **7** in 89% yield. The μ-chloro dimer **7** was converted quantitatively to the mononuclear PPh_3 adduct **8** upon reaction with 2 equiv. of PPh_3 in benzene. The 6-membered *exo*-cyclic complexes **6–8** are all stable to heat, air and moisture in the solid state. However, complex **7** proves to be much less stable in solution than **6** and **8**, as it degrades over time in common solvents at room temperature.

Oxazoline **2** reacted with $Pd(OAc)_2$ in acetonitrile to produce the μ-acetato cyclopalladated complex, which was converted in situ to the μ-chloro analog **11** using LiCl with an overall yield of 60% (Scheme 4). Contrary to our findings for oxazoline **1**, the cyclopalladation of **2** also proceeded successfully in acetic acid at 76–80 °C, giving complex **11** in 83% yield upon reaction of the μ-acetato dimer with LiCl. After treatment of a benzene solution of **11** with 2 equiv. of PPh_3, the mononuclear complex **12** was obtained in 85% yield (Scheme 4).

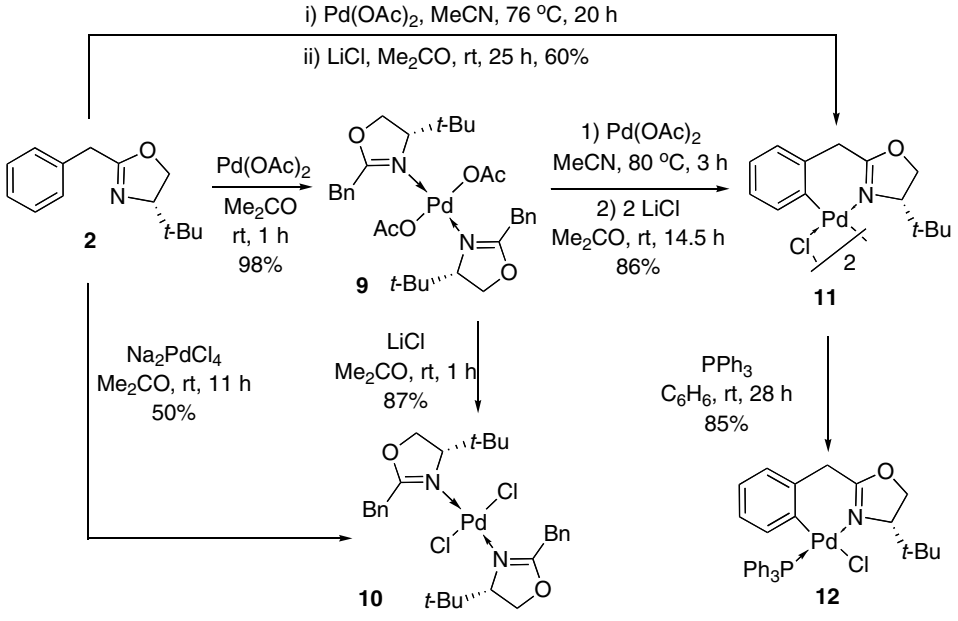
Oxazoline **3** has two different kinds of (sp^2)C–H bonds that are susceptible to palladation. Thus, the cyclopalladation reaction of **3** could produce a six-membered *endo* and/or *exo* palladacycle, via the activation of the *ortho* (sp^2)C–H of the 2-and/or 4-benzyl substituent on the oxazoline ring, respectively. The cyclopalladation of **3** took place regiospecifically in acetic acid, acetonitrile and dichloromethane (Scheme 5) to produce only one *endo* isomer as indicated by the presence of only one set of signals in the ^1H and $^{13}C–\{^1H\}$ NMR spectra of both the crude and pure cyclopalladated product **13**. Complex **13** was converted to the corresponding mononuclear derivative **14** containing PPh_3 as an auxiliary ligand (Scheme 5).

3. Spectral characterization of complexes

Oxazolines **1–3** and complexes **4–13** were characterized by IR and NMR (^1H, $^{13}C–\{^1H\}$ and $^{31}P–\{^1H\}$) spectroscopy;



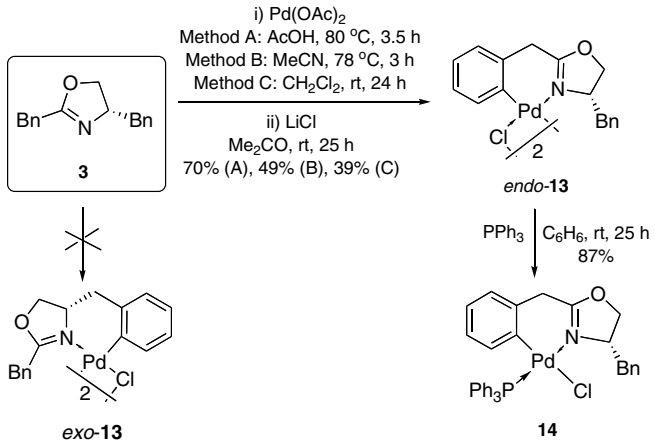
Scheme 3.



Scheme 4.

the signal assignment in ^{1}H and ^{13}C–{^{1}H} NMR spectra was done using 1D NOE, DEPT and HSQC experiments. The IR data confirmed the presence of the N–Pd bond in the coordination and cyclopalladated complexes. In the spectra of compounds **5**–**8** and **10**–**14**, the signals of the C=N bond vibrations were shifted to lower wavenumbers compared to those of free oxazolines ($\Delta\lambda = 5$–$27\ cm^{-1}$). These values are within the range of those reported for other oxazoline-derived Pd(II) complexes [48,50,54].

The ^{1}H NMR spectra of the cyclopalladated dimers **6**, **7**, **11**, and **13** are fully consistent with *ortho*-metalation of the phenyl ring. The 5H or 10H multiplets assigned to the aromatic protons in the spectra of free oxazolines **1**–**3** were replaced by 4H or 9H multiplets in the spectra of the dimeric complexes **6**, **7**, **11**, and **13**. According to the DEPT and ^{13}C–{^{1}H} NMR data, one of the aromatic CH groups in oxazoline **2** was replaced with a quaternary aromatic carbon in the respective cyclopalladated complexes **11** and **12**. PPh_3 adducts **8**, **12** and **14** exist in solution as single



Scheme 5.

isomers, as indicated by the presence of only one signal at δ 32.54, 34.41 and 33.52 ppm, respectively, in their ^{31}P–$\{^1H\}$ NMR spectra and one set of signals in their ^{13}C–$\{^1H\}$ NMR spectra. The chemical shift values of the ^{31}P–$\{^1H\}$ NMR signals are consistent with those reported for *trans-P,N* adducts [48,50].

The OCH_2 protons of 4-monosubstituted oxazoline rings are diastereotopic. Consequently, each of the three hydrogens of the oxazoline ring displayed a separate signal in the ^1H NMR spectra of compounds **1**–**14**. The assignment of these signals was done by analyzing ^{13}C–$\{^1H\}$, DEPT and HMQC spectra. 1D NOE experiments were carried out to differentiate between the diastereotopic OCH_2 protons. The results of these experiments for complex **8** are presented in Fig. 1.

