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Effect of the rigidity and flexibility features of 2-pyridinyl or 8-quinolinyl based N–N* chiral ligands on the stereochemical properties of [Pd(N–N*)Cl_2] complexes

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Abstract

The [Pd(N–N*)Cl_2] complexes have been obtained, as yellow solids, in almost quantitative yields; N–N* indicate bidentate chiral ligands (S_a)-**1**, (S_a)-**2**, (S,S)-**3**, (R,R)-**4**, containing the rigid 2-pyridinyl or 8-quinolinyl building block skeleton and the C_2-symmetric chiral framework *trans*-2,5-dimethylpyrrolidinyl or (S)-(+)-2,2′-(2-azapropane-1,3-diyl)-1,1′-binaphthalene. The ligands pairs have the same C_2-symmetric chiral framework but different building block skeleton, beyond that for the basicity in the N-donor atoms, for rigidity and flexibility features. The N–N* ligands act as chelating ligands leading a square planar geometry. The compounds [Pd(S,S-**3**)Cl_2] and [Pd(R,R-**4**)Cl_2] have been also characterised by X-ray diffraction. The rigidity and flexibility features of (S,S)-**3** and (R,R)-**4** ligands induce a different orientation of the *trans*-2,5-dimethylpyrrolidinyl moiety with respect to the pyridinyl and quinolinyl plane. This work shows that intrinsic rigidity and flexibility are not enough to define the ligand properties and to preview the effects that they induce on the reactivity of the metal complex.

Keywords: Chiral ligands; Palladium(II) complexes; X-ray analysis; Rigidity–flexibility ligand

1. Introduction

The design and synthesis of novel ligands have become an area of increasing interest that could lead to new and efficient transition metal catalysts [1]. Metallorganic chemistry has for a long time matured the fundamental principles of the homogeneous catalysis, broadening therefore its possible applications [2]. In this contest, the features of the coordinated ligand in determining the electronic properties of the metal centre (that it is the active site of the catalytic process), and the energy barrier for the reaction, assume particular importance [3]. However, specific molecular characteristics of the ligands, such as shape, bite angle, flexibility, rigidity, symmetry, frameworks properties must be also considered. The effect of flexibility and rigidity of the chiral coordinated ligands on the transition metal catalyst performance has been widely studied and applied in homogeneous asymmetric catalysis [2]. For example, the role of chiral bidentate ligands with cyclic ring structures, which could be used in asymmetric catalysis to restrict conformational flexibility of the ligand, has been emphasised and it has been assumed that the efficiency of chiral transfer can be enhanced through the ligand rigidity [4]. It is generally accepted that a chiral ligand which can form a rigid ligand–metal complex is essential for effective chiral recognition and that the increase of the ligand rigidity is the key for the development of highly enantioselective reactions [2,4].

The ligand flexibility was correlated to natural bite angle and it is normally defined as the accessible range of bite angles within less than 3 kcal/mol excess strain energy from the calculated natural bite [5]. However the flexibility, as ligand properties descriptor, has been also used in a

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generalised and less rigid way. For example, several studies have tried to correlate the efficiency of Pd(II) catalysts in the copolymerisation of CO and ethene to the high flexibility of chelating diphosphines backbone [6].

Recently [7,8], we synthesised N–N* bidentate chiral ligands starting from the rigid 2-pyridinyl or 8-quinolinyl building block skeleton and the C_2-symmetric chiral framework trans-2,5-dimethylpyrrolidinyl or (S)-(+)-2,2′-(2-azapropane-1,3-diyl)-1,1′-binaphthalene (Fig. 1). Each ligand showed different basicity in the N-donor atoms; the pK_a values for dialkyl substituted azepine and dialkyl substituted pyrrolidine are *ca*. 9 and 10, respectively, whereas the pK_a values for pyridine and quinoline are very close to 5. Moreover, the ligands pairs having the same C_2-symmetric chiral framework but different building block skeleton showed different rigidity and flexibility since a sp^2 or sp^3 carbon atom spacer separate the chelating arms in each ligand. Our studies about the induction of enantioselectivity in palladium catalysed allylic substitution reaction of 1,3-diphenylallyl acetate with dimethylmalonate [7] and about diastereoselectivity and configurational stability at the metal centre in half-sandwich (η^6-*p*-cymene)ruthenium(II) and (η^5-C_5Me_5)rhodium(III) complexes [8] showed that we can not explain the results obtained from these ligands (Fig. 1) only considering their rigidity and flexibility features. We found that the stereochemical arrangement of the chiral frameworks in the coordinated ligand is the factor determining the optical activity of the reported half-sandwich metal complex.

