

First Allylpalladium Systems Containing Chiral Imidazolyipyridine Ligands – Structural Studies and Catalytic Behaviour

Amaia Bastero,^[a] Antonio F. Bella,^[a] Fernando Fernández,^[b] Susanna Jansat,^[b] Carmen Claver,^{*[a]} Montserrat Gómez,^{*[b,c]} Guillermo Muller,^[b] Aurora Ruiz,^[a] Mercè Font-Bardía,^[d] and Xavier Solans^[d]

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Palladium/chiral imidazolyipyridine systems were tested in allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-I) and 3-acetoxy-1-phenyl-1-propene (II), paying particular attention to the influence of the amine nitrogen hybridisation on their catalytic behaviour. Allylpalladium complexes **9–11** containing optically pure imidazolines were synthesised and fully characterised both in solution (NMR) and the solid state (single-crystal X-ray diffraction). NMR studies

showed four species in solution for complex **9** containing the unsymmetrical 1-phenylallyl group, while for **10** and **11**, involving the symmetrical 1,3-diphenylallyl moiety, two species, *endo* and *exo*, were identified. In the solid state, only *endo* isomers crystallised for each complex.

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Introduction

In comparison with ligands containing oxazoline groups,^[1] chiral imidazolines have been used less in catalysis, despite the structural analogy between the two heterocycles.^[2] For imidazolines, the additional nitrogen atom in place of oxygen provides a further point for tuning the ligand basicity by changing the nature of the R³ group, and consequently a new modifiable region to be considered in selective catalytic processes (Figure 1).

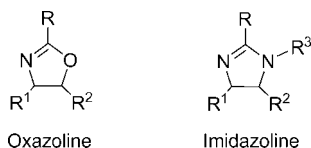


Figure 1. Oxazoline and imidazoline heterocycles.

The first enantioselective catalytic application of chiral imidazolines appeared in 1997 when Achiwa and co-

workers published their research about Pd-catalysed allylic alkylation using chiral thioimidazoline ligands, obtaining moderate activities but excellent enantioselectivities (up to 96% *ee*),^[3] comparable to those obtained with thioether-oxazolines.^[4] Later, chiral phosphanylimidazolines were tested in Ir-catalysed enantioselective hydrogenation,^[5,6] giving in some cases better asymmetric inductions than those involving analogous phosphanyloxazolines.^[5] This kind of ligand has also been used in Pd-catalysed asymmetric Heck reactions, yielding better enantioselectivities than BINAP and phosphanyloxazolines.^[7] Besides mono(imidazolines), bis(imidazolines) have also been used in catalysis. Therefore, chiral tridentate 2,6-bis(imidazolyl)pyridines, structurally analogous to pybox ligands,^[8] have been tested in Ru-catalysed asymmetric epoxidation reactions.^[9] In addition, C₂-symmetric bis(imidazolines) have also been prepared and successfully used in Pd-catalysed allylic alkylation,^[10,11] giving asymmetric inductions comparable to those obtained with analogous bis(oxazolines).^[1d]

Concerning imidazolyipyridines, our investigation on Pd-catalysed copolymerisation of carbon monoxide and styrene, which represents the first catalytic work involving this type of ligand,^[12] showed that the electronic nature of the R³ substituent (Figure 1) could somehow control the stereoregularity of the polyketones obtained,^[13,14] in contrast to the comparable oxazolyipyridine systems, affording invariably highly syndiotactic polymers.^[15] At the same time, Davies et al. reported the use of chiral imidazolyipyridines in Ru-catalysed Diels–Alder reactions and the synthesis and full characterisation of the first complex containing a chiral imidazoline group.^[16]

- [a] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
 Fax: +34-977559563
 E-mail: carmen.claver@urv.net
- [b] Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
- [c] Laboratoire Hétérochimie Fondamentale et Appliquée, UMR CNRS 5069, Université Paul Sabatier, 118 route de Narbonne, 31120 Toulouse cedex 9, France
 Fax: +33-5-61558204
 E-mail: gomez@chimie.ups-tlse.fr
- [d] Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

With regard to structural studies, few metal complexes containing chiral imidazoline moieties have been fully characterised.^[17] Only our palladium complexes of type $[\text{PdClR}(\kappa^2\text{-}N,N'\text{-L}^*)]$ ($R = \text{Cl}, \text{Me}$),^[13,14] rhodium compounds, $[\text{Rh}(\text{cod})(\kappa^2\text{-}N,N'\text{-L}^*)]\text{BF}_4$,^[14] and Davies' ruthenium complexes, $[\text{RuCl}(1,3,5\text{-trimethylbenzene})(\kappa^2\text{-}N,N'\text{-L}^*)]\text{SbF}_6$,^[16] have been published involving chiral imidazolylpyridines.

Following our research in allylic alkylation,^[18] we have carried out a catalytic and structural study with imidazolylpyridines (Figure 1) to compare their behaviour with those containing analogous oxazoline derivatives (like ligands **7** and **8**, see Table 4).^[19,20] For this purpose, we have chosen a short family of imidazolylpyridines coming from 1,2-diphenylethylenediamine, by varying the substituent nature on the amine nitrogen atom ($R = \text{H}, \text{Me}, \text{Bn}, \text{Ts}$, Figure 2). The influence of heterocycle stereochemistry on catalysis has also been considered [(R,R) -**1**, (S,S) -**2** and rac -(R,S)-**3**, Figure 1]. Allylpalladium intermediates have been synthesised and fully characterised in order to show a relationship with the catalytic behaviour observed.