Coupling constant values in the ^1H NMR spectra of the heterocycles **1**–**3** and complexes **4**–**14** in $CDCl_3$ can be used to determine the oxazoline ring conformation in these compounds. The values of the torsion angles H^S–C(O)–C(N)–H and H^R–C(O)–C(N)–H were estimated using the computer program MestRe-J, which calculates the torsion angles applying the Haasnoot–de Leeuw–Altona equation [85]. Using the coupling constants $^3J_{OCH^S,NCH} = 8.9$ and $^3J_{OCH^R,NCH} = 7.4$ for free oxazoline **1**, values of 16° and 135° were obtained for the H^S–C(O)–C(N)–H and H^R–C(O)–C(N)–H torsion angles, respectively. This suggests a slightly twisted $\delta(S)$ conformation for the oxazoline ring in preligand **1** (Fig. 2). The same twisted $\delta(S)$ solution conformation is predicted for the heterocycle in **2**. The oxazoline ring conformation in complexes with the *endo* palladacycle **11** and **12** in solution can be considered achiral, with no twist to either direction.

According to the reported X-ray data for six-membered palladacycles, they usually adopt a boat conformation in the solid state (palladacycles **B**, **C**, **E**, **F**, **L** and **M**, Chart 1) [6,10,14,16,17,33,86], although palladacycles of type **I** have a half-skew chair conformation [23,24,27,28,30]. Consideration of molecular models of mononuclear cyclopalladated complexes **8**, **12** and **14** suggests boat conformations A and/or B (Fig. 3). The rigidity of the palladacycles was checked by variable temperature (−60 to +60 °C) ^1H NMR experiments using the mononuclear complexes **8** and **12** in $CDCl_3$. Minor changes in the multiplicities and resonance frequencies of the benzylic protons in the spectra of **8** and **12** over the studied temperature range suggested that both the *exo* and *endo* palladacycles in these complexes have a rigid conformation in solution. In order to determine the conformation of the *exo* palladacycle in

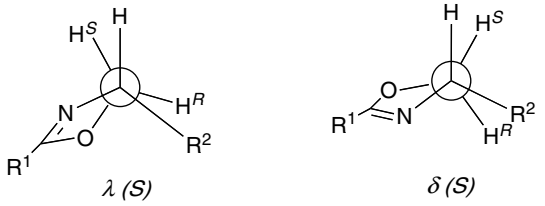


Fig. 2. Two possible chiral twisted [$\delta(S)$ and$\lambda(S)$] conformations [48] of the oxazoline ring in (*S*)-2,4-disubstituted oxazolines.

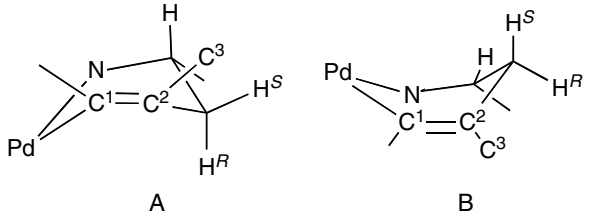


Fig. 3. Possible boat conformations of the *exo* palladacycle in complexes **6**–**8**.

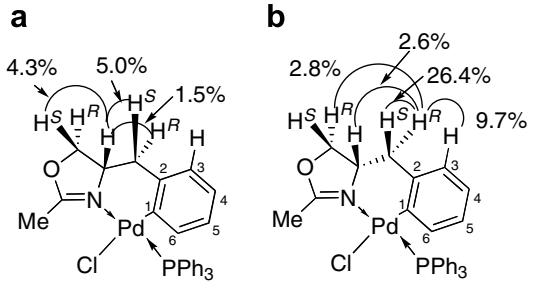


Fig. 1. Results of the 1D NOE experiments for complex **8**: (a) irradiation of the NCH signal; (b) irradiation of the $ArCH^R$ signal.

compound **8**, 1D NOE studies were carried out (Fig. 1). The observed NOE data are consistent with conformation B (Fig. 3). Unfortunately, it was impossible to determine the *endo* palladacycle's conformation in complexes **11**–**14** using NMR spectroscopy.

4. X-ray structural analysis of complexes 6 and 14

^{1}H and ^{13}C–{^{1}H} NMR spectra for the crude and purified product in the reaction of oxazoline **3** with $Pd(OAc)_2$ (Scheme 5) contain only one set of signals. This suggests complete regioselectivity of the reaction under the used conditions. However, NMR data did not allow differentiation between two possible palladacycles in complex **13** and its derivative **14**. The *endo* structure of the palladacycle in compound **14** was unambiguously confirmed by the single crystal X-ray diffraction study. The molecular structure of complex **14** with the *endo* palladacycle is presented in Fig. 4. The crystal structure of complex **6** with the six-membered *exo* palladacycle was also determined; a picture of it is shown in Fig. 5. As expected, the coordination geometry around the palladium atom in both structures **6** and **14** is approximately square-planar.

X-ray structures have been reported for two oxazoline-derived complexes with six-membered palladacycles: the acetato PPh_3 adduct with palladacycle **L** and the μ-bromo-dimer with palladacycle **M** (Chart 1). The palladacycles in both complexes are *endo*, with the oxazoline C=N moiety within the metal-containing ring. Overall, structural features of complex **14** are similar to those reported for complexes **L** and **M**. For example, the Pd–C bond lengths in palladacycles **L**, **M** and **14** equal 1.995(3), 1.997(9) and 1.996(3) Å, respectively. These values are within the range reported for oxazoline-derived five-membered *endo* metalacycles (1.992–2.052 Å) [38,48,53,54]. The Pd–N bond lengths in **L**, **M** and **14** are 2.079(3), 2.079(3) and 2.067(3) Å, respectively. These values are lower than that known for the imine-derived six-membered *C*,*N*-palladacycle **I** (R = Ph, Chart 1; 2.138 Å),[24] but slightly higher than those reported for oxazoline-based five-membered *endo* palladacycles, 2.012–2.072 Å [38,48,53–55]. The lengths of the C=N bonds in three palladacycles **L**, **M** and **14** are 1.266, 1.203 and 1.276 Å, respectively. They are slightly lower than the values found for oxazoline-based five-membered *endo* palladacycles, 1.265–1.307 Å [38,48,53–55] and imine-derived five-membered *exo* derivatives, 1.253–1.321 Å.[33] The torsion angles C–Pd–N in the palladacycles **L**, **M** and **14** are similar to one another (87.95, 85.73 and 86.36°), but quite different from those found in oxazoline-derived five-membered *endo* palladacycles (78.57–80.87°) [38,48,53–55].

All three *endo* palladacycles **L**, **M** and **14** have the boat conformation (Fig. 4). The oxazoline ring in complex **14** adopts the chiral twisted conformation $\lambda(S)$ with a torsion angle H^S–C(O)–C(N)–H of 14.78° (see Fig. 2). For comparison, the oxazoline ring's conformation in **M** can be described as $\delta(S)$ with a torsion angle H^S–C(O)–C(N)–H of 9.21°; the oxazoline ring in **L** is almost planar.