This work reports on the reaction of the chiral ligands hereafter named (S_a)-**1**, (S_a)-**2**, (S,S)-**3**, (R,R)-**4** (Fig. 1) with [Pd(PhCN)$_2$Cl$_2$]. The square-planar geometry of the reaction products and the presence of only two chlorine in *cis* position to coordinated ligand N-donor atoms allowed us to have information about the stereochemical of the coordinated ligands, since no bulky ligands were present in the coordination over and under the coordination plane of the metal centre that could influence their coordination.

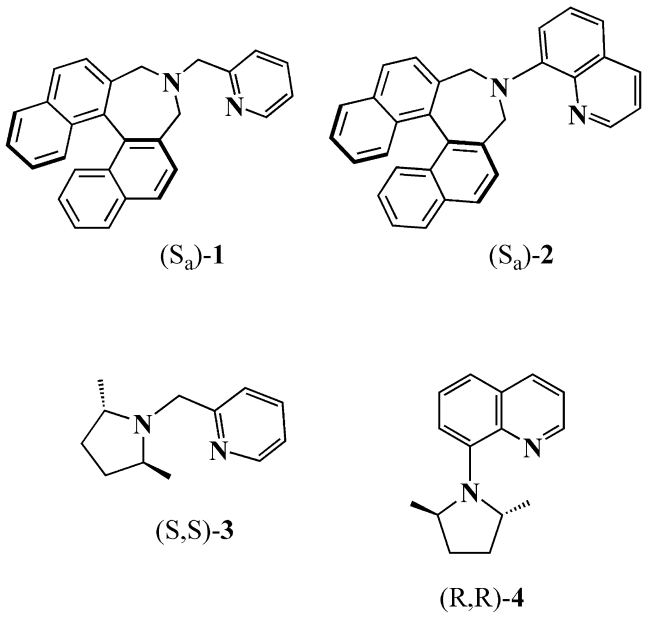

Fig. 1. Used ligands.

2. Results and discussions

2.1. Synthesis of [Pd(N–N*)Cl$_2$] (N–N* = (S_a)-1, (S_a)-2, (S,S)-3, (R,R)-4) complexes

We previously reported the synthesis and characterisation of the ligands (S_a)-**1**, (S_a)-**2**, (S,S)-**3** and (R,R)-**4**. [Pd(N–N*)Cl$_2$] complexes **5-8** (N–N* = (S_a)-**1**, **5**; (S_a)-**2**, **6**; (S,S)-**3**, **7**; (R,R)-**4**, **8**), were synthesised by adding to a CH_2Cl_2 solution of [Pd(benzonitrile)$_2$Cl$_2$] the ligand N–N*, in the same solvent, in the 1:1.2 complex:ligand ratio. After about 3 h at room temperature, the work-up gave the products [Pd(N–N*)Cl$_2$], in almost quantitative yields, as yellow solids. The use of (R,R)-**4** instead of (S,S)-**4** allowed us to obtain crystals suitable for X-ray diffraction analysis as palladium complex. Compounds **5**–**8** were characterised by elemental analysis and ^{1}H NMR spectroscopy; crystal structures of compounds **7** and **8** were determined by X-ray diffraction. A X-ray diffraction study of the compound [Pd(S_a-**2**)(CH_3)Cl], obtained from **6**, has been recently reported [7].

The experimental data allowed to establish that (S_a)-**1**, (S_a)-**2**, (S,S)-**3** and (R,R)-**4** ligands act, in the compounds **5**–**8**, as chelating ligands leading a square planar geometry. In particular, ^{1}H NMR spectroscopy clearly showed the coordination of the ligands to the metal centre by both the dinitrogen anchoring arms.

In palladium(II) complexes **5**–**8**, all ligands bear hydrogen atoms bound to carbon close to the two nitrogen atoms that can be used as diagnostic in evidencing chelation to the metal centre, since they are the most affected and shifted when compared to the resonances of the free ligands. In fact, after coordination, the α-proton (–CH) of the pyridinyl or quinolinyl fragment are shifted downfield, while the methylene group from azepine fragment (–CH_2) or pyrrolidinyl methyl substituents (–CH_3) are splitted into two pairs of different and well-separated signals.

