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Chiral bis(oxazoline) ligands. Synthesis of mono- and bi-metallic complexes of nickel and palladium

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The co-ordination behaviour of the chiral bis(oxazoline) ligands *ortho*-, *meta*-, and *para*-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene (**A**, **B**, **C**, respectively) has been studied. Palladium and nickel complexes were synthesized and characterized in solution and in the solid state. With regard to *N*,*N*′ co-ordination, **A** gave bidentate monometallic species, while **B** and **C** gave bimetallic compounds, with one or two bridging chiral molecules between two palladium atoms. Complexes with the C_2-symmetrical ligand **A** showed a loss of symmetry both in solution and in the solid state, due to the phenyl spacer group between the two oxazoline moieties in the seven-membered ring. The crystal structure of a monometallic complex has been determined. Palladation with these ligands was also tested. Ligand **A** did not give metallated species, but **B** and **C** gave mono- and bis-cyclopalladated compounds, respectively.

Introduction

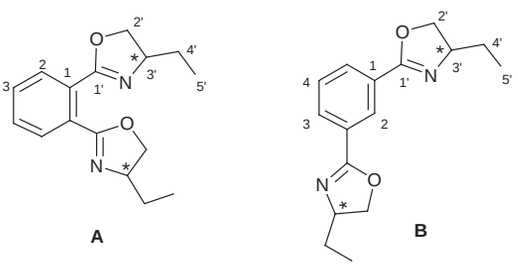
In last decade bis(oxazolines) have found efficient applications in several asymmetric organic processes:[1] Diels–Alder reactions catalysed by different metals (Mn, Fe, Co, Ni, Cu, Zn);[2] allylic substitution (Pd);[3] hydrosilylation of ketones (Rh);[4] cyclopropanation of olefins (Cu);[5] *etc.*

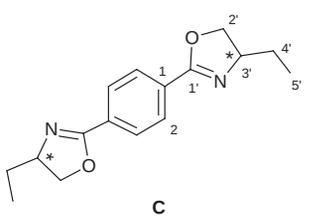
The increasing knowledge about metallic precursors has enabled modifications of nitrogen ligands in order to achieve better activity and selectivity in asymmetric organic reactions. For some processes, precursors and intermediate catalytic species have been isolated. For example, several studies (NMR spectroscopy and X-ray diffraction) of ionic allylic palladium complexes with *N*,*N*′-chelate ligands (precursors and intermediate species in allylic substitutions) have been done,[6] and diaryloxycarbonylruthenium complexes (active species in cyclopropanation reactions) have been characterized.[7] However, for transformations such as copper-catalysed cyclopropanations of olefins, the precursors and intermediates for the catalytic cycles are only suggested by indirect evidence. The postulated active species are carbene complexes, but, to date, these compounds have not been isolated, due to their easy decomposition.[8]

In addition, theoretical and computational studies have been used to obtain more information about organic processes and precursors in order to correlate experimental data with calculated parameters.[9]

In general, the proposed interaction between the metal and bis(oxazoline) ligand is chelation, giving monometallic *N*,*N*′-bound metal precursors. However, for pybox ligands [pybox = 2,6-bis(3,4-dihydrooxazol-2-yl)pyridine],[10] the ligand is three-co-ordinated to the metal by pyridine and oxazoline nitrogen atoms, and for aryl bis(oxazolines) the ligand may be co-ordinated by carbon and nitrogen oxazoline atoms, as in the terdentate palladium complex described recently.[11]

In this paper we describe the synthesis and characterization of complexes of Ni^{II} and Pd^{II} with chiral bis(oxazoline) ligands. We studied the *N*,*N*′-co-ordination behaviour of these ligands, depending on the relative position of the oxazoline moieties on the phenyl group. Therefore, we obtained mono- (for **A**) and bi-metallic (for **B** and **C**) species. The activation of the C_{aryl}–H bond was also investigated. In spite of the electron-withdrawing oxazoline substituents, ligands **B** and **C** afforded cyclometallated compounds.





Results and discussion

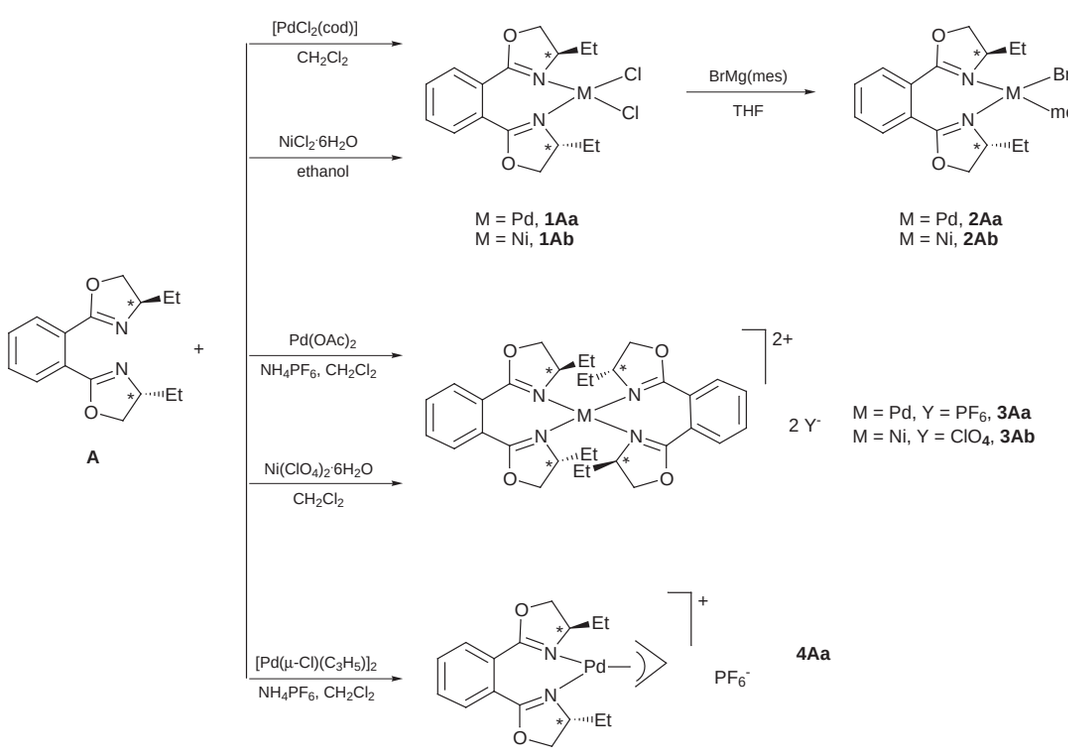
Synthesis of bis(oxazoline) ligands

Ligands **A**, **B** and **C** [(*R*,*R*)-1,2-$(EtOx)_2C_6H_4$, (*R*,*R*)-1,3-$(EtOx)_2C_6H_4$, and (*R*,*R*)-1,4-$(EtOx)_2C_6H_4$, respectively] were prepared following standard methods with minor modifications (see Experimental section).[12] Reactions between *ortho*-, *meta*-, and *para*-bis(cyano)benzene and L-(-)-2-aminobutanol, in the presence of a catalytic amount of zinc chloride, produced good yields of bis(oxazolines). The optical purity was analysed by gas chromatography (β cyclodex chiral column). For ligands **B** and **C** only one isomer was obtained, but for **A** a mixture of *RR* (80%) and *RS* (20%) isomers was isolated. This diastereomeric mixture was treated with nickel perchlorate in ethanol, yielding an orange solid. This compound was recrystallized from acetonitrile as orange crystals. From these crystals the isomer *RS*