Complexes **6**, **7** and **8** are the first representatives of cyclometalated oxazolines with a six-membered *exo* palladacycle. Therefore, structural parameters of complex **6** will be compared with the six-membered *endo* palladacycles **L**, **M** and **14**, as well as with a few known X-ray data for cyclopalladated imines containing *exo* metalacycles of the same size. The Pd–C and Pd–N bond lengths found in dimeric **6** are 1.973 and 2.026 Å, respectively. These values are in good agreement with the data reported for other

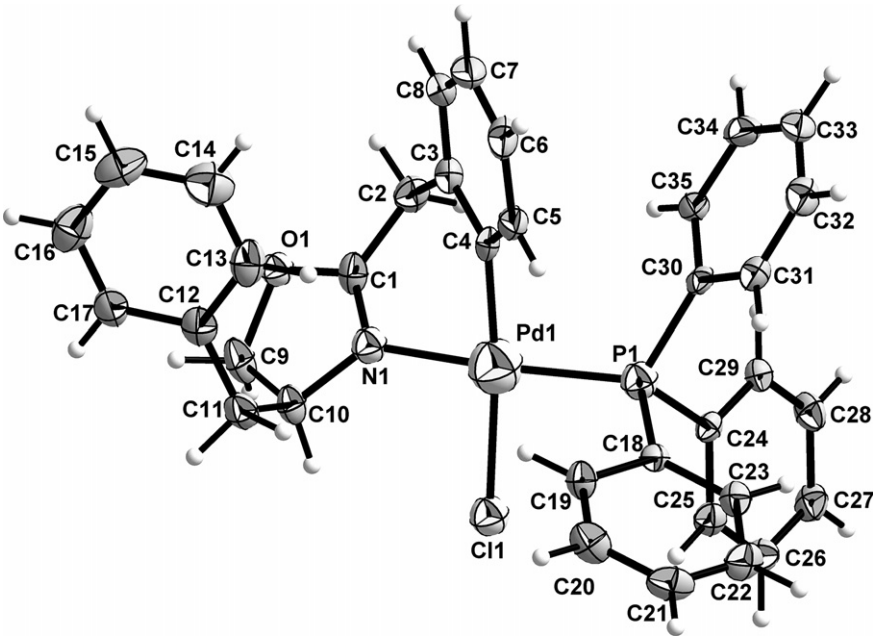


Fig. 4. Molecular structure of compound **14** drawn at 50% probability ellipsoids.

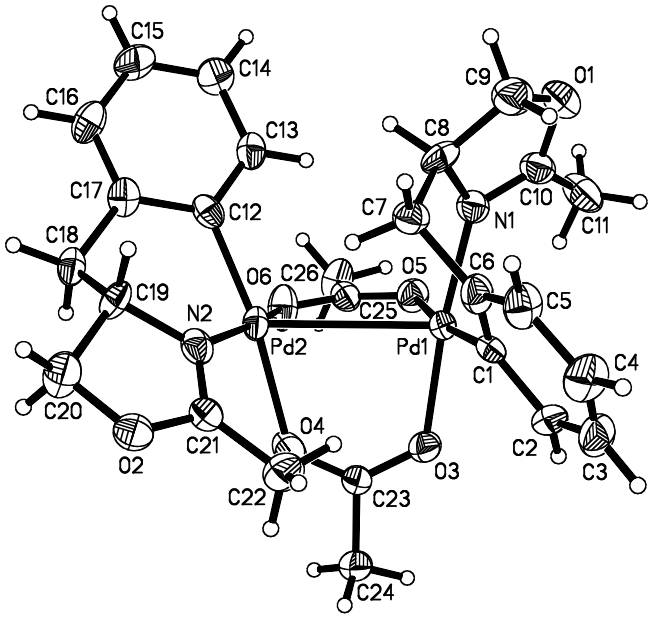


Fig. 5. Molecular structure of compound **6** drawn at 50% probability ellipsoids.

oxazoline-based palladacycles of different types. The length of the C═N bond in **6** (1.306 Å) is slightly longer than that found in the *endo* palladacycles **L**, **M** and **14** (1.203–1.276 Å) and comparable to that in five-membered *exo* palladacycles (1.253–1.321 Å) [33].

Both palladacycles in complex **6** adopt the boat conformation as do other six-membered oxazoline-based derivatives. It is interesting that one palladacycle in dimer **6** has boat conformation A, while the other adopts conformation B (Fig. 3). The solid state conformation of the two oxazoline rings in compound **6** can be described as $\delta(S)$ with torsion angles H^S–C(O)–C(N)–H of 22.75° and 28.62°.

The X-ray crystal structure of dimer **6** revealed its *anti* configuration. The same geometry was found in the X-ray structures of other oxazoline-derived μ-acetato dimers with five-membered palladacycles [55,60]. As with other μ-acetato dimeric complexes, compound **6** has a so-called open-book geometry [48,60] with a rather short Pd(1)–Pd(2) distance (3.044 Å). For comparison, the non-bonding Pd(1)–Pd(2) distance in μ-acetato dimer **P**, $R^1 = R^2 = Me$, $R^3 = H$, is 3.160 Å [55].

5. Conclusions

We have shown that six-membered *exo* and *endo* palladacycles can be synthesized successfully in good to excellent yields by direct palladation of oxazolines with $Pd(OAc)_2$ in acetonitrile and by reacting the corresponding coordination complexes with $Pd(OAc)_2$ in the same solvent. Complexes **6**–**8** represent the first examples of oxazoline-based six-membered *exo* palladacycles. The regiospecific cyclopalladation of **3** has demonstrated that the formation of six-membered oxazoline-derived palladacycles follows the *endo* rule.

6. Experimental

6.1. General methods and materials

All reactions were performed using standard bench top procedures with no special precautions to eliminate air. Purifications by column chromatography and preparative thin layer chromatography (TLC) were carried out using Natland silica gel 60 (230–400 mesh). Analytical TLC was performed on Whatman silica gel 60 (F_{254}) 250 μm pre-coated plates. Compounds were visualized on TLC plates using UV light (254 nm) and iodine stain. Routine ^1H (500 MHz), ^{13}C–{^1H} (126 MHz), and ^{31}P–{^1H} NMR (202 MHz), as well as DEPT, COSY, and HSQC spectra were recorded in $CDCl_3$ using a Bruker AVANCE 500 spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ as the internal standard (^1H and ^{13}C–{^1H}) or $P(OEt)_3$ as the external reference (^{31}P–{^1H}). Spin–spin coupling constants, *J*, are given in Hz. IR spectra were recorded on an ATI Mattson Genesis Series FT-IR. Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Optical rotations were measured in a 1 dm cell using an Autopol III automatic polarimeter. Elemental analyses were performed by Atlantic MicroLabs Inc., Norcross, GA. Benzene was refluxed over K/benzophenone ketyl, distilled under N_2 and kept over 3 Å molecular sieves. Acetone was distilled over $KMnO_4$, followed by distillation over anhydrous $CaSO_4$. Other solvents were dried by distillation over CaH_2. Prior to use, $Pd(OAc)_2$ was dissolved in hot benzene, followed by filtration and solvent removal in vacuo. All other chemicals were used as purchased from commercial sources (Sigma–Aldrich or Acros Organics).