In particular, ^{1}H NMR spectrum of compound **5** at 298 K in $CDCl_3$, showed in the aromatic region a downfield shift of the doublet relative to α-hydrogen of pyridine fragment from δ 8.51 to δ 8.97 ppm after coordination. In the aliphatic region two pairs of well-defined signals appeared for the four azepinic diastereotopic methylenic protons [δ 5.75 (d, 1H, ^2J 15 Hz, CH_2), 4.83 (d, 1H, ^2J 14 Hz, CH_2), 4.45 (d, 1H, ^2J 14 Hz, CH_2), 4.43 (d, 1H, ^2J 12 Hz, CH_2)], instead of the two expected doublets in the free (S_a)-**1** ligand.

As far as the other palladium(II) complexes are concerned, there are similar strategic signals to be considered: for compound **6** δ 9.65 (dd, 1H, α-quinolinyl proton), 6.06, 4.94, 4.48 and 4.14 (d, 1H, each one CH_2 azepinic); for compound **7** δ 9.05 (d, 1H, α-pyridinyl proton), 4.55 and

3.61 (d, 1H, each one CH_2 methylenic proton), 1.93 and 1.61 (d, 3H, each one CH_3 pyrrolidinyl); for compound **8**: δ 9.62 (dd, 1H, α-quinolinyl proton), 2.19 and 1.06 (d, 3H, each one CH_3 pyrrolidinyl).

2.2. Crystal and molecular structure of [Pd(S,S-3)Cl_2] (7) and [Pd(R,R-4)Cl_2] (8)

Crystals of **7** and **8** were obtained by slow diffusion of hexane in a dichloromethane solution of the compound. The view of the molecular structure models of [Pd(S,S-**3**)Cl_2] (**7**) and [Pd(R,R-**4**)Cl_2] (**8**) together with the atom numbering systems are shown in Figs. 2 and 3. Selected bond distances and angles are given in Tables 1 and 2, respectively.

In the compound **7** the palladium atom is coordinated by two chlorine atoms and by two nitrogen atoms from the bidentate chelating ligand (S,S)-**3** in a distorted square planar geometry: only the N(8) atom deviates remarkably [0.125(3) Å] from the mean plane through the four coordinated atoms and the metal centre. The five-membered Pd(1)N(1)C(6)C(7)N(8) chelating ring adopts a rough envelope conformation, with N(8) deviating by −0.743(4) Å from the mean plane through the other four atoms. The bite angle of 81.3(1)° for N(1)–Pd(1)–N(8) is smaller than the ideal value of 90°, due to the bite size. However, the steric hindrance of the ligand on the chlorine atoms causes an enlargement of the adjacent angles [92.83(8)° for N(1)–Pd(1)–Cl(1) and 95.53(7)° for N(8)–Pd(1)–Cl(2)], while the Cl(1)–Pd(1)–Cl(2) [90.58(4)°] angle tends to the expected value.

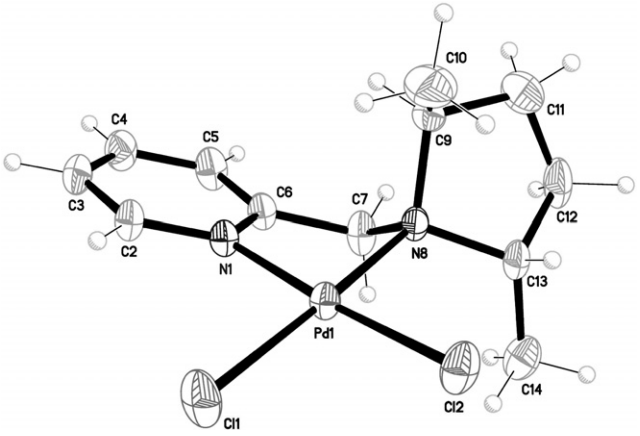

Fig. 2. ORTEP view of the crystal structure of **7** with atom numbering scheme and ellipsoids at the 30% probability level.

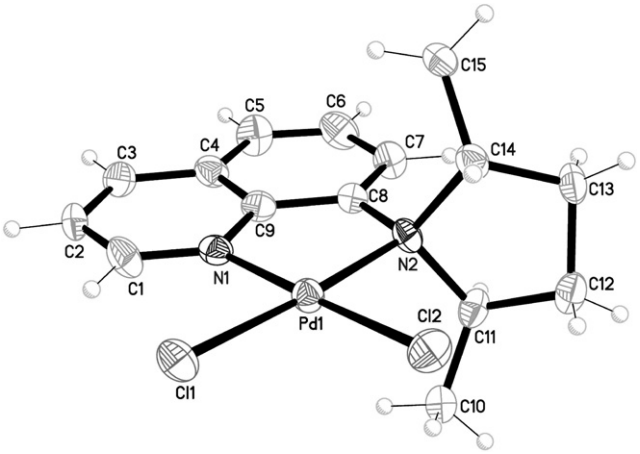

Fig. 3. ORTEP view of the crystal structure of **7** with atom numbering scheme and ellipsoids at the 30% probability level.