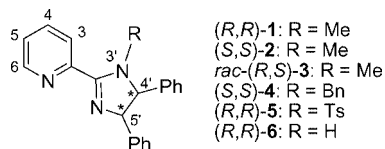


Figure 2. 2-(4',5'-Diphenyl-3'-R-imidazolyl)pyridines **1–6** with numbering scheme.

Results and Discussion

Palladium Complexes

Ionic palladium complexes **9–11** containing 1-phenyl- (**9**) and 1,3-diphenylallyl groups (**10** and **11**) were prepared from the corresponding palladium precursor and the appropriate chiral imidazolylpyridine ligand, (R,R) -**1** for **9**, (S,S) -**2** for **10** and (S,S) -**4** for **11**, in the presence of ammonium hexafluorophosphate (Scheme 1), according to the methodology previously described.^[19,21]

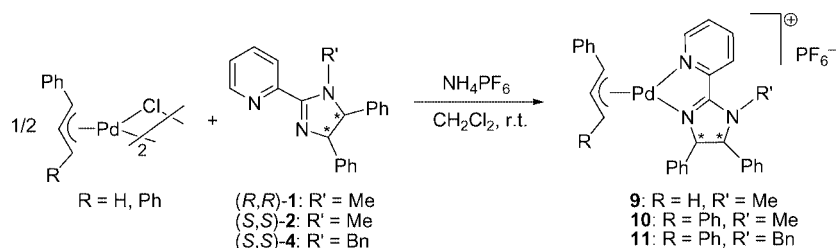
These compounds were obtained as monometallic complexes of general formula $[\text{Pd}(\eta^3\text{-1-Ph-3-R-C}_3\text{H}_7)(\text{L})]\text{PF}_6$ [**9**: $R = \text{H}$, $n = 4$, $L = (R,R)$ -**1**; **10**: $R = \text{Ph}$, $n = 3$, $L = (S,S)$ -**2**; **11**: $R = \text{Ph}$, $n = 3$, $L = (S,S)$ -**4**], where L acts as a $\kappa^2\text{-}N,N'$ -bidentate ligand affording a five-membered palladacycle. Complexes **9–11** were fully characterised by the us-

ual techniques. IR spectra showed strong signals at 1559–1549 cm^{-1} corresponding to the $\text{C}=\text{N}_{\text{imine}}$ moiety and at about 835 cm^{-1} assigned to P–F stretching of the PF_6^- anion. Mass spectra exhibited a peak corresponding to the $[\text{Pd}(\eta^3\text{-1-Ph-3-R-C}_3\text{H}_7)(\text{L})]^+$ fragment.

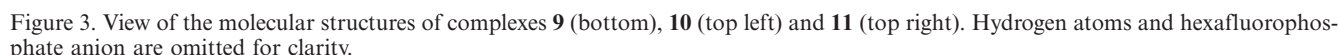
Suitable monocrystals of **9**, **10** and **11** for X-ray diffraction measurements were obtained from dichloromethane solutions of the corresponding complexes by slow diffusion of hexane.

In these structures (Figure 3), the palladium atom shows a distorted square-planar coordination, bonded to two nitrogen (N7 and N1) and two terminal allylic carbon atoms (Table 1), which are nearly coplanar (N1–C12–C14–N7 is about 4.8° for **9** and **10**, and 1.9° for **11**). These complexes crystallised as *endo* isomers, meaning that the central allylic carbon atom and the phenyl substituent at 5'-position on the imidazoline ring point in opposite directions.

In a previous study based in neutral and cationic Pd complexes involving this kind of ligand, it was found that the C–N bond lengths were sensitive to the R substituents at 3'-position, providing information about the electronic delocalisation through the amidine fragment.^[14] Therefore, in order to analyse the electronic density involved in the C–N bonds, N_{amine} (N4) and N_{imine} (N1) with their common bonded C atom (C5), we have compared the bond length difference between C5–N4 and C5–N1 . For **9** and **10**, the difference is slightly smaller than for **11** [$\Delta(\text{N1–C5} - \text{N4–C5}) = 0.051 \text{ \AA}$ for **9**; $\Delta(\text{N1–C5} - \text{N4–C5}) = 0.054 \text{ \AA}$ for **10**; $\Delta(\text{N1–C5} - \text{N4–C5}) = 0.069 \text{ \AA}$ for **11** (Table 1)]. Comparing these figures with those of related compounds, $[\text{PdClMe}(R,R\text{-2})]$ ($\Delta = 0.037 \text{ \AA}$) and $[\text{PdClMe}(R,R\text{-5})]$ ($\Delta = 0.139 \text{ \AA}$),^[14] we can state that complexes containing ligands (R,R) -**1** and (S,S) -**2** {complexes **9**, **10** and $[\text{PdClMe}(R,R\text{-1})]$ } have C–N bonds of a similar nature, with bond lengths intermediate between those for single and double bonds; while for **11**, containing (S,S) -**4**, both single and double bonds are present. In addition, IR spectra for **9–11** exhibit C=N stretching absorptions (1559–1549 cm^{-1} , see Experimental Section) at lower frequency than those observed for allylpalladium complexes containing bis(oxazolines) (1650–1670 cm^{-1})^[22,18a] or oxazolylpyridines (1630–1660 cm^{-1})^[19] consequently, weaker $\text{C}=\text{N}_{\text{imine}}$ bonds for imidazoline than for oxazoline derivatives are observed. These structural data point out an electronic delocalisation between the two nitrogen atoms of the imidazoline heterocycle, mainly when the substituent on the N_{amine} atom is a methyl group [ligands (R,R) -**1** and (S,S) -**2**].