6.2. (*S*)-4-Benzyl-2-methyl-2-oxazoline (*1*)

A solution of L-phenylalaninol (1.5828 g, 0.10468 mol) in CH_2Cl_2 (20 mL) was added drop-wise to a pre-cooled (0 °C, bath temp.) suspension of ethylacetimidate hydrochloride (0.1924 g, 0.01557 mol) in CH_2Cl_2 (25 mL). The resulting milky-white reaction mixture was stirred under N_2 at rt for 24 h and then diluted with water (150 mL). The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2 (3 × 75 mL). The combined CH_2Cl_2 solutions were dried over anhydrous $NaSO_4$. The drying agent was removed by filtration, the solvent was evaporated, and the crude product was distilled in vacuo, to afford 1.2001 g (65%) of the pure product as a colorless oil. Bp 120–123 °C at 6 mm Hg [lit.[87] (63–65 °C at 0.12 mm Hg)]; R_f 0. 27 (1:2 pet. ether–EtOAc); IR (thin film of $CDCl_3$ soln, *v*, cm^{-1}): 1674 (C═N); $[\alpha]_D^{24}$ −63.3° (*c* 1.71, MeOH) [lit.[88] $[\alpha]_D^{23}$ −47.9° (*c* 1.70, MeOH); lit.[87] $[\alpha]_D^{25}$ −49.3° (*c* 2.83, $CHCl_3$); lit. [89] $[\alpha]_D^{25}$ −50.7° (*c* 2.83, $CHCl_3$)]; ^1H NMR (δ, ppm): 1.97 (br. d, 3H, $^5J_{HH} = 1.2$, Me), 2.64 (dd, 1H, $^2J_{PhCH^R,PhCH^S} = 13.8$, $^3J_{PhCH^R,NCH} = 8.5$, PhCH^R), 3.08 (dd, 1H, $^3J_{PhCH^S,NCH} = 5.4$, PhCH^S), 3.93 (dd, 1H, $^2J_{OCH^R,OCH^S} = 8.4$, $^3J_{OCH^R,NCH} = 7.4$, OCH^R),

4.17 (t, $^3J_{OCH^S,NCH} = 8.9 OCH^S$), 4.36 (m, 1H, NCH), 7.19–7.24 (m, 3H, *o*- and *p*-CH arom.), 7.26–7.31 (m, 2H, *m*-CH arom.); $^{13}C–\{^1H\}$ NMR (δ, ppm): 14.0 (Me), 41.6 (Ph*C*H_2), 67.4 (NCH), 71.8 (O*C*H_2), 126.5 (*p*-CH arom.), 128.5 (*m*-CH arom.), 129.2 (*o*-CH arom.), 138.0 (*ipso*-C arom.), 165.1 (OCN).

6.3. (*S*)-2-Benzyl-4-tert-butyl-2-oxazoline (**2**)

$Cd(OAc)_2$ (0.1532 g, 0.5748 mmol) and phenylacetonitrile (1.3 mL, 0.011 mol) were added to a solution of (*S*)-*tert*-leucinol (1.3331 g, 11.380 mmol) in chlorobenzene (43 mL). The mixture was refluxed under N_2 for 5 days. The solvent was evaporated, and the residue was dissolved in petroleum ether and filtered through celite. After solvent evaporation, the crude product was further purified by vacuum distillation to obtain 1.9222 g (79%) of **2** as a colorless oil. Bp 90–95 °C/0.07 mm Hg; R_f 0.57 (1:2 pet. ether–EtOAc); IR (thin film of $CDCl_3$ soln, ν, cm^{-1}): 1670 (C=N); $[\alpha]^{22}_{633}$ −61.0°, $[\alpha]^{22}_{D}$ −70.0°, $[\alpha]^{22}_{546}$ −83.4°, $[\alpha]^{22}_{435}$ −143°, $[\alpha]^{22}_{365}$ −253° (*c* 0.264, CH_2Cl_2); ^1H NMR (δ, ppm): 0.88 (s, 9H, *t*-Bu), 3.62 and 3.66 (two d, 2H, $^2J = 19.5$, PhCH_2), 3.85 (dd, 1H, $^3J_{OCH^S,NCH} = 10.0$, $^3J_{OCH^R,NCH} = 8.0$, NCH), 4.01 (t, 1H, $^2J_{OCH^R,OCH^S} = 8.7$, OCH^R), 4.15 (dd, 1H, OCH^S), 7.23–7.31 (m, 5H, CH arom.); $^{13}C–\{^1H\}$ NMR (δ, ppm): 25.0 [(C*Me*$_3$), 33.6 [*C*Me$_3$], 34.9 (Ph*C*H_2), 68.9 (O*C*H_2), 75.7 (NCH), 126.9 (*p*-CH arom.), 128.5 (*m*-CH arom.), 128.9 (*o*-CH arom.), 135.4 (*ipso*-C arom.), 165.8 (OCN). Anal. Calc. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 76.78; H, 8.67; N, 6.50%.

6.4. (*S*)-2,4-Dibenzyl-2-oxazoline (**3**)

Compound **3** was synthesized using the same procedure as for **2**. The yield of **3** from 0.92 mL (8.0 mmol) of phenylacetonitrile and 1.21 g (7.97 mmol) of L-phenylalaninol after 4 days of reflux and purification by vacuum distillation was 1.59 g (84%). IR (neat, ν, cm^{-1}): 1665 (C=N). ^1H and $^{13}C–\{^1H\}$ NMR data are identical to those reported previously [90].

6.5. (*S,S*)-Diacetatobis-(4-benzyl-2-methyl-2-oxazoline)-palladium(II) (**4**)

(*S*)-4-Benzyl-2-methyl-2-oxazoline (156.2 mg, 0.8914 mmol) was dissolved in acetone (7.0 mL) and $Pd(OAc)_2$ (100.1 mg, 0.4459 mmol) was added to the stirred solution at rt. After 1.5 h, the solvent was evaporated. The crude product was recrystallized from Et_2O–petroleum ether to give **4** (242.4 mg, 95%) as yellow crystals. M.p. 123–124 °C; R_f 0.29 (95:5 EtOAc–MeOH); IR (thin film of $CDCl_3$ soln, ν, cm^{-1}): 1666, 1651, 1624, and 1601 (C=N and C=O); ^1H NMR (δ, ppm): 1.86 (s, 3H, Me), 2.52 (s, 3H, Ac), 2.80 (dd, 1H, $^2J = 13.7$, $^3J_{PhCH^R,NCH} = 10.4$, PhCH^R), 4.03 (t, 1H, $J = 8.3$, OCH^R), 4.14 (t, $J = 9.2$, OCH^S), 4.21 (m, 1H, NCH), 4.35 (dd, 1H, $^3J_{PhCH^S,NCH} = 3.7$, PhCH^S), 7.14–7.27 (m, 5H, CH arom.); $^{13}C–\{^1H\}$ NMR (δ, ppm): 15.0 (Me), 22.8 (*Me*CO_2), 41.0 (Ph*C*H_2), 66.0 (NCH), 72.5 (O*C*H_2), 126.7 (*p*-CH arom.), 128.8 (*m*-CH arom.), 129.3 (*o*-CH arom.), 137.0 (*ipso*-C arom.), 170.7 (OCN), 177.6 (C=O). Anal. Calc. for $C_{26}H_{32}N_2OPd$: C, 54.31; H, 5.61; N, 4.87. Found: C, 54.57; H, 5.63; N, 4.98%.