Table 1 Selected ^{1}H NMR data[a] (δ, 500 MHz, $CDCl_3$, 298 K) for complexes containing ligand **A**

Complex	5′	4′	3′	2′	Mesitylene[b]
1Aa	1.032 (t, 7.5)	1.83 (dq, 8.5; 7.5)	4.16 (m)	4.28 (m)	—
	1.080 (t, 7.5)	1.98 (dq, 8.5; 7.5)	4.77 (m)	4.30 (m)	—
		2.21 (dm, 7.5; 4.0)		4.68 (dd, 9.5; 9.0)	—
		2.62 (dm, 7.5; 4.0)		4.73 (dd, 10.0; 8.5)	—
rac-**1Aa**[c]	1.037 (t, 7.5)	1.72 (dq, 7.5; 4.0)	4.83 (m)	4.29 (t, 7.5)	—
		2.72 (dm, 7.5; 4.0)		4.73 (dd, 10.0; 9.0)	—
major-**2Aa**	0.89 (t, 7.5)	1.63 (m, 2 H)	3.50 (m)	4.15 (t, 8.5)	*o*-Me: 2.15; 2.28
	1.09 (t, 7.5)	2.40 (m, 1 H)	4.84 (m)	4.21 (dd, 8.5; 5.5)	*p*-Me: 2.89
	2.60 (m, 1 H)		4.30 (t, 9.0)	4.61 (dd, 10; 8.5)	Aromatic: 6.40; 6.56
minor-**2Aa**	0.44 (t, 7.5)	0.73 (m)	3.48 (m)	4.26 (t, 9.0)	*o*-Me: 2.12; 2.23
	1.13 (t, 7.5)	1.78 (m)	4.89 (m)	4.37 (t, 8.5)	*p*-Me: 2.86
		2.05 (m)		4.58 (dd, 10.0; 8.5)	Aromatic: 6.36; 6.43
		2.52 (m)		n.d.	
major-**2Ab**	0.88 (t, 7.5)	1.76 (m, 2 H)	4.80 (m, 2 H)	4.45 (m, 4 H)	*o*-Me: 2.10; 2.88
	1.07 (t, 7.5)	2.24 (m)			*p*-Me: 3.46
		3.14 (m)			Aromatic: 6.25; 6.42
minor-**2Ab**	1.19 (t, 7.5)	0.40 (m)	4.92 (m, 2 H)	4.05 (m, 2 H)	*o*-Me: 2.08; 2.81
	0.38 (t, 7.5)	1.62 (m)		4.20 (m, 2 H)	*p*-Me: 3.52
		1.96 (m)			Aromatic: 6.20; 6.34
		3.25 (m)			
3Aa	1.05 (t, 7.5)	1.74 (m)	4.30 (m)	4.52 (dd, 8.5; 7.5)	—
	0.96 (t, 7.5)	1.82 (m)	4.33 (m)	4.58 (dd, 8.5; 7.5)	—
		1.88 (m)		5.10 (m, 4 H)	—
		2.00 (m)			

[a] Multiplicity (d, doublet; t, triplet; m, multiplet) and coupling constants (in Hz) in parentheses. [b] Multiplicity for mesitylene protons was singlet. [c] All signals observed were of complex **1Aa** plus *rac*-**1Aa**



Scheme 1

was recovered by deco-ordination (treatment with potassium cyanide in ethanol, see Experimental section). Analogously, from the solution, the isomer *RR* was isolated.

N,*N*′-Co-ordination chemistry of bis(oxazoline) ligands

With regard to *N*-donor behaviour, ligands **A**, **B**, and **C** differed in the kind of metallic species that they could stabilize. Ligand **A** gave monometallic complexes in which it is bidentate, whereas **B** and **C** gave bimetallic compounds, in which they are bridging.

For **A**, neutral palladium and nickel complexes (**1Aa**, **1Ab**) were synthesized by substitution of labile ligands, followed by treatment with Grignard compound (**2Aa**, **2Ab**), see Scheme 1. The nickel complex **1Ab** was paramagnetic; the magnetic susceptibility value (3.17 μB) at room temperature is consistent with two unpaired electrons, corresponding to a d^8 electronic configuration in a tetrahedral environment. Other neutral complexes were diamagnetic and their ^{1}H NMR spectra were studied (see Table 1).

The ^{1}H NMR spectra for complex **1Aa** at variable temperatures (313–233 K) showed that the two oxazoline fragments were non-equivalent in the whole range (see Table 1). For the C_2-symmetrical ligand **A** the existence of isomers could be due to the axial chirality. Upon co-ordination, rotation around single bonds (C_{aryl}–$C_{oxazoline}$) is restricted by bonding to the two

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

Pd–N(1)	2.010(5)	N(1)–C(1)	1.469(7)
Pd–N(2)	2.006(5)	N(1)–C(5)	1.277(7)
Pd–Cl(1)	2.297(2)	N(2)–C(14)	1.506(8)
Pd–Cl(2)	2.289(2)	N(2)–C(12)	1.272(7)
N(1)–Pd–N(2)	85.8(2)	N(2)–Pd–Cl(2)	94.02(14)
N(1)–Pd–Cl(1)	88.94(2)	N(2)–Pd–Cl(1)	174.66(13)
N(1)–Pd–Cl(2)	179.2(2)		

nitrogen atoms. So, an efficient bidentate co-ordination towards a single metal atom in the *aRaR* or *aSaS* isomers is not possible due to the highly strained ring (*aR* or *aS* means the configuration of the chiral axis according to the Cahn–Ingold-Prelog rules[13]). Therefore, only the *aRaS* isomer can stabilize the non-planar seven-membered ring (see Chart 1, id refers to equivalent ethyl groups). Thus, the C_2-symmetry loss is due to the bridged phenyl between two oxazoline moieties. The X-ray diffraction determination of **1Aa** (see Fig. 1) showed that the C_2 axis did not exist in the solid state, and showed two non-equivalent oxazoline moieties and therefore, two non-equivalent chloro positions. This behaviour contrasts with other C_2-symmetrical bidentate ligands {like CHIRAPHOS [(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane] or Pfaltz bis-oxazolines} that co-ordinate to the metal center in a C_2-symmetrical fashion in solution, although they may show asymmetrical distortions in the solid state.[15] Complex **1Aa** showed the expected distorted square-planar co-ordination geometry of the core $PdCl_2N_2$ (see Table 2). The Pd–N distances (2.006–2.010 Å) and the Pd–Cl separations (2.297–2.289 Å) are consistent with reported values for related compounds.[16] The torsion angles between each oxazoline moiety and the phenyl group are 56.4 and 43.1° [N(2)–C(12)–C(11)–C(6) and N(1)–C(5)–C(6)–C(11), respectively]. Although atropoisomers may exist, due to the two chiral axes Pd–N, only one isomer is observed (*aRaS*) in the solid state and in solution, as discussed previously. The phenyl bridge between two oxazoline fragments in the seven-membered ring breaks the C_2 symmetry.