Scheme 1. Allylpalladium complexes **9–11** containing chiral ligands (R,R) -**1**, (S,S) -**2** and (S,S) -**4**.



	9	10	11
Pd1-N1	2.053(4)	2.096(4)	2.109(3)
Pd1-N7	2.124(4)	2.147(5)	2.137(3)
Pd1-C12	2.168(5)	2.173(5)	2.173(4)
Pd1-C13	2.087(5)	2.122(5)	2.145(4)
Pd1-C14	2.107(5)	2.137(5)	2.163(4)
N1-C5	1.289(6)	1.304(6)	1.291(5)
N4-C5	1.340(6)	1.358(6)	1.360(5)
N1-Pd1-N7	77.24(15)	77.64(15)	76.53(12)
C12-Pd1-C14	67.9(2)	67.77(18)	68.11(15)

The Pd–C distances in *trans* position to both nitrogen atoms, Pd1–C12 versus Pd1–C14, point to a higher *trans* influence for N_{imine} than for N_{pyridine}. Therefore, the differences in the distance between palladium and both terminal allylic carbon atoms [$\Delta(\text{Pd1}–\text{C12} – \text{Pd1}–\text{C14})$] are 0.036 and 0.010 Å for **10** and **11** respectively. However, the electronic effect of the R substituent on N_{amine} is not reflected in the

¹H NMR spectroscopy allowed the determination of the structure of these complexes in solution.^[19,24] For complex **9**, four isomers were observed in deuterated chloroform solution at room temperature, with a relative ratio 46:31:15:8 for **9a/9b/9c/9d**. Only for the two major isomers, **9a** and **9b**, were all carbon and proton atoms assigned. The isomers detected are formed because of (i) the relative position of the central allylic carbon atom and the phenyl substituent at the 5'-position on the imidazoline ring (giving *exo* and *endo* isomers, see above) and (ii) the substitution on the allyl moiety. 2D NOESY experiments exhibited interconversion between **9a** and **9d** and between **9b** and **9c**, but no π - σ - π allyl isomerisation was observed.

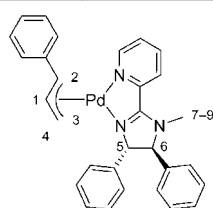
Concerning relative chemical shifts, the signals of the terminal allyl protons (H^3 and H^4 , Table 2) for the two major isomers ($\delta = 2.19\text{--}3.33$ ppm for **9a** and **9b**) are upfield-shielded relative to those of the other two isomers ($\delta = 3.51\text{--}4.25$ ppm for **9c** and **9d**), a fact that can be attributed to the spatial proximity of the phenyl group at the heterocycle 5'-position; similarly, the signal of the H^2 proton of **9c** is also upfield-shifted with respect to **9a** and **9b** [$\delta = 3.96$ (**9c**) vs. 4.52 and 4.53 ppm for **9a** and **9b**, respectively, Table 2]; H^5 is also sensitive to the allyl group and for **9c** its signal is more than 1 ppm upfield-shifted because of the close allylphenyl group [$\delta = 3.86$ (**9c**) vs. 4.84 and 5.00 ppm for **9a** and **9b**, respectively]. Consequently, the two major isomers could be attributed to *exo* and *endo* isomers where the phenylallyl group is located in *cis* position relative to

the pyridine nitrogen atom, while **9c** corresponds to one of the minor isomers where the phenylallyl group is located in *trans* position relative to the pyridine nitrogen atom. These data lead us to propose the structures shown in Figure 4.

Table 2. Selected ^1H NMR (CDCl_3 , 400 MHz, 298 K) chemical shifts for **9** (signal multiplicity in parentheses).^[a]

	9a	9b	9c	9d ^[b]
H ¹ (central)	5.76 (td)	5.69 (td)	5.87–5.95 (m)	n.d.
H ² (<i>anti</i> -Ph)	4.52 (d)	4.53 (d)	3.96 (d)	n.d.
H ³ (<i>anti</i>)	2.19 (ddd)	2.72 (d)	3.51 (d)	n.d.
H ⁴ (<i>syn</i>)	3.33 (dd)	2.79 (dd)	4.25 (d)	4.14 (d)
H ⁵	4.84 (d)	5.00 (d)	3.86 (d)	n.d.
H ⁶	4.90 (d)	4.86 (d)	4.41 (d)	n.d.
H ^{7–9} (CH_3)	3.31 (s)	3.29 (s)	3.21 (s)	n.d.

[a] Proton labels:



[b] n.d. means not distinguished.

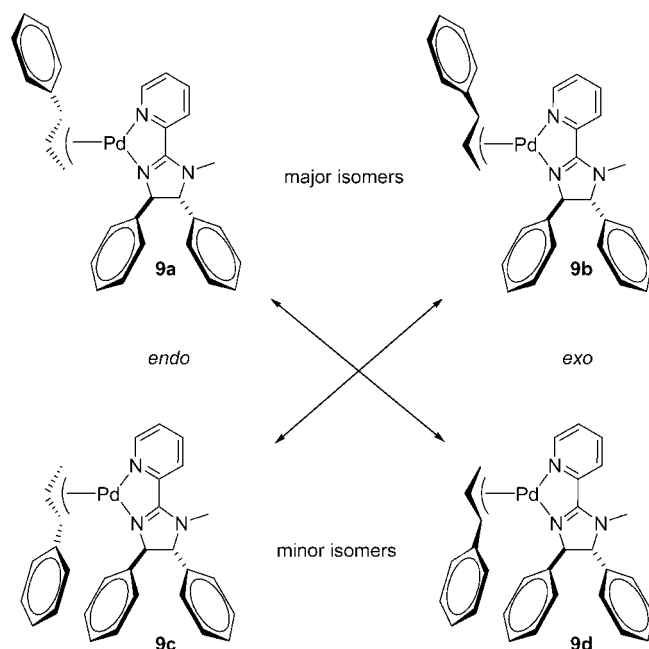


Figure 4. Proposed structures for the four isomers of **9** observed in solution (arrows indicate the isomer interconversion observed by 2D NOESY, between **9a** and **9d**, and **9b** and **9c**).