6.6. (*S, S*)-Dichlorobis-(4-benzyl-2-methyl-2-oxazoline)-palladium(II) (**5**)

A solution of (*S*)-4-benzyl-2-methyl-2-oxazoline (54.8 mg, 0.313 mmol) in acetone (2.0 mL) was added to a suspension of Na_2PdCl_4 (46.7 mg, 0.159 mmol). The mixture was stirred under N_2 at rt for 2 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and filtered through celite. Concentration of the filtrate, followed by addition of pentane, led to precipitation of the product as a yellow powder. Further purification by column chromatography, with benzene as the eluent, resulted in the isolation of 66.7 mg (81%) of the pure product. M.p. 133–134 °C; R_f 0.75 (1:1 toluene–EtOAc); IR (thin film of CH_2Cl_2 soln, ν, cm^{-1}): 1665 (C=N); $[\alpha]^{22}_{633}$ +157°, $[\alpha]^{22}_{D}$ +192°, $[\alpha]^{22}_{546}$ 241° (*c* 0.200, CH_2Cl_2); ^1H NMR (δ, ppm): 2.56 (s, 3H, Me), 2.85 (dd, 1H, $^2J_{PhCH^R,PhCH^S} = 13.8$, $^3J_{PhCH^R,NCH} = 10.7$, PhCH^R), 4.09 (t, 1H, $J = 8.6$, OCH^R), 4.23 (dd, 1H, $^3J_{PhCH^S,NCH} = 4.3$, PhCH^S), 4.28 (t, $J = 9.4$, OCH^S), 4.60 (m, 1H, NCH), 7.22–7.35 (m, 5H, CH arom.); $^{13}C–\{^1H\}$ NMR (δ, ppm): 16.0 (Me), 41.3 (Ph*C*H_2), 66.0 (NCH), 72.9 (O*C*H_2), 127.0 (*p*-CH arom.), 128.9 (*m*-CH arom.), 129.2 (*o*-CH arom.), 136.4 (*ipso*-C arom.), 170.3 (OCN). Anal. Calc. for $C_{22}H_{26}Cl_2N_2OPd$: C, 50.07; H, 4.97; N, 5.31. Found: C, 50.58; H, 4.94; N, 5.22%.

6.7. (*S,S*)-Di-μ-acetatobis-{2-[2-(2-methyl)oxazolin-4-yl]-methylphenyl-*C,N*}dipalladium(II) (**6**)

Method A. A mixture of (*S*)-4-benzyl-2-methyl-2-oxazoline **1** (54.2 mg, 0.309 mmol) and $Pd(OAc)_2$ (71.2 mg, 0.317 mmol) in acetonitrile (5.0 mL) was refluxed for 3.5 h. The mixture was allowed to cool to rt and filtered through celite. The solvent was evaporated, and the crude product was recrystallized from bezene–petroleum ether to obtain 93.4 mg (89%) of **6**. *Method B.* $Pd(OAc)_2$ (25.3 mg, 0.113 mmol) was added to an acetonitrile solution (5.0 mL) of coordination complex **4** (64.4 mg, 0.112 mmol). The reaction mixture was refluxed for 1 h. Evaporation of the solvent followed by recrystallization of the crude product from Et_2O–petroleum ether yielded 65.4 mg (86%) of **6**. M.p. 197–198 °C (with dec.); R_f 0.38 (98:2 EtOAc–MeOH); IR (thin film of $CDCl_3$ soln, ν, cm^{-1}): 1657; $[\alpha]^{23}_{633}$ −46.6°, $[\alpha]^{23}_{D}$ −70.8°, $[\alpha]^{23}_{546}$ −46.6°, (*c* 0.116, CH_2Cl_2); ^1H NMR (δ, ppm): 1.99 and 2.00 (two s, 3H each, Me and Ac), 2.82 (dd, 1H, $^2J_{PhCH^R,PhCH^S} = 14.5$, $^3J_{PhCH^R,NCH} = 8.6$, PhCH^R), 3.06 (dd, 1H, $^3J_{PhCH^S,NCH} = 3.9$, PhCH^S), 3.63 (m, 1H, NCH), 3.80 (t, 1H, $J = 9.5$, OCH^R), 4.19 (t, $J = 8.6$, OCH^S), 6.69 [br. d, 1H, $J = 6.7$, CH(6) arom.], 6.83 [br. t, 1H, $J = 6.9$,

CH(4) arom.], 6.88 [br. t, 1H, $J = 6.8$, CH(5) arom.], 7.19 [d, 1H, $J = 7.5$, CH(3) arom.]; $^{13}C–\{^1H\}$ NMR (δ, ppm): 14.3 (*Me*CN), 24.4 (*Me*CO_2), 40.3 [Ph*C*H_2], 62.5 (NCH), 72.7 (OCH_2), 124.0 [CH(5) arom.], 124.6 [CH(4) arom.], 127.0 [CH(6) arom.], 134.5 [CH(3) arom.], 135.4 [C(1) arom.], 137.6 [PdC(2) arom.], 171.7 (OCN), 180.4 (OCO). Anal. Calc. for $C_{26}H_{30}N_2O_6Pd_2$: C, 45.97; H, 4.45; N, 4.12. Found: C, 46.23; H, 4.53; N, 4.19%.

6.8. (S,S)-Di-μ-chlorobis-{2-[2-(2-methyl)oxazolin-4-yl]-methylphenyl-C,N} dipalladium(II) (7)

LiCl (28.20 mg, 0.6652 mmol) was added to an acetone (10.0 mL) solution of complex **6** (191.7 mg, 0.2822 mmol), and the mixture was stirred at rt for 1 h. The solvent was evaporated, and the residue was dissolved in Et_2O and filtered through celite. The crude product was recrystallized from CH_2Cl_2–hexanes to afford the pure **7** (157.9 mg, 89%) as a yellow powder. M.p. 198–220 (dec.); R_f 0.45 (1:2 benzene–EtOAc); IR (nujol mull, ν, cm^{-1}): 1647 (C=N); $[\alpha]^{24}_{633}$ −173°, $[\alpha]^{24}_{D}$ −216°, $[\alpha]^{24}_{546}$ −284°, (*c* 0.878, CH_2Cl_2); ^1H NMR (δ, ppm): 2.35 (s, 3H, Me), 2.64 (d, 1H, $^2J_{PhCH^R,PhCH^S} = 14.7$, PhC*H*^{R}), 3.72 (dd, 1H, $^2J_{OCH^R,OCH^S} = 8.3$, $^3J_{OCH^S,NCH} = 12.7$, OCH^S), 3.99 (br. dd, 1H, $^3J_{PhCH^S,NCH} = 6.5$, PhC*H*^{S}), 4.49 (br. s, 1H, NCH), 4.60 (t, 1H, $^3J_{OCH^R,NCH} = 9.0$, OCH^R), 6.72 [br. d, 1H, $J = 6.7$, CH(6) arom.], 6.83 [m, 1H, CH(4) arom.], 6.89 [br. t, 1H, $J = 6.8$, CH(5) arom.], 7.20 [br. d, 1H, $J = 7.5$, CH(3) arom.]; $^{13}C–\{^1H\}$ NMR (δ, ppm): 15.4 (Me), 38.6 (Ph*C*H_2), 59.7 (NCH), 73.3 (OCH_2), 124.5 [CH(5) arom.], 125.5 [CH(4) arom.], 127.9 [CH(6) arom.], 134.4 [C(1) arom.], 135.1 [CH(3) arom.], 138.9 [PdC(2) arom.], 171.9 (OCN). Anal. Calc. for $C_{22}H_{24}Cl_2N_2O_2Pd_2$: C, 41.80; H, 3.83; N, 4.43. Found: C, 41.74; H, 3.95; N, 4.30%.