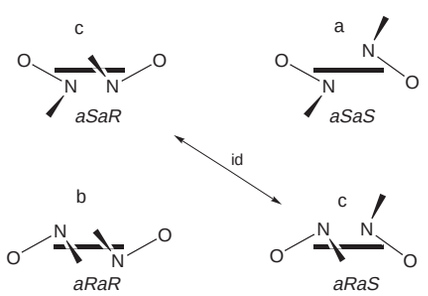


Chart 1

The ^{1}H NMR spectra for complexes **2Aa** and **2Ab** confirmed the non-equivalence of the two co-ordination positions *trans*- to N atoms due to the formation of two isomers, in a relative proportion of 2:1, depending on the halogen position substituted by the organic group. This non-statistical ratio reflects the larger steric hindrance between ethyloxazoline and mesitylene groups in the minor isomer. So, mesitylene exhibited two pairs of singlets in its aromatic region (δ 6–6.6) and two groups of three singlets in its methyl zone of the two different mesitylene groups (δ 2–3). In addition, four oxazoline moieties were distinguished (see Table 1). For **2Aa** the major isomer was separated by recrystallization.

Palladium complexes with *rac*-**A** were also prepared: *rac*-**1Aa** and *rac*-**2Aa**. The spectra of these complexes exhibited the sum of two diastereoisomers: *RaRaSR* (equivalent to *SaRaSS*) and *RaRaSS* (*SaRaSR*). The resonances of the former isomer have been analysed above. In the *meso* form, for *rac*-**1Aa**, both chloro

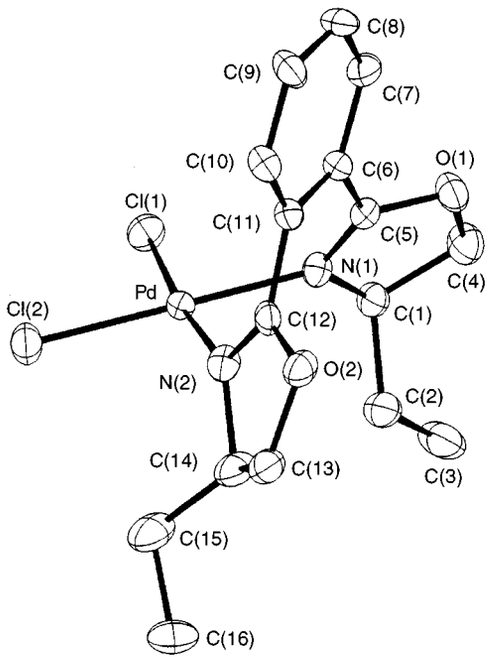


Fig. 1 An ORTEP view of the structure of complex **1Aa** [$PdCl_2$-{(*R*,*R*)-1, 2-$(EtOx)_2C_6H_4$}] showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity.

co-ordination positions are equivalent, with only one type of oxazoline group (see Table 1).

Ionic nickel and palladium complexes were also synthesized from metallic salts (**3Aa** and **3Ab**) and from neutral dimeric species [{Pd(η^3-C_3H_5)(μ-Cl)}$_2$] (**4Aa**). Palladium ionic complexes with bidentate ligands of formula $[Pd(N–N)_2]Y_2$ (where N–N is phenanthroline or bipyridine derivative ligands) have been known for a long time,[17] due to their application in catalytic processes. Van Leeuwen and co-workers[18] have recently described another synthetic route from $[PdCl_2(C_6H_5CN)_2]$ in two reaction steps, isolating neutral monosubstituted [$PdCl_2$-(N–N)] compounds as intermediates. In our study, a high yield of $[Pd(\mathbf{A})_2][PF_6]_2$ was obtained in one reaction step, starting from palladium acetate and ammonium hexafluorophosphate. During the course of this study, Milani *et al.*[19] have also published a one-pot synthesis method for preparing this kind of ionic complex, using protonated bipyridine and phenanthroline ligands.

The ^{1}H NMR study of these complexes showed that the nickel complex **3Ab** was very labile in solution. The ligand was substituted by the solvent, either in co-ordinating (acetone, acetonitrile) or non-co-ordinating solvents (chloroform, dichloromethane) even at a low temperature. At variable temperatures (223–298 K), in deuteriated chloroform solution, the 'free' ligand spectrum was observed over the whole range. However, the analogous palladium complex, **3Aa**, was less labile, exhibiting only partial deco-ordination, of **A** after 24 h in chloroform or dichloromethane solutions. This complex is expected to be a mixture of two isomers, *syn* and *anti*, depending on the position of the bridge phenyl relative to the co-ordination sphere. However, the *syn* complex is less stable due to steric interactions, as shown by molecular mechanics calculations. The ^{1}H NMR spectrum showed one isomer, with two inequivalent oxazoline moieties (see Table 1).

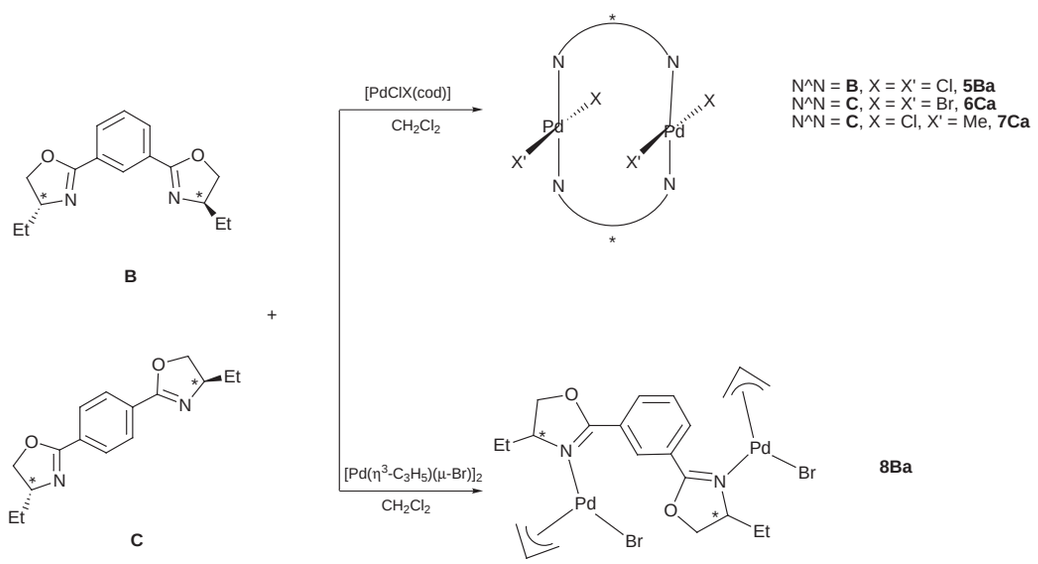
The ^{1}H NMR spectra for the allylic palladium complex **4Aa** showed a dynamic behaviour and broad signals were observed in the temperature range studied (223–323 K).