For complexes **10** and **11**, only two isomers were observed in deuterated chloroform solution, with a relative ratio of about 6:1. Most of the resonances for minor isomers are overlapped by signals corresponding to those of major species. 2D NOESY experiments exhibited, in both cases, interconversion between both isomers and no π - σ - π allyl isomerisation was detected. Because of the steric hindrance between both phenyl groups, from the imidazoline ring and allyl group, the major species for each complex could be assigned to the *endo* isomer.

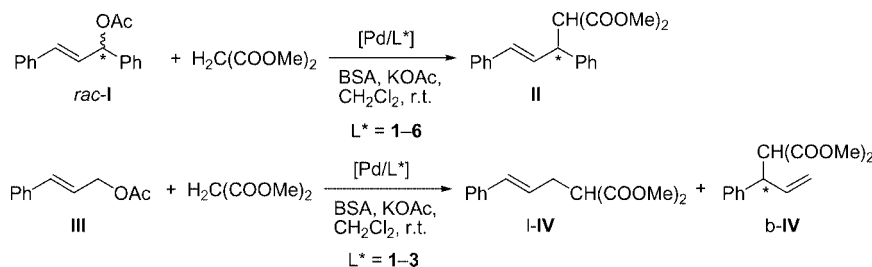
Pd-Catalysed Allylic Alkylation

Asymmetric allylic alkylation of the racemic substrate *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-**I**) and 3-acetoxy-1-phenyl-1-propene (**III**) with dimethyl malonate under basic Trost conditions^[25] was carried out using a Pd catalytic systems containing 2-(4',5'-diphenyl-5'-substituted-imidazolyl)pyridines **1–6** (Scheme 2). The results are summarised in Table 3. Catalytic precursors were generated in situ from $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ and the appropriated ligand ($\text{Pd}/\text{L} = 1:1.25$).

For the allylic alkylation of *rac*-**I**, we observed that the most active palladium systems were those containing a methyl group in the 5'-position of the imidazolyl ring, ligands (*R,R*)-**1**, (*S,S*)-**2** and *rac*-(*R,S*)-**3** (Entries 2, 4 and 5, Table 3). Benzyl and tosyl derivatives [ligands (*S,S*)-**4** and (*R,R*)-**5**, respectively] led to less active catalysts (Entries 7 and 9, Table 3), especially the $\text{Pd}/(\text{R,R})$ -**5** system, which showed a very low conversion [36% after 48 h of reaction (Entry 9, Table 3)].

The activity trend shown by these Pd/L^* systems correlates quite well with the N_{amine} hybridisation character. Actually, methyl derivatives containing sp^2 -hybridised N_{amine} (ligands **1**, **2** and **3**) are more active than benzyl [(*S,S*)-**4**], whose N_{amine} atom exhibits a significant sp^3 character and is clearly more active than the tosyl derivative, which contains an sp^3 -hybridised N_{amine} atom (Entries 2, 4, 5, 7 and 9, Table 3).

Concerning the enantioselectivity, only the $\text{Pd}/(\text{S,S})$ -**4** system gave a significant asymmetric induction, up to 19% *ee* (Entry 7, Table 3). The low enantioselectivity observed is probably due to the higher *trans* influence of N_{imine} than that of $\text{N}_{\text{pyridine}}$ (see above), directing the nucleophile attack towards the terminal allylic carbon atom *trans* to the imine nitrogen atom. In that position no steric hindrance coming



Scheme 2. Allylic alkylation of *rac*-**I** and **III** catalysed by Pd/L^* systems ($\text{L}^* = \mathbf{1-6}$).

Table 3. Allylic alkylation of *rac*-**I** and **III** catalysed by palladium systems containing imidazolylpyridines, Pd/L* (L* = **1–6**).^[a]

Entry	L*	Substrate	Time [h]	Conversion [%] ^[b]	ee of II [%] ^[b]	I-IV/b-IV ^[b]
1	1	I	5	41	0	–
2	1	I	24	97	0	–
3	2	I	5	34	0	–
4	2	I	24	100	0	–
5	3	I	24	81	0	–
6	4	I	5	0	–	–
7	4	I	24	46	19 (<i>S</i>)	–
8	4	I	48	99	15 (<i>S</i>)	–
9	5	I	48	36	0	–
10	5	I	96	94	0	–
11	1	III	24	100	–	13:1
12	2	III	24	100	–	13:1

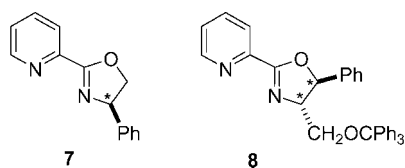
[a] Results from duplicated experiments. Pd/L*/substrate = 1:1.25:50. See Scheme 2. [b] Conversions based on substrate **I** or **III** determined by ¹H NMR spectroscopy; enantiomeric excesses (absolute configuration in parentheses) determined by HPLC and l(inear)/b(ranched) ratio, by GC.

from the 6-position of the pyridine group exists to discriminate this attack between both *endo* and *exo* isomers. In addition, the electronic effect due to the N_{amine} substituent can contribute to this lack of enantioselectivity. An increase of pyramidal arrangement around the N_{amine} atom means a decrease of π -electron delocalisation between the amine and imine nitrogen atom (see above) and consequently N_{imine} becomes a better donor Lewis centre, favouring the stability of cationic intermediate catalytic species responsible for the enantioselectivity control. The lack of enantioselectivity for (*R,R*)-**5** (Entries 9 and 10, Table 3) could be due to electronic factors.