The Pd(1)–N(1) [2.017(3) Å] bond length is significantly shorter than Pd(1)–N(8) [2.075(3) Å], but both are in the range for pyridyl-amine complexes of palladium [9]. The difference in the bond distances of 0.058 Å is related to the hybridisation of the two nitrogen atoms [N(1) sp^2 vs. N(8) sp^3] and the steric hindrance on the pyrrolidinyl N atom. The different nature of N-donor atoms is shown also by the Pd-Cl bond distances which are slightly different, Pd(1)–Cl(1) and Pd(1)–Cl(2), respectively, 2.288(1) and 2.2980(9) Å. In two comparable known complexes with a pyridine-amine chelating ligand on palladium, the Pd–Cl bond distances *trans* to N-pyridine were found longer than those *trans* to N-pyrrolidine: in the case in which the amine was represented by a pyrrolidine fragment the difference is 0.0142 Å [10], instead in the case in which there was a secondary amine it is 0.0134 Å [11].

A similar situation is found in the crystal structure of the complex **8**. The asymmetric unit of **8** contains four discrete molecules, displaying comparable dimensions. So in this discussion average values for the structural parameters are used. Further, there are four water molecules and two disordered dichloromethane molecules. The palladium atom shows the same coordination sphere of complex **7**: a distorted square planar coordination involving two chlorine atoms and the two nitrogen atoms of the bidentate chelating ligand (R,R-**4**): the max deviation from the plane through the coordinated atom and the metal centre was found for N(2) [0.06(1) Å], but is lower than that of N(8) in complex **7**. The five-membered Pd(1)N(1)N(2)C(8)C(9) chelating ring is planar [max deviation for N(1) −0.01(1) Å] with a mean bite angle N(1)–Pd(1)–N(2) of 83.3(7)°, slightly greater than that found in **7**. However, the enlargement of this angle might be related to the decreasing of the Cl(1)–Pd(1)–Cl(2) angle [88.2(2)°], while the two adjacent angles remain quite similar [93.1(6)° for N(1)–Pd(1)–Cl(1) and 95.2(5)° for N(2)–Pd(1)–Cl(2)].

As in the compound **7**, the different nitrogen atoms hybridisation in the ligand influences the Pd coordination and induces differences in the Pd–N [2.01(2) Å Pd(1)–N(1) vs. 2.10(2) Å Pd(1)–N(2)] and Pd–Cl [2.290(6) Å Pd(1)–Cl(1) vs. 2.299(6) Å Pd(1)–Cl(2)] bond lengths.

In the chelating ligands (S,S)-**3** and (R,R)-**4** the tetrahedral geometry of the coordinated nitrogen forces the pyrrolidinyl fragment to be almost orthogonal to the mean plane of the chelating ring (see Fig. 4).

Table 1
Bond lengths (Å), angles (°) and torsion angles (°) for [Pd(S,S-3)Cl_2] (**7**)

Pd(1)–N(1)	2.017(3)	C(6)–N(1)	1.354(4)
Pd(1)–N(8)	2.075(3)	C(7)–N(8)	1.496(4)
Pd(1)–Cl(1)	2.288(1)	C(9)–N(8)	1.526(5)
Pd(1)–Cl(2)	2.2980(9)	C(13)–N(8)	1.518(4)
C(2)–N(1)	1.342(4)		
N(1)–Pd(1)–N(8)	81.3(1)	N(8)–C(7)–C(6)	109.2(3)
N(1)–Pd(1)–Cl(1)	92.83(8)	C(7)–N(8)–C(13)	110.7(3)
N(8)–Pd(1)–Cl(2)	95.53(7)	C(7)–N(8)–C(9)	108.3(3)
Cl(1)–Pd(1)–Cl(2)	90.58(4)	C(13)–N(8)–C(9)	103.3(3)
C(2)–N(1)–C(6)	119.2(3)	C(7)–N(8)–Pd(1)	102.1(2)
C(2)–N(1)–Pd(1)	127.4(2)	C(13)–N(8)–Pd(1)	117.0(2)
C(6)–N(1)–Pd(1)	113.3(2)	C(9)–N(8)–Pd(1)	115.3(3)
C(12)–C(13)–N(8)–C(7)	74.0(4)	C(14)–C(13)–N(8)–C(7)	−55.0(4)
C(11)–C(9)–N(8)–C(7)	−90.9(4)	C(10)–C(9)–N(8)–C(7)	146.5(3)