For ligands **B** and **C**, bimetallic species with one and two bridging ligands were prepared (see Scheme 2). The reaction between **B** or **C** and starting palladium complexes [PdCl-(X)(cod)], where X = chloride or methyl group, afforded bis-

Table 3 Selected ^{1}H NMR data[a] (δ, 500 MHz, $CDCl_3$, 298 K) for complexes with ligands **B** and **C**

Complex	5′	4′	3′	2′	Other
5Ba	1.15 (m)	1.55 (m) 1.75 (m)	[b]	4.35 (m)	aromatic: 7.45 to 9.91 (m)
8Ba[c]	0.93 (t, 7.5) 0.95 (t, 7.5)	1.60 (m) 1.80 (m) 2.05 (m) 2.15 (m)	4.50 (m)	4.10 (m) 4.70 (m)	allyl: $H_{central}$ 5.40 (h); H_{anti} 2.73, 2.83, 2.95, 2.99 (d, 12); H_{syn} 4.30 (m), 3.60, 4.0 (d, 6)
9Ba	1.31 (t, 7.5) 1.32 (t, 7.2) 1.91 (t, 7.7) 1.95 (t, 6.5)	2.42 (m) 3.38 (m) 3.94 (m)	4.43 (m)	4.49 (m) 4.50 (m) 4.7 (m) 4.82 (m)	aromatic: 8.01 (pdd, 7.7, 1.7) 7.53 (m)
10Ba	0.99 (m)	1.50 (m)	4.65 (m)	4.63 (m)	aromatic: 6.9–7.7 (m)
6Ca	0.88 (t); 0.91 (t); 1.13 (t); 1.14 (t) (7.5)	1.30; 1.44; 2.10; 2.96 (m)	4.60 (m)	4.21; 4.28; 4.65; 4.70 (m)	aromatic: 7.50; 7.68 (m); 9.2–9.0 (m)
7Ca	1.01 (t, 7.7)	1.27 (m) 2.60 (m)	4.60 (m)	4.14 (m) 4.57 (m)	aromatic: 8.71–9.25
11Ca	1.15 (t, 7) 1.16 (t, 6)	2.15 (m) 2.95 (m)	4.57 (m) 4.69 (m)	4.30 (pt, 8.4) 4.67 (pt, 8.6)	aromatic: 8.89–9.22
12Ca	1.17 (t, 7.5)	2.16 (m) 2.98 (m)	4.60 (m)	4.32 (t, 7.9) 4.70 (dd, 7.9, 9.8)	aromatic: 9.01 (s) 7.71 (m) 7.42 (m) $\delta(^{31}P)$ 29.6

[a] Multiplicity (d, doublet; h, heptuplet; p. pseudo; t, triplet; m, multiplet) and coupling constants (in Hz) in parentheses. [b] Overlapped signal. [c] Measured at 223 K.



Scheme 2

(oxazoline)bispalladium compounds (**5Ba**, **6Ca** and **7Ca**). The complexes were characterized by NMR spectroscopy (see Table 3). The ^{1}H NMR spectrum for **6Ca** showed eight signals of the same intensity in the aromatic region, showing the non-equivalence of the two bridging ligands.

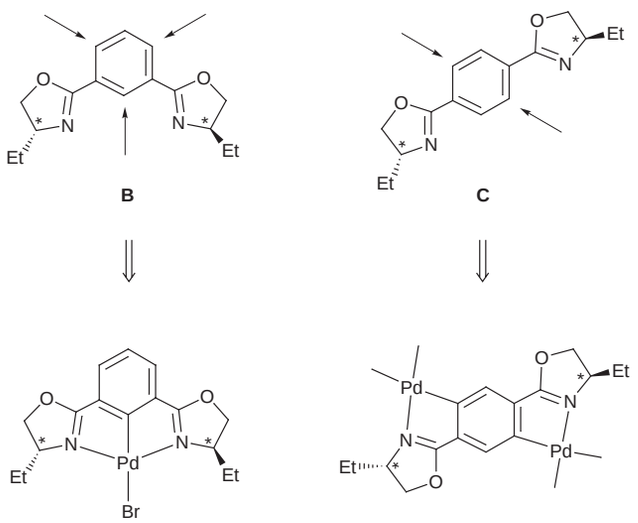
Starting from the allylic palladium complex [{$PdBr(\eta^3$-$C_3H_5)$-(μ-Br)}$_2$] a bimetallic compound with **B** was also obtained, but with only one bridging ligand, **8Ba**, even with an excess of ligand. Proton NMR studies were carried out at different temperatures (323–223 K). For the allyl group, $H_{central}$ exhibited one signal at δ 5.5 in the whole temperature range, with a narrow pseudo heptuplet at 323 K. Above room temperature, H_{anti} and H_{syn} of the allyl system showed one broad signal each (δ 3.0 and 4.0, respectively). At room temperature, H_{syn} split into two broad signals and at 273 K both protons showed two broad signals, being sharper and more defined at 223 K: H_{anti} showed four doublets at δ 2.80 (12 Hz) and H_{syn} showed two doublets and a multiplet at δ 3.80 (6.0 Hz) and 4.40, respectively. Coalescence between H_{anti} and H_{syn} was not observed in the range of temperatures studied. Therefore, allylic rotation around the Pd–π–allyl group was slow enough on the NMR timescale for distinguishing allylic protons. At 223 K two allyl groups are differentiated, with two non-equivalent *anti* and *syn* protons for each. The aromatic zone was more complicated, with different configurations at low temperatures due to the slow rotation, on the NMR timescale, around single C_{aryl}–$C_{oxazoline}$ bonds. Any contribution of the π–σ–π allyl movement was not detected.

Palladation chemistry of bis(oxazoline) ligands

It is well known that the cyclopalladation reaction proceeds by an electrophilic attack by the metal on the aryl group,[20] this being favoured when electron donating ligands are bonded, in *ortho* and *para* positions, to the metallated carbon. However, in the literature, there are several examples of the activation of C–H with electron-withdrawing substituents.[21] Also, for the oxazoline group, which is a strong electron-withdrawing substituent, cyclometallated compounds have been described with one oxazoline moiety on the aromatic system.[22] However, metallation may be less favoured with two oxazoline substituents on the phenyl group. Moreover, steric factors may be very important, impeding the process if the substituent *ortho* to the metallation is not co-ordinating. For **B** and **C** the positions to be activated are indicated by an arrow in Scheme 3.