The Pd/(*R,R*)-**6** system was not active, doubtless because of the NH deprotonation of the imidazoline group under the basic catalytic conditions used. In this case, the plausible palladium intermediate containing the anionic imidazolylpyridine ligand could induce a less electrophilic character on the allyl moiety than cationic allylic intermediates involving bidentate neutral ligands.

The most active catalytic systems [Pd/(*R,R*)-**1** and Pd/(*S,S*)-**2**] were used in the allylic alkylation of 3-acetoxy-1-phenyl-1-propene (**III**), under the same conditions described above for *rac*-**I**, showing a high regioselectivity towards the linear isomer, I-IV/b-IV ratio = 13:1 (Entries 11 and 12, Table 3).

From a structural point of view, the imidazoline ring is close to the oxazoline heterocycle. When we compare the catalytic results obtained for *rac*-**I** alkylation with (5'-phenyl-oxazolynyl)pyridine and (4',5'-disubstituted)oxazolynylpyridine ligands **7** and **8**, respectively (Table 4), we observe that Pd/**7** and Pd/**8** catalysts are more active and selective than the most active and selective imidazoline derivatives [ligands (*R,R*)-**1**, (*S,S*)-**2** and (*S,S*)-**4**, respectively; Entries 4 and 5 vs. 1, 2 and 3, Table 4].

Table 4. Allylic alkylation of *rac*-**I** catalysed by palladium systems containing imidazolyl- [(*R,R*)-**1**, (*S,S*)-**2**, (*S,S*)-**4**] and oxazolynylpyridines (**7**, **8**).

Entry	L*	Time [h]	Conversion [%] ^[a]	ee of II [%] ^[a]	Reference
1	1	5	41	0	this work
2	2	5	34	0	this work
3	4	24	46	19 (<i>S</i>)	this work
4	7	2.5	86	55 (<i>R</i>) ^[b]	[20]
5	8	2	84	25 (<i>S</i>)	[19]

[a] Conversions based on substrate **I** determined by ¹H NMR spectroscopy; enantiomeric excesses (absolute configuration in parentheses) determined by HPLC. [b] Determined by ¹H NMR spectroscopy using Eu(hfc)₃ as the chiral shift reagent.

The higher electronegativity of oxygen with respect to nitrogen avoids any π -delocalisation between oxygen and nitrogen atoms in the oxazoline heterocycle. Then the Lewis base character of the N_{imine} atom in oxazolines is more important than that for analogous imidazolines, especially for those containing an sp²-hybridised amine nitrogen atom. Therefore, this behaviour becomes crucial to understand the activity and selectivity diminution of imidazolylpyridines compared to related oxazolines.

Conclusion

We have found the fine-tuning effect of the remote N_{amine} centre on the Pd-catalysed allylic alkylation reaction. The delocalisation of the nonbonding electron pair of N_{amine} causes a basicity diminution in N_{imine}, which is directly bonded to the metal atom. This effect seems to be directly related with the activity and asymmetric induction of Pd/imidazolylpyridine catalytic systems.

Experimental Section

General Remarks: All compounds were prepared under purified nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen.^[26] [Pd(η^3 -1-phenylallyl)(μ -Cl)]^[27] and ligands (*R,R*)-**1**,^[14]

(*S,S*)-**2**,^[16] (*R,R*)-**5**^[14] and (*R,R*)-**6**^[14] were prepared as described previously. NMR spectra were recorded with Varian XL-500 (¹H, standard SiMe₄), Varian Gemini (¹H, 200 MHz; ¹³C, 50 MHz; standard SiMe₄), Bruker DRX 250 (¹³C, 62.9 MHz, standard SiMe₄) and Varian Mercury 400 (¹H, 400 MHz; ¹³C, 100 MHz, standard SiMe₄) spectrometers, using CDCl₃ as solvent, unless stated otherwise. Chemical shifts were reported downfield from standards. IR spectra were recorded with FTIR Nicolet 520 and Nicolet 5700 spectrometers. Electron-spray mass spectra were obtained with a Mass ZQ Micromass instrument. High-resolution mass spectra were obtained with a Waters LCT Premier spectrometer operated in ESI mode. The GC analyses were performed with a Hewlett-Packard 6890-Network GC system gas chromatograph [30 m HP5 (5% phenyl)methylpolysiloxane column] with an FID detector. Enantiomeric excesses were determined by HPLC on a Chiralcel OD column. Elemental analyses were carried out by the Serveis Científics-Tècnics de la Universitat de Barcelona with an Eager 1108 microanalyser. Optical rotations were measured with a JASCO P-1030 polarimeter.