Table 2
Bond lengths (Å), angles (°) and torsion angles (°) for [Pd(R,R-4)Cl_2] (**8**)

Pd(1)–N(1)	2.01(2)	Pd(1)–N(2)	2.10(2)
Pd(1)–Cl(1)	2.290(6)	Pd(1)–Cl(2)	2.299(6)
N(1)–C(1)	1.31(3)	N(1)–C(9)	1.37(3)
N(2)–C(8)	1.47(3)	N(2)–C(14)	1.56(3)
N(2)–C(11)	1.56(3)		
N(1)–Pd(1)–N(2)	83.3(7)	N(1)–Pd(1)–Cl(1)	93.1(6)
N(2)–Pd(1)–Cl(2)	95.2(5)	Cl(1)–Pd(1)–Cl(2)	88.2(2)
C(9)–N(1)–Pd(1)	113(1)	C(8)–C(9)–N(1)	119(2)
N(2)–C(8)–C(9)	118(2)	C(8)–N(2)–Pd(1)	107(1)
C(14)–N(2)–C(8)–C(7)	61(3)	C(11)–N(2)–C(8)–C(7)	−57(3)

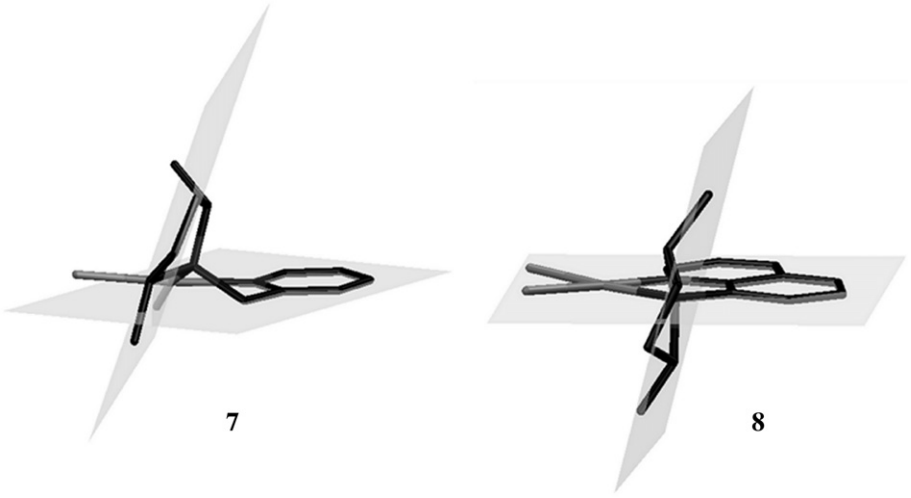

Fig. 4. Molecular stick representation for the compounds **7** and **8** in which the two orthogonal mean planes of the chelating ring and pyrrolidinyl fragment are showed.

In **8** this fragment is perfectly planar due to the quinolinyl delocalisation and the mean plane of the dimethyl-pyrrolidinyl moiety forms a dihedral angle of 76.4(3)° with this plane. Instead in **7**, because of the reduced bite delocalisation (greater flexibility), this fragment is not flat but the orthogonality is maintained [dihedral angle of 72.6(2)°].

In **7**, the analysis of the puckering coordinates [12] of the pentatomic pyrrolidinyl ring showed an envelope conformation, [E_2, $\phi_2 = 32.7(8)°$, $q_2 = 0.413(4)$], with the C(13) atom as apical atom. Instead, in **8** the pyrrolidinyl ring showed a twisted conformation [$^3T_4$, $\phi_2 = -88(2)°$, $q_2 = 0.45(2)$], with the C(13) and C(12) deviating from the mean plane [−0.27(2) Å, and 0.30(2) Å], in order to

minimise the steric interactions with the more rigid aromatic fragment.

Furthermore in Figs. 2 and 3 it is clear that the presence of the different C atoms spacers in the chelating ring causes a different orientation of the pyrrolidinyl moiety: in fact, while in complex **8** the pyrrolidinic N atom is on the plane of the quinoline [C(8) sp^2-spacer], in **7** this atom is out the plane of the pyridine [C(7) sp^3-spacer]. The angle between the mean plane through N(1)C(2)C(3)C(4)C(5)C(6) and the mean plane C(7)N(8)Pd(1) is 46.6(2)° (Fig. 5).