For **B**, two different cases are possible: mono- and bis-metallation, depending on the activated C_{aryl}–H bond. If position 3 were activated, bis-cyclometallated compounds would be isolated. Meanwhile, if activation was in position 2, monopalladation would be observed. When 1 equivalent of **B** reacted with 2 equivalents of Na_2PdCl_4 only co-ordination products were obtained. However, when 1 equivalent of **B** reacted with 1 equivalent of $Pd(O_2CMe)_2$ a monopalladated product was isolated (**9Ba**), after refluxing for three days (see Scheme 4). The ^{1}H NMR spectrum for **9Ba** exhibited the loss of the aromatic proton between the two oxazoline moieties. In addition, two sets of signals for oxazoline protons were observed, showing a non-symmetrical structure in solution. This behaviour showed that the formation of a terdentate compound is favoured, although the activated position is *ortho* to two electron-withdrawing groups. These results are consistent with the formation of a terdentate complex with a *meta*-bis(oxazoline) ligand, by an oxidative addition reaction.[11]

For **C**, a symmetrical bis-metallated compound was isolated (**11Ca**) by reaction with Na_2PdCl_4 (see Scheme 4). When **9Ba** and **11Ca** were treated with triphenylphosphine, mono- (**10Ba**) and bi-metallic (**12Ca**) complexes were obtained, respectively.



Scheme 3

The ^{1}H NMR spectrum for **12Ca** showed a symmetrical compound, with one resonance for the aromatic protons of the oxazoline groups (singlet at δ 9.00) and only one kind of oxazoline protons (see Table 3). The ratio between oxazoline and phosphine signals is in agreement with one oxazoline group per triphenylphosphine ligand.

For **A** no metallation was observed with Na_2PdCl_4 or $Pd(O_2CMe)_2$. In both cases, only co-ordination products were isolated.

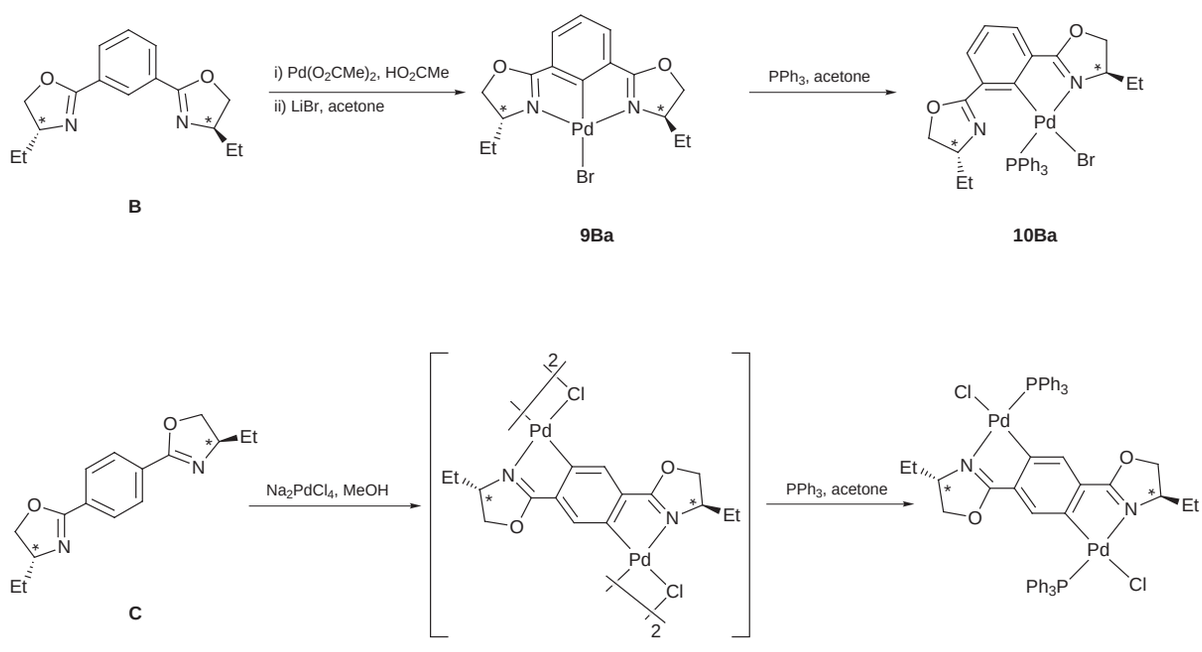
Conclusion

A series of bis-oxazolines, based on the relative position of the two oxazoline moieties on the phenyl group, allowed a study of *N*,*N*′-co-ordination behaviour, as well as a study of C_{aryl}–H bond activation. The proximity of two nitrogen atoms when the *ortho*-bis(oxazoline), **A**, interacts with a metal center facilitates chelate co-ordination, while for *meta*- and *para*-bis(oxazoline) ligands, **B** and **C**, only bridging co-ordination is observed. The most interesting structural feature for **A** is the loss of C_2 symmetry when it is co-ordinated in an *N*,*N*′-bidentate way. Therefore, for complexes with **A**, two *trans* positions to nitrogen atoms are non-equivalent, both in the solid state and in solution, and isomers can be distinguished in halogen substitution processes, as in the formation of **2Aa** and **2Ab**. This co-ordination behaviour explains the low asymmetric induction observed with *ortho*-bis(oxazolinyl)aryl ligands in organic transformations, such as Cu-catalysed cyclopropanations[5] or Pd-catalysed allylic substitutions.[3] In the latter case the nucleophile has different, but similar energetic positions to attack on the substrate and hence more accessible transition states, and thus low enantiomeric excesses are obtained. In addition, cyclopalladation processes enable metallacycles to be obtained with **B** and **C**. Ligand **C** stabilizes bis-metallated compounds by two C_{aryl}–H bond activations on the phenyl group, while for **B** a terdentate complex is obtained due to selective activation of the C_{aryl}–H bond between two oxazoline substituents.

Experimental

General

All compounds were prepared under a purified nitrogen atmos-



Scheme 4

phere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures[24] and distilled under nitrogen. L-(-)-2-Aminobutanol (Janssen) was used without previous purification, $ZnCl_2$ (Merck) was purified by the standard procedure[24] and [{PdCl(η³-C_3H_5)(μ-Cl)}$_2$],[25] [$PdCl_2$(cod)],[26] and [PdCl(Me)(cod)][27] were prepared as described previously. The NMR spectra were recorded on Varian XL-500 (^{1}H, standard $SiMe_4$), Gemini (^{13}C, 50 MHz, standard $SiMe_4$), and Bruker DRX 250 (^{31}P, 101 MHz, standard H_3PO_4) spectrometers. Chemical shifts are reported downfield from standards. The IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. The FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. The GC analysis, for chiral ligands, was performed on a Hewlett-Packard 5890 Series II gas chromatograph [25 m FS-cyclodex-β-I/P column: heptakis-(2,3,6-tri-*O*-methyl)-β-cyclodextrin–polysiloxane] with a flame ionization detector. The GC-MS analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column) interfaced to a Hewlett-Packard 5971 mass selective detector. Magnetic measurements were carried out at variable temperature (300–4 K) on polycrystalline samples with a pendulum type magnetometer (Manics DSM8) equipped with a Drusch EAF 16 UE electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's tables. Optical rotations were measured on a Perkin-Elmer 241 MC spectropolarimeter. Conductivities were obtained on a Radiometer CDM3 conductimeter. Elemental analyses were carried out by the Serveis Cientifico-Tècnics de la Universitat de Barcelona in an Eager 1108 microanalyzer. The molecular mechanics calculations were performed using the Spartan program, version 5.0 (Wavefunction Inc., Irvine, CA, USA, 1997).