(4'*R*,5'*S*)-2-(3'-Methyl-4',5'-diphenyl-2'-imidazolyl)pyridine [*rac*-(*R,S*)-3**]:** (4'*R*,5'*S*)-2-(4',5'-Diphenyl-2'-imidazolyl)pyridine^[12] (0.100 g, 0.33 mmol) was dissolved in THF (3 mL) and treated with NaH (9.5 mg, 0.4 mmol) for 1 h. MeI (22.4 μL, 0.36 mmol) was then added dropwise at room temperature. After 7 h, the solvent was removed under reduced pressure, giving a paste, which was purified by column chromatography yielding a white solid (77.8 mg, 75%). ¹H NMR (200 MHz, CDCl₃, 298 K): δ = 8.72–7.26 (m, 14 H, aromatic), 4.99 (d, 1 H, *J* = 10.4 Hz), 4.36 (d, 1 H, *J* = 10.4 Hz), 2.99 (s, 3 H) ppm. ¹³C NMR (100.6 MHz, CDCl₃, 298 K): δ = 164.6 (C=N), 149.2 (CH), 137.1 (CH), 129.2–127.11 (CH), 125.3 (CH), 124.9 (CH), 79.0 (CH), 77.4 (CH), 34.4 (CH₃) ppm. HRMS-ESI: *m/z* calcd. for C₂₁H₂₀N₃ 314.1657; found 314.1647 [M + H]⁺.

(4'*S*,5'*S*)-2-(3'-Benzyl-4',5'-diphenyl-2'-imidazolyl)pyridine [(*S,S*)-4**]:** (4'*S*,5'*S*)-2-(4',5'-Diphenyl-2'-imidazolyl)pyridine^[16] (0.100 g, 0.33 mmol) was dissolved in THF (3 mL) and treated with NaH (9.5 mg, 0.4 mmol) for 1 h. Benzyl bromide (42.5 μL, 0.36 mmol) was then added dropwise at room temperature. After 5 h, the solvent was removed under reduced pressure, giving a brown paste, which was purified by column chromatography yielding a white solid (96.6 mg, 75%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.73–6.97 (m, 19 H, aromatic), 5.67 (d, 1 H, *J* = 15.6 Hz), 5.03 (d, 1 H, *J* = 9.2 Hz), 4.45 (d, 1 H, *J* = 9.2 Hz), 3.96 (d, 1 H, *J* = 15.6 Hz) ppm. ¹³C NMR (100.6 MHz, CDCl₃, 298 K): δ = 162.8 (C=N), 148.5 (CH), 136.9 (CH), 128.8–126.9 (CH), 125.6 (CH), 122.6 (CH), 77.4 (CH), 73.6 (CH), 49.1 (CH₂) ppm. HRMS-ESI: *m/z* calcd. for C₂₇H₂₄N₃ 390.1970; found 390.1980 [M + H]⁺. [α]_D²⁰ –4.90 (*c* = 0.88, CHCl₃).

(η³-1-Phenylallyl)[(4'*R*,5'*R*)-2-(3'-methyl-4',5'-diphenyl-2'-imidazolyl)pyridine-*N,N*]palladium(II) Hexafluorophosphate (9**):** Ligand (*R,R*)-**1** (0.050 g, 0.160 mmol) and [Pd(μ-Cl)(η³-1-Ph-C₃H₄)]₂ (0.043 g, 0.083 mmol) were dissolved in dichloromethane (25 mL) at room temperature under nitrogen overnight. NH₄PF₆ (0.156 g, 0.960 mmol) was then added and the mixture was stirred for 3 h. Then the mixture was washed with water (6 × 20 mL). The aqueous phase was extracted with dichloromethane (3 × 10 mL). All the organic extracts were dried with Na₂SO₄, filtered off and the solvent was then evaporated to afford a yellow solid. The product was recrystallised from a mixture of dichloromethane and hexane (0.061 g, 56% yield). IR (KBr): ν̄ = 1559 (C=N), 838 (PF₆) cm⁻¹. C₃₀H₂₈F₆N₃PPd (681.94): calcd. C 52.84, H 4.14, N 6.16; found C 53.28, H 4.26, N 6.02. ESI⁺ MS: *m/z* = 536.1 [M – PF₆]⁺ (calcd.

536.975 for C₃₀H₂₈N₃Pd⁺). ¹H NMR (400 MHz, 298 K): **Isomer a** (46%): δ = 2.19 (ddd, 1 H, *J* = 12.4, 1.6, 1.2 Hz), 3.31 (s, 3 H), 3.33 (dd, 1 H, *J* = 7.0, 1.6 Hz), 4.52 (d, 1 H, *J* = 11.6 Hz), 4.84 (d, 1 H, *J* = 10.8 Hz), 4.90 (d, 1 H, *J* = 10.8 Hz), 5.76 (td, 1 H, *J* = 12.1, 7.0 Hz), 6.80–8.35 (aromatic protons, 19 H); **Isomer b** (31%): δ = 2.72 (d, 1 H, *J* = 12.0 Hz), 2.79 (dd, 1 H, *J* = 7.2, 1.2 Hz), 3.29 (s, 3 H), 4.53 (d, 1 H, *J* = 11.6 Hz), 4.86 (d, 1 H, *J* = 10.8 Hz), 5.00 (d, 1 H, *J* = 11.2 Hz), 5.69 (td, 1 H, *J* = 12.0, 6.8 Hz), 6.80–8.35 (aromatic protons, 19 H); **Isomer c** (15%): δ = 3.21 (s, 3 H), 3.51 (d, 1 H, *J* = 12.8 Hz), 3.86 (d, 1 H, *J* = 8.4 Hz), 3.96 (d, 1 H, *J* = 11.2 Hz), 4.25 (d, 1 H, *J* = 7.2 Hz), 4.41 (d, 1 H, *J* = 8.0 Hz), 5.90 (m, 1 H), 6.80–8.35 (aromatic protons, 19 H) ppm. ¹³C{¹H} NMR (100.6 MHz): **Isomer a** (46%): δ = 35.0 (CH₃), 55.5 (CH₂), 76.9 (CH), 80.2 (CH), 80.3 (CH), 109.4 (CH), 126.0 (CH), 127.0 (CH), 127.8 (CH), 127.9 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 129.2 (CH), 129.5 (CH), 130.0 (CH), 136.4 (C), 137.9 (C), 140.9 (C), 140.9 (CH), 146.6 (C), 149.4 (CH), 165.8 (C=N); **Isomer b** (31%): δ = 34.8 (CH₃), 55.0 (CH₂), 77.0 (CH), 80.2 (CH), 80.9 (CH), 110.2 (CH), 126.1 (CH), 127.2 (CH), 127.7 (CH), 128.0 (CH), 128.4 (CH), 128.8 (CH), 129.0 (CH), 129.1 (CH), 129.5 (CH), 130.0 (CH), 136.2 (C), 137.7 (C), 140.7 (C), 140.9 (CH), 146.5 (C), 149.6 (CH), 165.9 (C=N) ppm.