3. Discussion

The results of this work, together with those we recently reported by our group [7,8], indicated that the rigid 2-pyridinyl or 8-quinolinyl building block skeletons induce the orientation assumed by the C_2-symmetric chiral framework *trans*-2,5-dimethylpyrrolidinyl or (S)-(+)-2,2′-(2-azapropane-1,3-diyl)-1,1′-binaphthalene, giving rigidity or flexibility to the ligand, and on the other hand do not directly determining the properties of the metal complex containing the coordinated ligand.

From the molecular structure of the complex [Rh(η^5-C_5Me_5)(S_a-**1**)Cl]SbF_6 [8] resulted that the orientation of the binaphthyl moiety of (S_a)-**1** ligand was angled downwards, in the less congested side of the molecule to minimise the steric interactions with the C_5Me_5 framework; this is possible because of the flexibility of the ligand due to the presence of the sp^3-spacer. In the [Rh(η^5-C_5Me_5)(S_a-**2**)Cl]PF_6 [8] compound the quinolinyl sp^2-spacer of (S_a)-**2** gave rigidity to the ligand and the binaphthyl moiety was placed upwards. This orientation of the binaphthyl moiety in the coordinated (S_a)-**2** ligand, due to the rigidity of the quinolinyl sp^2-spacer was confirmed by the X-ray diffraction structural parameter found for the compound [Pd(S_a-**2**)(CH_3)Cl] [13], obtained from the here reported [Pd(S_a-**2**)Cl_2]. The orientation of the binaphthyl group in the complex [Rh(η^5-C_5Me_5)(S_a-1)Cl]SbF_6 induces a minor steric interaction on the coordination plane formed by the Cl and the ligand nitrogen atoms with respect to the case assumed in the complex [Rh(η^5-C_5Me_5)(S_a-2)Cl]PF_6.

The structural determination, by X-ray diffraction, of the complexes [Pd(N–N*)Cl_2], (N–N* = (S,S)-**3** and (R,R)-**4**) here reported, indicated that the *trans*-2,5-dimethylpyrrolidinyl chiral framework in the complexes **7** and **8** was oriented almost orthogonal to the coordination plane. However, the effect of the different rigidity and flexibility induced to the ligand by the 2-pyridinyl or 8-quinolinyl building block is the modification of the stereochemical configuration of the ligands in a significant way. In fact in the compound **7**, the sp^3-carbon spacer induces flexibility to the (S,S-**3**) ligand and allows the *trans*-2,5-dimethylpyrrolidinyl moiety to be tilted out of the plane of pyridine. Owing to the rigidity induced by the sp^2-quinolinyl-spacer, in the compound **8** there is a more extended planarity involving the N atom of *trans*-2,5-dimethylpyrrolidinyl.

Fig. 5. Molecular stick representation for the compound **7** showing two not orthogonal mean planes through N(1)C(2)C(3)C(4)C(5)C(6) and C(7)N(8)Pd(1).

It is noteworthy that the *trans*-2,5-dimethylpyrrolidinyl chiral framework assumed the orthogonal orientation, with respect to pyridinyl or 8-quinolinyl moiety, in a square planar coordination of the metal centre, in which no important repulsive interactions are present.

We previously demonstrated that the catalytic results in the palladium catalysed allylic alkylation reactions [7] and the diastereoselectivity and configurational stability at the metal centre in half-sandwich (η^6-*p*-cymene)ruthenium(II) and (η^5-C_5Me_5)rhodium(III) complexes [8] can be explained only by considering overriding the stereochemical of the C_2-symmetric chiral framework *trans*-2,5-dimethylpyrrolidinyl or (S)-(+)-2,2′-(2-azapropane-1,3-diyl)-1,1′-binaphthale-ne.

In conclusion, the results here reported, together with those about the reactivity of complexes containing (S_a)-**1**, (S_a)-**2**, (S,S)-**3**, (R,R)-**3**, (S,S)-**4** and (R,R)-**4** ligands, further confirm that only the intrinsic rigidity and flexibility are not enough to define the ligand properties and to preview the effects that they induce on the reactivity of the metal complex. It seems opportune to introduce a parameter that it is related to the situation determined over and under the coordination plane formed by the metal and the chelating ligand donor atoms.