Syntheses

1,*x*-Bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene ligands: A (*x* = 2), B (*x* = 3), and C (*x* = 4). The oxazolines **A**, **B** and **C** were synthesized following published procedures with minor modifications.[12,28] L-(-)-2-Aminobutanol (6.63 g, 74.40 mmol), 1,*x*-bis(cyano)benzene (*x* = 2, 3 or 4; 2.5 g, 19.50 mmol), and $ZnCl_2$ (180 mg, 1.32 mmol) were dissolved in 25 cm^3 of toluene and refluxed under nitrogen for some hours (24 h, for **A**; 96 h, for **B**; 72 h, for **C**), until no nitrile was observed (reaction monitored by gas chromatography). The reaction mixture was filtered, washed with water, and the organic phase dried over anhydrous Na_2SO_4 and distilled under vacuum, affording a yellow oil. The product was purified by SiO_2 column chromatography (ethyl acetate–hexane, 2:1 for **A** and **B**, 4:1 for **C**). For **A**, a mixture of diastereoisomers was obtained, *RR* (80%) and *RS* (20%). Yields: **A** 4.47 g, 84%; **B** 2.23 g, 50%; **C** 3.73 g, 70%. $[\alpha]_D^{25}$ = +100 (**A**); +135.44 (**B**); +120.05 deg cm^3 g^{-1} dm^{-1} (**C**) (*c* 0.1 g per 100 cm^3, $CHCl_3$). ^{1}H NMR data ($CDCl_3$, 500 MHz): **A**, *δ* 0.99 (H**5′**, 3 H, t, *J* 7.2); 1.62 (H**4′**, 1 H, m); 1.73 (H**4′**, 1 H, m); 4.20 (H**3′**, 1 H, m); 3.98 (H**2′**, 1 H, t, *J* 8.0); 4.42 (H**2′**, 1 H, dd, *J* 9.0, 8.0 Hz); 7.73 (H**2**, 1 H, m); 7.44 (H**3**, 1 H, m); **B**, *δ* 0.98 (H**5′**, 6 H, t, *J* 7.2); 1.59 (H**4′**, 2 H, m); 1.74 (H**4′**, 2 H, m); 4.23 (H**3′**, 2 H, m); 4.04 (H**2′**, 2 H, t, *J* 8.0); 4.46 (H**2′**, 2 H, dd, 9.0, *J* 8.0); 8.47 (H**2**, 1 H, t, *J* 1.5 Hz); 8.04 (H**3**, 2 H, dd, 8.0, *J* 1.5); 7.42 (H**4**, 1 H, t, *J* 8.0 Hz); **C**, *δ* 0.96 (H**5′**, 3 H, t, *J* 7.2); 1.59 (H**4′**, 1 H, m); 1.75 (H**4′**, 1 H, m); 4.20 (H**3′**, 1 H, m); 4.03 (H**2′**, 1 H, t, *J* 8.0); 4.46 (H**2′**, 1 H, dd, 9.0, *J* 8.0 Hz); 7.95 (H**2**, 2 H, s). ^{13}C NMR data ($CDCl_3$, 50 MHz): **A**, *δ* 9.1 (C**5′**); 27.4 (C**4′**); 67.3 (C**3′**); 71.6 (C**2′**); 127.5 (C**1**); 128.8, 128.4 (C**2**); 129.3 (C**3**), 162.7 (C**1′**); **B**, *δ* 9.9 (C**5′**); 28.6 (C**4′**); 68.0 (C**3′**); 72.2 (C**2′**); 128.2 (C**1**); 128.1, 128.4 (C**2**, C**5**); 130.8 (C**4**), 162.8 (C**1′**); **C**, *δ* 10.0 (C**5′**); 28.6 (C**4′**); 68.1 (C**3′**); 72.3 (C**2′**); 130.3 (C**1**); 128.1 (C**2**); 162.9 (C**1′**).

{1,2-Bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}-dichloropalladium(II) 1Aa. The compound [$PdCl_2$(cod)] (1.57, 5.50 mmol) and **A** (1.50 g, 5.50 mmol) were dissolved in 30 cm^3 of dichloromethane at room temperature and stirred for 8 h (the reaction was monitored by TLC until no free **A** was observed). The reaction mixture was filtered over Celite, concentrated to *ca*. 15 cm^3 under reduced pressure and hexane added. A yellow solid separated, which was recrystallized from dichloromethane and diethyl ether (1.94 g, 78%), mp (decomp.) = 130 °C. (Found: C, 42.53; H, 4.66; N, 6.22. Calc. for $C_{16}H_{20}Cl_2N_2O_2Pd$: C, 42.74; H, 4.48; N, 6.23%). MS (FAB positive): *m*/*z* 415 (M − Cl), 377 (M − 2 Cl), 272 (**A**).

{1,2-Bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}-dichloronickel(II) 1Ab. The compound $NiCl_2$·$6H_2O$ (1.31 g, 5.50 mmol) and **A** (1.50 g, 5.5 mmol) were dissolved in 30 cm^3 of absolute ethanol. The reaction mixture was warmed to 60 °C for 24 h (the reaction was monitored by TLC until no free **A** was observed), filtered, concentrated to *ca*. 15 cm^3 under reduced pressure, and hexane added. A blue solid was obtained after cooling the solution in a refrigerator overnight. The product was separated by filtration, washed with diethyl ether and dried under reduced pressure (1.16 g, 54%), mp (decomp) = 70 °C (Found: C, 47.31; H, 5.33; N, 7.08. Calc. for $C_{16}H_{20}Cl_2N_2NiO_2$: C, 47.81; H, 5.02; N, 6.97%). MS (FAB positive): *m*/*z* 366 (M − Cl), 330 (M − 2 Cl), 272 (**A**).

{1,2-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}-bromo(2,4,6-trimethylphenyl)metal(II), 2Aa (M = Pd) and 2Ab (M = Ni). A THF solution 16 cm^3 (3.8 mmol) of the Grignard compound, BrMg(Mes) (Mes = mesityl),† was added slowly over a solution of the dichloro derivative (**1Aa** 0.85 g, 1.9 mmols; **1Ab**, 0.5 g, 1.24 mmol) in 25 cm^3 of THF. The reaction mixture was stirred for 30 min at room temperature. Excess of Grignard compound was eliminated by hydrolysis with distilled water. The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated to *ca*. 15 cm^3 under reduced pressure, and hexane added. A white solid was obtained after cooling the solution in a refrigerator overnight. The product was separated by filtration, washed with diethyl ether and dried under reduced pressure (**2Aa**, 0.72 g, 66%; **2Ab**, 0.66 g, 65%). For **2Aa**: mp (decomp) = 133 °C (Found: C, 56.17; H, 5.92; N, 4.83. Calc. for $C_{25}H_{31}BrN_2O_2Pd$: C, 51.97; H, 5.41; N, 4.85%). MS (FAB positive) *m*/*z* 495 (M − Br), 377 (M − Br − Mes), 272 (**A**). For **2Ab**: mp (decomp) = 160 °C (Found: C, 56.34; H, 6.02; N, 5.66. Calc. for $C_{25}H_{31}BrN_2NiO_2$: C, 56.64; H, 5.89; N, 5.29%). MS (FAB positive) *m*/*z* 447 (M − Br), 330 (M − Br − Mes), 272 (**A**).