(η³-1,3-Diphenylallyl)[(4'*S*,5'*S*)-2-(3'-methyl-4',5'-diphenyl-2'-imidazolyl)pyridine-*N,N*]palladium(II) Hexafluorophosphate (10**):** Ligand (*S,S*)-**2** (0.075 g, 0.240 mmol) and [Pd(μ-Cl)(η³-1,3-Ph-C₃H₃)]₂ (0.084 g, 0.13 mmol) were dissolved in dichloromethane (20 mL) at room temperature under nitrogen overnight. NH₄PF₆ (0.123 g, 0.760 mmol) was then added and the mixture was stirred for 24 h. Then the mixture was washed with water (6 × 15 mL). The aqueous phase was extracted with dichloromethane (3 × 10 mL). All the organic extracts were dried with Na₂SO₄, filtered and the solvent was then evaporated to afford a yellow oil. The product was recrystallised from a mixture of dichloromethane and hexane (0.095 g, 52% yield). IR (KBr): ν̄ = 1556 (C=N), 838 (PF₆) cm⁻¹. C₃₆H₃₂F₆N₃PPd·0.2C₄H₁₀O·0.5CH₂Cl₂ (815.29): calcd. C 54.95, H 4.33, N 5.15; found C 55.09, H 4.02, N 5.07. FAB⁺ MS: *m/z* = 613.8 [M – PF₆]⁺ (calcd. 613.077 for C₃₆H₃₂N₃Pd⁺). ¹H NMR (400 MHz, 298 K): **Isomer a** (88%): δ = 3.18 (s, 3 H), 3.83 (d, *J* = 8.4 Hz, 1 H), 4.11 (d, *J* = 11.2 Hz, 1 H), 4.41 (d, *J* = 8.4 Hz, 1 H), 4.81 (d, *J* = 11.6 Hz, 1 H), 6.23 (t, *J* = 11.6 Hz, 1 H), 6.86–8.29 (aromatic protons, 24 H) ppm. ¹³C{¹H} NMR (100.6 MHz): **Isomer a** (88%): δ = 34.6 (CH₃), 72.4 (CH), 74.6 (CH), 79.2 (CH), 79.4 (CH), 107.6 (CH), 126.0 (CH), 126.0 (CH), 126.8 (CH), 127.7 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.4 (CH), 128.9 (CH), 129.1 (CH), 129.3 (CH), 129.4 (CH), 130.2 (CH), 136.4 (C), 137.4 (C), 138.4 (C), 141.0 (C), 141.1 (CH), 145.9 (C), 149.6 (CH), 165.2 (C=N) ppm.

(η³-1,3-Diphenylallyl)[(4'*S*,5'*S*)-2-(3'-benzyl-4',5'-diphenyl-2'-imidazolyl)pyridine-*N,N*]palladium(II) Hexafluorophosphate (11**):** Ligand (*S,S*)-**4** (0.029 g, 0.075 mmol) and [Pd(μ-Cl)(η³-1,3-Ph-C₃H₃)]₂ (0.025 g, 0.037 mmol) were dissolved in dichloromethane (10 mL) at room temperature under nitrogen overnight. NH₄PF₆ (0.037 g, 0.220 mmol) was then added and the mixture was stirred for 72 h. Then the mixture was washed with water (6 × 15 mL). The aqueous phase was extracted with dichloromethane (2 × 10 mL). All the organic extracts were dried with Na₂SO₄, filtered and the solvent was then evaporated to afford a yellow gum. The product was recrystallised from a mixture of dichloromethane and hexane (0.021 g, 33% yield). IR (KBr): ν̄ = 1549 (C=N), 832 (P–F) cm⁻¹. C₄₂H₃₆F₆N₃PPd (833.01): calcd. C 60.48, H 4.35, N 5.04; found C 60.90, H 4.95, N 5.16. ESI MS: *m/z* = 688.1 [M – PF₆]⁺ (calcd. 688.194 for C₄₂H₃₆N₃Pd⁺). ¹H NMR (500 MHz, 298 K): **Isomer a** (86%): δ = 3.90 (d, *J* = 6.0 Hz, H), 4.15 (d, *J* =

Table 5. Crystal data for **9**, **10** and **11**.