4. Experimental

4.1. General methods

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Freshly distilled solvents were used throughout and dried by standard procedures. Published methods were used to prepare the compound (S_a)-(+)-2,2′-[2-(methyl-2-pyridyl)-2-azapropane-1,3-diyl]1,1′-binaphthalene[14] (S_a)-**1** and (S_a)-(-)-2,2′-[(7-quinolinyl)-2-azapropane-1,3-diyl] 1,1′-binaphthalene (S_a)-**2**, (S,S)-(−)-2-(2,5-dimethyl-pyrrodin-1-ylmethyl)-pyridine (S,S)-**3** and (R,R)-(+)-8-(2,5-dimethyl-pyrrodin-1-yl)-quinoline (R,R)-**4**[15]. All other reagents were purchased from Sigma–Aldrich. ^{1}H NMR spectra were recorded with a Bruker AMX R300 spectrometer referenced to internal tetramethylsilane. Standard Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

4.2. Preparations

4.2.1. [Pd(N–N*)Cl$_2$] (5–8)

The [Pd(N–N*)Cl$_2$] complexes with N–N* = (S_a)-**1** (**5**), (S_a)-**2** (**6**), (S,S)-**3** (**7**), (R,R)-**4** (**8**), were synthesised in the same way with the following procedure.

To a solution of [Pd(benzonitrile)$_2$Cl$_2$] (20 mg, 52.1 mmol) in CH_2Cl_2 the ligand (**1**–**4**) was added (62.6 mmol) and the colour of the mixture switched from orange to slight yellow. After 3 h the solvent was removed *in vacuo* and the residue washed with hexane. Recrystallisation from CH_2Cl_2/hexane in 3:1 *ratio* yielded the complex as yellow solid.

4.2.2. [Pd(S_a-1)Cl$_2$] (5)

Yield: 85% (25 mg, 0.044 mol). ^{1}H NMR ($CDCl_3$): δ 8.97 (dd, 1H, ^3J 6 Hz, ^4J 2 Hz, Ar–H), 8.28 (d, 1H, ^3J 8 Hz, Ar–H), 8.07 (d, 1H, ^3J 8 Hz, Ar–H), 8.00-7.88 (td, 3H, ^3J 8 Hz, ^4J 2 Hz, Ar–H), 7.83 (td, 1H, ^3J 8 Hz, ^4J 2 Hz, Ar–H), 7.72 (d, 1H, ^3J 8 Hz, Ar–H), 7.48 (m, 3H, Ar–H), 7.28 (m, 5H, Ar–H), 5.75 (d, 1H, ^2J 15 Hz, CH_2), 4.83 (d, 1H, ^2J 14 Hz, CH_2), 4.45 (d, 1H, ^2J 14 Hz, CH_2), 4.43 (d, 1H, ^2J 12 Hz, CH_2), 3.64 (d, 1H, ^2J 15 Hz, CH_2), 3.02 (d, 1H, ^2J 12 Hz, CH_2). Anal. Calc. for $C_{28}H_{22}Cl_2N_2Pd$ (563.81): C, 59.65; H, 3.93; N, 4.97. Found: C, 59.61; H, 3.92; N, 4.91%.

4.2.3. [Pd(S_a-2)Cl$_2$] (6)

Yield: 81% (25.3 mg, 0.042 mol). ^{1}H NMR ($CDCl_3$): δ 9.65 (dd, 1H, ^3J 5 Hz, ^4J 2 Hz, Ar–H), 8.43 (dd, 1H, ^3J 8 Hz, ^4J 2 Hz, Ar–H), 8.28 (d, 1H, ^3J 8 Hz, Ar–H), 8.08 (dd, 2H, ^3J 8 Hz, ^4J 4 Hz, Ar–H), 8.00 (dd, 2H, ^3J 19 Hz, ^4J 8 Hz, Ar–H), 7.87 (dd, 1H, ^3J 8 Hz, ^4J 2 Hz, Ar–H), 7.63 (dd, 1H, ^3J 5 Hz, Ar–H), 7.56 (t, 1H, ^3J 7 Hz, Ar–H), 7.49–7.40 (m, 5H, Ar–H), 7.31 (t, 1H, ^3J 7 Hz, Ar–H), 7.21 (d, 2H, ^3J 4 Hz, Ar–H), 6.06 (d, 1H, ^2J 14 Hz, CH_2), 4.94 (d, 1H, ^2J 12 Hz, CH_2), 4.48 (d, 1H, ^2J 14 Hz, CH_2), 4.14 (d, 1H, ^2J 12 Hz, CH_2). Anal. Calc. for $C_{31}H_{22}Cl_2N_2Pd$ (599.85): C, 62.07; H, 3.70; N, 4.67. Found: C, 62.12; H, 3.64; N, 4.61%.