Bis{1,2-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}palladium(II) hexafluorophosphate 3Aa. To a solution of $Pd(O_2CMe)_2$ (0.50 g, 2.23 mmol) in 25 cm^3 of CH_2Cl_2 was added NH_4PF_6 (1.0 g, 4.46 mmol). Then, the ligand **A** (1.20 g, 4.41 mmol) was added and the reaction mixture stirred at room temperature for 24 h, yielding a white solid. The product was filtered off and washed with distilled water several times until ammonium salts were removed. The solid was then washed with diethyl ether and dried under reduced pressure (1.80 g, 86%), mp (decomp.) = 281 °C. (Found: C, 40.50; H, 4.13; N, 6.00. Calc. for $C_{32}H_{40}F_6N_4O_4PPd$: C, 40.84; H, 4.28; N, 5.95%). MS (FAB positive) *m*/*z* 795 (M^{2+} + PF_6), 650 (M^{2+}), 377 (M^{2+} − **A**).

Bis{1,2-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}nickel(II) perchlorate 3Ab. The salt $Ni(ClO_4)_2$·*x*H_2O (0.50 g, 1.94 mmol) and **A** (1.06 g, 3.88 mmol) were dissolved in 30 cm^3 of absolute ethanol. The reaction mixture was stirred at room temperature for 30 min, yielding a pale yellow solid. The

† Prepared by reaction of magnesium metal (0.5 g, 20 mmol) with bromomesitylene (1.51 cm^3, 10 mmol) in 20 cm^3 of THF, at 40 °C for 1 h. The reaction was monitored by GC.

product was separated by filtration, washed with diethyl ether and dried under reduced pressure (1.39 g, 89%), mp (decomp.) = 195 °C (Found: C, 47.54; H, 5.26; N, 7.01. Calc. for $C_{32}H_{40}Cl_2N_4NiO_{12}$: C, 47.90; H, 5.03; N, 6.98%). MS (FAB positive) *m*/*z* 602 (M^{2+}), 330 (M^{2+} − **A**).

Deco-ordination of complex 3Ab. To complex **3Ab** (1.0 g, 1.25 mmol) and potassium cyanide (0.52 g, 8 mmol) 20 cm^3 of ethanol were added. The reaction mixture was stirred at room temperature until a colorless solution was obtained. The solvent was then removed under reduced pressure, and 25 cm^3 of dichloromethane was added. The mixture was washed with water until no free cyanide was observed in the aqueous phase. The organic phase was dried over anhydrous Na_2SO_4, filtered off, and the solvent removed under reduced pressure, affording a white oil.

(η³-Allyl){1,2-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]-benzene-*N*,*N*′}palladium(II) hexafluorophosphate 4Aa. To a solution of di-μ-chloro-bis[(η³-allyl)palladium] (0.34 g, 0.75 mmol) in 20 cm^3 of absolute ethanol were added NH_4PF_6 (0.24 g, 1.5 mmol) and **A** (0.41 g, 1.5 mmol). The reaction mixture was stirred at room temperature for 3 h (the reaction was monitored by TLC until no free **A** was observed), then concentrated to *ca*. 10 cm^3 under reduced pressure and hexane added, producing a white solid. The product was filtered off, washed with diethyl ether and dried under reduced pressure (0.28 g, 76%), mp (decomp.) = 140 °C (Found: C, 40.51; H, 4.62; N, 5.15. Calc. for $C_{19}H_{25}F_6N_2O_2PPd$: C, 40.41; H, 4.46; N, 4.96%). MS (FAB positive) *m*/*z* 421 (M^+), 650 (M^{2+}), 377 (M^+ − **A**), 272 (**A**).

Bis{μ-1,3-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}tetrachlorodipalladium(II) 5Ba. The complex [$PdCl_2$(cod)] (0.40 g, 1.40 mmol) and **B** (0.38 g, 1.40 mmol) were dissolved in 30 cm^3 of dichloromethane. The reaction mixture was stirred at room temperature for 5 h (the reaction was monitored by TLC until no free **B** was observed), then concentrated to *ca*. 15 cm^3 under reduced pressure and hexane added. A yellow solid was obtained after cooling the solution in a refrigerator overnight. The product was separated by filtration and recrystallized from dichloromethane and diethyl ether, producing an orange solid (0.30 g, 60%), mp (decomp.) = 200 °C (Found: C, 42.65; H, 4.45; N, 3.23. Calc. for $C_{16}H_{20}Cl_2N_2O_2Pd$: C, 42.70; H, 4.48; N, 3.13%). MS (FAB positive): *m*/*z* 828 (M^+ − 2Cl).

Bis(η³-allyl)-μ-{1,3-bis(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]-benzene-*N*,*N*′}dibromo-dipalladium(II) 8Ba. Di-(μ-bromo)-bis-[(η³-allyl)palladium] (1.36 g, 3.0 mmol) and **B** (0.40 g, 1.50 mmol) were dissolved in 20 cm^3 of CH_2Cl_2. The reaction mixture was stirred under reflux for 3 h (the reaction was monitored by TLC until no free **B** was observed), then concentrated to *ca*. 10 cm^3 under reduced pressure and hexane added. A yellow solid was obtained after cooling the solution in a refrigerator overnight. The product was separated by filtration and recrystallized from dichloromethane and hexane (0.96 g, 93%), mp (decomp.) = 200 °C (Found: C, 35.92; H, 4.21; N, 3.81. Calc. for $C_{11}H_{15}BrNOPd$: C, 36.34; H, 4.16; N, 3.85%). MS (FAB positive): *m*/*z* 645 (M − Br), 564 (M − 2 allyl − Br).

{2,6-Bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]phenyl-*C*,*N*,*N*′}-bromopalladium(II) 9Ba. The compound $Pd(O_2CMe)_2$ (0.23 g, 1.0 mmol) and **B** (0.14 g, 0.50 mmol) were dissolved in 10 cm^3 of chloroform. The reaction mixture was refluxed for 3 d (the reaction was monitored by TLC until no free **B** was observed). Lithium bromide (0.09 g, 1 mmol) was then added and the mixture refluxed for 2 h, filtered over Celite and the solvent removed under reduced pressure. After addition of diethyl ether a yellow solid was obtained, which was recrystallized from dichloromethane and hexane (0.78 g, 45%), mp (decomp.) = 180 °C (Found: C, 41.00: H, 4.10; N, 6.30. Calc. for $C_{16}H_{19}BrN_2O_2Pd$: C, 41.98; H, 4.15; N, 6.12%). MS (FAB positive): *m*/*z* 377 (M − Br).