6.9. (S)-Chloro-{2-[2-(2-methyl)oxazolin-4-yl]-methylphenyl-C,N}(triphenylphosphine)palladium(II) (8)

PPh_3 (131.0 mg, 0.4995 mmol) was added to a stirred solution of dimer **7** (157.9 mg, 0.2498 mmol) in benzene (10.0 mL). After 12 h, the solvent was evaporated to obtain a pale-yellow solid, which was purified by trituration with petroleum ether to afford 287.0 mg (99%) of the pure product. M.p. ⩾140 °C (dec.); R_f 0.75 (98:2 EtOAc–MeOH), 0.29 (1:2 pet. ether–EtOAc); IR (nujol mull, ν, cm^{-1}): 1657 (C=N); $[\alpha]^{22}_{633}$ −64.6°, $[\alpha]^{22}_{D}$ −82.2°, $[\alpha]^{22}_{546}$ −105.7°, $[\alpha]^{22}_{435}$ −256.2°, $[\alpha]^{22}_{405}$ −369.8° (*c* 0.219, CH_2Cl_2); ^1H NMR (δ, ppm): 2.24 (br. d, 3H, $^5J_{HH} = 1.0$, Me), 2.68 (d, 1H, $^2J_{PhCH^R,PhCH^S} = 14.1$, PhC*H*^{R}), 3.68 (dd, 1H, $^2J_{OCH^R,OCH^S} = 8.4$, $^3J_{OCH^R,NCH} = 12.0$, OCH^R), 3.92 (dd, 1H, $^3J_{PhCH^S,NCH} = 6.6$, PhC*H*^{S}), 4.54 (t, 1H, $^3J_{OCH^S,NCH} = 9.2$, OCH^S), 4.77 (m, 1H, NCH), 6.29 [br. dt, 1H, $J_{HH} = 8.0$, $^5J_{PH} = 1.7$, CH(5) arom.], 6.50 [br. dd, 1H, $^3J_{HH} = 7.3$, $^4J_{PH} = 5.4$, CH(6) arom.], 6.70 [m, 2H, CH(3) and CH(4) arom.], 7.28 (m, 6H, *m*-CH of PPh_3), 7.38 (m, 3H, *p*-CH of PPh_3), 7.56 (m, 6H, *o*-CH of PPh_3); $^{13}C–\{^1H\}$ NMR (δ, ppm): 14.9 (Me), 40.6 (Ph*C*H_2), 60.4 (NCH), 72.4 (d, $^4J_{CP} = 1.3$, OCH_2), 123.2 [CH(4) arom.], 125.5 [d, $^4J_{CP} = 4.1$, CH(5) arom.], 127.6 [CH(3) arom.], 128.0 (d, $^3J_{CP} = 10.9$, *m*-CH of PPh_3), 130.2 (d, $^4J_{CP} = 2.0$, *p*-CH of PPh_3), 131.1 (d, $^1J_{CP} = 50.7$, *ipso*-C of PPh_3), 134.9 (d, $^2J_{CP} = 11.5$, *o*-CH of PPh_3), 135.7 [PdC(1) arom.], 136.6 [d, $^3J_{CP} = 10.5$, CH(6) arom.], 152.9 [C(2) arom.], 170.6 (d, $^3J_{CP} = 4.6$, OCN); $^{31}P–\{^1H\}$ NMR (δ, ppm): 32.54. Anal. Calc. for $C_{29}H_{27}ClNOPPd$: C, 60.22; H, 4.71; N, 2.42. Found: C, 60.39; H, 4.65; N, 2.43%.

6.10. (S,S)-Diacetatobis-(2-benzyl-4-tert-butyl-2-oxazoline)palladium(II) (9)

An acetone solution (2.6 mL) of 2-benzyl-4-*tert*-butyl-2-oxazoline (215.3 mg, 0.9908 mmol) was added to a suspension of $Pd(OAc)_2$ (112.5 mg, 0.5011 mmol) in acetone (1.0 mL). The reaction mixture was stirred under N_2 at rt for 1 h. The solvent was evaporated, and the resulting yellow residue was crystallized from CH_2Cl_2–petroleum ether to obtain 349 mg (98%) of the pure product. M.p. 106–109 °C; R_f 0.49 (EtOAc); IR (thin film of $CDCl_3$ soln, ν, cm^{-1}): 1658 (shoulder), 1639, 1603 (C=N and C=O); $[\alpha]^{22}_{633}$ + 18.4°, $[\alpha]^{22}_{D}$ +33.1°, $[\alpha]^{22}_{546}$ +71.8°, (*c* 0.250, CH_2Cl_2); ^1H NMR (δ, ppm): 1.26 (s, 9H, *t*-Bu), 1.85 (s, 3H, Ac), 3.82 (dd, 1H, $^3J_{OCH^S,NCH} = 10.2$, $^3J_{OCH^R,NCH} = 6.8$, NCH); 4.19 (dd, 1H, $^2J_{OCH^R,OCH^S} = 9.3$, OCH^R), 4.23 (t, 1H, OCH^S); 4.75 (d, 1H, $^2J_{PhCH^R,PhCH^S} = 15.7$, PhC*H*), 5.17 (br. d, 1H, PhC*H*), 7.25–7.36 (m, 5H, CH arom.); $^{13}C–\{^1H\}$ NMR (δ, ppm): 23.1 (*Me*CO_2), 26.0 [C*Me*$_3$], 33.9 [*C*Me$_3$], 36.5 (Ph*C*H_2), 70.1 (OCH_2), 73.6 (NCH), 127.1 (*p*-CH arom.), 128.5 (*m*-CH arom.), 129.4 (*o*-CH arom.), 134.3 (*ipso*-C arom.), 172.5 (OCN), 177.5 (Me*C*O_2).

6.11. (S,S)-Dichlorobis-(2-benzyl-4-tert-butyl-2-oxazoline)palladium(II) (10)

Method A. A solution of (*S*)-2-Benzyl-4-*tert*-butyl-2-oxazoline **2** (50.0 mg, 0.230 mmol) and Na_2PdCl_4 (33.5 mg, 0.114 mmol) in acetone (5.0 mL) was stirred for 11 h at rt in a flask equipped with a $CaCl_2$ drying tube. The solvent was evaporated and the crude product was purified by flash column chromatography, using toluene and 1:1 toluene–EtOAc as eluents. A yellow powder (34.9 mg (50%) was isolated as a mixture of two isomers in a 2:1 ratio. *Method B*. The pre-ligand **2**(87.7 mg, 0.404 mmol) was added to a suspension of $Pd(OAc)_2$ (54.8 mg, 0.204 mmol) in acetone (1.5 mL). The reaction mixture was stirred under N_2at rt for 1 h. A saturated solution of LiCl (17.6 mg, 0.415 mmol) in acetone (1.6 mL) was added and the mixture was stirred for an additional 1 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and filtered through celite. Purification of the crude product by column chromatography, using benzene as the eluent, afforded 106 mg (87%) of **10** as a yellow solid. M.p. 165–167 °C; R_f 0.40 (benzene); IR (thin film of

CH_2Cl_2 soln, ν, cm^{-1}): 1643 (C=N); $[\alpha]^{21}_{633}$ +173°, $[\alpha]^{21}_{D}$ +227°, $[\alpha]^{21}_{546}$ +303°, (*c* 0.180, CH_2Cl_2); ^1H NMR (δ, ppm): 1.30 (s, 9H, *t*-Bu), 4.09–4.63 (m, 5H, overlapping signals of PhCH_2, OCH_2 and NCH); 7.26–7.48 (m, 5H, CH arom.); ^{13}C–{^1H} NMR (δ, ppm): 26.3 (CMe_3), 34.0 (CMe$_3$), 36.4 (PhCH_2), 70.4 (OCH_2), 74.1 (NCH), 127.4 (*p*-CH arom.), 128.7 (*m*-CH arom.), 129.3 (*o*-CH arom.), 133.5 (*ipso*-C arom.), 171.4 (OCN). Anal. Calc. for $C_{28}H_{38}Cl_2N_2O_2Pd$: C, 54.96; H, 6.26; N, 4.58. Found: C, 55.02; H, 6.27; N, 4.50%.