	9	10	11
Empirical formula	C ₃₁ H ₃₀ Cl ₂ F ₆ N ₃ PPd	C ₃₇ H ₃₄ Cl ₂ F ₆ N ₃ PPd	C ₄₂ H ₃₆ F ₆ N ₃ OPPd·H ₂ O
Formula mass	766.85	842.94	852.12
Crystal size [mm]	0.30 × 0.27 × 0.05	0.2 × 0.18 × 0.02	0.2 × 0.1 × 0.1
Temperature [K]	120(2)	120(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	18.781(5)	39.157(8)	10.113(6)
<i>b</i> [Å]	9.728(3)	10.708(2)	26.731(11)
<i>c</i> [Å]	17.523(5)	17.471(4)	15.026(6)
β [°]	92.297(4)	103.537(4)	107.46(2)
Volume [Å ³]	3199.0(16)	7122(3)	3875(3)
<i>Z</i>	4	8	4
Density (calculated) [Mg/m ³]	1.592	1.572	1.461
Absorption coefficient [mm ⁻¹]	0.859	0.780	0.586
θ range for data collection [°]	2.17–26.02	1.98–26.73	2.60–30.00
Reflections collected [<i>I</i> ≥ 2σ(<i>I</i>)]	6272	7569	8370
Independent reflections	6272 [<i>R</i> (int) = 0.0000]	7569 [<i>R</i> (int) = 0.0000]	8489 [<i>R</i> (int) = 0.0000]
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^[a]	<i>R</i> ₁ = 0.0492, <i>wR</i> ₂ = 0.1332	<i>R</i> ₁ = 0.0530, <i>wR</i> ₂ = 0.1237	<i>R</i> ₁ = 0.0608, <i>wR</i> ₂ = 0.1043
<i>R</i> indices (all data) ^[a]	<i>R</i> ₁ = 0.0791, <i>wR</i> ₂ = 0.1480	<i>R</i> ₁ = 0.0928, <i>wR</i> ₂ = 0.1370	<i>R</i> ₁ = 0.0612, <i>wR</i> ₂ = 0.1044
Gof on <i>F</i> ²	1.120	1.051	1.423
Largest diff. peak/hole [e/Å ³]	1.308/−0.696	0.762/−1.401	0.424/−0.382

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

8.8 Hz, H), 4.41 (d, *J* = 14.4 Hz, H), 4.50 (d, *J* = 6.4 Hz, H), 4.83 (d, *J* = 9.6 Hz, H), 5.05 (d, *J* = 14.4 Hz, H), 6.31 (t, *J* = 9.2 Hz, H), 6.87–7.97 (aromatic protons, 29 H) ppm. ¹³C{¹H} NMR (100.6 MHz): **Isomer a** (86%): δ = 49.6 (CH₂), 72.3 (CH), 74.4 (CH), 76.9 (CH), 79.6 (CH), 107.8 (CH), 126.0 (CH), 126.0 (CH), 126.8 (CH), 127.7 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.4 (CH), 128.9 (CH), 129.1 (CH), 129.3 (CH), 129.4 (CH), 130.2 (CH), 136.4 (C), 137.4 (C), 138.4 (C), 141.0 (C), 141.1 (CH), 145.9 (C), 149.6 (CH), 165.6 (C=N) ppm.

Palladium-Catalysed Allylic Alkylation of *rac*-3-Acetoxy-1,3-diphenyl-1-propene (I): The catalytic precursor was generated in situ from [Pd(η³-C₃H₅)(μ-Cl)]₂ and the appropriate ligand (0.02 mmol of Pd source and 0.025 mmol of chiral ligand) in CH₂Cl₂ (2 mL) for 30 min before adding the substrate. *rac*-3-Acetoxy-1,3-diphenyl-1-propene (0.252 g, 1 mmol), dissolved in CH₂Cl₂ (2 mL), was added followed by dimethyl malonate (0.396 g, 3 mmol), BSA (0.610 mg, 3 mmol) and a catalytic amount of KOAc. The mixture was stirred at room temperature until total conversion of the substrate (monitored by TLC, unless stated otherwise). The solution was then diluted with diethyl ether, filtered through Celite, and washed with saturated ammonium chloride solution (4 × 10 mL) and water (4 × 10 mL). The organic phase was dried with anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO₂; ethyl acetate). The enantiomeric excesses were determined by HPLC on a Chiralcel OD column, using hexane/2-propanol, 99:1, as eluent in a flow of 0.3 mL/min.

Palladium-Catalysed Allylic Alkylation of (*E*)-3-Acetoxy-1-phenyl-1-propene (III): The procedure was analogous to the one described for *rac*-3-acetoxy-1,3-diphenyl-1-propene (**I**). The product was purified by column chromatography (SiO₂; ethyl acetate). Regioselectivity was determined by GC.

X-ray Crystallographic Study: Yellow crystals of **9**, **10** and **11** were selected and mounted on a Bruker SMART-CCD-1000 area detector single crystal diffractometer with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å). Crystal data are summarised in Table 5. Preliminary unit cell constants were calculated with a set of 45 narrow-frame (0.3° in ω) scans. Data were collected using the

φ-ω scan method. Absorption corrections were applied using the SADABS program.^[28] The structures were solved by direct methods using the SHELXS-97 computer program^[29] for crystal structure determination and refined by full-matrix least-squares method on *F*², with the SHELXL-97 computer program.^[30] The weighting schemes employed were $w = 1/[\sigma^2\{F_o^2 + (0.08259P)\}^2 + 0.0000P]$ for **9**, $w = 1/[\sigma^2\{F_o^2 + (0.0678P)\}^2 + 0.0000P]$ for **10** and $w = 1/[\sigma^2\{F_o^2 + (0.0079P)\}^2 + 4.7017P]$ for **11**, where $P = (|F_o|^2 + 2|F_c|^2)/3$. Hydrogen atoms were included in calculated positions and refined in riding mode. CCDC-291543 (for **9**), -614143 (for **10**) and -613925 (for **11**) contain the supplementary crystallographic data for this paper. 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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