{2,6-Bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl)]phenyl-*C*,*N*}-bromo(triphenylphosphine)palladium(II) 10Ba. Complex **9Ba** (0.25 g, 0.27 mmol) and triphenylphosphine (0.14 g, 0.54 mmol) were dissolved in 10 cm^3 of dichloromethane. The reaction mixture was refluxed for 3 h (the reaction was monitored by ^{31}P NMR until no free phosphine was observed), then filtered over Celite and the solvent removed under reduced pressure, affording a brown solid. The product was separated by filtration and recrystallized from dichloromethane and hexane (0.09 g, 50%), mp (decomp.) = 165 °C (Found: C, 56.40; H, 4.68; N, 3.96. Calc. for $C_{34}H_{34}BrN_2O_2PPd$: C, 56.72; H, 4.76; N, 3.89%). MS (FAB positive): *m*/*z* 639 (M − Br).

Bis{μ-1,4-bis[(4*R*)-4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}tetrabromodipalladium(II) 6Ca. The compound $Pd(O_2CMe)_2$ (1.23 g, 5.50 mmol) and **C** (1.50 g, 5.50 mmol) were dissolved in 20 cm^3 of chloroform. The reaction mixture was warmed at 40 °C for 24 h (the reaction was monitored by TLC until no free **C** was observed), then filtered over Celite and the solvent removed under reduced pressure, affording a dark brown oil which was dissolved in 10 cm^3 of CH_2Cl_2. Lithium bromide (0.54 g, 6.18 mmol) was then added and the reaction mixture stirred at room temperature for 1 h. The mixture was again filtered over Celite and 10 cm^3 of diethyl ether were added. A brown solid was obtained after cooling the solution in a refrigerator overnight. It was filtered off and recrystallized from dichloromethane and diethyl ether, affording a dark red solid (0.99 g, 50%), mp (decomp.) = 170 °C (Found: C, 35.56; H, 5.18; N, 3.72. Calc. for $C_{16}H_{20}Br_2N_2O_2Pd$: C, 35.65; H, 5.10; N, 3.74%). MS (FAB positive): *m*/*z* 916 (M − 2 Br), 837 (M − 3 Br), 728 (M − 4 Br − C_2H_5).

Bis{μ-1,4-bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2-yl]benzene-*N*,*N*′}dichlorodimethyldipalladium(II) 7Ca. The complex [PdCl(Me)(cod)] (0.10 g, 0.38 mmol) and **C** (0.103 g, 0.38 mmol) were dissolved in 20 cm^3 of dichloromethane. The reaction mixture was stirred at room temperature for 4 h (the reaction was monitored by TLC until no free **C** was observed). The solvent was removed under reduced pressure, and diethyl ether then added. A white solid was obtained after cooling the solution in a refrigerator overnight. The product was separated by filtration and recrystallized from dichloromethane and diethyl ether (0.16 g, 50%), mp (decomp.) = 185 °C (Found: C, 47.48; H, 5.42; N, 6.88. Calc. for $C_{17}H_{23}ClN_2O_2Pd$: C, 47.57; H, 5.40; N, 6.53%). MS (FAB positive): *m*/*z* 828 (M − Cl), 757 (M − 2 Cl − 2 Me).

{2,5-Bis[(4*R*)-(4-ethyl-3,4-dihydrooxazol-2′-yl]phenyl-C,*N*}-dichlorobis(triphenylphosphine)dipalladium(II) 12Ca. The compound $PdCl_2$ (0.18 g, 1.0 mmol) and LiCl (0.085 g, 2 mmol) were dissolved in 10 cm^3 of methanol and 3 cm^3 of water. The mixture was warmed to 40 °C and stirred for 6 h until the palladium chloride dissolved. Ligand **C** (0.14 g, 0.5 mmol) dissolved in 8 cm^3 of methanol was then added. The reaction mixture was refluxed for 1 d. The yellow solid (**11Ca**) obtained was separated by filtration and washed with diethyl ether. This residue (0.30 g) was treated with triphenylphosphine (0.18 g, 0.66 mmol) in 10 cm^3 of chloroform. The reaction mixture was refluxed for 2 h (the reaction was monitored by ^{31}P NMR until no free phosphine was observed). The solvent was removed until *ca*. 5 cm^3 and diethyl ether added. A yellow solid was obtained after cooling the solution in a refrigerator overnight. The product was separated by filtration, washed with diethyl ether and dried under reduced pressure (0.27 g, 60%). The product was purified by column chromatography (SiO_2) with diethyl ether and ethyl acetate (1:1) as an eluent, mp (decomp.) = 215 °C (Found: C, 56.48; H, 4.28; N, 2.35. Calc. for

Table 4 Crystal data for complex **1Aa**

Formula	$C_{16}H_{20}Cl_2N_2O_2Pd$
M	449.64
Crystal dimensions/mm	0.1 × 0.1 × 0.2
T/K	293
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	10.498(4)
b/Å	11.953(9)
c/Å	14.112(2)
V/Å^3	1771(2)
Z	4
D_c/g cm^{-3}	1.687
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0422, 0.0948
(all data)	0.0513, 0.1385
Goodness of fit	1.057

$C_{26}H_{24}ClNOPPd$: C, 57.91; H, 4.48; N, 2.60%). MS (FAB positive): *m*/*z* 1042 (M − Cl), 1007 (M − 2 Cl).

Crystallography

The crystallographic data for complex **1Aa** are summarized in Table 4. Crystals were obtained by slow diffusion of diethyl ether over a dichloromethane solution of the complex.

The crystal data were measured on an Enraf-Nonius CAD4 four circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71069$ Å), using the ω–2θ scan technique. 2626 Reflections were measured in the range $2.23 < \theta < 29.95°$, 2603 of which were non-equivalent by symmetry [R_{int} (on I) = 0.017]. 2404 Reflections were assumed observed [$I > 2\theta(I)$]. Three reflections were measured every 2 h as orientation and intensity controls, and significant intensity decay was not observed. Lorentz-polarization but not absorption corrections were made.

The structure was solved by direct methods, using the SHELXS computer program[28] and was refined by the full-matrix least-squares method with the SHELXL 93 computer program,[29] using 2553 reflections (very negative intensities were ignored). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0610\ P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$ values of f, f' and f'' were taken from ref. 30. The extinction coefficient was 0.0000(8). The chirality of the structure was defined from the Flack coefficient,[31] 0.03(6). Nine H atoms were located by a difference synthesis and refined with an overall isotropic thermal parameter and 10 H atoms were computed and refined with an overall isotropic thermal parameter using a riding model. The final R (on F) factor was 0.042, wR (on $|F|^2$) = 0.095 and goodness of fit = 1.057 for all observed reflections. The number of refined parameters was 234. The maximum and minimum peaks in the final difference synthesis were 0.954 and −0.445 e Å^{-3}, respectively.

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