6.12. (*S,S*)-Di-μ-chlorobis-[2-(4-tert-butyl-2-oxazolin-2-yl)methylphenyl-C,N]dipalladium(II) (**11**)

Method A. A mixture of (*S*)-2-benzyl-4-*tert*-butyl-2-oxazoline **2** (37.8 mg, 0.174 mmol) and $Pd(OAc)_2$ (39.1 mg, 0.174 mmol) in acetonitrile (3.0 mL) was heated in an oil bath at 76 °C (bath temp.) for 20 h. The solvent was evaporated and the residue was dissolved in acetone (4.5 mL). LiCl was added and the mixture was stirred at rt for 25 h. Evaporation of the solvent, followed by purification of the crude product by dry column flash chromatography, using 1:1 hexanes–CH_2CH_2 as the eluent, afforded 37.5 mg (60%) of a yellow powder as the pure product. *Method B*. The complex was synthesized from (*S*,*S*)-diacetatobis-(2-benzyl-4-*tert*-butyl-2-oxazoline)palladium(II) **9** (326.5 mg, 0.4954 mmol) and $Pd(OAc)_2$ (111.8 mg, 0.4978 mmol), followed by ligand metathesis with LiCl according to the procedure described for compound **7**. The pure complex (304.6 mg, 86%) was obtained after column chromatography with benzene and 20:1 CH_2Cl_2–EtOAc as eluents. M.p. ⩾143 (dec.); R_f 0.65 (9:1 toluene–EtOAc), 0.43 (49:1 benzene–EtOAc); IR (thin film of $CDCl_3$ soln, ν, cm^{-1}): 1658 (C=N); $[\alpha]^{22}_{633}$ +38.3°, $[\alpha]^{22}_{D}$ +44.5°, $[\alpha]^{22}_{546}$ +54.4°, $[\alpha]^{22}_{435}$ +81.2° (*c* 0.260, CH_2Cl_2); ^1H NMR (δ, ppm): 0.99 (s, 9H, *t*-Bu), 3.45 (d, 1H, $^2J_{PhCH^R,PhCH^S} = 17.7$, PhC$H^A$), 4.08 (dd, 1H, $^3J_{OCH^S,NCH} = 9.7$, $^3J_{OCH^R_{,}NCH} = 4.9$, NCH), 4.28 (d, 1H, PhCH^B), 4.39 (t, 1H, OCH^S), 4.46 (dd, 1H, $^2J_{OCH^R,OCH^S} = 9.2$, OCH^R), 6.81 [m, 1H, CH(3) arom.], 6.89 [m, 2H, CH(5) and CH(6) arom.], 7.30 [m, 1H, CH(4) arom.]; ^{13}C–{^1H} NMR (δ, ppm): 25.9 [C(CH_3)$_3$], 34.0 [C(CH$_3$)$_3$], 37.3 [PhCH_2], 72.3 (OCH_2), 72.4 (NCH), 124.2 [CH(5) arom.], 125.4 [CH(4) arom.], 126.1 [CH(6) arom.], 133.7 [C(1) arom.], 136.6 [CH(3) arom.], 138.5 [PdC(2) arom.], 171.0 (OCN).

6.13. (*S*)-Chloro-[2-(4-tert-butyl-2-oxazolin-2-yl)-methylphenyl-C,N](triphenylphosphane)palladium(II) (**12**)

A solution of dimer **11** (55.5 mg, 0.0775 mmol) and PPh_3 (42.8 mg, 0.163 mmol) in benzene (7.0 mL) was stirred under N_2 at rt for 28.5 h. The solvent was evaporated and the pale-yellow residue was triturated with hexanes, followed by slow crystallization from benzene–pentane to obtain **12** (81.6 mg, 85%) as pale-yellow crystals. M.p. 183–185 °C; R_f 0.36 (17:3 benzene–EtOAc); IR (thin film of $CDCl_3$ soln, ν, cm^{-1}): 1658 (C=N); $[\alpha]^{18}_{633}$ +19.1°, $[\alpha]^{18}_{D}$ +22.8°, $[\alpha]^{18}_{546}$ +28.3°, $[\alpha]^{18}_{435}$ +53.6°, $[\alpha]^{18}_{405}$ +68.1° (*c* 0.0640, CH_2Cl_2); ^1H NMR (δ, ppm): 0.82 (s, 9H, *t*-Bu), 3.42 (d, 1H, $^2J = 16.1$, PhCH^A), 4.25 (d, 1H, PhCH^B), 4.47 (dd, 1H, $^2J_{OCH^R,OCH^S} = 9.0$, $^3J_{OCH^R,NCH} = 5.0$, OCH^R), 4.53 (t, 1H, $^3J_{OCH^S_{,}NCH} = 9.6$, OCH^S), 4.74 (dd, 1H, NCH), 6.24 [t, 1H, $J = 7.3$, CH(5) arom.], 6.52 [t, 1H, $J = 6.7$, CH(6) arom.], 6.62 [t, 1H, $J = 7.3$, CH(4) arom.], 6.81 [d, 1H, $J = 7.2$, CH(3) arom.], 7.28 (m, 6H, *m*-CH of PPh_3), 7.36 (m, 3H, *p*-CH of PPh_3), 7.58 (m, 6H, *o*-CH of PPh_3); ^{13}C–{^1H} NMR (δ, ppm): 25.5 [CMe_3], 34.1 [CMe$_3$], 38.7 [PhCH_2], 70.2 (d, $^3J_{CP} = 2.3$, NCH), 72.8 (d, $^4J_{CP} = 1.8$, OCH_2), 122.7 [CH(4) arom.], 125.4 [d, $^4J_{CP} = 4.1$, CH(5) arom.], 126.0 [CH(3) arom.], 127.9 (d, $^3J_{CP} = 10.6$, *m*-CH of PPh_3), 130.2 (d, $^4J_{CP} = 2.1$, *p*-CH of PPh_3), 131.2 (d, $^1J_{CP} = 50.5$, *ipso*-C of PPh_3), 135.0 (d, $^2J_{CP} = 11.5$, *o*-CH of PPh_3), 136.0 [PdC(1) arom.], 138.8 [d, $^3J_{CP} = 11.1$, CH(6) arom.], 151.5 [C(2) arom.], 171.6 (d, OCN); ^{31}P–{^1H} NMR (δ, ppm): 34.41. Anal. Calc. for $C_{32}H_{33}ClNOPPd$: C, 61.95; H, 5.36; N, 2.26. Found: C, 62.21; H, 5.48; N, 2.27%.