4.2.4. [Pd(S,S-3)Cl$_2$] (7)

Yield: 89% (17.1 mg, 0.046 mol). ^{1}H NMR ($CDCl_3$): δ 9.05 (d, 1H, ^3J 6 Hz, Ar–H), 7.94 (td, 1H, ^3J 8 Hz, ^4J 2 Hz, Ar–H), 7.65 (d, 1H, ^3J 8 Hz, Ar–H), 7.40 (t, 1H, ^3J 7 Hz, Ar–H), 4.55 (d, 1H, ^2J 15 Hz, CH_2), 4.12 (m, 1H, CH), 3.61 (d, 1H, ^2J 15 Hz, CH_2), 3.03 (m, 1H, CH), 2.29 (m, 1H, CH_2), 2.10 (m, 1H, CH_2), 1.93 (d, 3H, ^3J 7 Hz, CH_3), 1.89 (m, 1H, CH_2), 1.63 (m, 1H, CH_2), 1.61 (d, 3H, ^3J 7 Hz, CH_3). Anal. Calc. for $C_{12}H_{18}Cl_2N_2Pd$ (367.61): C, 38.99; H, 5.45; N, 7.58. Found: C, 38.94; H, 5.41; N, 7.55%.

4.2.5. [Pd(R,R-4)Cl$_2$] (8)

Yield: 82% (17.2 mg, 0.043 mol). ^{1}H NMR ($CDCl_3$): δ 9.62 (dd, 1H, ^3J 5 Hz, ^4J 1 Hz, Ar–H), 8.43 (dd, 1H, ^3J 8 Hz, ^4J 2 Hz, Ar–H), 7.90 (dd, 1H, ^3J 7 Hz, ^4J 2 Hz, Ar–H), 7.78–7.70 (m, 2H, Ar–H), 7.58 (dd, 1H, ^3J 8 Hz, ^4J 5 Hz, Ar–H), 5.69 (m, 1H, CH), 3.76 (m, 1H, CH), 2.74 (m, 1H, CH_2), 2.27 (m, 1H, CH_2), 2.12 (m, 1H, CH_2), 2.19 (d, 3H, ^3J 7 Hz, CH_3), 1.97 (m, 1H, CH_2), 1.06 (d, 3H, ^3J 7 Hz, CH_3). Anal. Calc. for $C_{15}H_{18}Cl_2N_2Pd$ (403.64): C, 44.63; H, 4.49; N, 6.94. Found: C, 44.68; H, 4.41; N, 6.92%.

4.3. Crystal structure determination of complexes 7 and 8

The intensity data of complexes **7** and **8** were collected at r.t. on a Bruker APEX 8 diffractometer, using a graphite monochromated Mo Kα radiation and equipped with

Table 3
Crystal data and structure refinement for **7** and **8**

	7	**8**
Empirical formula	$C_{12}H_{18}Cl_2N_2Pd$	$C_{62}H_{84}Cl_{12}N_8O_4Pd_4$
Formula weight	367.58	1856.37
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions	$a = 12.769(3)$ Å $b = 15.394(3)$ Å $c = 7.291(2)$ Å	$a = 12.0509(16)$ Å $b = 17.150(2)$ Å $c = 19.375(3)$ Å $\beta = 91.07(1)°$
Volume	1433.2(5) Å^3	4003.6(10) Å^3
Z	4	2
Absorption coefficient	1.648 mm^{-1}	1.330 mm^{-1}
Theta range for data collection	2.07–24.99°	4.27–25.00°
Reflections collected	2001	21646
Independent reflections [R_{int}]	1838 [0.0109]	12752 [0.0449]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1838/0/154	12752/34/805
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0185$, $wR_2 = 0.0455$	$R_1 = 0.0627$, $wR_2 = 0.1701$
R indices (all data)	$R_1 = 0.0201$, $wR_2 = 0.0463$	$R_1 = 0.0735$, $wR_2 = 0.1867$
Absolute structure parameter	−0.04(4)	−0.06(4)
Largest differences in peak and hole	0.253 and −0.281 e Å^{-3}	1.632 and −1.118 e Å^{-3}

area detector. The data collection, cell refinement and reduction were carried out with the SMART and SAINT programs [16a].

The two structures were solved by Direct Methods, by using the Sir 2004 program [16b] and refined by weighted full-matrix least-square procedures (based on F^2) (SHELX-97) [16c]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were introduced into the geometrically calculated positions and refined using the *riding model*. Absolute configurations of both structures are in agreement with synthetic route; inversion of configurations did not give better results during structure refinement.

Crystallographic and experimental details for the three structures are summarised in Table 3.

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Appendix A. Supplementary material

CCDC 655460 and 655461 contain the supplementary crystallographic data for **7** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.09.012.

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