6.14. (*S,S*)-Di-μ-chlorobis-[2-(4-benzyl-2-oxazolin-2-yl)-methylphenyl-C,N]dipalladium(II) (**13**)

Complex **13** was synthesized using three different methods: *Method A*. A mixture of (*S*)-2,4-dibenzyl-2-oxazoline **3** (50.8 mg, 0.202 mmol) and $Pd(OAc)_2$ (45.7 mg, 0.204 mmol) in acetic acid (6.0 mL) was heated in an oil bath at 80 °C for 3.5 h, followed by ligand metathesis with LiCl (10.2 mg, 0.241 mmol) in acetone (7.0 mL) at rt for 25 h. Complex **13** was isolated in 70% overall yield after purification by flash column chromatography, using benzene as the eluent. *Method B*. When a mixture of **3** (50.8 mg, 0.202 mmol) and $Pd(OAc)_2$ (46.6 mg, 0.208 mmol) in acetonitrile (5.0 mL) was heated in an oil bath at 78 °C for 3 h, followed by ligand metathesis with LiCl (11.0 mg, 0.260 mmol) in acetone at rt, complex **13** was isolated in 49% overall yield. *Method C*. A solution of **3** (56.1 mg, 0.223 mmol) and $Pd(OAc)_2$ (51.0 mg, 0.227 mmol) in CH_2Cl_2 (5.0 mL) was stirred at room temperature for 24 h. The crude product was reacted with LiCl in acetone to obtain complex **13** in 39% yield. M.p. 134–137 °C; R_f 0.51 (24:1 benzene–EtOAc); IR (thin film of CH_2Cl_2 soln, ν, cm^{-1}): 1664 (C=N); $[\alpha]^{30}_{633}$ +57.4°, $[\alpha]^{30}_{D}$ +61.9°, $[\alpha]^{30}_{546}$ +85.4°, $[\alpha]^{30}_{435}$ +243.2° (*c* 0.13, CH_2Cl_2); ^1H NMR (δ, ppm): 2.86 (dd, $^2J_{PhCH^A,PhCH^B} = 13.7$, $^3J_{PhCH^A,NCH} \approx 8.9$, PhC$H^A$), 3.41 (dd, 1H, $^2J_{PhCH^C,PhCH^D} \approx 17.6$, $J \approx 9.9$, PhCH^C), 3.51 (dd, 1H, $^3J_{PhCH^B,NCH} \approx 3.5$, PhC$H^B$), 4.20 (br. t, 1H, PhC$H^D$), 4.29 (dd, 1H, $J \approx 17.0$, $J \approx 9.5$, OCH), 4.42 (dt, 1H, OCH), 4.68 (m, 1H, NCH), 6.79–7.49 [m, 9H, CH arom.]; ^{13}C–{^1H} NMR (δ, ppm): 37.0 (PhCH_2), 40.5 (PhCH_2), 65.3 (NCH), 74.3 (OCH_2), 124.6 [CH(4) arom.], 125.6 [CH(5) arom.], 126.6 [CH(3) arom.], 126.9 (*p*-CH of Ph), 128.5 (*m*-CH of Ph), 129.6

(*o*-CH of Ph), 133.7 (*ipso*-C of Ph), 135.5 [PdC(1) arom.], 137.1 [CH(6) arom.], 138.0 [C(2) arom.], 171.0 (OCN). Anal. Calc. for $C_{34}H_{32}Cl_2N_2O_2Pd_2$: C, 52.06; H, 4.11; N, 3.57. Found: C, 51.95; H, 4.10; N, 3.57%.

6.15. (*S*)-Chloro-[2-(4-benzyl-2-oxazolin-2-yl)-methylphenyl-*C,N*](triphenylphosphane)palladium(II) (**14**)

A solution of the μ-Cl dimer **13** (84.0 mg, 0.107 mmol) and PPh_3 (60.9 mg, 0.232 mmol) in benzene (10.0 mL) was stirred at rt for 25 h. The solvent was evaporated and the pale-yellow residue was triturated with pentane to obtain **14** (122.4 mg, 87%) as a cream-white solid. M.p. 204–207 °C (dec.); R_f 0.55 (2:1 benzene–EtOAc); IR (nujol, ν, cm^{-1}): 1651 (C=N); $[\alpha]_{633}^{27}$ +50.9°, $[\alpha]_{D}^{27}$ +57.8°, $[\alpha]_{546}^{27}$ +71.6°, $[\alpha]_{435}^{27}$ +159.8° (*c* 0.212, CH_2Cl_2); ^{1}H NMR (δ, ppm): 2.80 (dd, $^2J_{PhCH^A,PhCH^B} = 13.6$, $^3J_{PhCH^A,NCH} = 7.5$, PhCH^A), 3.20 (dd, 1H, $^3J_{PhCH^B,NCH} = 4.4$, PhCH^B), 3.35 (d, 1H, $^2J_{PhCH^C,PhCH^D} = 16.3$, PhC$H^C$), 4.14 (d, 1H, PhC$H^D$), 4.26 (dd, 1H, $^2J_{OCH^R,OCH^S} = 8.5$, $^3J_{OCH^R,NCH} = 7.5$, OCH^R), 4.50 (t, 1H, $^3J_{OCH^S,NCH} = 9.4$, OCH^S), 5.36 (m, 1H, NCH), 6.32 [t, 1H, $J = 7.3$, CH(5) arom.], 6.69 [t, 2H, $J = 7.2$, CH(4 and 6) arom.], 6.79 [d, 1H, $J = 7.0$, CH(3) arom.], 6.99 (d, 2H, $J = 7.1$, *o*-CH arom.), 7.03 (t, 2H, $J \approx 7.5$, *m*-CH arom.), 7.10 (t, 1H, $J \approx 7.2$, *p*-CH arom.), 7.30 (m, 6H, *m*-CH of PPh_3), 7.37 (m, 3H, *p*-CH of PPh_3), 7.60 (m, 6H, *o*-CH of PPh_3); ^{13}C–{^{1}H} NMR (δ, ppm): 38.4 [Ph*C*H_2], 40.1 (Ph*C*H_2), 63.1(NCH), 74.5 (OCH_2), 123.1[CH(4) arom.], 125.5 [d, $^4J_{CP} = 4.8$, CH(5) arom.], 126.4 [CH(3) arom.], 126.5 (*p*-CH of Ph), 128.0 (d, $^3J_{CP} = 10.7$, *m*-CH of PPh_3), 128.2 (*m*-CH of Ph), 129.9 (*o*-CH of Ph), 130.2 (d, $^4J_{CP} = 2.4$, *p*-CH of PPh_3), 131.2 (d, $^1J_{CP} = 50.1$, *ipso*-C of PPh_3), 135.0 (d, $^2J_{CP} = 11.3$, *o*-CH of PPh_3), 135.5 (*ipso*-C of Ph), 136.0 [PdC(1) arom.], 139.4 [d, $^3J_{CP} = 12.1$, CH(6) arom.], 151.0 [C(2) arom.], 171.6 (OCN); ^{31}P–{^{1}H} NMR (δ, ppm): 33.52. Anal. Calc. for $C_{35}H_{31}ClNOPPd$: C, 64.23; H, 4.77; N, 2.14. Found: C, 64.17; H, 4.88; N, 2.13%.

6.16. X-ray structure determinations for **6** and **14**

X-ray quality crystals of **6** and **14** were obtained from benzene-petroleum ether and benzene-pentane, respectively. A crystal (approximate dimensions $0.15 \times 0.05 \times 0.02$ mm^3 for **6** and $0.50 \times 0.05 \times 0.05$ mm^3 for **14**) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for data collection at 173(2) K [91]. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 30 and 27 reflections, respectively. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 60 s and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30° steps in ω at four different ϕ settings and a detector position of −28° in 2θ. The intensity data were corrected for absorption and decay (SADABS) [92]. Final cell constants were calculated from 2154 and 2552 strong reflections, respectively, from the actual data collection after integration (SAINT) [93].

The structures were solved and refined using Bruker SHELXTL [94]. The space groups $C2$ and $P2_12_12_1$ were determined for **6** and **14**, respectively, based on systematic absences and intensity statistics. A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0409$ and 0.0287 and $wR_2 = 0.1055$ and 0.0641 (F^2, all data), respectively.

7. Supplementary material

CCDC 651903 and 651904 contain the supplementary crystallographic data for **6** and **14**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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